Preparation of nanocone ZnO thin film and its aging effect of photoluminescence

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A B S T R A C T

In this work, a nanocone ZnO thin film was prepared by electron beam evaporation on a Si (1 0 0) substrate. The structural properties of the film were investigated by X-ray diffraction (XRD), atomic force microscopy and laser Raman scattering, respectively. The aging effect of the nanocone ZnO thin film was studied by photoluminescence spectra. The structural analyses show that the prepared ZnO thin film has a hexagonal wurtzite structure and is preferentially oriented along the c-axis perpendicular to the substrate surface. The photoluminescence spectra show that with the increase of aging time, the green emission of the nanocone ZnO thin film gradually decreases while the ultraviolet emission somewhat increases. The reason for this phenomenon is likely that the green-emission-related oxygen vacancies in the film are gradually filled up. The Raman scattering analyses also suggest that the intensity of the Raman peak related to oxygen vacancies in the nanocone ZnO thin film declines after the film is aged in air for a year. Therefore, the authors think the green emission is mainly connected with oxygen vacancy defects.

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1. Introduction

ZnO is a II–VI group wide band-gap compound semiconductor. At room temperature, it has a wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV. Many experimental results show that ZnO has an excellent excitonic emission performance, so it is an ideal material for the fabrication of short-wavelength optoelectronic devices, especially for the fabrication of ultraviolet light-emitting devices such as ultraviolet light-emitting diodes, ultraviolet lasers, etc. ZnO materials usually show two luminescent regions: a narrow ultraviolet peak and a wide green emission band. For the ultraviolet emission, it is generally attributed to transition of electrons between valence band and conduction band or/and recombination of free excitons [1,2]. However, for the green emission, although lots of researchers studied the green emission of ZnO by experiments or theoretical analyses, the green emission mechanism is controversial as yet. Some researchers think that the green emission is connected with oxygen vacancy defects [3–5], some researchers ascribe the green emission to the electron transition from the bottom of the conduction band to the antisite

defect O_{Zn} level [6,7], and others think the green emission is associated with oxygen interstitial defects [8]. For the fabrication of ultraviolet light-emitting devices based on ZnO materials, it is necessary to deeply investigate the stability of luminescent performance and the green emission mechanism of ZnO materials.

In regard to the study of ZnO materials, although many ZnO nanostructures such as nanorods, nanotubes, nanowires, nano-belts, etc. have been prepared, ZnO thin films are still the materials which are investigated most deeply and most extensively. Due to the difference in deposition techniques and preparation conditions, the prepared ZnO thin films will possess different structures including dense thin films, porous thin films and nanostructured thin films. Among these, the nanostructured ZnO thin films attract much attention due to some special features like larger surface area, stronger gas adsorption performance, etc. They can be used in various applications such as light-emitting devices, biosensors, gas sensors, solar cells, etc. In this work, we prepared the nanocone ZnO thin film by electron beam evaporation on a Si substrate and mainly investigated its aging effect by photoluminescence.

2. Experiment

The ZnO thin film was prepared by electron beam evaporation (PMC90S, Protech Korea Ltd.) on a Si substrate. High purity

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(99.999%) ZnO particles were used as source materials. The substrate material is Si (1 0 0). Before deposition of the ZnO thin film, the Si substrate was thoroughly cleaned. The deposition chamber was pumped down to 2.66×10^{-3} Pa before deposition of the film, then Ar (18 sccm) and O_2 (50 sccm) were introduced into the chamber (working pressure: 2.67×10^{-2} Pa). The electron gun voltage and working current were 7.11 KV and 78 mA, respectively. A quartz crystal thickness controller was used to control the thickness of the film. The thickness of the prepared ZnO thin film was ∼300 nm. The film was annealed at 800 °C in air for an hour. In order to study the aging effect of photoluminescence of the film, it was cut into two pieces. One of them was sealed in a plastic bag which was evacuated in order to reduce its oxygen content and placed into a cool and dry chamber; the other was placed on a glass-surface vessel in air at room temperature. After they were aged for six and twelve months, their photoluminescence spectra were recorded, respectively.

The crystalline orientation and crystal phase of the film were investigated by an X-ray diffractometer (Bruker D8 Advance). The surface morphology of the film was observed by an atomic force microscope (CSPM4000) in contact mode. The structural feature was determined by laser Raman scattering. The photoluminescence spectra were employed to investigate the aging effect of the film. The excitation source was a Xe lamp and the excitation wavelength was 325 nm. All the measurements were performed at room temperature in air.

3. Results and discussion

3.1. The microstructure of the prepared ZnO thin film

Fig. 1 shows the X-ray diffraction pattern of the prepared ZnO thin film. From this pattern, it can be seen that there is only one peak located at 34.5°, which corresponds to the diffraction of the (0 0 2) plane of ZnO with a wurtzite structure. This shows that the prepared ZnO thin film has a hexagonal wurtzite structure and is preferentially oriented along the c-axis perpendicular to the substrate surface. Fig. 2(a) and (b) are the two-dimensional and three-dimensional surface morphologies of the film. From Fig. 2(b), it is clear that the surface of the film is covered with dense and uniform nanocone ZnO grains whose average height is about 50 nm. These ZnO nanocones are all grown perpendicular to the substrate surface, which is in agreement with the XRD analysis. The formation of the nanocone structure mainly results from annealing treatment. The evolution of the surface morphology originating from annealing treatment will be reported elsewhere.
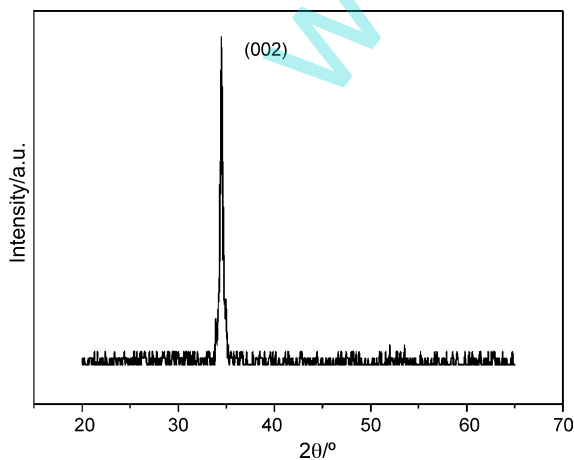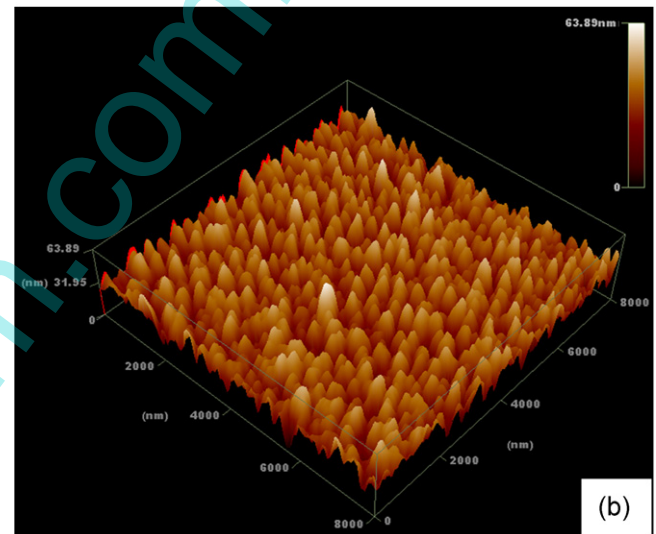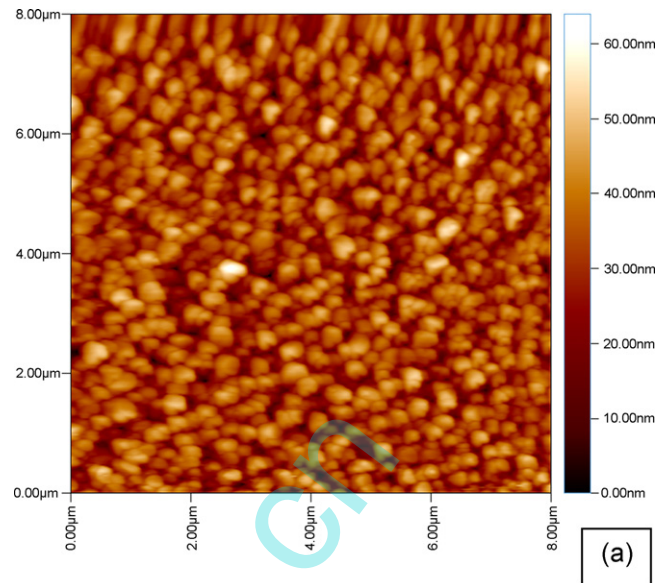

Fig. 1. XRD pattern of the prepared ZnO thin film.

Fig. 2. Two-dimensional (a) and three-dimensional (b) surface morphology of the prepared ZnO thin film.

3.2. The aging effect of photoluminescence of the nanocone ZnO thin film

The luminescence property of ZnO thin films is always an important aspect for the study of ZnO materials. In particular, for the green emission of ZnO, many researchers carried out relatively systematical experimental studies in order to have more knowledge of green emission mechanism. Some researchers investigated the influence of different annealing temperatures on the green emission [9,10], some researchers investigated the influence of different annealing atmosphere on the green emission [11,12], and others investigated the influence of doping on the green emission [13]. Although most of researchers all think the green emission is connected with oxygen-related defects such as oxygen vacancy, oxygen interstitial and oxygen antisite, its emission mechanism is in dispute as yet.

In this work, we mainly studied the effect of aging time on the photoluminescence of the nanocone ZnO thin film. In order to distinguish the aging effect under oxygen-surplus condition from that under oxygen-deficient condition, we stored the samples in different ways which has been described in experiment section.
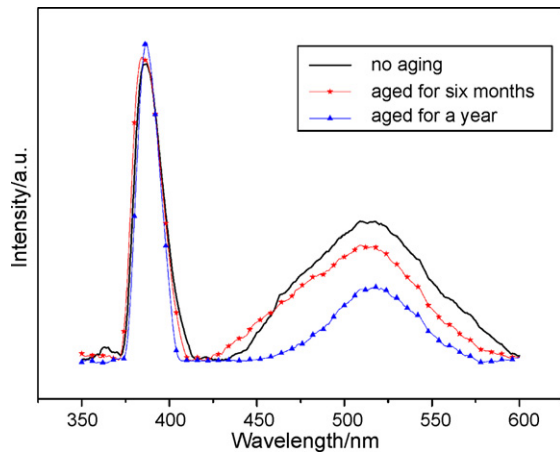
Fig. 3. Photoluminescence spectra of the nanocone ZnO thin film.

Fig. 3 shows the photoluminescence spectra of the nanocone ZnO thin film which was placed on a glass-surface vessel for aging. It is clear that the nanocone ZnO thin film has a strong ultraviolet emission peak centered at 385 nm or so and a wide green emission band. With the increase of aging time, the green emission gradually decreases while the ultraviolet emission somewhat increases, which is similar to the result reported by Shan et al. [12,14]. However, for the hermetically stored sample, the intensity of its green and ultraviolet emission hardly changed with the increase of aging time. Its photoluminescence spectra are not shown here. This means that in different aging environments, the density of defects leading to the green emission was changed differently. We speculate that the green emission is mainly connected with oxygen vacancy, because the density of oxygen interstitial and oxygen antisite could not vary so much without thermal activation energy. Some research results show that states near the surface of the film play an important role in the luminescence [15]. In this work, the ZnO thin film was annealed at 800 °C. The high annealing temperature made many oxygen atoms on the surface of the film desorbed, which resulted in numerous oxygen vacancy defects in the film. In the aging process, due to the larger surface area and stronger gas adsorption ability of the nanocone ZnO thin film, oxygen molecules in air can be absorbed on the surface of the film and some gradually penetrated into the film [16]. As a result, some oxygen vacancies near the film surface were filled up, which led to the intensity of the green emission gradually decreased. But the absorbed oxygen is hard to penetrate into the deeper location of the film; therefore, the ZnO thin film still keeps a certain intensity of green emission. It is worthy to note that Lord et al. [17] studied the aging effect of electrical property of As-doped ZnO thin films. They found that the resistivity of the films was much changed after aged for a period of time. Lord et al. [17] think that the large change of the resistivity mainly results from the fast decrease of oxygen vacancies in the As-doped ZnO thin films in aging process. This conclusion is in agreement with our results. From the above results, it can be known that with the prolonging of aging time, the ultraviolet emission of the ZnO thin film is stable while the green emission is unstable. Therefore, under common conditions, ZnO materials are suitable for the fabrication of ultraviolet light-emitting devices and unsuitable for the fabrication of green light-emitting devices.

3.3. Raman scattering spectra of the nanocone ZnO thin film

Fig. 4 displays the Raman scattering spectra of the nanocone ZnO thin film aged in air. The light source is an Ar$^+$ laser with a wavelength of 514.5 nm. Due to a strong Raman peak at 520 cm^{-1}
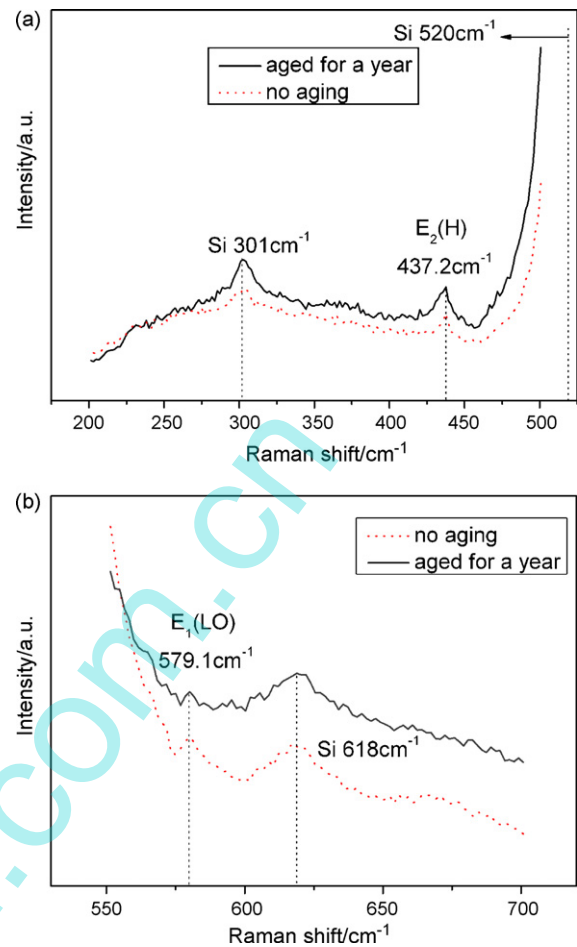

Fig. 4. Raman scattering spectra of the nanocone ZnO thin film.

of single crystal Si, the Raman scattering spectra were measured in two regions: 200–500 cm^{-1} and 550–700 cm^{-1}. From Fig. 4 (a), it can be seen that in the range of 200–500 cm^{-1} there are two Raman peaks. One of them lies at 301 cm^{-1}, belonging to the Si substrate; the other lies at 437.2 cm^{-1} which corresponds to $E_2(H)$ mode of ZnO. The $E_2(H)$ mode is the band characteristic of wurtzite-structured ZnO [18] and its Raman peak intensity is connected with the crystalline quality of the ZnO thin film. From Fig. 4, it is clear that after the film is aged in air for a year, the peak intensity of $E_2(H)$ mode is enhanced, which means that the crystalline quality of the film is improved to some extent. In the range of 550–700 cm^{-1}, there are also two Raman peaks. The peak at 618 cm^{-1} belongs to the Si substrate. The other peak at 579.1 cm^{-1} corresponds to $E_1(LO)$ mode of ZnO. The $E_1(LO)$ mode is related to some defects such as oxygen vacancy and zinc interstitial [18,19]. After the film is aged in air for a year, the peak intensity of $E_1(LO)$ mode obviously declines; this phenomenon also occurred in the study of Yang et al. [20]. It means the density of defects in the film dropped. Considering the results of photoluminescence, we think the reduced defects are mainly oxygen vacancies.

4. Conclusion

The green emission is the most common visible emission of ZnO thin films. If one wants to fabricate stable ZnO-based short-wavelength optoelectronic devices such as ultraviolet light-emitting diodes, ultraviolet lasers, etc. he has to effectively control the green emission. However, if he wants to effectively control the green emission, he has to get a good knowledge of the green

emission mechanism first. Although some models on the green emission mechanism have been suggested, it is still in dispute as yet. In this work, the aging effect of photoluminescent behavior of the nanocone ZnO thin film shows that the green emission is related to oxygen vacancy defects. This result is helpful to deeply understand the green emission mechanism of ZnO materials. In view of the complexity of the green emission mechanism of ZnO, we are carrying out further aging experiments—we store the nanocone ZnO thin films in N_2, O_2 and water, respectively, and then study the aging effect of their photoluminescence. These aging experiments on ZnO thin films are important for deepening the understanding of the green emission mechanism.

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