NANOSTRUCTURED ZnO AND ZAO TRANSPARENT THIN FILMS BY SPUTTERING–SURFACE CHARACTERIZATION

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Abstract. Zinc oxide (ZnO) and aluminum zinc oxide (ZAO) transparent thin films with different thickness were prepared by dc magnetron sputtering technique using metallic targets onto silicon and Corning glass substrates. Surface investigations carried out by Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) have shown a strong influence of deposition technique parameters on the film surface topography. Film roughness (RMS), grain shape and dimensions were found to correlate with the deposition parameters. The results revealed that the target composition has a radical effect on ZnO and ZAO film characteristics. XRD analysis revealed that all films grown by dc magnetron sputtered are polycrystalline regardless of target composition. The correlation of conductivity measurements with film RMS has shown a strong influence of surface on film electrical properties. Since the film surface characteristics are determined by the growth conditions, the gas sensing characteristics of these films are also strongly influenced and consequently may be enhanced by the control of the film growth parameters.

1. INTRODUCTION

Zinc oxide is one of the earliest discovered metal oxide gas sensing materials. It is an n-type semiconductor of wurtzite structure with a direct energy wide-bandgap of about 3.37 eV at room temperature [1]. As a consequence, it absorbs UV radiation due to band-to-band transitions [2] at $\lambda < 368$ nm, while, it can be used as transparent electrode in solar cells and flat panel displays as well as for the fabrication of gratings in optoelectronic devices, as a window material in antireflection coatings and in optical filters. Furthermore, ZnO is used as a semiconducting gas sensor [3,4] due to its conductivity changes when exposed to oxidizing gases such as ozone. Until now ZnO-based elements have attracted much attention as gas sensors because of their chemical sensitivity to volatile and other radical gases, their high chemical stability, suitability to doping, non-toxicity, and low cost. Their resistivity may be lowered further by extrinsic doping with group III elements such as B, Al, Ga or In. Amongst them, Al-doped ZnO thin films are considered as candidate materials for organic electroluminescence displays [5]. Furthermore, as expected, the physical properties of ZnO films are generally dependent on deposition parameters [6] and post-deposition conditions such as post annealing [7].

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The sensitivity of nanostructured ZnO gas elements is relatively high and is related to the grain-size effect [8]. Many deposition techniques [1,3,4] have been applied for the production of ZnO films in order to improve the properties of the films. Sputtering is preferred among these techniques due to its relative high deposition rates, good film properties and process stability [1]. Due to the interest related to the specific properties of these transparent metal oxide thin films, recent studies are focused in the correlation of surface and interface topology with deposition parameters and physical properties. Among these, efforts for understanding the correlation of microstructures and electrical properties of ZnO thin film are essential. In the present work, we report on the effect of plasma gas flow ratio (O_2 to Ar) on the variation of morphology of ZnO and ZAO thin films and the corresponding effects on the film conductivity.

2. EXPERIMENTAL DETAILS

The deposition of the ZnO and ZAO films was carried out in an Alcatel dc magnetron sputtering system using 99.999% pure metallic targets under different conditions. The base pressure in the chamber was $\leq 5 \cdot 10^{-7}$ mbar. Films with thickness about 100 nm were deposited onto Corning 1737F glass and silicon substrates in an oxygen-argon atmosphere. The deposition constant parameters were the total pressure ($8 \cdot 10^{-3}$ mbar), the substrate temperature at 27 °C (RT), and the film thickness. The depositions were done for two different plasma current settings (I=0.44 A and I=0.25 A). The surface morphology (grain size and surface roughness) was measured with a Nanoscope III atomic force microscope (Digital Co. Instruments, USA) using a normal silicon nitride tip (125 μm) in Tapping Mode scanning the surface with an oscillating tip to its resonant frequency (200-400 kHz). All measurements were made at room temperature (RT). In the present study the RMS roughness of the surface is defined as: RMS(nm)=$[\Sigma(z_i-z_{ave})^2/N]^{1/2}$ where z_i is the current value of z, z_{ave} is the mean value of z in the scan area, N is the number of points. Grain radius and features dimensions were evaluated using the Cross Section Analysis Menu facilities of NanoScope III Program. We have measured grain radius values for 18 grains per sample. The mean value of grain radius is given by the formula: GR(nm)=$\Sigma gr_i/18$, where gr_i is the measured grain radius of each grain.

X-ray diffraction (XRD) using a Rigaku diffractometer with CuK$_\alpha$ X-rays was applied in or-der to determine the crystal structure of the deposited films. The conductivity measurements were carried out in a special designed reactor [9,10] at room temperature in a home made system at FORTH. The mechanism responsible for the conductivity changes in ZnO films is the formation and annihilation of oxygen vacancies. UV irradiation of the sample with energies above the bonding energy between Zn and O leads to a transformation of an oxygen atom from a bound state to the gaseous state. For photoreduction the samples were directly irradiated in vacuum by the UV light of a mercury pencil lamp at a distance of approximately 3 cm for 20 min in order to achieve a steady state. For the subsequent oxidation ozone was produced upstream in the presence of UV and the chamber was backfilled with oxygen and ozone at a pressure of 560 Torr. This treatment lasted 40 min, after which no further changes of the conductivity could be observed. Finally, the chamber was evacuated and the photoreduction–oxidation cycle described above was repeated a few times. An electric field (1 or 10 V cm^{-1}) was applied during the whole cycling procedure to the samples and the electrical current was measured with an electrometer. Current-voltage (I-V) measurements were always performed before the cycling started in order to ensure the ohmic nature of the contacts.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows surface AFM images of ZnO (a), (b), (c) and ZAO (d), (e), (f) thin films deposited at room temperature, under varying Ar-to-O_2 flow ratios. AFM characterization of the films surfaces revealed a granular, polycrystalline morphology with grain size and roughness decreasing as the oxygen partial pressure decreases for two plasma current settings I=0.44 A and I=0.25 A. The grain size measured as described above was varying from 50 to 20 nm for ZnO and from 75 to 30 nm for ZAO. Since the plasma current is correlated with the growth rate in the sense that high plasma current corresponds to a high deposition rate the above microstructural changes are directly attributed to the film growth rate variation. At the same time, the growth rate increases when the O_2 concentration decreases due to the increased presence of Ar atoms in the plasma. Under these conditions one should expect that the grain size should decrease with increasing deposition rate and consequently with decreasing O_2 concentration in the plasma. Contrary to the above we observed that films deposited at high O_2 ratio (Figs. 1a and 1d) have shown bigger, better-formed grains. However,
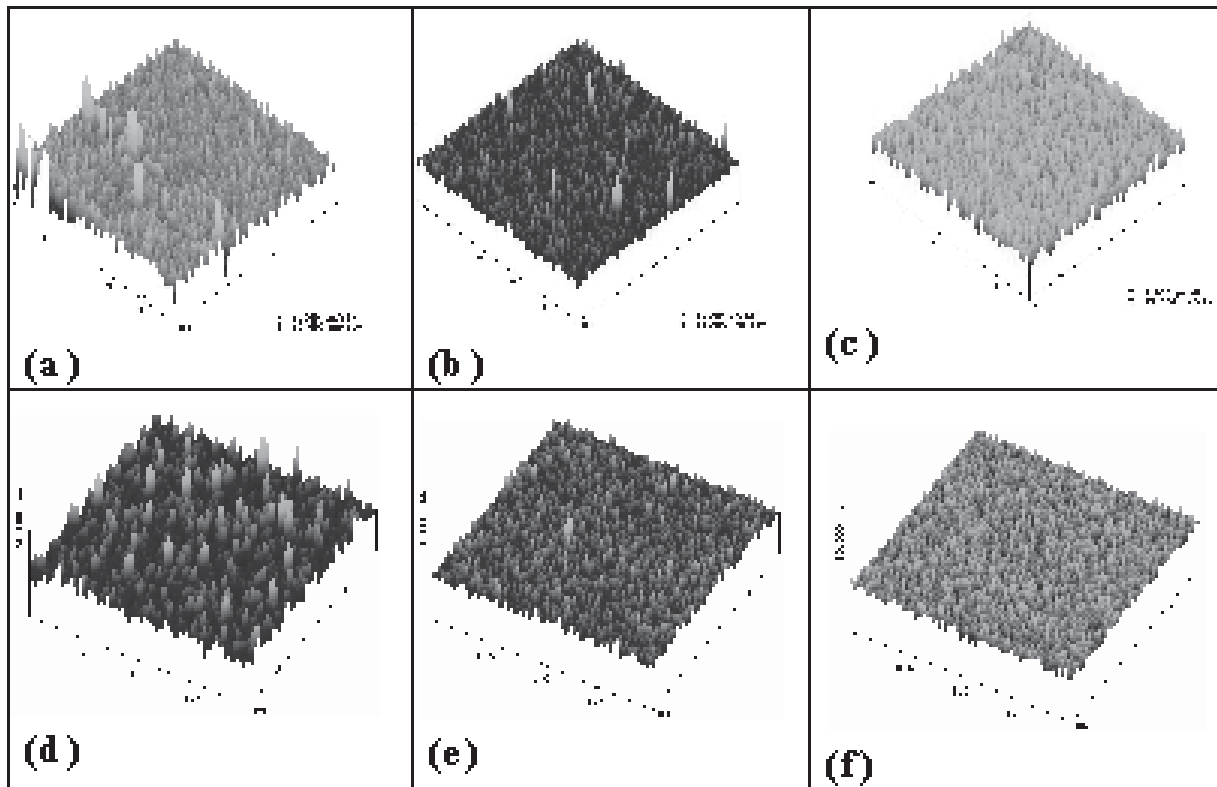
Fig. 1. AFM 3D images of as-deposited ZnO, and ZAO thin films at room temperature with O_2 plasma concentration of respectively (a) 100%, (b) 73%, (c) 60% ZnO and (d) 100%, (e) 80%, and (f) 75% ZAO.

we observed that they formed by the aggregation of many small particles, whereas those deposited at higher Ar ratio (Figs. 1c and 1f) had a uniform grain distribution but of smaller size.

These observations may be attributed to the role of oxygen as a plasma gas, which may generate high-energy oxygen neutral atoms. Such a formation of high-energy oxygen neutral atoms has also been reported by Tomminaga *et al.* [11] in 1981. It is generally believed that the formation of grain agglomerations for films deposited in the presence of high concentration oxygen gas (O_2 flow ratio of 100%) might be due to re-sputtering of high-energy neutral oxygen atoms. As oxygen content in plasma gas increases, re-sputtering effect by high-energy neutral oxygen atoms can increase. Subsequently it might accelerate grain growth (or aggregation of particles) and thus change the surface topology of the film particularly at the initial stage of the film growth process. Change in the film topology may also be amplified with increasing film thickness by shadowing effect, resulting in the enhancement of grain agglomeration. It is thus not surprising that

ZnO thin films deposited in a pure O_2 atmosphere have larger grains.

Fig. 2 shows the surface roughness variations of the ZnO thin films deposited at different O_2/Ar ratios. The scan area for surface roughness was 5×5 μm. The measured surface roughness (RMS) was the highest for the film deposited at 100% O_2 for ZAO films at both plasma current values while no clear correlation of the RMS for the ZnO thin films with O_2/Ar ratio was observed. This is probably due to the catalytic effect of Al in the ZAO film structure as an extra source of defect formations compared with the ZnO films.

XRD spectra of all deposited films indicate that our films are polycrystalline with (002) and (103) basal plane reflections of wurtzite ZnO.

The effect of O_2/Ar gas ratio on the conductivity changes under ozone exposure for two plasma currents was studied. Results have shown that the film conductivity strongly depends on O_2/Ar ratio. The photoreduction treatment resulted in an increase of the conductivity of up to seven orders of magnitude for ZnO thin films and up to six orders of magnitude
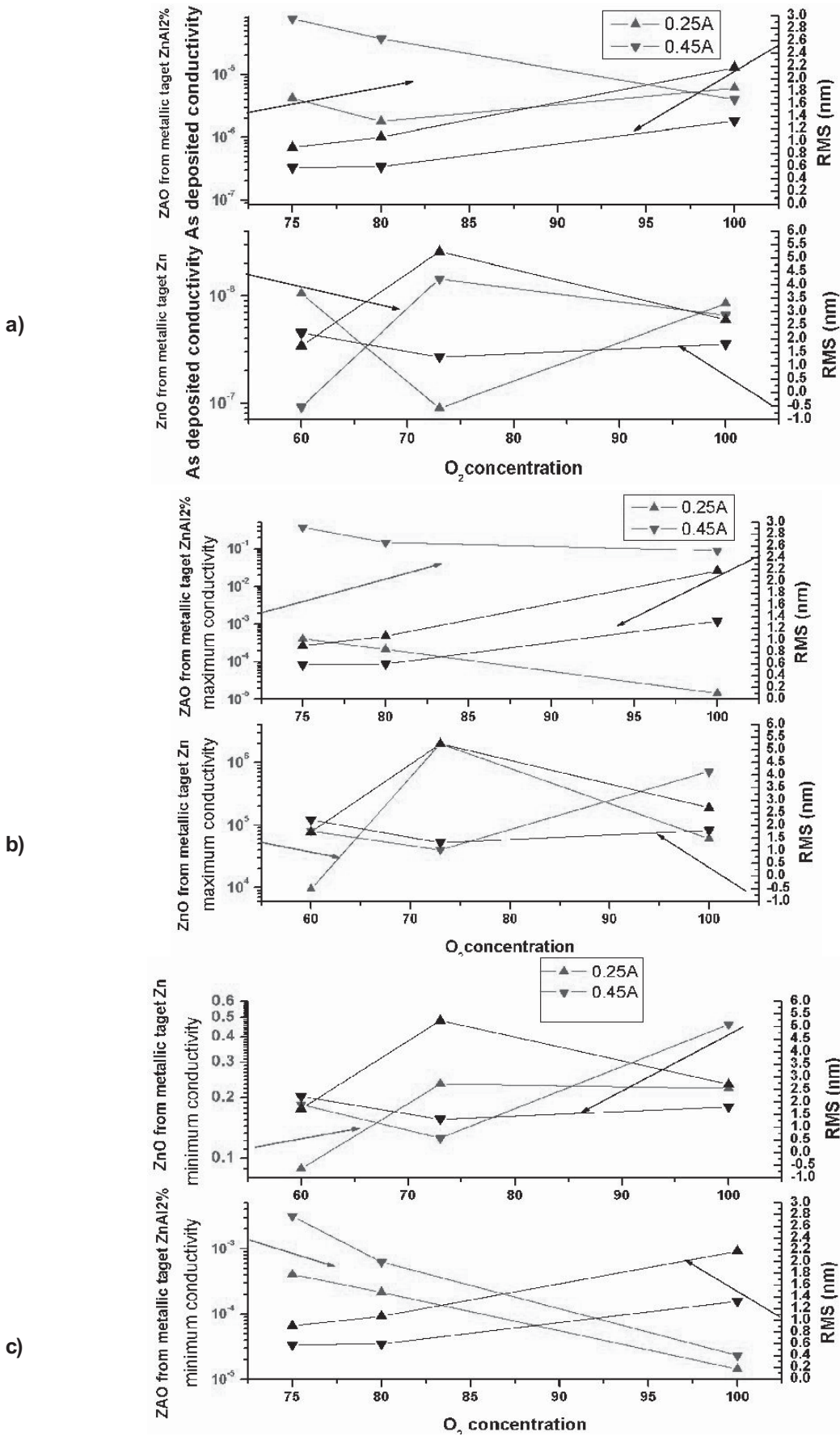
Fig. 2. (a) As deposited conductivity and RMS variation with O_2 concentration. (b) maximum conductivity and RMS variations with O_2 concentration. (c) minimum conductivity and RMS variations with O_2 concentration.
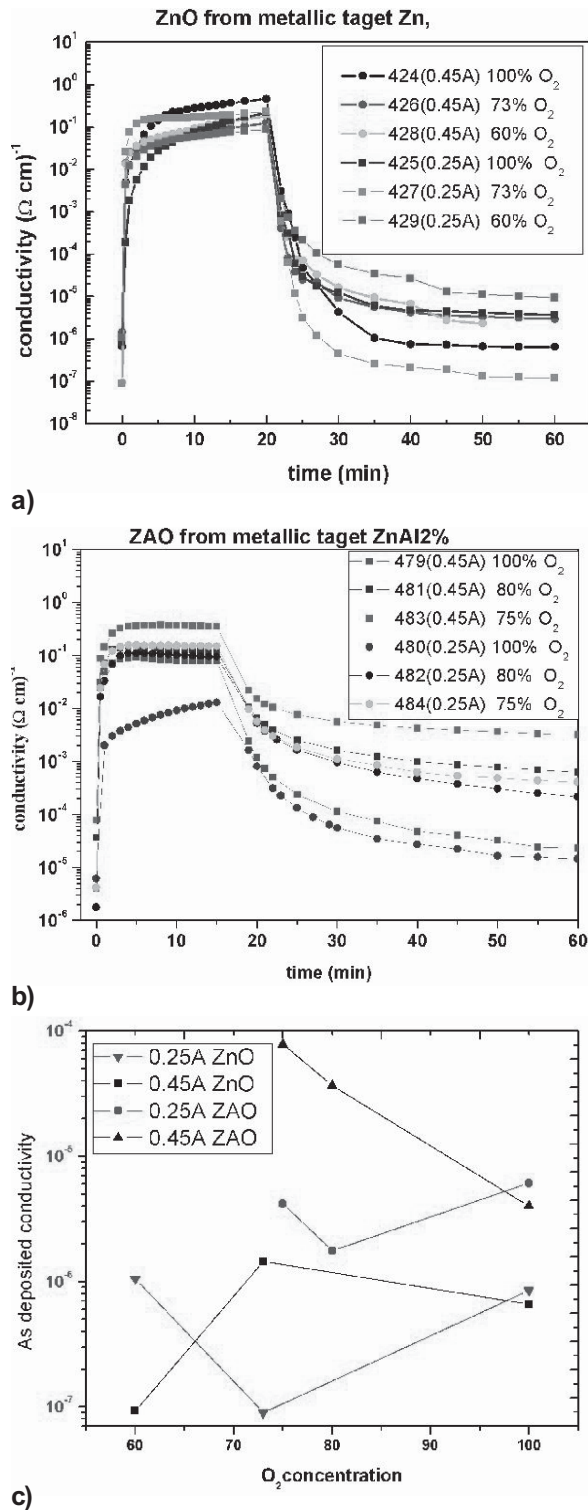
a)

b)

c)

Fig. 3. Conductivity changes under UV exposure in ozone atmosphere for films with different thickness: (a) ZnO, (b) ZAO, (c) As deposited conductivities for ZnO, ZAO thin films variation with O_2 concentration.

for ZAO thin films. Subsequent ozone oxidation lead to conductivity values changes of up to six orders for the ZnO films and up to four orders for ZAO thin films as shown in Figs. 3a and 3b. This behavior was completely reversible through many cycles of photoreduction and oxidation treatments. It is significant to note that the as deposited ZAO films conductivity was systematically higher than that of ZnO films probably due to the presence of Al dopant as shown in Fig 3c. To a lesser degree, this was also reflected in the conductivity of the films at the photoreduced state (i.e. after UV illumination). It should be noted that ZAO films demonstrated more stable and relatively higher values at this state regardless of deposition rates. Subsequent ozone exposure leads to the decrease of film conductivities to minimum values (although higher than the as deposited ones) possibly due to some oxygen vacancies annihilation (see Figs. 3a and 3b). Finally, comparing the conductivity changes with surface RMS from AFM measurements (Figs. 2a, 2b, and 2c), it can be seen that they follow each other in the sense that as the RMS increases, the conductivity decreases due to the enhancement of carrier scattering. Fig. 2 shows also the RMS and conductivity changes with O_2 concentration. As the O_2 concentration decreases the ZAO thin films RMS decreases while this was not clear for the ZnO films.

4. CONCLUSIONS

In this work the effect of gas flow ratio of O_2 to Ar as plasma gas on the variation of morphology of ZnO and ZAO thin films was studied as well as their effects on film conductivity changes. AFM characterization of the films surfaces revealed a granular, polycrystalline morphology with roughness decreasing as the oxygen partial pressure decreases. The films deposited at high O_2 ratio have shown bigger, better-formed grains, formed by the aggregation of many small particles, whereas the films deposited at higher Ar ratio had uniform grain distribution. O_2 to Ar ratio strongly influence the film surface morphology with implications in film conductivity modulation. Comparing the conductivity changes with surface RMS from AFM measurements it was shown that they follow each other in the sense that as the RMS increases, the conductivity decreases.

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