Control the crystal growth of Al-doped ZnO thin film prepared by pulsed laser deposition and the influences on its optical and electrical properties

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Abstract. In this work, highly transparent and highly conductive thin films of Al-doped ZnO (AZO) are achieved by pulsed laser deposition (PLD). By changing substrate temperature in the range of room temperature to 500°C during the deposition process, the preferential growth direction of AZO crystal is controlled and, therefore, the surface morphology, optical and electrical properties of AZO thin films are able to be manipulated. X-ray diffractograms as a function of the substrate temperature clearly illustrate the ability to control the preferential growth direction of AZO. At the low substrate temperature, the growth along [002] direction corresponding to c-axis of hexagonal ZnO is only observed. By elevating the substrate temperature, not only crystallinity of AZO thin film is further improved but also the competition of crystal growth along the [002], [001] and [101] directions are occurred due to the increase of total energy and surface mobility of cluster/atom. The AZO films obtained by all preparation conditions exhibit an n-type semiconducting characteristics, furthermore, the carrier concentration and the carrier mobility of AZO thin films can be optimized to reach 4.10×10^{20} cm^{-3} and 7.53 cm^2/Vs, respectively. The excellences in both carrier concentration and mobility of AZO thin film lead to very low resistivity of 2.08×10^{-3} Ωcm. In addition, the wide optical band gap of ~3.50 eV together with the high transparency over 90% in visible region is obtained from the AZO thin films. The exceptional optical and electrical properties of AZO thin film demonstrate that such material has enough potential to become a promising candidate using in optoelectronic applications.

1. Introduction

Transparent conductive oxide (TCO) is attractive interested as transparent electrode used in numerous applications such as solar cell, smart windows, organic light emitting diodes (OLEDs), touch screen and display technology. Among TCO material commonly and commercially utilized as transparent electrode, indium tin oxide (ITO) is favourable candidate because of its excellence in electrical and

optical properties. However, ITO thin film suffers from high cost of indium (In) source and unstable of electrical properties at high temperature operation [1]. Recently, III-A group metal doped ZnO have been proposed to replace ITO thin film owing to the outstanding properties like wide direct band gap (~3.4 eV), large exciton binding energy (~60 meV at 25ºC), non-toxicity and high environmental stability. Among III-A group, Aluminum (Al) demonstrates promising candidate compared with indium (In) or gallium (Ga) in case of lower cost and toxicity. Therefore, aluminum-doped zinc oxide (AZO) has enough potential to become the alternative material to replace ITO. Regarding to AZO fabrication technology, pulsed laser deposition (PLD) system is alternatively used to prepare AZO thin film because of providing crystallinity and preserving chemical composition [2]. For PLD parameters, energy density of ablated laser, repetition rate, working pressure and substrate temperature can be adjusted to acquire desired AZO properties. It is generally known that substrate temperature directly relates to the total energy and surface mobility of cluster/atom. In this work, AZO thin films were fabricated via the PLD at different substrate temperature in the range of room temperature (RT) to 500ºC. Crystal structure, surface morphology, electrical and optical properties of AZO thin films are characterized by x-ray diffraction (XRD), atomic force microscope (AFM), hall measurement and uv-visible spectrophotometer, respectively.

2. Methods

AZO thin films were fabricated on quartz and SiO_2/Si wafer via pulsed laser deposition system (Twente Solid State Technology, The Netherlands). $ZnO:Al_2O_3$ target with atomic ratio of 98%:2% is purchased from Kurt J. Lesker. Initially, the substrate was ultrasonically cleaned by alcohol process then directly transferred to the PLD chamber evacuated to $1x10^{-7}$ mbar. After that, the PLD chamber was fulfilled with $Ar:O_2$ atmosphere with the ratio of 10:1 until the working pressure reach to $1x10^{-1}$ mbar. Then AZO target was ablated by KrF excimer laser (IPEX-700, Lightmachinary, Inc. Com., λ=248 nm) at the fluency, repetition rate and total pulse of 0.70 J/cm^2, 5 Hz and 6000 shots, respectively. The substrate temperature was precisely controlled in range of RT, 200ºC, 300ºC, 400ºC and 500ºC, respectively. Finally, the fabricated AZO thin films were cooled down in O_2 ambient. Crystal structure of AZO thin films is performed via x-ray diffractometer (Rigaku) with Cu-Kα (λ=1.54 ***Å***) radiation. The diffractrograms (2θ = 30º – 50º) obtains from both wide angle XRD (WXRD; $\theta/2\theta$ scan) and grazing incident XRD (GIXRD; 2θ scan with incident angle ~0.03º). Atomic force microscope (Seiko, SPA400) is introduced to investigate the surface morphology with scanning area of 2 μm^2. Hall measurement set up (Ecopia HMS-3000) based on Van Der Pauw structure is employed to examine the electrical properties at RT with magnetic field of 0.5 T. Finally, the transmittance is collected from 200 nm to 850 nm via UV-visible spectrophotometer (PG Instrument T90+).

3. Results and Discussion

AZO thin films deposited as function of substrate temperature were characterized by WXRD to determine the orientation of the crystal growth along the perpendicular direction respect to the substrate. The diffractogram of AZO thin films are presented in figure 1(a). The unheated sample does not show any diffraction pattern whereas the heated samples clearly show the dominant diffracting peak at 34.50º corresponding to the growth of wurtzite ZnO in (002) plane (JCPDS card no. 086254). Interestingly, the decrease of peak intensity observed in the samples prepared by substrate temperature over 300ºC suggests the change of crystal growth. To obtain further information related to the growth of AZO crystal, GIXRD was applied and the results were presented in figure 1(b). the AZO thin film prepared at RT exhibits two weak diffracting peaks at 32.20º and 36.50º assigned to the growth of AZO along (100) and (101) planes. By elevating the substrate temperature, the preferential growth along (002) plane is clearly observed [3]. However, the alternative growth plane is observed for the sample obtained at substrate temperature over 300ºC. Notice that, thickness of obtained thin films was approximately from 150 nm to 180nm. The conversion of crystal growth behaviour can be described from the difference of formation energy in each preparation condition. For unheated film, the

formation energy only acquires from laser energy. Thus, cluster/atom arriving at substrate has low surface mobility and insufficient energy to form high crystallinity. By increasing substrate temperature, the cluster/atom obtains sufficient energy to form (002) plane. The further increase in substrate temperature results in the formation of AZO bulk phase indicated by the appearance of (100), (002) and (101) planes owing to excess formation energy. It is worth mentioning that no diffracting peak related to the formation of Zn, Al or Al_xO_y phase is appeared. This result indicates that, in AZO thin films, Al acts as dopant in ZnO matrix.

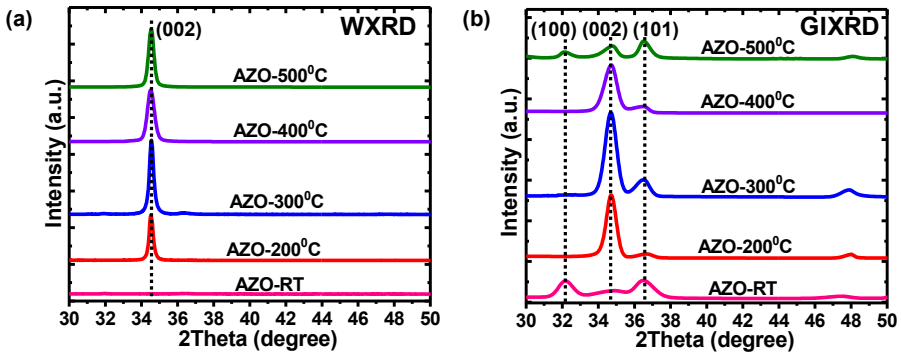

Figure 1. X-ray diffractrogram of AZO thin films prepared as function of substrate temperature using (a) wide angle x-ray diffraction (WXRD), (b) grazing incident x-ray diffraction (GIXRD) with grazing angle of 0.3°

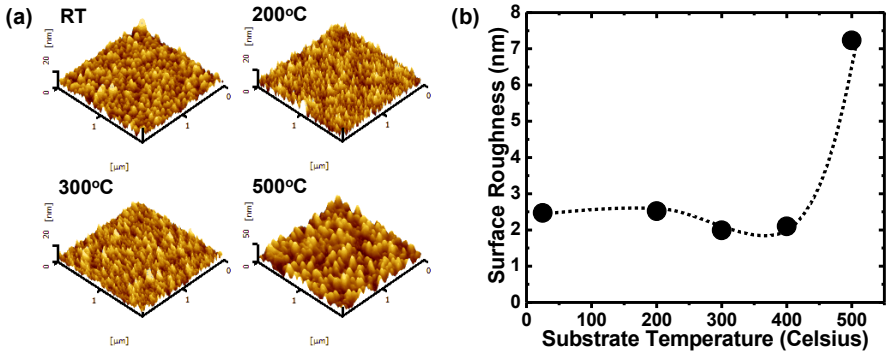

Figure 2. (a) AFM micrograph of AZO thin films at different substrate temperature and (b) surface roughness as a function of substrate temperature

Surface morphology of AZO thin films prepared by controlling substrate temperature from RT to 500°C are performed via AFM (see figure 2(a)). It clearly observes that the surface morphology of AZO thin films is homogenous without morphological defects e.g. crack, void and whisker on the surface. In addition, the surface grain boundary as well as surface roughness (shown in figure 2(b)) of AZO thin films gradually decrease by increasing substrate temperature from RT to 300°C but those dramatically increases when substrate temperature reached to 500°C. It is well known that, by elevating substrate temperature, the surface mobility of cluster/atom on the substrate surface is enhanced, leading to the formation of large surface grain boundary [4]. Electrical properties of AZO thin films obtained from Hall measurement suggest that all prepared conditions exhibit n-type semiconductor. The carrier concentration and the carrier mobility of AZO thin films as function of substrate temperature are shown in figure 3(a). The carrier concentration tends to increase from 1.35×10^{20} to 4.10×10^{20} cm^{-3} by increasing substrate temperature from RT to 300°C while the declination of carrier concentration is occurred when substrate temperature is higher than 300°C. The enhancement of carrier concentration at RT to 300°C and the declination at over 300°C are attributed

to the improvement and deterioration of crystallinity, respectively. Additionally, the thin film resistivity as low as 2.08x10^{-3} Ωcm is achieved at the substrate temperature of 300^{O}C.

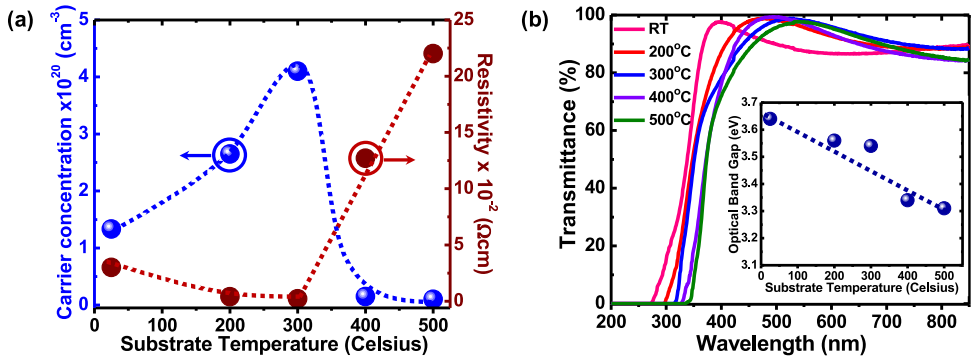

Figure 3. (a) Carrier concentration and resistivity, (b) optical transmission spectrum and (inset b) calculated optical band gap of AZO thin films prepared as a function of substrate temperature

Figure 3(b) displays optical transmittance in the range of 200 to 850 nm of AZO thin films prepared on quartz. The prepared AZO thin films exhibit wide band gap with the absorption edge ~380 nm and high optical transmittance in visible region over 90%. To determine the optical band gap of AZO thin films, Tauc's equation for direct band gap was employed. The optical band gap of AZO thin films is performed in the inset of figure 3(b). Our obtained optical band gaps are in the range of 3.30 to 3.65 eV which agrees with those obtained in the literatures [2, 5, 6]. As demonstrated results, the prepared AZO thin film provides enough potential to be used as the alternative transparent electrode.

4. Conclusions

In conclusion, the crystal growth of AZO thin films is controlled via substrate temperature during deposition process. The transition of crystal growth from (002) plane to bulk phase is resulted from the increase of formation energy directly obtained from temperature of the substrate. Furthermore, substrate temperature not only controls the crystal growth but also has an influence on the surface mobility of cluster/atom on the substrate surface which directly determine the surface morphology of AZO thin film. By controlling preparing condition, the AZO thin film with high optical transmittance over 90% in visible region and low resistivity of 2.08x10^{-3} Ωcm was acquired. Consequently, the prepared AZO thin film in this work demonstrates the possibility to be utilized as an alternative transparent conducting electrode.

5. Acknowledgements

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