Application of Cathodoluminescence to EPMA

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. Figure 1 is a schematic diagram showing various signals obtained when an electron beam irradiates a specimen surface.

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>
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| 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                                             |
| Biological specimens | • Observation using luminescent dye                                      |

Table 1.
solid specimens, but the CL method permits only the analysis of light-emitting specimens, 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 this 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 4 is a backscattered 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 consisted 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 layer (it is about 500 µm) 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 streak left when the surface of the specimen was polished. Scratches of this degree have virtually no affect 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.
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). 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 this 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 cathodoluminescence 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. Fugenbake. 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 (AIN) 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 band gap of AlN is 6.1 eV, and a CL peak can also be obtained from the vicinity of a wavelength of 200 nm. Therefore, yttriatite is used as filler for this substrate, and it is considered that the peak at the longer wavelength side normally
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)₃. Each specimen was made by pressing a powder specimen. The Al₂O₃, Al(OH)₃ 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


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.