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High quality ZnO thin films grown by plasma enhanced chemical vapor deposition

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High quality ZnO thin films have been grown on a Si(100) substrate by plasma enhanced chemical vapor deposition using a zinc organic source [$Zn(C_2H_5)_2$] and carbon dioxide (CO_2) gas mixtures at the low temperature of 180 °C. The dependence of ZnO thin film quality on the gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 (GFRRZC) is studied by using x-ray diffraction (XRD), optical absorption (OA) spectra, and cathodoluminescence (CL) spectra. High quality ZnO thin films with a *c*-axis-oriented wurtzite structure are obtained when the GFRRZC is 0.33. XRD shows that the full width at half maximum of (0002) ZnO located at 34.42° is about 0.2°. At room temperature, a pronounced free exciton absorption peak around 365 nm is clearly observed. Also, a strong free exciton emission without deep level defect emission is observed around 385 nm, and its temperature dependence is studied from the photoluminescence spectra. These observations indicate the formation of a high quality ZnO film. Additionally, nitridation of the Si surface caused by releasing NH_3 plasma into the deposition chamber is an effective way to improve film quality. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1415545]

I. INTRODUCTION

Recently much attention has been paid to short wavelength lasers for use in high density information storage.[1–3] It is widely accepted that ZnO is one of the most promising materials for producing an ultraviolet laser at room temperature due to its wide direct band gap (E_g = 3.3 eV) and large excitonic binding energy of 60 meV. To obtain high quality ZnO thin films a variety of techniques may be used such as molecular beam epitaxy (MBE),[4,5] metalorganic chemical vapor deposition (MOCVD),[6] magnetron sputtering,[7,8] pulsed laser deposition,[9,10] and so on. In the present article plasma enhanced chemical vapor deposition (PECVD) is employed to prepare ZnO thin film using a zinc organic source [$Zn(C_2H_5)_2$] and carbon dioxide (CO_2) gas mixtures.

PECVD has several advantages in preparing ZnO thin films. The thin film quality can be improved by a film densification process induced by plasma bombardment and ultraviolet ray irradiation. Furthermore, the low energy plasma can enhance the interface reaction. Unlike MOCVD, reactants used in PECVD are decomposed by the plasma, not by thermal energy. Thus the growth does not need a high temperature environment, which will reduce the strain induced by the different thermal expansion coefficients of the growth layer and the substrate. Additionally, before growing the thin films, the substrate can be cleaned by using plasma to remove the native oxide layer of Si, which is crucial to grow high quality thin films.

There is much interest in obtaining materials on a Si substrate in order to obtain optoelectronic integration. However, there are few papers dealing with the growth of ZnO thin films on a Si substrate,[11–13] and in particular, the growth of ZnO thin film on a Si substrate by PECVD. In this article the dependence of ZnO thin film quality on the gas flow rate ratio of $Zn(C_2H_5)_2$ to CO_2 (GFRRZC) is studied by x-ray diffraction (XRD), optical absorption (OA) spectra, cathodoluminescence (CL) spectra, and the temperature dependence of photoluminescence (PL) spectra. The mechanism of nitridiation of the Si surface by the NH_3 plasma is discussed.

II. EXPERIMENTAL PROCEDURE

ZnO thin films are grown by PECVD from the gas mixture of diethylzinc and carbon dioxide. The gas flow rate is controlled by different gas flow meters. Due to its low vapor pressure, the gas flow rate of diethylzinc is controlled by adjusting the gas flow rate of hydrogen. Since CO_2 is an intergas at room temperature, reactants can be blended adequately before entering into the plasma chamber. The Si substrates are chemically treated by a standard RCA process[14] before being loaded into the growth chamber which has a background pressure of less than 4×10^{-4} Pa. After the argon and hydrogen are let into the chamber, the Si substrate is heated to 180 °C which is monitored by a cuprum-constantan thermocouple. Then the rf source is loaded into the chamber. The argon and hydrogen plasmas induced from the rf occur in the chamber to remove the oxide layers for 15 min. Then ammonia gas is introduced into the plasma chamber to nitride the Si surface for 15 min. The diethylzinc source is packaged in a steel cylinder cool well and is kept refrigerated at 6 °C by a CW-1 type fine controlled temperature semiconductor device.

Generally the gas flow rate ratio has an obvious influence on the thin film quality. In our experiment the quality of the ZnO thin films depends strongly on the GFRRZC. To stress this problem and optimize the experimental param-

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TABLE I. The deposition conditions of ZnO thin films.

Sample	GFRR of $Zn(C_2H_5)_2$ to CO_2	(rf) power (W)	Temperature of the substrate (°C)	Gas flow rate of Argon (sccm)
a	1:0	35	180	4
b	1:0.5	35	180	4
c	1:1	35	180	4
d	1:2	35	180	4
e	1:3	35	180	4
f	1:4	35	180	4

eters, a set of samples with different GFRRZC are prepared. The working pressures vary from 80 to 100 Pa. The detailed growth conditions are listed in Table I.

The crystalline quality of the ZnO layers is examined by x-ray diffraction using a rotating anode x-ray diffractometer with Cu $K\alpha_1$ radiation of 1.54 Å. The OA spectra are measured by a UV-360 recording spectrophotometer (Shimadzu) at room temperature. CL spectra are measured under the 10 kV accelerated voltage with 6 μA electronic current. The temperature dependent PL spectra are obtained using the 325 nm line of a He–Cd laser and a PL microprobe measurement system (J-Y company, France). Measurements below room temperature were taken by placing the sample cells in a cryogenic unit. The temperature range was 83 to 383 K. The nitridation of the Si surface is studied by XRD and CL spectra.

III. RESULTS AND DISCUSSION

A. The dependence of ZnO thin film quality on the GFRRZC

Figures 1(a)–1(f) show the x-ray diffraction spectra of the ZnO thin films prepared by PECVD with different GFRRZCs. With no CO_2, Fig. 1(a), there is a Zn(0002) peak and a very weak ZnO (1000) peak, which is from the surface oxide layers of the Zn thin film. As the gas flow rate of CO_2 is increased, the intensity of the (0002) zinc peak significantly decreases, while the intensity of the ZnO peaks increases, as shown in Fig. 1(b). With a further increase of CO_2, the diffraction intensity of the (0002) ZnO peak grows dramatically and dominates the XRD spectra. Finally a preferred (0002) oriented ZnO thin film is obtained. Additionally, with increasing CO_2, the full width at half maximum (FWHM) of (0002) ZnO at 34.42° becomes smaller and smaller except for sample f. FWHMs of samples c, d, e, and f are 0.36°, 0.26°, 0.20°, and 0.35°, respectively. The Scherrer formula[15] is

$$d = 0.94\lambda/B \cos\theta,$$

where d, λ, θ, and B are the mean grain size, the x-ray wavelength of 1.54 Å, Bragg diffraction angle, and the linewidth at half maximum of the peak around 34.42°, respectively. According to this formula, the mean grain sizes of sample c, d, e, and f are 24, 33, 43, and 25 nm, respectively. If the CO_2 gas flow rate is increased further, the ZnO thin film quality will decline. From the above results we find that the optimized GFRRZC is 1:3. When oxygen ions are deficient, an increase of CO_2 will give 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 is 1:4, excess oxygen ions will form oxygen gas within the film, resulting in many microvoids and defects, which will prevent large size ZnO grain formation.

Figure 2 show the OA spectra for samples b–e at room temperature. The absorption peak of the free exciton is clearly visable near the absorption edge as the GFRRZC decreases, i.e., CO_2 gas flow rate increases.[16] This is because ZnO has a large exciton binding energy of 60 meV at room temperature. Thus the OA spectra of ZnO films display an
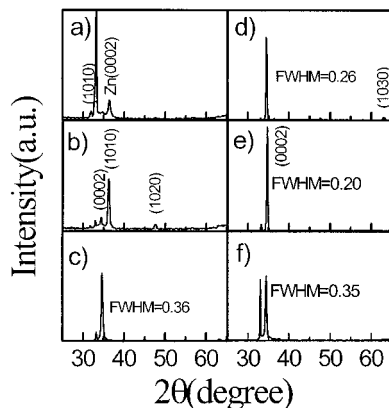

FIG. 1. X-ray diffraction patterns of the ZnO thin films grown on Si(100) substrates treated by NH_3 plasma under a different gas flow rate ratio of Zn $(C_2H_5)_2$ to CO_2 (GFRRZCs): (a) 1:0, (b) 1:0.5, (c) 1:1, (d) 1:2, (e) 1:3, and (f) 1:4.
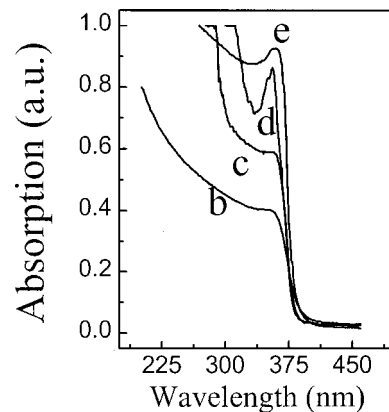

FIG. 2. The absorption coefficient of ZnO thin films grown under different GFRRZCs. (a) 1:0.5, (b) 1:1, (c) 1:2, and (d) 1:3.
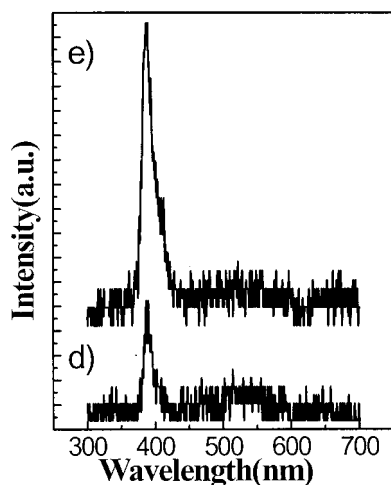
FIG. 3. CL spectra of ZnO thin films grown at different GFRRZCs: (a) 1:2 and (b) 1:3.
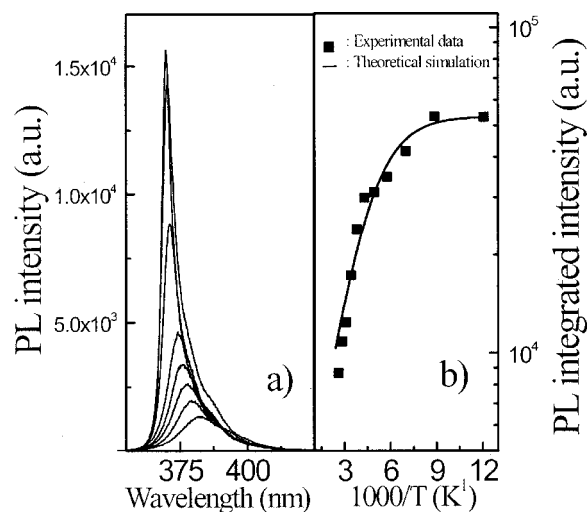

FIG. 4. Left: The dependence of PL spectra on temperature (a). Right: the integrated PL intensity dependence on the temperature (b). The square data points are experimental points simulated by the theoretical formula, equation $I(T) = I_0/[1 + A * \exp(-\Delta E/k_B T)]$.

exciton effect. In general, the exciton effect is closely correlated with film quality. Figure 2 suggests that high quality ZnO films have been prepared when the GFRRZC decreases from 2 to 0.33. When the CO_2 flow rate is lower, the ZnO films are of poor quality, which is verified by the XRD spectra, shown in Fig. 1. With an increasing CO_2 flow rate, the quality of the thin films improves. As a result, an exciton effect is observed in the OA spectra.

CL spectra were measured by a CL spectrometer with an anode acceleration voltage of 10 kV and an electron beam current of 6 μA. Only the luminescence of samples d and e can be observed and they are shown in Fig. 3. Sample d has a strong UV band emission at about 385 nm with a weak deep level emission around 520 nm related to oxygen vacancies.[17] As the CO_2 is increased, for sample e, the UV band emission is several times stronger at the expense of the green emission. The CL spectra are consistent with the ZnO thin film quality characterized by XRD. The improved crystal quality and orientation of ZnO films, namely reduced defects, will enhance the free-exciton transitions.

To confirm that the UV band is due to transitions of free-excitons, temperature dependent PL spectra are measured for sample e in the temperature range of 80–383 K, as shown in Fig. 4(a). It is remarkable that there is only one UV PL band without any luminescence related to deep level defects, even at high temperature. The PL is quenched by temperature. The PL intensity exponentially decreases with increasing temperature due to the thermal ionization of exciton and thermally activated nonradiative recombination mechanisms. The dependence of integrated PL intensity of the UV band on temperature is given in Fig. 4(b). The temperature dependence of the PL intensity can be expressed by the equation[18,19]

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

where ΔE is the activation energy of the thermal quenching process, k_B is Boltzmann constant, I_0 is the emission inten-

sity at 0 K, T is the thermodynamic temperature, and A is a constant. When fitting this theoretical formula to fit our experimental data, as shown Fig. 4(b), we find ΔE is 59.4 meV. This value is in agreement with the exciton binding energy of 60 meV in a bulk ZnO crystal. Thus we can conclude that the UV band is from free exciton recombination.

B. The effect of nitridation of the Si surface on the film quality

During the experiment we found it was necessary to clean the Si surface with argon and hydrogen plasmas, followed by the NH_3 plasma. In order to investigate the effect of nitridation of the Si surface by NH_3 plasma on thin film quality, epitaxial ZnO thin films were grown on Si(100) with (sample a) and without (sample b) nitrogen-passivated Si(100) substrates under the optimized GFRRZC of 1:3. Figure 5 shows the differences in XRD between sample a and b.
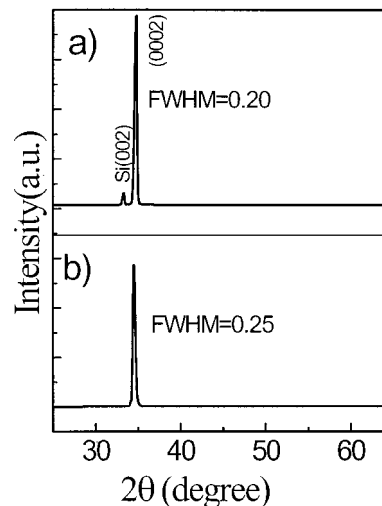

FIG. 5. X-ray diffraction patterns of ZnO thin films with and without treatment by NH_3 plasma under the optimal GFRRZC of 1:3.
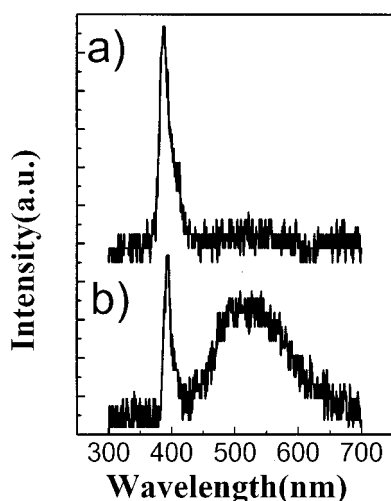
FIG. 6. CL spectra of ZnO thin films grown on a Si(100) substrate with and without treatment by NH_3 plasma.
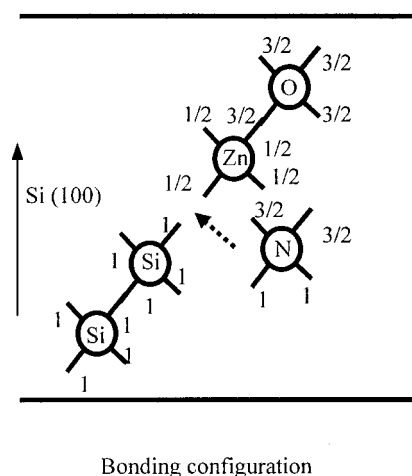

Bonding configuration

FIG. 7. Bonding configuration of the ZnO/Si(100) interface. The numbers represent the number of electrons contributed to each bond. An interface with the sequence Si–Si–Zn–O will have interface bonds with a total of 3/2 electrons, whereas the insertion of an N monolayer will leave all bonds with two electrons.

The FWHM of the (0002) ZnO XRD peak located at 34.42° is 0.2° for the Si surface treated with NH_3 plasma, as shown in Fig. 5(a), however, the FWHM is 0.25° for the Si surface untreated by nitridation, as shown in Fig. 5(b). The mean grain sizes of the films are 43 and 35 nm, respectively. The crystal quality of thin film is improved by treating the Si substrate with NH_3 plasma. To study the effect of nitridation on luminescence, the CL spectra are measured for the two samples with a 10 kV acceleration voltage and 6 μA electronic current, as shown in Fig. 6. There is a stronger excitonic emission with a weak emission around 520 nm related to deep-level defects for the Si substrate treated by nitridation, as shown in Fig. 6(a). However, there is a much stronger deep level emission around 520 nm with a weak excitonic emission for the substrate untreated by NH_3 plasma, as shown in Fig. 6(b). This means that the Si substrate treated with NH_3 plasma has less oxygen vacancies,[17] resulting in the improvement of thin film quality.

The larger lattice mismatch of ZnO and Si makes the epitaxial growth much more sensitive to the surface condition of Si. It is crucial to remove the oxide layer on the Si surface for the growth of high quality ZnO thin films. The argon and hydrogen plasmas can remove the native oxide layer of the Si surface. However, the hydrogen-terminated surface is not stable, and the hydrogen-desorbed surface is easily oxided by the residual oxygen. Yamauchi[20] employed arsenic vapor in plasma to stop oxidization on the Si surface. Because the As–Si bond is much stronger than the H–Si bond, the arsenic surface layer can protect the Si surface from oxidation.[20] In our experiment ammonia gas is introduced into the chamber and discharged for 15 min. Nitridation of the Si surface by the plasma of NH_3 is carried out. This can stop the Si surface from being oxided by residual oxygen because the N–Si bond is stronger than the As–Si bond. Finally, the Si surface is passivated by nitrogen atoms without oxygen. This passivated surface is useful for the growth of high quality ZnO thin films.

An imbalance in the interface charge is one of the serious problems associated with the growth of a polar semiconductor on a nonpolar one. The chemistry at the interface plays an important role at the initial stage of growth. Reactions between the layer species and the substrate atoms can form compounds at the interface. Previous results for both ZnSe/Si(001) and ZnS/Si(001) have found evidence that the presence of an As monolayer at interface leads to a better quality overlayer.[21] Nitrogen atoms have the same number of valence electrons as As atoms. Thus a similar effect can be expected for a Si(100):N interface. The effect of a N monolayer at the interface can be understood in terms of the electron counting argument:[21] In bulk ZnO, each Zn (O) atom contributes 1/2 (3/2) electrons to each of the four bonds surrounding it, and in bulk Si each atom contributed exactly one electron per bond. At a (100) interface between the Si and Zn plane of ZnO, therefore, each interface bond will receive a total of 3/2 electrons instead of the two electrons required, as shown in Fig. 7. A reaction between the Si atom and Zn atom forms a ZnSi compound. The balance in the interface charge is broken. The abrupt interface is energetically unfavorable. It will cause many defects when the ZnO thin films are growing. If, however, there is a N monolayer between the Zn layer and the Si in the sequence Si–N–Zn–O, the N layer has five electrons per atom and can contribute one electron to each of the two Si atoms below it and 3/2 electrons to each of the two Zn atoms above it. Now all the bonds have two electrons. Thus the oxygen vacancy declines. The balance of charge at the interface is helpful for growing high quality ZnO thin films.

IV. CONCLUSIONS

ZnO thin films on a Si(100) substrate are prepared by PECVD from the gas mixtures of diethylzinc and carbon dioxide at low temperature (180 °C). The optimized GFRRZC is 1:3 deduced from the XRD, OA spectra, and CL spectra. The UV band comes from the free exciton emission, tested by the temperature dependent PL spectra. Nitridation of the Si surface is an important stage for the growth of ZnO

thin films. It can protect Si from oxygen and keep the balance of charge at the interface. The quality of ZnO thin films is improved with nitridation of the Si surface. The results indicate that high quality ZnO thin films can be obtained by the PECVD technique assisted by a surface nitridation process.

ACKNOWLEDGMENTS

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