

Relationship between Crystal Structure and Photoluminescence Properties of ZnO Films Formed by Oxidation of Metallic Zn

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ZnO nanowires were formed on ZnO films by the oxidation of Zn at a temperature of 600 °C in air. The maximum intensities of the (002) and (101) diffraction peaks were observed for the ZnO film with nanowires on its surface. The finding that the intensities of the (002) and (101) peaks simultaneously exhibited maximum values conflicts with the conventional XRD patterns reported in many other studies on ZnO films. The highest intensity of the (002) peak results from the better crystalline quality than films prepared at other oxidation temperatures, and the highest intensity of the (101) peak is attributed to the higher density of nanowires. In addition, the ZnO film with nanowires exhibited the strongest UV emission intensity.

Keywords: zinc oxidation, zinc oxide film, nanowires, oxidation temperature, surface morphology, crystal structure

1. INTRODUCTION

ZnO is a II-VI semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, making it one of the most attractive materials for potential application in optoelectronic devices such as ultraviolet light emitting diodes and diode lasers. In addition, ZnO exhibits a n-type characteristic with a large free electron concentration originating from native defects such as oxygen vacancies and zinc interstitials. Owing to its high electrical conductivity and high optical transparency it is suitable for transparent conductive oxide films utilized as the front electrodes in thin film solar cells.^[1-3] Recently, it has been suggested that use of a nanostructured substrate yields improved performance in solar cells, as it enhances the carrier transfer from the active region to the contacts. In particular, vertical nanowire arrays are superior to nanoparticle films with respect to electron transport to the substrate electrode. Thus, the preparation of ZnO nanowires on ZnO electrodes has attracted growing attention in relation to solar cell devices.^[4-6]

Many methods such as metal organic chemical vapor deposition,^[7] pulse laser deposition,^[8] magnetron sputtering,^[9] a sol-gel method,^[10] and electrodeposition^[11] have been used to produce ZnO nanowires. Recent reports have also described the fabrication of high quality ZnO films via thermal oxidation of metallic Zn,^[12,13] a straightforward method with low cost. Thus, the preparation of ZnO nanowires on ZnO films by low temperature oxidation of Zn can be an effective

approach for fabricating high efficiency solar cells.

In this paper, we report on the formation of ZnO nanowires on a ZnO film upon oxidation of metallic Zn in air in a temperature regime as low as 450°C, and the relationship between the crystal structure and the photoluminescence properties of the ZnO films is elucidated.

2. EXPERIMENTAL PROCEDURE

ZnO films were prepared by oxidation of metallic Zn films deposited by thermal evaporation of Zn. The thermal evaporator consisted of a vacuum chamber, a diffusion pump, and a rotary pump. After evacuating the vacuum chamber to 1×10^{-6} Torr, the deposition of Zn was conducted onto a sapphire (0001) substrate via its evaporation at RT to form a Zn film. During the evaporation of Zn, the pressure was kept below 5×10^{-6} Torr. The distance between the zinc source and the substrate was 16 cm. In order to form a Zn film, a W boat containing the metallic Zn source was heated with a current of 40 A. The thickness of the deposited Zn films was about 200 nm. After depositing the Zn films, the substrates with Zn films were placed in an alumina crucible and the crucible was inserted into the center of an electric furnace for oxidation of the specimens. The oxidation was performed in a temperature range of 300°C to 900°C for 1 h under atmospheric pressure in air. After thermal oxidation, the samples were cooled to RT. The crystal structures of the films were analyzed by X-ray diffraction (XRD) using Cu-K α radiation operated at 40 kV and 30 mA. The surface morphologies and components of the oxidized Zn films were characterized

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using a scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) spectroscope, respectively. The photoluminescence (PL) at RT was measured using a He-Cd laser with a wavelength of 325 nm as an excitation source.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns were taken to examine the crystal structure of the films. Figure 1 shows the XRD patterns of the films prepared by the oxidation of Zn films at temperatures of 300°C, 450°C, 600°C, 750°C, and 900°C. The diffraction patterns for the oxidized films could be indexed to a hexagonal wurtzite structure of ZnO. For the film oxidized at 300°C, mixed peaks reflecting Zn and ZnO were observed, indicating incomplete oxidation of Zn. The peaks from Zn exhibit that the Zn film is in a polycrystalline phase with a hexagonal close packed crystal structure. After oxidation at a temperature over 450°C, metallic Zn is completely oxidized into ZnO with a hexagonal wurtzite structure. No peaks from Zn are detected in the patterns. The lattice parameters of ZnO calculated from the diffraction peaks are $a = 0.324$ nm and $c = 0.519$ nm, which are in good accordance with those of ZnO single crystal. This is indicative of high quality ZnO films. On the other hand, as shown

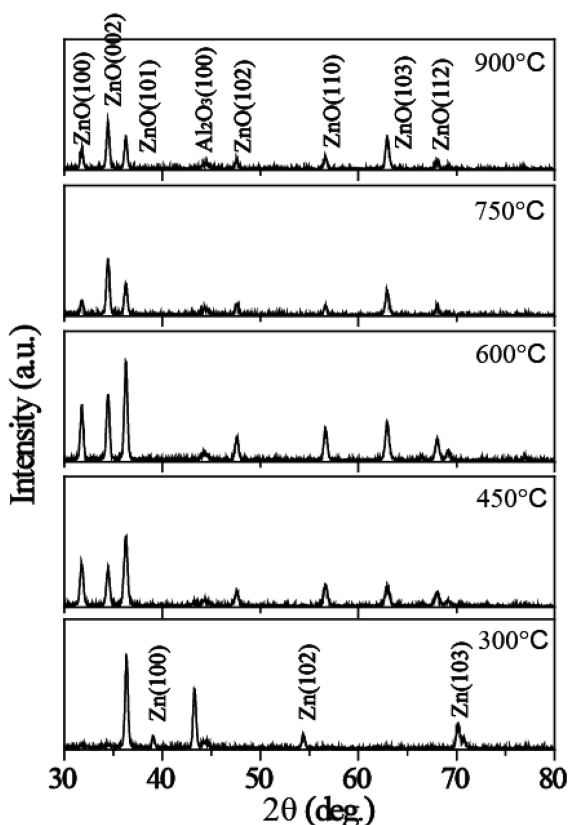


Fig. 1. XRD patterns of the ZnO films prepared by the oxidation of Zn in air for 1 h at temperatures ranging from 300°C to 900°C.

in the XRD patterns, it is clear that the oxidation temperature affects the crystalline structure of ZnO film. The (002) orientation is enhanced with the oxidation temperature, and reaches a maximum at 600°C. With an increase in oxidation temperature from 600°C to 900°C, the intensity of (002) diffraction then decreases. The intensity of the (101) peak also increases with an increase of oxidation temperature up to 600°C, and then decreases quickly as the temperature is increased to 900°C. This does not agree with the results in many other reports on ZnO films synthesized by the oxidation of metallic Zn. In these works, as the intensity of the (002) diffraction peak increased, the intensity of the (101) peak decreased. However, in our results, the intensities of the (101) and (002) peaks exhibit maximum values for the film oxidized at 600°C. Above 600°C, with a decrease in the intensity of the (002) peak, the intensity of the (101) peak also decreases. This is also not consistent with previous observations of ZnO films produced by thermal oxidation of Zn.^[14,15] For ZnO, the (002) plane is close-packed and has the lowest surface energy. Thus, the ZnO film has a tendency to grow preferentially with this plane parallel to the substrate. On the other hand, the (101) plane has been observed for ZnO films prepared with a high oxidation rate, which leads to inclusion of the absorbed oxygen atoms in the ZnO lattice. This results in the growth of unfavorable crystalline planes such as (100) and (101). Thus, with oxidation temperature, the ZnO film should demonstrate preferential growth in the (101) direction. However, our XRD results shows that the intensity of the (101) peak decreases with the oxidation temperature. In addition, the crystal orientation is sensitive to the oxidation temperature. ZnO crystallites grow preferentially with the (101) plane at temperatures up to 600°C, whereas ZnO grows with a dominant (002) texture above 750°C. This demonstrates that the dominant texture of the ZnO film is dependant on the oxidation temperature. It is also observed that the relative intensities of the (002) and (101) peaks are changed with oxidation temperature.

The EDX spectrum was measured on the oxidized films for characterization of the components. Figure 2 shows a typical EDX spectrum for a sample prepared by oxidation at 600°C. Note that no elements other than zinc and oxygen are detected in the film. Similar EDX spectra were observed for the films oxidized at temperatures over 450°C. The EDX spectra also confirm that the Zn films were completely oxidized into ZnO without any impurities.

In order to explore the mechanism underlying structural evolution with oxidation temperature, the surface morphological evolution of the ZnO films was investigated in accordance with oxidation temperature. The surface morphologies of the ZnO films were observed by SEM. Figure 3 presents SEM images of ZnO films prepared at oxidation temperatures in a range of 300°C to 900°C. For the ZnO film oxidized at 300°C, the surface is not dense or rugged, and flake

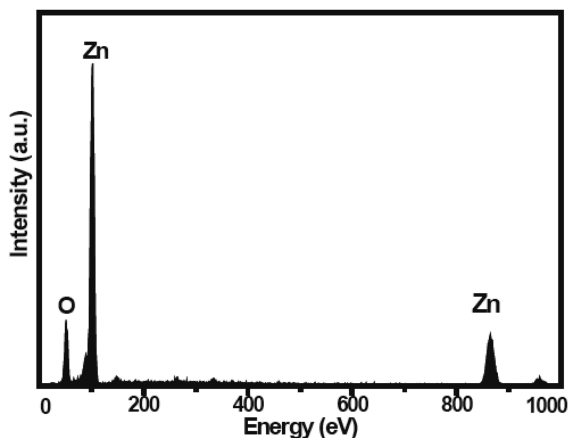


Fig. 2. EDX spectrum measured for the ZnO film prepared by the oxidation of Zn in air for 1 h at a temperature of 600°C.

type grains with a hexagonal shape are observed. The surface morphology is the same as that of the as-deposited Zn film. At an oxidation temperature of 450°C, fine particles with a spherical shape are observed. When oxidized at 600°C, numerous nanowires with a diameter below 50 nm and a length of several micrometers are formed on the film surface. The nanowires disappear at temperatures above 750°C. With a further increase of oxidation temperature, the size of the grains increases accordingly due to grain growth caused by Ostwald ripening.

These observations raise the question of why ZnO films show different morphologies at different oxidation temperatures. When oxidized at 300°C, below the melting point of Zn (419°C), the oxidation of Zn film is carried out through the diffusion of Zn atoms and oxygen atoms in the solid

phase. Hence, ZnO is formed while maintaining the surface morphology of the as-deposited (original) film, but the metallic Zn is not completely transformed into ZnO. In the case of oxidation at 450°C, higher than the melting point of Zn, Zn transforms to a liquid phase in the thin oxide film, which is formed naturally on the surface of the Zn film in air. Since the vaporization rate of liquid Zn is more rapid than that of solid Zn, rapid evaporation of Zn atoms from the liquid takes place at cleavages or grain boundaries in the rugged natural oxide layer. In turn, the rapidly evaporated Zn atoms react quickly with oxygen in the air at the cleavages or grain boundaries, resulting in wire-like growth. This is in agreement with the results in a report by Ren *et al* on the synthesis of ZnO nanowires on a Zn substrate by thermal oxidation at a temperature as low as 400°C.^[16] They also suggested that nanowires formed along linear defects in the Zn substrate such as dislocations and grain boundaries, which can act as favorable sites for nanowire nucleation as well as effective diffusion paths. At 600°C, the nanowires are formed with high density. The observation that ZnO nanowires were formed without the presence of a catalyst verifies that the nanowires were synthesized via a vapor-solid (VS) mechanism. With an increase of the oxidation temperature from 600°C to 900°C, the ZnO film becomes denser and the grain size becomes larger, as shown in Fig. 1, which induces a reduction of cleavages or grain boundaries on the film surface.

Generally, it has been reported that ZnO films formed by oxidation of a Zn film become denser and the grain size increases due to the coalescence of small grains as the oxidation temperature is increased.^[13] Accordingly, the nanowires gradually disappear from the film surface and are not

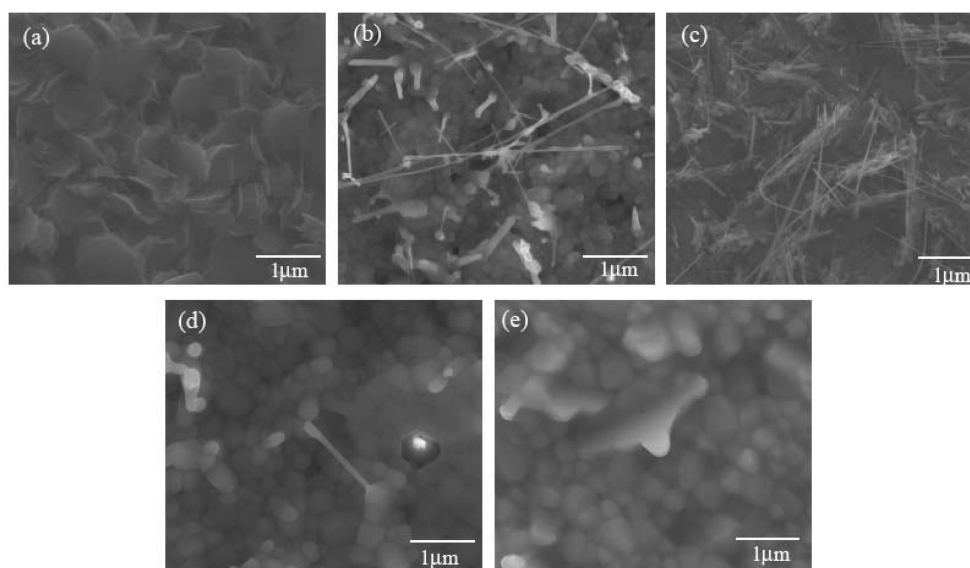


Fig. 3. Surface images taken using SEM for the ZnO films prepared by the oxidation of Zn in air for 1 h at temperatures of (a) 300°C, (b) 450°C, (c) 600°C, (d) 750°C, and (e) 900°C.

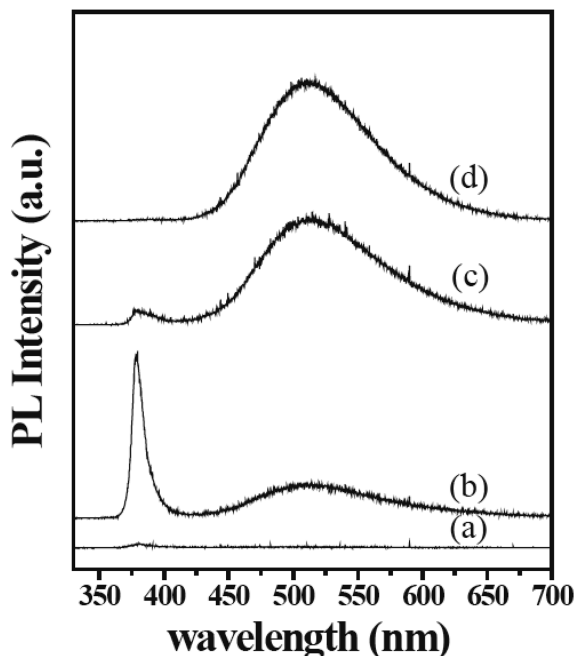


Fig. 4. Room temperature PL spectra of the ZnO films prepared by oxidation at different temperatures of (a) 300°C, (b) 600°C, (c) 750°C, and (d) 900°C.

observed at temperatures above 750°C. In addition, the grain size in the films increases with an increase of the oxidation temperature. The grain growth can be explained by Ostwald ripening. Large grains grow at the expense of smaller grains during Ostwald ripening. As a result, the small grains become smaller, whereas the large grains become larger until the smaller grains eventually disappear. The driving force for Ostwald ripening is the reduction of total surface energy.

We can now infer a correlation between the XRD data and the morphology. In the XRD patterns of the ZnO film prepared at an oxidation temperature of 600°C, the intensity from the (002) plane with the lowest surface energy is the strongest. This means that the ZnO film has better crystal quality and lower defect concentration than the films produced at other temperatures. This explains why the peak intensity from the (101) plane, an unfavorable crystal plane, is the strongest in the ZnO film prepared at 600°C. Xu et al. reported that for ZnO nanowires synthesized on an oxidized Si substrate, (100), (002), and (101) peaks were relatively strong and the (101) peak was the strongest.^[17] This is in good agreement with our XRD results. As shown in Fig 2(c), numerous ZnO nanowires are formed on the surface of the ZnO film prepared at 600°C. Accordingly, it is suggested that the strong (101) peak in the ZnO film prepared at an oxidation temperature of 600°C can be ascribed to the ZnO nanowires formed with high density on the film surface. The intensity of the (101) peak appears to reflect the density of ZnO nanowires.

The relationship between PL spectra and the crystalline structure of the ZnO films was investigated. Figure 3 presents room temperature PL spectra of the ZnO films prepared by oxidation at different temperatures. Two main emission peaks are observed for all the samples: a UV emission peak at 380 nm and a green emission peak around 500 nm. It is well known that the UV emission is attributed to a free excitonic transition^[18,19] and the green emission has a close relation with intrinsic defects such as oxygen vacancies and interstitial Zn ions in the ZnO lattice.^[20] Thus, the peak intensity of the UV emission is an indicative of the crystalline quality of the ZnO film. The high intensity of the UV emission indicates high crystalline quality of ZnO. The peak intensity of the UV emission increases with an increase of oxidation temperature up to 600°C, and then decreases quickly, finally disappearing at 900°C. Meanwhile, the defect-related green emission becomes stronger as the oxidation temperature is increased. The PL data coincides well with the XRD data. The highest intensity of UV emission was obtained for the ZnO film having diffraction peaks with the strongest intensity and the smallest full-width at half-maximum (FWHM). That is, the highest UV emission intensity in the PL spectrum of the ZnO film prepared at 600°C results from this film having the highest crystalline quality with a low concentration of defects. On the other hand, it has been reported that ZnO has a tendency to become non-stoichiometric due to desorption of oxygen at high temperatures above 700°C.^[21] Thus, with an increase of oxidation temperature from 600°C up to 900°C, the oxygen introduced into ZnO would be desorbed and the film would become more non-stoichiometric. This would lead to an increase in the density of oxygen vacancies in the films. Consequently, the peak intensity of the defect-related green emission increases remarkably.

Then, why do films showing stronger UV emission intensity have ZnO nanowires on their surface? At the relatively lower temperatures of 450°C and 600°C, the thickness of the ZnO film formed in the initial oxidation stage is very low due to the slower oxidation rate. Consequently, the absorbed oxygen on the surface may react at cleavages in the film with Zn vapor evaporated from the melted liquid Zn inside the ZnO film. This results in the formation of the ZnO nanowires. Furthermore, the slower oxidation rate provides sufficient time for the oxygen to react with the Zn at relative equilibrium conditions, thus leading to the formation of high quality ZnO films with good stoichiometry. This also results in enhanced intensity of UV emission. However, at temperatures above 750°C, the fast oxidation rate forms a thick and dense ZnO film over the surface, suppressing the growth of nanowires. The fast oxidation rate introduces a large number of defects into the ZnO films, which are responsible for the green emission.

4. CONCLUSIONS

The surface morphology of ZnO films synthesized by thermal oxidation of Zn was significantly changed with increasing oxidation temperature. In particular, from 600°C, ZnO nanowires with a diameter of less than 50 nm and a length of several micrometers were formed on the surface of the ZnO film. The formation of the nanowires is related to the surface state of the film, which is characterized by numerous cleavages in the rugged oxide layer. The maximum intensity of the (002) peak reflects the best crystalline quality, while the highest density of ZnO nanowires leads to the maximum intensity of the (101) peak in the XRD patterns. The film surface covered with nanowires also has ultrahigh surface sensitivity due to its larger surface area, which opens up possible application to chemical sensors and catalysts. The ZnO film with nanowires on its surface also showed strong UV emission, while green emission was enhanced in the ZnO films with spherical large grains. These features are thought to be related to the oxidation rate of the Zn films.

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