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Investigation of growth mode in ZnO thin films prepared at different temperature by plasma-molecular beam epitaxy

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Abstract

High-quality ZnO thin films on c-plane sapphire (Al_2O_3) substrates were prepared by plasma-molecular beam epitaxy (P-MBE). The influence of growth temperature on growth mode of ZnO was investigated. Real-time monitored by reflection high-energy electron diffraction (RHEED) images show that, below 500 °C, ZnO thin film was grown by three-dimension (3D) growth mode. While the two-dimension (2D) growth mode was obtained above growth temperature of 650 °C. Atomic force microscopy (AFM) images present that the surface morphology of ZnO thin film with 2D growth is improved and X-ray rocking curves (XRC) indicate that the full width at half maximum (FWHM) of the ZnO (0 0 2) peak becomes narrow. From the photoluminescence (PL) spectra, ultraviolet (UV) emission peak exhibits obvious blue-shift for the samples grown at lower temperature, which is attributed to the effect of the quantum confinement arisen from small crystal grain sizes. The minimum carrier concentration of $N = 7.66 \times 10^{16}\,cm^{-3}$ was obtained in the ZnO thin films with the 2D grown, which is closed to that of bulk ZnO.

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1. Introduction

As a wide gap semiconductor, ZnO is a promising candidate for use in light-emitting devices operating in the ultraviolet wavelength region because of its direct band gap of 3.37 eV at room temperature and its large exciton binding energy of 60 meV [1,2]. For the realization of these devices based on ZnO, it is necessary to grow high quality ZnO thin films with low residual carrier densities and low dislocation densities. Two-dimensional (2D) growth mode was demonstrated

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to be an effective approach to the realization of high-quality ZnO films [3]. The previous research on the growth mode of ZnO thin films has been reported by choosing lattice-matched substrates, such as bulk crystal ZnO [4] or $ScAlMgO_4$ [5], and so on. Because the lattice-matched substrates are hard to obtain, most of the works are focused on c-plane Al_2O_3 substrate with lattice mismatch of about 18% for ZnO [6,7]. So far, many groups have achieved preparation of single crystalline ZnO thin films on Al_2O_3 substrate by employing the various methods including surface polarity controlling [8], MgO [9] and GaN [10] buffer layer growth and post-growth annealing [11]. However, in spite of the 2D growth mode has been realized on the direct growth on Al_2O_3 substrate [7], the systemic research on the dependence of growth temperature on the growth mode has not been reported yet.

In this paper, ZnO films were grown on c-plane Al_2O_3 substrate by plasma-molecular beam epitaxy (P-MBE) without buffer layer. The influence of growth temperature on growth mode of ZnO film was studied by measurements of the morphological, structural, optical and electrical properties.

2. Experimental procedure

Al_2O_3 (0 0 1) was used as substrate and the chemical treated process was the same with Ref. [6]. Before growth, the substrate was treated by O-plasma at 650 °C for 30 min in order to remove surface contaminant and obtain oxygen terminated Al_2O_3 surface [6]. Elemental zinc with 99.9999% purity was used as precursors. Atomic oxygen is activated from O_2 gas (99.999%) by an RF plasma source (Oxford Applied Research). The Zn beam flux and O_2 partial pressure in the growth chamber were kept at 4×10^{-5} Pa and 6×10^{-3} Pa, respectively. The growth temperature was varied from 350 to 700 °C at an interval of 50 °C. The growth process was monitored by in situ reflection high-energy electron diffraction (RHEED). The thicknesses of all samples are about 400 nm.

Surface morphology of the samples was further investigated by atomic force microscopy (AFM) in the tapping mode. Rigaku O/max-RA X-ray system and D/Max 2400 double crystal diffractometer were used to characterize the ZnO films structures. The optical properties were studied by photoluminescence (PL) spectroscopy. The 325 nm line of a He–Cd laser was used as the excitation source. Hall effect measurements were performed by a standard four-probe van der Pauw method in a magnetic field of 0.320 T.

3. Results and discussion

3.1. Morphologic and structural properties of ZnO thin films grown in different growth mode

Fig. 1 shows the RHEED patterns of the substrate exposed to O-plasma at 650 °C for 30 min (Fig. 1a), the samples grown at 350 °C (Fig. 1b), 550 °C (Fig. 1c) and 650 °C (Fig. 1d), respectively. After plasma treatment, the substrate presents a streaky pattern (Fig. 1a), which indicates a well-ordered and flat Al_2O_3 surface was obtained. For the grown samples, RHEED results exhibit different patterns with changing growth temperature, as seen in Fig. 1b–d. For the sample grown at 350 °C, a spotty pattern indicates that a rough surface was formed with island growth mode. This mode remains till the growth temperature was increased to 500 °C. As the growth temperature was increased from 550 °C (c) to 650 °C (d), sharp streaky RHEED patterns appear gradually. It implies that the transition from 3D to 2D growth mode takes place. To understand the effect of the growth temperature on surface morphology, AFM measurements were performed on the ZnO thin films surfaces. Fig. 2 shows the $2 \times 2\,\mu m^2$ surface roughness images of the samples grown at 350, 450, 550 and 650 °C, respectively. With increasing the growth temperature, the root-mean-square (RMS) roughness of ZnO samples gradually decreased from 6.5 to 3.4 nm, which is relative with the changing of mean grain size. The growth mode dependent on the growth temperature can be seen clearly by the measurements of the mean grain sizes. In the 3D growth mode, the ZnO thin films consist of many grains with the mean sizes of 20–25 nm in Fig. 2a

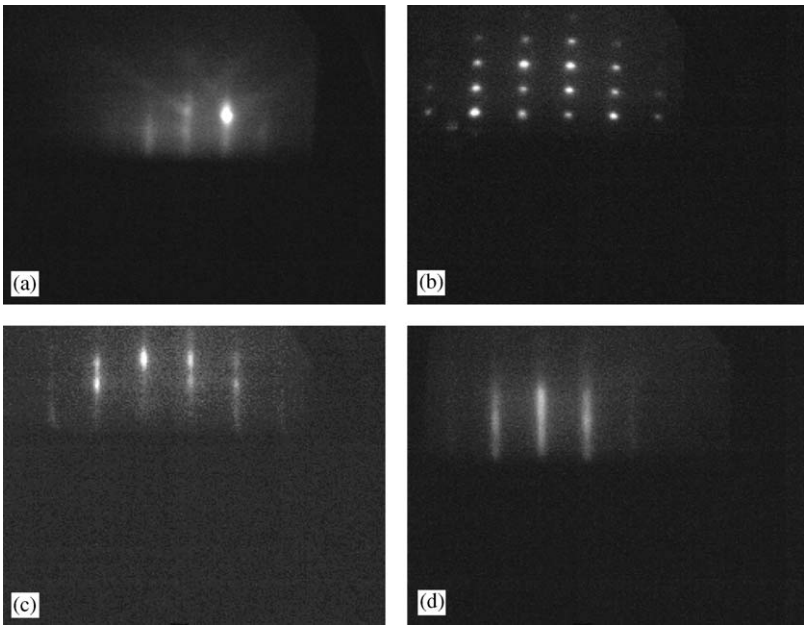

Fig. 1. The RHEED patterns of Al_2O_3 substrate treated by O-plasma (a) and ZnO thin films grown at 350 °C (b), 550 °C (c) and 650 °C (d).

and 25–30 nm in Fig. 2b, respectively. For growth temperature of 550 °C, the crystal grain size is more than 100 nm. While at 650 °C, the crystal grain size becomes upwards more than 200 nm. The dependence of temperature on the grain size can be explained by the migration and the diffusion of the reactants. At low temperature, atoms absorbed on the substrate surface have low mobility, which leads to 3D nucleation. In this case, ZnO epilayer has a small grain size and a rough surface. With increasing temperature, the enhancement of the atomic migration ability results in the forming of larger grain, and decrease of the surface roughness. This evolution reveals a transition of the growth mode from the 3D to 2D with increasing growth temperature. The 2D growth mode would be preferable for the growth of high-quality ZnO films [7].

Fig. 3 shows the XRD spectra of the samples. Besides the diffraction peak of Al_2O_3 (0 0 6) at 41.67°, only wurtzite structural ZnO (0 0 2) and (0 0 4) diffraction peaks can be observed for the samples. The appearance of ZnO (0 0 l) peaks indicates that ZnO thin films were grown along a c-axis orientation of the Al_2O_3 substrate. The full widths at half maximum (FWHMs) of XRC for the ZnO (0 0 2) diffraction peaks decreases from 0.88° to 0.20° with increasing growth temperature from 350 °C to 650 °C, while at 700 °C, the FWHM increases to 0.78°. Because the lattice mismatch between the ZnO and Al_2O_3 substrate is about 18% in c-plane, large numbers of mismatch defects will be introduced in the ZnO films. This is one reason for the broadening of the diffraction peak in the measured XRC. On the other hand, the grain size is also a factor that influences the FWHM of the diffraction peak. With increasing growth temperature, the larger grain size results in the decreasing of the FWHMs. When the growth temperature exceeds 700 °C, the broadening of the FWHM can be ascribed to the effect of thermal mismatch due to different thermal expansion coefficient between the ZnO and Al_2O_3.

3.2. *Optical and electrical properties of ZnO thin films grown in 2D and 3D growth mode*

PL measurements were performed at RT on the ZnO films, as shown in Fig. 4. The main features of the PL spectra are similar for all the samples,

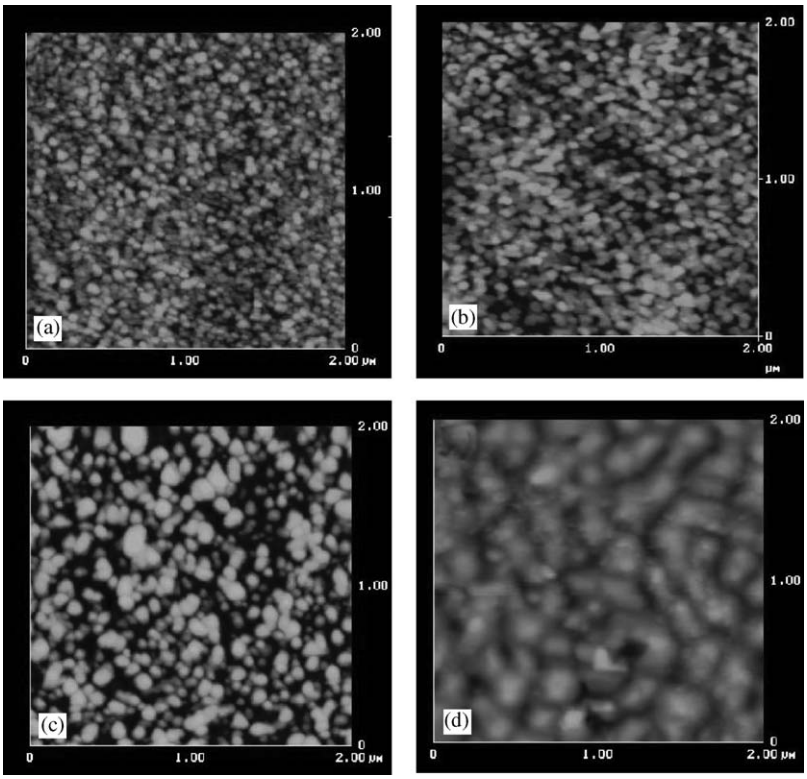

Fig. 2. The AFM images of ZnO films grown at 350 °C (a), 450 °C (b), 550 °C (c) and 650 °C (d).

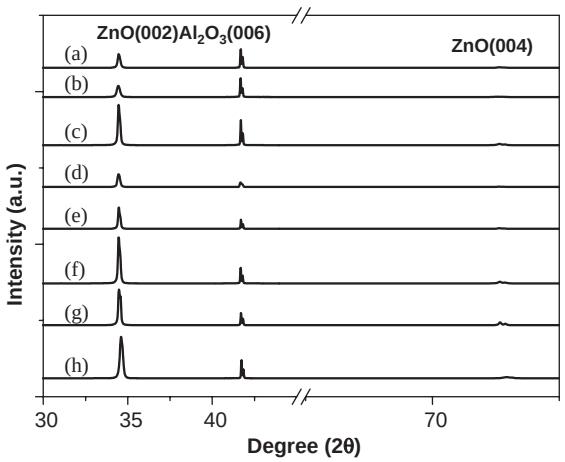

Fig. 3. The XRD spectra of ZnO films grown at different growth temperatures. (a)–(h) are the ZnO thin films grown from 350 °C to 700 °C at an interval of 50 °C.

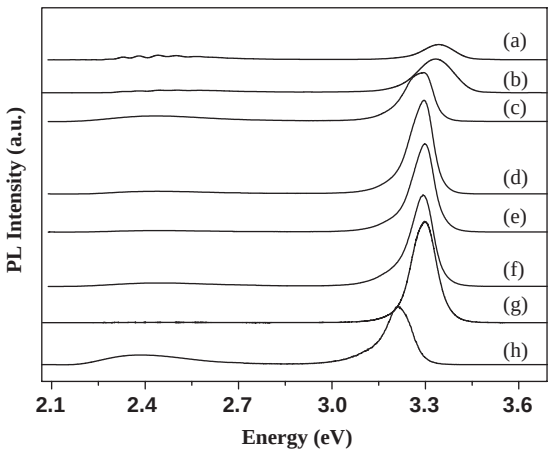

Fig. 4. Room temperature PL spectra of all samples grown at different temperatures. (a)–(h) are the spectra of ZnO thin films grown from 350 °C to 700 °C at an interval of 50 °C.

which consists of a strong ultraviolet (UV) and weak visible emission. The UV peak and the visible emission originated from emission of near-band-gap of ZnO and recombination of oxygen vacancies (V_O) defects, respectively [14]. For the ZnO films grown with the 3D growth mode shown

in Fig. 4a–d, the energy positions shift from 3.357 to 3.297 eV with increasing growth temperature. As the growth temperature increases from 500 to 650 °C, there are no noticeable change for the positions of all UV peaks located at 3.295 eV. According to previous report [12], this emission peak was assigned as the emission from free exciton. For the sample grown at 700 °C, the UV peak shifts to 3.212 eV. The origination of which will be reported elsewhere. As can be seen in AFM images, the ZnO thin films grown with 3D growth mode consists of many small ZnO grains. The small grain size will result in the blue shift of PL peak due to the quantum confinement effect comparing with the ZnO bulk material [13].

All the ZnO films show n-type conduction at RT in Hall effect measurement. As the growth temperature is increased from 350 to 650 °C, the carrier concentration decreases gradually from $N = 1.06 \times 10^{19}\,\mathrm{cm}^{-3}$ to $N = 7.66 \times 10^{16}\,\mathrm{cm}^{-3}$. When the growth temperature reaches 700 °C, the carrier concentration increases to $N = 8.5 \times 10^{18}\,\mathrm{cm}^{-3}$. The changing of carrier concentration is in agreement with that of the intensity of the visible emission related to V_O, as seen in Fig. 4. However, the V_O is a deep defect though considered an intrinsic donor in ZnO. Zhang et al. had proposed that the interstitial Zn (Zn_i) as another donor which would play an important role in the electrical properties, because the Zn_i level is shallower than the level of V_O [14]. A low growth temperature will lead to the formation of high-density Zn_i in ZnO films due to the lower migration ability. With increasing temperature, these defects that can contribute to the carrier concentration are decreased. However, high-density defects caused by thermal mismatch will result in the increasing of carrier concentration at high temperature. In the optimum growth condition (650 °C), the carrier concentration has a minimum of $N = 7.66 \times 10^{16}/\mathrm{cm}^3$ which is close to that of bulk ZnO [15].

4. Conclusions

The influence of growth temperature on the quality of ZnO film prepared by P-MBE was investigated. From growth temperature of 350 to 500 °C, the growth is governed by 3D growth mode, resulting in a rough surface morphology. With the further increasing growth temperature, the surface morphology is improved due to transition from 3D to 2D growth mode. The control of the growth mode from the 3D growth to 2D growth is realized by changing the growth temperature. The ZnO films with better structural, optical and electrical properties were obtained in the 2D growth mode. This indicates that the growth temperature may improve the quality of ZnO film on c-Al_2O_3 due to controlling the growth mode.

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