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Optical property of hexagonal nanocrystalline zno film on Si substrate prepared by plasma-enhanced CVD

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Abstract

In this paper, a two-step low-temperature growth method is reported for the fabrication of ZnO film. Hexagonal nanocrystalline ZnO film has been grown on a Si(1 0 0) substrate by plasma-enhanced chemical vapor deposition (PECVD) at a comparatively low temperature of 150 °C. The X-ray pattern shows that the film has a *c*-axis preferential orientation in the (0 0 0 2) crystal direction. SEM image indicates the film with a thickness of 300 nm consists of nanocrystallites with hexagonal cross-section, and the diameters of the nanocrystallites range from 100 to 120 nm.Room temperature photoluminescence (PL) spectrum exhibits a strong ultraviolet emission and the defect-related emission is negligibly weak. Possible reasons for low-temperature growth of high-quality Si-based ZnO film are discussed.

Keywords: Two-step growth; Hexagonal ZnO nanocrystallite; PECVD; Photoluminescence

1. Introduction

ZnO has a wide direct band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV, which makes it a potential material for excitonic laser diodes and low-threshold semiconductor lasers in the ultraviolet (UV) region [1–3]. These applications all require high-quality epitaxial layers. In general case, ZnO thin films growth has been mostly performed on sapphire substrates [4,5]. Compared with sapphire, silicon wafers have several fundamental advantages. They are cheap, conductive, and easy to cleave. In particular, from the view of combination with advanced Si-microelectronics technology, ZnO growth on Si is very valuable. However, it is well known that direct growth of epitaxial ZnO films on Si is extremely tough because of the large lattice mismatch and difference in crystal structure between ZnO and Si.

In previous work, we have reported the method of nitridation of Si surface by NH_3 plasma to obtain high-quality ZnO thin films grown by plasma-enhanced chemical vapor deposition (PECVD) [6]. In the present paper, besides nitridation of Si surface, a two-step growth method by controlling the oxygen content in the source gas mixture during nucleation and growth step was carried out for the formation of ZnO film by PECVD. The morphological and structural properties were characterized in detail.

2. Experiments

ZnO film was deposited on silicon (1 0 0) wafer at a low temperature of 150 °C by employing PECVD system, which was introduced previously [6]. Diethylzinc (DEZn) was used as the Zn source, and high-purity Ar was used as carrier gas. High-purity CO_2 was served as oxygen source. Before deposition, Si substrate was heated to 150 °C, and ammonia gas was introduced into the plasma chamber to nitride the Si surface for 30 min. For the first step, an equal flux of DEZn and CO_2 was used to grow the first layer for 5 min. Then, CO_2 flow was reduced to 10% of the gas mixture and the growth of ZnO film was continued for 1 h. The sample grown by the two-step process was labeled

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sample A. As compared, sample B was prepared under the same growth conditions as the first step of sample A, except that growth time was prolonged to 1 h.

The crystalline quality of the ZnO films was examined by X-ray diffraction using a rotating anode X-ray diffractometer (Rigaku) with CuK_α radiation of 1.54 Å. The surface morphologies were studied using field-emission scanning electron microscope (SEM) and AFM. The micro-photoluminescence of the ZnO nanocrystalline films was recorded using a JY UV-Lamb micro-Raman spectrometer in a back-scattering geometric configuration. The excitation wavelength was the 325 nm line of a He–Cd laser.

3. Results

Fig. 1 shows the X-ray diffraction patterns of samples A and B. It indicates that both films possess a hexagonal wurtzite ZnO crystal structure. For sample B, except a strong (0 0 2) diffraction peak, several weak diffraction peaks could be found, such as (1 0 1) (1 0 2) (1 0 3). However for sample A, only one dominant (0 0 2) peak at $2\theta = 34.485^\circ$ is observed, while no other peaks appear. It implies that sample A strongly prefers *c*-axis orientation. And compared with sample B, the full-width half-maximum (FWHM) of the (0 0 2) peak of sample A reduces from 0.27° to 0.23°, which is comparable with the previously reported values from ZnO films grown by more sophisticated techniques such as molecular beam epitaxy (MBE) [4]. The XRD results indicate that the crystalline quality of sample A has been improved after the two-step growth process.

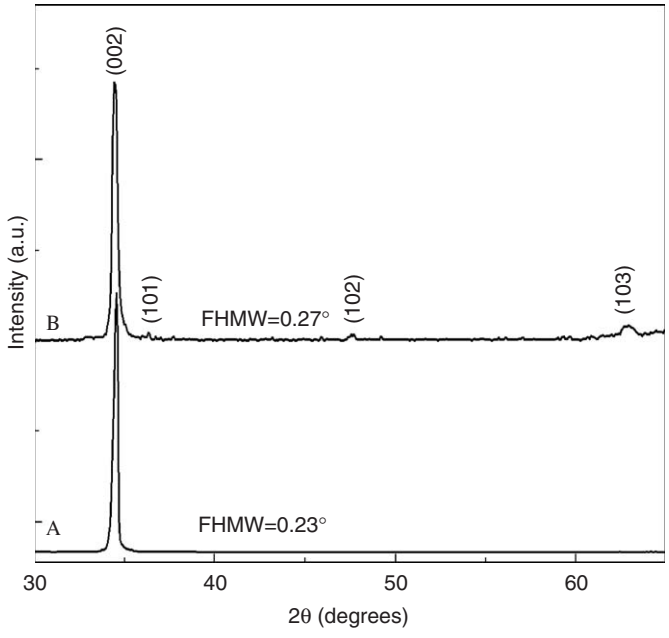

Fig. 1. The XRD patterns of the ZnO thin films at different growth processes, two step (a) and one step (b).

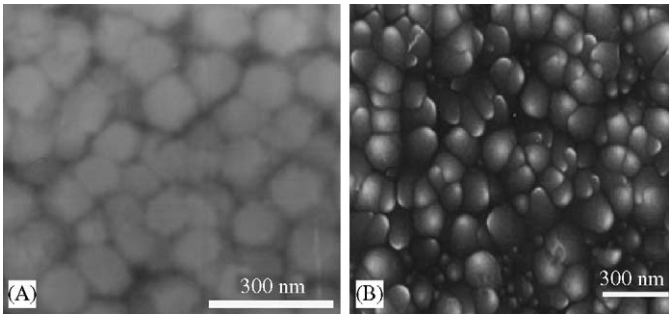

Fig. 2. SEM images of samples A and B.

Fig. 2 shows SEM images. Sample A consists of nanocrystallites with hexagonal cross-section. The diameters of the nanocrystallites have a basically uniform distribution, ranging from 100 to 120 nm.However, sample B is composed of irregular sized grains with the diameters in the range of 30–100 nm.The reduction of the average of ZnO grains corresponds to the increase of FWHM of the (0 0 2) peaks for sample B, which is consistent with the results from XRD patterns. The root mean square (RMS) surface roughness as determined by AFM ($2 \times 2\,\mu m^2$ area scans) (not shown here) is found to be 6.0 and 8.3 nm for samples A and B, respectively. The smoother surface is obtained for sample A, which implies that the film quality has been improved after two-step growth process.

Fig. 3 explicates the room temperature PL spectra of ZnO films grown by one-step and two-step process, respectively. It is remarkable that the near-band-edge (NBE) emission (located at around 3.26 eV) dominates the room temperature PL patterns, and the deep level (DL) emission is barely observable, as illustrated in Fig. 3. Sample A has a more intense UV emission intensity compared with sample B. The lineshape of the UV emission band for sample A is close to symmetric, whereas the UV emission band of sample B exhibits an asymmetric lineshape, with a tail on the low energy side. The FWHM of sample A decreases to 168 meV from 216 meV for sample B. These results accordingly imply the optical property of sample A has been improved.

In order to better understand PL property of sample A, PL spectrum measured at 81 K is shown in the inset Fig. 3. The strongest band, located at 3.299 eV, is tentatively attributed to one longitudinaloptical (LO)-phonon replica of the free excitonic emission. This is because the energy difference between this emission peak and its higher energy side shoulder, located at 3.370 eV, is 71 meV.The energy of 71 meV is similar to that of LO-phonon of ZnO [7]. Therefore, the higher energy side shoulder E_A (3.370 eV) is naturally assigned to the free exciton emission, whose value is consistent well with others reported [8]. The lower energy side of the strongest band arises three shoulders peaked at 3.223, 3.147 and 3.071 eV, respectively. The energy difference of each neighbor is close to LO-phonon energy of ZnO. Hence the three shoulders are attributed to phonon replicas of free excitons.

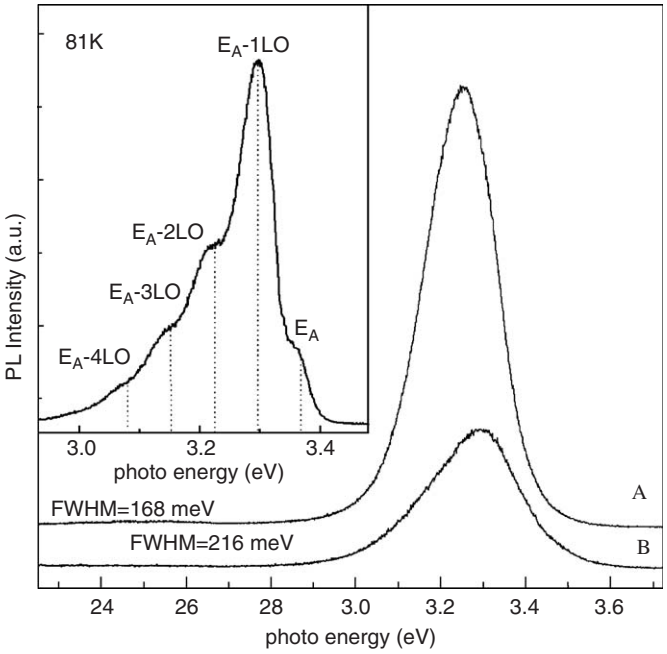

Fig. 3. Room temperature photoluminescence spectra of the ZnO thin films of samples A and B. The inset shows the near-band-edge emission at 81 K of sample A.

4. Discussions

From the above analysis, we can conclude that sample A exhibits higher qualities in structural, morphological and PL prosperities compared with sample B. The methodology of the two-step growth is derived from Ref. [9], where it is reported that sufficient oxygen is required for a high nucleation density. However, under oxygen-deficient condition, nucleation of ZnO on the bare substrate surface is difficult. Currently, a two-step growth method has been established by changing growth rate at different oxygen content in the gas mixture. In the first step, the amount of oxygen is enough to ensure a high nucleation density, and a seed layer is formed for the next growth. In the second step, the oxygen flow is reduced to form an oxygen-deficient condition. In this case, ZnO will grow preferentially on the pre-existing ZnO sites that have been formed during the first step. In addition, due to the faster vertical growth rate along *c*-axis compared to the lateral directions, hexagonal cross-section nanocrystalline ZnO film with *c*-axis as the preferential orientation is developed. But some slight cracks are observed from the image of SEM in the surface. The possible reason is that the effect of the density of seed layer on the substrate surfaces after the first step. Within a certain time period, the longer the first time is, the more ZnO nuclei form on the substrate surface. If the growth time of the first step is prolonged, one speculates that the cracks will decrease. Therefore, strictly speaking, we have obtained the film consisting of high areal density of hexagonal crystallite.

In present paper, a two-step growth method is different from that of the introduction of low-temperature buffer layers, which is based on changing the growth temperature in different growth phases. In general, the growth temperature of buffer layer is not lower than 400 °C, and the formal growth temperature is in the range 600–700 °C. However, we prepared high–quality ZnO film by using a two-step method at low temperature of 150 °C. The growth temperature decreases remarkably, which is very significant in applications of ZnO.

5. Summary and conclusion

ZnO films on a Si(1 0 0) substrate were prepared by PECVD at low temperature of 150 °C. The quality of ZnO nanocrystalline film is improved by employing a two-step growth. We have demonstrated high crystal quality with a *c*-axis preference, and a strong sharp NBE UV PL at 380 nm without evidence of extrinsic visible spectrum PL. The free exciton emission and four LO-phonon replicas dominated the UV band at the cryogenic PL spectrum. The results indicate that high-quality ZnO thin films can be obtained by the PECVD technique assisted by a two-step growth process at low growth temperature.

Acknowledgments

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