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The morphological, electrical, and vibrational characteristics of zinc to zinc suboxide

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In this paper, we have prepared Zn – ZnO_x from Zn metallic by thermal oxidation under air ambient with various oxidation durations. The root mean square roughness values are quadratic dependent with oxidation duration and the maximum value of root mean square is 65 nm. The current-voltage characteristic of Al contacts on samples show resistivity increases with oxidation durations. It may due to the formation of ZnO on Zn layer. These results are in good agreement with the observed trend in Raman spectra. The intensity of $E_2(high)$ was increasing with oxidation duration. Thus, the formation from Zn to ZnO_x becomes dominant. The absorption band at 535 cm^{-1} indicates the presence of Zn - O compound.

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1. Introduction

Zinx oxide, (ZnO) has attracted many researchers' attention due to the wide bandgap (3.37 eV) and high exciton binding energy (60 meV) at room temperature. Owing to the unique properties of ZnO, it has been used as a promising material in optoelectronic applications. Besides, ZnO is also a non-toxic material as well as it can be prepared using low-cost and various techniques such as sol-gel, spray pyrolysis, magnetron sputtering, evaporation – oxidation and hydrothermal method [1-11]. Among the preparation methods, evaporation- oxidation or we group it into the "bottom - up" growth method is relatively less reported. To the best of our knowledge, some physical properties of zinc - zinc suboxide, Zn-ZnO_x have not been reported. Through this study, a better understanding about the characteristic of the conversion of Zn to ZnO can be obtained. In this work, we report a simple evaporation – oxidation process for the conversion of metallic Zn to ZnO_x in air ambient. The morphological, electrical, and vibrational properties were obtained using atomic force microscopy, current-voltage measurement, Fourier transform infrared spectroscopy, and Raman measurement respectively.

2. Experimental details

The deposition of Zn metallic thin film is similar with our previous work [10]. After deposition, the samples were transferred into the furnace. The temperature of the furnace was fixed at 600 °C prior to the oxidation process. Thermal oxidation was performed under air ambient for 1, 2, 3, 4, 5, and 6 minutes and the samples were assigned as a, b, c, d, e, and f, respectively. The surface morphology of the sample was investigated by atomic force microscopy (AFM) (ULTRAObjective) using non-contact mode. The Raman measurements were performed at room temperature using Jobin Yvon HR800UV system. An argon ion laser (514.5 nm) was used as an excitation source for Raman measurements. Fourier transform infrared spectroscopy (FTIR, model: Perkin Elmer spectrum GX) measurement was performed to determine the presence of zinc species. The Al circular-shaped contacts with diameter of 1mm were deposited on the samples using thermal evaporator. Current-voltage (I-V) measurement was carried out by Keithley Model 82 with bias voltage range from -1 V to +1V. All the characterizations were performed at room temperature.

3. Results and discussions

Fig. 1 shows the AFM topographies of sample a and b. From Fig. 1, the grain size of sample a is about 200 nm, while that of sample b is about 400 nm. We also observed the packing distribution of sample b is less than sample a. Thus, we suggest that the increase in grain size with oxidation duration may be due to Zn spherical nano-particle received minimum thermal energy to reform from 8 nano-particles to 1 nano-particle in order to achieve lower surface per volume ratio.

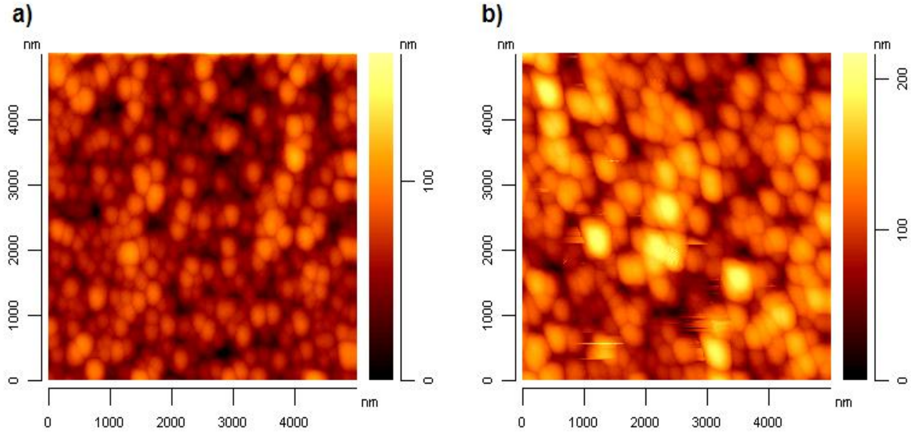

Fig. 1. AFM topographies of sample a and b with scan area $5 \times 5\ \mu m^2$.

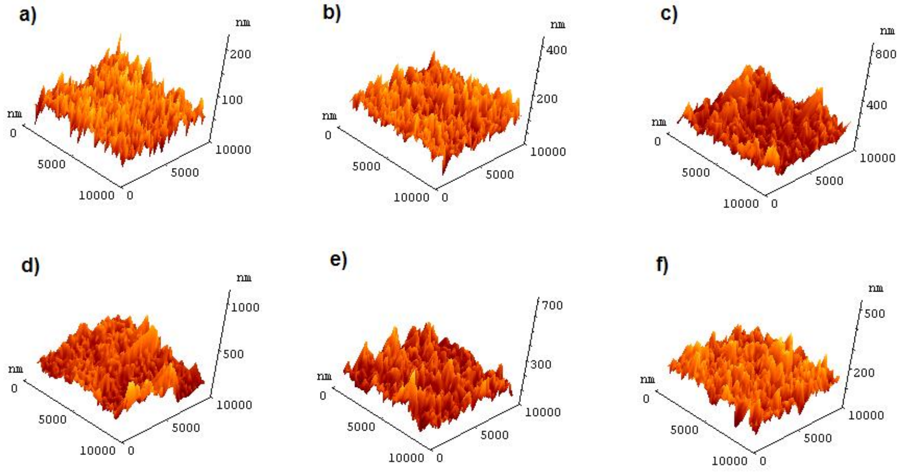

Fig. 2. 3D AFM topographies of sample with oxidation duration of a) 1, b) 2, c) 3, d) 4, e) 5, and f) 6 minutes, with scan area of 10 ×10 μm^2.

Fig. 2 shows the AFM 3D topographies of the samples under the scan area of $10 \times 10\ \mu m^2$. The roughness root means square (RMS) of the experimental data and curve fitting were plotted against oxidation duration, as shown in Fig. 3. The maximum value achieved is 65 nm, which corresponded to sample d. From the data, the best curve fitting equation are shown as below,

$$Rms(nm) = at^2 + bt + c \qquad (1)$$

where, Rms is root mean square roughness and t is oxidation duration.

Since the experimental data exhibit quadratic behaviour, the constant parameters were found to be

$$a = -5.45(nm/\min^2),\ b = 42.26(nm/\min),\ c = -24.42(nm).$$

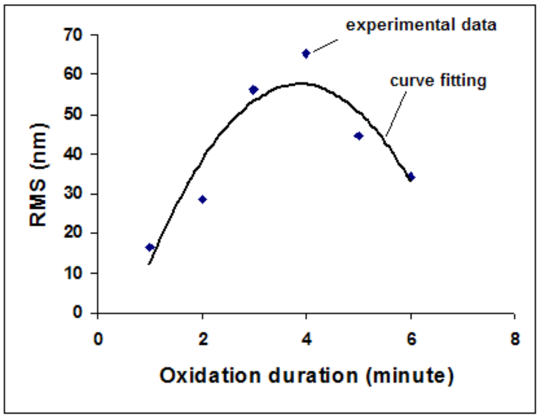

Fig. 3. RMS roughness (with scan area of $10 \times 10\ \mu m^2$ *) of the samples versus oxidation duration.*

Fig. 4 shows the I-V characteristic of non-annealed Al contacts on the samples. From the I-V characteristic, the resistivity of the samples increases with oxidation duration. During heat treatment under air ambient, the samples undergo oxidation process. The formation of ZnO increases with oxidation duration, since undoped ZnO has higher resistivity.

ZnO has a wurtzite crystal structure which belongs to the space group C_{6v}^4 with two formula units in primitive cell. The zone center optical phonon can be classified according to the following irreducible representations: $\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1$ [12].

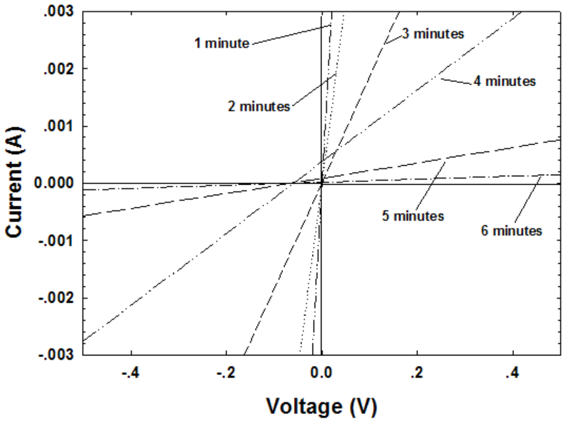

Fig. 4. I-V characteristics of Al contacts on the samples.

The E_2 is non-polar and Raman active modes, whereas the B_1 modes are silent modes. A_1 and E_1 modes are polar modes and are both Raman and infrared active. Fig. 5 shows Raman measurements of the samples. For comparison, as deposited Zn metallic sample was used in Raman measurements. The sample annealed for 6 minutes exhibited peaks at 334, 438, 570 and 1099 cm^{-1}, which could be assigned to $E_2(high)$-$E_2(low)$, $E_2(high)$, $A_1(LO)$ and $A_1(2LO)$ phonon modes respectively [6,12,13]. From Raman spectra, the appearance of $E_2(high)$ peak begins for samples oxidized for 2 minutes. The intensity of the $E_2(high)$ peak increases with oxidation duration due to the formation of ZnO. This data show that the majority Zn has been transformed to ZnO. The peak which appeared at 570 cm^{-1} for all samples was assigned as zinc interstitials located in the samples.

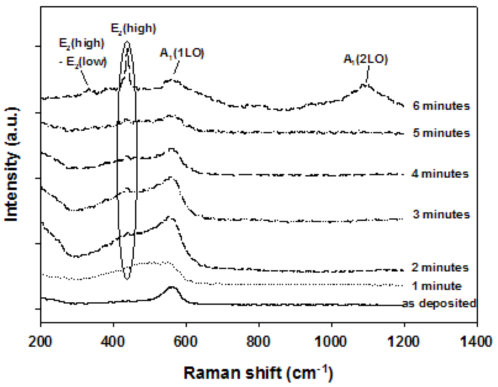

Fig. 5. Room temperature Raman spectra of the samples.

Fig. 6 shows the absorbance spectra in range of 400 – 1700 cm^{-1} for sample d. The absorption band at 535 cm^{-1} is assigned to Zn – O group [3]. The band at 785, 903, 1021 cm^{-1}are attributed to $\nu_2(CO_3^{2-})$ and $\nu_1(CO_3^{2-})$, respectively [8]. The bands in the range of 1300 – 1700 cm^{-1} are related to carboxylate ion and hydroxyl groups. The absorption bands at 1318 and 1457 cm^{-1} are attributed to asymmetric and symmetric stretching vibration of carboxylate ion while the bands at 1660 cm^{-1} is due to hydroxyl bending modes [3, 8].

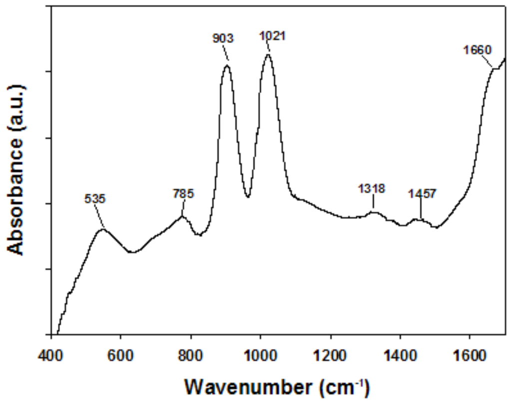

Fig. 6. Infrared absorption spectrum of samples d in range 400 – 1700 cm^{-1}.

4. Conclusions

In summary, we have prepared Zn – ZnO$_x$ from Zn metallic by thermal oxidation under air ambient with various oxidation durations. The morphological, electrical and the vibrational characteristic of the samples have been investigated. The AFM topography and RMS roughness of the samples have been intensively studied. The distributions of the RMS values are quadratic and dependent on oxidation duration. The maximum value of

RMS is 65 nm. The I-V characteristic of Al contacts on samples show resistivity increases with oxidation durations. It may due to the forming of ZnO on Zn layer. These results are in good agreement with the trend in Raman spectra. The intensity of $E_2(high)$ increases with oxidation duration. It shows the formation from Zn to ZnO_x becomes more dominant. The absorption band at 535 cm^{-1} also shows the presence of Zn - O compound. On the other hand, bands in 700 – 1700 cm^{-1} are related to stretching vibration of carboxylate ion.

Acknowledgments

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