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The photoluminescence of ZnO thin films grown on Si (1 0 0) substrate by plasma-enhanced chemical vapor deposition

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Abstract

High-quality ZnO thin films have been grown on a Si(1 0 0) substrate by plasma-enhanced chemical vapor deposition (PECVD) using a zinc organic source ($Zn(C_2H_5)_2$) and carbon dioxide (CO_2) gas mixtures at a temperature of 180°C. A strong free exciton emission with a weak defect-band emission in the visible region is observed. The characteristics of photoluminescence (PL) of ZnO, as well as the exciton absorption peak in the absorption spectra, are closely related to the gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2. Full-widths at half-maximum of the free exciton emission as narrow as 93.4 meV have been achieved. Based on the temperature dependence of the PL spectra from 83 to 383 K, the exciton binding energy and the transition energy of free excitons at 0 K were estimated to be 59.4 meV and 3.36 eV, respectively.

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1. Introduction

ZnO is a semiconductor with many attractive features. The versatile physical properties, such as piezo-electrical, ferro-electrical, electro-optical, acousto-optical and luminescence characteristics, rendered many potential applications of ZnO. ZnO has exerted a strong fascination upon several scientists and has grown in interests, especially since R.F. Service reported its potential application as an UV laser diode [1]. Recently, optically pumped stimulated emission and lasing of ZnO have been demonstrated, even at room temperature [2–4].

Most research on the photoluminescence (PL) of ZnO thin films has investigated samples that were grown on Al_2O_3, $ScAlMgO_4$ or $MgAl_2O_4$ substrates [2–8]. In order to combine the optoelectronic properties with large-scale integration technology, it is necessary to investigate the growth of ZnO thin films on Si substrates. Recently, some researchers have prepared ZnO thin films on Si substrates by MBE [9]. However, to the limits of

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our knowledge, there are still no reports on ZnO thin films prepared on Si substrates by plasma-enhanced chemical vapor deposition (PECVD), which report good luminescence properties. In this paper ZnO thin films were prepared by employing PECVD using a zinc organic source ($Zn(C_2H_5)_2$) and carbon dioxide (CO_2) gas mixtures at a temperature of 180°C. The absorption spectra and the temperature-dependent PL were studied on a set of ZnO thin films with different gas flow rate ratios of $Zn(C_2H_5)_2$ to CO_2 (GFRRZC).

2. Experimental procedure

ZnO thin films were grown by PECVD from the gas mixture of diethylzinc and carbon dioxide. The PECVD system and the experimental procedure have been discussed in detail previously [10]. A set of samples with different GFRRZCs was prepared to study the PL properties. The detailed growth conditions are listed in Table 1.

The quality of the crystalline ZnO thin films was examined by X-ray diffraction using a rotating anode X-ray diffractometer with Cu K_α radiation of 1.54 Å. The optical absorption spectra were measured at room temperature by an UV-360 Recording Spectrophotometer (Shimadzu). A deuterium lamp was used as the light source with the wavelength range of 200–460 nm. The signals were detected by an R_{456}-type photoelectric multiplier with a high resolution of 0.1 nm. The normal PL and the temperature dependent PL spectra were obtained using the 325 nm line of a continuous He–Cd laser operating at 30 mW and a PL microprobe measurement system (J–Y company, French). Measurements of the temperature-dependent PL spectra in the range of 83–383 K were taken by placing the samples in a cryogenic unit cooled by liquid nitrogen.

Table 1
The deposition conditions of the ZnO thin films

Sample	GFRRZC	(RF) Power (W)	Temperature of the substrate (°C)	Gas flow rate of Argon (sccm)
a	1:0.5	35	180	4
b	1:1	35	180	4
c	1:2	35	180	4
d	1:3	35	180	4
e	1:4	35	180	4

3. Results and discussion

Fig. 1(a)–(e) show the X-ray diffraction spectra of the ZnO thin films prepared by PECVD with different GFRRZCs. The quality of the ZnO thin films was closely related to the GFRRZCs. As the gas flow rate of CO_2 was increased, the diffraction intensity of the (0 0 2) ZnO peak grew dramatically and began to dominate the XRD spectra. Finally, a preferred (0 0 2) orientated ZnO thin film was obtained at the GFRRZC value of 1:3. Furthermore, with increasing CO_2, the full-width at half-maximum (FWHM) of the (0 0 2) ZnO peak at 34.42° became smaller and smaller except for sample e. FWHMs of sample b, c, d and e were 0.36°, 0.26°, 0.20° and 0.35°, respectively. From our experiments, it was found that the optimized GFRRZC was 1:3. Our interpretation is that different roles are played by oxygen based on its concentration in the gas. When oxygen ions are deficient, an increase of CO_2 gives zinc ions more chances to react with oxygen ions to form an ordered ZnO thin film. If CO_2 is excessively supplied, i.e. the GFRRZC was 1:4, excess oxygen ions form oxygen gas within the film, resulting in more microvoids and defects, which prevents the formation of large size ZnO.

Fig. 2 shows the absorption spectra (the dash curve) and the PL spectra (the solid curve) measured at room temperature. Because ZnO has a large exciton binding energy of 60 meV, an obvious exciton effect will always appear in the absorption spectra of high-quality ZnO films [11]. As the ZnO thin film quality improves, a pronounced exciton absorption peak located at 3.4 eV was observed. For the PL spectra, the main emission properties were closely dependent on the GFRRZCs, and the UV band emission dominates with a very weak deep-level defect emission. The UV band was assigned to be the free exciton

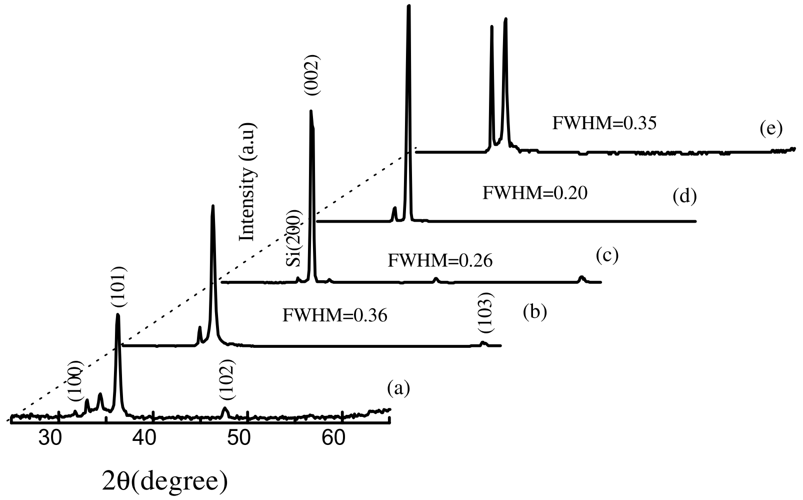

Fig. 1. X-ray diffraction patterns of the ZnO thin films grown on Si(1 0 0) substrates with different GFRRZCs: (a) 1:0.5; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:4.

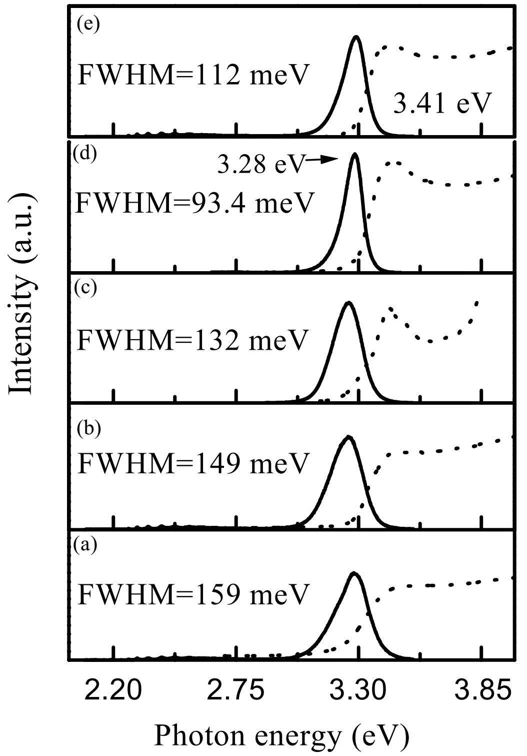

Fig. 2. The right traces show the absorption spectra (dotted curve), and the left traces show the PL spectra of ZnO thin films prepared at low temperature of 180°C with different GFRRZCs: (a) 1:0.5; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:4.

recombination [12,13], which was confirmed by the temperature-dependent PL spectra discussed below. As shown in Fig. 2, there was about 120 meV of Stokes shift between the PL spectra and the absorption spectra. In general, many effects such as electron–phonon coupling, lattice distortions, interface defects and point defects may cause a red shift of the emission line from the absorption edge. The FWHMs of the PL spectra became more narrow with the decrease of the GFRRZC from 4 to 0.25, which are 159, 149, 132, 93.4 and 112 meV, respectively. When the quality of ZnO thin films was relatively poor, the grain size of ZnO has a larger distribution, leading to a broader PL band. When the quality of the thin films improved, the grain size of ZnO became larger and more homogeneous, resulting in a narrower FWHM. It was remarkable that the deep-level emission band around 2.5 eV was very weak, even if the CO_2 was deficient. In general, a lot of oxygen vacancies will be produced at a deficient CO_2 gas mixture. However, a very weak deep-level emission is correlated with a low deep-level defect density. This can be explained by the fact that lots of oxygen vacancies were terminated by the excited hydrogen [14]. However, there were always defects to bound the free excitons in the films. As a result, a low-energy tail from the bound excitons in the

PL spectra was observed, as shown in Fig. 2. For better ZnO thin film quality, less density of defects states were present, indicting a relatively low density of the bound exciton states. Thus, with improvements in the quality of the ZnO thin film, the low-energy tail decreased and the symmetry of the shape of the UV band was enhanced.

To confirm that the UV band was due to the transitions of free excitons, temperature-dependent PL spectra were measured for sample e in the temperature range of 80–383 K, as shown in Fig. 3(a). It was noticed that there was only one UV PL band without any luminescence related to the deep-level defects, even at high temperature. The PL was slowly quenched with increasing temperature, and the PL intensity nearly exponentially decreased due to the thermal ionization of excitons and thermally activated nonradiative recombination mechanisms. The dependence of the integrated PL intensity of the UV band on temperature is shown in Fig. 3(b). The temperature dependence of the integrated PL intensity can be expressed by the equation [15,16]

$$I(T) = \frac{I_0}{1 + A * \exp(-\Delta E/k_B T)}, \quad (1)$$

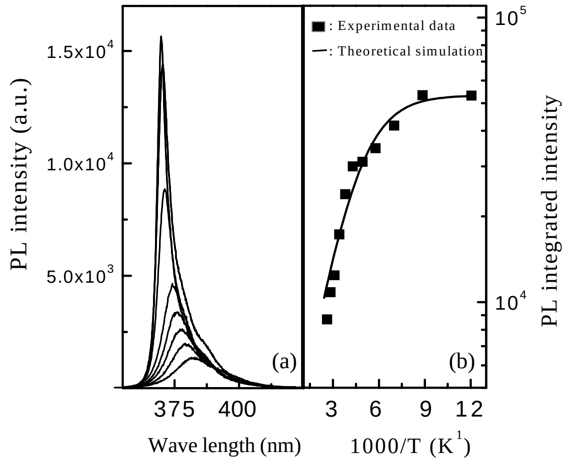

Fig. 3. Left: the dependence of PL spectra on temperature (a). Right: the integrated PL intensity dependence on temperature (b). The square data points are experimental points, and the solid curve is a fit to the equation $I(T) = I_0(1 + A^* \exp(-\Delta E/k_B T))$.

where ΔE is the activation energy of the thermal quenching process, k_B is the Boltzman constant, I_0 is the emission intensity at 0 K, T is the thermodynamic temperature, and A is a constant. By fitting our experimental data using Eq. (1), as shown in Fig. 3(b) by the solid line, ΔE is estimated to be 59.4 meV. This value is in excellent agreement with the exciton binding energy of 60 meV in bulk ZnO. We thus believe that the UV band was from free exciton recombination.

The excitonic origin of the UV emission was also clearly present in the dependence of the transition energy on the temperature, as shown in Fig. 4. With increasing temperature, the peak energy had a red shift. It is well known that for the temperature-dependent dilatation of the lattice and a temperature-dependent electron-lattice interaction, the variation in the energy gap with temperature is expected due to a shift in the relative position of the conduction and valence bands. The experimental data were estimated by the theoretical equation, $E_g = E_0 - \alpha T^2/(T + \beta)$ [17]. The transition energy of free exciton at 0 K was found to be 3.36 eV. The fit to the exciton

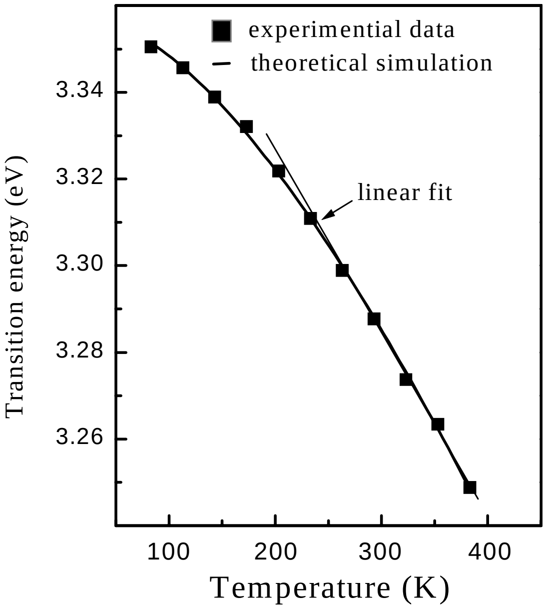

Fig. 4. Temperature dependence of the peak energy positions. The square data points are experimental points, and the solid curve is a fit to equation $E_g = E_0 - \alpha T^2/(T + \beta)$.

emission peak energy is almost linear at high temperature (293–383 K) with a slope of 0.33 meV K^{-1}, which is consistent with D.M. Bagnall's result [12].

4. Conclusion

ZnO thin films on Si(1 0 0) substrates were prepared by PECVD from gas mixtures of diethylzinc and carbon dioxide at low temperature (180°C). Pronounced exciton effects were observed in the absorption spectra as the ZnO thin film quality improved. The characteristics of the luminescence of ZnO were found to be closely related to the sample preparation parameters. At an optimized condition, that is a GFRRZC value of 1:3, a strong free exciton emission with FWHM of the PL band reaching 93.4 meV was obtained. The UV band coming from the free exciton emission, as well as the free excitonic transition energy, was studied by measurements of the temperature-dependent PL spectra. The exciton binding energy and the transition energy (0 K) were estimated to be 59.4 meV and 3.36 eV, respectively.

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