Development of Novel Optical Fiber System for Cathodoluminescence Detection in High Voltage Transmission Electron Microscope

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We have installed a new system to observe cathodoluminescence (CL) in a high voltage transmission electron microscope (HVTEM). The system is constructed of a ball lens for collection of CL, an optical fiber and a multi-channel optical detector. The system can be operated without any disturbance of TEM observation. The system was proved to be very useful to observe CL in HVTEM and will be a powerful tool to investigate production mechanisms of luminescence centers by observing CL changes with incident electron energy and flux (displacement damage effect), and temperature, together with simultaneous TEM observations of microstructure changes.

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1. Introduction

We have developed a new equipment to observe cathodoluminescence (CL) in a high voltage transmission electron microscope (HVTEM). CL in SEM or TEM has been used as a useful tool to study correlations of optical properties of semiconductors and insulators with their microstructure.¹⁻³⁾ Fortunately or unfortunately, electron energies ordinary used in SEM and TEM are below ~ 200 keV, which is not enough to induce elastic displacements of atoms and ensure no-micro-structure change during measurements of CL spectra. If we can use higher energy electron beam, *in-situ* observation of luminescence change accompanied with microstructure change caused by atomic displacement becomes possible. In addition, observation with changing temperature would help to investigate dynamic processes of radiation damage due to atomic displacement effects. This motivated us to equip a CL detection system in HVTEM.

2. Experimental Setup

Figure 1 shows a schematic illustration of the present CL detection system equipped into HVTEM (JEM-1300NEF, JEOL Ltd.) at Research Laboratory for High Voltage Electron Microscopy of Kyushu University. An optical fiber system was sheathed in a stainless tube and directly inserted through a small hole with 2 mm in diameter at an angle of 46 degrees from the electron beam without any disturbance of TEM observation. Therefore all equipments in HVTEM, such as a temperature variable sample holder and other analyzing tools can be used during the collection of CL signals. The optical fiber is made of UV grade SiO₂ with a core diameter of 600 μ m. A ball lens of 1 mm in diameter on the front head of the fiber enhances detection efficiency. The fiber system is movable to be inserted only at measurements of CL signals.

Fig. 1 Schematic illustration of the optical fiber system for TEM-CL detection.

CL is lead to an external multichannel optical spectrometer (PMA-12, Hamamatsu Photonics) through a SMA905 optical fiber connector.

3. Result

Figure 2 shows examples of observed spectra of TEM-CL for a single crystal α -Al₂O₃ (sapphire, Furuuchi Chemical Corp.) with the shape of a TEM disk of 3 mm in diameter and ~ 150 μ m in thickness induced by irradiation of a 1.25 MeV electron beam with a diameter of 10 μ m and flux of 1.3×10^{22} electrons/m²·s. The observed TEM-CL spectrum is very fine owing to the stainless sheath, which suppressed luminescence of the optical system induced by reflected or scattered electrons in a TEM system previously reported.⁴⁾

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Fig. 2 TEM-CL spectra of α - Al_2O_3 measured at RT under irradiation of 1.25 MeV electrons with a flux of 1.3×10^{22} electrons/ $\text{m}^2\cdot\text{s}$. Inset in the figure shows a typical CL spectrum of α - Al_2O_3 ⁵⁾ for a comparison.

For comparison, a CL spectrum of α - Al_2O_3 reported by P. Jonnard *et al.*⁵⁾ was shown in the inset of the figure in which the solid and dashed lines were induced by 4 keV electron beam irradiation with electron fluxes of 9.4×10^{19} and 9.4×10^{18} electrons/ $\text{m}^2\cdot\text{s}$, respectively. The present CL spectrum is composed of intense line emission at 690 nm (1.8 eV) accompanying a few satellite peaks and a broad band emission peaked at 330 nm (3.8 eV). In present work, we used thick specimen ($\sim 150 \mu\text{m}$) for the confirmation of CL detection. Considering the detection limit of the present system, the specimen thickness can be reduced by a factor of 1/100 (assuming the luminescence intensity is proportional to the thickness). Utilization of high-voltage TEM would allow to use a rather thick sample for simultaneous observations of TEM and luminescence.

The intense line emission is assigned as the emission of Cr^{3+} included as impurities. It is known that the wave length of the line emission and its satellite structures are varied reflecting local atomic arrangements surrounding Cr ions.⁶⁾ Broad band emission at 330 nm is attributed to the emission of F^+ center, which is an oxygen vacancy trapping one electron. In the observed spectra, no emission of F center (oxygen vacancy trapping two electrons) at around 410 nm (3.0 eV) appeared.⁵⁾ In general, CL spectra for Al_2O_3 show double band emissions attributed to F and F^+ centers. Such double band emissions, in particular, the intensity ratio of F^+/F emission changed with the flux and the fluence as shown in the inset of Fig. 2. With increasing the flux and/or the fluence, the intensity ratio of F^+/F increases.⁷⁾ It seems that the present irradiation flux of 1.3×10^{22} electrons/ $\text{m}^2\cdot\text{s}$, was too high to appear the F center emission.

The benefit of the HVTEM-CL appears in the observation of dynamic changes in the spectra. Figure 3 shows time sequences of the F^+ emission intensity. At earlier stage of the irradiation (or at lower fluences), the F^+ emission intensity increased nearly linearly with increasing irradiation time (fluence), while it saturated over the fluence of $\sim 1.5 \times 10^{25}$ electrons/ m^2 . The linear increase with the fluence can be correlated to the linear increase of the number of oxygen

Fig. 3 Electron fluence dependence of F^+ emission intensity at RT .

Fig. 4 Temperature dependence of saturated F^+ emission intensity ranging from RT to 120 K.

vacancies as the source of the luminescence centers produced by an atomic displacement effect of the high-voltage electron irradiation. The appearance of small deviation from the linearity at fluencies around 4×10^{24} electrons/ m^2 suggests the existence of some additional mechanisms for the increase of emission intensity, which will be investigated in future. Meanwhile, the saturation of the intensity suggests the balance between production of oxygen vacancies and their annihilation by recombination of vacancies and interstitials, and transformation to different defects, such as clustering to multiple vacancies, dislocations and so on.

Using the temperature variable sample holder, the temperature dependence of HVTEM-CL intensity was successfully measured. We observed the change of saturated F^+ emission intensity ranging from 120 K to RT . After 4.0×10^{25} electrons/ m^2 irradiation at RT , then we cooled a specimen with liquid nitrogen, and measured CL intensity change caused by cooling under continuous irradiation. The result was shown in Fig. 4. The intensity increased with decreasing temperature down to around 190 K to show a maximum value, and then decreased. Similar temperature dependence of F^+

emission intensity was previously reported.⁸⁾ Such observed temperature dependence of the F^+ emission intensity might not be caused by a simple origin. Since trapped electrons at F^+ centers are relaxed by either radiative or non-radiative transition, and the non-radiative transition is thermal-activated process, the ratio of radiative and non-radiative transitions is varied with temperature. In addition, saturated concentration of F^+ centers must be changed with temperature. Detailed investigation of the temperature dependence of the luminescence intensity with and without displacement damage will give useful information on the production or annihilation mechanism of the luminescence centers.

4. Conclusion

The newly developed HVTEM-CL detection system is proved to be a powerful tool to investigate production mechanisms of luminescence centers by observing CL changes with incident energy and flux (displacement effect), and temperature, together with simultaneous TEM observations of microstructure changes.

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