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Individual cathode luminescence spectroscopy of zinc oxide particles based on *in situ* transmission electron microscopy

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1. Introduction

Emission from nanometer-sized semiconductor particles and localized structures was dominated by their size, external shape and defects, in particular, for excitonic stimulated emission in addition to their crystal structure and chemical elements. These structural factors have been investigated by electron microscopy since materials themselves are in less than micrometer or nanometer scale. The emission spectra from in integrated nanometer structures in films and aggregates of the particles have been compared with statistical structural features, e.g. average size, common external shape and diffractively analyzed orientational relationships. While such statistical evaluation retains the reliability, we need microscopic analyses of optical properties of individual nanometer structures to design their integrated systems. Scanning near-field microscopy (SNOM) is an innovative method to perform it [1, 2]. The spatial resolution has reached to a few tenths nanometers [3]. We expect the progress in SNOM, on the other hand, we know that the resolution and new functions can be developed by combination with other microscopy. In this paper, we demonstrate individual cathode luminescence spectroscopy of nanometer-sized particles based on *in situ* transmission electron microscopy by optical fiber probes as used in SNOM. We selected a wide band gap semiconductor, zinc oxide (ZnO) as a specimen.

2. Experimental method

The experimental method in this study was developed based on *in situ* high-resolution TEM combined with functions of atomic force microscopy (AFM) and scanning tunneling microscopy [4]. Figure 1 shows the experimental setup of the present study. First we prepared ZnO particles by an inert-gas evaporation method; Zn was heated in He gas of 13 kPa in a vacuum chamber. ZnO particles of 10 – 50 nm in diameter formed and moved up to a stainless sheath cooled at 77 K. The particles were scraped and dispersed on a nanometer-sized tip of Si cantilevers, as used in AFM. The cantilever was attached to the front of a tube piezo on a cantilever holder of the transmission electron microscope in University of Tsukuba. An optical fiber probe was attached in another holder. Both the cantilever and fiber holders were then inserted into the microscope. The particles on the cantilever-tip were manipulated to approach a tip of the opposing fiber by piezo-driving. We selected the particles and irradiated electron beam accelerated to 200 keV and resultant cathode luminescence was detected by a spectrometer. A series of these manipulations were performed at room temperature and at 102 K in a vacuum of 10^{-6}-10^{-5} Pa. The structure of the particles and their dynamics during the procedure were observed *in situ* by bright-field imaging and lattice imaging of high-resolution TEM using a TV capture system. We confirmed that the spatial-resolution in the lattice imaging was 0.14 nm and the time-resolution of the image observations was 17 ms. The high-resolution imaging and signal detection in this system were coincidentally recorded and analyzed for every image using our own software.

3. Results and discussion

Figure 2 shows a bright-field image of the configuration of the specimen and fiber probe. An aggregate of ZnO particles is observed in the upper left of

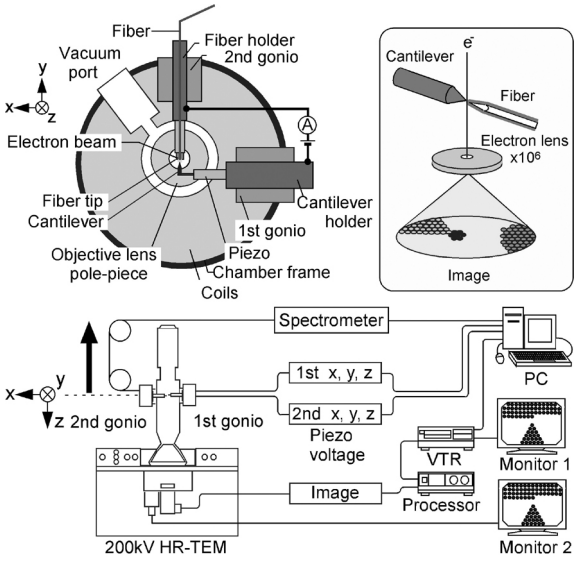

Fig. 1 Experimental setup of the present study based on *in situ* TEM.

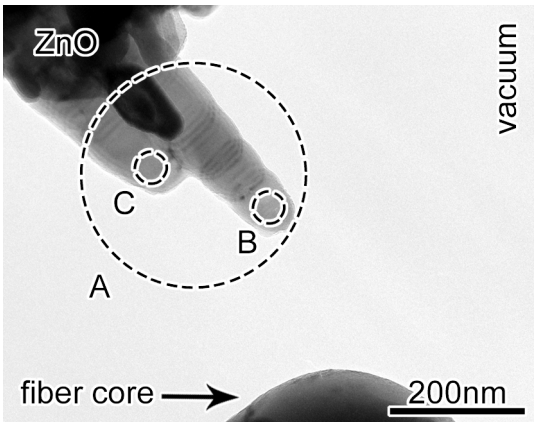

Fig. 2 Bright-field image of the configuration of the specimen and fiber probe. Circles of broken lines, A, B and C represent areas of electron irradiation to stimulate cathode luminescence.

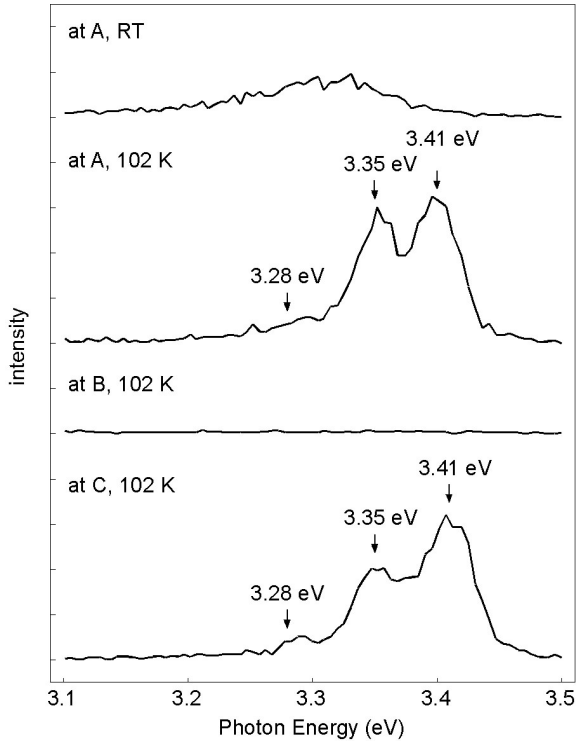

Fig. 3 Cathode luminescence spectra from area A at RT and at 102 K, and area B and C at 102 K.

Fig.2. The width in shorter direction is ~ 50 nm. The tip of the fiber, which is a part of aperture, is observed in the bottom. We irradiated electron beam in areas indicated with A, B and C. The diameter of area A is 300 nm. In area A, seven particles are included at the irradiation. The diameter of areas B and C is 30 nm. In these areas, the electron beam irradiated one particle. The distance between the particles and aperture is 300 – 500 nm. Thus, as shown in here, it is easy to observe the size, external shape, and distance between the probe and specimens, which are essential parameters in SNOM.

Figure 3 shows cathode luminescence spectra from areas A at room temperature and 102 K, and B and C at 102 K. In area A, a broad spectrum appears around 3.31 eV at room temperature. As the temperature decreases to 102 K, three peaks are observed. The peaks of these components were found to be 3.28, 3.35 and 3.41 eV from the Gaussian fitting. These components are the near band-edge emission [5]. The peaks, 3.35 and 3.41 eV are attributed to excitons bound to neutral acceptors and free excitons, respectively. The peak at 3.28 eV is caused by the phonon replica of the bound excitons. In area C, which is contained in area A, the spectrum shows the same peaks with those in area A, while no peak is observed in the spectrum from area B, which is also a part of area A. Selected-area electron diffraction showed similar patterns in areas B and C. This implies that the crystal structure and orientational relationship of the particle in area B is the similar to those in area C. Since the difference in the spectra in Fig. 3 is clear, it is deduced that defect concentration in area B is higher than that in area C although the concentration hardly contributes to the diffraction pattern.

4. Conclusion

The optical fiber probes as used in SNOM were installed in high-resolution TEM. Cathode luminescence from ZnO particles of 10 – 50 nm in the diameter was measured at room temperature and 102 K based on TEM imaging. It was found that the excitonic stimulated emission from the ZnO particles with the same crystal structure and orientational relationship at 102 K were deduced to be influenced significantly by defects that amount was not detected by the selected-area electron diffraction.

Acknowledgment

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