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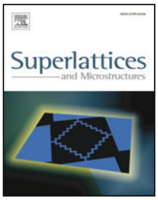

Hydrogen desorption effect on cathodoluminescence of ZnO

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ABSTRACT

The effects of the low-energy electron beam on ZnO single crystals were investigated by cathodoluminescence (CL), Time-of-Flight Electron Stimulated Desorption (TOF-ESD) and Temperature Programmed Desorption (TPD). Under e-beam irradiation, the ultraviolet (UV) emission decreases exponentially for O-face, while it increases and then decreases for Zn-face. Meanwhile, a large desorption of H^+ is observed by TOF-ESD for both O- and Zn-faces. On the other hand, an increase of H in the irradiated volume is observed after stopping the e-beam irradiation. Similar H_2 desorption is found by TPD for both faces. These data suggest that the decrease of the UV intensity is related to H desorption.

1. Introduction

ZnO is a promising fluorescent material for Field Emission Displays (FEDs) due to its wide bandgap, its high exciton-binding energy and its large variety of morphology [1–3]. However, a degradation of the luminescence is observed when ZnO is irradiated by the electron beam [4]. This degradation of the intensity under e-beam irradiation is a great drawback for FED applications because it shortens the lifetime of display devices. Recently, by irradiating faces with different surface polarity of ZnO by e-beam, we have found that different reactions take place at O- and Zn-faces [5]. The ultraviolet (UV) intensity of O-face decreases exponentially with irradiation time, while that of Zn-face first increases

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and then decreases. The decrease of UV intensity is similar for both faces. Moreover, we have found that, after hydrogenation, the decreasing component becomes larger, while the increasing component is not affected [6]. These observations suggest that the reactions induced by the e-beam irradiation happen near the surface, and that hydrogen may be a key for the luminescence degradation. In this work, to confirm the role of hydrogen, we have compared the effects of the electron beam on O- and Zn- faces of ZnO single crystals by cathodoluminescence (CL), Time-of-Flight Electron-Stimulated Desorption (TOF-ESD) and Temperature Programmed Desorption (TPD).

2. Experimental details

Specimens were ZnO single crystals grown by hydrothermal method. CL measurements were performed by using Ultra-High Vacuum Scanning Electron Microscope (UHV-SEM) with Gemini electron gun (Omicron, Germany) equipped with a CL system (Horiba, Japan) [7]. The vacuum of the analysis chamber was less than 2×10^{-10} mbar in order to prevent gas adsorption during CL measurement. The O- and Zn- faces of the same sample were irradiated by the electron beam for 1 h. The observed area was 22 μm × 15 μm scanned by an electron beam for every 90 ms. During the electron beam irradiation, the CL spectra were recorded by every 20 s. Since the reactions induced by the e-beam happen near the surface, the accelerating voltage was chosen at 1.5 kV, which corresponds to an electron range of 30 nm as calculated from the Kanaya–Okayama model [8]. The beam current was kept at 1 nA. All measurements were performed at room temperature.

TOF-ESD measurements were performed with a Scanning Electron-Stimulated Desorption Ion Microscope (SESDIM), composed of an UHV system with a pencil-type SEM and a TOF-ESD analyzer [9]. The vacuum was less than 2×10^{-10} mbar. The TOF-ESD spectra were taken with an electron energy of 0.5 keV and a specimen bias of 10 V, while the e-beam irradiation was done at 1.5 keV. When a positive specimen bias is applied, the flight-time of ions from the specimen to the detector is given by:

$$t = L(2m)^{0.5}(E_k^{0.5} + (E_k + qV_s)^{0.5})^{-1}$$

where E_k is the kinetic energy of the desorbed ion, V_s the specimen bias, q the electric charge, m the mass of the ion and L the flight distance of the Time-of-Flight instrument.

TPD measurements were carried out in an UHV system (ESCO, WA1000S, Japan), in which the vacuum was less than 4×10^{-10} mbar, at a heating rate of 30 °C min^{-1}.

3. Results and discussion

Fig. 1 shows the CL spectra taken after 20 and 3600 s of irradiation for O- and Zn-faces. The luminescence spectra of ZnO consist of a narrow strong band in the ultraviolet (UV) region and a broad weak band in the visible (VIS) region. The UV emission is related to the excitonic emission and the recombination via shallow-level, while the VIS emission to defects, such as O vacancy, or impurities, like Li or K, which are common in ZnO crystal by hydrothermal growth [10,11]. After 3600 s of e-beam irradiation, the UV and VIS intensities are changed, although their shapes are almost the same as those after 20 s. For O-face, the UV intensity decreases from 3400 to 500 cps while the VIS intensity decreases from 170 to 50 cps. For Zn-face, the UV intensity decreases from 4500 to 2900 cps while the VIS intensity decreases from 860 to 340 cps. Although the VIS variation is similar for the both faces, the UV intensity decreases much more for O-face than for Zn-face.

To clarify the irradiation effects, the CL spectra were recorded every 20 s during 3600 s. Fig. 2 shows the evolutions of the UV intensity during the electron beam irradiation at 1.5 kV and 1 nA for O- and Zn-faces. For O-face, the UV intensity decreases exponentially from 3500 to 500 cps. While for Zn-face, the intensity first increases, reaches a maximum at 6400 cps in 1 min and then decreases exponentially to 3500 cps. The decrease of the UV intensity is similar for O- and Zn-faces, while only an increase is observed of Zn face. Since the measurements were performed at a pressure less than 2×10^{-10} mbar, we may suppose that the probability of the gas adsorption from the chamber is low. Consequently, it is reasonable to suppose that the variation of the CL intensity is related to some defect reactions or gas desorption.