Ultra-Fast Spectrometric Cathodoluminescence Scanning Microscopy for Materials Analysis

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We have constructed a cathodoluminescence (CL) detection system that records the CL spectra emitted from each point raster-scanned by the incident electron probe in a conventional scanning electron microscope. The CL spectrum is detected by a 3 channel high-speed high-sensitive photoelectron multiplier array set behind the spectrometer. The shortest signal sampling time is 8 s for a frame of 512×512 pixels and all the imaging and spectroscopic signals are stored in two 8-megabyte files. Maximum image size is 2048×2048 pixels. The microscope displays a spectral accurate full color (whole spectrum) CL image, twenty-nine monochromic images and the spectrum of each point in the corresponding secondary electron image. The spatial resolution of CL image reaches 25 nm by reducing the quantum noise and the phosphorescent delay effect using a slow signal sampling time of 40 s with a 6-keV incident electron probe. Some examples are demonstrated using SnO2-doped ZnO-BaO ceramics and photosensitive cyanine dyes. [doi:10.2320/matertrans.MC200901]

(Received July 3, 2009; Accepted October 26, 2009; Published December 9, 2009)

Keywords: cathodoluminescence microscopy, scanning microscopy, cathodoluminescence spectroscopy, ZnO-BaO2 ceramics, photosensitive organic dye

1. Introduction

Light emission produced by the electron beam is called cathodoluminescence (CL), which provides the information of the electronic structure of the materials, especially for the electrons of outer shells. Scanning electron microscope (SEM) combined with CL detection system allows us to map panchromatic (all wavelength) or monochromatic CL images. Panchromatic CL images show only the distribution of the particular wavelength. Although the monochromatic CL image is very useful for the analysis of highly structured materials such as nano-fabricated semiconductor devices, it needs long time to map the images of various CL wavelengths with repeated observations. It is almost impossible to map CL across a wide wavelength range of several hundred nanometers, CL of which ordinary semiconductor materials and organic materials emit, without any structural damage or contamination.

The first system to map a CL image of all visual wavelengths in one frame scan was developed by Ogawa and Koike.1) In this system, the CL emitted from the specimen is collected with a hemispherical mirror and detected with three photoelectron multiplier tubes separately in three bands, 400 nm~500 nm, 500 nm~600 nm and 600 nm~700 nm, divided using two dichroic mirrors. The CL signals are stored in a digital memory of 512×512×3 words. This RGB CL SEM was successfully employed in the field of biomedical science,2) and then applied to the characterization of GaInP/GaInP and CdZnSe/ZnSe laser diodes,3) and ceramic varistors.4) After some reconstruction in the detection system,5) this microscope has been extensively applied to the investigations of high-tech materials, such as SiC6) and GaN-based laser diodes.7,8) Most successful was a series of studies on adsorption behavior of photosensitizing dye J-aggregates on AgBr emulsion crystals, whose results were reviewed in Refs. 9) and 10). Throughout these studies, we have analyzed the CL images giving attention only to the difference and change of tint or color rather than the CL wavelength.

The CL peak intensity and shape as well as wavelength are important parameters in understanding materials properties. When the CL is collected and divided into only three windows, as in the case of the RGB CL SEM,1) a limited amount of information is gathered. Alternatively, by collecting a series of monochromatic images of various wavelengths, we can measure with greater certainty the CL spectrum at each point.

In this paper we describe a new design for a CL detection system that records the CL spectra emitted from each point raster-scanned by the electron beam in a SEM, the idea11) and some results12) of which were preliminarily presented. In our new system, CL spectra of all points on the observed specimen are recorded with ultra-fast speed or in one frame scanning, simultaneously with secondary electron (SE) image. Thus, the microscope attached with this system displays a spectral full color (whole spectrum) CL image, monochromatic images and the spectrum of each point on the corresponding SE image, across a range of wavelength of the spectrometer used.

2. Design of CL Detection System

At first, our new ultra-fast spectrometric CL SEM was designed to record CL spectrum in the visible range at each pixel point in the SE image in a very short time. For such a high-speed acquisition, we limited the spectral resolution within Δλ ≈ 10 nm and employed new sequence for a faster digital sweep generation. A 32 channel high-speed high-sensitive photoelectron multiplier array (PMA) was used as the detector, which has a significantly high scanning speed as
compared with high-resolution CCD sensors with 512 or more channels. Block diagram of the present CL microscope is shown in Fig. 1. Both SE and CL emissions are emitted from a spot upon which the electron beam probe is incident. The SE signals are stored in a digital memory corresponding to the pixel address on the specimen surface. The CL emission is collected with an ellipsoidal mirror placed above the specimen and directed to the spectrometer, Jobin Yvon HR-320, placed in the air outside the microscope. The CL spectrum is detected by PMA, Hamamatsu Photonics H7260-04. After the amplification with Analog-Digital (AD) conversion, CL signals are stored in the memory with the same address where SE signals were stored. In our system, two AD conversion boards are used each of which accommodates sixteen channels. The width of detectable wavelength of CL spectrum is 300 nm with a 300 line/mm grating, and any range of 300 nm wide between 180 nm to 700 nm can be chosen by turning the grating. In most case we use 300–600 or 400–700 nm range, while 180–480 nm range for deep-UV materials.

The scanning incident electron probe is controlled by two ramp waves for beam deflection. They are digitally generated and converted to DC voltage at DA converter board in the control computer. During observation, the switching between D/A and A/D processes to output the ramp waves and to acquire SE and CL signals generally occurs repeatedly whenever the probing beam moves on the specimen by one pixel. It requires a few clock cycles of the computer and the accumulated time-loss in this switching cannot be ignored. In order to avoid such a delay, we employed following sequence: Two ramp waves for X-Y scan are created in advance and sent out to the DA converter board, and the scanning beam position that is the address of the pixel is obtained by measuring the voltages of two ramp waves simultaneously with CL and SE signals. With this method, it takes 8 s for the system to collect a 512×512 pixel microscopic image with full CL spectrums at every pixel point.

Two channels of the AD are used to measure the beam position. Another channel is used to measure the SE signals. The remainders of the twenty-nine (=32-2-1) channels can be used for CL spectra. Therefore, twenty-nine of thirty-two cells of the PMA are connected to AD channels. Our routine work uses a 300-groves/mm grating with a blaze wavelength of 500-nm, and the spread of CL spectra is slightly larger than 10 nm/channel on the window of the PMA, accordingly. This means that we can detect CL spectra of 300 nm in width, e.g. across a wavelength from 400 to 700 nm.

The signal depth is 11 bits/channel, and all the thirty-two channel signals (29 CL, 1 SE and 2 beam positions) are addressed just the same in the data file. All image data of 512×512 pixels occupies two 8 megabyte text files and one header file. These files are displayed as SE image, CL spectra and full color CL image in three windows of the main console. Signal accumulation can be made by repeating the frame scans. The CL spectrum displayed is of the point which the mouse pointer in SEM image indicates. Thus, we can display successively the CL spectrum varying with the move of the pointer, reflecting the variation of electronic states, trace element concentrations, structure, stress and strain in the specimen.

3. Some CL Observations

The CL image acquisition speed of the new spectrometric CL scanning microscope exceeds that of the previous RGB 3-band CL microscope by Koike et al. and also of other commercially available systems. However, the acquisition time of our system can be slowed by an order of magnitude for specimens that have slow luminescence decays or are very weak emitters. Image size can be chosen from 128×128, 256×256, 512×512, 1024×1024 and 2048×2048 pixels. The sampling time, which is here defined as the acquisition time for one frame, is proportional to the square of the size. The hyper spectral dataset or file creates so quick increases in size that we typically used a 512×512 size. When one frame scan is over, twenty-nine monochromic CL images have been recorded and stored. A composite full color CL image over a detection range of ∼400–700 nm can be displayed using these stored monochromic images. In Fig. 2 a full color CL image of SnO₂-doped ZnO-Bi₂O₃ ceramics is illustrated together with five examples from the twenty-nine monochromatic images that constitute the full color image. The ceramics has a nonlinear current-voltage characteristic and is used as varistor. The sample observed in this paper was prepared, according to a standard ceramic procedure, by mixing and sintering ZnO powders with the addition of 1 mol% of Bi₂O₃ and 0.1 mol% of SnO₂. For SEM studies, it was cut in half and mounted in an acrylic resin. Cross sections of the samples were mechanically ground and polished, followed by etching in dilute hydrochloric acid.

We examined the noise reduction effect by repeated observations. Figure 3 shows an example of the repeated observations, indicating that the noise appearing in the dark region is significantly suppressed and the contrast is enhanced with accumulation. Therefore, the noise reduction by repeated scanning is effective for specimens that are not influenced by the electron beam irradiation. The CL spectrums in Fig. 3(e) to (j) show how the CL signal from the small area is enhanced by the repeated observation while the surrounding background signals remain dark. The CL spectrum of a region marked by red square in the SEM image (a) is shown in (e), (g) and (i). With increasing accumulation from 2 times for (e) to 8 for (i), the peaks between 500 nm to 550 nm become eminent, and a small green dot appears in CL micrograph as seen in (d).

One is often under the impression that a CL image is mapping light emitted from the point upon which the electron probe is just incident. This means that CL emission is assumed to complete before the probe moves to the next pixel, without phosphorescent delay. If phosphorescent decay is slower than the acquisition time per pixel then tailing will be observed in the CL image. This tailing is seen in Fig. 4(c). The tailing cannot be removed by processing, and the only alternative is to extend the acquisition time per pixel. Figures 4(d) and (f) show images recorded in a sampling time extended to 80 s. It is clear that the longer sampling time has reduced the tailing and enhanced the signal to noise and the spatial resolution of the image.

The escape depth of CL photons is longer than that of secondary electrons. Since CL signal involves lights generated by the incident electrons spread deeply and widely.
Fig. 1 Block diagram of the ultra-fast spectrometric cathodoluminescence microscope.

Fig. 2 CL images of SnO$_2$ (0.1%)-doped ZnO-Bi$_2$O$_3$ (1%) ceramics. The full color CL image (upper center) was constructed by 29 monochromatic images which had been recorded and stored successively over a detection range of ~400–700 nm. Five examples from the 29 monochromatic images are also presented. Indication of Ch. 5, 450 nm shows that the image was recorded with the 5th cell of the PMT and stored using the 5th channel of AD and the center of the cell was set to 450 nm in wavelength.

Fig. 3 Noise reduction and signal enhancement of CL image by signal accumulation. (a) SE image of the SnO$_2$-doped ZnO-Bi$_2$O$_3$ ceramics. (b)–(d) Full color CL images recorded in a frame scan speed of 8 s and accumulated twice (b), four times (c) and eight times (d). 

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<tr>
<th>Accumulation</th>
<th>Two Times (b)</th>
<th>Four Times (c)</th>
<th>Eight Times (d)</th>
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<tr>
<td>Red square (weak signal)</td>
<td>(e)</td>
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<td>Blue square (no signal)</td>
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inside the specimen, the spatial resolution of CL image is worse than that of the corresponding SE image. Generally, the resolution of CL images is several tens of nm to sub μm. This can be improved by lowering the energy of the incident electrons and also by using a longer sampling time (mentioned above). In our system using a conventional W-filament SEM, the spatial resolution as high as 25 nm was obtained using the incident electron probe of 6 keV and a longer sampling time of 40 s/frame. Figures 5(a) and 5(b) show SE and full color images of the ZnO-Bi₂O₃ ceramics, respectively, and Figs. 5(c)–(h) show CL spectra from some points on the surface, which were recorded with this high resolution. The spectra in Figs. 5(e) and (f), the points for which leave a space of 25 nm (one pixel distance) with each other, indicates the spatial resolution of this system.

As seen in Fig. 5(b), the cutout plane, which can be regarded as the matrix inside the grain (see Fig. 5(j)), emits too weak luminescence to perceive, and strong blue-green CL is emitted near the surface of the grain or grain boundary. Tanaka et al.15) observed three CL peaks from the Bi-doped ZnO varistor; two are the intense 378 and 389 nm peaks, which were assigned to the intrinsic properties of inside ZnO grains, and the other is the strong broad 526 nm peak, which were ascribed to deep levels related to the oxygen deficiencies formed at grain boundaries. Bougrine et al.16) also reported that the CL spectra of undoped and Sn-doped ZnO films exhibit the common 382 nm peak but the undoped ZnO emits an intensive blue-green light (520 nm) and a red emission (672 nm) while the Sn-doped ZnO emits a new light of 463 nm and the extension of
blue-green light which are typical of the intrinsic behavior of the material, a grain-like structure inherent to the surface morphology. Our results are consistent with these observations. No observation of CL inside the grains is due to the detection range of 400~700 nm of our spectrometer. The strong near-band-edge emission around 380 nm is recorded as shown in Fig. 5(i). A variety of spectra were observed at different points in the grain boundary and near the grain.

**Fig. 5** (a), (b) SE image and full color CL image of the SnO$_2$-doped ZnO-Bi$_2$O$_3$. (j) Schematics of the cross section along A-A’ in (a). (c)–(h) CL spectra (400–700 nm) of points marked in (a). (i) CL spectra (200–500 nm) of inside grain.

**Fig. 6** (a) SE image of 1,1’-2,2’-cyanine microcrystals. (b) Structural formula of the cyanine. (c) Enlarged image of the area enclosed by a square in (a). (d–o) CL spectra of points marked in (a) and (c). Lights of various wavelengths are emitted from different points of crystals. Especially from the corners and edges, sharp luminescence that is characteristic of J-aggregates emits.
boundary; for example, a sharp peak around 510 nm in Figs. 5(c), 5(e) and 5(f) and a wide range emission, as if white light, including a broad blue peak (~460 nm), the sharp blue-green peak (~510 nm), a broad green-yellow peak (~560 nm), a broad-read peak (~660 nm) and so on. Here we do not argue any further because structural and compositional analyses of each point are necessary for complete explanation.

Figure 6 demonstrates CL observation of photosensitive cyanine dye J-aggregates (named for the discoverer E. E. Jerry). The cyanine dye J-aggregates have played a most important role in the silver halide photographic process: receiving photons of exposing light and releasing photoelectrons to inject into silver halides for latent image formation. Although CL microscopy observes the reverse process (receiving electrons and releasing photons) to the photographic process, it has greatly contributed to investigations of the aggregation, adsorption and structure of such photosensitive dyes.\(^9,10\) The dyes are so sensitive to electron irradiation that the color of CL, that is, the energy state of the J-aggregates changes by even one incident beam scanning.\(^9,10\) The present ultra-fast spectrometric CL-SEM displays its most power to investigation of such electron-sensitive materials. Figure 6 shows CL lights of different wavelengths from various sides of the 1,1', 2,2'-cyanine microcrystals. The J-aggregates are known to have several nanometers in size and show characteristic of very narrow band light absorption. The sharp peak at ~600 nm in wavelength is conjugated with the J-aggregates of this cyanine, which are formed in the small particles (Figs. 6(d), 6(e)) and the edges and corners of larger crystals (Figs. 6(g), 6(i), 6(m), 6(n) and 6(o)). Another strong peak appears at ~620 nm also the edges or corners (Figs. 6(g), 6(k) and 6(m)). Besides these strong peaks green yellow broad peaks also appear (Fig. 6(f)), especially the flat surfaces of the crystals (Figs. 6(h) and 6(l)). The local difference of the spectra in the cyanine dye crystals is interesting, suggesting different molecular conformation.

In this system, the detection range of the spectrum and the spectral resolution can be changed using a grating with appropriate groove density and blaze wavelength, over wide wavelength range including deep ultraviolet. This system is attachable in any SEM. Thus, the SEM should become a key tool to analyze locally and visually the electronic structure of nanostructures such as UV opto-electronic semiconductor, ceramics, polymer and organic molecule devices.

4. Conclusion

A CL detection system has been designed and constructed. It detects, stores and maps both the CL and SE signals emitted from each (pixel) point raster-scanned by the incident electron probe. This system detects CL signals using a 32 channel high-speed high-sensitive photoelectron multiplier array settled behind the spectrometer. The spectrometer accepts CL from the ellipsoidal mirror installed in the SEM used. The signal sampling time for a frame of 512×512 pixels is as short as 8 s and all the imaging and spectroscopic signals are stored in two 8-megabyte files. The microscope can display a spectral accurate full color (whole spectrum) CL image, twenty-nine monochromatic images and the spectrum of each pixel point on the corresponding SE image. The spatial resolution of CL image reaches 25 nm by slow scanning for reducing the quantum noise and the phosphorescent delay effect, with the 6 keV incident electron probe and a sampling time of 40 s/frame. The detection range of the spectrum and the spectral resolution can be change by use of the grating with appropriate groove density and blaze wavelength, over wide wavelength range including deep ultraviolet. This system is attachable in any SEM. Thus, the SEM should become a key tool to analyze locally and visually the electronic structure of nanostructures such as UV opto-electronic semiconductor, ceramics, polymer and organic molecule devices.

Acknowledgements

Mr. M. Fujimoto and Mr. M. Izumo, Kyoto Institute of Technology, helped us to construct the CL detection system in the spectrometric CL scanning microscope. The ZnO-Bi\(_2\)O\(_3\) specimens were kindly provided by Drs. A. Rečnik and N. Daneu, Jožef Stefan Institute, Slovenia. The authors deeply appreciate their cooperation.

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