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Growth and properties of ZnO nanotubes grown on Si(1 1 1) substrate by plasma-assisted molecular beam epitaxy

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Abstract

ZnO nanotubes were epitaxially grown on a Si(1 1 1) substrate by plasma-assisted molecular beam epitaxy using a two-step process. First, a low-temperature ZnO layer was deposited on the Si substrate at a temperature of 300 °C, which was treated by an O_2^+-plasma for 30 min. Second, a ZnO layer that showed tubular-like nanostructure was grown on this treated layer at 550 °C using the same flow rate of the O_2 and zinc. No catalyst or templates were required for the formation of the ZnO nanotubes. Field-emission scanning electron microscopy (SEM) and X-ray power diffraction (XRD) experiments showed that the ZnO nanotubes were single crystals of pure hexagonal wurtzite structure growing along the [0 0 0 2] direction. The diameters of the nanotubes were in a range of 10–90 nm, and the average size of the nanotubes was 50 nm. Room-temperature photoluminescence (PL) measurements of the ZnO nanotubes showed ultraviolet peaks at 3.290 eV with a full-width at half-maximum (FWHM) of 104 meV, which was comparable to those found in high-quality ZnO films. The PL spectrum at 81 K showed a sharp free-exciton emission with an FWHM of 22.1 meV. The SEM, XRD and PL results indicated that the prepared ZnO nanotubes have potential applications in optoelectronic devices. Possible reasons for the growth of ZnO nanotubes were discussed.
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1. Introduction

Zinc oxide is a well-known direct wide band-gap wurtzite-type semiconductor with a large band-gap energy of 3.37 eV at room temperature. It is an excellent semiconductor material as a potential replacement for other wide band-gap materials like GaN and SiC. Furthermore, due to its large exciton binding energy of 60 meV, the excitons in ZnO are thermally stable at room temperature, and thus ZnO has significant advantages in optoelectronic applications, such as UV lasing. Optically pumped stimulated emissions have been demonstrated in ZnO films [1,2]. The traditional problem in ZnO is to obtain p-type conductivity. Recent researches indicate great progress in the growth and understanding of p-type ZnO layers, which suggest the potential of ZnO in applications as electronics and optoelectronic devices [3–6]. One-dimensional nanoscale semiconductor materials, especially one-dimensional materials of ZnO, are of interest due to their remarkable physical and chemical properties. This study will result in further understanding of some basic scientific properties of ZnO nanomaterials.

Owing to their promising uses in electronic and optical devices, various one-dimensional nanomaterials of ZnO with different morphologies, including nanotubes [7], nanowires [8], nanorods [9] and nanobelts [10] have increasing drawn attention. Different fabrication methods have been reported for the ZnO one-dimensional nanostructures. The vapor transport process with the assistance of catalysts and/or templates, such as Au [11], Co [12], carbon nanotubes [13], etc., has been commonly used method. The major advantage of this process is the controllable growth of the ZnO nanostructures, but the main disadvantage is the remains of the foreign catalyst and template, which may influence the purity of the ZnO nanostructure. Zhang et al. [7] obtained ZnO nanotubes of high qualities on a sapphire (0 0 1) substrate by MOCVD, but sapphire is not conductive and also relatively expensive, which may pose a serious limitation for the application of the nanotubes in optoelectronic devices. Si wafers, as a conductive and low-cost material, are an optimal substrate, and they also provide the potential for integration of the nanotubes with silicon-based devices.

In this paper, we report the growth and properties of ZnO nanotubes grown on Si(1 1 1) substrates by plasma-assisted molecular beam epitaxy (P-MBE) without any catalyst or template, thereby avoiding potential problems with the "purity" of the ZnO nanotubes.

2. Experiment

ZnO nanotubes were deposited on a Si(1 1 1) substrate by P-MBE. The Si(1 1 1) substrate was cleaned with ethanol for 5 min, acetone for 10 min, followed by ethanol for an additional 5 min. Next, the surface oxidized layer was etched with $H_2SO_4{:}H_2O_2$ (3:1) for 10 min, $HF{:}H_2O$ (1:20) for about 1 min, $HCl{:}HNO_3$ (3:1) for 10 min and then with $HF{:}H_2O$ (1:20) for about 1 min. Finally, the surface was washed with de-ionized water and blow dried in dry nitrogen. Elemental Zn with a purity of 6 N and O_2 gas with 5 N purity were used as groups II and VI sources, respectively. After chemical cleaning and etching, the substrate was then heated for 5 min at 300 °C to remove contamination and then thermally cleaned at about 650 °C for 30 min. Then the substrate was inserted into the growth chamber.

Atomic oxygen was produced from ultrapure O_2 gas with 5 N purity by an Oxford Applied Research RF (13.56 MHz) plasma source with an electrostatic ion trap (EIT) operated at 500 V during growth. If the EIT is opened during growth, only the atomic oxygen reaches the surface of the substrate; if not, the O_2^+-plasma also reaches the substrate surface. In this work, a low-temperature ZnO thin layer was firstly deposited on the Si(1 1 1) substrate at 300 °C for about 200 s at the substrate temperature of 300 °C, Zn flux at 1×10^{-6} mbar, and O_2 flow rate at 1 sccm with the EIT open. Then, the EIT was closed and the ZnO thin layer was treated with an O_2^+-plasma for 30 min. Finally, with the EIT open, a ZnO layer that showed tubular-like structure was grown on this treated thin layer at 550 °C for 2 h with the same flow rate and flux of the O_2 and zinc.

To characterize the crystal structure of these nanotubes, X-ray power diffraction (XRD) experiments were performed using a D/maxrA X-ray diffraction spectrometer (Rigaku) with a CuKα line at 1.54 Å. Field-emission scanning electron microscope (SEM) measurements were also conducted to investigate the surface morphology of the sample. For the optical characterization, photoluminescence (PL) spectra were measured in the wavelength range of 350–625 nm at room temperature and at 81 K. The 325-nm line of a He–Cd laser operated at a power of 50 mW was used as the excitation source.

3. Results

Fig. 1 shows typical SEM images of the ZnO nanotubes grown on the Si substrate. From Fig. 1(a), which shows the top images of the sample, it is seen that all of the ZnO nanotubes have hexagonal shapes with a density of about 1×10^8 cm^{-2}. Figs. 1(b) and (c) show the SEM images with an inclination angle (45°) with respect to the nanotubes. The nanotubes show a regular alignment, which is preferentially vertical with a divergence of less than $\pm 30°$ on the Si(1 1 1) substrate, and the nanotubes have a uniform lateral size in a range of 10–90 nm.

Fig. 2 shows the crystal structure and orientation of the ZnO nanotubes grown on the Si(1 1 1) substrate, which was determined by making $\theta - 2\theta$ scans. Seven main peaks appear at $2\theta = 28.44°$, $31.77°$, $34.42°$, $36.24°$, $47.52°$, $62.90°$ and $67.96°$, which are the weak Si(1 1 1) substrate peak, the (1 0 1) ZnO peak, the (0 0 2) ZnO peak, the (1 0 1) ZnO peak, the (1 0 2) ZnO peak, the (1 0 3) ZnO peak and the (1 2 2) ZnO peak, respectively. In the XRD spectrum, very weak peaks corresponding to the Si substrate can also be observed, indicating formation of a substantial number of nanotubes covering most of the substrate. The XRD spectrum reveals that the as-synthesized products are the pure hexagonal wurtzite phase of ZnO with lattice constants of $a = 3.25$ Å and $c = 5.20$ Å. It is worth noting that the peak intensity of the (0 0 2) plane is much higher than for other orientations. The full-width at half-maximum (FWHM) of
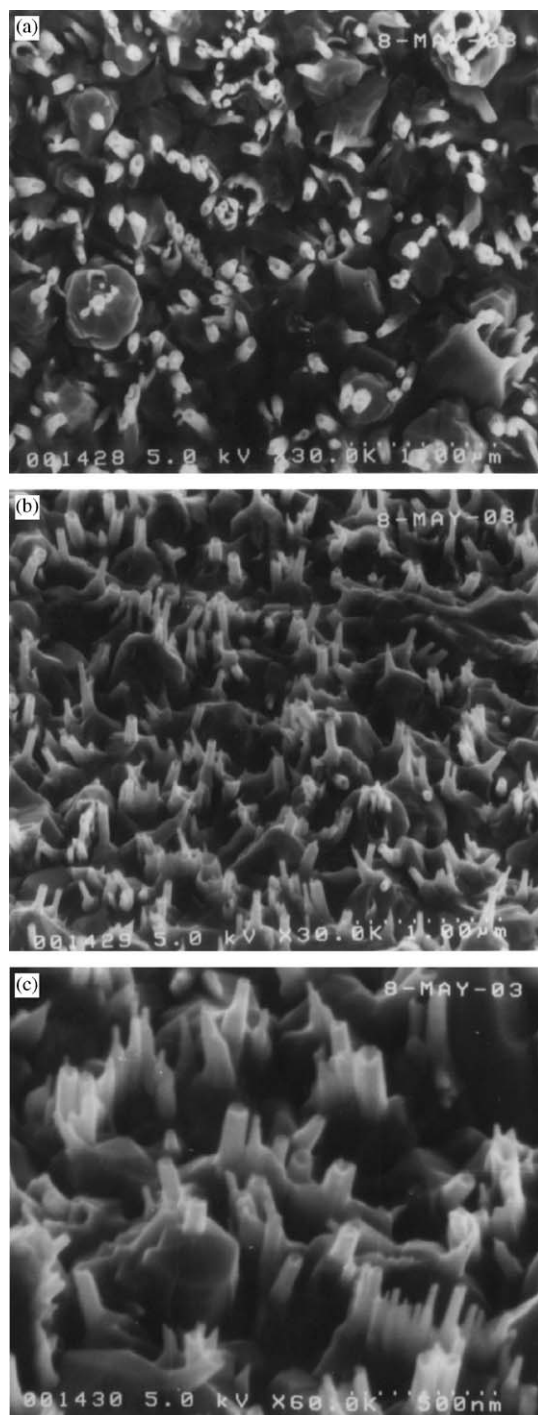

Fig. 1. FE-SEM of ZnO nanotubes grown on Si(1 1 1) substrate by P-MBE. The top image of the sample is shown in (a), an image with an inclination angle of 45° is shown in (b), and an enlarged image with an inclination angle of 45° is shown in (c).
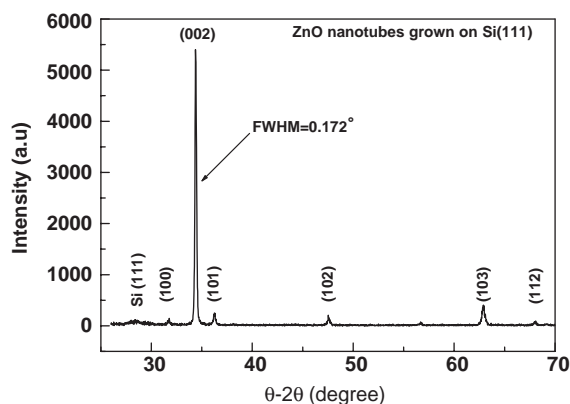
Fig. 2. XRD pattern of ZnO nanotubes grown on Si(1 1 1) substrate by P-MBE.

Fig. 3. PL spectrum of ZnO nanotubes grown on Si(1 1 1) at room-temperature substrate by P-MBE.

(0 0 2) is only 0.172°. According to the Scherrer formulation [14], the mean grain size of the sample is 50 nm. All these results are consistent with the aligned growth of ZnO nanotubes on the Si(1 1 1) substrate, and their preferential growth along [0 0 0 2] direction with a diameter in the range of 10–90 nm, as demonstrated by SEM. Both the SEM image and XRD pattern demonstrate good crystal quality of the ZnO nanotubes on the Si(1 1 1) substrate grown by P-MBE via treating a low-temperature ZnO layer by an O_2^+-plasma.

Fig. 3 shows the PL spectrum for ZnO nanotubes deposited on the Si(1 1 1) substrate at room temperature. An intensive near-band UV emission centered at 3.290 eV is shown for the prepared samples. The FWHM height is 104 meV. The UV emission is ascribed to the recombination of the free exciton. Further results on this peak will be published elsewhere. The deep-level emission occurs around 2.4–2.5 eV. It is caused by the intrinsic defects in ZnO nanotubes grown on Si(1 1 1) substrate, and the PL intensity is much weaker than the UV emission. The weak deep-level emission and dominant exciton emission suggest that the ZnO nanotubes have a low density of defects and high optical qualities.

Fig. 4 shows the PL spectrum at a temperature of 81 K for ZnO nanotubes deposited on the Si(1 1 1) substrate. There are five near-band-edge emissions located at 3.370, 3.315, 3.242, 3.170 and
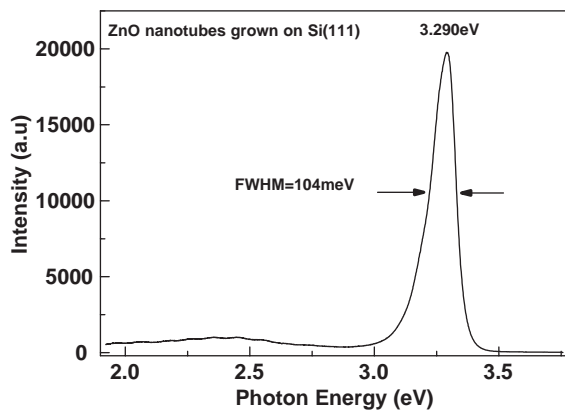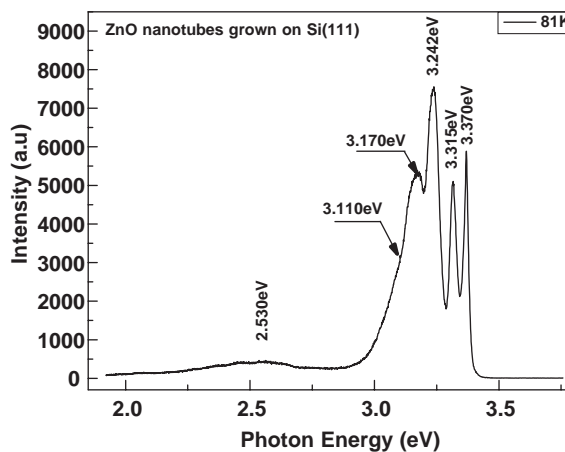

Fig. 4. PL spectrum of ZnO nanotubes grown on Si(1 1 1) substrate at the temperature of 81 K by P-MBE.

3.110 eV with a weak deep-level emission located at 2.5–2.6 eV. The strong emission line located at 3.370 eV has an FWHM of 22.1 meV. In view of its energy position, the line at 3.370 eV can be assigned to the free-exciton emission, and the emission observed at 3.315 eV can be assigned to the bound excitonic emission at neutral donors. The 3.315 eV peak is accompanied by two phonon replicas observed at 3.242 and 3.170 eV. A shoulder on the low-energy side of the near-band-edge emission at 3.110 eV should be assigned

to the bound excitonic emission at neutral acceptors. More detailed studies will be discussed later. The above results of ZnO free-exciton emission at 81 K with a narrow FWHM of 22.1 meV indicate that high-quality ZnO nanotubes have been grown on the Si(1 1 1) substrate by P-MBE using the treatment process of the low-temperature ZnO layer by an O_2^+-plasma.

4. Discussion

The possible growth mechanism for the ZnO nanotubes on the Si(1 1 1) substrate by P-MEB is assigned to the treatment process of the low-temperature ZnO layer by the O_2^+-plasma. In our previous work [15], the same low-temperature ZnO layer was introduced as a buffer to improve the quality of ZnO thin films grown on the Si(1 1 1) substrate by P-MBE, which can reduce the effects of the oxide layer on the Si surface and the lattice mismatch on the quality of the ZnO films. In the case with the EIT open through the whole growth process, the low-temperature ZnO buffer layer was not treated by the O_2^+-plasma and the quality of ZnO films was greatly improved. No ZnO nanotubes were observed on the Si(1 1 1) substrate. So, we can conclude that it is the treatment process of the initial low-temperature ZnO layer by the O_2^+-plasma that is crucial for the growth of ZnO nanotubes on Si(1 1 1) substrate. Moreover, we have fabricated well-aligned ZnO nanotubes on the sapphire substrate using the same treatment process involving a low-temperature O_2^+-plasma [16].

Because of the difference in the thermodynamic stability of the polarity surface and nonpolarity surface of the material, which makes the migration abilities of atoms differ, the surface with high stability is unfavorable to atomic migration. So atoms on the (0 0 2) surface are the more stable since the (0 0 2) face of ZnO is more stable than other faces. When the low-temperature ZnO layer which is grown on the Si(1 1 1) surface by the Stranski–Krastanow (S–K) model is treated by O_2^+-plasma, the atoms of the (0 0 2) ZnO surface are unfavorable to move compared to the atoms of other surfaces. A ring-like structure formed on the Si(1 1 1) surface, which was observed from the initial images presented elsewhere [16]. It is this ring-like structure, which provides a good "template" that allows the formation of the ZnO nanotubes on Si(1 1 1) substrate. Though the detailed dynamics are not clear, we can conclude that ZnO nanotubes can be obtained by the treatment process, which provides the ring-like "template" structure studied by our experiments. ZnO nanotubes with high density, preferred orientation, smooth morphology, well structure, and high optics could be obtained via optimizing the growth condition, such as changing either the growth temperature, the thickness of the low-temperature ZnO layer, or the treatment time, etc.

5. Conclusion

Pure hexagonal wurtzite structure ZnO nanotubes with a diameter of $\sim$50 nm were epitaxially grown on a Si(1 1 1) substrate by P-MBE via a treatment process involving a low-temperature ZnO layer and O_2^+-plasma. The treatment process provided a "template" for the growth of ZnO nanotubes on the Si(1 1 1) substrate, and played a crucial role in the formation of ZnO nanotubes on the Si(1 1 1) substrate. Possible reasons for the growth of ZnO nanotubes were discussed. The ZnO nanotubes showed good structural and optical qualities as characterized by SEM, XRD and PL measurements. The observation of the free-exciton emission for ZnO nanotubes at 81 K with a narrow FWHM of 22.1 meV strongly suggested that the nanotubes were of high optical quality. These nanotubes can potentially be used in various devices, such as energy-storage devices, solar cells and gas sensors, and the nature of the hexagonal cross section suggests high potential as photon micro-cavities.

Acknowledgements

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