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Ultraviolet emission characteristics of chemical solution – derived zinc oxide films

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ZnO films showing near band edge emission were prepared on silica glass substrates by sol-gel using a zinc naphthenate precursor. As-deposited films were prefired at 250 °C for 60 min and at 350 °C for 30 min, followed by final annealing at 600 °C. Crystal structure, surface morphology, surface roughness, transmittance at visible spectra range and photoluminescence were examined. Highly oriented ZnO film was obtained by annealing at 600°C for the film prefired at 350 °C. Photoluminescence was discussed on the basis of the results of the crystallinity and surface structure.

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1. Introduction

ZnO, a II-VI compound semiconductor, has emerged as a promising material to be used in exciton-related optical devices because of its large band gap of 3.37eV at room temperature and large exciton-binding energy of 60 meV [1, 2].

ZnO films have been prepared by various dry process such as metal organic chemical vapor deposition (MOCVD), magnetron sputtering and molecular beam epitaxy (MBE) [3-6]. Wet processes such as spray pyrolysis and sol-gel method [2, 7-10] are also valuable for the preparation of the ZnO film. Moreover, metal naphthenates as starting materials are more advantageous than metal alkoxids, in terms of stability in air and ease of handling [9, 10].

Preparation of the coating solution using zinc naphthenate was easy by the addition of toluene, while a complicated procedure was needed for coating a metal alkoxide-derived solution. Furthermore, it should be noted that vaporization of additives, such as alcohol, H_2O and catalyst etc. during pre-firing and final heat treatment might cause cracks and pores in the product layer, and this disturb the preparation of high-quality oxide layers.

The present authors suspected that the films might be excessively or locally heated to high temperatures, such as 600°C, because the organic compounds that decompose and evolve during the pyrolysis are rapidly burned out. This may cause random nucleation and heterogeneous crystal growth, thus disturbing high orientation or epitaxy. Thus, comparison between the prefiring temperatures was considered to be important in order to achieve homogeneous nucleation giving the high orientation.

The properties of ZnO films are much influenced by not only the growth method, but also by prefiring process parameters; therefore, it is important to evaluate the influence of prefiring on the properties of ZnO. The large exciton-binding energy permits excitonic recombination well above room temperature. Exciton provides a sensitive indicator of material quality [11]. Photoluminescence (PL) is very sensitive to the quality of crystal structure and to the presence of defects. The green luminescence from high-quality undoped ZnO film dominates the defects-related part of PL spectrum.

In present study, pre-firing temperatures were varied at 250 °C and 350 °C in order to make the effect of organics on the properties of the ZnO clearer.

2. Experimental

Zinc naphthenate (Nihon Kagaku Sangyo Co., Ltd., Japan) was used as precursor in the sol-gel process by diluting the sol with toluene. The concentration of metal ion in the coating solution was about 4 wt%.

Thin films were fabricated by spin coating onto 2.5 cm × 2.5 cm × 1 mm substrates made of silica glass at a rotation speed of 1500 rpm for 10 sec. After each deposition, the coating film was pyrolyzed in air at 250 °C for 60 min and 350 °C for 30 min to decompose the organic species. For multiple coatings, the above-mentioned processes were repeated five times to obtain the resultant films with a thickness of approximately 497nm. The resultant films were directly annealed in a preheated furnace at 600 °C for 30 min in air.

The phase evaluation of the films was examined by an high resolution X-ray diffractometer (HRXRD, X'pert-PRO, Philips, Netherlands). The surface morphology of the films was evaluated from the field emission - scanning electron microscopy (FE-SEM, S-4700, Hitachi, Japan) micrographs. Growth mechanism and surface roughness of the films were studied by a scanning probe microscope (SPM, Nanoscope IV, Digital Instruments, U.S.A.). The transmittance in the visible spectra range was measured ultraviolet – visible – near infrared spectrophotometer (CARY 500 Scan, VARIAN, Australia). The transmittance was automatically calibrated against a bare glass substrate as a reference sample, and the absorption coefficient was obtained from the transmittance curve. Room temperature PL was carried out by the excitation of the He-Cd laser with 325 nm.

3. Results and discussion

Fig. 1 shows XRD θ - 2θ scans of the ZnO thin films pyrolyzed at 250°C for 60 min (a) and at 350°C for 30 min (b), followed by final annealing at 600 °C. A strong (002) peak is observed at 2θ = 34° for the film prefired at 350 °C. When the pyrolysis temperature was too low, 250 °C, weak (002) ZnO peak was confirmed. The peak intensity of ZnO thin films was significantly affected by pyrolysis temperature although the final heat-treatment temperature was the same. The lower peak intensity of resultant film shown in Fig. 1 (a) may be attributed to the presence of residual organic components. The ZnO pyrolysis at 250 °C was assumed to contain many residual carbon or carbon hydroxides. In this case, crystallization of the film and decomposition of organic compounds concurrently proceeded during final heat treatment. Crystal growth may be suppressed by residual carbon during the final heat treatment, resulting in the low peak intensity of ZnO thin film.

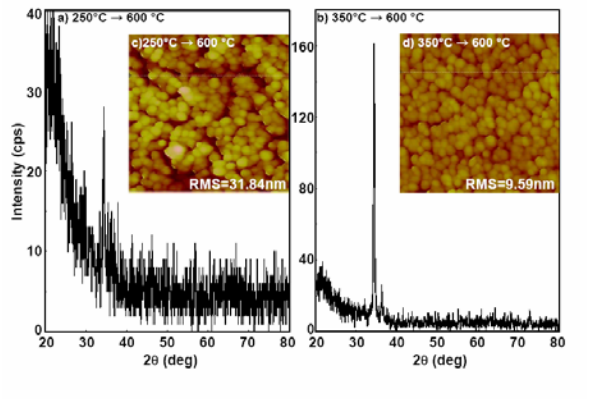

Fig. 1. XRD spectra and SPM images of finally annealed films prefired at 250 ℃ for 60 min [(a) and (c)], and at 350℃ for 30 min [(b) and (d)].

To evaluate the surface roughness and morphology of the films, SPM analysis was performed. Fig. 1 shows the SPM images ($10 \times 10\ \mu m^2$) of ZnO thin films pyrolyzed at 250 °C (c) and at 350 °C (d), followed by final annealing at 650 °C. With an increase in prefiring temperature, the root-mean-square (RMS) roughness decreased from 31.84 nm to 9.59 nm. Rougher surface structure containing some pores was identified for the films prefired at 250 °C. Formation of grain boundary micropores is quite obvious from the SPM images as shown in Fig. 2 (c). As the prefiring temperature decreases, amount of organics in the prefired film increases and therefore the decomposition and the crystallization may occur almost simultaneously. Since the structural relaxation of the prefired film, which is induced by the decomposition, can take place only before the crystallization, the simultaneous decomposition and crystallization may give the film less chance to be structurally relaxed, resulting in micro-porous structure.

Fig. 2 shows the transmission spectra of the annealed ZnO thin films. All the films exhibit a high transmittance (>80%) in visible spectra region and show a sharp fundamental absorption edge at about 0.38 ~ 0.4 μm, which is very close to the intrinsic band-gap of ZnO (3.2 eV). Fig. 2 (b) shows the FE-SEM image of the fracture cross-section of the ZnO film on silica glass substrate prefired at 350 °C, which is followed by final annealing at 600 °C. The fractured cross-section of the ZnO film with an approximately 457 nm thickness appears dense and uniform. This suggests that the bonding strength between the substrate and the film is sufficiently strong.

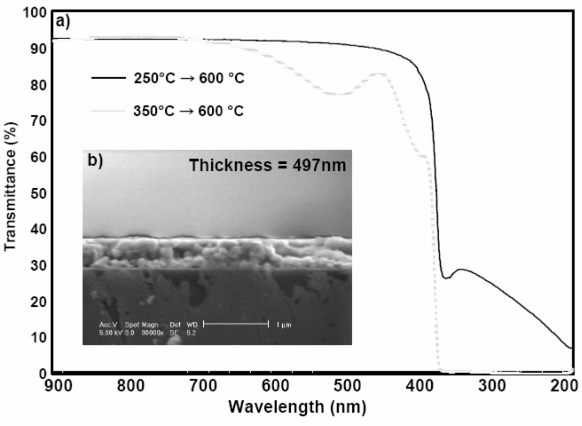

Fig. 2. Transmittance (a) and cross-sectional FE-SEM image (b) of the finally annealed films.

Fig. 3 shows the PL spectra of the samples. In ZnO two bands are observed in the PL spectra, a narrow UV emission band at ~ 380 nm corresponding to band edge emission due to free exciton emission and the other a broad green emission band near ~ 500 nm related to the defects. The radiative UV emission is fundamental peak of

ZnO and determines the crystal quality, where as green peak is attributed to the presence of defects, non-stoichiometry and crystal imperfections [12]. As shown in Fig. 3, the peak intensity corresponding to green emission has been found to increase with decrease of prefiring temperature. The larger green emission peak of the film prefired at 250°C is thought to be due to the rougher and porous surface as shown in Fig. 1. The origin of the green emission is attributed to defects; oxygen vacancies, zinc interstitials, etc. [13]. It is clearly observed from the Fig. 3, the defect-related green emission was disappeared when the prefiring temperature increases from 250 °C to 350 °C. This is due to the improvement of crystallinity in the ZnO film and is in agreement with the XRD measurements.

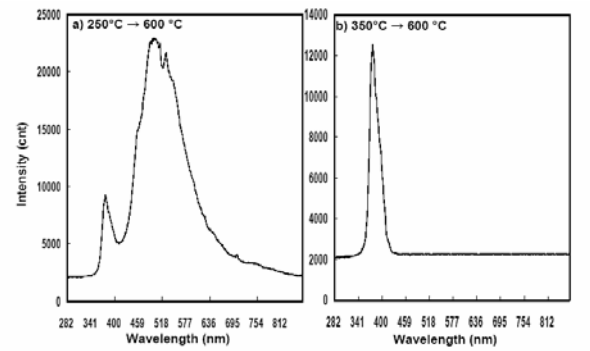

Fig. 3. PL spectra of the annealed films prefired at 250℃ for 60 min (a) and at 350℃ for 30 min (b).

4. Conclusions

Highly *c*-axis oriented ZnO film was prepared on silica glass substrates by a sol-gel process using zinc-naphthenate precursor. When the prefiring temperature was too low, 250 °C, crystallization and orientation of the films were difficult to occur. The XRD peak intensity of ZnO films was significantly affected by prefiring temperature although the final annealing temperature was the same. With an increase in prefiring temperature, the RMS roughness abruptly decreased. The defect-related green emission was disappeared when the prefiring temperature increases from 250 °C to 350 °C.

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