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Electrical and optical properties of ZnO films grown by molecular beam epitaxy

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ABSTRACT

Zinc oxide (ZnO) films have been grown on sapphire by molecular beam epitaxy (MBE), and it is found that the grain size of the ZnO films increased with increasing the growth temperature. Photoluminescence (PL) study shows that the intensity ratio of near-band-edge emission to deep-level-related emission (NBE/DL) of the ZnO is significantly enhanced with increasing the growth temperature, and the dependence of the carrier mobility on the growth temperature shows very similar trend, which implies that there is a community factor that determines the optical and electrical properties of ZnO, and this factor is suggested to be the grain boundary. The results obtained in this paper reveal that by reducing the grain boundaries, ZnO films with high optical and electrical properties may be acquired.

1. Introduction

As a wide band gap semiconductor, zinc oxide (ZnO) has attracted much attention in recent years, and the attention is mainly derived from the potential applications of ZnO in light-emitting devices [1,2] and lasing diodes [3,4] for its large band gap (3.37 eV) and high exciton binding energy (60 meV) [5]. Undoped ZnO usually shows n-type conduction, therefore, to realize the above-mentioned applications, reproducible and efficient acceptor doping of ZnO is necessary. However, this issue is still unresolved up to now although numerous efforts have been paid [6–8]. Obtaining ZnO films with high structural and optical quality is a fundamental step to p-type doping. ZnO tends to form three-dimensional columns instead of two-dimensional films for its hexagonal wurtzite nature and the large mismatch (18%) between the ZnO film and the commonly employed sapphire substrate [9]. Consequently, many grain boundaries were resulted. It is accepted that dangling bonds, surface defects or some impurities will concentrate at the grain boundaries [10]. However, how the grain boundaries will affect the optical and electrical properties of the ZnO films has not been demonstrated clearly yet, although it is of vital significance and importance in obtaining high structural and optical quality ZnO [11–13].

In this paper, ZnO films have been prepared on sapphire substrates in a plasma-assisted molecular beam epitaxy (MBE) technique, and the dependence of the optical and electrical properties of the ZnO films on growth temperature was studied.

2. Experimental

The ZnO thin films were deposited on sapphire (α-Al_2O_3) substrates by a VG-V80H plasma-assisted MBE. The sapphire substrates were cleaned in an ultrasonic bath in ethanol for 5 min, acetone for 10 min, followed by de-ionized water rinsing for 5 min. Then the substrates were etched in H_2SO_4:H_3PO_4 = 3:1 at 160 °C for 15 min. Finally, the surface was washed with de-ionized water and blow dried using nitrogen. After chemical cleaning and etching, the substrates were heated at about 750 °C for 30 min in a preparation chamber to remove the possible adsorbed surface contaminations. Then the substrates were loaded into the growth chamber.

The precursor used for the ZnO film growth is elemental Zn (6N in purity) and radical O, note that the radical O was produced in a radio-frequency plasma cell with the operating power being fixed at 300 W. The O_2 flow rate was fixed at 3.0 sccm and the zinc precursor temperature at 245 ± 0.1 °C during the growth process. The background pressure in the chamber was less than 1×10^{-9} mbar, and the pressure was maintained at 1×10^{-5} mbar

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during growth. A series of ZnO films were grown on sapphire substrates at different temperature in the range from 500 to 900 °C. When the growth process was over, the samples were cooled down to room temperature at a slow rate of 0.3 °C/s to avoid any possible damages caused to the films due to the large thermal mismatch between ZnO and sapphire.

To characterize the structure of the films, a Rigaku O/Max RA X-ray diffractmeter (XRD) with the CuKα line of 1.54 Å as the radiation source was employed. The morphology of the films was observed by a field emission scanning electron microscope (SEM, Hitachi S-4800). Photoluminescence (PL) spectra were recorded in a JY-630 micro-Raman spectrometer using the 325 nm line of a He–Cd laser as the excitation source. Electrical characteristics of the films were studied in a Hall measurement system (LakeShore Company, Model 7707).

3. Results and discussions

Figure 1(a) displays the SEM image of the sample grown at 500 °C. A rough surface with many irregular nodes can be observed, and the cross-section image exhibits a loose structure with stubbles grown vertically on the substrate, that is there are many boundaries inside the films. Fig. 1(b) and (c) show the surface morphology of the samples grown at 600 and 700 °C, respectively. Much smoother surfaces have been acquired although a few crystallites still can be seen in these two patterns. The crystallites are roughly hexagonal-shaped, note that the hexagonal patterns on the surface are an aid to see the shape of the grains. Such hexagonal crystallites are thought to be individual ZnO columns [14]. The crystallites are almost undetectable when the growth temperature reaches 800 and 900 °C. Cross-section images show that the ZnO films grown at 800 and 900 °C are dense and almost boundary-free. One can see from the SEM image that the density of the grain boundary is decreased with increasing growth temperature.

To confirm the crystal structure of the samples, XRD patterns are shown in Fig. 2. Besides the diffraction from the sapphire substrate at 41.68°, only one peak can be observed in the pattern of each sample, and the peak can be indexed to the diffraction from (0 0 0 2) facet of wurtzite ZnO. Note the doublet peaks are the diffractions irradiated by the CuKα1 (1.5406 Å) and Kα2 (1.5444 Å) lines. The strong (0 0 0 2) diffraction peak indicates that ZnO films are all crystallized in wurtzite structure with a *c*-axis preferred orientation.

Room temperature PL spectra of the ZnO films are shown in Fig. 3, note that the spectra have been normalized according to the height of their near-band-edge (NBE) emission. All the spectra show sharp NBE emissions at about 3.28 eV and weak broad deep-level-related (DL) emissions at about 2.35 eV. One can see from the figure that with increasing the growth temperature, the intensity ratio between NBE and DL emission is greatly enhanced, as shown in Fig. 4. The variation of the NBE/DL with the growth temperature can be understood as follows: Just as we have noted, the density of grain boundary in the ZnO films decreases with increasing the growth temperature, and impurities and/or defects have a preferential accumulation at the domain boundaries [10,14]. These impurities or defects will capture carriers, thus quench the NBE emission and enhance the DL emission. As a result, the NBE/DL emission ratio increases with increasing the growth temperature.

Also shown in Fig. 4 are the Hall mobility data of the ZnO films grown at different temperature. The mobility changed a little while the growth temperature is below 700 °C, but increased greatly from 20 to 51 cm^2/VS when the growth temperature reaches 800 °C, then to 81 cm^2/VS at 900 °C, which is close to the highest mobility value (~100 cm^2/VS) predicted by Kawasaki and co-workers for ZnO films grown on sapphire substrate [15]. A noteworthy phenomenon is that the variation trend of the mobility with growth temperature is very similar to that of NBE/DL, which suggests to us that the Hall mobility may be affected by the same factor that causes the DL emission. Therefore, it is supposed that

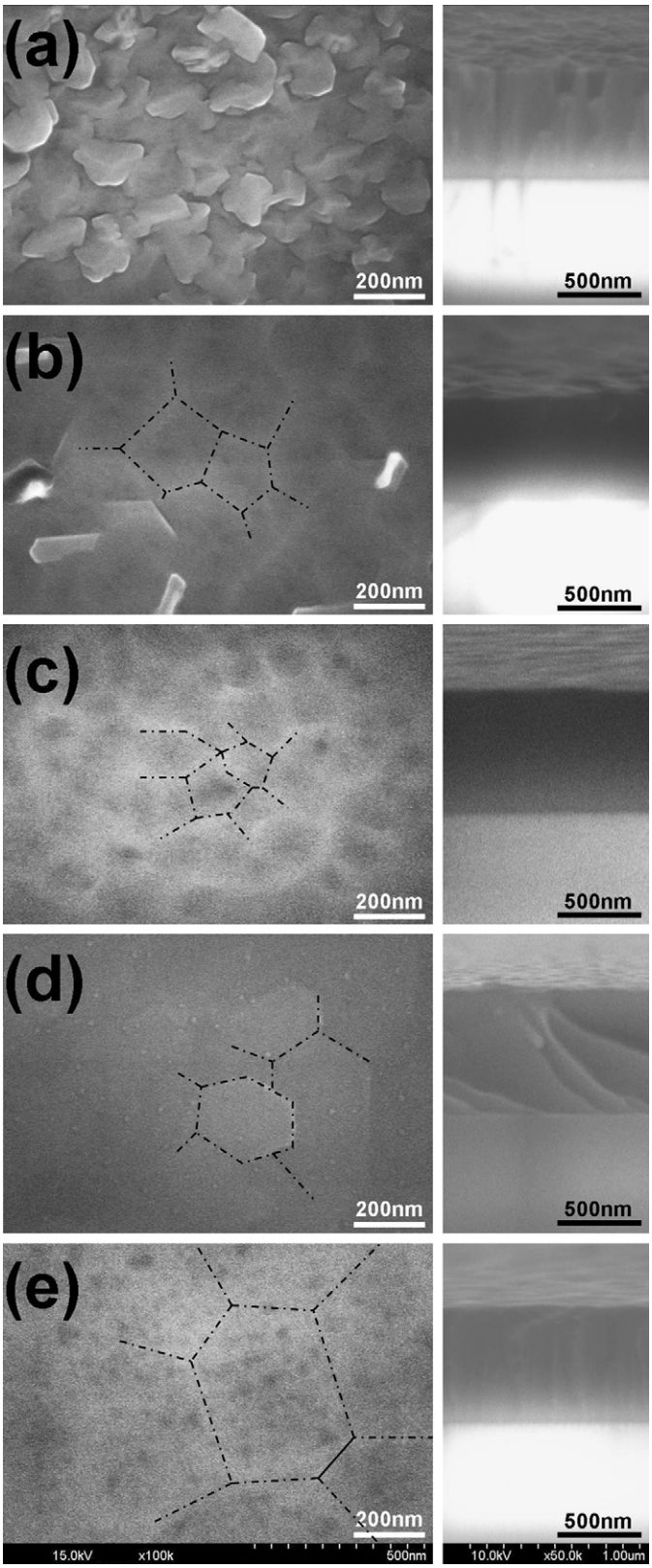

Fig. 1. Plan-view and cross-section SEM images of ZnO films grown at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C.

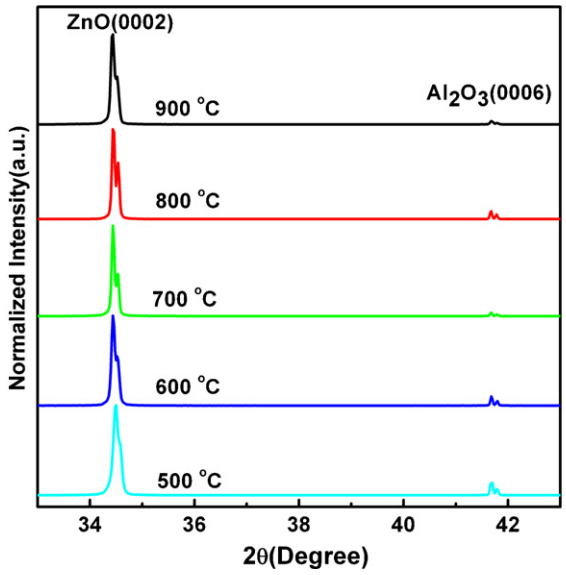

Fig. 2. XRD patterns of the ZnO films grown on sapphire substrates prepared at different growth temperature.

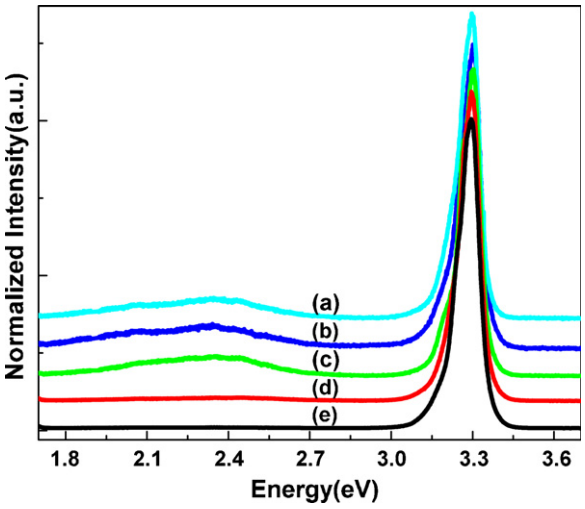

Fig. 3. Normalized PL spectra of the ZnO films grown at different temperature: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C.

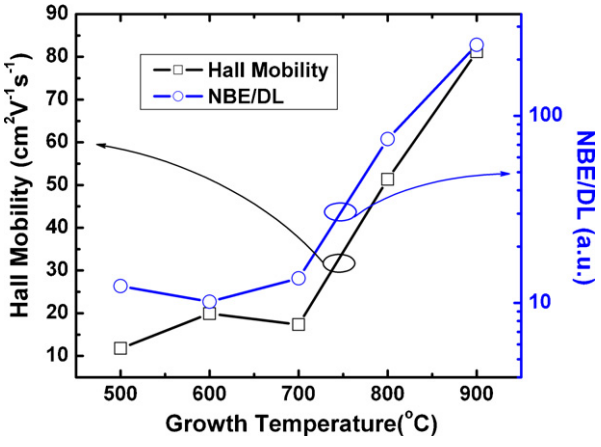

Fig. 4. The dependence of the Hall mobility and NBE/DL ratio of the ZnO films on the growth temperature.

the grain boundary may be the key factor that affects the mobility and DL emission of ZnO films. What corroborates our supposal is that Sun et al. have demonstrated theoretically that grain boundaries are dominant factor responsible for the very low carrier mobility in ZnO [16]. It is rational that grain boundary will exert great influence on the mobility of ZnO because the carriers in the films have to hop between the columns due to the existence of grain boundary. In the hopping process, the structural defects or adsorbed contaminations concentrated at the grain boundary will inevitably scatter the carriers. As a result, the mobility of the ZnO films is drastically decreased.

4. Conclusions

ZnO thin films have been prepared on sapphire substrates by MBE technique. It is found that with increasing growth temperature, the structural properties of the films have been improved. The carrier mobility and ratio of the emission from NBE and DL of ZnO is significantly enhanced, and the dependence of the carrier mobility and NBE/DL ratio on the growth temperature shows very similar trend. The trend is closely linked with the density of grain boundary, which suggests that the grain boundary may be a key factor affecting the electrical and optical properties of ZnO films. The results shown in this paper indicate that ZnO films with high optical and electrical properties, which is a significant step towards the p-doping of ZnO, may be obtained by reducing the grain boundaries, and higher growth temperature is favorable for reducing the boundaries.

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