

Temperature-dependent photoluminescence of ZnO layers grown on 6H-SiC substrates

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Temperature-dependent photoluminescence (PL) of ZnO layers grown on 6H-SiC substrates has been described. The PL spectra were dominated by free exciton (FX) emission throughout the whole temperature range, which reflects shallow nonradiative centers in high crystalline ZnO layers. The temperature-dependent exciton peak energy as well as intensity quenching due to overlapping of FX and D^0X (donor-bound exciton) bands has been addressed with an inclusion of donor-bound exciton-like defects. The D^0X linewidth of ~ 8 meV exhibited the thermal activation energy of ~ 16 meV, closely consistent with the exciton-defect binding energy. This particular bound-exciton peak suggests that it dissociates into a FX and a neutral-donor-bound-like defects pair complex with the increase of temperature. © 2004 American Institute of Physics. [DOI: 10.1063/1.1649451]

I. INTRODUCTION

Wide band-gap semiconductors are currently the subject of interest for investigations in response to the industrial demand for optoelectronics devices. Among the available wide band-gap materials, ZnO is promising which has a direct band-gap energy of 3.4 eV that can be adjusted in the range of 2.4–5.2 eV by alloying with CdO or MgO.^{1,2} The most exciting physical properties of ZnO are its large exciton-binding energy of ~ 60 meV,² which can be tuned up to ~ 120 meV by controlling the active ZnO layers in quantum structures.³ This large exciton-binding energy of ZnO layers indicates the potential for excitonic recombination at a temperature well above room temperature (RT).⁴ Toward these goals, a great deal of effort has been made on ZnO layers grown mostly on Al₂O₃ substrates. However, structural and optical characterizations indicated the presence of large residual strain, structural defects including mosaics, and donor-bound exciton emission (D^0X) with a high carrier concentration.⁵ These result from the large lattice mismatch (f_m) between the ZnO epilayer and Al₂O₃ substrate of $\sim 19\%$. It is noted that the lattice constants of ZnO along the a and c axes are 3.246 and 5.213 Å while those for the Al₂O₃ substrate are 4.758 and 12.99 Å, respectively.

Since the large f_m in a ZnO/Al₂O₃ heterostructure seems to be a limitation in optoelectronics, the use of an alternative substrate such as SiC may overcome these problems. Recently, there have been many reports on GaN layers including quantum dots grown on 6H-SiC substrates.⁶ The lattice constants of 6H-SiC substrate along the a and c axes are 3.08 and 15.117 Å, respectively. Considering the ZnO lattice constant, the f_m for the ZnO/6H-SiC heterostructure has been estimated to be $\sim 5\%$. This smaller f_m may explore ZnO epitaxy with superior crystalline and optical properties. Recently, we have reported the fundamental structural properties of epitaxial ZnO layers grown on 6H-SiC substrates by

metalorganic chemical-vapor deposition (MOCVD).⁷ In this article, it is shown that the ZnO crystalline quality grown on 6H-SiC substrate is superior than that grown on the Al₂O₃ substrate.⁸ It was found that a 6H-SiC substrate greatly improves the crystallinity of ZnO epilayers, which may be a result of smaller f_m that is less than $\frac{1}{4}$ of the Al₂O₃ substrate. From the view point of smaller f_m , the strain-dependent study is under the way and will be discussed elsewhere. From these samples, however, the dominant optical properties were discussed together with the higher ZnO crystallinity, but the details of optical properties of ZnO layers grown on the 6H-SiC substrates are yet not addressed.

In this article, temperature-dependent photoluminescence (PL) of ZnO layers grown on 6H-SiC(0001) substrates has been demonstrated. The temperature-dependent PL spectra showed the exciton peak energy as well as intensity quenching by overlapping the FX and D^0X bands with the increase of temperature. The physical mechanism of this quenching and/or overlapping has been attributed to the speculation of probable inclusion of phonons and/or defects in the optical bands. We also deduced the activation energies of FX and D^0X bands, consistent with exciton-defect binding energy.

II. EXPERIMENT

ZnO layers were grown directly on 6H-SiC(0001) substrates by MOCVD. The substrate cleaning and processing have been discussed in detail elsewhere.⁷ For the growth of ZnO layers, the flow rate of DEZn was controlled by adjusting the flow rate of carrier gas N₂. After the initial flow of DEZn, the substrate T_{sub} was heated to the growth temperature T_g . The flow of O₂ was started in the temperature range of $T_{\text{Zn}} \leq T_{\text{sub}} \leq T_g$. The substrate was then maintained at T_g for the successive growth of ZnO layers at 450 °C. In this study, the flow rate of DEZn was kept at 6.5 sccm, while the O₂ flow rate was 10 sccm. The grown ZnO layers were characterized by PL measurements.

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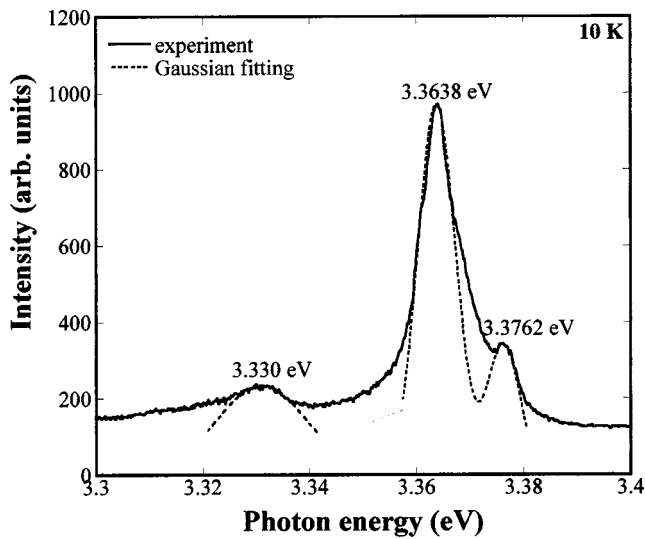


FIG. 1. PL spectrum of ZnO layer grown on 6H-SiC substrate. The PL measurement was performed at ~ 10 K under the He gas temperature. The dashed line shows the Gaussian fitting of the experimental data.

III. RESULTS AND DISCUSSION

To discuss the PL properties of ZnO layers grown on the 6H-SiC substrates, it would be useful to briefly review the crystalline properties. The x-ray measurements diffracted the *c*-axis oriented growth of the ZnO layer on the 6H-SiC substrate. The diffraction space mapping in the vicinity of symmetric SiC(0006) and ZnO(0002) diffraction peaks showed no tilting between the *ab* planes of SiC and ZnO. Considering the x-ray diffraction (XRD) θ - 2θ measurements, the full-width at half maximum (FWHM) was recorded as 0.05° , which is minimum yet for the MOCVD-grown ZnO layers on Al_2O_3 substrates⁸ but comparable to that of molecular-beam epitaxy (MBE)-grown ZnO layers.⁹ Therefore, we observed the best crystalline properties of ZnO layers grown at the substrate temperature of 450°C and considered for the temperature-dependent PL measurements.⁷

Figure 1 shows the PL spectra of ZnO layers with dominant 3.3762, 3.3638, and 3.330 eV peaks originated from FX,¹⁰ D^0X ,¹¹ and neutral acceptor-bound exciton (A^0X) bands,¹² respectively. To estimate the peak positions as well as FWHMs, the PL data were fitted using a Gaussian equation, which is in fairly good agreement with the experimental data to the extent that the width or area could be estimated and discussed separately for both the exciton bands. Therefore, we estimated the FWHMs of the FX, D^0X , and A^0X peaks, which correspond to 7.1, 8.3, and 16.6 meV, respectively. It is noted that these values are the lowest ever in the MOCVD-grown ZnO layers. It is also added that the deep-level emission was completely absent even at RT in the ZnO/6H-SiC heterostructures.⁷

To clarify the origins of these peaks, temperature-dependent PL measurements were performed in the range of 4–300 K and are plotted in Fig. 2(a). The assigned FX, D^0X , and A^0X bands were dominantly observed from the temperature range of 4–120 K. This series of PL spectra, however, illustrates that (i) the exciton emissions are shifted to the lower energy with the increase of temperature and (ii) as the

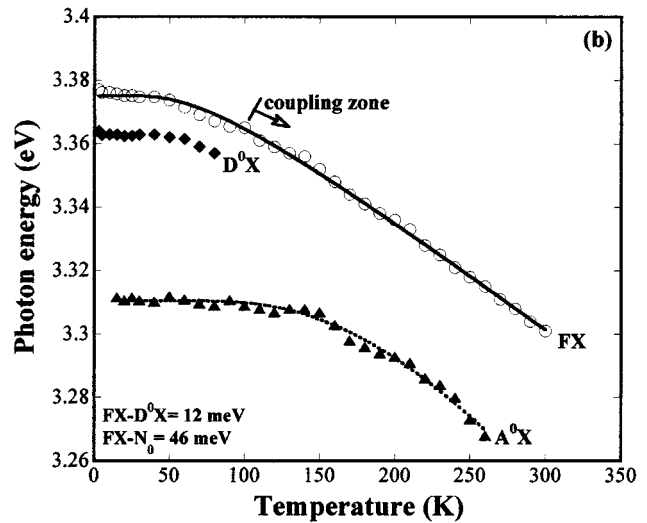
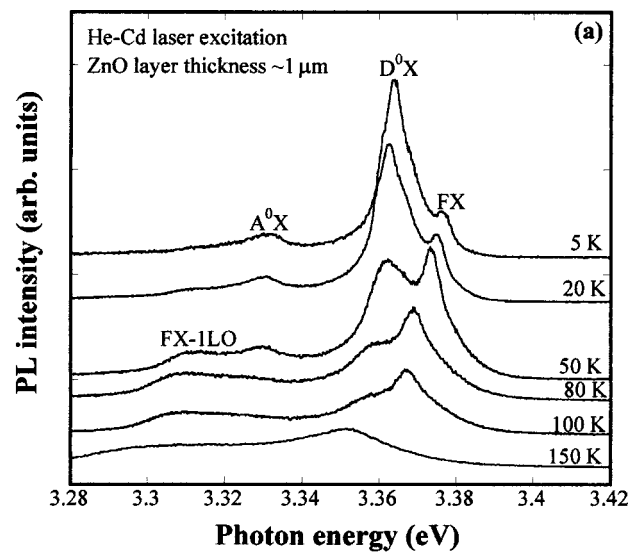


FIG. 2. (a) PL spectra with the dominant FX, D^0X , and A^0X peaks for the selected temperatures, and (b) photon energies are plotted against the temperature. The solid lines represent the fitting results based on the Eqs. (1).

temperature is increased, the FX and A^0X peak intensities become stronger compared to the D^0X peak. It carries out that the bound-exciton emissions appear to be thermally quenched at temperatures above approximately ~ 120 K, thereby the D^0X band is absent by superposing with the FX and prevented adequate identification of the D^0X position.

The variation of FX, D^0X , and A^0X peak energy positions as a function of temperature is plotted in Fig. 2(b). The figure shows that the excitons energies decrease gradually with the increase of temperature. From this result, the energy difference between the FX and D^0X as well as that between the FX and A^0X were estimated to be ~ 12 and ~ 45 meV, respectively. These values are in fairly good agreement with the reported values for the bulk ZnO.^{10–12} In addition, the D^0X band disappears at temperatures above ~ 120 K, and the FX band seems to squeeze after the D^0X peak disappears. Therefore, the convergence of the FX and D^0X bands, coupled with the line broadening of each of these peaks,

showed a coupling zone of excitons with an increase of temperature.

A shift in the exciton energy as a function of temperature results essentially from the optical band shift. It is noted that this phenomena is based on the assumption that the exciton binding energy is temperature independent since this drives from both the thermal expansion and exciton-phonon interaction. The corresponding temperature dependence from both the mechanisms is very similar, and all of the phonons, in principle, contribute to the band shift. This overall contribution to the band shift can be reproduced by the Einstein approximation using the effective phonon energy $\hbar\omega$, and in this case, the variation of exciton energy with the temperature is given by

$$E(T) = E(0) - \lambda / [\exp(\hbar\omega/k_B T) - 1], \quad (1)$$

where $E(0)$ is exciton energy at $T=0$ K, and λ is a proportional coefficient. The estimated value of $\hbar\omega$ (17.96 meV) is apparently higher than the maximum energy of a lower frequency group of ZnO bulk phonons of ~ 12 meV.¹⁴ This parameter fluctuation is not clear from this study but it is expected that the f_m may contribute to these results since ScAlMgO₄ substrate has been used for the ZnO layer in Ref. 14.

To clarify the luminescence properties of ZnO layers grown on 6H-SiC substrates, the PL peaks intensities of the FX and D^0X as a function of temperature are plotted in Fig. 3(a). The FX and D^0X peak intensities have a reverse role with the increase of temperature at ≤ 40 K. The FX peak intensity once increases from 4 to ~ 40 K and then gradually decreases, while the D^0X peak intensity decreases rapidly and disappears completely above ~ 120 K. However, the inclination of the FX and D^0X lines is completely independent, which acknowledges the contribution of the origin of different peaks. For FX emission, the peak intensity is quenched from 4 to 120 K with a ratio of ~ 1.6 , while for D^0X the ratio is ~ 10.2 . Therefore, the D^0X peak intensity decreases ~ 15 times faster than that of the FX. This indicates the higher quality of ZnO materials grown on the 6H-SiC substrates is possibly subject to the smaller f_m and lower residual carrier concentration.

To clear up this argument, the ratio of FX/ D^0X peak intensities is plotted in the inset of Fig. 3(a). It shows that the FX/ D^0X ratios increase with the increase of temperature. Viswanath *et al.*¹⁵ also observed an analog result and inferred that with the increase of temperature the D^0X dissociates into a FX and a neutral donor. Based on this approach, and the work of Reynolds *et al.*,¹⁶ we conclude that the thermal dissociation of the bound excitons results in the creation of FXs and a neutral-donor-like defect-pair complex.

Figure 3(b) shows the Arrhenius plot of integrated PL intensities of FX and D^0X peaks. The D^0X peak integrated intensity decreases independently with the increase of temperature. On the other hand, the FX peak integrated intensity becomes constant from 4 to ~ 70 K and is quenched gradually at temperatures above ~ 70 K. This overall temperature quenching behavior can be described by the equation

$$I_{\text{PL}} = I_0 / [1 + a \exp(-E_a/kT)], \quad (2)$$

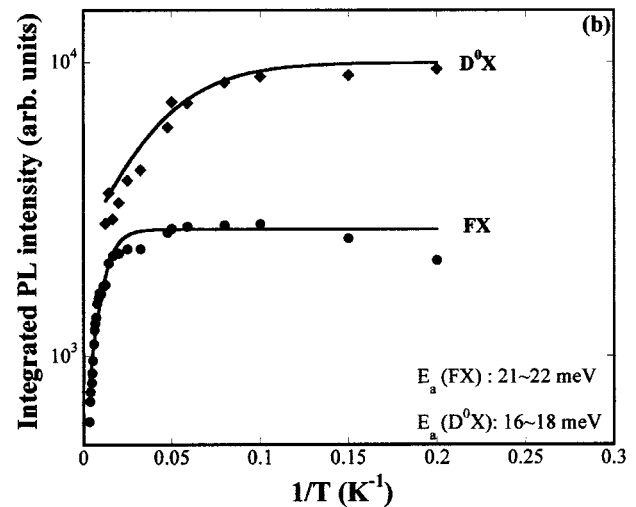
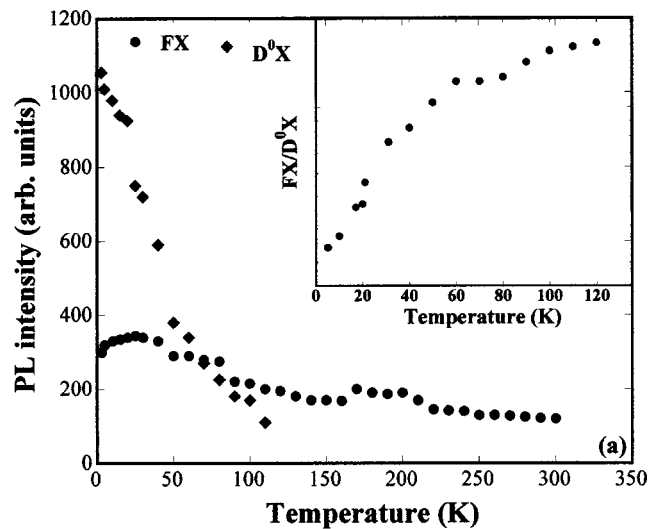


FIG. 3. (a) PL intensity of FX and D^0X as a function of temperature. The inset shows the FX/ D^0X intensity ratio as a function of temperature, and (b) integrated PL intensity of the FX and D^0X as a function of inverse temperature. The plotted data were fitted with solid lines using the Eqs. (2).

where E_a is the activation energy, k is a Boltzmann constant, and a is a proportional constant. E_a is ~ 22 and ~ 16 meV for the FX and D^0X , respectively. Therefore, the E_a of D^0X is in good agreement with the exciton-to-defect binding (localization) energy since it has been reported that the binding energy of the exciton to the defect-pair complexes ranges from 10 to 20 meV.¹⁰

The temperature-dependent PL properties of ZnO layers grown on 6H-SiC substrates suggested that the FX band was dominated even at RT while the D^0X was suppressed below ~ 70 K. This dominant FX emission is hardly seen in the MOCVD-grown ZnO/Al₂O₃ heterostructures.^{6,8-17} Therefore, these observations in the ZnO/6H-SiC heterostructures can be attributed into three ways: (i) smaller f_m of $\sim 5\%$; (ii) $+c$ polarity; and (iii) low impurity level.¹⁸ In particular, a clearcut hexagon morphology was observed in atomic force microscopy, indicating a $+c$ polarity in the ZnO epitaxy grown on the 6H-SiC substrate.¹⁸ It has been reported that GaN layers grown on 6H-SiC substrates always show a $+c$

polarity.¹⁹ In addition, the quenching and/or overlapping of the FX and D^0X bands as a function of temperature can be attributed to the trapping of excitons in optical bands by phonon involvement and thereby the sudden change in the integrated PL intensity at ~ 70 K.

IV. CONCLUSION

The dominant FX emission was observed even at RT, while the D^0X disappeared at temperatures above ~ 120 K. The temperature-dependent exciton peak energy, as well as intensity quenching, has been attributed to the overlapping of FX and D^0X bands by introducing the donor-bound-like exciton defects. The activation energy of D^0X was estimated to be ~ 16 meV, which is consistent with the exciton-to-defect binding energy. Further analysis on the D^0X suggested that a FX and a neutral-donor-like defect-pair complex occurs with the increase of temperature.

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