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Light emission due to dislocations in wurtzite ZnO bulk single crystals freshly introduced by plastic deformation

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An arbitrary number of dislocations were freshly introduced in wurtzite ZnO bulk single crystals by plastic deformation at high temperatures (923–1123 K), and the optical properties were examined by photoluminescence spectroscopy. ZnO, including a high density (more than $10^9\ \mathrm{cm}^{-2}$) of dislocations, showed excitonic light emission with photon energies of 3.100 and 3.345 eV, as well as their LO-phonon replicas, at a temperature of 11 K, and the intensities increased with increasing dislocation density. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2831001]

With a wide band gap of 3.4 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has rapidly emerged as a promising base material for short-wavelength electronic and optoelectronic devices. Despite considerable success in optimizing their growth and structural quality, ZnO epitaxial layers still contain a high density of defects that influence the electronic and optoelectronic properties. The most characteristic defect, investigated by transmission electron microscopy (TEM), is high-density (typically 10^9–$10^{11}\ \mathrm{cm}^{-2}$) dislocations passing through entire layers.[1,2] As reported in a large number of studies of GaN, it is generally known that dislocations can influence the device performance. Even though ZnO has the same crystal structure as GaN, the influence of dislocations in ZnO has not been fully elucidated. Cathodoluminescence spectroscopy in a scanning electron microscope[3–7] and scanning capacitance microscopy[8] have revealed that localized energy levels exist near the dislocations, and it is considered that the levels could be associated with acceptor states.[9] It has been proposed that several luminescence peaks, at photon energies of 3.335,[10] 3.314,[11] and ~3.1 eV,[12,13] are related to extended defects including dislocations, even though these relationships are controversial. In this work, the optical properties of dislocations were clarified by means of photoluminescence (PL) spectroscopy of ZnO bulk single crystals in which an arbitrary number of dislocations were newly introduced by plastic deformation, at temperatures comparable to the typical temperatures for the fabrication of ZnO-based devices. Two emission lines were found to be related to dislocations.

Fresh dislocations were introduced into wurtzite ZnO bulk single crystals (a *n*-type carrier concentration of $5\times10^{13}\ \mathrm{cm}^{-3}$ and a grown-in dislocation density of $10^4\ \mathrm{cm}^{-2}$), purchased from Goodwill (Russia), by compressive deformation at elevated temperatures. The compressive axis was inclined at 45° with respect to the $[0001]$ direction, with the surface of one side parallel to the $(10\bar{1}0)$ plane. Compression tests were conducted in a flowing high-purity argon gas atmosphere at temperatures in the range of 923–1123 K, under a constant shear strain rate of $4\times10^{-4}\ \mathrm{s}^{-1}$, up to a shear strain of about 0.3. Details of the compression process will be published elsewhere.[14] Some specimens were only heated at the above-mentioned temperatures without any deformation. The structural nature was characterized by TEM with a 120 keV electron beam, so that the radiation enhanced dislocation motion[7] would be negligible. The optical properties were characterized by PL spectroscopy. Specimens were illuminated with a 325 nm laser light from a 15 mW He–Cd laser at a temperature of 11 K. The probe size was 0.015 mm in diameter, and the excitation density P ranged from 3×10^{-2} to $35\ \mathrm{W/cm}^2$. PL lights were collected by a photomultiplier tube detector through a 32 cm monochromator, and the spectral resolution was about 0.4 meV.

In deformed specimens, high-density (on the order of $10^9\ \mathrm{cm}^{-2}$) dislocations were introduced (e.g., Fig. 1). Many dislocations passed through the specimens, with the rest forming dislocation loops, as indicated by the arrowheads in Fig. 1. A conventional two-beam TEM method revealed that no dislocation was dissociated,[15] and that the Burgers vector of the dislocations was $(a/3)[11\bar{2}0]$, $(a/3)[2\bar{1}\bar{1}0]$, or $(a/3)[1\bar{2}10]$. The dislocation loops were identified as being interstitial type by the inside-outside contrast method. Three-dimensional TEM revealed that many parts of a dislocation lay on a (0001) basal plane or a plane inclined with respect to the {0001} planes (most likely one of the $\{10\bar{1}1\}$ pyramidal planes[6]). Many dislocations contained jogs, indicating that a

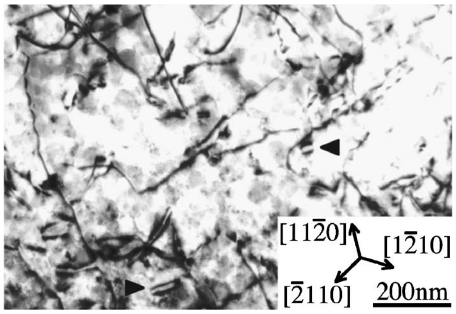

FIG. 1. The typical TEM image of a specimen heated at 1123 K under compressive stress.

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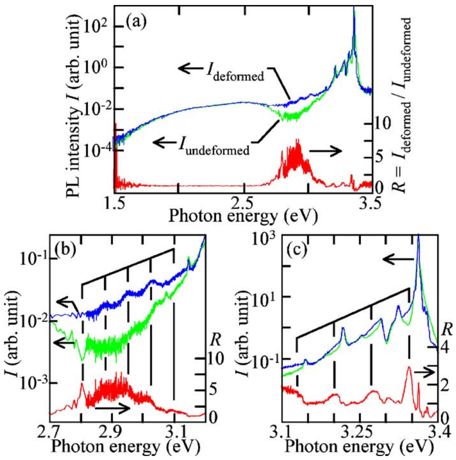

FIG. 2. (Color online) (a) A PL spectrum of a specimen heated at 923 K under compressive stress (black curve) or without stress (gray curve), and the intensity ratio *R* (see the text). A part of (a) is magnified in (b) and (c).

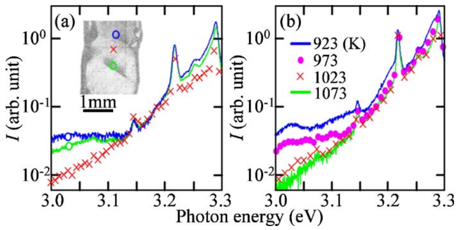

FIG. 3. (Color online) (a) Position dependent PL spectra for a specimen deformed at the temperature of 973 K. The inset shows the optical micrograph of the specimen and the marks in the inset indicate the observed areas. (b) Deformation temperature-dependent PL spectra.

high density of point defects would be introduced via the climb motion of the dislocations. In a deformed specimen, extremely dark regions along slip planes were observed by optical microscopy [see the inset in Fig. 3(a)], even though the identity of the defects was unclear. Other types of extended defects, such as twins and stacking faults, were not observed by TEM.

Figure 2 shows a typical PL spectrum obtained from a specimen deformed at a temperature of 923 K, as well as that from an undeformed specimen, which was annealed at the same temperature without stress. Both specimens exhibited near-band-edge emissions due to free excitons [peaking at 3.390 eV ($\mathrm{FX}_B^{n=1}$) and 3.378 eV ($\mathrm{FX}_A^{n=1}$)] (Ref. 17) and excitons bound to neutral donors [3.373 eV ($D_2^0X_B$) and 3.361 eV ($D_2^0X_A$)],[17] neutral acceptors [3.354 eV ($A_1^0X_A$)],[17] or unknown defects [3.335 eV (Ref. 10) and 3.314 eV (Ref. 11)], as well as their LO-phonon replicas. They also exhibited green (2.43 eV), yellow (2.18 eV), and red (1.91 eV) emissions.[17] The intensity of the emission lines for the deformed specimen I_{deformed} and that for the undeformed one $I_{\mathrm{undeformed}}$ were examined, and the intensity ratio $R = I_{\mathrm{deformed}}/I_{\mathrm{undeformed}}$ was estimated. R was found to be ~ 1 for the above-mentioned emission lines.[18] Similar results were obtained irrespective of the deformation temperature. The emission lines were therefore considered not to be related to dislocations.

In the deformed specimen, additional emission lines peaking at 3.100 eV [Fig. 2(b)] and 3.345 eV [Fig. 2(c)], as well as their LO-phonon replicas, were observed. The intensities varied depending on the dislocation density. High intensities of the emission lines were obtained from a region in which a dark band was observable by optical microscopy [Fig. 3(a)]. High intensities of the emission lines were also obtained from the specimens deformed at low temperatures [Fig. 3(b)], in which a high density of dislocations would be introduced.[19] The results indicate that the emission lines arose via the introduction of dislocations.

PL spectra for a deformed specimen were obtained with several values of excitation density P [Fig. 4(a)], and the PL intensity at the photon energies of 3.100 or 3.345 eV was fitted with a function, $I = I_0 P^{\alpha}$, in which I_0 or α was a constant [Fig. 4(b)]. α was estimated to be 1.10 for the emission line at 3.100 eV and 1.13 for that at 3.345 eV, similar to the intrinsic excitonic emissions, e.g., $\alpha = 1.16$ for the $D_2^0X_A$ emission [Fig. 4(b)]. This indicates that the emission line arose via an excitonic recombination.[20] It can therefore be concluded that the origin of the emission line was the excitons bound to a defect related to dislocations. Considering that the exciton binding energy in ZnO is of the order of 20 meV,[21] the depths of the defect level related to the 3.100 and 3.345 eV emissions were roughly estimated to be 0.28 and 0.03 eV, respectively.

We now discuss the origin of the emission lines related to dislocations peaking at 3.100 and 3.345 eV. Specimens with dislocations introduced by indentation[3,4,6,22] or mechanical milling[12,23] at room temperature have been studied, and no dislocation-related lines have been observed. These results indicate that (1) the intensity of a near-band-edge emission line decreases[3,4,6,12] but measurably recovers by annealing above 873–1073 K,[3] (2) the intensity of the yellow emission line, that could be associated with Zn vacancies,[24] increases[3,12] but then decreases by annealing above 873–1073 K,[3,22] and (3) the emission line (peaking at 3.1208 eV) presumably due to pairs of Zn-vacancy acceptors and Zn-interstitial donors,[23] which were not observed in our specimens deformed at 923–1123 K, are induced.[12,23] (4) An emission line with a photon energy around 3 eV, similar to the dislocation-related line at 3.100 eV, is induced by annealing at 773–1073 K.[22] These results suggest that the dislocation-related lines arose via thermal migration of point defects at temperatures above 773–1073 K. Actually, transmission electron holography reveals that localized energy levels exist near dislocations, and that the origin of the levels are related to point defects in the vicinity of dislocations rather than to the dislocation cores.[9] The dislocation-related lines are not observed in specimens annealed after ion implantation,[24] indicating that they do not arise only by the introduction of point defects. Therefore, the origin of the dislocation-related lines was probably point-defect complexes involving dislocations.

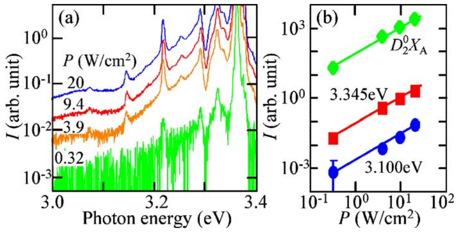

FIG. 4. (Color online) (a) PL spectra for a deformed specimen (at a temperature of 973 K) at several *P*'s. (b) *P*-dependent PL intensity of an emission line.

Finally, it is interesting to note that the introduction of dislocations at high temperatures (773–1073 K) did not influence the PL intensities of the emission lines except the dislocation-related lines. This characteristic of ZnO may be an advantage over GaN, since GaN does not exhibit such a phenomenon and all the PL intensities decrease with the introduction of dislocations.[25]

In conclusion, emission lines related to dislocations freshly introduced by plastic deformation of bulk ZnO at elevated temperatures were identified by PL spectroscopy. It is suggested that point defect complexes involving dislocations gave rise to these emission lines. This finding may help to elucidate the influence of dislocations and point defects on the electronic and optoelectronic properties of semiconductors.

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