Atomic-Resolution Characterization Using the Aberration-Corrected JEOL JEM-ARM200CF at the University of Illinois – Chicago

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Modern aberration-corrected scanning transmission electron microscopes (STEM) provide a multitude of characterization techniques that can be applied across a wide-range of length and temperature scales. At the University of Illinois at Chicago, the aberration-corrected, cold-field emission JEOL JEM-ARM200CF is capable of atomic-resolution imaging, electron energy-loss (EEL) as well as energy-dispersive X-ray (XEDS) spectroscopy in a temperature range between 80 – 1,300 K. The capabilities of this instrument will be demonstrated using a number of studies focusing on both structural and chemical properties of materials including NbH, SrTiO3, CdTe and ferritin protein. The central theme of these studies is microscope versatility, which is realized through the ability to perform atomic-scale chemical characterization while retaining high spatial imaging resolution. Of particular interest to many studies is the visualization of light elements, such as N, O or H, using simultaneous high-angle annular dark field (HAADF) and annular bright field (ABF) imaging. Novel in-situ capabilities will be demonstrated using graphene liquid cells. Finally, we will demonstrate the effects of a new silicon drift detector, the Oxford X-MaxN 100TLE on performing atomic-column resolved XEDS mapping at varying length scales and energy resolution.

Introduction

A better understanding of the mechanisms that influence a material’s property on the atomic level is essential for developing new functional nano-devices for electronics, energy and biological applications, it is essential that we gain an understanding. Even more so than on the macroscopic level, when a component has been miniaturized for use in nano-devices, surfaces, interfaces, and individual defects dominate its properties by changing the material’s structural, compositional and bonding behavior. If working and reliable devices are to be successfully fabricated, it is imperative that we understand the structure-property relationships of these defects, interfaces and surfaces.

Over the last decade, analytical transmission electron microscopy (TEM) and scanning TEM (STEM) have emerged as the primary tools for exploring the structure-property relationships of novel nano-materials [1-15], in particular the atomic and electronic structures of defects, interfaces, or nano-particles [16-20]. The scanning transmission electron microscope (STEM) fitted with a probe-side aberration corrector, such as the JEOL JEM-2200FS or the JEOL JEM-ARM200F [21-24] yields unparalleled spatial resolution of both heavy and light chemical species. With spatial resolution of aberration-corrected high-resolution phase contrast imaging (HRTEM) and high angle annular dark field, HAADF, (or Z-contrast) imaging in aberration-corrected STEMs now reaching the fundamental limit of the Bohr radius, \(a_0 = 50 \text{ pm}\), the focus is shifting to increasing the chemical resolution and visualizing all constituent atomic species, while retaining spatial resolution. To that end, electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (XEDS) are being pushed to the point where atomically-resolved chemical maps are possible with both techniques [25, 26]. The implementation of silicon drift detectors (SDD) with larger active detector areas in XEDS have greatly aided this advancement, leading to the demonstration of single atom sensitivity [27].

Many material systems are utilized in devices under conditions (i.e. temperatures, pressures or fields) that are substantially different from those present inside an electron microscope column. In a conventional atomic-resolution transmission electron microscope, atomic-resolution studies have previously been limited to ambient temperatures and under high vacuum \((P_{\text{v}} = 10^{-3} \text{ Pa})\) due to the inability to get in-situ holders into the small gap of an ultra-high-resolution objective lens pole-piece. Over the
last decade, the field has advanced significantly, and in-situ capabilities are now available to study the dynamic behavior of materials in environments other than the high-vacuum of the TEM column. Novel sample stage designs have enabled in-situ heating up to 1,300 K with atomic resolution, in-situ gas and liquid experiments with nano-meter resolution, as well as time-resolved imaging with better than nanosecond resolution.

This paper will demonstrate the capabilities of the JEOL JEM-ARM200CF at the University of Illinois at Chicago, a probe aberration-corrected STEM equipped with a cold-field emission electron source, a post-column EEL spectrometer and the new Oxford X-MaxN 100TLE SDD-XEDS detector. We will demonstrate that atomic-resolution imaging of light elements, including N, O and H is possible using ABF imaging, while the cold-field emission electron source allows for EELS with an energy resolution of better than 400 meV. In addition, we will highlight our newly developed graphene liquid cell approach of encapsulating biological samples, such as ferritin proteins in a liquid between two single layers of graphene.

Experimental

The JEOL JEM-ARM200CF installed in the Research Resources Centre (RRC) at the University of Illinois at Chicago (Fig. 1) is equipped with a cold field emission gun, 5 annular detectors, a Gatan Enfina EELS spectrometer and the new Oxford X-MaxN 100TLE SDD EDS detector and was installed in our laboratory in late 2011. The spatial resolution that can now be routinely achieved using the JEOL JEM-ARM200CF exceeds 70 pm at 200 kV primary energy (see Fig. 2(a)) and 100 pm at 80 kV primary energy. The energy resolution of the EEL spectra at any energy between 80 and 200 kV is 350 meV (see Fig. 2(b)). The stability of the instrument was measured using a long-exposure HAADF image without drift correction, and was determined to better than 150 pm/min. In addition to the double tilt holders, we also took delivery of a Gatan double-tilt liquid He cooling stage, a Protochips Aduro double tilt heating stage, a Fischione tomography stage, as well as a Nanofactory STM-TEM stage and a Protochips Poseidon liquid flow cell. In addition, we have still access to the Gatan double tilt heating and the double tilt LN₂ cooling stage, which were purchased in 1998 for use in the UIC JEM-2010F.

In this paper, we will show results from several of these in-situ stages, including the Gatan LN₂ cooling stage and the home-made graphene liquid cell. These results are meant to demonstrate the wide range of experiments that can be conducted on a daily basis in the ARM200CF. At this point, it is important to note that switching between TEM and STEM mode can be done without disturbing the alignment or stability of the instrument significantly. For example, when switching from TEM to STEM mode, it is possible to achieve atomic resolution nearly immediately after the coma and astigmatism have been manually corrected. At the highest imaging resolution, we notice that during the first 60-120 minutes after entering STEM mode, some adjustment of the focus and stigmator is necessary. Once the ARM200CF has been in STEM mode for two hours, the instrument is completely stable.

The UIC JEOL JEM-ARM200CF is located in an open-access user-facility, which allows qualified users to use the instrument 24 hours, 7 days per week on an hourly user-charge basis [28]. It is, therefore, crucial that any of the experimental setups required by the user are not affecting the performance of the instrumentation for the subsequent users. To date, we have not experienced any significant influence of any in-situ experiments or

Fig. 1. The JEOL JEM-ARM200CF at the University of Illinois at Chicago.
low-voltage measurements on the vacuum column or energy-stability performance for more than a few hours after the completion of the experiments.

Results and Discussion

Here, we will discuss the results from several experiments conducted using the JEOL ARM200CF at the University of Illinois at Chicago. The materials that were characterized include SrTiO$_3$ thin films on GaAs, 8-NbH, polycrystalline CdTe and ferritin proteins in a graphene liquid cell.

**Low voltage characterization of SrTiO$_3$/GaAs interfaces**

Over the past few years, ultrathin metal-oxide films on polar semiconductor surfaces have received much attention due to the occurrence of novel interfacial properties, including ferroelectricity, superconductivity and the presence of an interfacial 2-dimensional electron gas [29-34]. The first successful growth of SrTiO$_3$ thin films on Si was reported more than two decades ago, and various techniques have been used to assemble a layer-by-layer crystalline oxide film and avoid the formation of the amorphous layer at the interface [35, 36].

The SrTiO$_3$/GaAs interfaces were studied experimentally and theoretically with various techniques in order to develop a fundamental understanding of the structure property relationships and it has been reported that the SrTiO$_3$ film prefers to be SrO terminated at the interface, regardless of the growth condition, and a submonolayer of Ti, hereafter referred to as a Ti pre-layer, between the oxide and semiconductor can release the Fermi level pinning after the thin film deposition.[37-39] However, due to the oxygen deficiency of the film, it was not possible to perform atomic resolution electron energy-loss spectroscopy (EELS) on the highly beam sensitive SrTiO$_3$/GaAs interface [40].

Using the JEOL ARM200CF at UIC, we conducted a detailed study of the atomic and electronic structures of the SrTiO$_3$/GaAs interface with and without a Ti pre-layer using HAADF imaging and EELS at 80 kV primary electron energy [41]. Figure 3 shows atomic-resolution Z-contrast images of a 4 monolayer thin SrTiO$_3$ film on GaAs (001), where the epitaxy is apparent with SrTiO$_3$(001) || GaAs (001) and SrTiO$_3$(110) || GaAs[100]. The interface between the SrTiO$_3$ film and the GaAs-support in Fig. 3 appears sharp with no obvious interfacial diffusion. Moreover, the images suggest that the oxide films start with a SrO layer at the As terminated GaAs interface, regardless of the fact that 0.5 ML of a Ti pre-layer was deposited on the GaAs surface prior to SrTiO$_3$ growth for the sample shown in Fig. 3(a)). As opposed to the experiments

![Fig. 2](image_url)

**Fig. 2** a) HAADF image at 200 kV of Si (110) with Fourier transform shown as insert. b) Zero-loss peak with indicated full width at half maximum.
conducted at 200 kV primary electron energy, the SrTiO$_3$/GaAs interfaces are now sufficiently stable to withstand atomic resolution imaging and spectroscopy for extended periods of time. Even several hours of analysis on a particular region of a sample has so far not shown any signs of beam damage, neither in Z-contrast imaging nor in spectroscopy.

The acquired Ti L- and O K-edges are shown in Fig. 4 and Fig. 5, respectively acquired using a convergence semi-angle of 30 mrad, a collection semi-angle of 35 mrad, with a 0.1 eV/pixel dispersion and a 3s dwell time. The top spectrum in Fig. 4 and Fig. 5 is taken from a SrTiO$_3$ bulk specimen thus providing a Ti$^{4+}$ fine structure as a reference. In Fig. 4, the crystal field splitting of Ti L$_1$ and L$_2$ edges can be clearly resolved in all the spectra taken from the SrTiO$_3$ thin film, which indicates that the Ti valence is close to 4+ throughout the films in both films with and without the Ti prelayer.[42] To further assess the Ti valence state, and thereby the oxygen stoichiometry of the films, the energy scale has been calibrated using the O K-edge onset, as shown in Fig. 4.

It can now be seen that in the film without the Ti pre-layer, the Ti L-edges for each location in the film are slightly shifted towards lower energy, again indicating a slight decrease in the Ti. More specifically, both L$_1$ and L$_2$ edges shift towards lower energies as the electron probe approaches the SrTiO$_3$/GaAs interface, indicating a decrease of the Ti valence from 4+ to a mixture state of 3+ and 4+[42]. Such phenomena could be caused by oxygen vacancies, or because the Ti-O bonding state on the TiO$_2$ columns in the thin film changed to Ti-As on the surface of the substrate. In addition, it is interesting to note here that a Ti signal is noticeable at least 2 layers into the GaAs support, indicating that some of the Ti has diffused into the GaAs support during the film synthesis.

In Fig. 5, the acquired O K-edges are fitted to their 5$^\text{th}$ nearest neighbors and compared with the reference spectrum taken from bulk SrTiO$_3$. The colored spectra correspond to the colored rectangles in Fig. 3. It is immediately noticeable that the O K-edge fine-structure in the SrTiO$_3$ thin films is significantly different from the bulk SrTiO$_3$, especially for the film grown without the Ti prelayer. More specifically, the pre-peak, which strongly scales with the presence of oxygen vacancies, is suppressed in the spectra taken from the films [43, 44], indicating the presence of oxygen vacancies. Furthermore, near the SrTiO$_3$/GaAs interface, the fine-structure of the O K-edge exhibits several peaks that were not found in the bulk SrTiO$_3$, nor in the films SrTiO$_3$ spectra. These additional peaks indicate the oxygen bonding with arsenic on the GaAs surface during the initial steps of the thin film synthesis. Finally, the integrated O K-edge intensity disappears completely in the GaAs support, even in the locations where a Ti signal was found. This further indicates that only the Ti diffuses into the support, while the oxygen remains in the SrTiO$_3$ film and on the GaAs surface.

Our low-kV imaging and spectroscopy study, therefore, shows, that while the atomic structure of the interfaces does not reveal any evidence of the Ti prelayer at the SrTiO$_3$ interface, the electronic structure of the films appears significantly different. The films grown without the Ti pre-layer appears to be more oxygen deficient, and exhibit strong interaction between the GaAs support and the interfacial oxygen, potentially forming As$_2$O$_3$. The deposition of the Ti pre-layer appear to alleviate the oxidation of the substrate and consequently lift the

Fig. 3 Atomic resolution HAADF image at 80 kV of SrTiO$_3$/GaAs a) with and b) without the Ti pre-layer. The colored rectangle highlight the area where EEL spectra where acquired. An atomic model is superimposed on the images and the interface is indicated by the dotted line.
Fermi-level pinning [41].

**Direct imaging of hydrogen in $\beta$-NbH**

Niobium, a $4d$ transition metal, has found many applications including hydrogen storage, heterogeneous catalysis, dielectric coatings, and superconducting devices, such as superconducting radio-frequency (SRF) cavities [45]. In the next generation accelerators, the performance of SRF cavities at moderate (i.e. 16-19 MVm$^{-1}$) and high electric (i.e. >35 MVm$^{-1}$) field gradients are critical [46]. Nevertheless, even after decades of research, a solid understanding of the microstructural defects limiting the medium and high field performance is still missing. What appears clear, however, is that Niobium hydride, if present, can be a major contributor to the degradation of the quality factor, $Q$, since hydride precipitates can only be superconducting by proximity effect, and their premature transition to the normal state will lead to strong losses [47, 48].

Here, we present an atomic-resolution study of the formation of $\beta$-NbH precipitates at room temperature in Nb grains near the cavity surfaces [49]. In addition, we demonstrate that atomic-resolution imaging is still possible at LN$_2$ temperatures, although spatial drift limits the dwell time per pixel to around 16 $\mu$s/pixel.

**Figure 6** shows a pair of HAADF and ABF...
images, acquired simultaneously, of a β-NbH precipitate in the [110] orientation. While the HAADF image appears very similar to that of pure Nb, the ABF image reveals additional atomic columns, which can be identified as hydrogen atomic columns. The insert in Fig. 6 shows the proposed structure of β-NbH [110] as well as the calculated image contrast using the multi-slice method. The contrast in the image calculations agrees with that measure in the experimental ABF images. Using a combination of ABF imaging, selective area electron diffraction and EELS, we confirmed that the phase image is β-NbH [110].

According to the phase diagram for Nb-hydride, there exist several other phases depending on the local hydrogen concentration and temperature. Therefore, in order to fully understand the role of hydride precipitates on the mid and high field gradient performance of Nb based SRF cavities, an imaging method capable of atomic-resolution at low temperature (e.g. LN₂ temperature) is needed. Using the Gatan double tilt LN₂ stage, we imaged bulk Nb [110] (Fig. 7(b)) and show that achieving atomic-resolution is possible at that temperature. However, due to the increase mechanical vibrations as a result of the nitrogen boiling off, we had to decrease the pixel dwell time to 16 µs/pixel and average over several images to achieve a presentable signal to noise ratio. If necessary, more sophisticated noise reduction procedures can be employed if repeated acquisition of short-exposure time images is not possible.

**XEDS analysis of defects in polycrystalline CdTe**

Polycrystalline CdTe thin film based photovoltaic devices are present leaders in thin film solar technology ([50], [51]). Commercial success of CdTe based devices stems from the nearly ideal band gap of the material which very effectively couples to our sun’s light spectrum as well as ease of manufacturing and low cost of the modules. However, to improve the conversion efficiency beyond 20%, it is critical to minimize the harmful effects of grain boundaries and lattice defects in CdTe. Direct atomic-scale structural and chemical investigation is desirable in order to identify atomic configurations which can act as carrier recombination centers. Likewise, it is necessary to confirm that passivants introduced into CdTe are able to diffuse and bind to the target defects.

Besides arbitrarily oriented grain boundaries, stacking faults and Σ3 twin boundaries, both lying on

![Fig. 6 Simultaneous HAADF and ABF images at 200 kV of β-NbH [110] clearly showing the hydrogen atomic columns in the ABF image.](image-url)
[111] planes, are very common planar defects in CdTe. These defects have the correct nearest-neighbor bonding, however stacking disorder becomes apparent in second (and beyond) nearest neighbors. While these interfaces have been deemed benign as far as carrier recombination centers are concerned, their role in attracting impurities and anti-site point defects remains unknown. In Fig. 8, we show an HAADF image and XEDS image of a stacking fault in CdTe along [110]. In this projection, Cd and Te atomic columns form a dumbbell-like structure with 162 pm column separation. The XEDS data clearly shows atomic resolution and the polarity of the planar defect can be readily identified. More precisely, the direction of the dumbbells at the stacking fault is rotated by 250° about [110]. Figure 8 shows that the terminating column of the left side of the interface is Te, followed by Cd. Such data will allow us to quantify possible changes in stoichiometry across twin boundaries and stacking faults, detect the presence of dopants, and determine the atomic structure of dislocation cores terminating such defects.

HAADF image and atomic-column resolved XEDS map of a Lomer-Cottrell dislocation along [-1-10] zone-axis in CdTe are presented in Fig. 9. More specifically, two intrinsic stacking faults are seen in the HAADF image and the XEDS spectrum image shows the integrated intensity of the Cd and Te L-peaks in the stacking faults. The dislocation core is located at the vertex of two intersecting stacking faults, and is composed of three Cd atomic columns and a single Te column (Cd,Te), as can be seen from the spectrum image map shown in Fig. 8. It should be pointed out here that without the availability of the XEDS spectrum image, the identification of the atomic columns in the dislocation core would not be possible, since the atomic numbers (Z) for Cd and Te are too close to be distinguished using HAADF imaging alone.

**Ferritin in a graphene liquid cell**

Nanoparticle growth, chemical reactions or biochemical activity often occur in the presence of a liquid. To study liquid sample in an electron microscope, several liquid cell designs have become commercially available in recent years that enable materials to be imaged in a carefully controlled liquid environment within the vacuum of a TEM. However, all suffer from a few key limitations that do not allow for ultra high-resolution imaging or spectroscopy:[52] 1) two Si$_3$N$_4$ layers (50-500 nm thick) used as electron transparent windows and 2) the thickness of the liquid.

Fig. 7 200 kV atomic-resolution ABF images at a) room and b) LN$_2$ temperature. Both images show the Nb atomic columns, but the Hydrogen columns are not very visible in the low temperature image due to the increased sample vibration.

Fig. 8 An HAADF STEM image acquired across a twin boundary, viewed with the Cd L (red) and Te L (blue) series overlaid. The scale bar is 1 nm and applies to the individual element maps.
liquid surrounding the sample. In these liquid cells, the imaging resolution is usually limited to nanometers. Electron energy-loss spectroscopy (EELS) is degraded by multiple scattering events in the thick window layers, and the strong core-loss signals associated with the presence of Si and N [53]. In addition to the increased sample thickness, radiation damage is a fundamentally limiting factor when examining beam sensitive materials and/or hydrates in TEM. It has been shown that coating the specimen with carbon, metal or grapheme [54-58], or lowering the temperature [57] have positive effects against radiation damage by reducing electrostatic charging, mass loss, loss of crystallinity, or defect formation rate [54-58]. These studies suggest that it is possible to reduce radiation damage to below breakage of covalent bonds. However, further reduction of radiation damage is needed for characterization of biological samples, since many biological structures and functions are related to the much weaker hydrogen bonds.

We have developed a biocompatible approach of encapsulating liquid containing samples in monolayers of graphene. This not only allows biological samples to be directly imaged at atomic resolution in a native liquid state without limitations from the window thickness (see Fig. 10), but also enables nm-scale analysis using EELS to quantify reactions in an aqueous environment [59]. It has to be pointed out here that any imaging or chemical analysis of graphene liquid cells required that the electron beam energy is lowered below 100 kV, and the images shown in Fig. 10 are taken at 80 kV.

Further, we have shown that the energy deposited by the incoming electrons is dissipated by graphene from the area irradiated at a rate equivalent to the beam current of several electrons per Å² per second [59]. This would therefore provide a reduction of radiation damage, allowing for high resolution imaging and spectroscopy of beam sensitive materials. Details, such as individual Fe atoms (see Fig. 10) or polypeptide of unstained protein, are resolved in a liquid environment. By carefully controlling the induced electron dose rate, we have shown that reactions, such as liquid/ gas phase transition (bubble formation and condensation), or nanoparticle/ nanowire growth can be initiated at selected locations in GLC, and recorded at nm resolution. This technique also allows us to perform a quantitative study of radiation damage effect on different encapsulated samples, such as water or protein, by observing local reaction processes.

Conclusion

Nearly two years after the delivery of the new JEOL ARM200CF to UIC, we have demonstrated the capabilities of the instrument to perform with sub-Å and sub-eV resolution in a variety of environments using a 200 kV primary energy electron beam. The spatial resolution is decreased in 1.0 Å for low energy imaging at 80 kV without any loss in the analytical capabilities of the instrument. In addition, the ARM200CF is capable of imaging samples in a liquid environment, at elevated or cryogenic temperatures in either TEM or STEM mode.

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Fig. 9 a) Atomic-column resolved XEDS map overlaid on top of the Z-contrast image in the <110> projection. L-C dislocation core (circled) is associated with the two dashed intrinsic stacking faults.
Fig. 10 HAADF (A and B) images of ferritin in a graphene liquid cell (GLC). Bubbles in (A) were formed in advance using the Ronchigram mode to confirm the presence of a liquid. In STEM mode, electron dose rate and pixel dwell time is optimized so that no further bubbles are formed during scanning. Single iron atoms are resolved in a liquid environment in image (B) near the edge of a GLC. A line profile across the upper left atom is shown as an inset of (B), with each pixel corresponding to 0.99 Å. The resolution of these images is optimized by taking images under the corresponding threshold area averaged dose rate of bubble formation at each magnification.

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