Structural and optical properties of ZnO epitaxial films grown on Al$_2$O$_3$ (11$ar{2}$0) substrates by metalorganic chemical vapor deposition

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Abstract. ZnO films with different thicknesses were grown on Al$_2$O$_3$ (11$ar{2}$0) substrates by metalorganic chemical vapor deposition. Characterizations using X-ray diffraction and scanning electron microscopy demonstrated the evolution from two-dimension growth to three-dimensional growth with increases in the film thickness. Photoluminescence spectra revealed a thickness dependence of exciton peak and stimulated emission due to exciton-exciton scattering was observed.

Keywords: ZnO, MOCVD, OMVPE, Al$_2$O$_3$, epitaxial growth, surface morphology, X-ray diffraction, photoluminescence, exciton-exciton scattering

1. Introduction

ZnO is a direct and wide band-gap (3.37 eV) compound semiconductor that is promising for short-wavelength optoelectronic devices. Lasing action in the ultraviolet spectral region has been observed from both disordered particles and thin films. In addition, ZnO has an exciton binding energy as large as 60 meV, being significantly larger than that of ZnSe (22 meV) and GaN (25 meV). Excitons in ZnO are therefore thermally stable at room temperature, which leads to exciton-involved lasing processes.

Many growth techniques have been used to obtain ZnO films such as radiofrequency (RF) magnetron, molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD). Among them, MOCVD has been widely used for high quality epitaxial growth of various semiconductors and it is the ideal production technology for growth of ZnO films. ZnO films have been grown by MOCVD on various types of substrates such as Al$_2$O$_3$ (0001), Al$_2$O$_3$ (11$ar{2}$0), Al$_2$O$_3$ (1T02), Si, SiC, SiO$_2$, GaAs and so on. Out of these substrates, Al$_2$O$_3$ (0001) and Al$_2$O$_3$ (11$ar{2}$0) were used more popular from the viewpoints of both high-quality ZnO films and low cost. However the large mismatch between the ZnO film and the Al$_2$O$_3$ substrate causes strong dependence of film properties on the film thickness. Evolution of the properties of ZnO films as changing the film thickness has been studied on Al$_2$O$_3$ (0001) substrates in case of
RF magnetron sputtering. It has been shown that, in the initial growth stage, ZnO layer follow a two-dimensional (2D) growth mode and is highly strained. However, the layer is well aligned to the substrate which is reflected by a small mosaic distribution (0.01°). With increasing the film thickness, a transition from 2D to three-dimensional (3D) growth takes place. The critical thickness of 2D growth of ZnO on Al2O3 (0001) substrates was estimated to be 4.5 nm.

In this letter, thickness-dependent characteristics of ZnO films grown by MOCVD are studied. Moreover, Al2O3 (11 20) substrate are used because ZnO films with better quality can be obtained compared with those grown on Al2O3 (0001) substrates. We report the variation as a function of film thickness of surface morphology, crystalline and optical properties of ZnO films grown on Al2O3 (11 20) substrates by MOCVD.

2. Experiment

The MOCVD system is the same as that used in our previous study. Oxygen gas (O2) and diethyl zinc (DEZn, Zn(C2H5)2) were used as precursors and nitrogen gas was used as the carrier gas for DEZn. Al2O3 (11 20) substrates were cleaned in an ultrasonic bath of organic solution and then placed into the reactor. At room temperature, O2 flow was started and the reactor pressure was fixed at 5 Torr. Then the substrate was heated to 500 °C and DEZn was introduced to start the growth. The flows of O2 and N2 were set to 30 sccm and 6.5 sccm, respectively. The temperature of DEZn was 4 ~ 5 °C. During the whole process, the reactor pressure was kept at the same value. The film thickness was estimated from the growth time and the growth rate, while the later was determined to be 168 nm/hr by measuring the thickness of a comparatively smooth sample. Since the actual surface is not smooth, the thickness shown in the following should be taken as an effective value. The surface morphology was examined using either a scanning electron microscope (SEM) or an atomic force microscope (AFM). X-ray diffraction (XRD) measurements were carried out using a triple-axis, four-crystal Philips X'pert diffractometer. The optical properties of films were investigated by photoluminescence (PL) spectroscopy at 4.2 K and room temperature using either the 325 nm line of a He-Cd laser or the third harmonic (355 nm) of a Nd:YAG laser as the excitation source.

3. Results and discussion

Figure 1 shows the SEM images of the surfaces of samples with film thicknesses of 28 nm, 56 nm, 168 nm and 336 nm. The film with a thickness of 28 nm (Fig. 1a) is characterized by a flat surface with a large number of holes (diameters: 20 ~ 50 nm), the latter are believed to be due to the strain effect. It has been reported that strain relaxation can cause pits (or holes) and islands. The pits and islands are even clear when the film thickness is 56 nm (Fig. 1b), from which elongated islands (length: ~100 nm, width: ~30 nm) were observed. These islands form networks of ZnO and the brighter points indicate preferred growth of ZnO at the ends of the islands. With further increase in the film thickness, nano-scale rods
(diameter: \(~20\ \text{nm}\)) were formed at such preferred positions and simultaneously the elongated islands became higher to form nano-scale walls (Fig. 1c). With increasing further the film thickness, nano-scale rods (diameter: \(\sim50\ \text{nm}\)) dominant the surface (Fig. 1d). The origin of the preferred growth at island ends is tentatively attributed to the higher density of dangling bounds at these points. These bounds lead to an increase in the surface energy. Preferable growth of adsorbed atoms or molecules at these positions is effective in reducing these bounds and consequently in keeping a smaller energy of the whole system. The results also suggest a method of fabricating networks consisting of nano-scale ZnO walls and rods. Such networks have been fabricated by vapor-liquid-solid (VLS) growth mode in which a high growth temperature (\(~900\ ^\circ\text{C}\)) and a catalyst are necessary.\(^{19}\) Our results suggest the possibility of obtaining such networks by a catalyst-free and low-temperature approach.

Figure 2a shows the \(\omega\)-rocking of ZnO (0002) Bragg reflection of the samples with different thicknesses. The full-width-at-half-maximum (FWHM) values, \(\Delta\omega\), are shown in Fig. 2b together with the FWHM values, \(\Delta2\theta\), obtained from \(2\theta-\omega\) scans as a function of film thickness. When the thickness is less than 56 nm, only one sharp peak with \(\Delta\omega = 0.005^\circ\) (18 arcsec) was observed in the rocking curve. This is less than that of ZnO/Al\(_2\)O\(_3\) (0001) prepared by sputtering (0.01\(^\circ\)),\(^5\) similar to those (12 ~ 14.4 arcsec) obtained from ZnO/Al\(_2\)O\(_3\) (0001) grown by MBE\(^6-8\) and better than that (39 arcsec) obtained from ZnO films grown on lattice-matched ScAlMgO\(_4\) substrate.\(^{10}\) The small \(\Delta\omega\) obtained from thinner films in this study demonstrates a small magnitude in the mosaicity and the excellent order along the growth direction of these films. In other words, the film is well-aligned with the c-axis being strictly parallel to the substrate normal within the entire film. This can be taken as an indicator of 2D growth.\(^5\) This is also supported by the large \(\Delta2\theta\) value, which reflects the deviation of lattice distance along the growth direction, observed from thinner films. The large \(\Delta2\theta\) value indicates a larger lattice distortion which is caused by lattice mismatch, while the existence of lattice mismatch indicates the 2D layer-by-layer growth. With further increasing the film thickness, a broader peak appeared and, when the film thickness is 84 nm, the latter dominant the rocking curve. The broad peak is centered at the same position as the narrow one, forming superimposed shape. For even thicker films (larger than 112 nm), only the broader one was observed. The \(\Delta\omega\) of the broad component changes from 0.6\(^\circ\) to 0.3\(^\circ\),
showing a decrease with increase in the film thickness. Compared with the result obtained for thinner films, the large $\Delta \omega$ values for thicker films reflect worse alignment of the film and can be attributed to the result of 3D growth. The $\Delta \omega$ value for thicker films is also small, indicating small magnitudes of strain in these films. The superimposed shape of the rocking curve observed in the regime of medium film thickness indicates the coexistence of 2D and 3D layers. Our results suggest the following growth model: when the thickness is less than 56 nm, ZnO follows a 2D layer-by-layer growth. However, a 3D growth mode is true when the film thickness is larger than 112 nm. Transition from 2D to 3D growth takes place in the thickness range of 56-112 nm. This model is similar to those observed in case of ZnO on Al$_2$O$_3$ (0001) grown by sputtering. The critical thickness within which 2D growth of ZnO is realized on Al$_2$O$_3$ (11$ar{2}$0) is estimated to be 56 nm. This is much larger than the value, 4.5 nm, obtained for ZnO on Al$_2$O$_3$ (0001), due probably to the small lattice mismatch in the former. In case of ZnO on Al$_2$O$_3$ (0001), the lattice mismatch is isotropic and the magnitude is 18.3 or 31.5% depending on the in-plane orientation. In case of ZnO on Al$_2$O$_3$ (11$ar{2}$0), however, the situation is much more different. The epitaxial relationship has been demonstrated to be ZnO (0001) // Al$_2$O$_3$ (11$ar{2}$0) and ZnO [010] // Al$_2$O$_3$ [001].

The lattice mismatch along the ZnO [010] direct ion is less than 0.08% when taking higher order matching (4 times $a_{\text{ZnO}}$ to $c_{\text{sapphire}}$, $a_{\text{ZnO}} = 0.325$ nm, $c_{\text{sapphire}} = 1.299$ nm). On the other hand, in the ZnO [210] direction which is perpendicular to both ZnO [010] and ZnO [001], the mismatch is about 2.4% according the configuration of Fig. 3c in Ref. 9 ($\sqrt{3}$ times $a_{\text{ZnO}}$ to 2 times O-lattice in Al$_2$O$_3$: $c_{\text{sapphire}} = \sqrt{3} a_{\text{sapphire}} = 0.2748$ nm).

PL spectra taken at 4.2 K for different films were shown in Fig. 3a. A broad emission peak located at ~3.25 eV was observed from the film with the smallest thickness. This peak is tentatively attributed to defect-related emission since the large magnitude of distortion in the lattice. For all of the films, band-edge emission due to donor-bound-exciton (denoted by D$_0$X) was observed and there is no green emission. The FWHM of exciton emission decreases from 14 meV (28 nm sample) to 7 meV (336 nm sample). It is noted that the D$_0$X peak shifts with film thickness. As shown in Fig. 3b, the D$_0$X peak energy exhibited a rapid blue-shift from 3.365 eV to 3.371 eV and then a gradual red-shift to 3.368 eV when the film thickness was increased from 28 to 336 nm. The maximum D$_0$X peak energy appeared at 3.371 eV and was observed from films with thicknesses of 56 and 84 nm, corresponding to the 2D-to-3D transition regime. The dependence of the emission energy on the film thickness is tentatively attributed to the strain-induced band-gap variation.

PL Intensity (a. u.)

Photon energy (eV)

D$_0$X

Emission Energy (eV)

168 nm, x1
112 nm, x1
84 nm, x5
56 nm, x40
42 nm, x100
28 nm, x1500

Film Thickness (nm)

3.372
3.370
3.368
3.366
3.364

Fig. 3 (a) PL spectra of different films at 4.2 K. (b) Dependence of D$_0$X emission energy on film thickness.
Under excitation of the third harmonic of a Nd:YAG laser (355 nm, pulse width 15 ns, repetition rate 50 Hz), stimulated emission was observed from samples with film thicknesses of from 84 nm to 168 nm. The incident angle of the laser beam was about 45°. The emission from the sample was collected and dispersed using a spectrometer (Trix 320) and a cooled CCD. Figure 4 shows the PL spectra observed from the sample with a thickness of 84 nm at room temperature. At low excitation intensity, only a broad peak (FWHM ~ 0.11 eV) due to spontaneous emission was observed. When the excitation intensity exceeds a threshold, a sharp peak emerged at 3.205 eV. This peak is attributed to the exciton-exciton scattering and assigned as $P_2$, in which an exciton is scattered from the $n = 1$ state to the $n = 2$ state by absorbing part of the energy emitted from another exciton. When the excitation intensity is increased, this peak shifted to 3.190 eV (denoted by $P$) in which the exciton was scattered to continuum states. The emission energy of exciton-exciton scattering is written as 

$$E_n = E_{ex} - E_b^E \left( 1 - \frac{1}{n^2} \right) - \frac{3}{2} kT$$

where $n = 2, 3, 4, \ldots$. $E_{ex}$ is the exciton energy, $E_b^E = 60$ meV is the binding energy of the exciton, and $kT$ is the thermal energy. $P$- and $P_2$-lines correspond to $n = \infty$ and $n = 2$, respectively. This equation predicts a separation between $P$ and $P_2$ lines to be 15 meV, which is equal exactly to that observed in this study. With further increasing the excitation intensity, $P$-line showed an even larger red shift in the emission energy. Within our experiments, the magnitude of the red shift of $P$-line was about 20 meV. This red shift may be caused by a few mechanisms such as band-filling effect and thermal effect. Inset in Fig. 4 shows the integrated emission intensity of the peak due to exciton-exciton scattering as a function of excitation intensity. A superlinear relationship was observed when the laser power was up to 31.8 kW/cm². At even higher excitation powers, the emission intensity of the $P$-line deviated from the superlinear relationship. The observation of the emission due to exciton-exciton scattering suggests such ZnO films grown by MOCVD can be used in UV-region light-emitting devices.

4. Conclusion

In conclusion, ZnO films grown by MOCVD on Al₂O₃ (11̅20) exhibited the evolution from 2D to 3D growth with increases in the film thickness.
thickness is smaller than 56 nm, 2D growth mode is obeyed. In the thickness range of 56 – 112 nm, transition from 2D to 3D takes place. Growth will be completely 3D mode in even thicker films. The photoluminescence spectra showed a thickness dependence of exciton peak. Stimulated emission due to exciton-exciton scattering was observed. We also presented a catalyst-free, low-temperature growth method of nano-scale ZnO networks made of nanowalls and nanorods.

Reference