Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition

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ZnO thin films were epitaxially grown on *c*-sapphire substrates by pulsed laser deposition at substrate temperatures of 500–800 °C. The crystal structure of ZnO films follow the epitaxial relationship of $(0001)_{ZnO} \| (0001)_{Al_2O_3} (10\bar{1}0)_{ZnO} \| (11\bar{2}0)_{Al_2O_3}$. Both room temperature and cryogenic temperature photoluminescence showed a remarkable band-edge transition, and clear excitonic structures could be seen at cryogenic temperature. The optical refractive index was measured in the range of 375–900 nm by varying angle spectroscopic ellipsometry. The simulation was carried out using a Sellmeier equation. © *1999 American Institute of Physics.*
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I. INTRODUCTION

Zinc oxide (ZnO) is a wide-band-gap semiconductor (3.3 eV). Like indium oxide and tin oxide, ZnO is both transparent in the visible region and electrically conductive with appropriate dopants such as aluminum. This unique property has been widely studied for its practical applications such as transparent conducting electrodes for flat panel displays, and solar cells.[1] Zinc oxide is also a piezoelectric material which has a reasonably large piezoelectric coefficient. Acousto-electrical devices, such as surface acoustic wave devices (SAW) have been fabricated with ZnO.[2] Due to its unique conducting mechanism based on oxygen vacancies, zinc oxide is also used in oxygen gas sensors.[3]

Very recently, because of the rapid growth of gallium nitride (GaN) based blue, green light emitting diodes (LED) and laser diodes (LD),[4,5] zinc oxide has received particular attention as a promising substrate material due to its isomorphic structure and near perfect lattice match to GaN, especially in its thin film form.[6,7] Since bulk ZnO is quite expensive and unavailable in large wafers for the time being, ZnO thin film, especially on sapphire, is a relatively good choice due to (1) it can heteroepitaxially grow on sapphire and Si(111) at low substrate temperatures,[8,9] (2) it is isomorphic to GaN (the lattice mismatch between GaN and ZnO is just 2.2%, even their band edge and deep-center photoluminescence show great similarities[10]), (3) it is transparent in the visible region and electrically conductive. Because ZnO is such a potential substrate of GaN growth, it is quite important to study the optical properties of ZnO on sapphire in order to design GaN LED and LD that perform well.

More recently, room temperature ultraviolet (UV) lasing from ZnO films grown on sapphire has been demonstrated by two research groups.[11,12] This makes it possible to fabricate ZnO-based UV light emitting devices. An understanding of the optical properties of ZnO on sapphire is also needed in this case to obtain the best performance.

Fabricating crystal quality ZnO on sapphire, and analysis of its optical properties, will be important for the aforementioned applications. In this article, ZnO thin films grown epitaxially on sapphire by pulsed laser deposition (PLD) at relatively low temperatures are reported. Photoluminescence (PL) measurement and variable angle spectroscopic ellipsometry (VASE) were employed to study the optical properties of PLD grown ZnO on sapphire. In fact, high quality heteroepitaxially ZnO has been grown on sapphire by PLD.[8]

II. EXPERIMENT

The 99.99% pure ZnO target used in our experiment was a commercial 1 in. diameter hot pressed and sintered disk. An ArF excimer laser (Lambda Physik) operating at 193 nm was used to ablate the ZnO target. Throughout the experiment, the excimer laser was set at a pulse energy of 150 mJ and a repetition rate of 10 Hz. The laser was focused on the target with an area of $1 \times 2.5\ mm^2$, producing an energy density of $6\ J/cm^2$. The deposition was conducted as follows: the pulsed laser deposition chamber was first turbopumped to a base pressure of 10^{-7} Torr, then oxygen gas was backfilled into the chamber through a mass flow controller. The chamber was kept at a constant pressure of 10 mTorr during the deposition. The distance between the target and the substrate was kept at 5 cm. The substrate temperatures used in our experiment ranged from 200 to 800 °C.

The crystallinity of the as-grown ZnO films was characterized by high-resolution x-ray diffraction (HRXRD) for both rocking curve measurement and in plane ϕ scan using copper $K\alpha$ radiation. Photoluminescence and VASE were both carried out to characterize the optical properties of the as-grown ZnO. The photoluminescence was excited by a

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TABLE I. Film thickness and crystal quality of epitaxially grown ZnO film on sapphire by pulsed laser deposition at various substrate temperatures. An ArF excimer laser operating at 193 nm with a pulse energy of 150 mJ and a repetition rate of 10 Hz was used for all the depositions.

Growth temperature	Film thickness	FWHM of x-ray rocking curve of ZnO (0002) peak
500 °C	650 nm	0.48°
600 °C	640 nm	0.25°
700 °C	600 nm	0.18°
800 °C	420 nm	0.18°

He–Cd laser operating at 325 nm and captured by a charge coupled device (CCD) camera through a monochromator. Low temperature photoluminescence was performed in a small chamber that can be cooled down to 10 K. The VASE was carried out by a variable angle spectroscopic ellipsometer from J. A. Woollam Co., ψ and Δ were obtained over the wavelength range of 350–900 nm. The refractive index and the film thickness were fitted by a Sellmeier relationship.

III. CRYSTAL STRUCTURES

In the present study, we found that the critical parameter determining the crystal quality of ZnO is the substrate temperature. The substrate temperature is crucial in that too low substrate temperature results in a low surface migration of adatoms, while too high substrate temperature causes the adatoms to re-evaporate from the film surface. Various temperatures ranging from 200 to 800 °C were used for growing ZnO film on sapphire (0001). The epitaxial growth of ZnO film begins from as low as 500 °C. ZnO is an interesting material in that even with low substrate heating (200 °C in this experiment), Zn and O atoms follow vertical packing, resulting in a single *c*-axis orientation. The best crystalline quality film was obtained at a substrate temperature of 700 °C and an oxygen pressure of 10 mTorr. Compared to the optimum condition (10^{-5}–10^{-4} Torr oxygen pressure) employed by Vispute *et al.*,[8] our 10 mTorr oxygen pressure is relatively higher. This may be due to the pressure-distance PD scaling law[13] in PLD. In PLD, a higher ambient gas pressure must accompany a shorter target-substrate distance in order to obtain the film with optimum quality. Although the target-substrate distance has not been mentioned in Ref. 8, we believe their target-substrate distance is longer than ours (5 cm). The difference in laser parameters (laser wavelength, laser fluence) may also be responsible for the

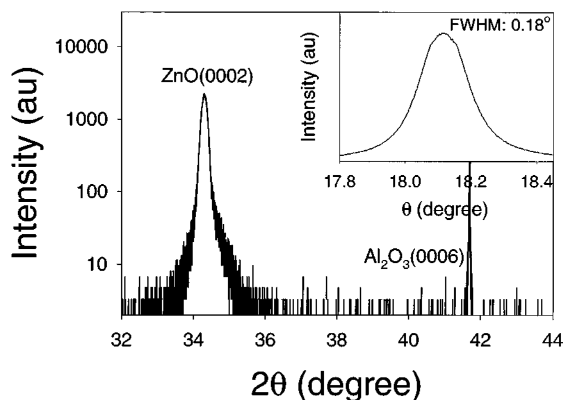

FIG. 1. XRD 2θ scan of ZnO grown on (0001) sapphire at a growth temperature of 700 °C. The inset shows the x-ray rocking curve of the film.

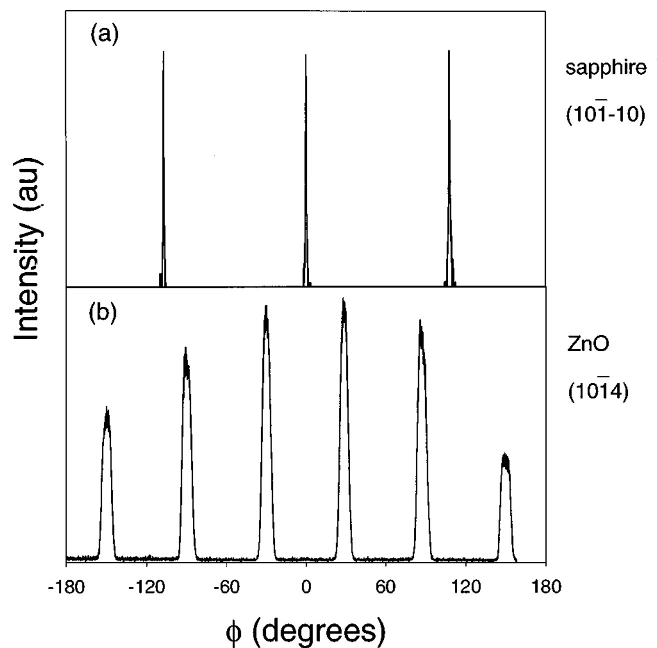

FIG. 2. XRD in plane ϕ scan of (a) $(10\bar{1}\text{-}10)$ plane of sapphire (0001), and (b) $(10\bar{1}4)$ plane of ZnO film grown on sapphire (0001) at 700 °C.

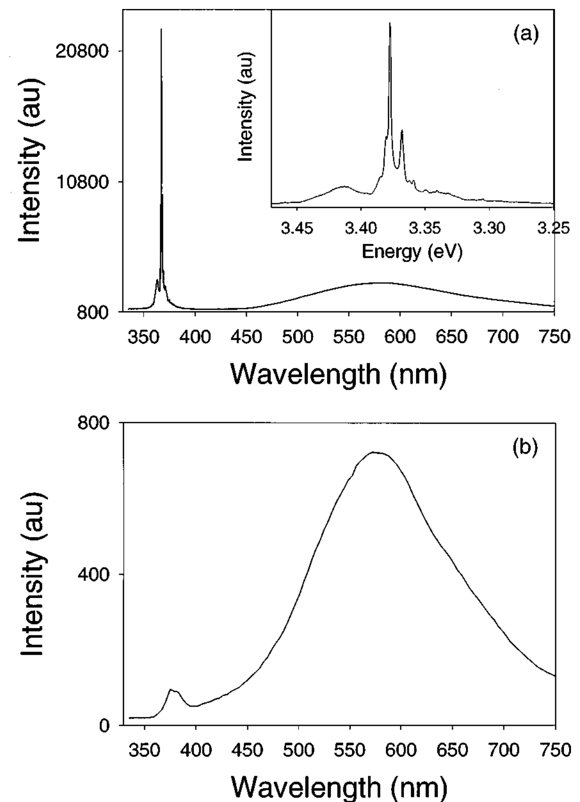

FIG. 3. (a) Photoluminescence spectrum of ZnO film grown on sapphire (0001) measured at a cryogenic temperature of 10 K. The inset shows the energy spectrum of the band-edge luminescence. (b) Photoluminescence spectrum of ZnO film grown on sapphire (0001) measured at room temperature.

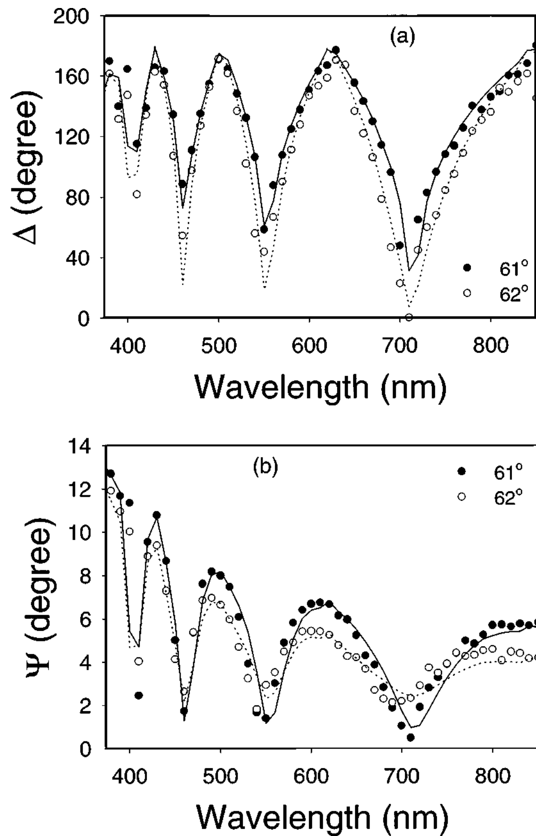

FIG. 4. Measured (closed and open circles) and calculated (solid and dashed lines) (a) Δ and (b) Ψ spectra of ZnO film on a sapphire (0001) substrate at two incident angles of 61° and 62°, respectively.

optimum oxygen pressure difference between Ref. 8 and our experiment. The films deposited at 800 °C showed similar crystalline quality to the ZnO film deposited at 700 °C. Table I lists the full width at half maximum (FWHM) of ZnO (0002) peak and the film thickness at different growth temperatures. All films (shown in Table I) were deposited by 50 thousand laser shots. It is quite obvious that the growth rate showed a continuous decrease as the substrate temperature increased.

HRXRD θ–2θ scan spectrum is shown in Fig. 1 for the ZnO film deposited at 700 °C and an oxygen pressure of 10 mTorr. The rocking curve (cf. inset of Fig. 1) shows that ZnO grows in single c-axis orientation with the c axis normal to the sapphire basal plane, indicating a heteroepitaxial relationship of $(0001)_{\mathrm{ZnO}}\|(0001)_{\mathrm{sapphire}}$. As shown in Fig. 1, the FWHM of ZnO (0002) rocking curve is 0.18°. The in-plane ϕ scan is shown in Fig. 2. The scanning planes used here were $(10\bar{1}\text{-}10)$[14] for sapphire, and $(10\bar{1}4)$ for ZnO. From the in-plane x-ray ϕ scan, it can be seen that the $(10\bar{1}0)$ plane of ZnO aligns with the $(11\bar{2}0)$ plane of sapphire. This indicates a 30° rotation of the ZnO unit cell with respect to that of sapphire. This phenomenon, observed before by other researchers,[8] is probably due to the large lattice mismatch between ZnO and sapphire (16%). Combining the results of XRD θ scan and ϕ scan, the epitaxial relationship between ZnO and sapphire is $(0001)_{\mathrm{ZnO}}\|(0001)_{\mathrm{sapphire}}$ and $(10\bar{1}0)_{\mathrm{ZnO}}\|(11\bar{2}0)_{\mathrm{sapphire}}$.

TABLE II. The best VASE fitting parameters of Sellmeier model.

A	B	C	D	E	Thickness	MSE
2.0065	1.5748×10^{6}	1×10^{8}	1.5868	2606.3	6119 Å	24.49

IV. PHOTOLUMINESCENCE

Photoluminescence of the epitaxially grown ZnO on sapphire(0001) was also characterized. The excitation source used was a He–Cd laser operating at 325 nm with an output power of 3 mW. The sample was mounted in a closed-cycle refrigerator that can be cooled down to 10 K. The PL signal from the sample was filtered by a monochromator (with a resolution of 2 nm) and picked up by a water-cooled CCD detector. A Corning color glass filter was used to suppress the scattered laser radiation. The cutoff wavelength of the filter at the ultraviolet side is about 340 nm.

Figure 3 shows a typical PL spectrum of epitaxially grown ZnO film on sapphire(0001) both at a cryogenic temperature of 10 K [Fig. 3(a)] and at room temperature [Fig. 3(b)]. Please note that the vertical scale of Fig. 3(a) is 30 times larger than that of Fig. 3(b). From Fig. 3(a), it can be seen that there is a clear band-edge luminescence from the cryogenic temperature measurement. The band-edge luminescence is enlarged and inserted in the inset of Fig. 3(a). At least three peaks can be identified; a free excitons peak at 3.413 eV, excitons bound to neutral donors at 3.377 eV, and excitons bound to neutral acceptors at 3.368 eV.[15,16] The other fine structures may be due to phonon replicas of either the donor or acceptor bound excitons. It can also be seen in Fig. 3(b) that, at room temperature, the green band emission dominates; the band-edge luminescence showed a broadened peak without fine structures. At room temperature, the band-edge luminescence has a remarkable redshift compared to the 10 K measurement. Both the room temperature and cryogenic temperature measurements showed green band emission from deep levels. This is believed to come either from oxygen vacancies or interstitial zinc.[10,17]

V. VARIABLE ANGLE SPECTROSCOPIC ELLIPSOMETRY (VASE)

The epitaxial ZnO films on sapphire appeared optically smooth by visual inspection. They should be suitable to apply the Sellmeier model. The measured VASE data (ψ, Δ) in the wavelength region of 350–1000 nm under an incident angle of 61° (closed circle) and 62° (open circle) are plotted in Fig. 4. The solid line and the dashed line are simulation fittings by a Sellmeier model for 61° and 62° incidence, respectively.

From the experimental data of Δ and ψ, the refractive index and extinction coefficient can be extracted through a Sellmeier equation fitting of Δ and ψ. The fit was done by minimizing the mean-square error (MSE) automatically by the ellipsometer's own computer program. Film thickness was also obtained as a by-product. The Sellmeier equation[18] for the refractive index, n, and the extinction coefficient, k as a function of wavelength in our model is expressed by

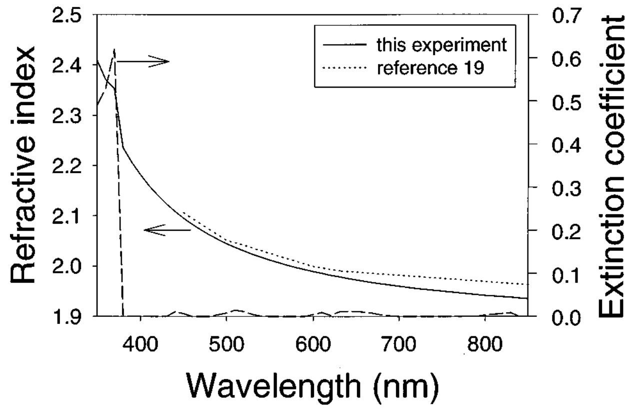

FIG. 5. Refractive index, extinction coefficient of ZnO film on sapphire as a function of wavelength. The dashed line shows the refractive index of ZnO from Ref. 19.

$$n(\lambda)^2 = A + \frac{B\lambda^2}{\lambda^2 - C^2} + \frac{D\lambda^2}{\lambda^2 - E^2}, \quad (1)$$

$$k(\lambda) = 0. \quad (2)$$

A, B, C, D and E are the fitting parameters, and λ is the wavelength of light (in Å). The Sellmeier model assumes that the film surface is smooth and that the sapphire substrate is of infinite thickness. k is considered to be zero because ZnO absorbs very little in the near UV and visible region. However, this fact can also be verified from our VASE data if a nonzero k is assumed.

The simulated n, as a function of wavelength, is plotted in Fig. 5 together with reference data from Ref. 19, and the fitting parameters are listed in Table II. In Fig 5, one can see the rugged experimental refractive index curve at less than 3800 Å wavelength range. This corresponds to a relatively large deviation of Δ and ψ in the same range which comes from the strong absorption of ZnO interband transition. The band gap is just about 3.3 eV as the room temperature PL showed. Also shown in Fig. 5 is an extinction coefficient assuming a nonzero k. It can be seen that k can be considered zero in the range of 4000–8500 Å, although there are small disturbances which are believed to come from the scattering at the back of sapphire substrate (the sapphire substrate used is one-side polished). This is why we have not considered the extinction coefficient as in Eq. (2). It can also be seen from Fig. 5 that our fitted refractive index, in the wavelength region of 4000–8500 Å, coincides well with that taken from Ref. 19. The value of the fitted film thickness (6119 Å) closely matches the film thickness measured by a profilometer (6000 Å).

VI. CONCLUSIONS

High quality ZnO films were epitaxially grown on sapphire(0001) substrate by pulsed laser deposition. These films are suitable for GaN-based III–V compound heterostructures. Optical properties including photoluminescence and refractive index were measured. PL measurement showed clear excitonic bandedge structures at cryogenic temperatures. Refractive index was extracted by fitting VASE of Δ and ψ by a Sellmeier equation. These data should be helpful to design high efficiency GaN-based light emitting devices on ZnO substrate or ZnO-buffered substrates.

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