Transactions of the Materials Research Society of Japan 30[4] 1235-1238 (2005)

Properties of ZnO Films by Dip Coating of Sol Gel Method

M. Rusop, K. Uma, T. Soga and T. Jimbo
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
Fax: 81-052-913-0611, E-mail: hambalah@gmail.com

The transparent c-axis oriented zinc oxide (ZnO) thin films have been prepared by sol gel method using zinc acetate as cations source, 2-methoxyethanol as solvent and monoethanolamine as sol stabilizer. Film deposition was performed by dip coating technique at a withdrawal rate of 10 mm/min on quartz and silicon substrates. The effect of annealing temperature in air ambient from 100 to 800°C on the structural, optical and electrical properties of the films is discussed. ZnO films annealed with higher temperature showed an extremely sharp (002) peak in the XRD patterns, indicates crystallization increased. The optical transmittance spectra of the films is found to change with annealing temperature and showed a very good transmittance (between 80 to 90%) with the films prepared at 600°C showed highest optical transparency within the visible wavelength region. The absorption edge analysis reveled that the optical band gap is found to increase with annealing temperature up to 3.5 eV at 600°C and decreased with higher temperature. Electronic transition was found to be direct transition type. The minimum electrical resistivity of 55 (Ω-cm) was obtained for the films annealed at 600°C.

Key words: Dip coating, sol gel, annealing, Electrical properties, Optical properties

1. INTRODUCTION

Transparent conducting oxide layers have been studied extensively because of their broad range of application such as transparent electrodes in display and in photovoltaic devices [1,2]. SnO_2 (undoped and doped) and indium-tin oxide (ITO) have been most used for transparent conducting electrodes on thin films because of their excellent in optical and electrical properties [3,4].

Recently, ZnO thin films prompted a great interest as a transparent conductor, owing to their promising properties. ZnO is an n-type wide band-gap semiconductor (E_g = 3.3 eV), and its electrical conductivity is mainly due to zinc excess at the interstitial position.

ZnO thin films have been prepared by a variety of thin films deposition techniques such as sol gel process method [6], chemical vapor deposition [7], pulsed laser deposition [8], r. f. magnetron sputtering [9], spray pyrolysis [10,11], etc. Among them, the sol gel technique offers the possibility of preparing a small and as well as a large area coating of ZnO thin films at a low cost for technological applications.

In this paper, the effect of annealing temperature in air ambient on the structural, optical and electrical properties of ZnO thin films prepared by dip coating of sol gel method are reported.

2. EXPERIMENTAL

The ZnO thin films were prepared by sol gel method. The sol gel was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 2H_2O$) in 2-methoxyethanol followed by addition of monoethanolamine (MEA) into the solution. The 2-methoxyethanol and MEA were respectively used as a solvent and solution stabilizer. The molar ratio of MEA to total metal ions in the solution was maintained at 1.0 and the concentration of total metal ion was 0.35M. The solution was stirred at 60°C for 3 hours to yield a clear and homogeneous sol gel solution, which served as the coating solution.

The solution then was stirring at room temperature. The film deposition was usually made 3 days after the solution was made at 100°C (deposition temperature) in order to react the hydrolysis process during film deposition. The ZnO thin film deposition was performed by dip coating technique at a withdrawal rate of 10 mm/min on quartz and p-type silicon substrates. After dip coated the film onto substrates, the films were dried for 10 min on hot plate at 100°C to evaporate the solvent and remove organic residuals.

The procedures from coating to drying were repeated for 2 times to get the thickness of approximately 250 nm. The films then inserted into the furnace and annealed for 30 min in air at various annealing temperatures in range from 100 to 800°C. The film thickness was measured by Alfa-Step Profiler. The crystsllinities of the ZnO flms were measured by an X-ray diffractometer with CuKα radiation (XRD). The optical properties were measured using the UV-VIS Spectrophotometer. The electrical resistance was measured by a 4-point probe method.

3. RESULTS AND DISCUSSIONS

The XRD patterns of ZnO thin films annealed at various temperatures are presented in figure 1. We found that in case of annealed at 100, 200 and 300°C, the (100), (002) and (101) peaks appeared and a small preferential growth was observed. However as can be seen in figure 1, with higher annealing temperature over 400°C, the (100) and (101) diffraction peaks are smaller compared to (002) indicating the preferred grain growth along the (002) plate for the films annealed at higher annealing temperatures. The XRD patterns of all the samples indicated enhanced intensities for the peaks corresponding to (002) plane, indicating preferential orientation along the c-axis. The relative intensity of the peaks corresponding to (002) plane increased with increasing annealing temperature.

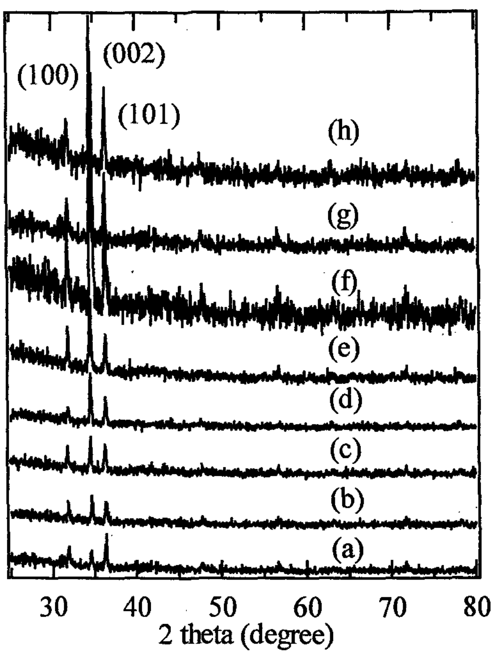

Fig. 1: The XRD patterns of ZnO thin films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, (f) 600, (g) 700, and (h) 800°C.

Since c-axis oriented ZnO thin films were also obtained by using other preparation methods such as laser ablation [8], r.f. sputtering [10] and chemical vapor deposition [12], this fact could be a common feature in all ZnO films. It is believed that the preferential orientation is caused by the minimization of internal stress and surface energy [12]. Amirhaghi et al. [13] also reported that c-orientation might be resulted from the facilitated growth along the c-axis due to the highest atomic density found along the (002) plane.

Another authors [14] reported the effects of a solvent and alkanolamine addition on a c-axis preferred orientation of ZnO thin films. The use of 2-methoxyethanol and MEA solvents of higher boiling points has resulted in a strongly preferred orientation of ZnO crystals. In this expriment, the ZnO films annealed at higher temperature was found to have more preferred (002) orientation may be because of the structural relaxation of the gel films (before crystallization) was more easily accepted by MEA and resultant organics at higher annealing temperature.

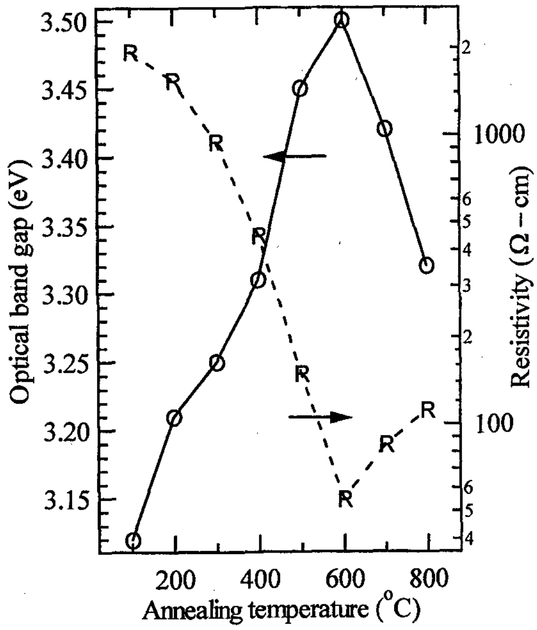

Fig. 2: The optical band gap (left-axis) and resistivity (right-axis) of ZnO thin films as a function of annealing temperatures.

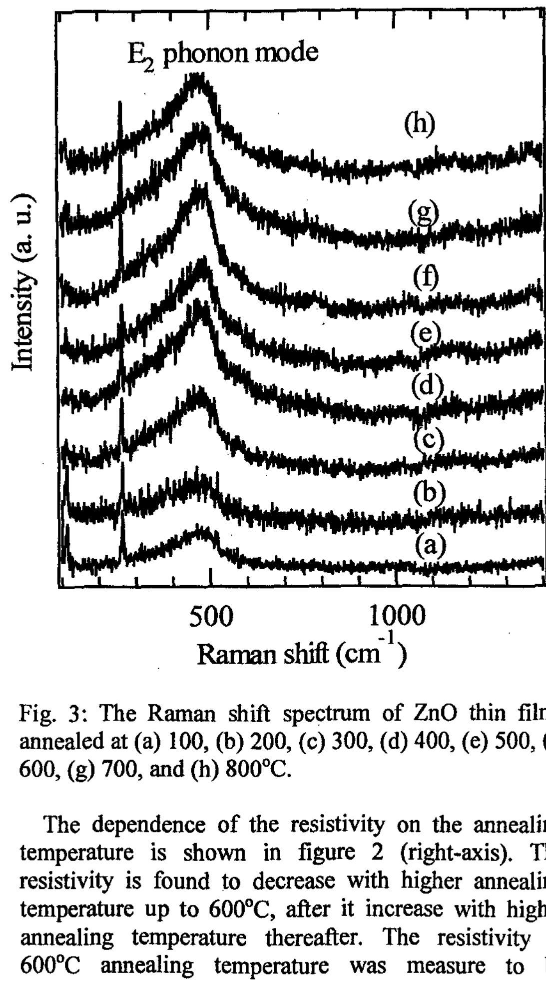

Fig. 3: The Raman shift spectrum of ZnO thin films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, (f) 600, (g) 700, and (h) 800°C.

The dependence of the resistivity on the annealing temperature is shown in figure 2 (right-axis). The resistivity is found to decrease with higher annealing temperature up to 600°C, after it increase with higher annealing temperature thereafter. The resistivity at 600°C annealing temperature was measure to be approximately 55 [Ω -cm]. We found there is a tendency that resistivity of the films were inversely proportionate to intensities of (002) orientation peaks as can be seen with comparing between figure 1 and 2. The decrease in resistivity with higher annealing temperature up to 600°C can be interpreted in terms of crystallite structure enhancement, that has been reported in the literature that the correspondence between the crystalline quality and the value of the preferred orientation quality [15].

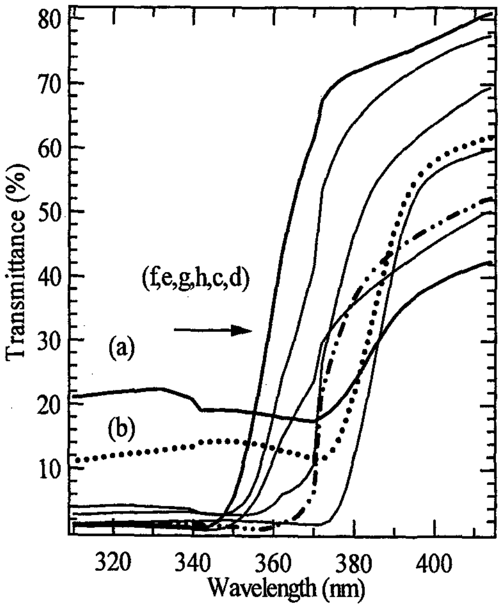

Fig. 4: The optical transmittance spectrum of ZnO thin films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, (f) 600, (g) 700, and (h) 800°C.

This phenomenon also well supported by other experimental techniques such as Raman spectroscopy (Fig. 3). Raman spectroscopy has shown the Raman shift peak (E_2 phonon mode) approximately at 470 cm^{-1} has increased and shifted to higher wave number with increased of annealing temperature peak at 600°C, after which it showing decreasing phase with higher annealing temperature above 600°C. The degradation of orientation is considered to increased resistivity at higher annealing temperature above 600°C.

We also have found by the Scanning electron microscopy (SEM) measurement that the grain size of films prepared at 600°C (not shown) was larger than that of the films prepared at other annealing temperatures. The grain size increased with annealing temperature up to the films prepared at 600°C, after which the grain size decreased with higher temperature. Carriers were scattered at the grain boundaries, so their mobility decrease with higher grain size. As the grain size increased, the grain boundary density of the films decreased, subsequently, the scattering of carriers at the grain boundaries decreased. Therefore, the resistivity value became lower for the films with bigger grain size prepared at 600°C. It is well known that n-type conductivity in non-stoichiometric ZnO is due to interstitial zinc atoms and oxygen vacancies [16].

Since the electrical conductivity of ZnO is directly related to the number of electrons, the electrons formed by the ionization of the interstitial zinc atom and the oxygen vacancies affect the electrical conductivity properties of ZnO crystal. The problem is why at higher annealing temperature above 600 °C the resistivity was increased again. The reason is might be due to the oxygen vacancies formed the oxygen annihilation from the ZnO crystals through the annealing process at higher annealing temperature above 600 °C. In addition, when the experimental was performed at higher annealing temperature above 600 °C, the carrier's concentration may increases by desorption (changing from an adsorbed state on a surface to a gaseous due to higher annealing temperature) of oxygen in the grain boundaries, which act as a traps for the carriers [17]. This affects the resistivity to decrease above 600°C of annealing temperature.

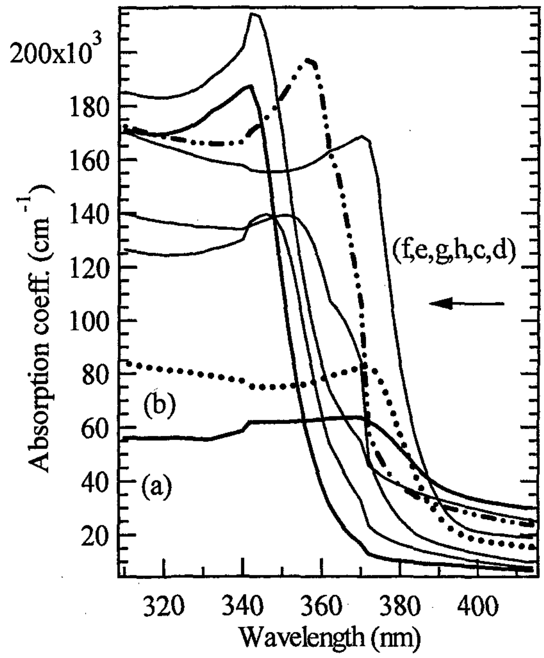

Fig. 5: The optical absorption coefficient spectrum of ZnO thin films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, (f) 600, (g) 700, and (h) 800°C.

The transmittance and reflectance spectra of TiO_2 film prepared at various annealing temperature are measured by UV-VIS Spectrophotometer in range from 300 to 1000 nm. Figure 4 and 5 showed the optical transmittance and absorption coefficient spectra of the films as a function of annealing temperatures in the wavelength in range 310 to 415 nm (3 to 4 eV).

The optical transmittance spectra of the films is found to changed with annealing temperature and showed a very good transmittance (between 80 to 90%) with the films prepared at 600°C showed highest optical transparency within the visible wavelength region. It can be seen that the transmittance spectrum decreased with higher annealing temperature over 600°C. Surface morphology also has a strong influence on the optical properties of the films. The increased in transmittance at 600°C may be due to decreasing optical scattering caused by the densification of grains followed by grain growth and the reduction of grain boundary density. It can be seen in figure 5 that there is a sharp decreased in intensity of transmitted light due to band edge absorption. The absorption edge for the films prepared at 600°C is at higher energy compared with other films, indicates highest optical transparency of the films.

To have an estimate of the optical band gap, absorption coefficient (α) of the ZnO films near the absorption edge was calculated from the transmittance (T) and reflectance (R) data using the simplified relation $T = (1-R)e^{-\alpha d}$, where d is the thickness of the films. From the equation, $\ln(T/(1-R)) = -\alpha d$, $\ln(1-R)/T)) = \alpha d$ and $\alpha = (1/d)(\ln(1-R)/T)$ are calculated.

The linear intercept of the tangent to the $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), will give an estimate of the optical band gap energy of a polycrystalline (direct band gap). Plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) is shown in figure 6. The direct optical band gap energy was evaluated from the plot (Fig. 6) and shown in figure 2 (left-axis) with the films annealed at 600°C shows highest band gap of 3.5 eV.

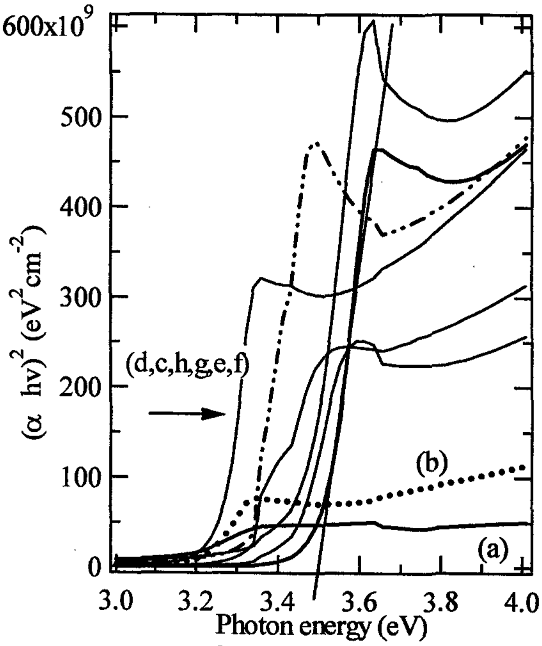

Fig. 6: The $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) of ZnO thin films annealed at (a) 100, (b) 200, (c) 300, (d) 400, (e) 500, (f) 600, (g) 700, and (h) 800°C.

4. CONCLUSIONS

The c-axis oriented ZnO thin films were prepared the on quartz and silicon substrates by the dip coating of sol gel method using $Zn(CH_3COO)_2 2H_2O$, 2-methoxyethanol and MEA. The effect of the annealing temperature from 100 to 800°C on the structural properties, optical transparency and electrical resistivity of the films were studied. The ZnO films exhibited increased c-axis orientation with higher annealing temperature. The films annealed at 600°C showed the preferred (002) orientation of ZnO films. The optical transmittance spectra of the films is found to change with annealing temperature and showed a very good transmittance (between 80 to 90%) with the films prepared at 600°C showed highest optical transparency within the visible wavelength region. The optical band gap is found to increase with annealing temperature up to 3.5 eV at 600°C and decreased with higher temperature. The electronic transition was found to be direct transition type. The minimum electrical resistivity of 55 (Ω-cm) was obtained for the films annealed at 600°C.

ACKNOWLEDGEMENTS

This work was supported by the Incorporated Administrative Agency New Energy and Industrial Technology Development Organization (NEDO) under Ministry of Economy, Trade and Industry (METI) and 21st century COE program at NIT.

REFERENCES

[1] M. Chen, Z.L. Pei, C. Sun, J. Gong, R.F. Huang and L.S. Wen, Mater. Sci. Eng. B 85 (2001) 212.
[2] J. Herero, M.T. Gutierrez, C. Guillen, J.M. Dona, M.A. Martinez, A.M. Chaparro and R. Bayon, Thin Solid Films 361-362 (2000) 28.
[3] J.W. Bae, S.W. Lee, K.H. Song, J.I. Park, Y.W. Ko and G.Y. Yeom, Jpn. J. Appl. Phys. 38 (1999) 2917.
[4] F.O. Adurodija, H. Izumi, T. Ishihara, H. Yoshikawa, H. Matsui and M. Motoyama, Jpn. J. Appl. Phys. 38 (1999) 2710.
[5] J.H. Lee, K.H. Ko and B. O. Park, J. Crystal Growth 247 (2003) 119.
[6] M.M. Kamalasanan and S. Chandra, Thin Solid Films 288 (1996) 112.
[7] Y. Kashiwaba, F. Katahira, K. Haga, T. Sekiguchi and H. Watanabe, J. Crystal Growth 221 (2000) 431.
[8] Y.R. Ryu, W.J. Kim and H.W. White, J. Cryst. Growth 219 (2000) 419.
[9] P. Nunes, D. Costa, E. Fortunato and R. Martins, Vacuum 64 (2002) 293.
[10] F.D. Paraguay, W.L. Estrada, D.R.N. Acosta, E. Andrade and M.M. Yoshida, Thin Solid Films 350 (1999) 192.
[11] P. Nunes, E. Fortunato and R. Martins, Int. J. Inorg. Mater. 3 (2001) 1125.
[12] D. Bao, H. Gu and A. Kuang, Thin Solid Films 312 (1998) 37.
[13] S. Amirhaghi, V. Craciun, D. Craciun, J. Elders and I.W. Boyd, Microelectron. Eng. 25 (1994) 321.
[14] M. Ohyama, H. Kozuka, T. Yoko and S. Sakka, J. Ceram. Soc. Jpn. 104 (4) (1996) 296.
[15] F.D. Paraguay, J. Morales, W. L. Estrada, E. Andrade and M.M. Yoshida, Thin Solid Films 366 (2000) 6.
[16] M.H. Sukkar and H.L. Tuller, Adv. Ceramics 7 (1984) 71.
[17] S. Major, A. Banerjee and K.L. Chopra, Thin Solid Films 122 (1984) 31.

(Received December 24, 2004; Accepted June 30, 2005)