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Growth characteristics and residual stress of RF magnetron sputtered ZnO:Al films

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Abstract

Transparent and conductive ZnO:Al films were deposited by RF reactive magnetron sputtering on glass substrates. The growth characteristics of the films as function of oxygen fraction and RF power were investigated by X-ray diffractometry, scanning electron microscopy and transmission electron microscopy; while the induced residual stress in the films was calculated by the Stoney's equation. It is shown that the deposits were flat and dense with a columnar structure in the cross-section morphology. A ZnO (0002) preferred orientation was obtained when the oxygen fraction used in the deposition process was larger than 12%. The growth rate reveals a maximum value depending on the oxygen fraction and RF power. All the deposits show a compressive stress which increased as the RF power was increased when the oxygen fraction in the deposition process was 8~10%, while it decreased as the oxygen fraction was 12~15%.

Keywords: Stresses; Physical vapor deposition; Transparent conductive oxide, RF magnetron sputtering; Thin films

1. Introduction

Transparent conducting oxide (TCO) thin films are characterized by their low specific electrical-resistance and high transparency in the wavelength of visible range. Zinc oxide thin films doped with group III atoms, including Al, In, Ga, etc. [1–4], have been fabricated as transparent and conducting films for such applications as photovoltaic electrodes [5], display devices [6], solar cells [7] and so on. Among the doped films, Al-doped ZnO is considered to be an outmost important material due to the highest conductivity and good transparency. Sputtering is considered to be a suitable technique to prepare ZnO:Al films because it has low cost and offers good uniformity in large area application. The sputtering parameters relating to the electrical and optical properties of the ZnO:Al films have been investigated thoroughly while their mechanical properties have been scarcely considered. Puchert et al. [8] related that the residual stress in the ZnO films could reach values as high as 10^9 Pa. The durability of thin films, which is influenced by their mechanical properties is very important for the coated products. In microelectronics technology, the mechanical stress is much important for the mechanical stability and the electrical properties of the film [9]. In this study, the growth characteristics and residual stress of the ZnO:Al films were investigated. The effect of sputtering power and oxygen fraction in the deposition on the residual stress was discussed.

2. Experimental

The ZnO:Al films were deposited onto Corning 1737 glass substrates by conventional planar reactive radio frequency (RF) magnetron sputtering using a 3 inch Zn–2 wt.% Al alloy target as described elsewhere [10]. During the sputtering process, the substrate temperature was set at 250°C, the RF power was varied from 80 to 100 W and the oxygen fraction was changed from 8 to 15%. After deposition, the structural characteristics were analyzed by X-ray diffraction (XRD, Rigaku, D/max. 3V) using Cu-K_α radiation, scanning electron microscopy (FE-SEM, Philip XL-40FEG) and trans-

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mission electron microscopy (TEM, JEOL, JEM 3010) while the composition of the films was analyzed by electron probe microanalyzer (EPMA). To determine the growth rate, the film thickness was measured by a conventional stylus surface roughness detector (Telcon, α-step 200). The residual stress of the deposits was measured by the curvature of the coated Corning 1737 glass using Stoney's equation [11] as follows:

$$\sigma = \frac{E_s \cdot h_s^2}{6(1-\nu) r h_f}$$

where E_s and ν are Young's modulus and Poisson ratio of the substrate and h_s and h_f are the thickness of the substrate and of the film, respectively.

3. Results and discussion

3.1. Film growth

Fig. 1 shows the growth rate of ZnO:Al films versus the oxygen fraction used in deposition at the total pressure of 2×10^{-3} Torr. It is shown that the growth rate increased initially with increasing the oxygen fraction and then decreased. Shinoki and Itoh [12] defined the reactive sputtering into two regions according to their reaction model by the critical partial pressure of reactive gas. For the first metallic region where the reactive gas is under the critical partial pressure, most of the sputtered species are in the metallic state and have a high deposition rate, while as it increases over the critical partial pressure, the growth rate decreases sharply due to the target poison effect. However, the growth rate in this study was very low at low oxygen fraction, this probably being due to the formation of high-energy negative ions during sputtering [13]. The ions were accelerated to bombard the substrate and consequently, the as-received zinc particle was re-sputtered or re-evaporated because it has a low melting point as well as a high vapor pressure. This in turn resulted in a dramatic change in the composition of the deposited films; therefore, the compositions analyzed by EPMA in Table 1 show that the zinc concentration was by far deviated from the stoichiometry as deposited at low oxygen fraction, which supported our suggestion. In this study, the growth rate reached a maximum value at the oxygen fraction of 12% and then decreased for RF power of 90 and 100 W. This indicates that a larger surface coverage by reactive gas happened at a higher reactive gas fraction. In addition, for the oxygen fractions of 12 and 15%, the growth rate increased at increased RF power, indicating that a higher ionization of the sputtering gas was obtained at high RF power.

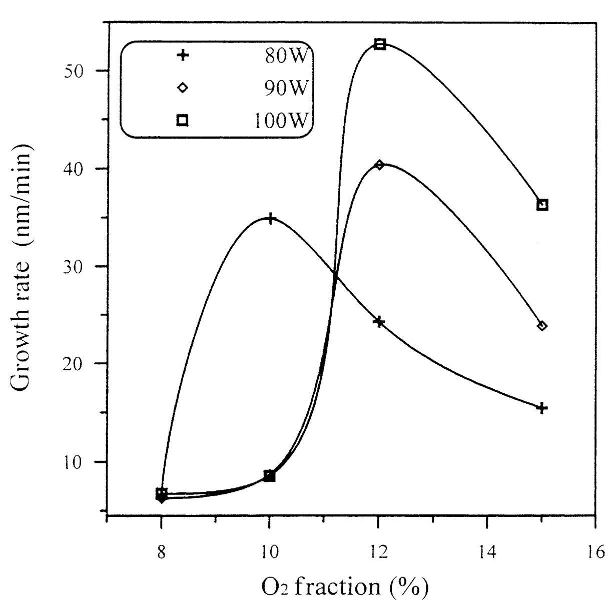

Fig. 1. Dependence of growth rate on oxygen fraction at a total pressure of 2×10^{-3} Torr.

3.2. Structure of ZnO:Al films

Fig. 2 shows the XRD diffraction patterns of the films deposited at various oxygen fractions and RF power of 90 W in Fig. 2(a), and at various RF powers and constant oxygen fraction of 12% in Fig. 2(b). The diffraction peak of the film located at about 36.5° as deposited at low oxygen fraction of 8% was attributed to the Al_2O_3 phase while no significant ZnO phase was found. The formation of Al_2O_3 may be a result of re-sputtering of as-received zinc species at the substrate by high-energy negative ions due to the low melting point of zinc, therefore, an excess Al left on the substrate to react with oxygen. When the oxygen fraction in the reaction chamber was large enough to poison the target, a ZnO (0002) preferred orientation was formed. The dominant constitution in the films changed from Al_2O_3 to ZnO

Table 1
Film compositions analyzed by EPMA

Deposition parameters		Chemical composition in at.%			
RF power (W)	O_2(%)	Si	O	Zn	Al
80	8	13.0116	53.4274	8.6089	24.9522
80	10	0.0078	52.4021	45.2186	2.3741
80	15	0.0030	52.0421	46.0886	1.8662
90	8	0.5291	59.1941	11.2195	29.0574
90	10	0.0066	52.8222	45.2183	1.9551
90	12	0.0052	52.8593	44.9363	2.1992
90	15	0.0074	52.5275	45.6540	1.8111
100	8	10.5528	52.7516	13.7498	22.9457
100	10	12.9315	53.4463	12.5104	21.1118
100	12	0.0038	52.1932	45.6934	2.1169
100	15	0.0081	52.9661	44.8950	2.1362

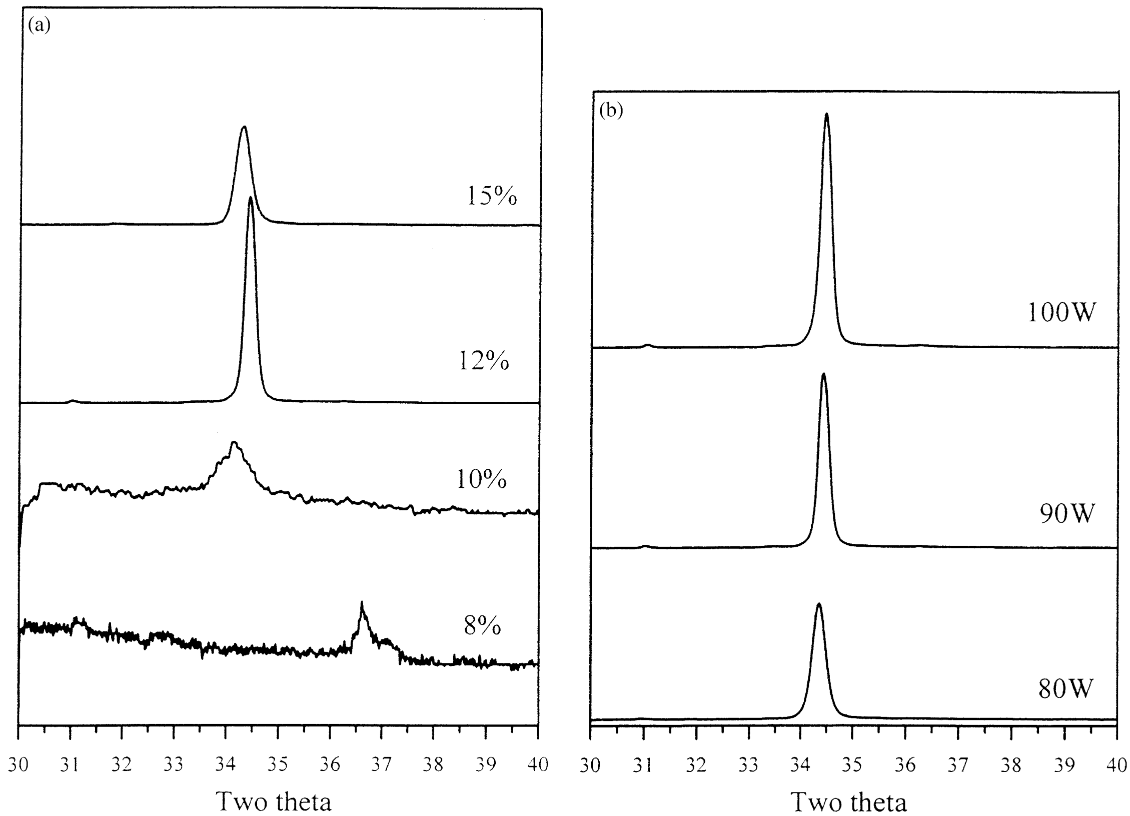

Fig. 2. XRD diffraction patterns of the AZO films deposited at (a) various oxygen fractions and RF power of 90 W and (b) various RF powers and oxygen fraction of 12%.

phase was found in every power level for a specific oxygen fraction in this study. It is shown that the deposited films have a low deposition rate and poor crystallinity under lower oxygen fraction. Only when the oxygen fraction was larger than a threshold value, ZnO:Al films with good crystallinity can be obtained. Fig. 2(b) shows the X-ray diffraction patterns for the ZnO:Al films deposited at oxygen fraction of 12% which is under the oxide region of Shinoki model [12] where the crystallinity was enhanced with increasing RF power. In addition, the deposited ZnO:Al films during this oxide region show a ZnO (0002) preferred orientation, implying a *c*-axis growth perpendicular to the substrate surface. This was due to the lowest surface free energy [14] of the most densely packed (0002) planes in the wurtzite ZnO structure.

The SEM surface and cross-section morphologies for the film deposited at 100 W and 12% oxygen fraction are shown in Fig. 3. The deposited film was dense with high energetic species bombardment features on the surface, while the cross-section micrograph reveals a columnar structure as it grew on the substrate. Usually, a columnar structure of the deposits is found in the sputtering process, however, it can be seen that the grain size is much smaller near the substrate surface

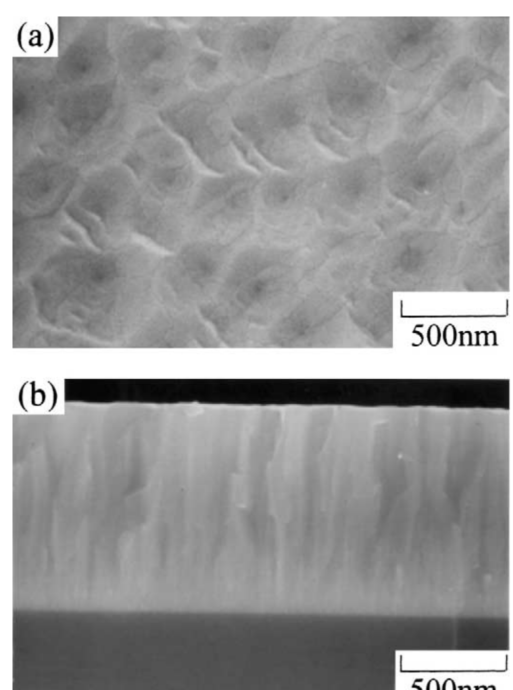

Fig. 3. SEM surface and cross-section morphologies for AZO film deposited at RF power of 100 W and oxygen fraction of 12%.

than the ones on the top of the film, implying a competing growth [15] of the deposited film. The columnar structure was further identified by the TEM analysis in Fig. 4, which shows a significant columnar morphology. The diffraction patterns demonstrate the ZnO hexagonal structure of the film while no other phases were found by the TEM analysis, although Sieber et al. [16] suggested the presence of secondary phases of ZnO_2 and ZnAlO.

3.3. Residual stress in the films

The residual stress in the films is composed of thermal stress and intrinsic stress, the former comes from the difference in the thermal expansion coefficients between the coating and the substrate, while the latter originates from the ingrown defects or structural mismatch between the film and substrate [17]. In this study, the dependence of total residual stress on the deposition parameters was investigated, in which the thermal stress could be considered as constant due to the same deposition temperature. Fig. 5 shows that the residual stress reached a high value as deposited at low oxygen fraction of 8% and then it decreased sharply with increasing oxygen fraction in deposition. After that, the residual stress increased gradually again with further increasing the oxygen fraction to 15%. It is well known that the total energy input at the growing films plays a critical role in stress development. The high stress for the films deposited at a low oxygen partial pressure was due to the atomic peening effect [18] by the high-energy negative ions, which induced structural defects and deviation from stoichiometry, therefore, increasing the residual stress. As the oxygen fraction increased to 10 or 12%, the sputtered species had an appropriate energy due to the partial oxidation of the target. Further increase in the oxygen fraction larger than 12% in the deposition process, most of the target surface was oxidized, which caused a low sputtering yield and low energy species. Therefore, the residual stress was increased due to the low energy for the as-received species to migrate on the substrate.

Fig. 6 shows that the residual stress increased with increasing the RF power as the oxygen fraction was 8–

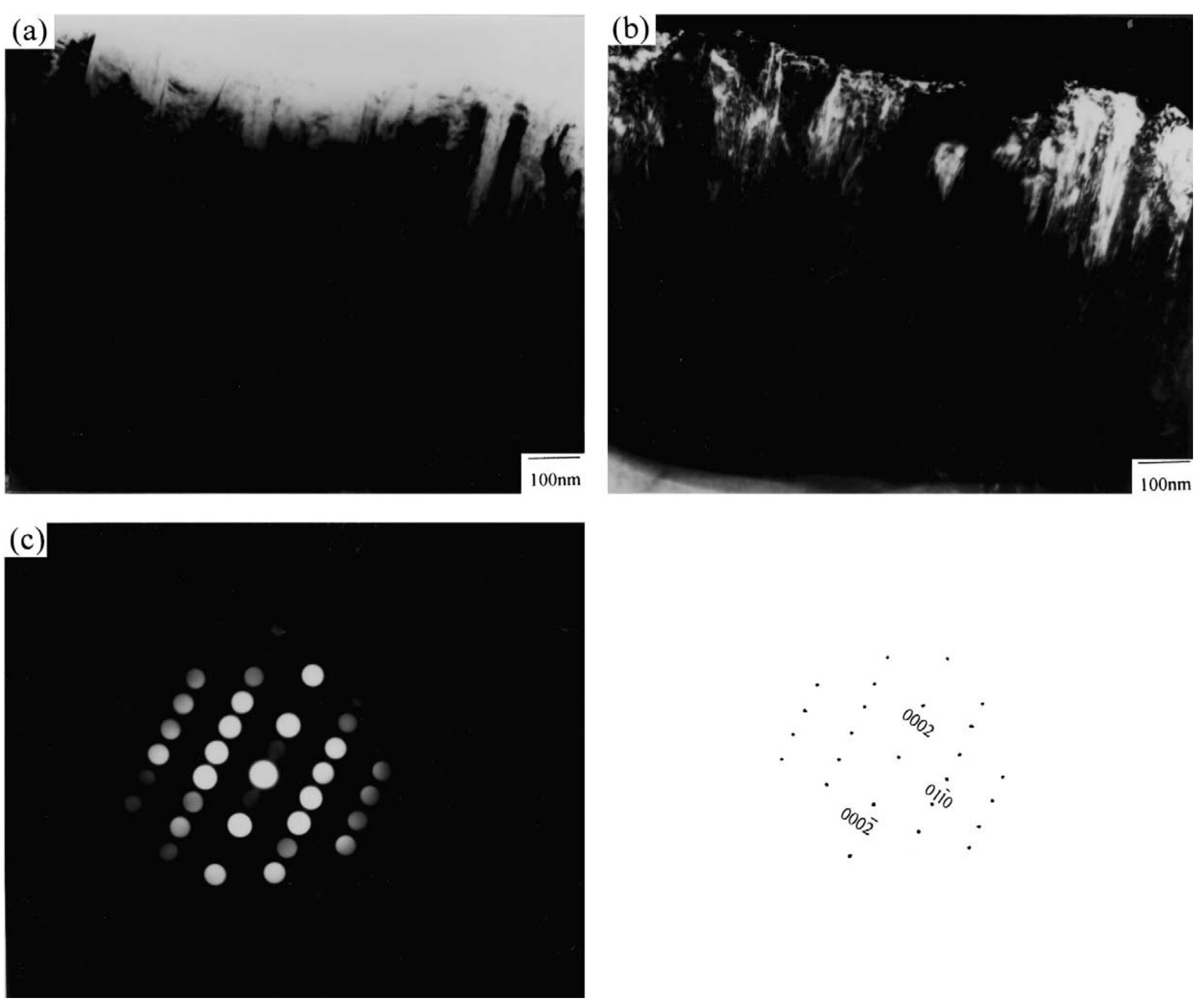

Fig. 4. TEM cross-section micrograph and diffraction pattern for AZO film deposited at RF power of 100 W and oxygen fraction of 12%.

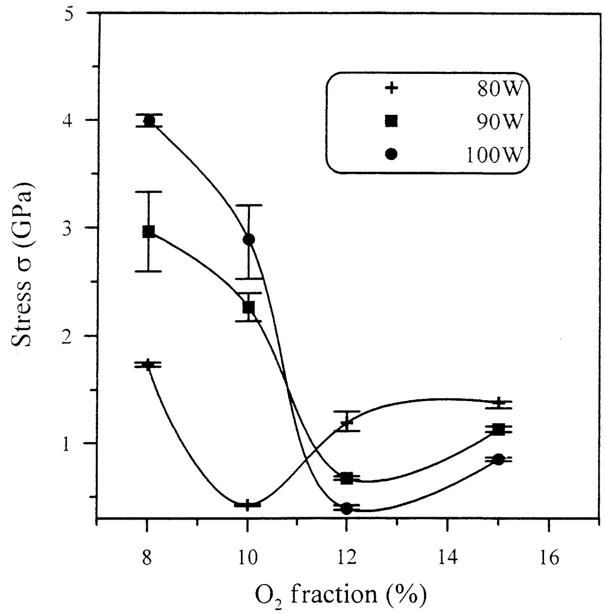

Fig. 5. Dependence of compressive stress on oxygen fraction in deposition.

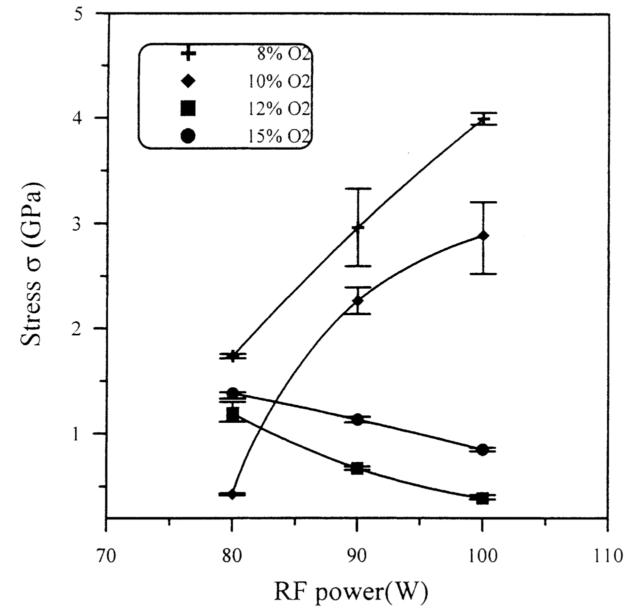

Fig. 6. Dependence of compressive stress on RF power in deposition.

10%. This can be explained by the resputtering and atomic peening effects [18] due to the high energy negative species bombarding the substrate under low oxygen partial pressure. It can be seen that the residual stress for the films deposited at 8% oxygen fraction was larger than those at 10% under every power value used, indicating a high bombardment effect for low oxygen partial pressure. However, the residual stress decreased with increasing the RF power at 12 and 15% oxygen partial pressures, implying that at the oxide region of reactive sputtering, the as-received atoms had the ability to migrate to the suitable sites on the substrate with the appropriate power and then reduced the ingrown stress. Davis [19] also suggested that high energetic bombardment could induce a stress relaxation effect, which was found in the oxide region in this sputtering process.

4. Conclusion

The effect of sputtering parameters on the structural characteristics and residual stress of transparent conducting ZnO:Al films was investigated. The deposited films were grown in a columnar structure perpendicular to the substrate and showed a smooth morphology with some high energetic species bombardment features for the films prepared under a high RF power. As deposited at a lower oxygen fraction, the growth rate was limited due to the resputtering effect which in turn resulted in a high compressive stress and a poor crystallinity with the presence of Al_2O_3 phase. While as the oxygen fraction was increased to poison the target, the resputtering effect was reduced and the deposits had a high growth rate as well as a low internal stress; nevertheless, it had a critical value of 12% oxygen fraction for the highest growth rate as well as the lowest compressive stress in the films.

Acknowledgements

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