Performance and Capabilities of JEM-3000F to Advanced Materials Characterization at Brookhaven National Laboratory

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In this report we describe some of the instrumentation and performance of our JEM-3000F field-emission TEM to the study of technologically important superconductor and magnetic materials. To illustrate the capability of our JEM-3000F, we highlight the more advanced techniques being performed in our lab. We focus on the performance of our microscope to carry out off-axis electron holography at medium- to high-resolution, as well as at low-magnification appropriate to magnetic studies. We present abbreviated results from coherent electron diffraction experiments using magnetic materials performed at our laboratory, which compliment the higher-magnification holography studies. We further present results of magnetic field calibration of the sample area of our JEM-3000F as a function of objective lens excitation, allowing quantitative in-situ magnetization and de-magnetization experiments to be performed. We present a sampling of results from field-calibrated magnetic imaging studies that we have carried out with our microscope that, along with the high- and low-magnification holography and coherent electron diffraction experiments, indicate a highly coherent electron source for our microscope. We also illustrate some of the spectroscopic capabilities of our TEM instrumentation.

1. Introduction

The combination of advanced analysis techniques and cutting-edge instrumentation in transmission electron microscopy (TEM) allows for powerful capabilities to the study of technologically exciting materials. The JEM-3000F field-emission TEM at Brookhaven National Laboratory is just such a microscope equipped with, for example, a Scanning Transmission Electron Microscopy (STEM) attachment, Energetic-Dispersive X-ray (EDX) detector, Annular Dark-field (ADF) detector, integrated Gatan Imaging Filter (GIF) for spectroscopy and energy-filtered imaging (giving the option for automatic magnification compensation of the GIF), and electron biprism for holographic studies. The microscope is equipped with two multi-scan CCD cameras mounted before and after the GIF, a Fuji Imaging Plate system replacing the conventional photographic plate system, and two TV-rate CCD cameras mounted, as well, above and below the GIF for in-situ recording and observation. A number of sample holders are also available for our microscope, including heating (to ~1400 K) and cooling (to ~15 K) holders, offering a rather wide range of experimental capabilities exploiting our unique combination of instrumentation. Equipped with a high-resolution pole-piece, our microscope has demonstrated 0.165 nm spatial resolution and energy resolution of 0.7 eV.

In this report we describe results from a sampling of some of the capabilities of our JEM-3000F, which highlight the more advanced techniques being performed in our lab. Due to limited space we refer the reader to the literature [1] for the high-resolution performance of our JEM-3000F. We focus here on the recent addition of our ability to perform off-axis electron holography studies where, as the number of research labs equipped for electron holography increase, it is valuable to have an assessment for a particular machine and holography setup to record holograms. An abbreviated discussion of the experimental parameters affecting the quality of holograms is included in Section 2, from which a general approach to characterizing and optimizing the microscope for a given application is presented. It is clear from the discussion that flexibility provided by free-lens control is critical to recording useful holograms for the JEM-3000F. We present an electron holography study of (001) twist boundaries in the Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) high-temperature superconductor in Section 3.1, and demonstrate the ability of this microscope to perform electron holography at medium- to high-resolution. In Section 3.2 we present results from the same Bi-2212 system using newly developed interferometric shadow-imagining-diffraction methods. In Sections 4.1 and 4.2 we present our calibration of the magnetic field at the sample area as a function of objective lens excitation using Hall probe measurements, as well as low-magnification holography and in-situ Foucault imaging studies of Nd$_2$Fe$_{14}$B permanent magnets. We round out this report in Section 5 by providing an example of the spectroscopy imaging capabilities of our microscope.

2. Characterization for Off-Axis Electron Holography

In conventional transmission electron microscopy (TEM), the phase of the image wave is lost on recording since only the image intensity (amplitude-squared) is detected. Off-axis electron holography, however, allows
retention of both the phase and amplitude of the image wave [2]. This is the primary advantage of off-axis electron holography since the phase carries information about the electric and magnetic fields of the sample. Off-axis electron holography is an interferometric technique requiring a coherent electron source, such as provided by a field-emission electron gun (PEG), and an electrostatic biprism situated below the sample. The sample is positioned off the optic axis of the microscope so that incident plane-wave illumination passes partially through vacuum (reference wave) and partially through the sample (object wave), as shown schematically in Fig. 1a. The biprism is oriented such that the reference and object waves pass on either sides of the wire, being brought together by a bias applied to the biprism. The resulting interference pattern (hologram) is recorded on a CCD camera, and the complex image wave (amplitude and phase) is mathematically reconstructed from the hologram intensity through knowledge of the interfering reference wave (i.e., plane-wave vacuum reference). Figure 1b shows a schematic of the highly astigmatic illumination used to record off-axis electron holograms. The illumination is generally stretched as much as possible perpendicular to the biprism wire (and, therefore interference fringes) in order to maximize the size of the coherence patch over the width, D, of the hologram.

In practice, the reconstruction process is more involved than implied above and depends critically upon recording holograms with a strong contrast of interference fringes. Additionally, specific experimental objectives impose criteria on the quality and characteristics of the recorded hologram. Experimental parameters directly affecting the fringe contrast include electron wavelength, gun brightness, virtual source size, illumination convergence angle, interference overlap distance, and size of illumination perpendicular to the interference fringes. On the other hand, depending upon experimental objectives, requirements on the interference fringe spacing, overlap distance, and magnification are imposed. Further consideration involving the overall intensity and exposure time required to record the hologram as related to the detection efficiency of the CCD camera is also needed. As a consequence, careful experimental design and detailed knowledge of microscope and CCD imaging characteristics affecting the recordable quality of holograms is needed to efficiently obtain useful data. Complicating matters in this regard is that for a given holography setup, i.e., geometry between microscope, biprism and CCD camera, the large number of experimental parameters are not necessarily independent from each other. It is evident that both practical considerations and some handle on an optimization approach is required to record useful data.

To begin, the detection quantum efficiency (DQE) of the CCD camera used to record holograms was determined according to the methods described in references [3, 4]. The DQE is a quantitative measure of the detection capabilities of the CCD camera, and depends upon spatial frequency as well as electron dose and exposure time. For our camera the DQE was found to be fairly uniform over the range of spatial frequencies up to the Nyquist limit for typical exposure times (<10 sec) and electron dose (~500 to 10000) average counts/pix) used in conventional TEM applications. Values of DQE -0.75-0.8 were obtained for low-to-mid spatial frequencies, whereas the DQE dropped to around 0.65-0.7 at frequencies near the Nyquist limit. (A value of DQE=1 indicates ideal detection characteristics.)

For holography applications, however, one is ultimately concerned with maximizing the beam coherence, which necessitates concern over the CCD detection capabilities at low dose and/or long exposure time. Under these conditions the rate at which counts (due to signal) are being generated at the CCD camera becomes important. (i.e., if the average beam intensity incident on the camera is such that only a small number of counts per second are being generated, one expects the signal to be lost within thermal and electrical noise generated by the camera, regardless of exposure time.) Figure 2 illustrates the effect of low intensity (average counts per pixel per second) on the DQE for our camera. As seen in the figure, a severe degradation in the camera’s detection capability exists for incident intensities <30 counts/sec. This provides a practical guideline in attempting to optimize microscope parameters for electron holography such that an average hologram intensity recorded at greater than about 50 counts/sec (for our camera) is necessary in order that the CCD camera not limit the accuracy of the reconstructed phase and amplitude. Within this limit then, one may examine the effect of various other experimental parameters on the precision of phase and amplitude determination.

The minimum variance in the reconstructed phase and amplitude determination, in general, is inversely proportional to the product DQE (q)uN, where q and u are the interference fringe contrast and spatial frequency, respectively, and N is the total electron dose of the hologram [5]. If one restricts consideration to holograms recorded at sufficient intensity as discussed above, the factor DQE(qu) is constant and so the observable signal amounts to maximizing uN. In terms of experimental parameters, the product uN, can be written as [6, 7]

\[ uN = \frac{A}{2D/d} e^{-2\pi d^2} \exp\left[-\frac{(2\pi R)^2}{D^2}ight] \]  

where A is the recorded area, the gun brightness, R, the source size at the sample, the illumination convergence semi-angle, the exposure time, the electron wavelength, and e the electron charge. The overlap distance D is the distance between points in the object plane brought to overlap in the image plane by the biprism, while d1 and d2 are the size of the illumination perpendicular and parallel to the interference fringes, respectively. (See, also, Fig. 1b.)

Equation [1] illustrates the complex interplay between the wide variety of experimental parameters affecting the quality of recorded holograms, but is not very practical in guiding the choice of those parameters. It is instructive, therefore, to define dimensionless quantities,

\[ \bar{q} = \frac{q}{D/d}, \quad \bar{u} = \frac{u}{d}, \quad \bar{N} = \frac{N}{d^2} \]

where \( \bar{q} \) is the probe current at the specimen, which relate to particular aspects of the holography experiment. The quantity \( \bar{q} \) is the coherence parameter of the illumination and is given by the ratio of the coherence width to source size [7]. Values of \( \bar{q} \) range from \( \bar{q} \approx 0 \) for essentially incoherent illumination to \( \bar{q} = 10 \) for effectively total coherence. The quantity \( \bar{u} \) depends on the illumination (as it effects \( d_1 \)), but specifically as a ratio \( D/d_2 \), upon the geometry of the holography setup including the intermediate and projector lens excitations. The geometric parameter \( \bar{q} \) (having, typically, values on the order 10^-2) also carries information about the biprism bias as it affects \( D/d_2 \) and affects coherence. Hence, along with the magnification implied by the intermediate and projector lens settings, \( \bar{q} \) carries the information required in consideration of specific experimental objectives such as desired resolution. The parameter \( \bar{u} \) depends upon the brightness characteristics of the gun, as well as the illumination system, and may be thought of as being described by factors affecting the average hologram intensity, i.e., as an imaging (intensity)

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Fig. 1. Schematic of (a) off-axis electron holography and (b) illumination conditions used to record holograms. Highly astigmatic illumination is used with illumination size denoted by d1 and d2 perpendicular and parallel, respectively, to the interference fringes. The hologram width is denoted by D.

Fig. 2. Low-dose detection quantum efficiency for Gatan multi-scan CCD camera located after Gatan Image Filter attached to JEM-3000F. Significant degradation in detector efficiency occurs below about 30 counts/sec per CCD pixel.
parameter. Typical values for $\alpha$ are within an order of magnitude or two of 10$^{-6}$ for a FEG.

Expressed in terms of these parameters describing various aspects of the holography experiment, the quantity to be maximized in Eqn. [1], $\alpha \beta n_p$, is proportional to the reconstructed phase and amplitude signal-to-noise ratio, and given by

$$D = \frac{I_1}{D_1/D_4} \exp(-20D/D_4).$$

Here, we have written $A \equiv D_4D_4/D_1$ being the fraction of the interference area ($\sim D_4D_4$) recorded, and approximated the gun brightness as $[8, 9]$. The factor $D_4$ is related to the physical size of the CCD detector and microscope magnification, but is somewhat incidental to this analysis and could be absorbed into $\alpha$ without loss of generality. It should be cautioned that the parameters $D_1$, $D_4$, and $\alpha$ are not independent from each other in terms of experimental variables so that a sanguine maximization of Eqn. [2] is not easily interpretable or even practical. The merit of Eqn. [2] is that the aspects of imaging ($D_1$), coherence ($D_4$) and geometry ($\alpha$) in holography experiments are displayed rather simply for their affect on measurement precision, and that the range of practically obtainable values for the parameters are easily known or calculable. This allows an assessment of the importance of each aspect by evaluating how $D$ varies with each parameter independently.

In particular, eliminating factors common to each partial derivative, and taking the orders of magnitude as discussed above ($D_1 \sim 10^{-6}$ and $D_4 \sim 10^{-1}$), one finds

$$D \sim 10^{-2} \quad (\text{imaging})$$

$$D \sim 40(D/D_4) \sim 10^{-3} \quad (\text{coherence}) [3]$$

$$D \sim (1 - 4(D/D_4)^2) \sim 10^{-6} \quad (\text{geometry})$$

for the relative effect of each experimental aspect on the measurement precision. It is clear from Eqn. [3] that the optimization approach to holography must involve, in order, the holography geometry as imbedded in $D_1/D_4$ followed by the microscope coherence. Optimization relative to the imaging intensity ought to be relegated to final considerations assuming a sufficient minimum intensity is met. We stress here that Eqn. [3] gives the relative changes of the phase and amplitude measurement precision with respect to the various parameters, hence provides a guide as to which aspect affects most dramatically the measurement precision. The parameters are not truly independent, however, so Eqns. [2 & 3] must be used with caution and practical optimization must proceed in a wider sense. Nevertheless, Eqns. [2 & 3] make a few additional important points to consider.

Firstly, free-lens control of the microscope is critical to obtaining the highest quality holograms for a given application. In particular, control of the imaging and projecting lenses over their affect on the geometric parameter $\alpha$ is crucial. Evermore so since embodied within $\alpha$ are the experimental requirements of resolution and field-of-view. Furthermore, control and flexibility over the illumination system is necessary to obtain the most coherent and parallel illumination possible with sufficient beam intensity. Another point made from Eqns. [2 & 3] is that an explicit prescription to optimize the experimental parameters for recording good quality holograms is not very feasible, and that the hologram quality will generally depend upon the application. This makes an overall characterization and assessment of a particular microscope to perform electron holography somewhat abstract or vague, and commands specific demonstration of the microscope’s capabilities for a given application. Bearing in mind this last point, we present results of two electron holography studies with our JEM-3000F TEM having rather different demands on resolution and field-of-view.

3. Measurement of Potential Variation and Lattice Displacement in Bi$_2$Sr$_2$CaCu$_2$O$_8$ Superconductors

Potential variations due to charge transfer, impurity segregation and/or lattice distortion across grain boundaries in polycrystalline superconductors play a crucial role in the transport properties of the material. Junction interfaces often act as weak links to the superconductor current, which, in turn, limits the critical current densities that may be obtained [10]. In high-T$_c$ superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) tapes and wires, (001) twist boundaries are predominant within the fabricated material due to its two-dimensional layered structure. However, it is not clear if superconducting critical current is found to be independent of twist angle for this system [11]. Moreover, local “impurity phases” of Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2223) or Bi$_2$Sr$_2$CuO$_4$ (Bi-2201), consisting of an additional or missing (Ca$_2$O$_4$) bilayer, respectively, are commonly observed adjacent to (001) twist boundaries [12]. Such grain boundary behavior is presently not understood. We have used off-axis electron holography to directly obtain the potential across these types of grain interfaces, which, we expect, will lead to new insight about the boundary properties.

3.1 High-Magnification Electron Holography

Our JEM-3000F is equipped for electron holography with a retractable biprism assembly consisting of a platinum wire $<0.5 \mu$m in diameter. The biprism wire is rotated $45^\circ$ and located approximately in the selected area aperture plane of the microscope. The multi-scan CCD camera located after the Gatan Image Filter (GIF) attached to the microscope was used to record holograms. (The second multi-scan CCD camera located before the GIF provides considerable flexibility in recording data, but was not used in this study [3]) Figure 3 illustrates the performance of our holography setup in terms of holographic fringe contrast, fringe spacing and hologram width for one of the standard holography modes (300 kV accelerating voltage, 100 kX magnification) available with our machine, i.e., no free-lens adjustments made. Measurements were made from holograms recorded on the smallest spot size and largest condenser aperture generally giving the best available fringe contrast. Adjusting the emission characteristics of the gun (first and second anode voltages) improved the fringe contrast slightly, but not dramatically.

Figure 3a shows the holographic fringe spacing (which controls the resolution of the reconstructed image wave) as a function of voltage applied to the biprism. For example, 2 Å fringes (giving ~6 Å resolution [13]) requires about 75 V bias applied to the biprism. Figure 3b, then, shows the hologram width and fringe contrast as a function of fringe spacing (consequent to biprism voltage) for the standard 100 kX mode. hologram fringe width (open circles in Fig. 3b) defines the maximum field for holographic reconstruction, but that the actual field-of-view may be limited by the size of the CCD array. More critically for this standard mode, however, is that the fringe contrast (closed circles in Fig. 3b) for higher resolution application is comparatively low: a minimum contrast around 20% being preferred for reliable phase and amplitude reconstruction. For example, a reconstructed image wave with 3 Å resolution requires ~1 Å fringes, which gives only ~5-10% fringe contrast with this mode. Considerably better quality holograms, however, can be obtained by adjusting the intermediate (12, 13, and 15) and projector (P) lenses to maximize the imaging system of the JEM-3000F through use of the projector hole.

For example, leaving the illumination system unchanged, but adjusting lens potentials of $I_1$: 0.01 $\pm$0.25 V and $P$: 5.65 $\pm$0.30 V (with $I_2$: 4.70 V and $I_3$: 2.14 V unchanged) increases the fringe contrast (at 153.9 V biprism bias) from about 8% in standard mode to about 26% contrast with the free-lens settings. The field-of-view on CCD decreases from 12.6 nm to about 9.5 nm due to a slight change in overall magnification, but more importantly, the hologram width, D, is dramatically decreased from ~175 nm to ~15 nm with negligible change of fringe spacing by going to the free-lens settings. Hence, the geometry ratio $I_2/D_i$ is made smaller in this example, and the importance of the holography geometry (imaging lens settings) on the quality of holograms is clear. (See also Fig. 1b.) We note importantly here that the above example was performed with the condenser stigmators giving the most stretched illumination possible for our machine. The fringe contrast may be additionally increased were it possible to increase the strength of the condenser stigmator coils, and, hence, seems to be a limiting factor in free-lens operation of holography for our microscope.

Nevertheless, in the study of Bi-2212 c-axis oriented grain boundaries, we proceeded to apply the above principles to find suitable conditions for recording good quality holograms with a minimum hologram width of a couple tens of nanometers and fringe spacing less than about 2 Å. Under these conditions, the reconstructed phase would have about 6 Å resolution corresponding to about 1/5 the Bi-2212 c-axis unit-cell dimension (suitable to observe the grain-boundary), while maintaining a field-of-view large enough to observe several unit-cells of each Bi-2212 grain to either side of the interface. One might then separate contributions to the holography map due to the intrinsic thickness of the boundary due to the bulk material and, thereby, since the electron phase is related to the sample potential, obtain a profile of the electrostatic potential distribution across the grain-boundary. Though a simplified prescription is being presented here, the motivation for studying grain boundaries in Bi-2212 by electron holography becomes clear as shown schematically in Fig. 4. Given the potential distribution across
the grain-boundary (upper plot in Fig. 4), one may directly obtain the associated charge distribution (lower plot in Fig. 4), to which structure one may relate physical properties of the interface such as electrical transport properties.

**Figure 5a** shows an electron hologram obtained from a (001) twist boundary in Bi-2212 where the grains have been tilted to a systematic row orientation to assure the interface is parallel to the electron beam. The fringe contrast in Fig. 5a is about 25% (as measured from the vacuum reference image, not shown) at the 70V biprism voltage used, and corresponds to a fringe spacing of 2.1 Å as measured after image calibration by the known lattice spacing of Bi-2212. Under these conditions, the field-of-view on the CCD camera is about 22.1 nm, allowing amplitude and phase profiles extending a few Bi-2212 c-axis unit-cell dimensions (3.1 nm) from the twist boundary to be easily obtained. **Figure 5b** and 5c show, respectively, the numeric reconstruction of the image amplitude and phase from the hologram shown in Fig. 5a. The grain-boundary potential, shown in **Fig. 5d**, was directly obtained from the phase image by averaging parallel to the interface and assuming a uniform slope to the sample thickness over the region. As seen in the potential profile, Fig. 5d, the interface potential is on the order of less than a few nanometers in width (where the c-axis unit cell dimension is 3.1 nm), and has a magnitude about 0.8 V. This result is consistent with

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**Fig. 3.** Summary of JEM-3000F performance to record holograms using standard holography mode at 100KX magnification. (a) Hologram interference fringe spacing as a function of applied biprism voltage. (b) Hologram width (open circles) and interference contrast (closed circles) as a function of fringe spacing consequent to biprism voltage.

**Fig. 4.** Schematic grain-boundary potential, V, and corresponding charge density, ρ, illustrating how recovery of phase information may provide insight to physical properties of grain-boundaries as the potential is directly related to reconstructed phase in electron holography. Here, ε₀ is the permittivity of the material.

**Fig. 5.** (a) Electron hologram of pure (001) twist boundary in Bi-2212 where 2Å holographic interference fringes run nearly perpendicular to the grain-boundary (GB). (b) Reconstructed image amplitude and (c) phase from the hologram shown in (a). (d) Potential obtained from profile of phase image along line AB in (c). Note that the periodic drops in the potential profile correspond to the BiO double-layer positions, which are also clearly seen in (a-c).

**Fig. 6.** (a) Experimental shadow-image diffraction (PARODI) pattern and corresponding intensity profile (above) from c-axis systematic row oriented Bi-2212 wedge. (b) Enlarged 0014 experimental disk rotated ~20° counter-clockwise to compare with (c) calculated 0014 disk. (d) Wedge thickness determined from EELS. (e) Measured c-axis charge density over Bi-2212 unit-cell obtained from analysis of similar patterns shown in (a). Measured charge transfer (solid line) with reference to formal valence is shown at the bottom of (e) and compared with first-principle calculations (dashed line).
analysis of holograms obtained from similar pure-phase Bi-2212 (001) twist boundaries where values ranging from about 0.5 to 2 V have been found. The dependence of measured grain-boundary potential with twist angle is under investigation, as well as a study of twist boundaries containing local ‘impurity’ phases of Bi-2223 and Bi-2201 where significant charge transfer is observed. These preliminary holography results compliment results obtained from similar boundaries using interferometric shadow-imaging diffraction methods, examples of which we present next.

3.2 Coherent Electron Diffraction
Quantitative convergent-beam electron diffraction (CBED) studies can reveal important information about bonding and ionicity for small unit-cell crystals [14-17]. Conventional CBED techniques, however, are not suitable to study of crystals with a large unit-cell such as high-temperature superconductors, partly because the wide range of incident beam directions and sample tilting results in overlapping diffraction disks. We have developed a new technique by introducing an additional dimension, thickness, into the diffraction pattern and focusing on the diffraction intensity variation not only as a function of excitation error, but also as a function of crystal thickness [18]. CBED results obtained from our technique with CBED methods (which focus the probe on the sample) in that we focus the electron probe above or below the sample. In doing so, we form shadow-images (dark-field images) of a large illuminated area within the diffraction-disks that contain not only orientation information (as with conventional CBED), but thickness-profiles, or Fradellius fringes, as well as for the many simultaneously recorded reflections. Since this method obtains dark-field images within each diffraction disk for many reflections in a single exposure (parallel recording), we term our method parallel recording of dark-field images, or PARODI.

Our PARODI method offers some distinct advantages over other techniques. First, dozens of reflections (for large unit-cell crystals) are recorded simultaneously, which ensures that the incident-beam illumination and exposure are exactly the same for all reflections. Secondly, the dark-field images are recorded in the back-focal plane of the objective lens where the objective lens aberration and transfer function can be neglected for quantitative analysis. Thirdly, for a wedge sample the discrete data-points within each reflection (corresponding to different sample thickness) are independent which results in a high ratio of experimental observations versus the number of fitting parameters in model calculations giving correspondingly higher levels of confidence. Fourthly, interference fringes due to planar defects (e.g., interfaces) show strong contrast even when the defect is viewed edge-on. And, finally, a wide range of reflections can be simultaneously analyzed in quantitative measurement of charge distribution and lattice displacement since electrons scattered at small angles are sensitive to charge arrangement, while electrons scattered at high-angle are sensitive to crystal distortion.

Figure 6a is an experimental PARODI pattern, with a line scan of the reflection intensity shown above it, from a wedge Bi-2212 crystal in systematic (001) orientation using the Fuji Imaging Plate system with our JEM-3000F. The top-left portion of the shadow-images within each disk of Fig. 6a corresponds to vacuum, as easily seen in the 000 disk, and the sample thickness increases from left to right in each shadow-image. Figure 6b shows an enlarged view of the 0014 reflection from Fig. 6a (after ~20° anti-clockwise rotation), and is compared with the intensity shown in Fig. 6c obtained from dynamical Bloch-wave calculations. The intensity oscillation in Fig. 6c originates from the thickness increase of the sample, as shown in Fig. 6d obtained from electron energy-loss spectroscopy. By quantitatively refining model calculations against the experimental patterns obtained by our PARODI method, we can determine the structure factors for low-order reflections very accurately, which can then be used to determine the charge distribution within the crystal. For example, the movement of 0.05 electron holes per unit-cell of YBa2Cu3O7-δ superconductor between the CuO2 layer and O chain, which correspond to rearranging 1 out of 5000 electrons in the crystal, changes the 001 structure factor by 0.1nm for electron scattering. Correspondingly, our PARODI, method, we can determine this structure factor with an accuracy of 0.09 nm [19]. Figure 6e shows the measured charge density distribution in Bi-2212 over a single unit-cell dimension, where the lattice planes are labeled above the charge density peaks. Below the charge density plot in Fig. 6e are difference profiles (using a formal valence model as reference) showing the charge transfer, ∆, along the Bi-2212 c-axis unit-cell direction based on our measurements (solid line) and based on first-principles calculations. These experimental results indicate excess valence electrons associated with the BiO double layers, which is consistent with HRTEM observation [1,20], and suggests a possible covalent nature to the BiO-BiO bond since such a high charge transfer is observed at the interstitial region of the double-layer. The charge transfer indicates that the charge distribution in the CuO2 and SrO planes are nearly equal while Ca is almost completely ionic with negligible charge transfer.

An exciting extension of our PARODI method is to the study of faulted crystals to accurately measure interface lattice displacements with a coherent source. Since the method is based on quantitative analysis of shadow images produced by coherent electron diffraction, it is an interferometric technique where the spatial resolution of the measurement is not limited by the wavelength of the fast electrons. Accuracy down to 1pm has been demonstrated in measuring displacements associated with stacking faults and grain boundaries in Bi-2212 [21]. Due to the highly coherent electron source, strong intensity oscillations parallel to the fault are present in the PARODI patterns when a planar fault exists within the shadow-image field-of-view. As an illustrative example, experimental and simulated shadow-images are shown in Fig. 7 (upper row and lower row of disks, respectively) for a stacking fault consisting of an additional (Fig. 7a) or missing (Fig. 7b) (Ca2Cu3O6) bilayer in Bi-2212. After quantitative model refinement against experimental data and careful error analysis, we arrive at displacement vectors R=0.320 ± 0.002 nm and R=0.319 ± 0.001 nm for the insertion or depletion, respectively, of (Ca2Cu3O6) bilayer in Bi-2212. These results are, to our knowledge, about a ten-fold improvement over any existing technique in determining local lattice displacements. Rigid body translations associated with (001) twist boundaries in Bi-2212 were also studied, where, for example, the lattice displacement across a near 13 boundary was determined to be R=0.026 ± 0.004nm. The combination of quantitative electron holography to provide approximate models of potential or charge distribution for complicated interfacial structures, and the powerful refinement capabilities of the PARODI method described here, offer exciting new possibilities to unparalleled studies of grain-boundary interfaces in the high-temperature superconductors.

4. Magnetic Imaging of NdFe2B Permanent Magnets
NdFe2B magnets are currently the most powerful permanent magnets having found wide application from generators to motors and computer devices. The technological importance of NdFe2B magnets is growing rapidly as their magnet properties are improved through chemistry and processing of this compound where its magnetic properties are known to be very sensitive to such microstructures as grain size, grain alignment and the presence of secondary phases [22,23]. Nevertheless, the energy products thus far achieved for this highly anisotropic material are significantly lower than theoretical upper limits, and our current understanding of the dependence of magnetic structure on microstructure in hard magnets is still quite limited. Knowledge of how magnetic structure is related to microstructure within NdFe2B permanent magnets may help address major issues of magnetism in magnetic materials such as an understanding of the role of domain wall depinning and reversed domain nucleation as factors that limit the coercivity of these hard magnets [22]. Light field emission electron holography combined with in-situ field-calibrated magnetization and demagnetization Lorentz or Foucault microscopy provides a quantitative approach to examining these important issues.

4.1 Low-Magnification Electron Holography
The standard low-magnification holography mode (objective lens very weakly excited) for our JEM-3000F suffers somewhat poorer performance compared to its standard medium- or high-magnification modes, or compared to similar modes for commercial microscopes from other manufacturers [21]. By using holographic fringe contrasts against 10% or lower for biprism voltages around 60 V, which gives 19.1 nm interference fringes and 4.2 μm hologram width. For this magnification, the field-of-view on our CCD cameras is 8.5 μm and 0.6 μm, respectively, for the cameras mounted above and below the GIF. The discussion of Section 2, hence, holds special pertinence here. Efforts to maximize the fringe contrast according to principles discussed above have, so far, met with only partial success. For example, we obtain 8-9% fringe contrast at 60 V biprism bias in the standard low-magnification mode.
But, by increasing the first intermediate lens from 0.01 V to 2.72 V through free-lens control of the microscope, leaving all other lenses untouched, the fringe contrast is dramatically increased to 58%. This gain, however, is tempered by the fact that the objective mini-lens (OM) cannot be increased sufficiently to focus the sample, and appears to be the primary factor limiting the overall performance of our machine for low-magnification holography applications. Nevertheless, the performance of our microscope can be improved beyond that of the standard-mode lens settings by going over to free-lens control where, though a labor-intensive practice, sufficiently strong contrast can be obtained for particular applications as shown below.

Figure 8a is an electron hologram recorded from a sintered Nd$_3$Fe$_5$B permanent magnet, and Figs 8b and 8c are, respectively, the reconstructed amplitude and cosine of the phase images. The hologram shown in Fig. 8a was recorded with lens potentials: C$_1$=3.42, OL=0.35, OM=6.25, I$_1$=0.01, I$_2$=4.60, I$_3$=1.09, and P=3.20; and 60.2V biprism bias. The fringe contrast (in vacuum) was 16% under these conditions giving 10.8 nm fringes over a 1.46 μm field-of-view on the CCD camera where the hologram covered the entire CCD array. Domain boundaries (marked by arrows in Fig. 8c) appear as discontinuities in the gradient of the phase image. Figure 8d shows a vector map of the calculated phase-gradient, which, neglecting contributions from sample thickness and electrostatic potentials in the sample, represents the projected magnetic induction. (Even accounting for contributions due to sample thickness and electrostatic potentials, one must be aware that the component of magnetic field parallel to the beam does not contribute to the final induction map so that interpretation must be performed with caution.) While being grossly oversimplified, Fig. 8d shows qualitatively the 180°-domain configuration (as thick arrows) present in the sample, and illustrates the potential for our microscope to perform quantitative magnetic studies. The quantitative potentiality of electron holographic methods, combined with more conventional, yet mainly qualitative, magnetic imaging techniques of Lorentz and/or Foucault imaging, discussed next, represents a powerful combination of capabilities of our JEM-3000F to the study of magnetic materials.

### 4.2 In-Situ Magnetic Imaging

To understand the relation between structure and properties of magnetic materials, it is crucial to be able to magnetize or demagnetize the sample in the microscope so that dynamic behavior of magnetic domain structure, such as orientation dependence and interaction with defects, can be studied in-situ. For magnetic imaging, samples are normally examined with the main objective lens (OL) of the microscope either switched off or slightly exited. The latter case is used for in-situ magnetizing experiments. Exact knowledge of the magnetic field excited in the specimen area of the electron microscope as a function of the OL potential allows one to take qualitative imaging of magnetic domain behavior obtained in the Lorentz and/or Foucault modes to a new level. For example, quantitative description of the evolution of the local domain structure versus the applied field becomes possible, as well as the ability to evaluate processes of magnetization and demagnetization. This may, for example, allow differentiation of the underlying mechanisms between reversed-domain nucleation or domain pinning that determines the coercivity of magnetic materials. To this end, the magnetic field in the sample area versus objective lens potential for our JEM-3000F was carefully calibrated by direct Hall probe measurements using a BELL610 gaussmeter [25]. As plotted in Fig. 9, the magnetic field at the sample area can be varied from 0.02 to 3 Tesla. Table 1, then, shows the magnetic fields present at the sample area corresponding to various standard operating modes of our microscope, including the "Hololow Mag" mode used for electron holography and conventional "Low Mag" mode used for Lorentz and Foucault imaging.

As an example of the utility of the approach described above, we elucidate the evolution of domain nucleation near grain boundaries of sintered Nd$_3$Fe$_5$B magnets, as recorded in the Foucault mode [26]. In the Foucault imaging mode, an aperture is placed slightly off-center from the transmitted beam in the back-focal plane of the imaging lens, i.e., objective mini-

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**Table 1.** Magnetic field at specimen area for JEM-3000F field-emission TEM.
lens of the JEM-3000F. Oppositely oriented domains (in projection), then, appear correspondingly bright or dark in the image depending, respectively, upon whether the magnetic (Lorentz) scattering is into or out of the aperture. Figure 10 shows the domain configuration present in an 84° grain-boundary (GB) region of a sintered NdFeB-Magnet for two different magnetic fields (3.3 Koe and 2.1 Koe corresponding to Fig. 10a and 10b, respectively) applied normal to the image-plane via the calibrated OL excitation. Due to its crystallographic orientation at 3.3 Koe, the left grain (G1) is near magnetic saturation (single-domain configuration) with a small nucleus of reverse-magnetization present, as shown in Fig. 10a. Upon further reduction of the applied magnetic field to 2.1 Koe, the reverse-magnetization nucleus abruptly expands to encompass the grain with equal width of reversal domains, as shown in Fig. 10b, suggesting grain G1 has reached a demagnetized state. In contrast, the right grain (G2) remains nearly saturated. The magnetization reversal near grain boundaries is further elucidated in Fig. 11 where the applied magnetic field (via the OL excitation) has been decreased to zero and, in fact, reversed. (The ability to reverse the OL lens current (hence, magnetic field) is a non-standard feature installed with our JEM-3000F.)

Reversal domain nucleation at grain boundaries is further illustrated in Fig. 11b, where 24 frames of a sequence showing consecutive images of the nucleation process of domains present near a grain-boundary (GB) region of NdFeB-B, where the in-plane easy magnetization axis (c-axes of NdFeB-B) appear parallel when projected onto the image. Figure 11b are enlarged images of the same domain area for frames 4-6 in Fig. 11a recorded at a rate of 24 frames per second under these in-situ demagnetizing conditions. (i.e., decrease and reversal of objective lens excitation.) The demagnetizing process usually takes place at grain boundaries where the nucleation of reversal (negative) domains occurs via sudden splitings of positive domains. This phenomenon is clearly seen in the frames of Fig. 11b where the nucleation of a positive domain near a positive-negative double domain configuration, enclosing a pair of newly generated 180°-domain walls.

The nucleation process shown in Fig. 11 is essentially irreversible, and may be considered as a cascade-like discharge of over-saturated magnetic charge (or poles) at the boundary [26]. The formation of reversal (or negative) domains through this process reduces the magnetostatic energy of each boundary by self-compensating the newly created N/S-poles at the grain boundaries. The final phase of the magnetization reversal process, not shown here, is completed very fast by simple lateral expansion of the many newly created domain walls within each encompassing grain. These in-situ magnetic studies coupled with the ability to perform electron holography promise for exciting research avenues into fundamental properties of advanced magnetic materials.

5. Detection Limit of EELS and Spectroscopy Imaging

Implicit in the technological performance of the materials discussed above is the role of off-stoichiometry and/or the addition of impurity dopants to improve their respective materials properties. For example, non-stoichiometric oxygen content in Bi-2212 is known to affect its superconductor properties [27], while doping NdFeB with small amounts Co or Ga impurities plays an important role in achieving high-energy products for the material [28-30]. One, therefore, cannot dismiss the importance of spectroscopic methods as an essential tool for advanced materials analysis, and we have undertaken a study of the detection limits using electron energy-loss spectroscopy (EELS) for light elements in biological samples (specifically, boron) for our JEM-3000F and GID setup. Spatial mapping of boron at low concentration is challenging, but of particular interest and importance for boron-neutron-capture therapy for cancer treatment.

To determine the detection limit using EELS, we used a series of samples with various boron contents deposited on carbon films as prepared by Ray Egerton’s group in Alberta [31]. For a perfect electron detector (detector quantum efficiency, or DQE=1), the minimum number of atoms (all chemical species) per unit area of specimen, I the incident-beam current, and T the recording time. The background extrapolation parameter, h, is associated with separating the core-loss signal (scattering cross section of the non-characteristic spectral background signal (scattering cross section of the non-characteristic signal) of a boron atom as follows: For a test film consisting mainly of 50 nm carbon, the number density N = D/(Au) = 4.5 × 10^15 cm^-2, where u is the atomic mass unit and T the sample thickness. For 300 keV incident electron energy, 10 m rad collection angle and 50 eV integration window, the cross section for boron K-shell ionization (δ = 0.0040 ξ 10^-14 cm^2) calculated using SIGMAK3 for the boron K-edge [32]. The cross section for the non-characteristic background is δ = 0.222δ = 1530 ξ 10^-14 cm^2, estimated from measurements of the non-characteristic background in typical spectra collected from 50 nm carbon samples with 0.2 % boron. The beam current for our instrument may be obtained from the TEM screen current, which was calibrated using a Faraday cup, and can be taken as 0.7 nA for these calculations. The MAF, then, can be calculated taking SNR = 10 (for 10 % measurement accuracy), h = 10 and acquisition time T = 6s, giving a value MAF = 0.0017. In other words, about 0.17 % of the boron should be measurable with 10 % accuracy.

Experimentally, we achieved about this accuracy on test films containing 0.2 % boron concentration on 50 nm thick carbon, the minimum boron-containing sample detected [31]. Boron concentration ratios measured on our JEM-3000F gave an average boron fraction of N/B = 0.0021 ± 0.0002, which was found, also, to be consistent with measurements on a JEM-2010 (LaB6) instrument equipped with a PEELS detector. Since the MAF is independent of the incident beam diameter, it should be possible map 0.2 % boron in STEM mode by acquiring spectra from each point with resolution as good as allowed by the radiation damage of the sample or by spherical aberration of the objective lens. Furthermore, the above calculations can be extended (not shown here) to energy-filtered elemental mapping to determine the minimum area (n×n pixels) in which boron can be detected, offering the possibility of mapping the spatial distribution of an element (boron) of interest. In particular, it should be possible to map 0.3 % variations in boron concentration when 16×16 pixels are binned in energy-filtered transmission electron microscopy (EFTEM) with our microscope. Figure 12a is a zero-loss image of three tobacco mosaic viruses imaged in EFTEM mode with our JEM-3000F. Figure 12b is the corresponding boron map of the same area. Figure 12b clearly shows an increase in boron signal in regions corresponding to positions of the TMV. Extending the above calculations and analysis, we estimate the number of boron atoms per unit area in Fig. 12b to be approximately 10^10 boron atoms per pixel (with a pixel size of 1nm^2) in the vicinity of the tobacco mosaic viruses.

6. Conclusions

We have illustrated some of the more advanced techniques to materials characterization that our JEM-3000F field-emission STEM is capable. Using coherent diffraction techniques newly developed in our laboratory (PARODI), we measure lattice displacements across grain-boundaries in high-temperature superconductors with picometer accuracy, as well as potential variations and charge transfer on sub-nanometer scales. We have taken in-situ magnetization studies using conventional Lorentz and Foucault imaging modes to new quantitative levels by careful calibration of the magnetic field applied to the sample area as a function of objective lens excitation. We have analyzed the detection limits of our spectroscopic capabilities and illustrated the sensitivity of energy-filtered imaging to detection of light elements. We have also demonstrated the ability to carry out both medium- to high-resolution electron holography studies of superconductor grain-boundaries and low-magnification holography studies of permanent magnets with our JEM-3000F.

Since all of the techniques described above require a highly coherent electron source and good high-tension stability, we may conclude that our JEM-3000F exhibits such qualities. Furthermore, the performance of our machine does not appear hindered by the multitude of various attached detectors and complex integration of experimental capabilities. For holography applications, the ability to freely control all the lens settings was found to be crucial in recording good quality holograms as the programmed settings give poor interference fringe contrast in the holograms. The strength of the objective mini-lens seems to be the limiting factor in low-magnification magnetic applications, while the strength of the condenser-stigmators appears to hinder the ultimate capability of our microscope for higher-magnification applications. Nevertheless, combined with the advanced techniques being performed in our laboratory, the demonstration to perform electron holography studies adds another dimension.
sion to the already uniquely powerful capabilities of our TEM instrumentation to the study of advanced materials.

7. Acknowledgements

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References


Fig. 10. Foucault images of domain configuration at 84° grain-boundary (GB) in Nd,Fe14B sample recorded at (a) 3.3kOe and (b) 2.1kOe fields applied normal to image plane via calibrated objective lens excitation. A small reverse-magnetization domain (circled) is present in grain G1 of (a) which expands to encompass the grain interior as the applied field is further lowered, as shown in (b).

Fig. 11. (a) Successive frames (1-6) of reverse-domain nucleation process near grain-boundary (GB) as recorded at 24 frames/sec in Foucault imaging mode during decrease and reversal of applied magnetic field normal to image plane. (b) Enlarged from circled regions of frames 4-6 showing domain splitting.

Fig. 12. (a) Zero-loss energy-filtered image of tobacco mosaic virus (TMV) and (b) corresponding energy-filtered boron map showing the concentration of boron associated with the virus.
TEM User Station with a Multimode CCD Camera

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Introduction
A major goal of CCD/TEM system integration is to improve laboratory productivity, especially in multi-user environments. Digital camera systems can provide visual feedback as well as easier and faster data collection relative to conventional viewing and film recording. In addition digital systems can reduce the total cost of recording relative to conventional film based systems.

Modern TEMs allow control by a camera system or other computer. Such control can add flexibility and customization of operating parameters to individual user needs. The challenge in system integration is to combine these new capabilities to produce a practical tool for the laboratory. This design objective demands that the system maintains quality and reliability, operates simply and intuitively, and remains cost-effective.

A "user station" is defined as a module that is optimized for producing high quality data with a minimum of encumbrances. It embeds both machine control and automation tasks, and employs a structured user interface, which anticipates the operations. The result is a minimum of "mouse clicking" and a well-structured flow of control and information.

System Components

CCD Camera Head

A multimode, progressive scan CCD camera is the starting point for sensor integration. It combines high speed, high sensitivity and high definition in a single module. Speed is needed for efficient control either by the user or by a computer-automated procedure, while sensitivity is important to avoid specimen damage. Finally high definition is needed to produce a worthwhile final product.

This system uses a specially modified Hamamatsu ORCA camera using a SONY ICX-061 CCD sensor. The clock speed of the camera is 14.7 MHz with a 12 bit A/D converter with a 1280 × 1024 pixel format. Thermal noise is minimized by use of a Pelletier cooler, which maintains the sensor at 5 degrees C. The camera has an electronic shutter; thus neither beam blanking nor mechanical leaf shuttering is needed for operation. The current system uses a 1024 × 1024 pixel sub-array and is operated at either full resolution (1 ÷ 1 binning) or half resolution (2 ÷ 2 binning). The maximum update rate of the camera is 18 f/s in binned mode and 9 f/s in full resolution mode. Exposure, timing and gain are controlled through an RS232 serial communications port. Digital image information is transferred at 14.7 MHz via 12 RS422 lipo-pairs. A more detailed specification is available from Hamamatsu [1].

TEM Configuration

The reliability and speed of the control software in large part depends on the stability and performance margin of the combined TEM and optical systems. A priority for the integrated system is predictability in the TEM's response to operator (i.e. computer) demands. In particular, maintaining alignment during magnification and brightness adjustments is important for minimizing computer searching and keeping the system responsive. The JEM-1230 meets these stability requirements.

The TEM control system is based on a Motorola processor running OS-9, which is a robust, small kernel operating system capable of multitasking. Communication between the Windows platform (camera control unit) and the TEM is via RS232 with handshaking. The control tasks are partitioned into modules: The in-depth "setup" procedures remain on the JEM-1230 monitor, while the routine operating parameters are integrated into the Windows platform.

An important feature is that the camera can be run at a 100 % duty cycle, meaning that a completed frame can be read while its succeeding frame is being exposed. This eliminates response lag and improves overall collection efficiency.

The SONY CCD well depth is approximately 12000 electrons, which is lower than traditional full frame cameras based on large format CCDs. This lowers the dynamic range of a single frame image [2]. In live imaging this limitation is not important, since generally the dose will be small for exposure times on the order of 100 ms and beam statistics rather than well depth will be the limiting factor.

For recording, where exposure times are on the order of 2 seconds, the limited well depth is a potential problem. This system uses digital frame integration to create a 16 bit deep, virtual well [3]. The fast clock-rate of the CCD and speed of the computer processor allow readout and frame summation to occur before pixel saturation for a very large range of operating conditions. Because the camera has a 100 % duty cycle, there is no dead time in this process and collection is 100 % temporally efficient. The dynamic range becomes limited by computer memory rather than the CCD cell dimensions.

Frame Grabber and Capture Software

The RS422 format signal is captured and buffered by a IC-PCI frame grabber from Coreco/Imaging Technology. The card has 4 MB of on-board memory and transfers data over a 100 MHz PCI bus. The control software has a 32 bit architecture and runs on a MS Windows NT platform. Data transfers are fast enough to support live imaging and real-time frame integration.

Phosphor

The projected electron image is converted to light with a 24 mm ÷ 24 mm P 43 phosphor screen with a phosphor density of approximately 5 mg/cm2 with a light output of about 3000 photons/electron at 100 keV. The output is green with a major peak between 540 and 560 nm. The decay constant [4] for P 43 is less than 1 ms so it is suitable for live imaging at 18 f/s. The estimated MTF at the Nyquist frequency of the screen is better than 50 % for 100 keV electrons. [5,6]

A single crystal scintillator, such as YAG, was not used for this application, because of its lower light output [2] and poorer point spread function [7] relative to the phosphor. Although Fourier transform based reconstruction procedures can be used to restore resolution from a YAG image, these techniques are not as effective in lower dose situations or live imaging where beam counting statistics limit the signal quality [8].

Optical Components

The lens needs to project the phosphor-generated images to the CCD and maintain resolution. A specially designed lens with a 0.293 magnification was built for this task. An Air Force test pattern generated by this lens/camera combination shows clean edges and a symmetric response for high contrast patterns. (Figure 2).

The lens response to low contrast detail is more reliably predicted by the measured MTF curves shown in Figure 3. The measurements indicate that over 70 % of the contrast pro-
duced by the phosphor is available for detection at the CCD sensor [9].

The lens has an MTF of greater than 70% at the Nyquist frequency of the CCD (75 lp/mm). This value is maintained across the entire CCD. The distortion of the lens is less than 0.5% across the field.

The maximum signal-to-noise ratio (SNR) of the system is determined by beam counting statistics, which follow the normal square-root dependence of a Poisson distribution. Statistical variations in photon emission and detection degrade the SNR by adding error to the measurement. The lens is about 0.5% efficient in transferring phosphor-generated photons to the CCD sensor surface [4]. Given a phosphor output of 3000 photons per incident electron, approximately 15 photons reach the sensor per imaging electron of which an average of 6 are actually detected. This process multiplies the signal to noise ratio by a factor of $\frac{6}{15}$, thus degrading the SNR by about 8% [10].

**Performance**

The design goal was to develop a TEM user-station that 1) uses the CCD camera to provide visual feedback to both the user and imbedded control procedures, and 2) sends control signals and information back and forth between the user (or user application) and the TEM subsystem. The key factors for evaluating the “user station” are:

1) **Live viewing**

The speed and sensitivity allow the specimen to be viewed at 18 f/s with imaging currents above 0.5 nA (corresponding to 5 pA/cm² on the film meter). This corresponds to a uniformly “spread” beam and allows the user to use the same conditions for viewing and recording. Each frame is normalized for structural inhomogeneities and illumination variations in the phosphor and optical chain. In live mode this normalization is done with 8 bit accuracy, since this involves less computation and since higher precision corrections are not statistically justified for short exposures. The final result is that normalization has no measurable effect on the speed of the system.

Display contrast is automatically set by the user station. The white and dark levels are calculated for each frame from analysis of the real-time intensity data. This works well in the absence of grid bars and holes in the specimen. Manual override is also possible for specimens with these “pathological” contrast conditions.

The normal viewing mode uses 2x2 binning, which results in TV quality image. This image can be converted to a KS170 format for VCR recording or live internet communication.

Focusing mode views a 512x512 pixel center region at 2x magnification. Although the frame update reduces to 9 f/s in the mode, the speed and signal quality are sufficient to achieve a high quality focus.

2) **Recording**

Normal recording is done with a 16 frame summation of the 12 bit data. Visually the effect of summation is striking as the integration increases from 1 to 4 frames and becomes less apparent after 8 frames.

The 16 frame integration produces an image with a maximum of 65535 levels. The result is 16 bits deep arithmetically, but statistically the image has less than 16 bits of dynamic range.

Based on the square root dependence on the error of the mean, the normal 16 frame summation adds two statistically significant bits to the dynamic range of the image.

The image is also dark field corrected using a (suitably scaled) 48 frame integration of the dark image. This image is extremely stable and does not need to be updated more than once every few months.

A new reference image still needs to be obtained every day, because it is affected by long-term mechanical variations and beam voltage changes. It is otherwise stable so that a single reference is adequate for an entire session.

The final image is also normalized with another 16 frame integrated reference image, which is a recording of a uniformly illuminated blank image. All the calculations are done in double precision arithmetic. The precision in the recording process is especially needed to extract detail in darker regions of the image as shown in Figure 4, where there are fine tonal differences in the crystalline region.

3) **TEM controls**

The visual feedback from the camera enables live control of the TEM through mouse driven commands, by reference to the image itself or through auto-functions.

**Exposure**: The user station has live image-base automatic control or exposure, which complements the JEM-1230’s analytically programmed intensity tracking. Users can work from 1000 to 200,000 or more without having to adjust brightness settings or re-centering illumination.

**Focus**: The live focus mode is linked to the

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**Fig. 1**: Cooled CCD camera and lens used on the 35 mm port of JEM-1230. Note that, although cooled to 5 degrees C, the camera does not have water lines.

**Fig. 2**: Air Force resolution target shows vertical and horizontal line-pairs with spacings of less than 75 lp/mm. Note the symmetry of the images.

**Fig. 3**: Measured modulation percentage (MTF) of the lens as a function of spatial frequency. S and T refer respectively to sagittal and tangential directions.
objective lens wobbler, such that the wobbler automatically turns on during focusing. The wobbler speed and amplitude are preset in the JEM-1230 controls for the 9 t/s focus mode update rate. The exposure time and gain are matched between focusing and live modes as well as for the recording mode.

**Magnification Control** : A thumbwheel control allows the magnification to be controlled from the screen.

**Automatic Illumination Reset** : An illumination reset icon is available for situations where the beam illumination is not optimal, due either to limitation in alignment or specimen thickness variations. The reset control optimizes the second condenser lens using the intensity histogram of the live image and a tracking algorithm.

**Automatic Alignment** : The JEM-1230 interface also allows control of the deflectors. However, speed of the control interface is an important consideration for alignment, which requires multidimensional control. This feature is under development.

**Recording** : The station automatically switches the camera to full resolution and matches the illumination conditions of the live mode by lowering the gain and lengthening exposure. The wobbler also automatically switches off for recording. Only images obtained in full resolution mode can be stored or analyzed.

**Annotation and Storage** : Images are recorded in either 8 bit or 16 bit TIFF files. The format is pre-selected. Initiating the save command prompts the user for the picture caption, which includes a micron bar. Magnification, voltage, specimen position and mode of operation are automatically read and inserted in the form. The caption is inserted in a blank area at the bottom of the recorded image. This information is also included in the comment tag of the TIFF header. All image save-events are recorded in a log, which includes the filename, time, and magnification.

**Case Save** : Data sets can be saved in a "Case" that automatically names and numbers the stored images. Each case is assigned a directory (using the same case prefix). The directory can be located in any available device. The history of all cases is saved in the root directory of the imaging computer.

**Stage Control** : The stage can be moved to any position in the live display by mouse clicking on a point in the display window. This control is compensated for rotation shifts resulting from imaging mode changes.

The position of a stored image is also recorded in the header of the TIFF file. On image recall the stage can be directed to this position by a mouse driven command.

The original TEM trackball control is retained as well for touch sensitive control. At any time the current stage position can be recorded. Backlash correction is done automatically.

**Measurement** : On line point to point and diffraction measurements are done directly on a final image. The magnification is automatically known and the TEM calibration is used.

The measurements are shown on the display and are burned in the image. A measurement table is written in text characters. The table can be annotated and saved for use in data reduction programs and spreadsheets.

![Fig. 4. Crystalline inclusion in a mitochondrion from a patient with a mitochondrial myopathy.](image)

**Montage** : A montage procedure records a rectangular array of images. Currently, this procedure is optimized for low magnification and stage control is used to place the images. The recorded images have a pre-determined amount of cropping and overlap. The images are automatically stitched and saved in a TIFF file.

**Hot Buttons** : Individual needs and preferences for additional software are met by programming icons to immediately port the recorded images to the individual applications. This enhances the capabilities of the systems without cluttering the user interface and reproducing existing functionality in standard imaging software.

**User Experience**

The "user station" is located in a multi-instrument, multi-user facility with both clinical and research activities. Typical examples, shown in Figures 5 and 6, illustrate the range of magnifications used and the definition available with the system.

Nearly all images are stored digitally and transferred to CD-R disks. An inkjet printer provides hard copy prints when required.

**References**

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Fig. 5. Double immunogold label of an absorptive cell from a crypt in the ileum. CFTR (a small gold) was seen on the membrane of the microvilli. Occasionally ClC4 (large gold) was seen on the structures.

Fig. 6. Inclusion in a mitochondrion from a mitochondrial myopathy.
Characterization of Guinier-Preston Zones by High-Angle Annular Detector Dark-Field Scanning Transmission Electron Microscopy

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Imaging of Guinier-Preston (GP) zones in aged Al-Cu alloys has been a long-standing problem for transmission electron microscopy (TEM), not only because of their small size (typically several nanometer), but also because of their coherent nature of the precipitation in a matrix, especially in their incipient stage. Thus, early TEM studies focused on the diffraction contrast of the surrounding matrix instead of the zone itself, and the resolution was later improved by the introduction of the weak-beak technique. With a high-resolution TEM, one can still not directly observe Cu atoms; it is the interpretation of images made by modeling and simulation that suggests the actual position of a precipitated layer(s). In this report we show, on the other hand, that the high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM) provides images interpretable without a prior knowledge of the structure of the GP zones, and has a potential to help advance our understanding on the coherent precipitation significantly.

Age-hardened alloys are everywhere: in aeroplanes, aluminum sashes, electrical connections for computer devices, and so on. The materials that have made possible the very existence of these human inventions are manufactured based on a single materials-science principle known as ageing. Here, supersaturated impurity atoms that dissolved in an otherwise pure metal gather around inside the metal as time goes by, and precipitate, sometimes in the form of a spherical cluster, sometimes in the form of a disc aligned in parallel to a crystalllographic plane of the metal matrix. These crystallographically coherent precipitations are collectively known as Guinier-Preston (GP) zones after the pioneering scientists who revealed the structure of the zones in the Al-Cu system by X-ray diffraction technique [1, 2]. Since these precipitate phases are highly coherent with the matrix, it is very difficult to identify their structure unambiguously even with high-resolution transmission electron microscopy (HRTEM). For example, in the Al-Cu system, the Cu atoms precipitate in parallel to the {100} planes of the Al matrix, and thus the phase contrast is highly sensitive to a number of experimental conditions, including the thickness of the specimen and defocus of the objective lens. This can be evidenced by a number of simulation works that have been reported so far in order to elucidate the structure [3-7]. High-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM), on the other hand, give a direct correspondence between object and image, primarily due to the incoherent nature of the image formation [8-10]. Thus for example, image reversion does not occur with defocus or with the change in thickness of a specimen, and resolution is preserved, even though the contrast is reduced. Therefore, it was expected that HAADF-STEM would reveal the structures of the zones in a clear-cut manner. We chose the Al-Cu system to investigate the possibility [11] since this is probably the most well-known system studied by a number of researchers.

Guinier [12] proposed the following reaction sequence would take place upon the aging (low-temperature annealing) of quenched Al-Cu alloys:

GP-I zone → GP-II zone (α phase) → α-phase

Fig. 1. (a) SAD pattern of the Al-3.3 wt% Cu alloy aged at room temperature for 100 days, showing streaks through [200] diffraction spots. (b) BF TEM micrograph, showing the GP-I zones with about 10 nm in length, parallel to {100} planes of the [001] oriented Al matrix.

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-phase (CuAl₂, stable phase).

This reaction sequence was broadly confirmed by the X-ray diffraction and other techniques, and the GP-I zone was thought to be composed of Cu monolayers parallel to the Al (100) planes. On the other hand, an ordered tetragonal structure was accepted as a model for GP-II, even though there exist two distinct views as for the arrangements of Al and Cu layers. That is, Guinier [13] initially suggested a tetragonal structure comprising Al₃(Al,Cu): Cu₃(Al,Cu):Al ordered layers with a c value of 0.77 to 0.79 nm, as supported by Silcock et al. [14], whereas Gerold [15] proposed a different model, in which Cu monolayers are separated by three Al layers. Interestingly, the latter model is frequently quoted in standard textbooks on physical metallurgy [16, 17].

We used JEOL-2010F equipped with a Schottky field emission gun, operating at 200 kV in the STEM mode for HAADF imaging [18, 19], while JEOL-3010 operating at 300 kV was used for conventional TEM observations. The HAADF-STEM images were recorded with a Gatan system, and presented here without any processing.

**Figures 1 (a) and 1 (b)** are a selected area diffraction (SAD) pattern and bright-field (BF) TEM images of the Al-3.3 wt% Cu alloy aged at room temperature for 100 days, taken along the [001] axis of the Al matrix. The streaks through the {200} diffraction spots of the Al matrix in the SAD patterns represent the shape function of the precipitates and essentially the same as the elongated diffuse streaks found independently by Guinier and Preston in their X-ray scattering patterns. The staggered contrast in the BF-TEM image arises from the strain fields around the GP-I zones, and was interpreted as the evidence of single-layered Cu precipitates [20].

**Figures 2 (a) and 2 (b)** are a series of high-resolution TEM images taken from exactly the same area of the Al-3.3 wt% Cu alloy under different defocus values, which differ each other by approximately 100 nm. Both the micrographs show the images of GP zones at the atomic level; yet, some Cu layers that are clearly visible in Fig. 2 (b), as indicated by arrows, are completely absent in Fig. 2 (a). It should be noted that some of the GP-zones are visible in both the photographs, whereas some are not, indicating that the contrast of the zone depends strongly on the size of the Cu layer, as pointed out by Karlík and Jouffrey [7]. These results suggest that it is practically impossible to simultaneously image GP-I zones having different sizes, even though an individual zone can be identified if the condition is met for a particular zone.
Figures 3 (a) and (b) are unprocessed HAADF-STEM images of the Al-3.3 wt% Cu alloy, taken along the [001] axis. These images were obtained with slight specimen drift during the image capturing process (which took about 20 seconds), and thus do not give the exact four-fold rotational symmetry. Nevertheless, the image of the matrix clearly reveals an atomically resolved face-centered cubic structure viewed along the [001] axis, implying that the resolution is indeed better than about 0.2 nm, the (200) spacing of the Al matrix. Densely populated GP-I zones are identified by bright line contrasts arising from Cu atom layers, because of their large Z value. It should be mentioned, however, that each GP-I zone is approximately in the form of a disc, which minimizes strain energy. Therefore, the bright line contrasts are the images of Cu discs viewed edge-on, and it is reasonable to expect weaker contrasts in the edges of each bright line. Among them, one can see a GP-I zone less than 2 nm in length (or the diameter of the disc), as indicated by the pair of arrowheads in Fig. 3 (a). In addition to commonly-known single layered GP-I, double layered GP-I zones have been frequently encountered, as indicated by the pairs of double arrowheads in Figs. 3 (a) and (b). This observation is in agreement with previous findings by TEM [3, 20, 22] and by field ion microscopy [23], although we have so far not detected GP-I zones with more than two layers, as reported by Phillips [21].

It should also be emphasized that the GP-I zones actually comprise a three-dimensional structure of planar Cu precipitates, as depicted in Fig. 4. Among them, only the GP zones whose planes are parallel to the incident beam are clearly visible in both HRTEM (Fig. 2) and HAADF-STEM (Fig.3) micrographs. However, close examination of HAADF-STEM images often reveals disc-like contrasts with approximately 2 nm in diameter viewed face-on, as indicated by the asterisks in Figs. 3(a) and (b). Since these are just the size of the discs, we may suggest that these dull bright discs represent GP-I platelets oriented normal to the electron beam. A detailed calculation of the contrast formation is required to verify the possibility of detecting GP-zones oriented normal to the beam.

When the alloy is annealed at higher temperatures, the GP-I zones are known to transform into the GP-II zones. Figure 5 is an HRTEM micrograph of the 4.3% Cu-Al alloy aged at 180 °C for 48 hours, showing the GP-II zones. This micrograph does not give clear-cut information as to the positions of Cu layers.

Figures 6 (a) and (b) are unprocessed HAADF-STEM images of the 4.3% Cu-Al alloy. Figure 6 (a) clearly shows two single Cu layers separated by three Al layers, supporting the Gerold's model of the GP-II zone [15]. In addition to the direct confirmation of the model, it can be seen that the GP-II possesses a step-wise edge, suggesting that, once it is nucleated, it may grow by a layer-by-layer mechanism. The structure of the GP-II zone, on the other hand, does not always conform to the Gerold's model. For example, Fig. 6 (b) shows a pair of Cu double-layers separated by a single Al layer. This image is a direct support to the earlier suggestion by Sato et al., who reported the same structure using HRTEM observation [3, 22].

Figures 7 (a) and (b) are also HAADF-STEM images of the Al-4.3 wt% Cu alloy. The three dominant parallel lines seen in both the micrographs arise from Cu layers, each of which are separated by four Al (200) spacings, in agreement with the Gerold's model of GP-II. In addition, Fig. 7 (a) shows a bright line, i.e., a Cu layer, about 2 nm in length, on the face of the GP-II, as indicated by the arrows. The spacing between the Cu layer and the GP-II is approximately 0.3 nm, which does not agree with any spacings arising from GP-II, but is close to 0.29 nm, the (002) spacing of the phase. Figure 7 (b) was taken from a different zone in the same sample. In this micrograph, regions of faint alternating contrast were observed on both the faces of the GP-II zone, as indicated by the white arrows. The spacing between the bright contrasts in both the region is 0.59 ± 0.02 nm, which is in fair agreement with the c value of the phase, 0.58 nm [14]. Thus, this HAADF-STEM micrograph indicates that the face of the GP-II can act as a nucleation site for the phase. Hence, our finding here strongly supports the earlier statement by Pennycook and Jesson, who wrote "No structures are excluded, so that unexpected interfacial arrangements, ordering, new interfacial phase, or transition zones will be immediately apparent" [24].

To summarize, we have shown that HAADF-STEM can be effectively used to clarify the structure of GP-zones. The information obtained by HAADF-STEM on the GP-zones is intuitively interpretable; GP-I zones as small as 2 nm in length can be identified among densely populated GP-I zones; a GP-I zone consisting of double Cu layers was also identified. It was also confirmed that so-called GP-II does not always possess the structure suggested by Gerold: a variant does exist, in which a pair of double Cu layers are separated by a single
Al layer. These findings demonstrate that HAADF-STEM is an extremely powerful technique, especially to elucidate the structure of coherent precipitates at the atomic level, where components of the precipitates can not be distinguished easily by conventional techniques.

References


Fig. 6. HAADF-STEM micrographs of the GP-II zones observed in the Al-4.3 wt% Cu alloy. Brighter lines correspond to Cu layers. (a) two Cu monolayers are separated by three Al layers. (b) two Cu double-layers are separated by an Al monolayer. This unusual structure was not frequently encountered, but it does suggest diverse nature of the structure of GP-II.

Fig. 7. HAADF-STEM micrographs of the GP-II zones observed in the Al-4.3wt%Cu alloy. (a) a Cu layer about 2 nm in length is seen on the top of the GP-II zone, as indicated by arrowheads. (b) faint, periodic contrasts with an interval of about 0.59 ± 0.02 nm are seen on both the faces of the GP-II zone, as indicated by the arrows, suggesting that the q' phase nucleates on the faces of the GP-II zone.
Structure of Quasicrystals Studied by Atomic-Resolution Electron Microscopy

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Introduction

The discovery of a metallic phase with symmetries forbidden to ordinary crystals and without any transnational order in 1984 [1], referred to as a quasicrystal, was a revolutionary event for crystallography, because the transnational order had been believed to be essential to generate the diffraction pattern composed of a set of function peaks. This had led to a redefinition of the term crystal to mean any solid having an essentially discrete diffraction diagram, which was declared by the International Union of Crystallography (IUCr) in 1991. Now quasicrystals have been firmly established as one of the well-ordered states of a solid. The central issue has been where atoms are in such a complex, non-periodic structure. Unlike the structure determination of crystals, for quasicrystals it is quite difficult to give a conclusive solution solely based on the diffraction intensity method because several nonperiodic structural models which differ in local atomic arrangements can generate a quite similar intensity distribution (in case of crystals, this is known as homometric structures). This is due to the local isomorphic nature of a quasilattice constructed by a set of multiple unit cells, which is a structural fundamental to describe the quasiperiodic transnational order. Therefore, a direct observation is essentially required for quasicrystals to converge a convincing atomic structure.

Atomic-resolution transmission electron microscopy is powerful to investigate the non-periodic structures in a real space, and thus it has been applied quite effectively for quasicrystal structures [2]. In addition to the high-resolution phase-contrast imaging used conventionally so far, a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with finely focused electron probe (∼2 Å) has recently become of great interest as a kind of atomic-resolution imaging, by which the relatively heavy atom positions emerge out with highlighted contrast in the image due to the Z (atomic number)-contrast nature [3]. This is useful for structural analysis of quasicrystals [4], since most of which are formed as intermetallic compounds with a well-ordered arrangement of different Z atoms. Here we describe the successful application of atomic-resolution phase-contrast and Z-contrast imaging for structural analysis of quasicrystals.

Imaging Basis

Figure 1 shows schematic drawings of principles of atomic-resolution phase-contrast and Z-contrast imaging process. In phase contrast imaging, a parallel beam irradiates the speci-
men, and the image is formed by interference between many beams; in Fig. 1, this is exemplified by direct and one diffracted beams. As well known, the image contrast may reveal an electrostatic potential under the Scherzer defocus condition which realizes the successful - 1/2 phase shift (ideally) of diffracted beams at the objective lens for a wide frequency range to result in totally 0 phase shift at the imaging plane. Hence the projected atomic positions are imaged as dark region; this is achieved only when the sample foil is thin enough (typically less than 5 nm for metallic foils), where weak phase object (WPO) assumption is valid. A spatial resolution is limited by the performance of the objective lens, which is often described by the contrast-transfer-function (CTF). On the other hand, a finely-focused beam with convergent angle of ~10 mrad is used for atomic-resolution Z-contrast imaging. The atomic columns are illuminated one by one as

![Fig. 2](image_url)
the probe scans across the specimen, generating a two-dimensional intensity map of scattered electrons at the annular detector, where the atomic positions always appear to be bright. When detecting the sufficient high-angle scatterings (>~50 mrad at 200 kV), the intensity is dominated by an inelastic, thermal diffuse scattering (TDS) of multiphonon scattering events, based on the Einstein model of independently vibrating atoms. Therefore, to a good approximation, the scattering is assumed as being generated incoherently from individual atoms, so that the image intensity is simply proportional to a sum of the (high-angle) scattering cross sections $TDS\int f^2(s)\left[1 - \exp(-2M\cdot s^2)\right]$, where the $f(s)$ is the atomic form factor, with
interpretation on the TM atom position, though; no significant signal from Al atoms (selective imaging). Thus, it would be difficult to discuss the entire atomic structure solely based on the Z-contrast imaging, even with the present best-resolution STEM [8]. Complementary, Al arrangement is derived from the phase-contrast images in which the image contrast is sufficiently high for the symmetric positions less than 1 Å (three Al at the core of the cluster) was successfully proved by contrast-fitting between the observed and calculated images [6]. This feature was further confirmed by the through-focus phase-contrast imaging; the contrast appearances observed at defocus values different from the Scherzer one were also analysed and are simulated based on the proposed atomic model.

**Zn2Mg12Ho Icosahedral Quasicrystal**

The Zn2Mg12Ho quasicrystal has a 3-dimensional (3D) quasiperiodic structure of an icosahedral symmetry ($m35$, Figs. 3 (a) and (b)). Therefore, in the images the 3D quasiperiodic atomic structure is projected, so that unfortunately we cannot derive the atomic model directly from the image contrasts [10]. Here we describe a verification of the atomic model proposed by X-ray diffraction analysis.

The structural fundamental of the icosahedral quasicrystal is known to be explained well based on the 3D Penrose lattice constructed by two types of rhombohedra. Although the atomic structure of the Zn2Mg12Ho icosahedral quasicrystal has not been fully determined yet, recent single-crystal x-ray diffraction analysis based on hyperspace crystallography have indicated that the Ho atoms sit at the even-body center site of the 3D Penrose lattice [11] (with hyperspace crystallography, the Zn2Mg12Ho is described as a 6D face-centered cubic lattice, resulting in sublattice ordering of the 3D Penrose lattice according to the even-odd parity). Particularly, the analysis has been made via model-free, ab initio method so that the validity of the proposed Ho sites needs to be checked by a direct observation of the real atomic structure. **Figure 3 (c) and (d)** show the high-resolution phase-contrast and Z-contrast images taken along the fivefold symmetry axis, respectively [12]. In the phase-contrast image, all projected atomic positions appear as dark regions, while the Z-contrast selectively highlights the projected atomic columns. As shown by encircled regions, characteristic decagon-contrasts with a diameter of about 1.5 Å are found in the images, indicating a local high-symmetric arrangement of atoms.

We note that the bright spots in Fig. 3 (d) are not pure element columns but actually composed of more than two element, namely, mixed columns, and the Ho is a minor constituent element in the Zn2Mg12Ho compound (Ho content is 10at.%). However, the Ho ($Z=72$) has a remarkably larger atomic number than that of others, Zn ($Z=30$) and Mg ($Z=12$), so that Ho-rich columns are expected to be significantly highlighted (assuming an ideal Z'-contrast condition, Ho contributes to the contrast by about 5 and 30 times stronger than Zn and Mg do). In fact, it was confirmed that the Z-contrast images are explained fairly well by the projected potential of only the Ho atomic arrangement [12]. Consequently, the observation strongly supports a validity of the proposed Ho site as well. The local appearances of the image contrasts are interpreted by the local configuration of Ho atoms, which is represented by a dodecahedron and an icosahedron with bond lengths of 5.44 Å, as shown in **Fig. 3 (e)**, projected atomic positions of which are inserted in the enlarged images located below Figs. 3 (c) and (d). We would point out that the phase-contrast image will be useful for further modeling of the full atomic structure, i.e. searching for the candidate sites for Zn and Mg atoms.

**Summary**

We have demonstrated that the atomic-resolution Z-contrast imaging provides a direct interpretation of the heavy atom position in the quasicrystalline compounds, although the relatively light atoms in the quasicrystalline structures are hardly imaged with the present resolution of STEM. Complementary, the phase-contrast imaging is applied to investigate details on a total atomic arrangement, especially focusing on the local symmetry of the quasicrystals. In the near future, STEM resolution would be significantly improved by equipping a Cs corrector (less than 1.0 Å electron probe is expected with 200kV STEM), by which all the atomic columns including the light atoms might be successfully imaged with Z-contrast mode.

**References**

Lithographic Performance and Mix-and-Match Lithography Using 100 kV Electron Beam System JBX-9300FS

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We evaluated the performance of 100-kV point electron-beam lithography system: JBX-9300FS and developed Mix-and-Match lithography process. Resolution on resist exposure is 30-nm using commercially available chemically amplified resist and is down to 10-nm-order using Calixarene resist. For high-throughput lithography, Mix-and-Match lithography process was developed including pattern preparation, and EB exposure time decreased to 1/3. These process technologies are useful for development of advanced CMOS devices.

Introduction
Recently, for the increase in the performance of logic devices, the feature size of CMOS devices is rapidly decreasing less than 100 nm as predicted by ITRS 1999 (International Technology Roadmap for Semiconductors). [1] Lithography technology is the key to realize sub-100-nm high-performance devices, then several types of high-throughput lithography tools are under development such as F2-excimer laser lithography, EUV (Extremely Ultra Violet) lithography and EPL (Electron Projection Lithography). On the other hand, advanced CMOS devices with a gate length of less than 100 nm should be also developed ahead of mass production. For this purpose, high-resolution point electron beam lithography is only a tool for the research and development of devices on a full wafer.

We have introduced an advanced point electron beam system, JBX-9300FS, which is designed for the development of advanced devices with a small feature size on a large silicon wafer. In this report, the performance of JBX-9300FS on lithography and development of Mix-and-Match lithography are described.

Lithographic Performance
Figure 1 shows a photograph of the first EB column installed at NEC Sagamihara plant. [2] Recently the size of silicon wafers increases with increasing chip size and device density, so that high productivity is obtained and production cost decreases. Currently, 8-inch wafers are used in both R&D and mass production, but 12-inch wafers are being introduced to the semiconductor industry. Research in sub-0.1-μm device continues intensively. In order to obtain high throughput, chemically amplified resists are commonly used in both optical and electron beam lithography. Therefore, it is necessary that a high-resolution electron-beam lithography system can handle a chemically amplified resist and large wafers for next generation process. JBX-9300FS has several advanced or new features to obtain high-resolution, high-accuracy and high-throughput for device development on large silicon wafers. [3] The electron column is operated at an acceleration voltage of 50 kV and 100 kV to obtain small beam diameter of 7 nm for 50 kV and 4 nm for 100 kV with a large deflection field of 1000 μm and 500 μm, respectively. Large deflection field contributes to obtaining high-throughput by reducing a number of stage motions. The maximum deflection clock is over 25 MHz. Dynamic focus and dynamic sigma correction are installed to obtain high-resolution and high-placement accuracy in a large field. An 8-inch wafer is available for full exposure and a 12-inch wafer is laudable. The system has an automatic wafer cassette loader, which can be used with an automatic coater and developer.

Figure 2 shows SEM (Scanning Electron

Fig. 1. First JBX-9300FS was installed at NEC Sagamihara plant in Japan. EB system is combined with in-line developer.
Microscope) photographs of negative resist, NEB22A3 (Sumitomo Chemical Co.) for a gate fabrication and positive resist, UV5 (Shipley Co.), for contact holes exposed by 50 kV electron beam. 30-nm-width line pattern and 100-nm-diameter-hole pattern were delineated. Commercially available chemically amplified negative resist has a resolution down to 30-nm.

We have investigated a mechanism for resist resolution and have developed a new type of resist, called calixarene. [4] We found that the resolution of an organic negative resist depends on the molecular size of its composed material of resist. [5, 6] The average molecular weight of an usual negative resist ranges from several thousands to several tens thousands and its molecular size or diameter ranges from a few nanometers to several tens nanometers. This resist shows a resolution of only ten nm. [7] It is important to obtain low molecular weight resin for high resolution. The roughness of the resist pattern is affected not only by molecular size of the resist but also by dispersion. [8] Calixarene resist pattern and its chemical structure is shown in Fig. 3. Calixarene used in this experiment consists of 6-phenol ring and has a low molecular weight of 972 with almost monodispersity. 10-nm-order resist pattern is delineated exposed at 100 kV. The resist shows ultrahigh resolution and high durability under halide plasma etching using HBr, CF₄, and Cl₂. Exposure characteristics are shown in Fig. 4. Sensitivity decreased as an acceleration voltage increased from 50 kV to 100 kV as a factor of 1.7. On the other hand, contrast is improved when an acceleration voltage of 100 kV compared with that at 50 kV. The sensitivities are same for the thickness of 35 and 100 nm due to high acceleration voltage.

We measured a deposited energy distribution at 50 kV and 100 kV on silicon wafer for proximity effect correction. We irradiated electron beam on NEB22A3 negative resist on silicon wafer without deflection. The deposited energy distribution in arbitrary unit is shown in Fig. 5. The deposited energy distribution curve for 100 kV near the beam-irradiated point is sharper and lower than that for 50 kV. This means a small forward scattering range and then a possibility of high-resolution patterning. The deposited energy distribution for 100 kV at around 10 μm is lower than that for 50 kV. This region of deposited energy depends on backscattered electrons. This deposited energy affects a long-range proximity effect. According to the results, proximity effect for 100 kV is smaller than that for 50 kV, therefore it has a possibility that high-density, high-resolution patterning is delineated by using 100-kV electron beam.

Mix-and-Match lithography

Point electron beam exposure has the advantage of high resolution, but has the disadvantage of low throughput. Therefore, EB lithography is applied for the specific layer including fine patterns such as gate layer, which cannot be delineated by optical lithography and the other layers including no fine patterns are delineated by the optical lithography. This strategy is called as Mix-and-Match lithography. [9,10,11] In this lithography, there is a problem of overlay error between patterns exposed by EB and optical lithography (stepper). JBX-9300FS has a feature called stepper distortion correction. When using this feature, distortion of field (or chip) exposed by a stepper is measured in advance and measured distortion data is stored in JBX-9300FS. Differences to an ideal position in a stepper exposure field of KrF stepper is about 30 nm for both x and y direction. When EB exposure, exposed patterns (or EB field) are distorted to be as same as that exposed by a stepper. Then high overlay accuracy is obtained between layers exposed by EB and by optical stepper. In Fig. 6, overlay error between patterns exposed by EB and by optical stepper with and without stepper distortion correction are shown. Due to the correction, overlay error distribution decreased from 35 to 20 and 28 to 15 nm in x and y direction, respectively. The residual average overlay error was observed due to insufficient calibration, and it can be reduced because of stable error value.

Other type of Mix-and-Match lithography is that one pattern layer is exposed by EB and optical stepper to obtain high-throughput. We call Intra-level Mix-and-Match lithography.[12] A pattern data in the same layer is divided into two, then one pattern data includes fine patterns smaller than a threshold length L₀.

![Fig. 2. Line pattern using negative resist, NEB22A3 on polysilicon layer (a) and UV5 (b) on silicon wafer exposed by 50 kV, 400 pA EB. Both are chemically amplified resist. Exposure doses are 48.4 μC/cm² for NEB22A3 and 28 μC/cm² for UV5.](image)

![Fig. 3. High-resolution calixarene resist pattern exposed at a dose of 100 mC/cm² by 100 kV, 400pA beam. Resist thickness is 35 nm. Design width is 5nm.](image)

![Fig. 4. Exposure characteristics of calixarene resist exposed at 50 kV and 100 kV. Resist sensitivity decreased as a factor of 1.7, but contrast increased.](image)

![Fig. 5. Deposited energy distribution on silicon wafer at 50 and 100 kV.](image)
as a criterion for EB exposure and the other pattern data includes rough patterns larger than Ls for optical stepper. In this Mix & Match lithography, it is desirable that a resist used can be exposed both by EB and optical stepper. NEB22A3 chemically amplified negative resist has high sensitivity both for EB and optical exposure, then this resist was used in our experiments.

Because there is an intrinsic pattern placement error due to each exposure tool, it is necessary to add supplementary pattern to avoid detachment between patterns exposed by EB and stepper. We developed a method to generate a supplementary pattern (overlap margin) by logical operation on figures using CAD [11]. A generation process is described in Fig. 7(a). We use ‘L’ shape overlaps to avoid detachment both in x and y directions. First, we divide a pattern into EB and optical patterns by using threshold length Ls, for example, 0.16 μm. Then, we move one pattern in ∆W and extract an overlap area as an overlap. Next, we move the overlap in opposite direction in ∆W and enlarge the overlap in ∆L, and extract an overlap area again. The value of ∆W and ∆L is decided according to a relative positional error in x and y direction between EB and optical stepper. Finally, we move these overlaps in ∆W and merge the overlaps and the divided pattern. The feature of this method is that there is no pattern size limitation, and we can handle fine patterns less than ∆W. The exposed resist pattern by Mix-and-Match lithography using this overlaps generation method is shown in Fig. 7(b). Large rectangle area for a gate pad and a fine line pattern for gate electrode were exposed by KrF stepper and point EB, respectively. Fine line pattern with a width of 40 nm without detachment was obtained.

The effect of Mix-and-Match lithography is shown in Fig. 8. Exposure area for EB decreased in 1/6 compared with an area for EB when exposed by EB exposure only. Exposure time for EB decreased in 1/3. This discrepancy in reduction ratio is due to blanking time, settling time of EB and stage motion.

**Summary**

We show lithographic performance of an advanced point electron beam system JBX-9300FS. This EB exposure system is designed for development of advanced CMOS devices with several features such as high acceleration voltage of 100 kV, large deflection field, high beam clock speed, dynamic focus/stepper correction and stepper distortion correction. Fine negative resist pattern with a width of 30 nm and positive contact hole pattern with a diameter of 100 nm were obtained. We also show 10-nm-order calixarene resist pattern. We developed Mix-and-Match lithography process to increase throughput without the sacrifice of resolution. Nanolithography using JBX-9300FS is useful for development of minute devices such as CMOS and single-electron transistors.

**References**


![Fig. 6. The effect of stepper distortion correction is shown. Distribution of overlay error is improved by the correction.](image)

![Fig. 7. (a) Process for adding overlap patterns. (b) Resist pattern exposed by Mix-and-Match lithography using EB and KrF.](image)

![Fig. 8. The effect of Mix-and-Match lithography is shown. Exposure area for EB decreased in 1/6, and exposure time for EB decreased in 1/3.](image)
The Remote Control Scanning Microscope with Web Operation Interface (WebSEM)

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Introduction

Recently, a network has started to be used in observation instruments centered on an SEM (scanning electron microscope) for various purposes such as compiling the observed images into a database. In order to utilize such a network for integrated control of the results obtained from an observation/analytical instrument including an SEM, and also to perform observation efficiently, it has become necessary for operators and administrators (using client PCs) to share data. For this reason, it is necessary to be able to observe images from an SEM, or to operate the SEM, from a remote site. To meet these requirements, we have developed a system for remotely controlling an SEM connected to a network.

In order to perform the remote control of an SEM, we have constructed a system based on the concepts set out below.

- The SEM can be operated on the client PC with the user interface constructed on a WEB Browser, regardless of the model of the SEM.
- The system can support multiple customers without installing special software on their client PCs.
- The client PC on a network can be connected easily to the SEM from anywhere.

Based on the above concepts, we have developed a remote control system for the SEM, which enables the SEM images and the SEM control functions to be displayed on a WEB Browser in an external client PC.

In this system, the operation interface is displayed on a WEB Browser; therefore, the SEM can be connected and controlled from anywhere at all, provided that a generally used browser (IE: Internet Explorer) is installed in the PC.

This system can be connected to FE (field emission) SEMs (JSM-6700F/6500F/6335F) on which an FE gun is installed, or with SEMs employing a thermal electron gun (JSM-5900/5900LV, JSM-5600/5600LV and JSM-5500/5500LV), from a client PC.

We have named this remote control system “WebSEM”, based on the above concepts.

Configuration of the WebSEM System

We describe the method of controlling the JSM-6700F that is connected to a LAN (Local Area Network), from a client PC that is connected to this network. Figure 1 shows a diagram of the hardware configuration in which the SEM is controlled from a client PC using a LAN.

The SEM, which is the server side, is connected to a video server for transferring live images, and is also connected directly to the LAN to permit communication between the SEM and the client PC. The client PC is connected to the network. If necessary, the simple operation panel can be connected to the serial port. Thus, at the server (SEM) side, it is necessary to add hardware to a standard SEM for image transfer and communication, however the client PC side does not need any special hardware. Also, the software necessary at the client PC side can be transferred from the server; therefore, there is no need to provide any special software in advance like the case of the hardware.

Figure 2 shows the contents of the signals for communication between the SEM (server) and the client PC. Both the image transfer part and the SEM control part of the JSM-6700F are connected to a LAN. In order to display the SEM image as a live display with 640 × 480 pixels, which is used as a means of high-quality image transfer via networks in the current image-transfer technologies, the original image with 1280 × 1024 pixels is resized to 640 × 480 pixels using a scan converter. The image signals are connected to a video server intended exclusively for image transfer, and the images are transferred from the video server to the client PC via the LAN.

As for the SEM control, in the WEB Browser environment, the SEM is controlled by command-level communication between the client PC and the SEM. The interface for SEM control is displayed on the WEB Browser on the client PC, as shown in Fig. 3. The user interface consists basically of an SEM image display and the SEM control part. The SEM live image is displayed at 640 × 480 pixels. In this case, the OS (operating system) used in the client PC is Windows 2000 (or Windows NT), which is a standard OS having good capabilities of network security and stability.

The live image displayed on the client PC consists of 640 × 480 pixels, which is sufficient for observation or image adjustment (such as focusing). The saved image needs to have higher image quality or more information in the image (image density). To permit observation with higher quality, it is necessary that an image consists of 1280 × 1024 pixels. To achieve this, the WebSEM has been designed to provide the functions as follows (shown in Fig. 2). When an operator performs the image-saving operations from a client PC, a high-quality image is saved in the

Fig. 1. The block diagram of WebSEM remote control system with JSM-6700F.
hard disk on the SEM (server) side, and then it is automatically transferred to and saved in the client PC. A high-quality image is automatically saved on the client PC when the operator at the client PC just specifies the save button. Thus, it is possible to observe a live image and also acquire a high-quality saved image with comfortable operations.

**User Interface**

In the WebSEM, we have constructed a user-interface screen on the WEB Browser in an SEM to permit the SEM control from any PC connected to the LAN. Figure 3 shows the graphical user interface (GUI). The WebSEM utilizes the GUI that is used in the JSM-6000 series and JSM-5000 series. This screen features a configuration that enables the SEM to be controlled by a mouse operation alone. The method of operating the user interface is described below. It is roughly classified into button operations and dragging operations using the mouse.

Figure 4 shows the setup buttons for the column, image adjustment and observation conditions. The menu part has image-saving button, scanning-speed select buttons, image freeze ON/OFF button, magnification select buttons, and auto function buttons. These button functions are used mainly for controlling a live image.

Beneath this group of buttons is the section used to adjust brightness, and focusing/astigmatism correction of the image. Operations of this image-adjustment section are made according to the method shown in Fig. 5. Figure 5 shows an example of contrast adjustment. To adjust the contrast, first click the mouse button at the contrast button, and a cursor will appear on the image screen. Next, drag the mouse up or down while keeping the mouse button pressed to change the contrast. At this time, the left mouse button is assigned to “fine step”, and the right button to “coarse step”. These buttons are used as necessary.

These operations can be used to other functions such as focusing, and each item is subjected to the adjustment on a live-image screen.

The button group on the right of the user interface of Fig.4 is used mainly to set the observation conditions. Using them, setting of the accelerating voltage including ON/OFF switching, magnification and other items are carried out. Clicking one of these buttons displays a setting dialog box shown at the right of Fig.4 (in the case of accelerating voltage). The Accelerating Voltage is selected from this dialog box, and then clicking the OK button completes the selection.

As described above, the basic operations of the SEM are performed using the buttons shown in Figures 4 and 5. When observing an image from a client PC under preset observation conditions, it is necessary to use the setup button shown at the right side of Fig.4. Selecting this setup button permits a direct setting of preset observation condition in a single operation. This is a very effective method for observing a specimen when the observation conditions for the specimen are known in advance.

By clicking the save button after setting the conditions for observation and image adjustment, a high-quality image can be saved (acquired) in the client PC automatically. After these operations, this image can be printed from the same client PC.

This system has a function of automatic stage shift. When the client clicks the right mouse button at the observing object on the observation-image screen to which the client wants to shift the stage, the position of the stage moves to the center of the observation image on the screen. The feature of this function is that the specified position always comes to the center of the screen. The image refresh speed depends on the traffic capacity of the server PC.
of the LAN. Therefore, this stage-centering function is useful for the client PC even when the image refresh is delayed.

**Operation Panel**

It is also possible to install an exclusive operation panel (Fig.6) on the client PC. The use of this operation panel provides the client with the feeling of directly operating the SEM, even when operating it on the client PC, thus improving operability. This is a particularly useful method for persons who are not familiar with controlling the SEM using a mouse. In consideration of operability, the operation panel is the same as that of the JSM-6700F and its functions are limited to those shown in Fig.6, including magnification, focusing and other items. However, since it is installed on the client PC side, the type of PC that can be used to perform SEM operations are limited.

**Application Example**

The following is an example of application of the WebSEM. **Figure 7** shows the case of a clean room. The outside client PC controls the SEM that is installed inside a clean room. There are many cases in which operating the SEM in a clean room is important, but it is difficult to enter the room frequently. In the case of an SEM that is installed in such a place, the administrator PC is connected to the SEM when information on the observed specimen needs to be exchanged between the SEM operator and the administrator.

By connecting the client PC to the SEM, the client can observe the same image as that seen by the SEM operator, in real time. This enables the client to confirm the image information with each other. Also, as necessary, the administrator can operate the SEM and give instructions. These operations allow information to be shared at all times. In addition, prompt action can be taken if a problem is found in the specimen, thus permitting efficient work.

As a demonstration of the remote control system, at the Annual Meeting of Japanese Society for Electron Microscopy held between May 10 and 12, 2001 we operated an SEM using ISDN (8 lines used at a speed of about 1Mbps) over a distance of about 900 km between Fukuoka (the conference site) and Akishima (JEOL). (Fig.8)

**Summary**

We have completed the WebSEM that provides a user interface for SEM control and SEM image observation built on a WEB Browser to enable the SEM to be remotely controlled.

This system has many potential applications, such as the following.

- It is possible to observe SEM images and control the SEM regardless of its model, from any PC whatever.
- When the SEM is installed in places such as a clean room where entering is difficult, it is easily possible to check the SEM image from outside and issue instructions to the SEM that is inside the place.
- It is possible to carry out SEM education including operation training at an external site.

Amidst of the rapidly evolving network environment, it is expected that the remote control WebSEM system using networks will be increasingly utilized to a variety of fields in the future.

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**Fig. 6. Operation panel for client PC.**

**Fig. 7. Application example of WebSEM.** Sharing of the information with the place inside and outside (for example Clean Room).

**Fig. 8. WebSEM remote control demonstration performed at Annual Meeting of Japanese Society for Electron Microscopy (9 to 12, May, 2001).**
High Precision Optical Coating Deposition System: NBPF-2

Bin Fan and Daiyu Son
OPTORUN Co., Ltd.

By taking advantage of rapid development of fiber optical communication, the optical coating technology has been improved greatly in recent years. A long-term stable, high deposition rate, high-precision real-time optical thickness control coating system becomes key equipment to make the filters for fiber optical communication application. In this paper, NBPF-2, an ion assisted deposition (IAD) based electron beam (EB) evaporation system has been introduced. Some special filters, such as 50 GHz DWDM Filter, Add Drop Filter and Gain Flattening Filter, which consist of hundreds of layers had been deposited with NBPF-2. The critical requirement for coating deposition system has been discussed in this paper.

**Keyword:** Optical Filters, IAD, EB Evaporation, Long-term Stability, Optical Monitor System.

1. Introduction

Rapid development in scientific and technological applications, especially the fiber optical communication, needs a lot of optical filters with special requirements. These optical filters consist of tens or hundreds of layers. It is usually made of two or more materials in which the thickness of the individual layers should be well controlled. The filters should be stable against exposure to the atmosphere or high power density fields. It means these filters must have a good microstructure and the coating materials should be environmentally stable. Since these filters should be easily reproducible from run to run in mass production, a long-term stable, high deposition rate, high-precision real-time optical thickness control coating deposition system becomes key equipment to make these filters.

In order to meet these requirements, a lot of coating engineers and scientists have been involved in this field and a large array of techniques is used to deposit optical coatings in recent years. IAD (Ion Assisted Deposition), APS (Advanced Plasma System) and IBS (RF Ion Beam Sputtering) are three commonly used energetic processes to deposit environmentally stable filters. IAD and APS processes use electron beam to evaporate the coating materials and use an ion source or a plasma source to assist the deposition. The benefit of using IAD and APS processes is that they can provide a high deposition rate and good uniformity. The filters made by these processes have an amorphous microstructure and low stress. Comparing with IAD process, APS process usually introduces a high insertion loss. The disadvantage of using IAD or APS process is poor repeatability. The uniformity and optical constant have a little shift from run to run. IBS process uses ion beam to bombard the target material and deposit the coating material on the substrate. IBS process has a very steady deposition rate and optical constant of coating material can repeat from run to run. But its low deposition rate, poor uniformity and high stress restrain the application of this process. In some situations, IAD process is the best one comparing with APS and IBS process.

In section 2, an IAD based EB evaporation system, NBPF-2, was introduced. Some special filters and the critical requirement for produc-

Fig. 1. Schematic alignment of NBPF-2.
ing these filters were discussed in section 3. Finally, the result was summarized in section 4.

2. IAD Based EB Evaporation System

In order to deposit the filters for fiber optical communication applications, an IAD-based system, NBPF2, was developed by OPTORUN Co., Ltd. This system includes two oil diffusion pumps and one Polycold which can evacuate the system from atmosphere to 1.3 × 10⁻⁹ Pa in 15 minutes. The automatic evaporation system is composed of two EB sources (JEOL) and one 16 cm type ion source (Ion Tech). The crucible of high and low material can rotate from 5 min/circle to 2 hour/circle. Usually, Ta2O5 and SiO₂ are used as high and low refractive index materials. About 3 kilogram Ta2O5 is pre-melted before evaporation. Substrate temperature and chamber temperature are controlled by two heating systems. The substrate is rotated by a magnetic sealed servo motor. The maximum rotation speed of substrate is about 1000 rpm. The deposition rate and physical thickness of evaporation are controlled with a six-piece exchangeable quartz crystal monitor. The optical thickness is controlled with an optical monitor system (transmittance mode) by measuring the substrate directly. The schematic alignment of the system is shown in Figure 1.

3. The Critical Requirement for Producing DWDM Filters

Numerous optical filters are used in fiber optical communication systems. Some filters widely used are listed in Table 1.

NBPF2 is specially designed for producing optical filter used in fiber optical communication. It must meet some critical requirements for producing these filters.

Long Term Stability of Deposition System

The filters used in fiber optical communication systems, such as 50 GHz DWDM Filters, Optical Add Drop Filters, usually consists of hundreds of layers. The coating process time of these filters need tens of hours. The specification of these filters needs a non-stop process. It means there are enough materials to deposit hundreds of layers in one batch run. And during the evaporation, the hardware trouble, such as arcing of the EB Gun, shutdown of Ion source must be avoided. NBPF-2 uses JEOL’s EB gun as an evaporation source. Since JEOL’s EB gun and power supply are specially designed, it effectively avoids the arcing during the coating process.

Substrate Temperature

The pass bandwidth of 50 GHz DWDM filter is only 0.3 nm. A little temperature variation will cause the center wavelength of the filter to shift despite the fact that a special substrate was used. And finally, this shifting induces a disappearing of optical monitor signal. NBPF-2 uses two loops PID heater control system. It can control the substrate temperature in 1°C.

Thickness Monitor System

The thickness monitor system is the most important factor to make DWDM filters. There

<table>
<thead>
<tr>
<th>Band Pass Filters</th>
<th>Edge Filters</th>
<th>Special Filters</th>
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<tbody>
<tr>
<td>50 GHz</td>
<td>0.98 Pump Filter</td>
<td>Gain Flattening Filter</td>
</tr>
<tr>
<td>100 GHz</td>
<td>1.48 Pump Filter</td>
<td>Dispersion Compensation</td>
</tr>
<tr>
<td>200 GHz</td>
<td>LWPF B</td>
<td>cam Splitter</td>
</tr>
<tr>
<td>400 GHz</td>
<td>SWPF</td>
<td>ASE Filter</td>
</tr>
<tr>
<td>Blue/Red Splitter</td>
<td>C/L Splitter</td>
<td>AR Coating</td>
</tr>
<tr>
<td>C/L</td>
<td>Splitter</td>
<td>PBS</td>
</tr>
<tr>
<td>Coarse WDM</td>
<td></td>
<td>Interleaver</td>
</tr>
<tr>
<td>Add Drop Filter</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The optical filters used in fiber optical communication system.

![Fig. 2. Some important parameter of optical monitor system.](image)

![Fig. 3. Uniformity of 3 cavity 100 GHz DWDM filter in 84 mm diameter.](image)
are two kinds of thickness monitor systems. One is an optical thickness monitor system. The other is a quartz crystal monitor system. Wavelength resolution, signal-to-noise ratio and long-term stability are most important specification for the optical monitor system. Wavelength resolution determines the minimum bandwidth of the filter which the optical monitor system can monitor. Signal-to-noise ratio and long-term stability of the optical monitor system determines how accurately the system can operate. Figure 2 shows some important parameters of OPTORUN’s optical monitor system. NBPF-2 uses an optical monitor system to control the optical thickness of sensitive layer and uses a quartz crystal monitor to control the deposition rate and the thickness of insensitive layer. By this thickness monitor system, OPTORUN Co., Ltd produces the 50 GHz DWDM filter automatically.

Uniformity

Uniformity is very important parameter for mass production of optical filters. It has a complex relationship with the system structure, vacuum pressure, EB gun spot size, ion beam current distribution and so on. Good uniformity not only improves the yield of every run, but also improves the monitor accuracy of the optical monitor system. Figure 3 and Figure 4 illustrate the relationship of uniformity and optical monitor system.

By adjusting the ion source and EB spot size, OPTORUN improves the uniformity of 100 GHz DWDM filter from 6nm to 3nm in 95 mm diameter.

Some Optical Filters Produced with NBPF-2

Figure 5 shows the transmittance spectrum of five-cavity 184-layer 50 GHz DWDM filter produced with NBPF-2. The pass bandwidth at 0.5dB loss point is more than 0.27 nm and the isolation bandwidth at 25 dB loss point is less than 0.55 nm. The insertion loss of this filter is less than 0.5 dB. The pass band ripple is less than 0.2 dB. This filter is automatically deposited by NBPF-2 for 16 hours. The result illustrates that NBPF-2 has a good performance in long-term stability, deposition rate and thickness monitor system.

Figure 6 is one Gain Flattening Filter produced with NBPF-2. The insertion loss error function of the filter is about 0.3 dB. We use our optical monitor system to control the quarter wavelength and non-quarter wavelength directly. It illustrates that NBPF-2 has a good long-term stability.

Figure 7 is four consecutive batches produced with NBPF-2. It shows that NBPF-2 has a good repeatability.

The transmittance of 100G 4C filter was measured at the monitor position:

- Batch1: BW@0.5dB=0.47, BW@-25dB=1.08 nm, CWL=1549.72 nm;
- Batch2: BW@0.5dB=0.47, BW@-25dB=1.09 nm, CWL=1549.71 nm;
- Batch3: BW@0.5dB=0.47, BW@-25dB=1.09 nm, CWL=1549.70 nm;
- Batch4: BW@0.5dB=0.46, BW@-25dB=1.10 nm, CWL=1549.70 nm.

Fig. 4. Uniformity effect on optical monitor system (Light spot size = 2mm).

Fig. 5. Five-cavity 184-layer 50 GHz DWDM filter produced with NBPF-2.

Fig. 6. Gain flattening filter produced with NBPF-2.
4. Conclusion
Some special optical filters have been deposited by OPTORUN’s IAD-based NBPF-2 system. It illustrates that NBPF-2 has a good performance in long-term stability, deposition rate and thickness monitor system.

5. About OPTORUN
OPTORUN Co., Ltd. designs, manufactures and distributes precision vacuum deposition systems for optical fiber communications. OPTORUN has grown rapidly in the fiber optic industry since it was found on 25th Aug. 1999.

It delivered the first version of DWDM filter deposition system in February 2000 and produced the first 100GHz DWDM filter in March 2000. OPTORUN has shipped a total of 27 deposition systems to DWDM filter manufacturers worldwide so far.

OPTORUN spends 15% of its sales amount in research and development. The R & D includes development of high-resolution and low-noise optical monitors, thickness control software, and critical thin films. OPTORUN is one of very few manufacturers that can demonstrate and deliver process of the making of 50/100 GHz filters and Gain Flattening Filters.

OPTORUN’s primary manufacturing facility is located in 10-1 Takeno, Kawagoe-city, Saitama, Japan.
The Latest Analytical Method and Future Potential with In-lens Thermal FEG

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Introduction
We developed a new field emission scanning electron microscope (FE SEM), Model JSM-6500F, which has an in-lens thermal FEG and is based on the concepts of multi-purpose and high-resolution observation and analysis. It has undergone improvement mainly in respect of spatial resolution. At present, a spatial resolution of 1.0 nm can be realized at an accelerating voltage of 15 kV, and a spatial resolution of 2.2 nm can be realized even at an accelerating voltage of 1 kV, by using a cold field emission gun (C-FEG) that has a small energy spread and also a semi-in-lens type objective lens.

The method of performing analysis using an FE SEM on which a C-FEG is mounted is restricted to quantitative and/or qualitative analysis by means of energy dispersive X-ray spectrometry (EDS). This is because it is in practice impossible to make use of the C-FEG for analysis using wavelength dispersive X-ray spectrometry (WDS) or cathode luminescence (CLD) because the maximum probe current of the C-FEG that can be obtained is no more than several nA, it is essential to perform flashing once every 10 hours or so, and also a stable probe current cannot be maintained over a long period.

Also, analysis using an EDS is limited to a high accelerating voltage; hence the excitation area of the X-rays widens, making it difficult to perform microscopic area analysis that effectively utilizes the characteristics of the FE SEM.

Recently, however, in various fields including the semiconductor field, it is becoming increasingly necessary to perform not only observation but also analysis of more microscopic areas, and the appearance of an FE SEM that is intended mainly for analysis is eagerly awaited.

In the case of an FE SEM that is intended for analysis, it is absolutely essential that a large probe current be obtained, and also that the probe current be stable. In order to ensure analysis over a more microscopic area, a finely focused electron beam is required even when the probe current is large.

Development of the In-lens Thermal FEG
An in-lens thermal FEG effectively combines a Schottky field emission electron gun and a first stage condenser lens (CL1) in order to efficiently condense the electron beam emitted from the emitter and provide a probe current of 200 to 400 nA. Figure 1 shows the difference between an in-lens thermal FEG and a conventional FEG. In the case of an in-lens thermal FEG, CL1 is directly beneath the FEG emitter, enabling a large probe current to be obtained efficiently. On the other hand, in the case of a conventional FEG, the electron gun emitter and CL1 are separated from each other; hence it is not possible to adequately condense the electron beam emitted from the emitter.

As a result of the adoption of an in-lens thermal FEG, the JSM-6500F can provide a probe current of 200 nA, which is 10 times that of a conventional SEM that uses a thermal FEG.

Also, if the aperture angle (θ) of the objective lens is optimum (optimum 0), the spatial resolution when a large probe current flows in the FE SEM will be affected by the spherical

Fig. 1. Comparison of In-Lens Thermal FEG and Conventional Thermal FEG

Fig. 2. SE image under analytical conditions.
Acc.V: 15kV, Ip.: 5nA, WD: 10mm

Fig. 3. SE image taken with a large probe current.
Acc.V: 15kV, Ip.: 100nA, WD: 10mm
shows 15kV, Ip.: 5nA

**Figure 4.** Probe current stability of JSM-6500F. Acc. V : 15kV, Ip : 5nA

![Fig. 4. Probe current stability of JSM-6500F.](image)

This shows a secondary electron image obtained under analytical conditions. We confirmed that the spatial resolution was 3 nm under conditions that are often used for analysis (accelerating voltage 15 kV, probe current 5 nA, and WD 10 mm). Figure 3 shows the observed image of evaporated gold particles that were deposited using an accelerating voltage of 15 kV, a probe current of 100 nA and a WD of 10 mm.

The Schottky field emitter used as the electron source features high brightness, small energy spread, and good stability [3]. The results of evaluating the stability are shown in Figure 4. We confirmed that the stability after 13 hours under conditions frequently used during analysis (accelerating voltage 15 kV, probe current 5 nA) was 1% or better.

**Application Example**

The following are examples of data obtained for applications that require a large probe current.

**Electron backscattered diffraction (EBSD)**

An EBSD is an instrument that has been attracting much attention recently in various fields. It assigns an index to the crystal orientation of a specimen. The general observation conditions used in an EBSD are an accelerating voltage of 15 kV to 25 kV and a probe current of 0.5 nA to 10 nA.

Conventionally, when performing EBSD analysis, a multi-purpose SEM (W-SEM) that has a tungsten hairpin filament is used because a large probe current and long acquisition time are required to perform measurement. However, in a W-SEM, the beam diameter under the above observation conditions increases to above 50 nm; hence it is not possible to obtain a pattern in the case of a specimen that has microscopic crystal grains such as subgrains.

Figure 5 shows an example of the results of EBSD analysis, which can only be obtained with an FE SEM. The results shown here are for a cross-section of cold-rolled steel. Steel sheet used in various fields such as the automobile industry is required to have excellent forming ability; hence the crystal orientation at the cold-rolling and heat treatment processes is controlled.

**Example of application to wavelength dispersive X-ray spectrometry**

In WDS, the probe current must be 100 nA or more and the beam must have a stability of 1% or lower per hour. In an FE-SEM installed with a C-FEG, it has been difficult to satisfy these conditions.

The JSM-6500F can meet these conditions. Figure 7 shows a measurement example obtained using the JSM-6500F.

This specimen is black ore (Fig.7(a)) which includes a layer that contains Pb and S. In EDS, the Pb and S peaks overlap each other, as shown in Fig.7(b). In WDS, the peaks are separate, as shown in Fig.7(c).

In this way, WDS, which has high energy resolution, permits quantitative and qualitative analysis of elements, including those that cannot be separated by EDS.

**Example of application to energy dispersive X-ray spectrometry**

EDS is the most commonly used method of analysis in an FE-SEM that has a C-FEG. The characteristic X-rays emitted from the specimen are generated from a range that depends upon the specimen and the accelerating voltage. Consequently, the lower the accelerating voltage, the smaller is the area over which analysis can be performed.

However, with the C-FEG, the probe current obtained at a low accelerating voltage becomes
small, preventing adequate sensitivity from being obtained, during EDS analysis.

This instrument permits adequate probe current to be obtained, even when the accelerating voltage is reduced to the lower limit at which X-rays are generated. As a result, superficial parts of the specimen, that is, areas where the X-rays are not dispersed, can be mapped.

**Figure 8** is a two-dimensional image of a lava from Miyake Island in Tokyo, Japan. **Figures 9(a) to (c)** are the results of EDS mapping of O, Mg and Al measured at an accelerating voltage of 15 kV and a probe current of 1.8 nA. **Figures 10(a) to (c)** are the results of EDS mapping of O, Mg and Al measured at an accelerating voltage of 5 kV and a probe current of 2.8 nA.

Thus, a large probe current can be obtained at a low accelerating voltage, enabling a sharp map to be obtained in a short period, even when mapping on the light element side where the image becomes blurred at a high accelerating voltage.

**Other conceivable applications**

The finely focused large probe-current electron beam available with this instrument can conceivably be used in many applications such as electron-beam pattern writing and CLD.

**Conclusion**

By using this in-lens thermal FEG, we were able to obtain a maximum probe current of 20 times that of a conventional thermal FEG. Because we were able to obtain a large probe current with an FE SEM, it is now possible to perform analysis using WDS, EBSD, and CLD, in addition to EDS.

By using the above-mentioned instrument that has a high spatial resolution and is capable of obtaining a more stable and large probe current, it is now possible to analyze the structure of a microscopic area of a specimen that could only be morphologically observed, but not analyzed, using a conventional instrument.

**References**

Application of Cathodoluminescence to EPMA

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†Application & Research Center, †Electron Optics Division, JEOL Ltd.

Introduction
Cathodoluminescence (CL) is a method conventionally used to analyze the crystal structure of a specimen [1], including trace impurities, lattice defects and crystal distortion. A CL collecting mirror and spectrometer are installed in a transmission electron microscope (TEM) or a scanning electron microscope (SEM), and analysis is performed over a minute area of the specimen. Large amount of analysis data concerning this method have been published. Recently, many reports of CL analysis using electron probe microanalyzers (EPMA) can also be seen. The cathodoluminescence device we introduce here is installed in an EPMA, and allows uniform CL analysis without lowering the quality of secondary electron images, backscattered electron images, and X-ray images obtained with a wavelength dispersive spectrometer. We intend to provide information from the specimens using both EPMA and CL data. In this paper, we introduce the spectrometer-type CL device installed in the JXA-8800 series and also some of the data obtained by the use of this device.

Principle and Features of Cathodoluminescence Method
Near infrared ~ visible light ~ near ultraviolet light generated when an electron beam irradiates a specimen is called cathodoluminescence. Characteristic X-rays analyzed using EPMA mainly are originated from the excitation of inner-shell electrons (100eV to 10keV), while CL is emitted by the excitation of the valence band or the molecular orbital (up to several eV). In the case of a semiconductor specimen, the CL energy is equivalent to the energy gap between the conduction band and the valence band. In the cathodoluminescence spectrum, various factors cause the level overlap. Conceivable reasons for this include the difference in crystal structures or compositions, the generation of impurity level, and the generation of trapping level due to lattice defects. Among these factors, the electron transition accompanying light emission makes the CL signal. A schematic diagram showing various signals obtained when an electron beam irradiates a specimen surface is shown in Figure 1.

The followings are the features of the CL method. They are not obtainable with EPMA.
- It is possible to analyze the distribution of trace impurities and also the distribution of defects. In the case of a semiconductor specimen, donor and acceptor elements are doped in order to form the PN junction. The highest concentration of these elements is of the order of several ppm, which is too low to permit element analysis using EMPA.
- It is possible to perform measurement over a minute area as small as that in characteristic X-ray analysis. In the case of a bulk specimen analyzed with EPMA, the characteristic X-ray distribution at the normal accelerating voltage has a spread of about 1 μm. In the case of CL as well, it is considered that as a rough guide the spread is about 1 μm, that is, of the same order as in EPMA [2]. Actually, CL is easily excited by scattered electrons and continuous X-rays in the EPMA instrument. Therefore, the CL emission range is wide. When a CL device is installed in a TEM and the CL distribution of a thin-section specimen is observed, as the area of scattered electrons in the thin film is small, the spatial resolution of the order of nanometer can be obtained. In the case of a bulk specimen, since the accelerating voltage used for normal EPMA analysis (several to 30 kV) will be much higher than the energy of CL, the CL excitation efficiency is independent of the accelerating voltage, and so the depth profile of CL can be easily obtained.
- Considering various conceivable factors involved in the CL generation process, it is extremely difficult to analyze the data and prepare the specimen. For example, when performing CL observation of the cross-section of a light emitting diode (LED) specimen (we will describe later), it has been found that CL did not appear along the streak left by the polishing.
- EPMA enables the analysis of a variety of

<table>
<thead>
<tr>
<th>Material field</th>
<th>Example of application of CL method</th>
</tr>
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</table>
| Semiconductor devices | - Device characteristics  
- Wavelength of emitted light  
- Distribution of trace defects and impurities in the specimen |
| Optical fiber | - Change in refractive index  
- Distribution of trace defects |
| Fluorescent materials | - Wavelength of emitted light  
- Identification of emitted area  
- Distribution of each light-emitting particle |
| Ceramic materials | - Distribution of grain boundaries and defects in sintering |
| Minerals, rocks | - Distribution of trace impurities  
- Structural non-uniformity  
- Stress distribution in minerals |
| Steel materials | - Analysis of oxide inclusion  
- Observation using luminescent dye |
| Biological specimens |

Table 1.

Fig. 1. Various signals obtained by the electron irradiation of specimen surface and the signal detection depth.
solid specimens, but the CL method permits only the analysis of light-emitting specimen, hence its field of application is limited.

As mentioned above though, the CL method is applicable only to a certain kinds of specimens, it has many merits not obtainable by the EPMA method. Particularly, it can obtain more data supplementing the composition data obtained mainly by instruments such as EPMA.

Application Scope of Cathodoluminescence

Conventionally, the cathodoluminescence method has been used widely for research of mineral specimens. Recently, it has especially come to receive attention for developing optical devices such as the commercialization of blue LEDs and laser diodes. It is also used in various fields such as large capacity memory devices, devices for optical communication network and materials for various kinds of displays. Table 1 shows the material fields in which the CL method is mainly used, and also examples of its use.

**Cathodoluminescence Device**

Conventionally, there are several kinds of cathodoluminescence devices that can be installed in EPMA. One of them is a spectrometer-type device, which incorporates a parabolic mirror mounted on the spectrometer port. This specially designed mirror is used for collecting the CL. The other is a panchromatic type-device, which is equipped with a photomultiplier mounted directly on the optical microscope port (there are also cases in which a filter allowing a specific wavelength to pass through it is used). The spectrometer-type cathodoluminescence device utilized in the following measurement examples uses the optical microscope port of the EPMA, as shown in Fig. 2. enabling a CL spectrum and a CL image of a specific wavelength to be obtained (it can also be installed in the JXA-8100, JXA-8600 and JXA-733 series). In the EPMA, the electron optical system, specimen stage and wavelength dispersive spectrometer are adjusted in accordance with the optical axis of the optical microscope coming with the EPMA. In this measurement, this optical microscope is used, and the CL is collected by a reflection objective mirror in the EPMA instrument, and extracted from the instrument. It is thus possible to analyze simultaneously both EPMA and CL signals without adding any changes to the EPMA instrument and also without interfering with normal EPMA analysis.

**Figure 3** shows a block diagram of the CL device. It consists of the optical fiber unit, which directs the CL from the CCD camera port of the JXA-8800, CL spectrometer, photomultiplier, photon-counting unit, drive system and power supply. The spectrometer is controlled by a PC. It is possible to acquire simultaneously a CL map from a specific wavelength or a panchromatic CL signal, together with a secondary electron image (SEI) or an X-ray map, from the EPMA instrument. Compared to an exclusive CL device in which the CL collecting mirror is placed very near the light-emitting source, the collecting solid angle
of the optical system is small. However, by the use of the photon-counting unit, CL intensity can be obtained sufficiently enough to practical purpose. Since the working distance of the specimen used in CL analysis is the same as that used in EPMA analysis, there is no need for position adjustment between the CL collecting mirror and the specimen. Also, it is important that the analysis point and probe current are extremely stable when the accelerating voltage and probe current are changed frequently. It is possible to perform CL mapping over a wide area of several centimeter square by moving the specimen stage at high speed. As we have described above, the major advantage of the cathodoluminescence method is to allow simultaneous analysis of the CL signal and other signals.

**Various Applications of the Cathodoluminescence Method**

We show various application examples of CL measurements. Particularly, since the comparison with the X-ray signal from EPMA is of great interest, many examples of area analysis are shown. We made cross-sectioned specimens by embedding them with room-temperature curing resin to cut them, and by polishing the cross-sectioned surface with 1 μm diamond paste. As the measurement results indicate, CL is easily affected by streak, therefore, depending upon the specimen and the observation area it is necessary to use other methods such as sputtering, FIB, and so on. After the specimen was polished, it was coated with about 10 nm thick carbon, in order to make it electrically conductive. Granular specimens were sputter-coated with gold to a thickness of about 10 nm. In the analyses described here, gold sputtering resulted in a more uniform coating, and the gold-sputtered film was more resistant to beam damage. Gold coated specimens can sometimes reduce the CL excitation from areas not irradiated by the electron beam, because of the effect of low-energy scattered electrons inside the EPMA instrument. Therefore, gold coating may be better for CL analysis. This is a subject that must be studied in the future.

When performing CL analysis over a small area, this analysis is usually done at a low accelerating voltage of about 1 kV. In the analyses described here, an accelerating voltage of about 10 to 15 kV was used in order to compare the results acquired from CL signals with those from X-ray signals. The specimens were left at room temperature during measurements.

**Applications of CL Observation of Optical Device**

**Red LED**

As an analysis example of optical device, we show a result of observation of a high-brightness red LED. The PN junction made of GaAsP or GaP is used for a red LED. The commercially available high-brightness LED used in this analysis consisted of a compound semiconductor with a multi-layer structure containing Ga, In, P, Al, and As, as shown in Fig. 4. Figure 5 is a cross-sectional electron image of the cross-section of a red LED. The enlarged image is that of multi-layer films consisting mainly of AlGaAs, AlInP, AlGaInP, AlInP, and AlGaAs-InP multi-layer, with GaAs substrate, going from the top. From the results of CL analysis of each layer, the AlGaInP layer was found to emit red light of 642.5 nm. This portion is considered to be the active layer. **Figure 5** shows the area analysis results for this multi-layer structure, including the X-ray images of Ga, In, P, Al, and As, and the image of 642.5 nm CL. Compared to the electron scattering area (it is 0.6 μm when GaAs bulk specimen is analyzed at an accelerating voltage of 10 kV), it is assumed that the low-energy CL emission area becomes wider than that of X-ray generation area. Although the thickness of the 642.5 nm CL emission area is wider (0.5 to 0.6 μm) than the thickness of the active layer (0.35 μm), it is possible to identify the light-emission position. Thus, even for observation of a normal cross-section specimen, there are cases in which the area resolution of the CL is maintained in the sub-micron area of 1 μm or less.

**Yellow LED**

**Figure 6** shows a backscattered electron image of the cross-section of a yellow LED and also the area analysis results for this LED, which include the X-ray images of Ga, As, and P, and the image of 580 nm CL. This LED consists of mixed crystals prepared on a GaP substrate and shows a gradual change in As concentration. From the results of area analysis, it can be seen that 580 nm yellow light is emitted from the GaAsP1-x surface layer with a thickness of 200 μm. This area should be a P-type GaAsP1-x layer doped with Zn as an acceptor. Since the concentration of the acceptor is below the element detection limit of the EPMA analysis, the acceptor cannot be detected. On the other hand, it is possible to indirectly show the thickness of the P-type region from the CL emission area. Incidentally, the light-emission area shown in the figure disappears at the position of the leak left when the surface of the specimen was polished. Scratches of this degree have virtually no effect on the characteristic X-ray signal, but have a great effect on CL analysis. It can be said that CL emission is also extremely sensitive to the state of the surface of the specimen.

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*Fig. 4. Cross-section of a red LED (backscattered electron image).*

*Fig. 5. Red LED’s multi-layers (642.5 nm CL image, and X-ray images of Al, Ga, As, In and P).*

*Fig. 6. Yellow LED. (backscattered electron image, 560 nm CL image, and X-ray images of each element).*

*Fig. 7. Cross-section of a white LED (backscattered electron image) and CL spectrum of GaN area in the white LED.*

*Fig. 8. Cross-section of a white LED (CL images of each wavelength).*
White LED [3]

A commercially available white LED consists of a blue GaN LED coated with a layer of fluorescent material, such as Yttrium-Aluminum Garnet (YAG), that emits yellow-green light. The blue light emitted by GaN excites the YAG, and the combination of blue and yellow-green light results in white light.

Figure 7 is a cross-sectional backscattered electron image of a white LED (50 to 2000 [1]). On a steel base, this LED consists of a sapphire (Al₂O₃) substrate, a GaN thin film, Au (Ni) electrodes, and a layer of YAG powder. Actually, blue light is emitted from the InGaN thin layer at the upper portion of the GaN thin film, but it could not be detected during the cross-section analysis because this layer was extremely thin.

Figure 8 shows a backscattered electron image of the area near the positive electrode of the specimen, and also the CL images of each wavelength, 560 nm, 370 nm, and 457.5 nm. It is considered that the image of 560 nm shows the yellow light emitted by YAG. 457.5 nm is the blue light emitted from the active layer at the upper portion of GaN, and 370 nm is the light emitted from the N-type doped GaN layer.

Applications of CL Observation of Mineral Specimen

The cathodoluminence method has been used to analyze mineral specimens for many years.

Conventionally, in JEOL EPMA, transmission light source, polarizer and analyzer are provided for a thin-section specimen, enabling the distribution of minerals in rock to be identified from the colors of each mineral. The cathodoluminescence method, on the other hand, enables analysis, over a small area, of changes in the intensity of the CL, which is caused by compositional changes, trace impurities or non-uniformity of structures inside the minerals.

As an example, Fig. 9 shows a secondary electron image, backscattered electron image, 487.5 nm CL image and X-ray maps of Si, Ca and Al in plagioclase contained in volcanic rock obtained from Mt. Fugen-dake. It is thought that when plagioclase is formed, the composition of the supplied magma is different. Therefore, layers of different compositions are formed, thus resulting in the formation of the zoning structure shown here. It can be seen that the bright CL contrast areas correspond to areas that are rich in Ca and Al. As the other example, we show the analysis results of quartz in the same rock. Figure 10 is a CL spectrum at an arbitrary point on the quartz. This quartz shows peaks at 430 nm and 642.5 nm. We made CL analysis and element analysis at both peak positions. The results are shown in Fig. 11. It can be seen that the contrast in the CL images of the respective peak positions are different from each other, and are not complementary. Also, we attempted to perform qualitative analysis using the contrast of the 430 nm CL image as a reference, but it was not possible to detect impurities other than Si and O.

Application of CL Observation of Ceramic Specimen

As an example of a ceramic specimen, we show the results of area analysis of commercially available sintered AlN.

Aluminum nitride (AlN) is a ceramic with high thermal conductivity and high electric sensitivity. It is used in a wide range of applications as a non-electro conductivity heat sink. Since AlN has a coefficient of thermal expansion close to that of silicon, it can be processed easier than other high thermally conductive ceramics, and can be bonded firmly to the metal used for the electrodes. It is, therefore, an indispensable material in the heat sink design that is used for semiconductors. Figure 12 shows the results of area analysis of the surface of a commercially available sintered AlN substrate, including a backscattered electron image, a CL image of the peak position of 360 nm obtained from a CL spectrum, and X-ray images of Al and N. In principle, the bandgap of AlN is 6.1 eV, and a CL peak can also be obtained from the vicinity of a wavelength of 200 nm. Therefore, yttrium is used as filler for this substrate, and it is considered that the peak at the longer wavelength side normally

Fig. 9. Zoning structure in plagioclase contained in volcanic rock (secondary electron image, backscattered electron image, 487.5 nm CL image and X-ray maps of Si, Ca and Al).

Fig. 10. CL spectrum of quartz in volcanic rock.

Fig. 11. Comparison of CL images of the two peak positions obtained from the CL spectrum of the quartz in Fig. 10.
obtained in the analysis of a Y2O3 specimen also appears. However, the CL intensity of the surrounding area of AlN was strong, hence it was almost impossible to detect a signal from the portion of the filler. It is considered that channeling contrast resembling a backscattered electron image, or contrast of grain boundary, does not easily appear because the analysis depth of the CL image is thought to be about the same as that of X-rays. However, the results obtained from this actual sample show a contrast reflecting the crystalline grain boundary. Also, dark and bright spots that do not reflect the distribution of the elements Al, N, Y and O, appear at the grain boundaries and also inside the grains.

**Application of CL Observation of Fluorescent Material**

It goes without saying that fluorescent material is suitable for CL analysis. Conventionally, it has been analyzed using the CL method [4]. The fluorescent material was prepared on electrically conductive tape from the fluorescent lamp, and it was investigated the distribution of the particles corresponding to each color of R, G and B. **Figure 13** shows the CL spectrum of the fluorescent particles. In this spectrum, it can be seen that the 612.5 nm peak is the main peak for the fluorescent particles emitting red light, the 545 nm peak for those emitting green light, and the 457.5 nm broad peak for those emitting blue light. A CL map was acquired for each peak, and the resulting data was artificially indicated as each color level of R, G and B (Fig. 14). It is easily possible to investigate the distribution of the particles for each color, the area ratio of each particle in the analysis area, and so on.

**Comparison of EPMA State Analysis and CL Analysis**

EPMA is not only used for elemental analysis, but has come to be extensively used for state analysis. However, for materials that emit light, it is also of great interest to compare the state analysis data with the CL spectrum. The following is an example in which the results of CL analysis indicate a remarkable difference in the spectra of the various compounds, compared with the results of state analysis by EPMA. The spectra shown in Fig.15 were obtained from three kinds of Al oxides, Al2O3, Al(OH)3 and Al(OH)4. Each specimen was made by pressing a powder specimen. The Al-sKα, X-ray spectra using the state analysis of these specimens show only very small differences. However, when CL analysis is used, there is a marked difference in the spectra. On the other hand, the CL spectrum is extremely sensitive due to impurity level below the detection limit of WDS analysis, defects, distortion, and so on. For this reason, it is necessary to take care at the time of sampling and handling the specimen, and also when interpreting the acquired CL data.

**Conclusion**

We have demonstrated the cathodoluminescence device installed in the EPMA, together with several examples of analyses. The obtained data shown here were limited to the ones, which we could obtain easily. Actually, very interesting data have seemed to be obtained from specimens analyzed by customers. Quite complicated factors are involved in the generation of CL. Since it is not easy to interpret the CL spectrum, it is important to accumulate various data in the future.

**References**


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**Fig. 12.** Sintered AlN (backscattered electron image, CL image, and X-ray images of Al and N).

**Fig. 13.** CL spectrum of fluorescent material on the wall inside of a fluorescent tube.

**Fig. 14.** CL images of fluorescent material R, G and B, and combination map.

**Fig. 15.** CL spectra of various Al oxide powders.
**EPMA Analysis of Insulating Materials Using the Thin Film Method**

**Introduction**

Where an uncoated insulating material is subjected to electron probe microanalysis (EPMA), the electrons lose their escape way. Hence an electric charge builds up on the surface of the specimen. For this reason, the surface of an insulating specimen is usually made conductive by coating with an electrically conductive material prior to observation and analysis. However, problems sometimes arise in the analysis of the same elements as those contained in the coated material, or in the case of trace element analysis that is affected by the absorption of X-rays by the coated film. Also, organic high polymer specimens, for example, are easily damaged by a low thermal conductivity during coating.

In this paper, consideration is made on the cause of charging, and methods of specimens treatment other than coating of a conducting film are reported together with some examples of analysis using these methods. Reported here are also the features of high spatial resolution X-ray data obtained using a thin film specimen.

**Study of Charge Prevention Methods**

We have studied several charge prevention methods in EPMA. First, the method of measuring the degree of charging is considered. In the case of electrically conductive specimen, the probe current $I_p$ is transformed to the absorbed current or sample current $I_s$ during passing through the specimen, the backscattered electron current $I_b$, the secondary electron current $I_s$ and the transmitted electron current $I_t$ as shown in schematically diagram Fig. 1(a). It is expressed by the following equation.

$$I_p = I_s + I_b + I_s + I_t \ldots (1)$$

Usually, with increasing the mean atomic number, the number of backscattered electrons increases. Consequently, in the case of bulk specimen, $I_t$ is 0, and $I_b$ is much smaller than $I_s$ or $I_s$. If $I_b$ is large, $I_s$ is small. Figure 1(b) shows the actual current, as a rough guide. The upper curve shows the ratio of the actual sample current obtained from the standard specimen for $\text{SiO}_2$ to $\text{Sb}$ with the probe current. The lower curve shows the backscattering coefficient according to Love and Scott (1978)[1].

![Figure 1](image1)

(a) Behavior of electrons when a specimen is exposed to an accelerated electron beam.

![Figure 2](image2)

(b) Outline of the method of supporting the specimen

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When the atomic number as $3\text{B}$ is small, the number of backscattered electrons is small, hence the sample current becomes about 94% of the probe current. For the atomic number 30, i.e. $3\text{Zn}$, the sample current is about 70% of the probe current. However, if the specimen is charged, electrons cannot pass through it, hence equation (1) will no longer hold, and $I_a$ becomes extremely small. (If the specimen is completely nonconductive, $I_a$ should be 0, but in actual cases, a very small and unstable current in the order of $10^{-12}$ $\text{A}$ flows.) Consequently, by monitoring $I_a$, it is possible to check the specimen charging to a certain extent. If the coated film on insulating material tears off during analysis, the sample current abruptly decreases and becomes unstable.

**Thin Film Method**

Shiraga[2] (Sumitomo Chemical Co., Ltd.) reported on the application of the thin film method to an organic polymer thin film. The thin film was placed on a copper grid used for TEM observation. Kobayashi and others[3] (Niigata University) reported a method analysing biological specimen, where its thin film was placed on a carbon stub and then carbon-coated. Referring to these methods, we studied the following two ways of analyzing thin film specimens without coating. In the first method a thin film was made using a microtome and mounted on a copper grid for TEM observation. In the second method the specimen was supported by an electrically conductive substrate. We monitored the sample current and investigated the effectiveness of these thin film analysis methods. The specimen was polyvinyl chloride (PVC), and its thin films were prepared using the microtome shown in Fig. 2 (a). After floating these thin films in distilled water, they were placed on a carbon stub and a silicon wafer. Also, as a means of supporting the specimen without substrate, the thin film was mounted on a copper grid for TEM observation, as shown in Fig. 2 (b). None of the specimens were treated by coating. The reason why the silicon wafer was used as the substrate was that it is electrically conductive, has a smooth and stable surface without holes and is easily obtainable. According to Kobayashi and others, it consisted of the carbon stub of sintered carbon molding material (Nikka Seiko), which was cut to dimensions 20 $\times$ 25 $\times$ 20 (height) $\text{mm}$, polished with water-proof sandpaper (#8000–1000) and then washed in distilled water. We measured the variation of sample current due to the change in the accelerating voltage.

**Thin film specimen with substrate**

Generally, the irradiated electrons cause heating in the specimen. The temperature $\Delta (\text{K})$ is expressed by the following equation (2).

$$\Delta = 1.14 \frac{I \cdot V}{K \cdot d} \quad \text{(2)}$$

$I$: Probe current ($\text{A}$)
$V$: Accelerating voltage (kV)
$K$: Heat conductivity (cal/cm $\cdot$ sec)$\cdot$K
$d$: Beam diameter ($\mu\text{m}$)

This equation shows that the temperature is increased when the probe current or accelerating voltage are increased and the beam diameter is reduced. Usually, soft specimens such as organic materials are affected by the beam bombardment because of their low melting points and low heat conductivity.

However, heat is generated inside the electron diffusion area in the bulk specimen. If the soft specimen is sufficiently thinner than the depth of electron diffusion and it is supported on a substrate with a large heat conductivity, the specimen will be resistant to heat damage by the irradiated electrons. The schematic illustration of a thin film specimen on a substrate is shown in Fig. 3.

**Substrate-less thin film specimen**

In the case of the thin film specimen placed on the copper grid for TEM observation, it was charged at a low accelerating voltage. As shown in Fig. 4, the thicker the specimen the higher the accelerating voltage at which charging is suppressed. For the specimen of 0.07 $\mu\text{m}$ thick, this voltage is approximately 3 kV, for the specimen of 0.2 $\mu\text{m}$ thick, it is approximately 5 kV, and for the specimen of 0.5 $\mu\text{m}$ thick, it is approximately 12 kV. Consequently, it can be said that the reduction of a thin specimen thickness is effective for reducing charging. However, in EPMA, if the film is made too thin, X-ray intensity becomes too weak to be detected. This point should be taken into account at the time of the specimen preparation. The optimum specimen thickness should be selected, considering upon the factors of

![Fig. 3. Schematic illustration of a thin film specimen on a substrate.](image)

When the thickness of a soft thin-film specimen is smaller than the depth of electron diffusion, the heat is generated inside the substrate, not in the thin film specimen.

![Fig. 4. Change in sample current with accelerating voltage for a PVC thin film (without substrate) on a copper grid.](image)

![Fig. 5. Comparison of mapping of BEI (backscattered electron images) for N, contained in an uncoated thin film specimen of the cross-section of a rice grain, a uncoated bulk specimen, and a specimen treated by Au coating.](image)
expected spatial resolution and the specimen density.

In the case of the thin film method, the increase in the accelerating voltage is effective to reduce the specimen charge, regardless of whether or not the specimen is placed on the substrate. This is the opposite to the above-mentioned case of a bulk specimen, for which the low accelerating voltage was used appropriately. It is thought that, if accelerated electrons possess a sufficiently high energy to pass through the insulating film, a kind of insulation breakdown may occur. The value of the allowable voltage depends upon the film thickness and the kind of specimen. For a bulk specimen, increasing the accelerating voltage reduces the diameter of the electron probe, permitting a high resolution image to be obtained. With the specimen supported on a silicon wafer, carbon stub or other substrates with good thermal conductivity, heat generated in the specimen is dissipated in the substrate, hence the damage caused by electron beam may be reduced even when the current is increased. Thin sections supported in this manner are stable even under high beam currents. This is fairly convenient for a soft specimen when the same area is analysed repeatedly, for example, when analysing a large number of elements by WDS.

When a low accelerating voltage was used and the uncoated specimen was tilted, the monitored value of \( I_e \) (sample current) was near zero. This makes it difficult to evaluate the effectiveness of this analysis method. The reason of this phenomenon comes from the following fact: In the case of insulating material, \( I_p \) provides surplus electrons to cause the specimen charging, so that the sample current \( I_a \) should be zero. However, if a very low accelerating voltage is selected or the specimen is tilted remarkably in order to avoid charging, the secondary electron emission efficiency \( \eta \) becomes unity. In other words, the ratio of the incident electrons to the emitted electrons becomes 1, and the balanced state exists on the surface of the specimen. In equation (1), if \( I_e = 0 \) and \( I_p \neq I_a + I_b \) hence \( I_a \) is roughly 0. On the other hand, in the case of electrically conductive bulk specimen, that is, \( I_e \neq 0 \), any absorbed electrons except \( I_a \) and \( I_b \) can pass through the specimen to the specimen holder. Consequently, the sample current \( I_a \) is much larger than 0. This is different from the mechanism taking place in the above-mentioned methods. However, in the low accelerating voltage method, the condition under which the specimen did not get charged was a low energy of about 1 kV. In EPMA, this energy is too low to cause the adequate X-ray excitation. Also, in the tilt method, the tilt angle differs depending upon the kind of specimen. Generally, a large angle of inclination is requested, but it imposes limits on the orientation of the X-ray spectrometer, the specimen, and so on. The measurement can only be performed under limited conditions. In contrast, in the case of thin film analysis, the sample current increases in proportion to the accelerating voltage, providing a stable charge suppression. Accordingly, the accelerating voltage sufficiently enough to excite the X-rays should be used. Even in the case of the specimen containing several compounds, provided that the accelerating voltage is sufficiently high to prevent charge-up on any of these compounds, there will be no possibility of local charging. In this respect as well, this method is superior to the low accelerating voltage and tilt methods.

From the above results it may be clearly seen that, thin film method is effective for analyzing insulating specimens without coating treatment, using EPMA. In the following, actual examples of the thin film specimen method are shown.

**Experiment**

All data were obtained by EPMA model JXA-8800R (JEOL).

For the specimens, we used a rice grain, paper, PVC, mica, mouse liver, and solder (which is conductive and was used to test for higher spatial resolution.)

The measurement conditions are as follows.

- **Analysis of the cross-section of rice grain**
  - Accelerating voltage: 15 kV
  - Probe current: 0.1 µA
  - Number of pixels: 400 \( \times \) 400
  - Pixel size: 0.5 \( \mu \) m
  - Analysis area: 200 \( \mu \) m \( \times \) 200 \( \mu \) m²
  - Acquisition time for 1 pixel: 80 msec
  - Acquisition method: Stage scan

- **Analysis of paper**
  - Accelerating voltage: 15 kV
  - Probe current: 1.8 nA
  - Number of pixels: 256 \( \times \) 256
  - Pixel size: 0.05 \( \mu \) m
  - Analysis area: 20.48 \( \mu \) m \( \times \) 20.48 \( \mu \) m²
  - Acquisition time for 1 pixel: 20 msec
  - Beam scan (10000)

- **Analysis of PVC**
  - Accelerating voltage: 15 kV
  - Probe current: 7.5 nA
  - Number of pixels: 256 \( \times \) 256
  - Pixel size: 0.05 \( \mu \) m
  - Analysis area: 12.8 \( \mu \) m \( \times \) 12.8 \( \mu \) m²
  - Acquisition time for 1 pixel: 20 msec
  - Acquisition method: Beam scan (10000)

- **Analysis of Mica**
  - Accelerating voltage: 15 kV, 25 kV
  - Probe current: 0.07 µ A
  - Number of pixels: 400 \( \times \) 400
  - Pixel size: 2.5 \( \mu \) m
  - Analysis area: 1000 \( \mu \) m \( \times \) 1000 \( \mu \) m²
  - Acquisition time for 1 pixel: 30 msec
  - Acquisition method: Stage scan

- **Analysis of mouse liver**
  - Accelerating voltage: 15 kV
  - Probe current: 0.1 µ A
  - Number of pixels: 400 \( \times \) 400
  - Pixel size: 0.16 \( \mu \) m
  - Analysis area: 64 \( \mu \) m \( \times \) 64 \( \mu \) m²
  - Acquisition time for 1 pixel: 100 msec
  - Acquisition method: Stage scan

- **Analysis of Solder**
  - Accelerating voltage: 25 kV

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![Fig. 6. Comparison of the results of O, Ca and C mapping, and the backscattered electron image, between the thin film method without coating and the bulk specimen method by Au-coating.](image)

![Fig. 7. Observation of the distribution of TiO₂ grains by mapping of Ti-K Kα in PVC. Comparison of specimens of 0.07 µ m thickness, 0.2 µ m thickness and 0.5 µ m thickness mounted on a copper grid (without substrate), silicon wafer and carbon stub, respectively.](image)
• Probe current: 1.9 nA
• Number of pixels: 256 × 256
• Pixel size: 0.04 μ m
• Analysis area: 10.24 × 10.24 μ m²
• Acquisition time for 1 pixel: 30 msec
• Acquisition method: Beam scan (× 10000)

Examples of Thin Film Analysis

Analysis of Rice Grain

We obtained CP composition image (backscattered electron image) and mapping of the element N using the uncoated thin film sampling method, the uncoated bulk specimen sampling method, and the Au-coated sampling method. Fig. 5 shows composition images. In the case of uncoated bulk specimen, the element distribution is irregular as a result of charging. A similar distribution was obtained for the specimen subjected to the Au coating, indicating that the charging effect remained. In contrast, in the case of the thin film without coating, a stable element distribution was obtained. This result reflects the distribution of the trace of N particularly well.

Analysis of Paper

Figure 6 shows a comparison of the CP (BEI) with X-ray maps for O, Ca and C in a bulk paper specimen together with those in a thin film specimen on a silicon substrate. As can be seen in the figure, in the thin film specimen the above elements are distributed along the contours of the pulp fibers. In contrast, in the case of the bulk specimen (treated with Au coating), the outline is not clear. This is thought to be due to the absorption of X-rays.

Analysis of PVC

Figure 7 shows the distribution of TiO₂ grains in PVC. From left to right, the thin film thicknesses are 0.07 μ m, 0.2 μ m and 0.5 μ m, which from the top to down the specimens are placed on a copper grid, on a carbon stub and on a silicon wafer. The granular distribution of TiO₂ can be observed.

Analysis of Mica

Mica is known as a nonconductive laminate, and is used as a support film in TEM observation. We placed a water droplet on a silicon wafer, and then placed a small mica lamina on the water droplet, followed by drying the specimen. The mica lamina adhered firmly to the silicon wafer. We then carried out X-ray mapping for Al and K in this specimen at accelerating voltages of 15 kV and 25 kV, and also acquired secondary electron images (SEI). The results are shown in Fig. 8. The periphery is thinner than the center part. Though Al and K mappings were possible even at 15 kV, the SEI image showed that the center area was charged to reduce the X-ray intensity. On the other hand, at 25kV, the electron beam seemed to reach the silicon wafer substrate and no evidence of charging was observed, giving appropriate distributions of Al and K maps.

Analysis of Mouse Liver Section

We sliced mouse liver section to make a thin specimen with a thickness of approximately 0.2 μ m, placed it on a copper grid (200 mesh), and obtained CP(BEI) and X-ray maps for N, C, Cl, Os and O. The results are shown in Fig. 9. The analyzed area was 600 μ m square. The gray, circular shape in the CP is the core of a cell, and gray cell tissue can be seen around it. The tissue is stained with osmium tetroxide; thus the stained area can be seen well. Cl is thought to come from the embedding resin. We also observed the distribution of N in the cell. C is observed at the black part inside the cell, and is thought to be blood vessel tissue.

Analysis of Metallic Pb-Sn Solder

Figure 10 shows the differences in the results of analysis of a thin film specimen (0.2 μ m thickness) and a bulk specimen of metallic solder. The upper half shows the results for the bulk specimen, and the lower half the results for the thin film. On the right are enlarged Pb distribution maps of part of bulk specimens and the thin film. The contours of the Pb distribution for the thin film specimen can be seen clearly, but the contours for the bulk specimen and the upper and lower part of the X-ray intensity is not abrupt at the boundary.

Discussion

The results obtained from the uncoated thin film specimen of a rice grain showed that there was little change in the specimen deformation even when the probe current increased. This indicates that this analysis method is effective, particularly for WDS analysis. According to various literatures[4], in general, Mg, P and other elements in a rice grain can be analyzed by EPMA, but little mention has been made concerning the distribution of light elements such as N. This may be due to the problems in sensitivity and sampling. The sensitivity for nitrogen and other ultra light elements has been greatly improved by the development of a high sensitivity LDE (Layered Dispersion Element: artificial superlattice) device having a small Rowland circle. By using this device in combination with the thin film method, we were able to acquire good quality data with high sensitivity, even for specimens that could not be analyzed by the thin film method alone. We also used the probe current of 0.1 μ A, and found that the specimen was virtually undamaged in spite of a high probe current. It is thus possible to analyze many kinds of elements in sequence. This is highly advantageous for WDS analysis in which the number of spectrometers is limited. Because the specimen is uncoated, there is no absorption of the X-rays due to absorption in the coating film, and also there is little irregularity in the X-ray intensity due to the separation of this film. This may be due to the fact that the substrate is a good electrical and thermal conductor, and so the heat due to the elec-
electron beam is radiated rapidly. Moreover, compared to a bulk specimen, the spatial resolution of the thin film also appears to be much improved.

Like the rice grain, the paper specimen contains many organic elements, hence analysis examples of paper by WDS are not many. However, EPMA analysis employing the Os stain method by Hamada and others is a revolutionarily important paper analysis method[5]. By using the thin film specimen, we were able to clearly observe the mineral content, such as t alc and kaolin for fillers, and also the contours of the pulp fibers. However, Si and C must often be analyzed as well. Therefore, it may be necessary in the future to change the substrate to the one not containing Si or C, and also to investigate into the applicability of this method for the paper analysis.

In the thin film analysis of PVC, we sampled three kinds of specimens with different film thickness, and placed them on the copper grid on the silicon wafer and on the carbon stub. From the results of Fig. 7, we can see that all of the thinnest specimens of 0.07  m disappeared during mapping acquisition. When the specimen is excessively thin, it seems to shrink, and become unstable. Our experience showed that the specimen of high weight polymer with low density, such as PVC, was difficult to subject EMPA analysis when the specimen thickness was 0.1  m or less. If the specimen is excessively thin, the amount of X-rays generated decreases too much, so that a care to the thickness must be taken. However, if the film thickness is 0.5  m or more, the merits of the thin film method are lost. These appropriate thickness depends upon the kind of specimen, and so it is best to prepare several specimens of different thickness in the range from 0.1 to 0.5  m. The appropriate thickness in EPMA analysis is different from the film thickness in TEM in where the thinner specimen is better.

Next, we compared the analysis results of thin film and bulk specimen of Pb-Sn alloy (solder), in order to investigate the degree of the spatial resolution improvement by adoption of a thin film. As was seen in Fig. 10, the X-ray intensity change at the boundary of the alloy phase at the time of the line analysis on the map, depends on the specimen thickness. The value obtained for the bulk specimen was about 640 nm, and for the thin film (0.2  m thick placed on the silicon substrate) was about 200 nm. This fact was supported by the Monte Carlo simulation shown in Fig. 11, where the use of a thin film reduces the diffusion of electron beam and so the area of X-ray generation.

From the above, the analysis method using uncoated thin film is extremely effective in EPMA. The advantages and disadvantages of this method and also future problems, are summarized.

Conclusions

In the analysis of uncoated thin films, using fairly high accelerating voltage, the electron beam passes right through the specimen. This reduces charging artifacts and improves spatial resolution of X-ray data. As the specimen damage is also small, this method is effective for WDS analysis, in which many kinds of elements are analyzed in sequence by repetitive analysis.

A layered dispersive element intended for high sensitivity spectroscopy permits the detection of ultra-light elements, since they were difficult to be detected in the analysis of organic thin films previously, and its adoption contributes to acquire good quality data.

For some specimens, empirical factors are necessary for controlling the thickness of thin film.

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References

Cryogenic Transmission Electron Microscope

Hideo Nishioka
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Introduction
The transmission electron microscope (TEM) that has been widely used in research in the fields of materials science and technology has now become capable of observing specimens at atomic resolution and is making valuable contributions to research and development of industrial products. In recent years, with the progress of molecular biology, the TEM has begun to be used in analyses of biological macromolecules such as proteins (enzymes) and viruses on the molecular level. Also, it is being applied to elucidating life phenomena, including those on the molecular level, as well as to development and improvement of industrial, pharmaceutical, and agricultural products.

Also, recently, strong demands for TEM observation of three-dimensional structures of biological macromolecules in the hydrated state (the native state in living bodies) at atomic resolution have been made.

However, there are two difficult problems in using the TEM for these purposes. First, the path of the electron beam must be in vacuum and, therefore, the specimen to be observed must also be kept in vacuum. Second, there is stronger interaction between the electron beam and the substances to be observed than in X-ray studies. Therefore, damage of the specimen due to electron-beam irradiation is large and must be reduced considerably.

A method for overcoming these difficulties and for observing the specimen at atomic resolution while keeping it in the hydrated state is the so-called ice embedding method for preparing a frozen specimen. Also, for reducing irradiation damage of the specimen by the electron beam, there is the cryogenic transmission electron microscope that is capable of observing a frozen specimen at an extremely low temperature. In this document, we will describe the method of observation fine biological macromolecules and other specimens.

Frozen Specimen Preparation (Ice-Embedding Method)
A method for observing fine specimens such as biological macromolecules or viruses floating in solution, using a TEM, staining in the hydrated state as it is, is the negative staining method. However, generally, when a specimen is dried, it is deformed by surface tension. To improve on this, there is the method of freeze-drying the specimen after negatively staining it with uranyl acetate. In this method, a rather three-dimensional-like image can be obtained (Fig. 1A) [1]. However, even using this method, the effect of the staining liquid remains. It is difficult to say that the specimen keeps its original shape. Also, only information about the specimen surface is obtained. Adrian et al. [2] have shown that it is possible to observe a specimen in the native state by rapidly freezing fine samples in liquid and embedding them directly in a thin film of amorphous ice (example: Fig. 1B, C). In other words, an unstained specimen embedded in ice is observed in the hydrated state as it is. Also, information about the inside of the specimen is obtained. We will briefly describe this ice-embedding (bare-grid) method of fine specimens below [3 to 7].

Procedures of the bare grid method
- On a #150 to #200 copper mesh, apply a carbon-evaporated micro grid (use a commercially available product or make it yourself [8]).
- Make the mesh hydrophilic by glow discharge or other means. (Use a commercially available hydrophilic-treatment device, for example, JEOL HDT-400.)
- Pick up the mesh with a pair of tweezers used for specimen preparation and place a drop of the solution containing the fine specimen on it (Fig. 2B).

Fig. 1. TEM images of influenza virus (A,B) and tobacco mosaic virus (C). A: Negative staining (the freeze-dry method, B: Ice embedding method.)
Set up the tweezers on a rapid freezing device (Leica EM CPC, for example; Figs. 2A and 2C).

Cut the mesh with a piece of filter paper (Wattmann #50) from both sides to absorb excess solution and form a thin film of liquid on the micro grid (Fig. 2C).

Immediately after that, plunge the mesh into a coolant (Table 1) such as liquid ethane (Fig. 2D). At this time, a thin film of amorphous ice forms and preparation of the frozen specimen embedded in ice is completed.

This frozen specimen is then transferred to a cryogenic TEM, avoiding contact with moisture in the air and kept at liquid nitrogen temperature, and is observed there. Or, the specimen is put in a mesh holder or some other container and stored in liquid nitrogen. However, caution is required because the specimen may decompose even in liquid nitrogen.

When the holes of the micro grid used are large, formation of a film of ice may be rather difficult. However, with practice, you can form a thin and broad film. When the holes are small, it may be easy to form a film but it is difficult to obtain a thin film. The thickness of ice varies depending on the thickness and the aperture ratio of the mesh used. Although there is a tendency that the thinner the mesh, the thinner the ice film that forms, if the mesh is too thin, it will become difficult to apply a micro grid to the mesh. When it is difficult to form a thin ice film, cover the mesh on which a micro grid is adhered further with a supporting film of colloidion, for example, or use a mesh covered only with a supporting film, and observe a thin ice film formed on the supporting film. However, the contrast of the specimen image deteriorates when you use this method.

Add several percent of an antifreeze (glycerin, glucose, sucrose, or trehalose, for example) to the liquid used for embedding the fine specimen. It facilitates formation of a thin ice film.

As coolant, liquid ethane, liquid propane, liquid nitrogen, and others are used (Table 1). Since propane sometimes contains a large amount of water and, when it does, its melting point increases rather remarkably, it is necessary to pay attention to the grade of propane. Also, since ethane and propane gases are flammable and there is a danger of explosion if a mixture of the air and these gases catches fire, the use of fire near these coolants is strictly prohibited. Remaining liquid propane must be disposed of by burning in a special-purpose propane incinerator. The freezing power of these coolants is much stronger than that of liquid nitrogen and special caution is required when handling them. If these coolants touch your skin, you will certainly suffer from frostbite.

**Electron Microscope**

1. **TEM**

   We will explain the cryogenic TEM suited to observation of the frozen specimen embed-

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**Table 1.** Performances of major cryo-electron microscopes.

<table>
<thead>
<tr>
<th>Electron microscope</th>
<th>Objective lens</th>
<th>Cooling system</th>
<th>Coolant</th>
<th>Accelerating voltage</th>
<th>Electron gun</th>
<th>Theoretical resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>JEM-3000SF</td>
<td>CTM type</td>
<td>Liquid He</td>
<td>300 kV</td>
<td>FEG</td>
<td>0.204 nm (at 4.2 K) (Image of lattice)</td>
<td></td>
</tr>
<tr>
<td>JEM-4010</td>
<td>High-resolution analysis</td>
<td>Using CTH</td>
<td>Liquid N2</td>
<td>400 kV</td>
<td>LaB6</td>
<td>0.17 nm</td>
</tr>
<tr>
<td>JEM-3010</td>
<td>High contrast</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JEM-2010 /2010F</td>
<td>High resolution analysis</td>
<td>Using CTH</td>
<td>Liquid N2</td>
<td>300 kV</td>
<td>LaB6</td>
<td>0.26 nm</td>
</tr>
<tr>
<td></td>
<td>High contrast</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>JEM-1230</td>
<td>High contrast</td>
<td>Using CTH</td>
<td>Liquid N2</td>
<td>200 kV</td>
<td>W or LaB6</td>
<td>0.32 nm</td>
</tr>
<tr>
<td>JEM-1010</td>
<td>High tilt angle</td>
<td>Using CTH</td>
<td>Liquid N2</td>
<td>100 kV</td>
<td>W or LaB6</td>
<td>0.45 nm</td>
</tr>
</tbody>
</table>

**Table 2.** Melting points and boiling points of various coolants.

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N2)</td>
<td>-209.9</td>
<td>-195.8</td>
</tr>
<tr>
<td>Ethane (C2H6)</td>
<td>-183.6</td>
<td>-88.6</td>
</tr>
<tr>
<td>Propane (C3H8)</td>
<td>-188</td>
<td>-42.1</td>
</tr>
</tbody>
</table>

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Fig. 2. (A) to (D) Rapid freezing device EM CPC (made by Leica) for preparation of the ice embedded specimen.
Fig. 3. (A) JEM-3000SFF equipped with the superfluid helium stage. (B) External view of the JEM-2010FEF equipped with the in-column \( \Phi \) filter.

Fig. 4. (A) Cross-section diagram of the superfluid helium stage of the JEM-3000SFF. (B) Cross-section diagram of specimen-exchange device. (C) Cross-section diagram in the vicinity of the cryo-objective lens of the JEM-2010/2010F/2010FEF.

2. Electron Gun

The electron gun suited to cryogenic TEM is the field-emission electron gun (FEG) (Table 3). Since the electron source of the FEG has high brightness and small, the beam is bright and its coherency is good. For this reason, the phase contrast of the image of the crystal lattice obtained is high and suited for analysis. However, if ultimate resolution is not pursued, you can get sufficiently good results even with the conventional thermal electron guns [9-11]. However, a thermal electron gun using a hairpin-type tungsten filament is not bright enough and it would be better to replace the filament with one of the LaB\(_6\) type.

3. \( \Phi \)-Filter

Recently, a TEM equipped with an in-column \( \Phi \)-filter has become available on the market (Fig. 3B). Since the zero-loss image obtained by the \( \Phi \)-filter TEM is formed by ded ice below (Table 2). Currently, two types of TEM have been developed. One is the JEM-3000SFF (Fig. 3A) developed jointly by Professor Yoshinori Fujiyoshi of Kyoto University and by JEOL. This system is capable of cryo-transfering a specimen to a TEM at liquid-nitrogen temperature. It is equipped with a top-entry specimen stage that can cool the specimen with superfluid helium and is capable of observing the specimen at this temperature. In other words, this instrument is to be used exclusively for cryogenic observation and is not suited for other uses. Fig. 4A shows the helium stage of the JEM-3000SFF and Fig. 5 shows a resolution performance picture taken at 4.2 K. In this instrument, the frozen specimen is set up on the top-entry specimen holder and it is further set on the TEM main body. It can be evacuated together with liquid nitrogen and is equipped with the cryogenic-transfer system that can transfer the specimen to the helium stage in vacuum at liquid-nitrogen temperature.

Another type of instrument is a combination of a conventional TEM (JEM-4010, -3010, -2010, -2010FEF, -1200, or -1010) and a cryo-transfer holder (CTH, Figs. 6A and 6C) that can transfer the specimen to liquid-nitrogen temperature into the TEM and observe it there. This type of instrument becomes a cryogenic TEM only when cryo-observation is performed by using the CTH. That is to say, this is an instrument suited also for purposes other than cryo-observation. The CTH is equipped with a covering (shutter) system at the top to prevent the specimen from being exposed to the air and contacting moisture when the specimen is cryo-transferred from the work stage to the TEM (Figs. 6B and 6D).

A device to prevent moisture brought into the column from adhering to the specimen (an anti-contamination device, ACD) is also necessary for the TEM because the specimen holder cooled by liquid nitrogen becomes a liquid nitrogen trap. All cryogenic TEMs are equipped with this device. Especially, the cryo-objective lens systems of the JEM-2010, 2010F, and 2010FEF have a design optimized for cryo-observation. The space in the vicinity of the specimen is surrounded with a liquid-nitrogen trap (ACD) as completely as possible to prevent contamination of the specimen (Fig. 4C).
zero-loss electrons, which have not lost energy, excluding electrons inelastically scattered in the specimen, a clear image with higher contrast can be obtained. For this advantage, the filter TEM has now been noted as a useful system for observation of thick specimens embedded in ice.

4. Image Observation

Since, in observation at a very low magnification (Low Mag, mesh image), a broad area of the specimen is irradiated by electrons, the observation time is limited to the minimum and the mode is switched to the Mag mode as quickly as possible to protect the specimen from damage. Alignment of the axes and other necessary adjustments are made prior to the specimen observation. Formerly, frozen specimens were observed while looking at a dark fluorescent screen in a dark room. However, recently, high-sensitivity TV-rate or slow-scan CCD cameras are available on the market. By using one of them, even a dark image which you could not notice on the fluorescent screen before can now easily be observed and, therefore, there is no longer any need to look at a dark image; thus, the efficiency of the work is greatly increased. Since the accuracy of focusing also increases, it would be better to install one of these cameras if possible.

5. Photographing Method

(1) Minimum dose system (MDS)

Proteins are broken down at room temperature by electron-beam irradiation of several tens of electrons per square nm. Because of this restriction, they could not be observed with a TEM at all. To overcome this difficulty, the cryogenic electron microscope method has been developed. This method reduces the damage due to electron-beam irradiation by cooling the specimen with liquid nitrogen and liquid helium. However, even if the specimen is cooled to an extremely low temperature, the temperature of the specimen increases due to electron-beam irradiation and the specimen will suffer damage. To solve this problem, the minimum dose system (MDS, Fig. 7A) has been developed. This is a method of photographing in which three modes are selected to minimize the irradiation damage. The electron beam is irradiated on the field of view for photographing only during the time needed to expose the film (PHOTO mode). Focus is adjusted at a field of view different from that for photographing (the field of view is moved to another place with the image shift and beam shift coils) (FOCUS mode). The field of view for photographing is searched for at low magnification with the minimum amount of electron irradiation required to barely notice the image (SEARCH mode). By using this method, observation and photographing of the specimen can be made with the minimum electron-beam dose. Although appropriate conditions can be set each time according to the susceptibility to damage and the size of the specimen, the photographing magnification, and other factors, each mode of MDS will be explained below for your reference.

SEARCH mode

Turn the Brightness knob fully counterclockwise (the fluorescent screen becomes completely dark) and select the diffraction mode. When the focus knob of the diffraction image is turned to defocused position, a bright real image will appear in the center spot. Adjust the amount of defocusing to make this image an appropriate size and search for the field of view you want to photograph. Adjust the projector lens alignment coil so that the field of view for photographing comes to the center of the fluorescent screen or TV.

FOCUS mode

Move the field of view to be photographed out of the fluorescent screen by using Image Shift and Beam Shift, while keeping the photographing magnification. After making sure that the spot is not in the range for photographing, converge the beam on a small spot (increase the brightness) and deliberately melt some ice. Bring the edge of the melted ice into focus. Since ice is a specimen which usually shows almost no contrast, it will be necessary to make the under-focus amount rather large (1 μm or more).

PHOTO mode

This is the mode for setting photographic conditions. Set the photographic magnification (it is usually set to 40,000 to 50,000 times or less.

Fig. 5. Photographic images of germanium-deposited film and a gold particle taken at 4.2 K.

Fig. 6. External view of the cryo-transfer holder and work bench. (A) and (B): CTH-11 (JEOL), (C) to (D): Gatan.
according to the brightness and electron beam dose to the specimen, the specimen size, the photographic film resolution, instability and the limit of performance of the TEM). Set the current on the film surface to 1 to 5 pA/cm² or less and manually set the exposure time to one-half of the optimum auto exposure or less (4 seconds or less is desirable because there is a specimen drift). When the photographing switch is pressed, the image is automatically photographed under the conditions selected. The alignment and lens data for each mode are memorized and controlled. Therefore, once they have been set, TEM observation can easily be made under these conditions.

(2) Image recording media
Since, when photographing a specimen embedded in ice, you cannot irradiate it with a large electron-beam doze, photographic films or other recording media having higher sensitivity are necessary. Figure 7B shows graphs comparing the sensitivities of a common TEM film (Fuji FG), a high-sensitivity film (Kodak SO-163), and an imaging plate (IP). SO-163 has 3 to 4 times higher sensitivity compared with FG, and the sensitivity of IP is 1000 times or more higher than that of FG. Although IP has the highest sensitivity, its resolution is poorer than those of the films. Therefore, when you take a photograph, you would get better to use FG or S-163. However, when taking a photograph of electron-diffraction images, the wide dynamic range of IP is useful [12].

Even if a photograph is taken of a good specimen, cooled to an extremely low temperature, and using MDS, in truth to avoid damaging the specimen by electron beam irradiation, confirmation of whether the specimen is actually in a good state is not done. Therefore, it is necessary to select a good picture after photographing as many fields of view as possible. When a good specimen is found, sometimes you need to photograph that single mesh repeatedly for several days.

Summary
Currently, the demand for cryogenic TEM observation of ice-embedded specimens is increasing. Development of techniques for preparing specimens and hardware including the transmission electron microscope and specimen-preparation devices necessary to meet the demands is also making rapid progress. However, many problems remain to be solved regarding this observation method, for example, enhancement of the transmission power of electrons (increase of the accelerating voltage), enhancement of resolution, realization of stable operation of the specimen stage, reduction of ice contamination, reduction of evaporation rates of liquid helium and liquid nitrogen, automatic specimen exchange, and automatic photographing. They must be solved by cooperation between manufacturers and users of the transmission electron microscopes to make the cryogenic TEM observation technique more powerful and useful.

References

Table 3. Comparison of various types of electron gun.

<table>
<thead>
<tr>
<th>Thermal electron gun</th>
<th>Field-emission electron gun</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten hairpin</td>
<td>ZrO/W (100)</td>
</tr>
<tr>
<td>LaB6</td>
<td>Shorty ZrO/W (100)</td>
</tr>
<tr>
<td>Brightness (A/cm²/ar) at 200kV</td>
<td>~5 x 10⁻⁷</td>
</tr>
<tr>
<td>Energy width</td>
<td>~2.3</td>
</tr>
<tr>
<td>Electron source size</td>
<td>~0.7</td>
</tr>
<tr>
<td>Using conditions</td>
<td>Pressure (Pa)</td>
</tr>
<tr>
<td></td>
<td>Temperature (K)</td>
</tr>
<tr>
<td></td>
<td>Current (A)</td>
</tr>
<tr>
<td></td>
<td>Short-term stability</td>
</tr>
<tr>
<td></td>
<td>Long-term stability</td>
</tr>
<tr>
<td></td>
<td>Current working efficiency</td>
</tr>
<tr>
<td>Maintenance</td>
<td>Easiest</td>
</tr>
</tbody>
</table>

Fig. 7. (A) MDS operation panel. (B) Conceptual diagram of MDS. The field of view point X to be photographed is searched for in the Search Mode at low magnification, the point Y near the point X is brought into focus, and a photograph of the point X is taken. Comparison of the sensitivities of Fuji FG with those of Kodak SO-163 (c) and Fuji IP (d).
System for Three-Dimensional Reconstruction of TEM Images Based on Computerized Tomography Method

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Introduction

The conventional continuous thin-section method for three-dimensional (3D) reconstruction in transmission electron microscopy is well known. However, this method has disadvantages such as that it requires complicated specimen preparation and cannot acquire sufficient information concerning quantification and resolution because height information depends on the thickness of the thin sections.

Recently, new research for 3D reconstruction in TEM (transmission electron microscopy) images based on the computerized tomography (CT) method has been conducted in many fields, and some papers on such themes have been published. The CT method reconstructs the distribution of a substance inside the body of an object based on the principle of the Radon transform-inverse Radon transform. The CT method using X-rays for medical applications is well known.

When applying this CT method to transmission electron microscopy, 3D reconstructed images involving internal information can be acquired simply by photographing TEM images by sequentially tilting the specimen stage in steps, without slicing the specimen. However, the CT method conventionally has been applied only to limited special cases due to practical problems of TEM-image formation conditions such as restriction on tilt angle of the specimen stage, identification of rotation axis, image rotation and image shift.

We have been discussing how to solve such problems using an image-processing and analytical method with advanced computer technology, based on digitalization of TEM images and increases in the performance of PCs. As a result, we have established an available algorithm and developed effective software, both of which are presented here.

Principle of CT Method

Computerized tomography (CT) is well known as an imaging diagnostic instrument for medical applications. The CT scanner for medical applications acquires cross-sectional images of a substance according to the distribution of the X-ray absorption coefficient. Applying this principle to TEM using electron beams leads to the System for Three-Dimensional (3D) Reconstruction of TEM Images, which is presented here.

Projection and Radon transform

The process of illuminating an object by X-rays or electron beams, whose cross sectional images are to be examined, and of acquiring their TEM images is called projection.

Consider the situation in which an object is to be illuminated by a beam (an X-ray beam or an electron beam) and the intensity of the beam after it has passed through the object is to be measured, as shown in Fig. 1. Let the distribution of the absorption coefficient of the beam over one cross section be \( f(x,y) \), and also the incident beam intensity and the intensity after passing the object be \( I_i \) and \( I_o \), respectively. Then, the following relation is obtained:

\[
\int_{-\infty}^{\infty} f(x,y)\, dx = \ln \frac{I_i}{I_o} \quad \text{And so,} \\
I_o = I_i e^{\int f(x,y)\, dx} 
\]

where \( ds \) is a distance element along the beam. Let the incident beam intensity \( I_i \) be constant.

Now, let a new coordinate system be introduced, which is rotated by an angle \( \theta \) from the x-y coordinate system. The \( \theta \)-direction projection \( p(r, \theta) \) is defined as

\[
p(r, \theta) = \int_{-\infty}^{\infty} f(r\cos\theta - xsin\theta, rsin\theta + xcos\theta)\, dx \\
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (x, y)/(x\cos\theta + y\sin\theta - r)\, dx \, dy \quad (1) 
\]

where \( \theta \) is the Dirac delta function, and \( r \) and \( x \) are expressed by the following respective equations:

\[
r = x\cos\theta + y\sin\theta \\
s = x\sin\theta + y\cos\theta 
\]

The integral transform of Eq. (2), which expresses the transform from \( f(x,y) \) to \( p(r, \theta) \), is called the Radon transform. Reconstructing the cross section from projections is the inverse Radon transform.

Back projection and inverse Radon transform

The transforming from \( p(r, \theta) \) to \( f(x,y) \) can be easily understood by using the 2D Fourier transform. The two-dimensional (2D) Fourier transform of \( f(x,y) \) is defined as

\[
F(\theta, \phi) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) e^{-j2\pi(x\cos\theta + y\sin\theta)}\, dx\, dy 
\]

Here, transform \( \theta = \theta \cos\phi \) and \( \phi = \theta \sin\phi \) to express \( F(\theta, \phi) \) using a polar coordinate \( \theta, \phi \), then

\[
F(\theta \cos\phi, \theta \sin\phi) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) e^{-j2\pi(x\cos\theta + y\sin\theta)}\, dx\, dy 
\]

When the variables are changed according to Eq. 3, Eq. 5 becomes

\[
F(\theta \cos\phi, \theta \sin\phi) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [f(x\cos\phi - x\sin\phi, x\sin\phi + x\cos\phi)]\, dx\, dy e^{-j2\pi r \, dr} 
\]

From Eq. 6, it can be said that the Fourier spectrum of the \( \theta \)-direction projection \( p(r, \theta) \) with respect to \( r \) shows a \( \theta \)-direction cross section of the spectrum obtained by 2D Fourier transformation of \( f(x,y) \), as shown in Fig. 2.
device is installed in TEM, the information on TEM films or printed images must be converted to digital data by a scanner or other similar devices. In doing so, the displacement of the field of view depending on the position or angle of the set film or printed image sheet cannot be avoided.

Two-dimensional simulation results showing how the displacement of the field of view affects the reconstruction are presented here.

**Figure 4** (b) shows an image reconstructed by projecting the original 2D images Fig. 4(a) by 1 listeps in the range from -90° to +90°. The reconstructed images of Fig. 4(c) to (e) are obtained by giving random positional displacements, with maximum displacements of 2%, 5% and 10%.

From these simulation results, the displacement must be less than 5% to be tolerable. This is equivalent to an accuracy of 10 pixels or better when the range to be reconstructed is assumed to be 200 pixels ±200 pixels. When a field of view is extracted from the field in the usual way, the accuracy of 10 pixels or better is required for the whole field of view. Therefore, for the whole field of view of 1 k x 1 k (pixels), an accuracy of 1% is required, and for 4 k x 4 k field, an accuracy of 0.25% or better is required. Such high accuracy must be quite difficult to achieve by only improving the mechanical accuracy. To solve this problem, we have developed and implemented an algorithm by which the same field of view is selectively extracted repeatedly.

**Identification of rotation axis**

As already described, in the CT method, the back projection is performed based on the same angle and same rotation axis as those which were used when the projection was performed. Although, as seen from the theory, the positional information of the rotation axis can be deduced to be especially important, it is impossible to determine the rotation axis even by observing the TEM image. For finding the rotation axis, marking the specimen surface has been proposed. However, this is impractical because complicated handling requires much time. Simulation results are presented in Fig. 5.

**Figure 5(a)** shows images resulting from Radon transform in 1 steps in the range from -90° to +90° in the same way as in Fig. 4(b), and reconstructed by back projection. The reconstructed images of Fig. 5(b) to (e) are obtained by giving uniform rotation axis displacements, 2%, 5%, 10%, and 30% displacements each as the maximum displacement. A 2% displacement of the rotation axis (4 pixels) makes images blurred. Also, it can be seen that 10% displacement of the rotation axis or more cannot be tolerated in image reconstruction.

From these simulation results, it can be seen that the requirement for the tolerable displacement of the rotation axis is much rigorous than for the displacement of field of view. That is, the accuracy for the rotation axis is the key for three-dimensional reconstruction of TEM images. This simulation has been performed using the one-dimensional projection for TEM images where the axis position is considered to vary sequentially according to sequentially prepared sections.

We have developed probabilistic algorithm

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**Problems When Applying to TEM Images**

Application of the CT method to TEM images was proposed many years ago, and much research has been performed since then. Today, greatly-improved computer processing allows the principle of the CT method to be examined easily. However, there has been no commercial, general-purpose software based on this principle. This is because application of the CT method to the TEM field must be limited to only special specimens and measurement conditions due to several problems specific to TEM. CT simulation results depending on the conditions of TEM parameters and the solution to overcome the problem specific to TEM are presented here.

**Displacement of field of view position (shift and rotation)**

TEMs are usually equipped with a fully eucentric specimen stage which allows tilted-specimen images of the same field of view to be acquired. However, the positioning accuracy of specimen stages is insufficient for practically reconstructing 3D images from high-magnification TEM images. Also, when no TV camera or SSCCD
to identify rotation axes by processing successive projection images.

**Restriction to tilting angle of specimen stage**

For full reconstruction by the CT method, projection in the range of projection angles from -90° to +90° is required. If the range of projection angles is restricted, the specified range of projection angles for the object cannot be reconstructed due to the lack of information at some projection angles. In practice, in an actual TEM stage, there are limitations on the projection angle and an apparent increase of the specimen thickness at high projection angles (except for spherical or cubic specimens), both of which make it impossible to acquire TEM images. As a result, for TEM images, reconstruction is performed using limited projections. The simulation results obtained under these limitations on projection angles are presented in Fig. 6.

**Figure 6 (a)** shows images resulting from Radon transform in 10 steps in the range of projection angles from -90° to +90° in the same way as in Fig. 4(b), and reconstructed by back projection. The reconstructed image of Fig. 4(b) is obtained in the range from -60° to +60°, and Fig. 4(c) from -45° to +45°. As seen in these figures, the areas without projections are dark, as the theory predicts. To solve this problem, we have tried a method based on interpolation and a probabilistic estimation method, but new problems such as virtual images have arisen. In our system, as a result of examination using actual TEM images, even when projection angles are restricted to lie in the range from -60° to +60° these problems can be eliminated by adjusting the conditions concerning the 3D reconstructed image observation.

**Number of projection sheets**

In principle, although projections acquired sequentially by varying the projection angle sequentially make it possible to cover the 2D Fourier space completely, such acquisition is impossible in practice. **Figure 7** presents the simulation results showing the relationship between reconstructed images and a number of projection sheets.

**Figure 7 (a)** shows images resulting from Radon transform with 10 steps in the range of projection angles from -90° to +90° in the same way in Fig. 4 (b), and reconstructed by back projection. The reconstructed image of Fig. 7(b) is obtained with 5 steps, (c) obtained with 10 steps, and (d) with 30 steps. From the simulation results, we see that reconstruction of images is possible even with 10 steps (17 sheets). However, in light of the restriction on projection angles it is believed that much more information becomes necessary. As a result, 20 sheets or more are considered to be necessary.

**Accuracy for stage angle**

The specimen stage is controlled manually when acquiring data. Angle errors due to mechanical movement of the stage (backlash and other phenomena) and angle reading errors occur at this time. Results of simulation of the reconstructed image as affected by such errors are presented in **Fig. 8**.

---

**Figure 8 (a)** shows images resulting from Radon transform in 10 steps in the range of projection angles from -90° to +90° in the same way as in Fig. 4 (b), and reconstructed by back projection. The reconstructed images from **Fig. 8 (b) to (e)** are obtained by randomly giving angle errors with maximum amplitude ranging from 0.5° to 5°. It can be seen that even if an angle error much bigger than 1° occurs for a projection angle of 1° image reconstruction is possible. It can be said that stage adjustment can usual-
Summary

From the simulation results of Fig. 4 to Fig. 8, the requirements for 3D reconstruction of TEM images are determined as follows:

- Displacement of specimen position: Within 5% of size of image to be reconstructed (to be corrected by image processing)
- Identification of rotation axis: Within 2% of size of image to be reconstructed (to be corrected by image processing)
- Stage angle: 60° or more (the lack of information is compensated by 3D image display)
- Number of projection sheets: More than 20 sheets (depending on object shape and image quality)
- Accuracy of stage angle: Error of 2° is tolerable.

General Description of System

Composition

The system is composed of the following four programs running on a PC:

- Projection Finder: Software for position correction and data extraction
  - Extracts the area to be reconstructed from the original image while correcting the position and tilting angle.
  - The algorithm of this software is now being prepared to be patented.
- Axis Estimator: Software for identifying rotation axis
  - Deduces the rotation axis using extracted images and shifts and rotates the image so that the center of the image coincides with the rotation axis. The algorithm of this software is also now being prepared to be patented.
- 3D Builder: Software for 3D image reconstruction
  - Reconstructs 3D images from the tilted images whose positions and rotation axes have been corrected and forms 3D data. The inverse Radon transform is processed by filtered back projection in real area to achieve high speed. A processing function to improve image quality using matrix iteration is also implemented.
- 3D Viewer: Software for viewing 3D data
  - The 3D data formed by 3D Builder are made to be viewed. 3D Viewer allows displaying an arbitrary new cross-sectional plane of Volume Rendering plane, equal-value plane, x-y, y-z, and z-x planes. Interactive object handling using a mouse is available.

How to input image data

Figure 9 shows how to input image data into the EBCT-3DR system. At present, this system is independent of the TEM used. In the case of a TV camera or a SSCCD, TEM-image data are to be input through a network or a media like an MO (magnetic-optical disk) into this system. In the case of silver halide photographs, a negative film or a printed photographic paper is scanned using a scanner to convert it to digital data to be input. In both cases, the software supports data files in the .TIF or .BMP formats.

Operating conditions

Recommended operating conditions (recommended environment) of the EBCT-3DR system are as follows:

- CPU: Intel Pentium III 500 MHz or faster
- OS: Microsoft Windows2000
- Main memory: 512 MB or more
- Usable hard disk space: 2 GB or more
- Display card: One provided with OpenGL acceleration function
- Hardware rendering card: AVS driver compatible
- Display: SXGA (1280 x 960 pixels) or more
- Scanner: Transparency adapter (with focus adjustment)
  - Resolution: Around 1200 dpi
Results of Reconstruction

Examples of reconstruction are presented below:

**Gyroid (molecules of high mass number)** (Fig. 10)

The specimens are offered by the courtesy of Dr. Hasegawa of Kyoto University and Dr. Jinnai of Kyoto Institute of Technology.

Photographing conditions are as follows:
- Stage tilt angle: +60° - 60°
- Number of projection sheets: 2.5 steps (49 sheets)
- Magnification: 20k

**Coated vesicle** (Fig. 11)

The specimens are offered by the courtesy of Dr. Usukura of Nagoya university and Dr. Morone of Japan Science and Technology Corporation.

Photographing conditions are as follows:
- Stage tilt angle: +60° - 60°
- Number of projection sheets: 2.5 steps (49 sheets)
- Magnification: 23k

**DNA-RFC (Replicated Factor C)** (Fig. 12)

The specimens are offered by the courtesy of Dr. Usukura of Nagoya university and Dr. Turimoto of Nara Institute of Science and Technology.

Photographing conditions are as follows:
- Stage tilt angle: +60° - 60°
- Number of projection sheets: 2.5 steps (49 sheets)
- Magnification: 180k

**Conclusion**

We have established an algorithm where the alignment of field of view and the identification of rotation axis, both of which were obstacles to applying the CT method to TEM images, can be performed by image processing. Using this algorithm, a system has been developed where 3D reconstruction of TEM images can be performed by acquiring only tilted TEM images. Also, several applied examples have revealed that this CT method is very effective in 3D TEM image observation.

The following are goals for further improvements of the 3D reconstruction CT method for TEM images:

**Speed-up of calculation**

The present system takes from several hours to more than ten hours for identification of field of view and rotation axis. In order to overcome this problem, improvement of the algorithm to speed up the calculation and implementation of hardware devices such as parallel arithmetic units are being examined now.

**Expanding functions for analysis of reconstructed 3D images**

Fields of application of the system will be expanded by adding new functions to various measurements (metrology and volume measurement) and shape recognition and other improvements.

**TEM to be made available on-line**

A fully automatic system, from tilted-image acquisition to 3D reconstruction, will be established by linking with the TEM remote-control function.

**References**


![Fig. 10. (a) TEM images of gyroid and (b) reconstructed images of gyroid. Image area: 70 100 25 nm.](image-url)
Fig. 11. (a) TEM images of coated vesicle and (b) reconstructed images of coated vesicle. Image area : 390 \( \times \) 390 \( \times \) 135 nm.

Fig. 12. (a) TEM images of DNA-RFC and (b) reconstructed images of DNA-RFC. Image area : 70 \( \times \) 90 \( \times \) 15 nm.
Development of Electron Beam 2D Pattern Metrology System

Manabu Saito
Semiconductor Equipment Division, JEOL Ltd.

We developed the Electron Beam 2D (two-dimensional) Pattern Metrology System for performing metrology of pattern-stitching accuracy at the stitching region in the writing field on an electron beam lithography pattern. This system can obtain SEM images of field stitching, and also perform two-dimensional metrology of location errors in stitched patterns, fully automatically according to a measurement recipe. The results of measurement are transferred to a data analysis system, and then subjected to various kinds of analysis after the finish of all measurements. In order to measure the stitching accuracy on an actual device pattern, which is fine and complex, we developed and evaluated a new metrology method. As a result, we found that it was possible to measure the stitching accuracy on an actual device pattern with reproducibility of 5 nm or less.

Introduction
Currently, as the design rules for semiconductor LSI patterns are rapidly being reduced in feature size, the importance of fine pattern lithography using an electron beam is increasing. When electron beam pattern writing is used on a wafer or a mask, the beam deflection range (pattern writing field) is narrow compared to the size of one chip, and there are many stitched patterns in the chip. Consequently, it is necessary to measure and control the stitching accuracy, and feed it back to the lithography system.

Conventionally, there was no suitable method of measuring pattern-stitching accuracy. For this reason, a test pattern that had marks at the periphery of the pattern writing field was drawn, and the positions of the marks was measured mainly using an optical measurement system, in order to measure the field positioning accuracy. However, along with the downsizing of the pattern, the optical metrology has now reached the limitation in resolution. Also, there are demands to be able to perform measurement on a complex pattern on an actual device without using dedicated marks for measurement.

In cooperation with Selete (Semiconductor Leading Edge Technologies, Inc.), we developed the 2D Pattern Metrology System that measures pattern-stitching accuracy using an SEM image. This system uses various new technologies to measure pattern stitching. Examples are the edge detection method, which reduces statistical fluctuations in the measured value due to roughness in the lithography pattern and noises in the SEM image, and a method that utilizes pattern matching on an image to measure the stitching in a complex actual pattern.

This system performs two-dimensional (XY) metrology of the pattern stitching on a fine pattern on an actual device, and transfers the results to the data analysis system, fully automatically. The analysis system displays the stitching between pattern writing fields and analyzes it. Also, it can easily display an SEM image of the stitching region.

We evaluated the performance of this system using a test wafer on which an electron beam lithography pattern had been processed on photoresist. A report on the evaluation is described below.

System Configuration
We constructed the system shown in Fig. 1.

The SEM electron optical column was based on that of the JWS-7555S, and an aberration corrector was built in the instrument, resulting in a high resolution of 3 nm or less (at 1 kV). A holder type loader/stage system was used to cope with various applications. At present, the system can perform measurement on a 200 mm (flat or v-notch) wafer, a 300 mm wafer and a

Fig. 1. System configuration.

Fig. 2. Principle of the "Pattern Matching Method". Dotted line indicates the pattern-stitching boundary.

\[ D_1 = (X_{iL}, Y_{iL}) - (X_{iR}, Y_{iR}) \]
\[ D_2 = (X_{iL}, Y_{iL}) - (X_{iR}, Y_{iR}) \]
\[ (dx, dy) = D_1 - D_2 \]
150 mm mask or reticle. The position of the XY stage is controlled by a laser interferometer. Measurement is performed fully automatically according to a measurement recipe created in advance.

The SEM image acquired to the frame memory is used to perform two-dimensional metrology of the stitching error. Measurement is performed by transferring the image to a pattern-matching engine or an edge-detection engine, and comparing it with a reference pattern image or a simulation model.

The results of measurement are sequentially transferred to the data analysis system, then after the finish of all measurements the GUI (graphical user interface) is operated, and the data is compiled and converted into visual form.

**Pattern-Stitching Accuracy Measurement**

We used two metrology methods for measuring pattern stitching accuracy. One is "Edge Set Separation Method" in which two-dimensional distance measurement is performed by separating the two stitched line patterns (represented as two edge point sets) from each other using a statistical approach and simulation model matching. Another is "Pattern Matching Method" in which the distance between patterns is measured comparatively by compiling the features of the complex pattern into a model and performing pattern matching. Here, an outline of the pattern matching method is described. Also, the measurement recipe and data analysis system are described.

**Metrology (Pattern Matching Method)**

Figure 2 shows the principle of this method. First, an image of a reference pattern is prepared. On the reference image screen, two rectangular areas, each of which has an arbitrary size, are specified on both sides of the stitching boundary. Then the pattern-matching models are created from the image features represented in those areas. Each model should contain some features that consist of a part on the device pattern. The distance between the model areas is memorized as $D$. Next, pattern matching is performed on the image of the target pattern for searching a part of the same shape as that of the pattern-matching model, and the distance between the search results ($D'$) is obtained. Finally, $D$ and $D'$ are compared with each other, enabling the shift ($dx$, $dy$) to be measured. As a reference pattern, it is reasonable to use a pattern that does not contain the stitching region.

In order to perform pattern matching accurately, it is necessary to include the features of the vertical and horizontal directions of the image in the model. So long as these features are included, it is possible to perform measurement with various types of patterns such as those shown in Table 1. It is sufficient that only a part of the pattern is included in the model area. In the case of a simple line & space pattern, which has only single direction feature, measurement can only be performed in the direction perpendicular to the line direction. In this method, if the pattern is complex, the distinctive features will increase, and the pattern matching accuracy will increase. Therefore, the measurement accuracy (reproducibility) will be improved.

**Measurement Recipe and Data Analysis System**

The flow of the data that is necessary for measurement is shown in Fig. 3. In order to specify the measurement position (that is, the field stitching position), a measurement position data file must be prepared in advance. In this system, this file can be created automatically by specifying the following conditions on GUI: the measurement start coordinates, the measurement end coordinates, and the number of measurement points. In addition, this system can link to various electron beam lithography systems, provided that, the formatted measurement position data file, which is extracted from a pattern data or a lithography result data of these lithography systems, is sent from them. A readable format (text format) is used to this file, and its format is disclosed to lithography system vendors or users upon request.

In addition to this system, another software was developed for the use of JEOL’s JBX-9000MV electron beam lithography system (mask writer). It automatically extracts the measurement point from the pattern data in the JBX-9000MV, in order to perform the stitching metrology of the reticle pattern written by this.
<table>
<thead>
<tr>
<th>Pattern</th>
<th>ISO1 (BAR) 180DRAM</th>
<th>ISO2 (DIAG) 180DRAM</th>
<th>NODE 180DRAM</th>
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<td><img src="image2" alt="SEM Image" /></td>
<td><img src="image3" alt="SEM Image" /></td>
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<td>dx, dy (3σ; nm)</td>
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<td>2.3, 1.6</td>
<td>4.7, 1.5</td>
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<th>150SRAM Contact (DOT)</th>
<th>280DRAM ISO</th>
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<td>x 50,000</td>
<td>x 30,000</td>
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<tr>
<td>Field-of-view size</td>
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<td>(6.7 x 5.3) μm</td>
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<th>160LOGIC GATE</th>
<th>180DRAM GATE (L&amp;S)</th>
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<td><strong>Magnification</strong></td>
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<td>(3.5, 11.0)</td>
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Table 1. Measurement results of 9 kinds of actual device patterns.
equipment. The linkage operation between this system and the software for the JBX-9000MV has been verified.

When performing measurement using the pattern matching method, a reference image is necessary, so a reference-image acquisition recipe is created and executed. Executing this recipe permits the automatic acquisition of the pattern-matching model at the measurement position that was specified in the measurement position data file, and enables the model data to be input in the data file. As a reference image, it is possible to use not only an SEM image, but also a bitmap image that was extracted from a CAD data.

After these operations, by executing the measurement recipe, the wafer stage moves to each measurement position, measurement is performed, and then the measurement results are sent to the data analysis system.

The data analysis system consists of a server that administrates a huge amount of data, and also a client PC that extracts the data on the server via the GUI and compiles it. The client PC can perform various kinds of analysis. One of the client PCs functions is the rail-road chart display of measurement data. The rail-road chart display of the measurement data enables the error and distortion in each field to be clearly visualized. (Fig. 4)

**Measurement Results**

Table 1 shows the measurement sample and the measurement results. First, we obtained the error caused by the measurement system. We employed the pattern matching method, and used the same stage position for obtaining both the reference image and the image of the target pattern so that the expected value of the measured stitching error could become (0, 0) nm. Then, we performed measurement at 25 points on each pattern. The actual measured values obtained in this experiment directly express the errors caused by the measurement system. We found that, although the results depended somewhat on the directionality of the pattern, it was possible to perform measurement with reproducibility of about 2 to 5 nm at 3 sigma. Regarding a pattern that had a strong directionality, the measurement accuracy fell to about 15 nm along with the reduction of the pattern matching accuracy.

Also, the degradation of measurement reproducibility due to loading and unloading of the wafer was about 1.5 nm with 10 measurements.

Next, we wrote isolation patterns of DRAM containing built-in designed stitching shift in the X and Y directions of ±40, 20 and 0 nm (25 kinds), and carried out measurement. We used the pattern containing a shift of (0, 0) nm as a reference, measured 25 kinds of patterns five times each, and obtained the average of them. The results are shown in Fig. 5. The vertical and horizontal directions show the measured shift (nm) for the X and Y directions, respectively. Plotting of the measured values was made on the graph. The point of X-Y intersection with each of the ±40, 20 and 0 nm scale marks (dotted lines) means the design value of the stitching shift. It can be seen that the measured values agreed with the design values.

As described above, it is also possible to use a bitmap image of a CAD pattern rather than an SEM image of a processed pattern as a reference image. If it is difficult to accurately create an actual pattern that has no stitching error, a reference image can be extracted from CAD instead, which is an effective way. Figure 6 shows the results of measurement using a bitmap image that was extracted from CAD as a reference image. A Y-direction bias of about 10 nm acted on all measured values. This bias can be considered to be a constant resulting from the difference between the SEM image and the CAD image (difference between the design profile and the processed pattern, the difference of contrast between the SEM images and the CAD images, and so on). In other words, the bias does not depend on the measurement position, so by appropriately determin-

The time required to perform measurement using the existing system was 42 seconds per point, including the stage shift time. We will reduce this time to 10 seconds by improving the system.

**Summary**

We developed the Electron Beam 2D Pattern Metrology System for performing metrology of the stitching accuracy on electron beam lithography patterns using SEM images. This system is capable of performing fully automatic metrology of the stitching accuracy in a fine and complex actual-pattern and the location error in patterns on a device, with reproducibility of 5 nm or less.

**Acknowledgements**

This two-and-a-half-year research was carried out with financial assistance from Selete covering part of the development expenses.

We would like to take this opportunity to thank the following researchers whose ideas and discussions enabled us to successfully complete our research. Selete: N. Endo, M. Yamabe, Y. Tomo, H. Takenaka, Y. Okuyama (former member: ELP-IDA), S. Matsui (former member: Himeji Institute of Technology), Sony: S. Moriya, NEC: H. Nozue, Oki Electric Industry: A. Endo, JEOL: N. Date, S. Norioka, H. Shimada, S. Takashima, K. Tanaka, K. Honda, T. Shinkawa, A. Tohyama, S. Seki, S. Kamata, H. Tanaka, K. Nakagawa, Y. Ogiwara, Y. Higashi.
Application of OBIC/OBIRCH/OBHIC (Semiconductor Failure Analysis)

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Introduction

When a laser beam, finely focused by an objective lens, irradiates a sample surface, various kinds of signals are emitted as result of interaction between the incident laser beam and the sample. Such various signals and photo effects are shown in Fig. 1 schematically. Visualization of these phenomena can be made by detecting these various photo effects caused by the interaction and by displaying them on a viewing screen synchronized with the scanning of the laser beam [1].

When the laser beam with energy higher than the band gap energy of the pn junction irradiates semiconductor devices, electron-hall pairs are generated and they flow in the semiconductor to make electron current. Detecting this current and displaying on a viewing screen, we obtain OBIC image, and they are used for failure analysis of semiconductor devices.

Applying a bias voltage to the wire in the wiring area of semiconductor, we can detect a current change due to the resistance change by scanning the focused laser beam over the surface. This is the Optical Beam Induced Resistance Change (OBIRCH) [2]. Laser beam irradiated area is heated and its resistance is increased. This results in less current. We are able to display this resistance change on a viewing screen by measuring the current change. We must always supply the bias voltage to the sample in order to detect small current change in this method.

We can detect so-called thermo-electromotive force of a material containing no pn junction, if it is heated by the laser irradiation. This can be used to detect defects or failures [3]. This current is called Optical Beam Heat Induced Current (OBHIC)[4].

Figure 2 shows a typical system block diagram of the unit for detecting and visualizing these phenomena. The typical system is consisted of a sample stage, laser source, optical microscope, signal amplifier, DC power supply, computer and viewing screen (CRT). We use different laser beam wavelength for different applications, and a DC Power Supply is used if necessary.

OBIC (Optical Beam Induced Current) Applications

Failure detection of pn junction

a) An example of a recombination center

When there is a recombination center like dangling bond, the recombination probability rises and trapped electrons increase to cause OBIC current decrease. As a result, OBIC images become dark. The black spot in the center of Fig. 3 shows the recombination center.

b) An example of a generation center

The OBIC current increases at the impurity position in the junction. The OBIC image is shown in Fig. 4. The position indicated by arrows is the generation center areas and they are brighter than the surrounding area.

Failure detection of inter-level short

When the wirings are shorted, the resistance between the wirings decreases locally and electric field concentration occurs there. They are called the weak point. As this makes OBIC...
current larger, the OBIC image becomes brighter than the other area as shown in Fig. 5.

Confirmation of the on and off states of transistor
When a transistor is switched on, electrostatic potential between the poles is almost equal and so OBIC current generation is small. Therefore, the contrast in the OBIC image is weak. The transistor at the left side in Fig. 6 is in the state of switched on and the OBIC contrast is weak. The other transistor at the right side is in the state of switched off and the OBIC current generation is higher than the left side transistor, so that image is brighter.

Failure detection of latch-up
We used a DRAM for this test. Figure 7 shows an example of detecting the defect in the cell driving area, which is consisted of several transistors. If we irradiate a laser beam with the wavelength for detecting OBIC on to this kind of sample, so-called the parasitic transistor is turned on and triggers all the other transistors. This phenomenon is called the latch-up, and we are not able to specify the parasitic transistor, as shown in Fig. 7(a). For specifying the parasitic transistor with this kind of sample, the Synchronized Dual Laser Beam Irradiation Analysis (SDLBIA) method is proposed. Figure 7(b) is an example obtained with this method [5].

Weak point detection of MOS transistor
In case of MOS transistor, OBIC current depends on the potential of electrostatic field. The OBIC current becomes stronger at the weak point where the electrostatic field concentrates in the insulating material. A typical image is shown in Fig. 8. The bright spot in the center of Fig. 8 shows that the OBIC current is larger than surrounding area. Four black spots around the bright spot are the marks of laser marker. After the OBIC investigation with this device, we made a thin cross section film including the weak point and investigated with a transmission electron microscope (TEM). Figure 9 shows a TEM image of the weak point.

OBIRCH (Optical Beam Induced Resistance Change) Applications

Failure detection by the via-hole chain TEG
Figure 10 shows an example of failure detection by via-hole chain TEG. We found two bright spots in the area. After investigation with the Laser Defect Analyzer, we made a cross section of the circled area marked with the in Fig. 10 with a Dual Beam FIB instrument. Figure 11 shows a secondary electron image from the cross section of this area, in which we can see a void due to failure formed during the production process.
**Failure detection at the pattern circuit**

Figure 12 shows OBIRCH current between one pad and the base plate while a low bias voltage was supplied. Figure 12(a) is a low magnification image of 90 and Fig.12(b) is a higher magnification of 7600. After investigation of the sample with the Laser Defect Analyzer, we made a cross section of this area with a Dual FIB instrument. Figure 13 shows a secondary electron image of the cross section of failure part. We can see that there is no connection between 1st and 2nd wirings.

**Failure detection at the via-hole chain with WELL**

Figure 14 shows a schematic drawing of the sample used for this measurement, and Fig. 15 shows the result obtained with laser beam irradiation of two different wavelengths. Figure 15(a) is the image taken with 1083nm laser beam (near infrared region). The OBIC phenomenon can be observed over whole WELL area. We cannot specify the specific malfunction part when we use the laser beam of the wavelength 1083nm. However, when a laser beam with wavelength of 1360nm (near infrared region), though OBIC is not generated, OBIRCH is generated. Thus the defective area is specified at the contact.

**Failure analysis of system LSI device**

A Logic-IC, which shown to have a failure between the power supply line and the ground line by Charged Device Model (CDM) test, was investigated with the Laser Defect Analyzer. Figure 16(a) is the optical image of the device and the Fig. 16(b) is the OBIRCH current image from the same area. All the bright spots in the Fig 16(b) show failures at the gate oxide film. The area encircled with white circle was enlarged. Figure 16(c) is the optical image and Fig. 16(d) the current image.

Fig. 17 shows the result of CDM test. I-V curve from the good device shows non-linear I-V curve but the curve from the faulty device shows the linear I-V curve. After the investigation of the device with the Laser Defect Analyzer, the Logic-IC was chemically treated and the top layer film was removed down to Poli-Si gate. Figure 18 shows a secondary electron image of the gate area. The gate oxide films of transistors are shown to be defective.

**OBHIC(Optical Beam Heat Induced Current)Applications**

**Failure detection of MR head**

In general, electrical probing is used to select defective chips in the Magnetic Resistance (MR) head review. Since the electrical probing does not identify the specific location of the defect in the chip structure, this selection process contributes little to the yield enhancement if a further analysis is not made. The Laser Defect Analyzer inspects the defective chips selected, and by the use of a current meter connected between terminals, the location of defect can be found by monitoring the current flow. Figure 19 shows an example of this process. The defective chip, whose resistance is 1/100 of the normal chip, was selected by the electrical probing. The laser beam with
the wavelength of 658 nm was used to take its OBHIC image. Figure 19(a) is a composite image of optical and OBHIC images showing the structure of MR head under magnification of 360. Figure 19(b) is the magnified image of the encircled area around the bright spot. At the center, the defective part exists. After the investigation with the Laser Defect Analyzer, the crosses section of defective area was made with a Dual Beam FIB. **Figure 20** is the secondary electron image of the area. This shows that the defect is located at the position about 5 μm in depth from the surface.

**Conclusion**

The Laser Defect Analyzer is a quite powerful instrument for the failure analysis of semiconductor device and the other materials. The use of instrument can contribute to the quality control of the production and enhancement of the yield management.

**References**

JAS-WPA Series
Wafer Surface Particle Analyzer

Hiroshi Terashima
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Introduction
A review station employing an optical microscope and a wafer review SEM (scanning electron microscope) has been used extensively as morphology-observation-based particle and defect inspection tools for yield management in the manufacturing process of semiconductor devices and LCD panels. Recently, an element analysis system consisting of a wafer review SEM installing an EDS and tools permitting FIB milling have appeared on the market, and are contributing to the identification of component elements and the structural analysis of particles and defects. In the particle analysis, however, even the element analysis methods, which are effective for analyzing particles consisting of elemental compounds such as metals, have insufficient ability to identify particles consisting of organic compounds (particularly organic compounds) having complex structure. In such cases, it is necessary to rely on morphological classification, and even skillful engineers feel it difficult to perform accurate substance identification. To overcome this problem, JEOL employs an entirely new approach, and is manufacturing and supplying the JAS-WPA series of wafer surface particle analyzer, which is a defect review tool for analyzing fine particles on the surfaces of wafers, based on Micro Raman Spectrometer. The outline of this instrument is given below together with measurement examples.

Outline of the Instrument
This instrument combines a laser Raman spectrometer and a review system for wafer inspection based on an optical microscope. The overall photograph of the instrument is shown in Figure 1. The review system has a wafer transfer function, an XY stage shift function that is linked to the positional information of defect (corresponding to the coordinate files of KLA/Tencor, Hitachi Electronics Engineering, and so on), and an auto focus function, enabling defective particles to be easily captured within the visual field of microscope. Overall, this instrument is a defect analysis tool having the function for observing the Raman scattering spectrum generated from a particle irradiated by a laser beam, in addition to the normal particle review function. The spectrum acquired by the Raman spectroscopy is characteristic of the substance concerned, and thus permits qualitative analysis. This spectral analysis method is particularly suitable for identifying specific compounds. The spatial resolution related to Raman measurement depends upon the wavelength of laser used and also the condensing rate (magnification) of the objective lens. When a diode laser (wavelength 532 nm) is used and the magnification of the objective lens is 1500, an irradiation beam diameter of 0.7 μm is attained. This instrument comes with high performance Windows-based software having various data-processing functions and a report-making function for improved processing of spectrum data, together with library-search software based on the spectrum comparison. Thus it enables even inexperienced persons to easily determine the substances contained in a particle. Furthermore, an extremely high rate of substance identification can be achieved by combining the customer's own database with the database constructed by JEOL. The following is the actual work procedure for particle analysis.

1. The wafer is extracted from the carrier by a robot arm, and then after global alignment it is transferred to the XY stage. (Compatible with all types of wafers: including 125/150/200 mm, V-notch and OF.)
2. The XY stage moves the particle accurately into the field of view of the microscope, based on the XY coordinate data sent from the defect inspection system. (Linked to the defect coordinate file. The XY stage positional accuracy: 1.5 μm.)
3. The pinpoint laser-beam irradiates the particle through the objective lens, to cause Raman scattering. (The laser irradiation power is only several hundred of μ W; therefore, the particle is almost undamaged.)
4. A spectrum is acquired by an ultra-high sensitivity Raman spectrometer, and the com-
In this paper, we present results of polypropylene and amorphous carbon analyzed by EDS. EDS, and shows another sub-

Fig. 2. µm size of particle was measured by WPA and identified as polypropylene.

Fig. 3. Another sub-µm size of particle was measured by WPA and identified as amorphous carbon.

Fig. 4. Results of polypropylene and amorphous carbon analyzed by EDS.

Fig. 5. Results of various size of polystyrene particles analyzed by WPA.

pounds are identified by library-search with the databases.

Example of Particle Analysis

Figures 2 and 3 show analysis examples of particles on a bare wafer. A satisfactory spectrum was obtained in the measurement period of several tens of seconds. From the results of the library-search (output to the third possibility shown on the right side of the chart), the particles were identified as polypropylene (the component elements are C and H) and amorphous carbon (the component element is C alone). The same specimen was subjected to the element analysis using SEM+EDS, and the results obtained are shown in the chart of Figure 4. In the EDS analysis, hydrogen cannot be detected, and so only carbon is detected in both kinds of particles. Therefore, they are identified as the same kind of particle. On the other hand, it can be seen that the Raman spectroscopy enables both kinds of particles to be clearly differentiated from each other. In this case, it is found that polypropylene comes from the wafer case, and amorphous carbon comes from the etcher, enabling appropriate dust preventive countermeasures to be taken. In addition, this method can identify a variety of substances, both organic and inorganic compounds. Examples of identifiable organic substances include various plastic materials (Teflon, polyester, acrylic resin, etc.), oils and fats (hydrocarbons, silicones, fluorine-contained compounds, etc.), and human proteins. Examples of identifiable inorganic substances include products of reactions between acids and alkalis such as film-degeneration substances typified by silicates, sulfates and nitrates. The WPA is a reliable tool that clarifies the cause of occurrence of defects and particles.

Limit Size in Measurement

Figure 5 shows the results obtained from the scattering measurement of polystyrene particles of various size on a wafer. From this data, it can be seen that the spectrum can be obtained even for a 0.2 µm size particle. When the beam diameter is larger than the particle diameter or the laser beam passes through the particle, the spectrum will be interrupted by the spectrum originating from the silicon substrate. However, by removing this interference using spectrum subtraction, it is possible to detect only the spectrum signal generated from the particle itself. Such data processing can be implemented as an automatic function. Effective use of this function enables to analyze plastic and carbon (amorphous carbon, graphite) particles with 0.2 µm or less in size.

Future Development

We intend to produce a lineup of dedicated wafer inspection systems compatible with 300 mm wafers. The spatial resolution of the order of sub-micrometers and excellent qualitative analysis capabilities offered by the Raman spectroscopy can be utilized for the analysis of particles not only on wafers but also on masks and FPD (flat panel display). For this reason, we are currently studying the manufacturing of a highly versatile model capable of coping with various kinds of specimen shapes.
Effective Methods to Prevent Charging in Auger Electron Spectroscopy

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1. Introduction

In rapid progress in downsizing technologies for semiconductors and functional materials, it is more important to carry out the evaluation and the analysis of sub-micro structures. Auger Electron Spectroscopy (AES) has been used as one of the effective analytical methods for these specimens. It uses a fine electron probe focused to several 10 nm, thus enabling microarea analysis that provides correspondence between the analysis point and the point on an SEM image. It also enables element analysis, state analysis and element mapping from the acquired Auger spectra. Auger application, however, is limited only to conductive specimens other than nonconductive and organic one, because of the use of a fine focused electron beam. In this point, AES has been inferior to X-ray photoelectron spectroscopy (XPS, ESCA) that is effective for analyzing nonconductive specimens. Therefore, many persons have carried out researches and experiments in order to apply AES to nonconductive specimens with high spatial resolution.

In the case of Auger analyses of nonconductive specimen, the tilting method has been used usually. This is a conventional method to prevent charging by tilting a specimen to increase the amount of escaping secondary electrons [1]. Recently, however, it has become difficult to utilize this method for more minute and complicated specimens included in insulators, for example, liquid crystal panels, ceramics circuit boards and VLSI devices. In this paper, we introduce two methods to prevent charging in Auger analysis; the charge-neutralization method [2] and the thin-film method [3]. The former is to use the fact that the charging on an insulator is neutralized with positive Ar ions during Auger analysis. The latter is to use the fact that most incident electrons pass through a cross-sectional thin specimen fabricated by FIB (focused ion beam) [3]. In addition to them, some applications are shown in this paper.

2. Charge-Neutralization Method

2.1 Purpose of Neutralizing Electric Charge

In the case of conductive specimens, incident electrons rapidly diffuse as free electrons by electromagnetic force. To a result, the specimen surface keeps the constant electrical state during Auger analysis. To the contrary, in the case of nonconductive specimens, however, incident electrons hardly diffuse both on the surface and in the specimen bulk. These electrons cause non-uniform electric fields and influence the kinetic energy and the direction of secondary electrons (included Auger electrons) on various parts of the specimen (Fig. 1). Consequently, SEM images and Auger spectra become abnormal. To overcome this problem, JEOL has developed a new ion gun where positive ions of an inert gas, such as Ar⁺, irradiate the specimen surface, thereby neutralizing (decreasing) the non-uniform electric field entirely.

2.2 Development of the Floating-Type Micro Ion Etching Device (FMIED)

JEOL has developed the FMIED as a new-type ion gun for charge neutralization and sput-

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Fig. 1. Purpose of charge neutralization.

Fig. 2. Schematic view of the floating-type micro ion etching device (FMIED).
tering. In the case of irradiation with ions from a conventional ion gun under non-sputtering condition, the lower was the ion energy, the lower was the ion current. Therefore, it was not possible to obtain a sufficient neutralizing effect. In order to overcome this, the FMIED was developed, which can provide high current density even at sufficient low ion energy (50 eV or less) to prevent sputtering. A schematic view of the FMIED is shown in Fig. 2, and its exterior view is shown in Fig. 3. Figure 4 shows a comparison of the ion current characteristics between the FMIED and a conventional ion gun; Micro Ion Etching Device (MIED4).

2.3 Neutralizing Conditions of FMIED

Several experiments were carried out to determine the appropriate neutralizing conditions of the FMIED.

For effective charge neutralization, it is necessary to make ion current as large as possible. Because the large ion current needs higher accelerating voltage generally, it had to find the appropriate ion energy for neutralization under non-sputtering condition. To acquire these conditions, it was examined if the natural oxide film on a Si wafer changed before and after the ion irradiation under various accelerating voltages. The results for the accelerating voltages of 20 eV and 50 eV are shown in Fig. 5.

In the case of the specimen irradiated by Ar ions of 50 eV, the oxygen intensity decreases along with the irradiation period. Therefore, it is clear that the oxide film was sputtered. On the other hand, in the case of the specimen irradiated by Ar ions of 20 eV, the intensity of Si and O was constant. So the sputtering could not be detected under this condition. Based on these facts, the Ar ions of no more than 20 eV was used as the appropriate neutralizing condition of the FMIED for the experiments described below.

2.4 Application of the Charge-Neutralization Method

Auger analysis was performed at an Au electrode surrounded by resin on a printed memory circuit board, which is shown in Fig. 6. The resin around the Au electrode was roughly covered with aluminum foils. For the ion gun conditions, the Ar ion energy used was 10 eV and the irradiation ion current was 0.1 μA (measured as the absorbed current on SiO2). Irradiation was performed using a 300 x 300 μm2 raster scan.

2.4.1 Effectiveness of neutralization depending on the accelerating voltage of the incident electron beam

For the incident electron beam, we applied two different accelerating voltages 5 kV and 10 kV to the Au electrode pattern and examine the difference in the effectiveness of neutralization. During this experiment, the Au electrode was grounded.

Figure 7 shows the difference in the secondary electron images before and during Ar ion irradiation, and Fig. 8 shows the Auger spectra measured at the electrode.

In the both cases of electron accelerating voltages, normal-contrast SEM images were obtained during charge neutralization. Without neutralization, the images was in an unstable of high contrast. Concerning the Auger spectra...
in the both cases, normal spectra were also obtained during the neutralization. Even small peaks of Ni were detected in these spectra clearly.

2.4.2 Change in the Auger spectra at a non-grounded electrode

Next, in the same way as described in the previous paragraph, a secondary electron image and Auger spectra were obtained from the Au electrode in the floating (non-grounded) state.

Figure 9 shows the difference in the secondary electron images before and during the Ar ion irradiation, and Fig. 10 shows the corresponding Auger spectra measured at the electrode.

The secondary electron image of Fig. 9 before the ion irradiation was different from that of Fig. 7 due to the charging of the electrode itself. During the ion irradiation, the Au electrode showed the same contrast as that of the resin part. It is considered that the Au electrode was also charged by positive Ar ions; therefore, its surface potential was as high as that of the resin parts.

Figure 10 shows the Auger spectra of the electrode surface measured under the following three conditions.
1) Before Ar ion irradiation
2) During Ar ion irradiation
3) After Ar ion irradiation, irradiation stopped

Without neutralization, the Auger spectra were distorted and few electrons were detected at the lower energy side. To the contrary, during neutralization, the spectra were distorted a little and shifted about 20 eV to the lower energy side. Particularly, the low energy electrons (1000 eV or less) decreased a little because the floating Au electrode itself became positively charged by Ar ions.

An interesting result was obtained. Normal Auger spectra were obtained even if ion irradiation was stopped while the electron beam kept to irradiate a spot (150 μm) only on the electrode. It is considered that the non-uniform electrical field was not generated not only on the electrode but also on the resin.

On the other hand, a similar phenomenon was found in quartz. Once Ar ions irradiated the surface of quartz tilted by 45° to the incident electron beam under charge-neutralization condition, normal Auger spectra continued to be obtained from the quartz surface for several hours without Ar irradiation. The mechanisms of these phenomena are currently under
3. Thin-film Method

3.1 Meaning of Thin-film Method

Even if the methods described in Sections 1 and 2 (the tilting method and charge neutralization) are applied, it is not possible to eliminate the charging effect completely. For example, charging always occurs on non-conductive surfaces whenever the fine electron beam is focused to a small area of 1 µm or less. Here, there is a new method, which is called “thin-film method”, that permits high spatial-resolution mapping as well as acquisition of Auger spectra even on such a minute nonconductive area. It involves fabricating a thin film from the specimen, placing it on a substrate (supporting film or graphite), and then analyzing it by the AES. An outline description and an application of this thin-film method are shown below.

3.2 Merits of the Thin-film Method

3.2.1 Prevention of charging by passing incident electrons through the specimen

It is well-known that the incident electron beam is transmitted through the specimen if it is thinned to a film about 100 nm thick, as shown in Fig. 11. This “thin-film method” utilizes this principle in Auger analysis effectively. The thin-film specimen is placed on a substrate (graphite) having a high electrical or thermal conductivity. In Auger analysis, this thin-film specimen is not charged because most of incident electrons can pass through the specimen. Also, heat will be mostly generated and diffused in the substrate, thus decreasing the damages to the specimen. In this case, although a large amount of electrons enter into the substrate, the Auger electrons only from the specimen can be detected due to the effect of their escape depth.

3.2.2 High spatial resolution near the edge

If the irradiation point of the electron beam approaches near the edge (within 1 µm or less from the edge) of a thick specimen, the backscattered electrons in the bulk may appear from the side of it, causing the generation of Auger electrons. In this condition, the detected electrons contain Auger electrons from the side of the specimen as well as from the analysis point. Therefore, the analysis result is complicated. However, if the specimen is made into a thin film, only the Auger electrons emitted from the surface will be detected even at the edge of the specimen, as little backscattered electrons are emitted from the side of it (in Fig. 12). This merit results in a higher spatial resolution of the Auger analysis, and also improves the accuracy of mapping.

3.3 How to Fabricate a Thin-film Using Micro-manipulator System and FIB

3.3.1 Fabrication of a thin-film specimen using FIB

First, FIB (focused ion beam) [3] is used to...
fabricate a cross-sectional thin specimen with a thickness of 0.1 µm or less and an area of 10 µm × 10 µm squares, as shown in Fig. 13.

Next, FIB-cutting is made in the bottom and both sides of the thin-film part to separate it from the bulk of the specimen.

3.3.2 Pickup of the thin film with the micro-manipulator system

This thin-film specimen fabricated by FIB is taken out from the vacuum to the micro-manipulator system. This system is a device combining an optical microscope with a hydraulic micro-manipulator (Fig. 14). It is possible to pick up and transfer specimens of several 10 µm in size by the employment of a special glass probe with a rounded head. The glass probe is made of a glass tube with about 1 mm diameter, made by pulling and cutting during heating. Finally the end part of the probe is heated further and is rounded to a radius of 1.5 to 2.5 µm. Figure 15 shows an actual pick up process using this special glass probe.

3.3.3 Observation and analysis

The picked-up specimen placed on electrically conductive graphite can be directly mounted on the specimen holder, thus enabling smooth Auger measurement of this specimen. The specimen picked up in 3.3.2 was just placed on the graphite without special treatment. It did not move to anywhere on the graphite. Electrostatic force is considered to fix the specimen. Therefore, Auger analysis could be easily performed without another treatment.

3.4 Application of the Thin-Film Method

Finally, the application of the thin-film method is shown below. Auger analysis was performed for a semiconductor module fabricated by means of the thin-film method (Fig. 16). As a result, it was found that fine Auger spectra and clear Auger images could be obtained even at SiO₂ and Si₃N₄ parts, without distortion and fuzziness (Fig. 17).

4. Summary

The Auger Electron Spectroscopy is an analysis method permitting element analysis and state analysis with a high spatial resolution of several 10 nm. However it has been difficult to analyze nonconductive specimens conveniently. Here, to analyze such a nonconductive specimen by AES, the charge-neutralization method and the thin-film method have been developed which support the tilting method. It is sure that the both methods are effective to prevent charging in Auger Electron Spectroscopy.

References