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ZnO Thin Films Prepared by the Electrochemical Method with Various Electrolytic Current

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Electrochemical deposition method has some advantages over the conventional methods such as large area deposition at low temperature. ZnO thin films were prepared by this method with various electrolytic current in a range of 4.5 - 122 μA/cm^2 to evaluate the relation of growth rate to the surface morphology. All samples showed 0002 preferred orientation tendencies. Furthermore, it was confirmed that the shape and size of grains depends heavily on the electrolytic current. The ZnO films deposited with electrolytic current of 22 - 71 μm/cm^2 had especially large hexagonal grains with sharp liner edges and flat planes.

Key words: electrochemical deposition, constant current electrolysis, ZnO thin film, grain size

1. INTRODUCTION

ZnO is a II-VI semiconductor with wide band gap of 3.3 eV [1] and large exiciton binding energy of 60 meV [2]. ZnO has spontaneous n-type conduction because of O vacancies [3] and/or Zn interstitials [4]. ZnO thin film is expected to apply transparent conductive film [5]. Low resistivity was achieved by doping Al [6, 7], Ga [8] and In [9]. In addition, there are several expected applications of ZnO such as light-emitting diode (LED) [10] and gas sensor [11]. There are many deposition methods for preparation of ZnO thin films, such as rf magnetron sputtering [12], molecular beam epitaxy (MBE) [13], pulse laser deposition (PLD) [14], chemical vapor deposition (CVD) [15], spray pyrolysis [16], and sol-gel method [17]. However, some of their equipments are very expensive. Other means need expensive and/or toxic raw materials. The deposition temperature and area of MBE, PLD and CVD are fairly limited, though epitaxial films can be prepared.

The electrochemical deposition (ECD) method [18, 19] has some advantages, for example enormously in-expensive and simple equipment, low operation cost, high efficiency in the use of element, large deposition area and low deposition temperature below 100 °C. However, ECD method is not used, by ordinary, for practical preparation of advanced functional thin films such as semiconductors, so far. The most serious issue of ECD method is lack of fine controllability of crystal growth in comparison to the others such as MBE, PLD and CVD.

In this paper, we focused on the surface morphology, especially the shape and size of grains, of ZnO thin films prepared by ECD method. The shape and size of grains affect light scattering. Therefore, it is very important to apply transparent electrodes of solar cells and others. Furthermore, control of them is a very important issue to reduce defects in the film and to improve the electrical transport properties which are essential for preparation of advanced ZnO devices such as LED. There are several factors effective to the surface morphology, such as pressure and kind of atmosphere in vapor phase growth, degree of super-saturation in liquid phase growth and deposition temperature in general. Among them, it is expected that deposition rate of the film is one of the most effective factor to the surface morphology. In case of ECD, the deposition rate is directly related to the number of electrons supplied per unit time per unit area, *i.e.*, the cathodic electrolytic current density, I_e, because the reactions for production of ZnO at the surface is limited by the supply of electrons [20].

In general, ECD is carried out under constant potential (C.P.) condition to maintain the potential in the optimum range for depositions [18]. However, the electrolytic current under C.P. condition, *i.e.*, the deposition rate wildly fluctuates during a deposition. Therefore, constant current (C.C.) method is employed in this study. The shape and size of grains of films prepared by ECD method with C.C. were investigated. Furthermore, relations between I_e and the surface morphology was evaluated and discussed.

2. EXPERIMENTAL

Fig. 1 shows the schematic view of the equipment for preparation of ZnO thin films. The electrolyte was an aqueous solution of $Zn(NO_3)_2$ [18] with concentration of 0.1 M [18]. Temperature of the electrolyte was fixed at 60 °C during a deposition. Working electrode was a polycrystalline Au film on glass substrate prepared by DC sputtering. The thickness and area of the Au is about 100 nm and 1 cm^2, respectively. 99.5 % Zn plate was used as a counter electrode. A reference electrode was an Ag/AgCl in saturated KCl. The I_e for a deposition was fixed at a value in range of 4.5 - 122 μA/cm^2. Total amount of charge supplied to the substrate was 2 Coulomb. After a deposition, the ZnO films were rinsed by water and blown with N_2 gas.

The θ–2θ X-ray diffraction (XRD) measurement was performed with CuKα radiation operated at 30 kV and 30 mA. The surface and cross section of the films were observed by scanning electron microscopy (SEM) to

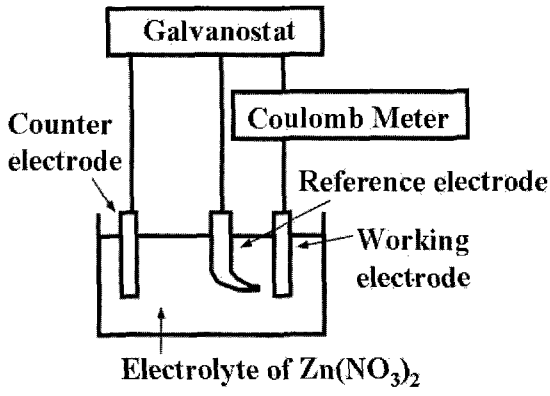

Fig. 1. A schematic view of the equipment for the electrochemical deposition method.

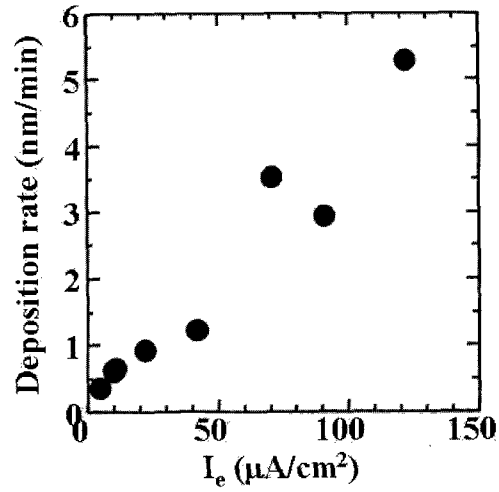

Fig. 2. Dependence of deposition rate on I_e.

evaluate the shape and size of grains and to estimate the film thickness.

3. RESULTS AND DISCUSSION

Fig. 2 shows the deposition rate versus I_e. The deposition rates at 4.5 and 122 μA/cm^2 are about 0.35 and 5.28 nm/min. The deposition rate increases almost linearly with increasing I_e. Therefore, it is presumed that the deposition rate is changed in accord with I_e, *i.e.*, the deposition rate is able to be changed by controlling I_e. It is confirmed that the cathodic potential during a deposition with constant I_e of 4.5 - 122 μA/cm^2 was almost in the optimum range for ZnO deposition [18].

The XRD patterns from the films deposited with various I_e are shown in Fig. 3. All diffraction peaks from all samples are confirmed as that corresponding to ZnO and Au. In some patterns, the intensity of 0002 diffraction peak is larger than any others, though the intensity of 0002 diffraction peak from ZnO powder is not the largest according to the JCPDS card #36-1451. To evaluate the 0002 preferred orientation tendencies, we use a parameter R_{0002} defined as follows. According to the JCPDS card, the diffractions with three largest intensities are 10-10, 0002 and 10-11. R_{0002} is defined as the ratio of the 0002 diffraction peak intensity, I_{0002}, to the sum of that of the three largest diffractions, *i.e.*, I_{0002} / ($I_{10\text{-}10}$ + I_{0002} + $I_{10\text{-}11}$). I_e dependence of the preferred orientation tendency parameter R_{0002} is shown in Fig. 4. All R_{0002} are larger than the value of random orientation derived from the JCPDS card, which means that the films show 0002 preferred orientation tendencies. Furthermore, the degree of 0002 orientation depends on I_e. R_{0002} increases up to 0.71 with increasing I_e to 42 μA/cm^2, and decreases.

The SEM images of the films are shown in Fig. 5. Magnification ratios of all images are unified. As is evident from the images, both shape and size of grains are changed drastically by I_e. Large grains were observed in the films prepared with I_e of 4.5 - 11 μA/cm^2 as shown in Fig. 5 (a) - (c). Though the diameters of the grains are up to 10 μm and more, they consist of very small sub-grains. Some of the grains show hexagonal-like

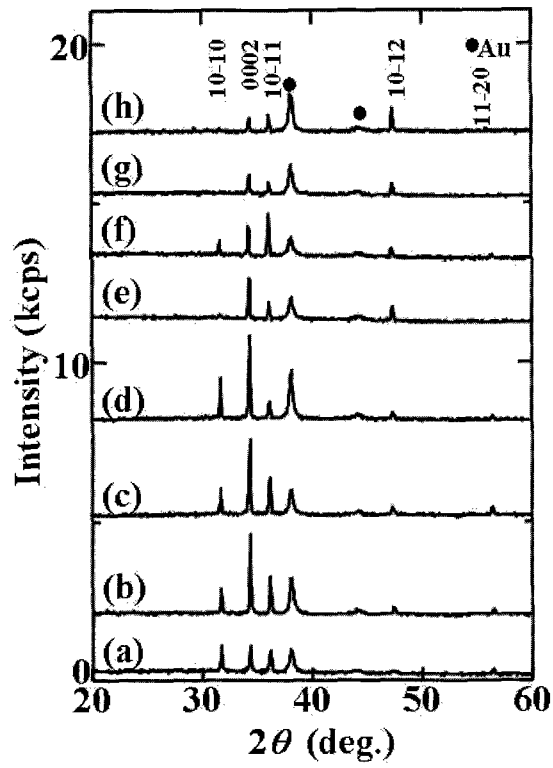

Fig. 3. θ–2θ scan XRD patterns from ZnO films prepared with I_e of (a); 4.5, (b); 9.9, (c); 11, (d); 22, (e); 42, (f); 71, (g); 91 and (h); 122 μA/cm^2. The filled circles indicate diffractions from Au as substrate.

shape with rounded corners. By increasing I_e, the shape of grains changes to hexagonal with sharp liner edges and flat planes. The average size of grains are less than 10 μm and decreasing with increasing I_e, as shown in Fig. 5 (d) - (f). The grain size is drastically reduced by increasing I_e

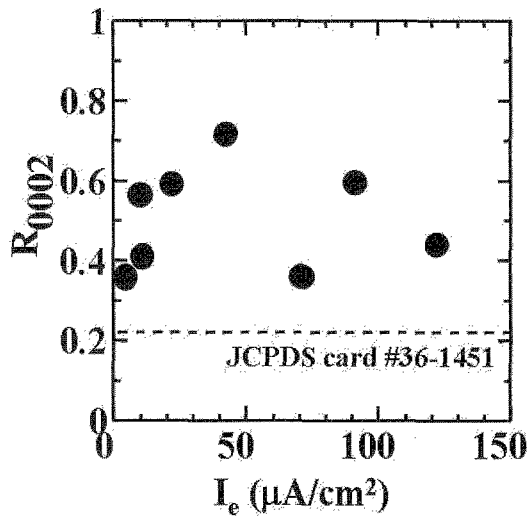

Fig. 4. Electrolytic current density dependence of the preferred orientation tendency parameter.

up to 91 μA/cm^2 and more. The average grain size shown in Fig. 5 (g) and (h) is less than 1 μm. Though, they have sharp edges and flat planes.

4. CONCLUSION

ZnO thin films were prepared by the ECD method with various I_e. The degree of 0002 preferred orientation depends on I_e. Both size and shape of grains strongly depends on I_e. The grain size is as large as several μm at I_e of 22 - 71 μA/cm^2.These results suggest the possibility for control the surface morphologies of ZnO thin films prepared by the ECD method and for novel application of ECD.

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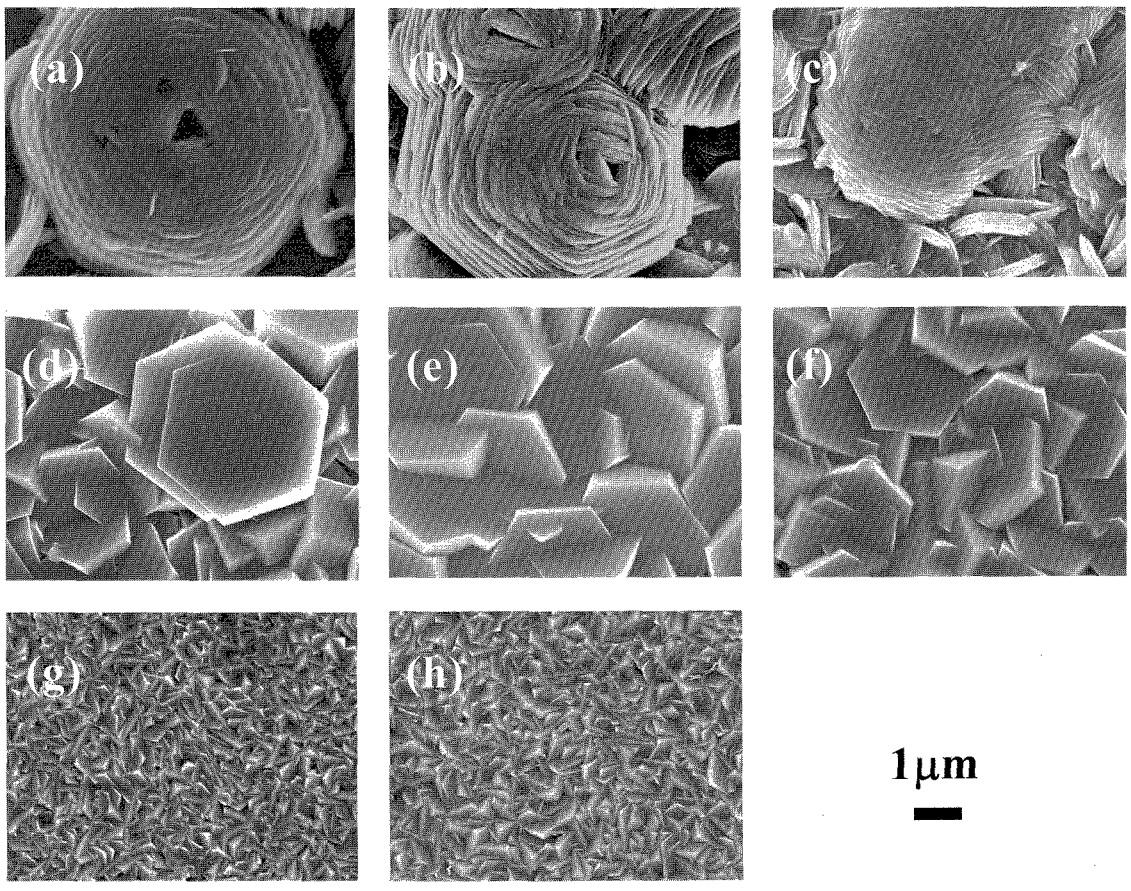

Fig. 5. SEM images of ZnO films prepared with I_e of (a); 4.5, (b); 9.9, (c); 11, (d); 22, (e); 42, (f); 71, (g); 91 and (h); 122 μA/cm^2. Magnification ratios of all images are unified.

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