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Comparative study of zinc oxide and aluminum doped zinc oxide transparent thin films grown by direct current magnetron sputtering

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Abstract

Pure and aluminum (Al) doped zinc oxide (ZnO and ZAO) thin films have been grown using direct current (dc) magnetron sputtering from pure metallic Zn and ceramic ZnO targets, as well as from Al-doped metallic ZnAl2at.% and ceramic ZnAl2at.%O targets at room temperature (RT). The effects of target composition on the film's surface topology, crystallinity, and optical transmission have been investigated for various oxygen partial pressures in the sputtering atmosphere. It has been shown that Al-doped ZnO films sputtered from either metallic or ceramic targets exhibit different surface morphology than the undoped ZnO films, while their preferential crystalline growth orientation revealed by X-ray diffraction remains always the (002). More significantly, Al-doping leads to a larger increase of the optical transmission and energy gap (E_g) of the metallic than of the ceramic target prepared films.

Keywords: Zinc oxide; dc magnetron sputtering; Surface morphology; Sensors

1. Introduction

ZnO thin films are highly attractive in the development of materials area, due to their interesting physical properties as high transparency in the visible and near-ultraviolet (UV–VIS) spectral regions, as well as their wide conductivity range and conductivity changes under photoreduction/oxidation condition. The conductivity and its changes under specific conditions for ZnO thin films depends upon several factors, such as the preparation technique, the in situ preparation parameters, the doping agent, the annealing temperature and atmosphere, and even the measurement conditions [1–4]. When ZnO films are doped with the appropriate metal atoms, such as Al, Sn, Cd, Ga, In, etc., their conductivity can be changed from values as low as 10^{-10} $(\Omega\ \mathrm{cm})^{-1}$ to values as high as 10^{4} $(\Omega\ \mathrm{cm})^{-1}$. The wide range of conductivities and conductivity changes upon different environmental conditions make ZnO films suitable materials for oxidant gas sensing layers [5–7]. Dopant presence determines significant changes of film physical properties as crystalline structure (associated to stoichiometry), surface topology (associated to adsorption of species onto surface), optical properties (associated with photoconductivity) which reflect directly on film ability to act as a sensing layer. In the case of ZAO films, previous works have reported that the presence of the dopant determines usually crystallinity alterations [8] or decreases of the transmittance significantly, to values under 70% [9], facts that are highly inconvenient for sensing applications. In this work ZnO and ZAO thin films prepared by dc magnetron sputtering and their structural and optical properties were studied comparatively.

2. Experimental

The deposition of the ZnO and ZAO films was carried out in an Alcatel dc magnetron sputtering system using 99.999% pure

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Zn, ZnAl2 at% (ZnAl2%) metallic and ZnO, ZnO: 2 at.%Al_2O_3 (ZnAl2%O) ceramic targets all fabricated by Heraeus TMD. The base pressure in the chamber was 5×10^{-7} mbar (5×10^{-5} Pa). Films with thickness about 100 nm were deposited onto Corning 1737F glass and silicon substrates in an oxygen–argon atmosphere (O_2/Ar). The deposition constant parameters were the total pressure (8×10^{-3} mbar), the substrate temperature at 27 °C (RT), and the total gas flow. The depositions were done for plasma current I = 0.44 A. The surface morphology was measured with a Nanoscope III atomic force microscope (AFM) (Digital Co. Instruments, USA) using in Tapping Mode a conventional silicon nitride tip (125 μm) oscillating to its resonant frequency (200–400 kHz). All measurements were made at RT. In the present study the morphology parameters were determined using the Scanning Probe Image Processor (SPIP image processing software for nano- and micro scale microscopy).

X-ray diffraction (XRD) using a Rigaku diffractometer with CuKα X-rays was done in order to determine the crystal structure of the deposited films.

3. Results and discussions

It is well known that sputtered ZnO films are highly textured with the c axis perpendicular to the substrate surface. The changes in crystal structure for films sputtered from different targets were investigated by X-ray diffraction (XRD). Fig. 1a displays XRD patterns of ZnO and ZAO films deposited on Corning glass. The XRD spectra are dominated by the hexagonal ZnO (002) plane confirming the strong (002) textures. The films exhibit only the (002) peak in the displayed $2\theta/\omega$ region and no metallic Zn or Al characteristic peaks are observed. The characteristic parameters given by XRD from the (002) plane are used to characterize the feature of these ZnO and ZAO films (grown at RT in a 100%O_2 or Ar for ceramic targets), which are shown in Fig. 1b. The diffraction angle of $2\theta/\omega$ ranges from 33.669° for ZnO films grown from Zn metallic target, to 34.16° for ZnO films grown from ceramic target. The

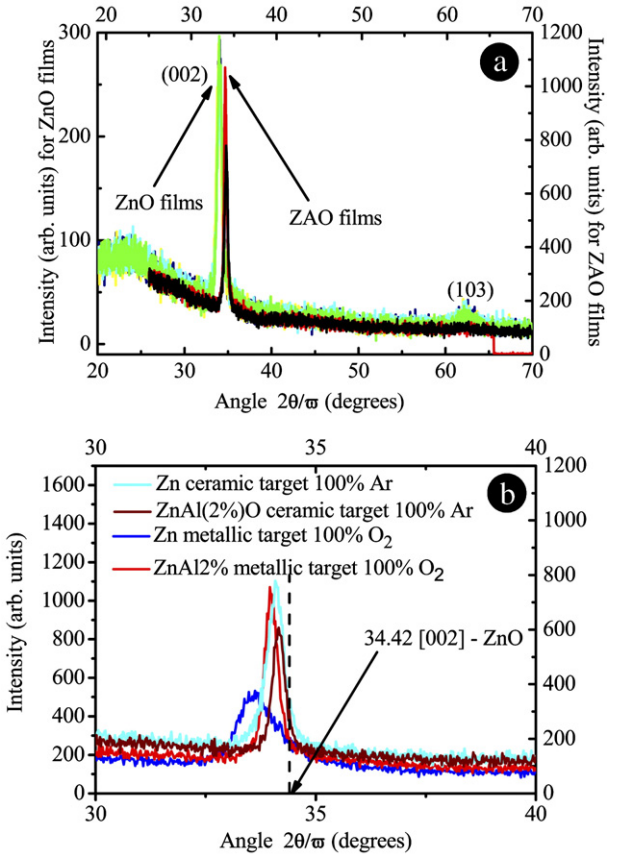

Fig. 1. a) XRD patterns of ZnO and ZAO films deposited on Corning glass; b) zoom on XRD pattern near (002) reflexion plane of ZnO and ZAO films (grown at RT in a 100%O_2 or Ar for ceramic targets).

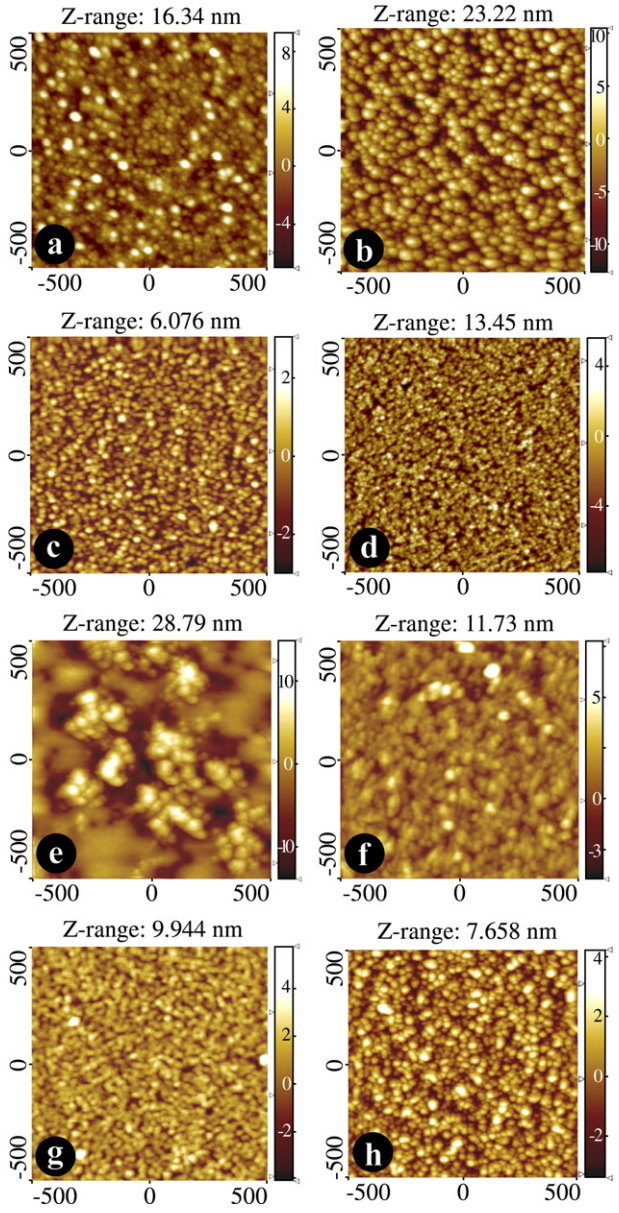

Fig. 2. AFM images of 1 × 1 μm scan size on films grown: a) from Zn metallic target in 80% O_2 concentration in plasma; b) in 100% O_2; c) from ZnAl2% metallic target in 80% O_2 concentration in plasma; d) in 100% O_2; e from ZnO ceramic target in 0% O_2 in plasma; f) in 20% O_2; g) from ZAO ceramic target in 0% O_2 in plasma; h) in 15% O_2.

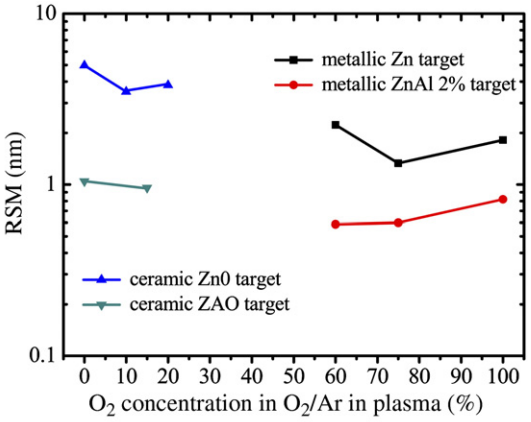

Fig. 3. RMS surface variation as a function of O_2 concentration in plasma for ZnO and ZAO films.

corresponding full width at half maximum (FWHM deg) of (002) diffraction ranges from 0.862° to 0.304°. In the case of ZAO films the diffraction angle of $2\theta/\omega$ ranges from 33.980° for films grown from ZnAl2% metallic target, to 34.085° for films grown from ceramic target. The corresponding FWHM deg of (002) diffraction ranges from 0.317° to 0.402°. The diffraction peak position of $2\theta/\omega$ approaches, but never reaches that of the bulk ZnO which has the value of 34.42°. It is obviously observed that the films show (002) textures and the (002) peak shifts to lower angle for metallic targets, as well as a decrease of film crystallinity reflected on lower peak intensity and crude peak broadening. Cebulla et al. [10] attributed the lower diffraction angles shift to a significant increase of compressive stress with decrease of oxygen concentration. This leads to a higher oxygen vacancies presence in the film, a fact which can explain the shift in the case of ZnO films from the extreme value of 33.669° for ZnO films grown from Zn metallic target in high O_2 concentrations and to the much closer value of 34.16° for ZnO films grown from ceramic target in high concentrations Ar. Kuroyanagi et al. [11] attributed the diffraction angle shifts from the (002) plane of Al-doped ZnO films grown by ionized deposition towards lower angles, to ionization of ZnO rather than Al-doping. Gupta et al. [12] have observed that sputtered ZAO films are in a uniform state of stress with tensile components parallel to *c* axis that could also result in a lower diffraction angle shift. These observations are in line with what was observed in this work for our ZAO films. However films grown under different O_2/Ar plasma concentrations did not show any significant variations in the XRD diffractograms.

AFM imaging of the surfaces of ZnO thin films deposited at room temperature from metallic and ceramic targets, under varying O_2/Ar flow ratios, are shown in Fig. 3. AFM characterization for the films deposited from a metallic target (Fig. 2a, b ZnO, c, d ZAO) revealed a granular, polycrystalline morphology with grain size decreasing and roughness increasing as the oxygen partial pressure in the plasma decreases. In the case of films grown from a ZnO ceramic target (Fig. 2e, f ZnO) the surface had a complete different morphology, which was mainly dominated by grains agglomerations and very tall features while films grown from ZAO ceramic target show a very smooth and homogeneous surface as shown in Fig. 2g, h. The grain size, derived with SPIP from AFM measurements, varied from 50 to 20 nm for ZnO deposited from a metallic

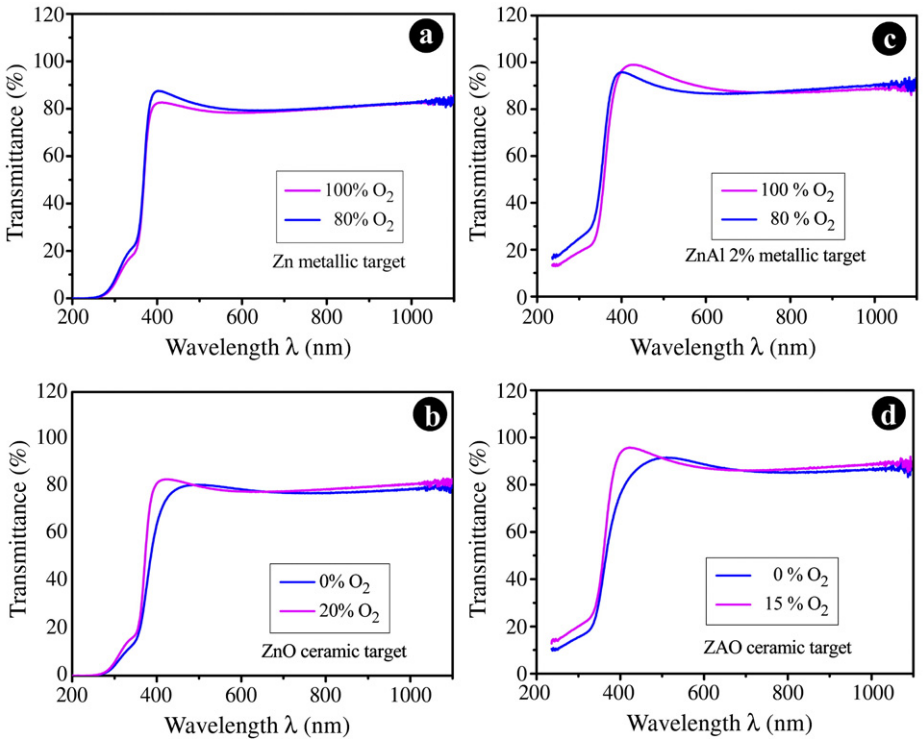

Fig. 4. UV–VIS transmittance spectra variation with O_2 concentration in plasma for films grown: a) from Zn metallic target; b) from ZnO ceramic target; c) from ZnAl2% metallic target; d) from ZAO ceramic target.

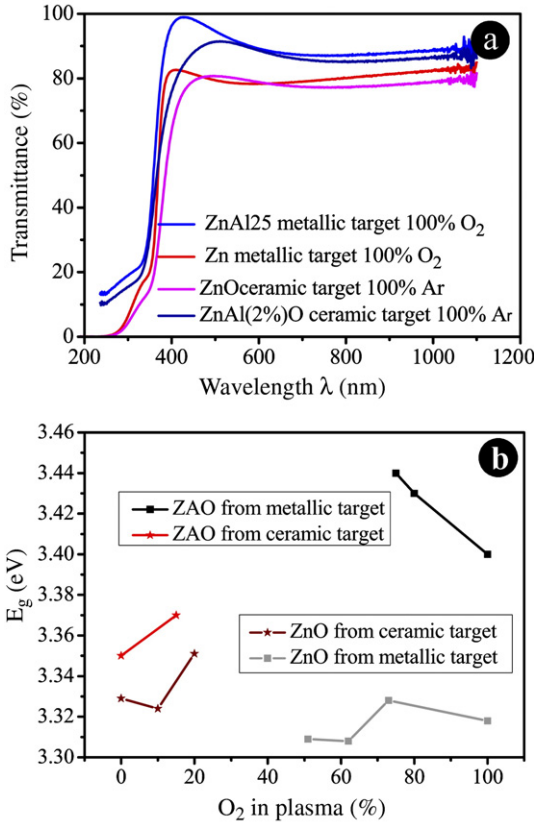

Fig. 5. a) UV–VIS transmittance spectra as a function of target material; b) E_g variation as a function of O_2 concentration in plasma for ZnO and ZAO films.

target. For ZnO films deposited from a ceramic target, agglomerates dimensions varied from 500 to 50 nm. The subgrain dimensions were measured and found to be in the range of 10–50 nm. For ZAO films grown from ZnAl2% metallic target, grain size was found to vary from 75 to 30 nm while for ZAO films grown from a ceramic target from 15 to 40 nm. The overall surface of ZAO films is formed by smaller and more homogeneous grains compared to the one of ZnO. The above mentioned microstructural changes can be directly attributed to the film growth rate variation. The growth rate increases when the O_2 concentration decreases due to the presence of Ar atoms in the plasma. For films grown from a metallic target, we observed that films deposited at higher O_2 ratio (Fig. 2a, c) have shown bigger, better-formed grains, whereas those deposited at higher Ar ratio (Fig. 2b, d) had a uniform grain distribution and smaller size. These observations may be attributed to the introduction of oxygen in the plasma, which could also generate high-energy oxygen neutral atoms. It is generally believed that the formation of grain agglomerations in the film deposited under the introduction of oxygen gas might be due to re-sputtering of high-energy neutral oxygen atoms [13]. As oxygen content in the 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 at the initial stage of the film growth process. For films grown from a ceramic target, the growth rate had a remarkable increase compared to the metallic target case for both ZnO and ZAO, due to the high Ar ion concentration in the plasma. The surface roughness (RMS) variations of the ZnO and ZAO thin films deposited at different O_2/Ar ratio are shown in Fig. 3. The scan area for surface roughness was 5×5 μm. It can be observed that the surface RMS is generally much smaller for ZAO films than for ZnO thin films. This points the role of Al dopant as a mineralizer or surfactant that significantly improves the texture of the layers.

The effect of O_2/Ar ratios in the plasma on the optical properties of the films was also investigated. Fig. 4 shows the normalized UV–VIS transmittance of different films grown from the four different targets on Corning glass at RT. All films exhibit a transmittance of higher than 80% in visible region and a sharp fundamental absorption edge. The visible transmission of these films has been observed to increase slightly when O_2 concentration in O_2/Ar plasma increases for all films grown from ceramic targets. In the case of growth from the metallic target, the variation in the visible transmission did not show any significant trend. However notable changes on UV–VIS transmittance were recorded subject to the nature of target as shown in Fig. 5a. We found out that ZAO films exhibit higher transmittance in visible region for both metallic and ceramic targets. More significantly, we observed that Al-doping enhances the optical transmittance of the ZnO films to values in the order of 90% which make them suitable for use as glass window material.

The optical band gap of ZnO and ZAO film was calculated to be in the range of 3.31 to 3.35 eV for ZnO films and from 3.35 to 3.43 eV for ZAO films based on the location of the absorption edge. The dependence of optical band gap on O_2/Ar ratios in the plasma revealing the optical band gap generally increases with increasing O_2 in the plasma and the target material are shown in Fig. 5b. Generally, the values for optical band gap of ZAO films were slightly higher. The conduction electrons in ZnO films are supplied from donor sites associated with oxygen vacancies or excess metal ions. In general the conduction characteristics of ZnO are primarily dominated by electrons generated from O_2 vacancies and Zn interstitial atoms which determine the shift of optical band gap to values smaller than the bulk $E_g \sim 3.37$ eV. The increase of the band gap with O_2 concentration can be associated with the decrease of the growth rates for all targets leading to a relative improved film stoichiometry, therefore a closer value of film E_g to the bulk material. For ZAO films, compared with pure ZnO films, the contribution from Al^{3+} ions on substitutional sites of Zn^{2+} ions and Al interstitial atoms determines the widening of the band gap caused by increase in carrier concentration. This is the well known Burstein–Moss effect [10] and is due to the Fermi level moving into the conduction band. According to the Burstein–Moss effect, the broadening of the optical band gap is

$$\Delta Eg = \left(\frac{\hbar^2}{2m^*_{vc}}\right)\left(3\pi^2 n\right)^{2/3},$$

where ΔE_g is the shift of doped semiconductor compared to undoped semiconductor, m_{vc}^* is the reduced effective mass, $\hbar$ is Plank constant, and n is carrier concentration. According to this

equation the band gap would increase with increasing carrier concentration. However, the band gap obtained for our ZAO films does not accurately follow the equation, and is much smaller than predicted (~3.9 eV) from Burstein–Moss theory at ~2 at.% Al-doped films [14,15]. This has been attributed to the merging of an impurity band into the conduction band, thereby shrinking the band gap and compensating the Burstein–Moss effect and it is in line with previous observations [14].

4. Conclusions

ZnO and ZAO thin films have been grown using dc magnetron sputtering from pure metallic Zn and ceramic ZnO targets, as well as from Al-doped metallic ZnAl2% and ceramic ZnAl2%O targets. All films have (002) texture, however for metallic targets the (002) peak shifts to lower angles and there is a decrease of film crystallinity. All films exhibit only the (002) peak and no metallic Zn or Al characteristic peaks were observed. The (002) diffraction peak position approaches but never reaches that of the bulk ZnO which has the value of 34.42°. Surface topology studied by AFM imaging of the surfaces of ZnO thin films deposited at room temperature from metallic and ceramic targets, under varying O_2/Ar plasma ratios showed that grain size and surface RMS are determined by growth conditions for each specific target and they can be controlled and reproduced for a specific application. All films exhibit a transmittance higher than 80% in the visible region and a sharp fundamental absorption edge. The optical band gap width of ZnO and ZAO film was simply estimated to be in the range of 3.31 to 3.35 eV for ZnO films and from 3.35 to 3.43 eV for ZAO films based on the location of the absorption edge. Al-doping leads to increased optical transmittance for both metallic and ceramic targets.

Acknowledgments

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References

[1] P. Nunes, B. Fernandez, E. Fortunato, P. Vilarinho, R. Martins, Thin Solid Films 337 (1999) 176.
[2] T. Minami, H. Nanto, S. Takata, Jpn. J. Appl. Phys. 24 (1995) L605.
[3] A. Suzuki, T. Matsushita, N. Wada, Y. Sakamoto, M. Okuda, Jpn. J. Appl. Phys. 35 (1996) L56.
[4] E. Jiménez González, J.A. Urueta, Sol. Energy Mater. Sol. Cells 52 (1998) 345.
[5] G. Kiriakidis, M. Suchea, S. Christoulakis, N. Katsarakis, Rev. Adv. Mat. Sci. 10 (2005) 215.
[6] M. Suchea, K. Christoulakis, N. Moschovis, G. Katsarakis, Thin Solid Films 515 (2006) 551.
[7] A.M. Gas'kov, M.N. Rumyantseva, Russ. J. Appl. Chem. 74 (2001) 440.
[8] M. Chen, Z.L. Pei, X. Wang, C. Sun, L.S. Wen, J. Vac. Sci. Technol. A19 (3) (2001) 963.
[9] K. Tominaga, H. Manabe, N. Umezu, I. Mori, T. Ushiro, I. Nakabayashi, J. Vac. Sci. Technol. A15 (1997) 1074.
[10] R. Cebulla, R. Wendt, K. Ellmer, J. Appl. Phys. 83 (1998) 1087.
[11] A. Kuroyanagi, J. Appl. Phys. 66 (1989) 5492.
[12] V. Gupta, A. Mansingh, J. Appl. Phys. 80 (1996) 1063.
[13] S. Mishra, C. Ghanshyama, N. Rama, R.P. Bajpai, R.K. Bedi, Sens. Actuators, B 97 (2004) 387.
[14] Z.C. Jin, I. Hamberg, C.G. Granqvist, J. Appl. Phys. 64 (1988) 5117.
[15] K.C. Park, D.Y. Ma, K.H. Kim, Thin Solid Films 305 (1997) 201.