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Structural and optical properties of ZnO films grown by two-step method using MOCVD

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Structural and optical properties of ZnO films, grown on Si(111) and prepared via two-step method by MOCVD using diethylzinc and H_2O as reactant gases, are studied using XRD, PL and AFM. For samples using two-step method, excellent crystallization quality and optical properties were obtained. Moreover, as increasing the growth temperature, the properties of ZnO films were improved further. AFM results indicated that the RMS of ZnO films using two-step method were all about 7.0 nm. Compared with the samples using single-step method, there is no obviously variation of RMS as increased the growth temperature for samples grown by two-step method.

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1. Introduction

Zinc oxide has gained considerable attention as a promising material for short-wavelength lasers and light-emitting diodes due to its wide band gap of 3.37eV and large exciton binding energy of 60 meV at room temperature [1]. It is known that the performance of a device is strongly affected by the material properties, and there are many intrinsic defects and impurities in ZnO films which will worsen the properties of optoelectronic devices. So, to obtain high performance light emitting devices, the fabrication of high quality ZnO epitaxial films is necessary. For the deposition of single crystal ZnO films, molecular-beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), pulse laser deposition (PLD) and other high-precision techniques have mainly been used [2-4], and often the substrates were single crystal. All this lead to high cost and expensiveness of ZnO films. Recently, several reports demonstrated a number of possibilities for yielding high-quality ZnO films via a small amount of H_2O vapor assistance, suggesting that H_2O vapor might be an efficient new oxygen source for the growth of ZnO [5-7]. And considering that only a small investment will be necessary as H_2O vapor is an abundant natural resource. In this work, diethylzinc (DEZ) and H_2O were used as reactant gases to explore the growth of high quality ZnO films at lower temperature. In addition, the direct growth of ZnO film on Si substrate is known as an extremely difficult task due to large tensile strain between film and substrate induced by lattice mismatch and different thermal expansion coefficient. Buffer layer is an effective method to reduce the effects of strain, and this technique has achieved great success for the growth of GaN and SiC on Si substrates and ZnO on $A1_2O_3$ substrates [8-10]. In this paper, to obtain high quality ZnO films, two-step growth method was used [11]. The first step was grown at lower temperature in a relatively short period of time. Then the ZnO films were deposited on the buffer layer at different temperature. The effect of buffer layer and the growth temperature on crystal quality, optical properties and surface morphologies of ZnO films were analyzed using XRD, PL and AFM methods.

2. Experimental procedure

Experiments were carried out on the MOCVD system which was designed and built by ourselves. The improved intake system is similar to sprinkler head. The schematic of ZnO reactor chamber was shown in Fig. 1. In this system, source materials are introduced into reaction chamber from different pipelines which were designed to avoid earlier reaction. Then the sprinkler head renders certain the uniformly mix and sufficiently reaction between sources near the surface of substrate. It is beneficial to epitaxial better crystalline quality of ZnO films using this intake system.

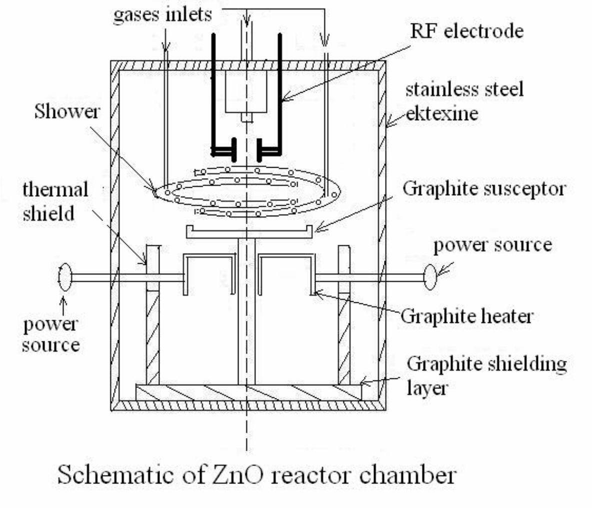

Fig. 1. Schematic diagram of ZnO reactor chamber

ZnO films were deposited on Si (111) substrates. Diethylzinc and H_2O were used as source materials. They were supplied to the growth chamber through bubbling systems using high purity nitrogen as carrier gas. During growth, DEZ and H_2O were kept in bubblers at -10□ and 2□ respectively. In order to eliminate the remnant amorphous silica layer thoroughly, the Si substrates were bombarded by Ar+ plasma in the growth chamber before the deposition of ZnO films [12]. At first, low temperature buffer layers were deposited at 200□ for 5min, and amorphous ZnO layers were obtained. Then the temperature of the substrates was raised to 400□~600℃ quickly and the growth process maintained for 25 min. The flow rate of DEZ and H_2O were both fixed at 5 sccm (standard-state cubic centimeter per minute). In order to analyze the effect of buffer layer, ZnO films without low temperature step was also investigated. The details of growth conditions were shown in Table 1. All samples were annealed in N_2 ambient (humidity: 23%) at 900 °C for 1 h after growth.

Table.1. Growth parameters for sample T1~T3, S1.

Sample	DEZ(sccm)	H_2O(sccm)	Temp(℃)	Time(min)
S1	5.0	5.0	400	30
T1	5.0	5.0	400	5*+25
T2	5.0	5.0	500	5*+25
T3	5.0	5.0	600	5*+25

*Low temperature buffer layers were deposited at 200□ for 5min.

Crystallinity of obtained films was analyzed by X-ray diffraction using a D-MAX/γA system with Cu*K*α radiation λ=0.154178nm in the range of 30^0~80^0. Optical properties were characterized by photoluminescence with He–Cd laser as a light source using an excitation wavelength of 325nm. Surface morphologies of ZnO films were observed using atomic force microscopy (AJ—IIIa AFM).

3. Results and discussion

3.1 Structural properties

Fig. 2 is the XRD patterns of ZnO films grown by two-step or not at 400℃. For sample S1, in addition to ZnO (002) diffraction peak, there are two other peaks corresponding to ZnO (102) and (103) planes can be observed. While, for sample T1, the intensity of ZnO (002) diffraction peak strengthened and the ZnO (102) and (103) diffraction peak disappeared. This result indicates that the crystallization of ZnO films has been significantly improved with a simple homogeneous buffer layer. It is because that the low temperature buffer layer can reduce the lattice mismatch between ZnO films and Si substrates effectively. Then many defects in films will be avoided and fine ZnO films will be obtained.

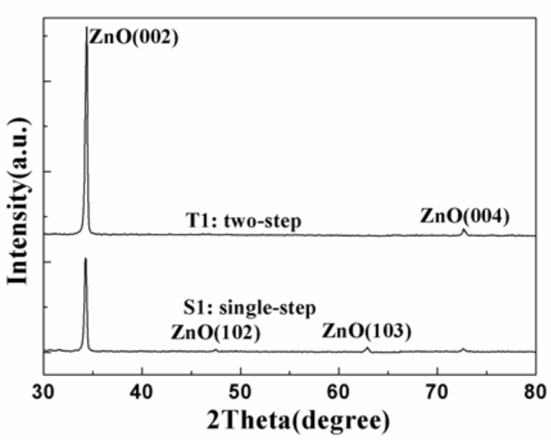

Fig. 2. XRD patterns of ZnO films prepared at 400 ℃. S1: single-step; T1: two-step.

The XRD patterns of ZnO films grown by two-step at different temperature are shown in Fig. 3. All the peaks of the XRD patterns can be indexed to ZnO with the hexagonal wurtzite structure. No excess diffraction peaks of impurities are observed. Strongest intensity of the diffraction peak corresponding to (002) plane indicates that all the samples have a c-axis preferential orientation. Moreover, as increasing the growth temperature, the intensity of ZnO (002) diffraction peak strengthened obviously and the second diffraction peak corresponding to the (002) plane of ZnO is also observed. This phenomenon indicates that the crystallinity of ZnO film is significantly improved as increasing the growth temperature. The reason is that the kinetic energy of nuclei is increased by higher temperature, and so the atoms adsorbed on the substrate surface are freely to spread to arrange in ideal lattice structure as possible.

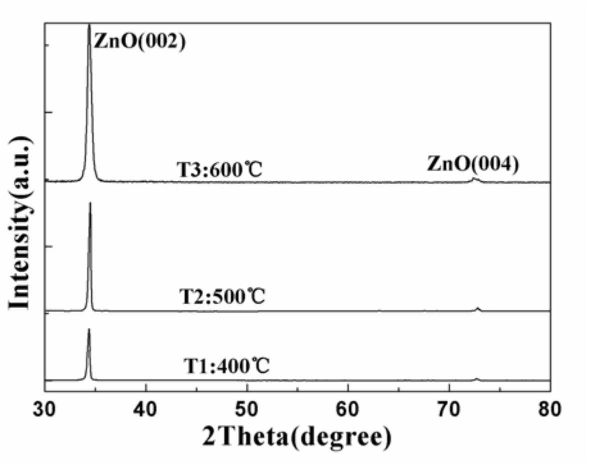

Fig. 3. XRD patterns of ZnO films prepared by two-step method at different temperature. T1: 400 ℃; T2: 500 ℃; T3: 600 ℃

3.2 Optical properties

The PL spectra of ZnO films with and without buffer layer were compared. The results are displayed in Fig. 4. For samples grown by single-step, the spectrum can be divided into the UV and the visible light parts. While, for samples grown by two-step, the broad visible peak disappeared and the intensity of the UV emission peak enhanced. Normally, the UV emission is attributed to an exciton transition and the visible bands are attributed to deep-level defects in ZnO, such as vacancies and interstitials of zinc and oxygen [13, 14]. The disappearance of the visible peak and the enhancement of the UV peak indicated that the crystal quality of ZnO films was improved effectively by two-step method.

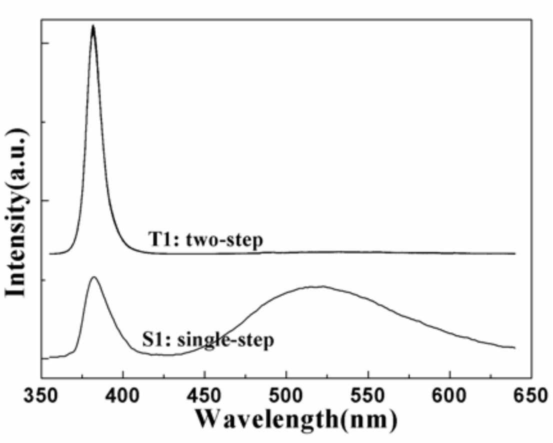

Fig. 4. PL spectra of ZnO films prepared at 400 ℃. S1: single-step; T1: two-step.

Fig. 5 illustrates the PL spectra of ZnO films grown by two-step at different temperature. As shown in the figure, all the samples have a strong emission in the UV range with a peak at 380 nm and no visible emission can be observed. The absent of visible emission indicating that all the ZnO films are of good optical properties. In addition, as increasing the growth temperature, the emission peak in UV range enhanced obviously. This variation tendency is consistent with the XRD results.

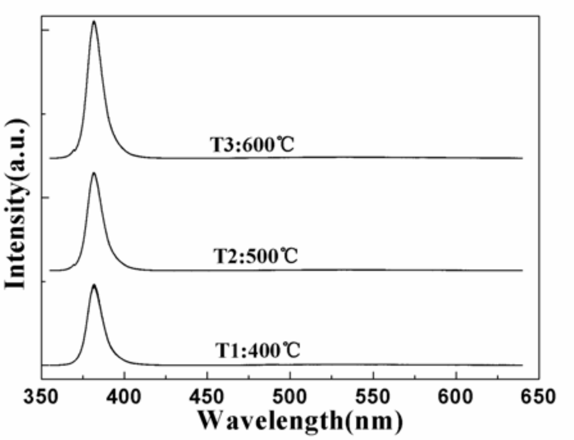

Fig. 5. PL spectra of ZnO films prepared by two-step method at different temperature T1: 400 ℃; T2: 500 ℃; T3: 600 ℃.

3.3 Surface morphology

To determine the surface morphology of ZnO films, AFM analysis was performed. For comparison, AFM image corresponding to ZnO film without buffer layer is shown in Fig. 6(a). Fig. 6(b) ~ Fig. 6(d) displays the AFM scans obtained for ZnO films by two-step at different temperature. The RMS roughness of sample S1 is 13.710nm. While, when two-step growth method was used, the RMS roughness decreased immediately and the result is 7.764nm. Furthermore, as increased the growth temperature, there is no obviously variation of grain size for ZnO films. It indicates that, based on two-step method, the growth temperature has little effect on the surface morphology of ZnO films.

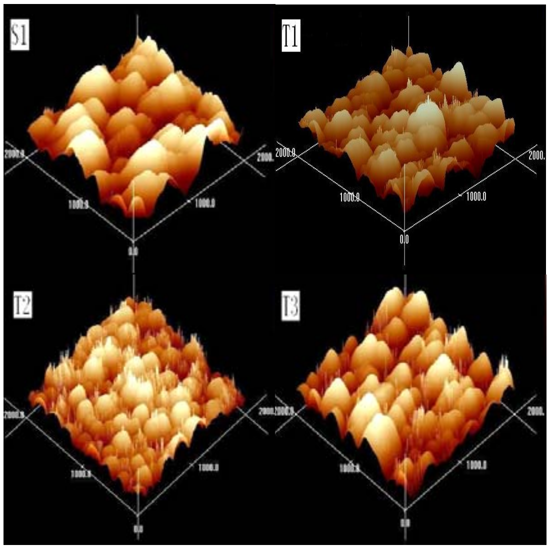

Fig. 6. AFM images of ZnO films (2μm×2μm): single-step (S1) at 400 ℃ and two-step at 400 ℃ (T1), 500 ℃(T2), 600 ℃(T3).

4. Conclusions

ZnO films have been grown on Si (111) substrates by Metal-Organic Chemical Vapor Deposition technique using diethylzinc and H_2O as reactant gases. XRD and PL results indicated that relatively better structural quality and optical properties of ZnO films were obtained by two-step growth method (with low temperature buffer layer). Moreover, as increased the growth temperature, the quality of ZnO films were improved further. AFM results indicated that two-step growth method reduced the RMS of ZnO films effectively. While, compared with the ZnO films by single-step, no obviously variation of grain size for ZnO films by two-step method was observed along with the increase of growth temperature.

Acknowledgements

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