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The effects of electron beam irradiation on the luminescence of ZnO single crystals were investigated by cathodoluminescence. We have found that the evolution of the intensity during the e-beam irradiation depends on the surface polarity. For O-face, the ultraviolet (UV) emission decreases exponentially and approaches an asymptotic value. For Zn-face, it first increases and then decreases. The decrease components are similar in both faces. If we halt the e-beam irradiation, the UV intensity recovers partially. These results suggest that the decrease in the UV evolution is related to metastable bulk defect reactions at the subsurface region while the increase is related to surface reaction such as electron-stimulated desorption. © *2008 American Institute of Physics.*
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I. INTRODUCTION

Field emission displays (FEDs) are expected to replace the liquid crystal displays and plasma displays because of their high-contrast wide-view angle and low power consumption.[1,2] For their development, high quality phosphors are indispensable. The requirements for FED phosphors are high luminescence efficiency under low-energy electron excitation and good stability under electron beam irradiation.[3] ZnO is a good candidate for this purpose. Indeed, its wide band gap, its high exciton-binding energy, and its large variety of morphology are attractive properties.[4–6] However, we have found that a degradation of the luminescence under e-beam irradiation takes place in nano- and bulk ZnO crystals.[7] This degradation of the intensity under e-beam irradiation is a great drawback for FED applications because it shortens the lifetime of display devices. Therefore, we must understand the degradation mechanisms and suppress this decrease to improve the ZnO FED devices.

To investigate the luminescence stability of ZnO under e-beam irradiation, we have studied ZnO single crystal by using cathodoluminescence (CL). We have irradiated the $-c(000\bar{1})$ and $+c(0001)$ facets, corresponding to O- and Zn-terminated surfaces of ZnO, respectively, with different electron beam conditions.[8]

II. EXPERIMENTAL DETAILS

Specimens were ZnO single crystals grown by hydrothermal method (Furuuchi Chemical Corporation, Japan). CL spectra were measured by using an ultrahigh vacuum (UHV) scanning electron microscope with Gemini electron gun (Omicron, Germany) equipped with a CL system (Horiba, Japan).[9] The vacuum of the specimen chamber was less than 2×10^{-10} mbar in order to prevent contamination during the measurement. The O- and Zn-faces of the same sample were irradiated by the electron beam for 1 h. The observed area was 22×15 μm^2 scanned by an e-beam for every 90 ms. During the e-beam irradiation, the CL spectra were recorded for every 20 s. The accelerating voltage (V_a) was varied from 1.5 to 20 kV, which corresponds to an electron range from 30 nm to 2 μm as calculated from the Kanaya–Okayama model.[10] The beam current (I_b) was varied from 400 to 2000 pA. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the CL spectra taken after being irradiated for 20 and 3600 s by using 5 kV and 1000 pA e-beam for O- and Zn-faces, respectively. The luminescence from ZnO consists 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 or impurities.[8,11] After 3600 s of e-beam irradiation, the UV and VIS intensities are changed while their shapes are similar to those after 20 s. For O-face, the UV intensity decreases from 8900 to 4800 cps while the vis intensity decreases from 2700 to 1900 cps. For Zn-face, the UV intensity increases from 13 000 to 17 000 cps while the vis decreases from 3800 to 2900 cps. Thus, the behavior of the UV peak depends on the polarity of the face. It is noted that the UV intensities of O- and Zn-faces at 20 s are different. This may be because the e-beam effects have ever started to happen during the first 20 s.

To clarify the irradiation effects, the CL spectra were recorded for every 20 s during 3600 s. Figure 2 shows the evolution of the UV peak intensity during the electron beam irradiation at 5 kV and 1000 pA for O- and Zn-faces, respectively. For O-face, the UV intensity decreases exponentially and approaches around 50% of the initial value. While for Zn-face, the intensity first increases, reaches a maximum at

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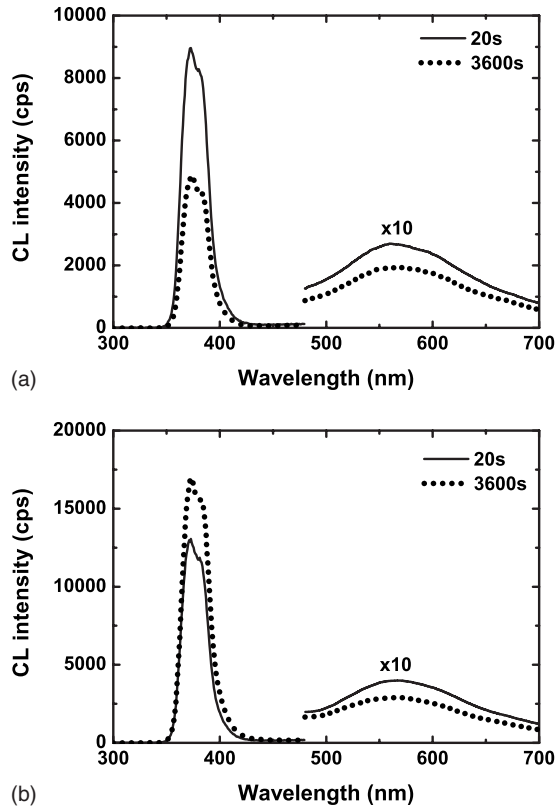b)Electronic mail: sekiguchi.takashi@nims.go.jp.

FIG. 1. (a) CL spectra for O-face after 20 and 3600 s of e-beam irradiation at 5 kV and 1000 pA. (b) CL spectra for Zn-face after 20 and 3600 s of e-beam irradiation at 5 kV and 1000 pA.

140% of the initial value in 5 min, and then decreases. To compare these behaviors, the increase and decrease components were fitted with exponential function

$$A_{\text{inc/dec}} \exp(-t/\tau_{\text{inc/dec}}),$$

where $A_{\text{inc/dec}}$ and $\tau_{\text{inc/dec}}$ correspond to the amplitude and time constant of the increase/decrease component, respectively. Table I shows the fitting parameters for the UV evolution of the O- and Zn-faces. Both decreasing parameters A_{dec} and τ_{dec} for O- and Zn-faces are comparable. This suggests that the same reactions responsible for the decrease component take place in both faces. On the other hand, the increase component exists only for Zn-face. A_{inc} is twice as large as A_{dec} while τ_{inc} is five times as large as τ_{dec}. The
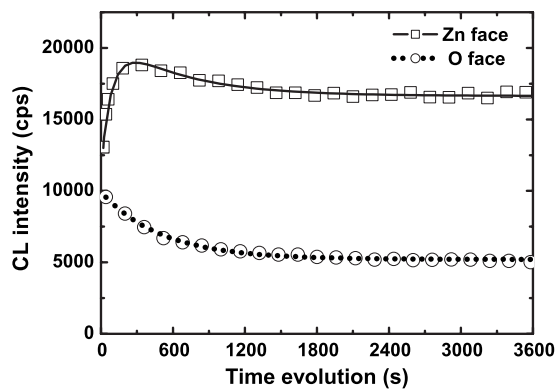

FIG. 2. UV intensity evolutions during the e-beam irradiation for O- and Zn-faces at 5 kV and 1000 pA.

TABLE I. Fitting values of the increase and decrease components for O- and Zn-faces at 5 kV and 1000 pA.

Face	Variation	A	τ
Zn	Inc	−8900	100
Zn	Dec	4500	600
O	Dec	4700	510

reactions responsible for the increase are quicker than those responsible for the decrease.

Figures 3(a) and 3(b) show the UV intensity evolutions in the function of V_a for O- and Zn-faces, respectively, at 1000 pA. For O-face, the intensity continuously decreases for each V_a. The final intensities are 15%, 30%, 50%, and 80% of the initial intensities while τ_{dec} are 100, 200, 500, and 850 s for 1.5, 2.5, 5, and 10 kV, respectively. The decrease percentage is larger and the decrease rate is faster for lower V_a. For Zn-face, the intensity always increases first and then decreases. For the increase part, τ_{inc} are 15, 35, 100, and 160 s for 1.5, 2.5, 5, and 10 kV, respectively. So, the UV intensity is faster to reach the maximum for lower V_a. For the decrease component, τ_{dec} is similar to that of the O-face. Thus, lower V_a induces a quicker reaction for both O- and Zn-faces. It suggests that the reactions happen mainly near the surface.

Figures 4(a) and 4(b) show the UV intensity evolutions in the function of I_b for O- and Zn-faces, respectively, at 5 kV. For O-face, the intensity always decreases and approaches about 50% of the initial intensity for different I_b. τ_{dec} are 940, 470, and 390 s for 400, 1000, and 2000 pA,
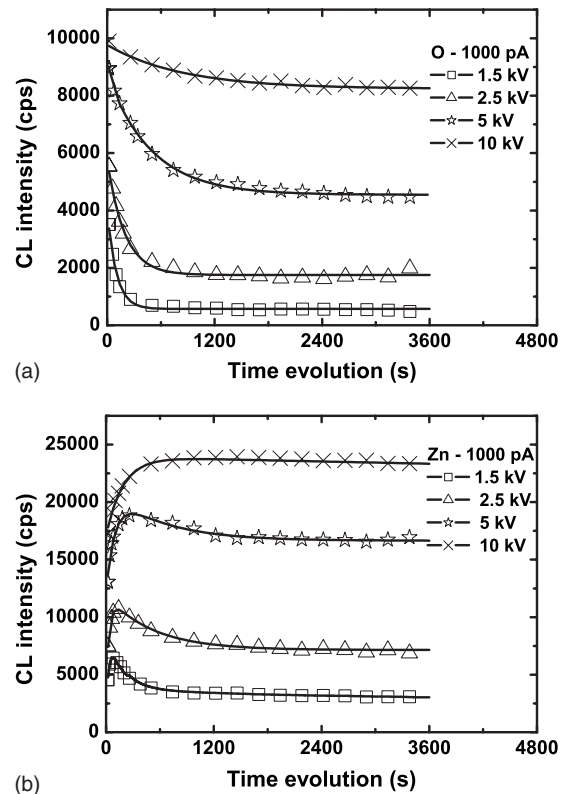

FIG. 3. (a) UV intensity evolutions of O-face during the e-beam irradiation in the function of V_a at 1000 pA. (b) UV intensity evolutions of Zn-face during the e-beam irradiation in the function of V_a at 1000 pA.
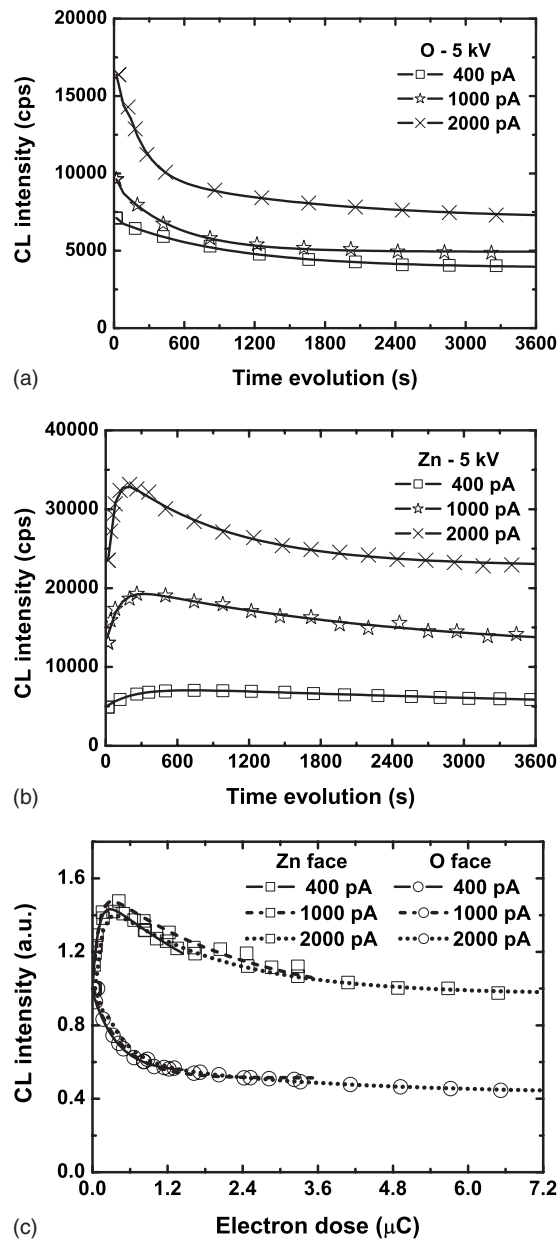
(a)

(b)

(c)

FIG. 4. (a) UV intensity evolutions of O-face during the e-beam irradiation in the function of I_b at 5 kV. (b) UV intensity evolutions of Zn-face during the e-beam irradiation in the function of V_a at I_b at 5 kV. (c) Normalized UV intensity evolutions during the e-beam irradiation in the function of the electron dose for O- and Zn-faces at 5 kV.
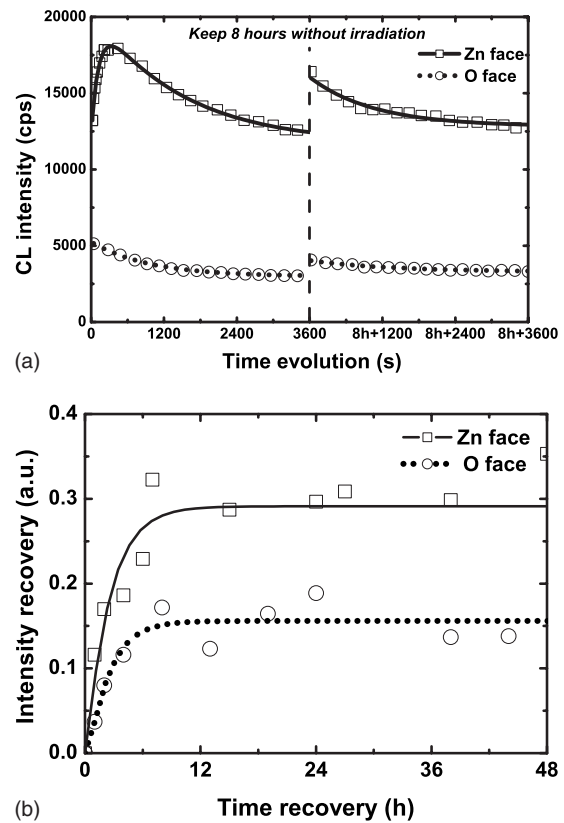

(a)

(b)

FIG. 5. (a) UV intensity evolutions for O- and Zn-faces before and after turning off the electron beam during 8 h at 5 kV and 400 pA. (b) Intensity recovery for O- and Zn-faces in the function of the e-beam halting time.

respectively. The decrease rate is faster for higher I_b. For Zn-face, τ_{inc} are 230, 100, and 50 s for 400, 1000, and 2000 pA, respectively. The UV intensity is faster to reach the maximum for higher I_b. For the decrease component, τ_{dec} is similar to that of the O-face. It suggests that I_b, and more precisely the electron dose, affects mainly the rate of reactions responsible for the CL intensity variation.[12] To confirm this point, Figs. 4(a) and 4(b) have been normalized and replotted against electron dose as shown in Fig. 4(c). The curves for different I_b coincide each other for both O- and Zn-faces. For O-face, the UV intensity decreases and approaches about 50% of the initial intensity with an electron dose of 1.0 μC. For Zn-face, the UV intensity increases until 140% of the initial intensity for an electron dose of

0.5 μC and then decreases until the initial intensity for an electron dose is of 1.8 μC. These results confirm that the electron dose affects the reaction rate.

To check the recovery of the e-beam effects, we turned off the e-beam, halted for a certain period, and then repeated the experiments. First, a 22×15 μm^2 area was irradiated for 1 h at 5 kV and 400 pA. Then, the sample was kept in the UHV chamber for 8 h without e-beam irradiation. Finally, the same area was measured again with the same condition. Figure 5(a) shows the recovery of UV intensity variation for O- and Zn-faces. The 8 h halting gives a recovery of the UV intensity to a certain extent for both faces. The UV intensity of the O-face recovers from 59% to 78% of its initial value while that of Zn-face from 94% to 124%. Interestingly, for Zn-face, no increase is observed after the 8 h halting. Figure 5(b) shows the intensity recovery in the function of the e-beam halting time for O and Zn-faces. In the first 10 h, the UV intensity recovers until 19% and 30% of the initial value for O- and Zn-surfaces, respectively. Then, no more recovery is observed. The recovery is limited to a certain extent. Furthermore, the recovery is more effective for Zn-face than for O-face. These results suggest that the e-beam induced reactions responsible for the decrease in the UV intensity are partially reversible while those responsible for the increase are irreversible.

We discuss the variation in the CL intensity in terms of e-beam stimulated reactions.[12–14] The variations in the CL intensity are larger for lower V_a, which suggests that they occur near the surface. For both faces, the variation is

quicker for lower V_a (Fig. 3) and higher for I_b (Fig. 4). It suggests that the variation rate is related to the electron density since the electron density is inversely proportional to $V_a^{4.25}$ and proportional to I_b.[10] A higher electron density induces a higher rate of reaction. It is also clear that at least two reactions are caused by the e-beam irradiation: one for the increase in the UV intensity and another for the decrease. The increase in the UV intensity is observed only for Zn-face. Moreover, this increase always happens at the beginning of the irradiation. Due to the influence of the polarity and the fact that it is the faster reaction, it is reasonable to suppose that the reactions responsible for the increase take place at the specimen surface. Since the measurements were performed at a pressure less than 2×10^{-10} mbar, we may suppose that the increase is less probably related to gas adsorption such as oxygen or hydrocarbons. Thus, we speculate that the reactions responsible for the increase are electron-stimulated desorption such as desorption of OH groups from the surface. The surface polarity may give a difference in the presence of these species between Zn- and O-faces, which may explain why the increase only occurs for Zn-face.[15] On the other hand, the decrease in the UV intensity is observed for both O- and Zn-faces. The decrease components of O- and Zn-faces are similar. These results suggest that the decrease is caused by bulk defect reactions at the subsurface region. Moreover, the partial recovery of the CL intensity also suggests that these defect reactions are reversible. Such metastability of defects is often observed in bulk semiconductors.[16–18] Although further experiments are needed to clarify these reactions, we speculate that H, O, or OH groups play a role in these CL behaviors.

IV. CONCLUSIONS

In conclusion, we have investigated the evolution of the CL intensity from ZnO single crystal under e-beam irradiation. We have found that this CL intensity evolution depends on the surface polarity. The UV intensity for O-face decreases exponentially while that for Zn-face first increases and then decreases. The decrease components are similar in both faces. We have also observed a partial recovery of the UV intensity after stopping the e beam for several hours. It is supposed that the decrease behavior is related to metastable bulk reactions while the increase behavior is related to surface reaction as electron-stimulated desorption.

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