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The electrical and vibrational characteristics of ZnO synthesized using the “bottom-up” growth method

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ZnO thin films were synthesized using the “bottom-up” method. The surface morphology of the ZnO films was determined by using atomic force microscopy. The resistivity was characterized by four point probe measurement. From Raman scattering measurement, the peak $A_1(LO)$ at 576 cm^{-1} is absent for sample with longer oxidation duration, which may be due to the interstitial Zn in the ZnO crystal. Infrared absorbance analysis suggested the presence of $Zn-OH$ bond in the translation and deformation mode in the range of 510-570 cm^{-1} and 950-1020 cm^{-1} respectively.

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1. Introduction

Wide-bandgap metal-oxide semiconductor such as zinc oxide (ZnO) has been widely investigated due to the outstanding potential in optoelectronic applications. The typical ZnO deposition techniques included magnetron sputtering [1-2], MOCVD [3], sol-gel or spray pyrolysis[4], evaporation-oxidation , “bottom-up” growth method [5-7] and hydrothermal [8] have been reported. Among the deposition techniques of ZnO, “bottom-up” growth method is attractive as it is cost effective for fabrication. The “bottom-up” method is defined as the direction of the Zn^{2+} and O^{2-} sources flowing in the opposite direction but chemically react at the same substrate to form a solid layer. To study the lattice or phonon characteristics, we need to have some suitable optical measurements, such as Raman scattering and Fourier transform infrared spectroscopy (FTIR). These measurements are non-destructive in principle and required no sample preparation. However, relatively less report are found that discuss about the vibrational properties of ZnO prepared using this deposition method.

In this report, we have studied morphological, electrical and vibrational properties by using atomic force microscopy (AFM), four point probe, Raman scattering and infrared absorbance spectroscopy respectively.

2. Experimental details

Zn thin films were deposited onto glass substrate using thermal evaporation method. Granulated Zn (>99% purity) was used as the source of evaporation. A few clean microscope glasses were used as substrates. The vacuum chamber was pumped down to background pressure of 5 × 10^{-5} mbar, and the evaporation current was fixed at 5 A. Deposition time was around 0.5 minutes and the thickness of the Zn thin film was about 0.3 micron. After deposition, the samples were transferred into the furnace. The temperature of the furnace was fixed at 600℃ before oxidation process. Thermal oxidation was performed under air ambient between 15 to 60 minutes. HR- XRD (PANalytical X’pert Pro MRD) with CuK$_{\alpha 1}$ radiation source (λ= 0.154 nm) was used to determine the crystalline quality of the samples. The resistivity measurements were carried out by four point probe (Changmin Tech CMT-SR2000N). The surface morphology of the sample was investigated by atomic force microscopy (ULTRAObjective) with non-contact mode. The Raman measurements were performed at room temperature using Jobin Yvon HR800UV system. An argon ion laser (514.5nm) was used as an excitation source for Raman measurements. FTIR (model: Perkin Elmer spectrum GX) measurement was performed to determine the presence of zinc species.

3. Results and discussion

Fig. 1 shows the AFM topography of the samples. The root mean square (RMS) roughness is 85, 70, 126, and 70 nm with oxidation duration of 15, 30, 45, and 60 minutes, respectively. The scan area for the sample oxidized at 15 and 45 minutes is 20 µm × 20 µm, while the scan area for samples oxidized at 30 and 60 minutes is 10 µm × 10 µm. The value of the RMS roughness for sample with oxidation duration of 45 minutes is the highest.

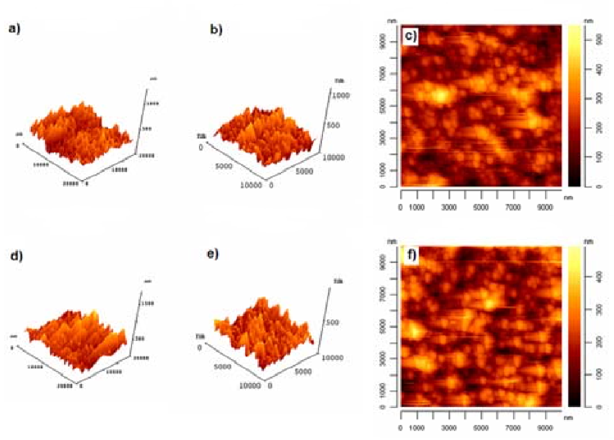

Fig. 1. AFM topography of the samples with oxidation duration of a)15 minutes, b) and c) 30 minutes, d) 45 minutes, e) and f) 60 minutes. The scan area of a) and d) is 20 µm × 20 µm, however the scan area for b), c), e) and f) is 10 µm × 10 µm.

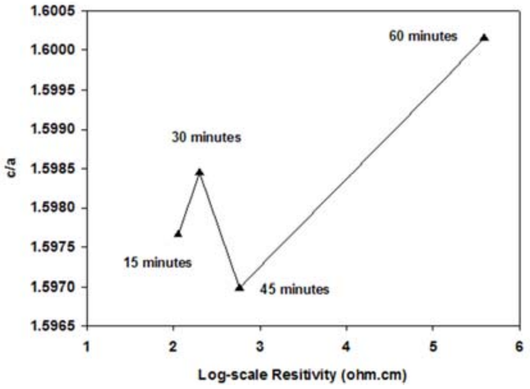

Fig. 2. The relation between ratio c/a and resistivity of sample with various oxidation durations.

Fig. 2 shows the dependence of the ratio of lattice constants c and a with resistivity. For a hexagonal unit cell, the interplanar spacing, d_{hkl} of the (hkl) plane is given by

$$\frac{1}{d_{hkl}^2}=\frac{4}{3}\frac{(h^2+k^2+hk)}{a^2}+\frac{l^2}{c^2} \tag{1}$$

From Bragg's law, the lattice constant, c, for allowed $(000l)$ reflection can be derived as

$$c=\frac{l\lambda}{2\sin\theta} \qquad 2)$$

Typically, the value of c/a increase with resistivity which could be due to the presence of additional oxygen atoms in the ZnO crystal during oxidation. However, the sample with 45 minutes oxidation duration shows relatively low c/a value.

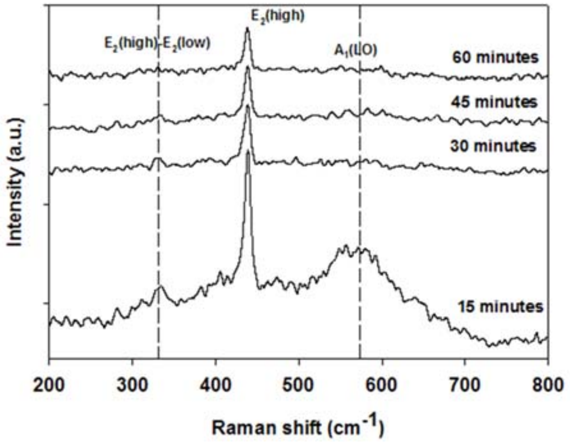

Fig. 3. Room temperature Raman scattering spectra of the samples.

Raman scattering measurement is a standard optical characterization technique for investigating various properties of materials such as electronic and lattice properties. Raman scattering is due to phonons which are relatively dominant in covalent crystal than in ionic crystal. So, ZnO are suitable for Raman scattering measurement since the ionicity is about 0.616, which means the behavior of ZnO between ionic and covalent. Wurzite crystal structure of ZnO belongs to space group $P6_3mc$ with two formula units per primitive cell. The Raman scattering experiments were carried out in the $z(x, x \text{ or } y)\overline{z}$ scattering configuration. The Raman active zone-center optical phonons are $A_1+2E_2+E_1$, where A_1 and E_1 are symmetry of polar phonons. Symmetry E_2 is non-polar mode and it has two frequencies; $E_2(low)$ is related with Zn sublattice and $E_2(high)$ is related with oxygen atom [9]. Fig. 3 shows the room temperature Raman scattering spectra of the samples. For the sample which was oxidized for 15 minutes, 3 peaks appearing at 335, 440 and 576 cm^{-1} are assigned to symmetry $E_2(high)-E_2(low)$, $E_2(high)$, $A_1(LO)$ respectively [10].The peak at 335 cm^{-1} is attributed to the second-order Raman process [9,10].The appearing of the peak $A_1(LO)$ may be due to the interstitial Zn in the ZnO crystal. For the samples oxidized at 30, 45, and 60 minutes, all of the Raman spectra do not reveal any $A_1(LO)$ peak. It may be due to the disordering of ZnO crystal is reduced, which decrease the scattering from the sidewalls with increase in oxidation duration in this experiment. In addition, the ratio of c/a is increasing with oxidation duration. This result indicates covalent behavior in ZnO decrease with oxidation duration. Therefore, the Raman scattering intensity decreases with oxidation duration.

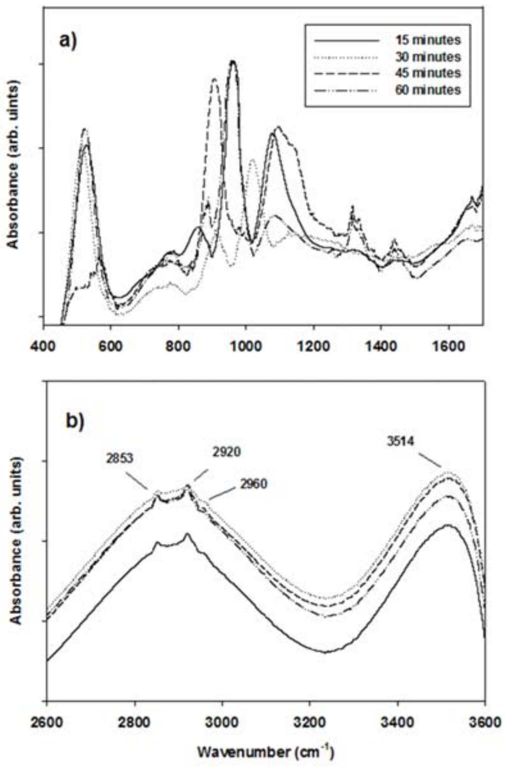

Fig. 4. Infrared absorbance spectra of the samples with wavenumber range a) 400-1700 cm^{-1}, b) 2600-3600 cm^{-1}.

Fig. 4 a) and 4 b) show the infrared spectra of ZnO samples with wavenumber ranging from 400 – 1700 cm^{-1} and 2600-3600 cm^{-1} respectively. Table 1 shows the corresponding absorbance peaks and their assignments for the samples [4]. Various absorbance peaks corresponding to vibration of coordinated group are observed. In the infrared spectra, the absorbance peak corresponding to $Zn-OH$ translation mode are observed and its located at 535, 511, 566, and 517 cm^{-1} for samples oxidized at 15, 30, 45, and 60 minutes respectively [4,8]. Only for the sample which was oxidized at 15 minutes, a peak was observed at 849 cm^{-1} and it is associated with $\nu_2(CO_3^{\ 2-})$ mode. However, for the first 15 minutes of oxidation, the absorbance peak which corresponds to H_2O rocking mode was absent. It may be due to the need for longer oxidation duration to decompose $\nu_2(CO_3^{\ 2-})$ to H_2O. Only the sample which was oxidized at 45 minutes shows the absence of peak associated to $Zn-OH$ deformation mode and it may be due to the higher roughness to release hydrogen atom. The peaks present in between 1082-1136 cm^{-1} of the samples are assigned to $\nu_1(CO_3^{\ 2-})$. The peaks are assigned to symmetry and asymmetry stretching vibration of carboxylate ion, and only can be found for oxidation duration of more then 30 minutes. It may be that more energy is needed to form carboxylate ion complex in ZnO crystal thus these peaks are only absent for low temperature oxidized samples [4,8]. The peaks with wavenumber range in between 2850 to 3514 cm^{-1} are assigned to $\nu(CH)$ and anion bound of H_2O [4].

Table 1. Summary of absorbance peaks and their assignments.

Annealed Durations Assignments/mode	15 minutes (cm^{-1})	30 minutes (cm^{-1})	45 minutes (cm^{-1})	60 minutes (cm^{-1})	Ref. [4] (cm^{-1})
$Zn-OH$ translation	535	511	566	517	520
$\nu_2(CO_3^{\ 2-})$	849	-	-	-	837
H_2O rocking	-	913	902	887	890
$Zn-OH$ deformation	957	1015	-	954	950
$\nu_1(CO_3^{\ 2-})$	1082	1134	1092	1078,1136	1050, 1120
Symmetry and asymmetry stretching vibration of carboxylate ion	-	-	1315,1435	1315	1360, 1405, 1460
$\nu(CH)$	2853,2920,2960	2853,2920,2960	2853,2920,2960	2853,2920,2960	2878, 2927, 2956
Anion bound of H_2O	3514	3514	3514	3514	3570

4. Conclusion

ZnO thin films were prepared by “bottom – up” growth method on microscope glass. The morphological properties indicate the highest RMS roughness for sample with 45 minutes of oxidation. The resistivity of the samples is dependent on the ratio of c/a. The Raman scattering spectra indicated the absence of the $A_1(LO)$ peak for the samples oxidized for 30, 45, 60 minutes. It may be due to the disordering of ZnO crystal is reduced, which decreases the scattering from the sidewalls. The results from infrared spectroscopy show the properties of Zn – O bond.

Acknowledgments

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