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Deep UV imaging by spectrometric full-colour cathodoluminescence microscopy

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Abstract. A new deep-UV cathodoluminescence (CL) microscopy is tried on studying design and fabrication of recent solid-state light-emitting (LE) devices that emit near 200 nm light. CL microscopy has enough energy for electronic excitation of deep-UV emitting devices and visualizes distribution map of their electronic structures. The deep-UV imaging system is constructed on our own spectrometric full-colour CL microscope that collects CL spectra at all pixel points of the specimen during regular SEM observation, and at the end of one frame scan, a set of CL spectra is accumulated in the control computer. One frame scan of 512x512 pixels needs 8 to 80 sec, which is unbeatable by any other commercial CL microscopes. Full-colour CL micrograph is constructed using the spectra. The detector, a 32-channel photoelectron multiplier array, has higher sensitivity in UV region than any solid-state linear sensors, and a grating of 300-nm blaze wavelength instead of one at 500-nm blaze wavelength for visible lights, provide CL micrographs of 180-700 nm lights for recent deep-UV LE devices. Some unforeseen light emissions between 200-350 nm regions are observed on various materials and they are discussed correlating with the structure observed in SEM micrographs.

1. Introduction
Recent solid-state light-emitting (LE) devices go into deep-UV emission, and some emit near 200 nm light that is almost limit wavelength to transmit in air. Such devices ask for fine designing and precise fabrication in elemental, chemical and crystal structure, density and distribution of defects and impurities, etc. All above must be controlled at nano-accuracy, and the fabrication process should receive both structural and chemical verifications. Elemental distribution and crystal structure can be studied by electron microscopy with EDX, but the electronic energy levels, a key structure as LE device, are hardly examined. The wavelength of absorbing or emitting lights from a LE device is a direct measure between two energy levels among which electrons transfer during excitation and/or relaxation. The excitation of deep UV emitting devices is easily made by electric currents, i.e. electroluminescence, and the light emitting sites and the wavelengths are optically imaged, which means the spatial resolution is in the level of optical microscopy. Higher spatial resolution is achieved by scanning probe microscopy such as near-field microscopy, but the excitation energy is limited to near UV region. Raman

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spectroscopy, X-ray or synchrotron orbital radiation (SOR) lights excite deep energy states, but they lack microscopic imaging ability. Cathodoluminescence (CL) microscopy is the sole analysing tool that can excite deep-UV states with a narrow electron beam to draw micrograph.

Commercially available CL microscopes are designed to measure spectra of visual light to near UV in high resolution with slow imaging rate e.g. several hours. Among the various properties of materials, electronic structure is most irradiation sensitive and generally receives damage during one frame observation. In the present study, we tried to measure CL images of 180 nm to 700 nm lights in four sequential observations in five minutes.

2. Experimental.

2.1 Design of Deep-UV CL imaging system [1]

Figure 1 shows the block diagram of our spectrometric CL microscope, which detects CL spectra of the point where the scanning electron beam is placed and stores both secondary electron micrograph (SEM) and CL spectra signals simultaneously in the control computer. One frame scan of 512x512 pixels ends in 8s to 80s, and signal accumulation is possible by repeating frame scans. For deep-UV imaging, we replaced the grating of Jovin-Yvon spectrometer to 300-nm blaze wavelength (600 line/mm grating) instead of one at 500-nm blaze wavelength (300 line/mm grating for visible lights). Multi-channel linear array sensor is placed at the focus of the grating. The number of channels of sensing device determines spectral resolution. Most commercial microscopes use linear CCD array of 1024 channels or more, and proudly declare the spectral resolution be 0.1 nm on the data sheet. However, by the quantum chemical reasons, any luminescence from solid materials is wide spread in wavelength and the FWHM (full-width at half maximum) is generally 10 nm or more. Avoiding CCD sensors of low sensitivity to deep-UV lights and slow data reading rate due to too many channels, we employed Hamamatsu Photonics, H7260-04 32-channel photoelectron multiplier (PMT) array as a detector for the wavelengths from 200 nm to 700 nm lights. As a result, our spectral resolution is 5 nm and the highest spatial resolution in the CL micrograph is 20 nm. CL spectrum is stored at the address of the memory corresponding to the scanning electron beam position (pixel position), and is used to display full-colour CL micrographs.

2.2. Specimen

The deep UV imaging is tested with ZnO varistors, #1 to #4, of four different SnO₂ concentrations, 0.1, 0.5, 2 and 10 % respectively. All of them contain 1% Bi₂O₃. The specimen has a grain structure and ZnO is inside the grains. SnO₂ controls grain growth and Sn-Zn spinel particles are formed inside grain. At the grain boundaries, Bi₂O₃ is believed to segregate and control the electronic properties [2] [3]. The shell and core of grains are well illustrated in the CL micrographs of visible light region [4].

Figure 2. A schematic diagram of the grain structure of ZnO varistor. The surface is cut and polished to show the cross section of grains. Arrow is a direction of observation.
3. Results and Discussion

Figure 3 is an example of CL micrograph taken using a grating of blaze wavelength 500 nm. With this grating, we record spectra of continuous 300 nm wavelengths in one scan, and for recording 200-700 nm, two measurements of 200-500 nm and 400-700 nm, are performed. In the figure, we can see strong luminescence peak at about 380 nm inside grain (see spectrum in subfigure 5) that is eminent in electroluminescence of ZnO materials. Luminescence over 400 nm is used to draw CL micrograph where wide green colour regions are grain surfaces and curved narrow green lines are grain boundaries being cross-cut on the specimen preparation. The CL micrograph composed with luminescence of 200-400 nm shows similar bright area distribution as that of 400-700 nm. However, several areas in the upper part of the figure are dark as compared to those in 400-700 nm CL micrograph.

Figure 4 shows CL spectra of various points of the specimen, ZnO #1. Strong and sharp CL peaks from 200 to 250 nm are from the edges or surfaces of grain boundaries as identified in the SEM image. This understanding can be enhanced with higher incident energy.

Figure 5 is the case of 30 keV beam of ZnO #2, where high-energy incident electrons penetrate inside grains and excite grain boundaries hidden from the specimen surface. Spectra taken at the grain boundary edges (red square) and at the middle of the grains (blue square) show similar distribution of CL spectra. It is well known that bulk ZnO emits luminescence at about 380 nm. This specimen contains both Bi₂O₃ and SnO₂, but we can ignore Sn-Zn spinel particles because of low SnO₂ concentra-
tion in Specimens #1 and #2. Bi$_2$O$_3$ segregates on the grain boundaries and control electronic properties [3]. Bi$_2$O$_3$ has several absorptions of lights between 3.60-4.20 eV i.e. 344-295 nm, and with increasing thickness, it reaches 6.20 eV or 200 nm [5]. The CL peaks in Fig. 5 are, therefore, from thick Bi$_2$O$_3$ accumulated on the grain boundaries.

With increasing SnO$_2$ concentration, X-ray analysis suggests formation of Sn-Zn spinel particles inside grain [3]. Figure 6 is the case of high SnO$_2$ concentration. At the grain boundaries identified in the SEM image, strong 210 nm emission is again seen. Some new peaks around 255-260 nm appear in the spectra 2, 3 and 8 of Fig. 6. They seem not from the boundaries but from inside the grain. As these peaks are hardly seen in the spectra of Specimen #1 and #2, we consider them from Sn-Zn spinel or related materials.

4. Conclusion
Deep-UV luminescence is successfully imaged in CL microscopy with CL spectrum in our spectrometric full-colour electron microscope. Thick segregation of Bi$_2$O$_3$ and Sn-Zn spinel formation is clearly seen by the spectra.

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