Amorphous $In_2Ga_2ZnO_7$ films with adjustable structural, electrical and optical properties deposited by magnetron sputtering

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Abstract: Amorphous $In_2Ga_2ZnO_7$ (IGZO) films with adjustable structure and properties were deposited on glass substrates by magnetron sputtering, and the corresponding parameters of growth temperature which would improve the electrical and optical properties of the IGZO films were further investigated. The IGZO films prepared at the temperature range from room temperature to 300 °C demonstrated smooth surfaces, and were constructed by numerous nanoparticles with amorphous phase and dense structure. Furthermore, the resistivity, carrier concentration and Hall mobility of the IGZO films showed obvious changes under different growth temperatures. From this study, it could be found that the IGZO film showed the smallest value of direct current resistivity at 300 °C, and displayed high transmittance in the visible light range. The band gap (3.80 eV) of the IGZO films was red-shifted slightly as the growth temperature increased.

OCIS codes: (310.0310) Thin film; (310.7005) Transparent conductive coatings.

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1. Introduction

Oxide semiconductors such as In_2O_3, ZnO and SnO_2 were intensively investigated as transparent and conductive electrodes of optoelectronic devices because of their controllable electrical and optical properties [1–3]. However, thin films deposited by using these oxide semiconductors are usually crystalline state, which would probably lead to fracture at alternating bending and even demand high growth temperature. In the past few years, transparent amorphous oxide semiconductors (TAOSs) were subjected to wide investigation as thin film transistors (TFTs), which were considered as a substitute for conventional silicon based TFTs and would be applied to active matrix flat panel displays [4]. Recently, TAOSs based on multi-cation systems, such as indium zinc oxide (a-IZO) [5], zinc tin oxide (a-ZTO) [6], zinc indium tin oxide (a-ZITO) [7] and indium gallium zinc oxide (a-IGZO) [8], have been extensively reported for TFT applications, particularly the a-IGZO TFTs, which have several advantages over other oxide TFTs [9], and can be fabricated by magnetron sputtering production line of silicon-based TFTs at low growth temperature.

As is well known, the successful fabrication of TFTs based on a-IGZO channel layer is determined by the physical properties of a-IGZO film. The a-IGZO films could be fabricated by using pulsed laser deposition (PLD) [10–13] and radio frequency (r.f.) magnetron sputtering (r.f.-MS) [14–16] at low growth temperature. For the sputtering-deposited a-IGZO films, the properties could be affected by the process parameters, such as power supply (r.f. or d.c. (direct current)), power, working pressure, oxygen partial pressure, growth temperature. Growth temperature is generally recognized as one of the important parameters for tailoring the structural, electrical and optical properties of sputtering-deposited films [17]. It was reported that amorphous $InGaZnO_4$ film deposited by r.f. magnetron sputtering constructed excellent prototype TFT devices with high mobility [14]. In addition, the deposition method was mainly based on r.f.-MS process, and the materials were usually focused on $InGaZnO_4$.

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However, the detailed relationship between the properties and growth temperature of amorphous $In_2Ga_2ZnO_7$ films has not been systematically investigated.

In this work, the a-IGZO films were deposited on glass substrate at different growth temperatures by using d.c. magnetron sputtering. The structural, electrical and optical properties were investigated to explore the relationship between growth temperature and the physical properties of the a-IGZO films. The effect of oxygen on conductivity was also investigated.

2. Experimental

A home-made polycrystalline $In_2Ga_2ZnO_7$ ceramic with a diameter of 3-inch was used as sputtering target. The a-IGZO films were deposited on glass substrates by using magnetron sputtering (Kaoduen, Taiwan). The base pressure of chamber was 5×10^{-6} Torr. During the deposition process, the working pressure was fixed at 6 mTorr, the d.c. power was 55 W, the rotating speed of substrates was 10 rpm (revolutions per minute), the oxygen content was 0.4 vol.% by controlling the argon and oxygen flow. The substrate temperature heated by halogen lamps was increased from room temperature (R.T.) to 300 °C. The substrate temperature was confirmed by thermocouple and temperature sticker with random error controlled within 5 degrees. a-IGZO films with a thickness of about 200 nm were fabricated.

The phase structure was measured by X-ray diffractometer (XRD) (AXS D8-ADVANCE, Bruker). The surface and cross-section morphologies were studied by field-emission scanning electron microscopy (FE-SEM) (S4800, Hitachi). The thickness was measured by a reflectometer (ST2000-DLXn, K-MAC) and confirmed by FE-SEM. The resistivity, carrier density and Hall mobility were measured by Hall Effect measurement (HMS-3000, Ecopia) at room temperature. The optical transmittance in the visible light range was measured by UV/VIS spectrophotometer (V-600, Jasco). The composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent, 710-ES).

3. Results and discussion

The phase structure of the IGZO films deposited on amorphous glass substrate was verified by X-ray diffraction method as shown in Fig. 1. It can be seen that the X-ray diffraction peaks originating from the IGZO films are invisible under different growth temperatures, which confirms the formation of amorphous structure regardless of growth temperature. The results indicate that the a-IGZO films can be obtained by d.c. magnetron sputtering under a wide growth temperature range, which are compatible with the existing fabrication technology of a-Si:H TFTs. The IGZO films of 1114 composition deposited by PLD were amorphous state at 500 °C, and turned to polycrystalline state at 600 °C [18].

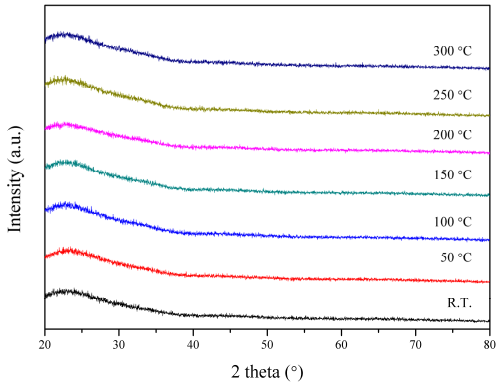

Fig. 1. XRD patterns of the IGZO films deposited at the growth temperature range from R.T. to 300 °C.

Surface microstructure of the a-IGZO films was analyzed by FE-SEM. Figure 2 shows the SEM images of the a-IGZO films deposited at different growth temperatures. It can be seen

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that the particle size of the a-IGZO films become larger when the growth temperature increases. The a-IGZO films show small particle size compared with the crystalline oxide films, such as IGZO and GZO films [18,19]. It could be observed from Fig. 2(a)-(g) that the average particle size of the a-IGZO films deposited at the temperature range of R.T.-200 °C is about 2-10 nm. However, the a-IGZO films deposited at 250 °C and 300 °C show larger particle size and have a size distribution of about 10-25 nm. Furthermore, the a-IGZO films deposited at different growth temperatures show flat surface, which is due to the amorphous tiny particles. Figure 2(h) indicates that the thickness of the a-IGZO film deposited at 300 °C is about 200 nm, and the a-IGZO film shows weak columnar crystals.

Figure 2 also shows that the surface gets rougher when the substrate temperature rises up to 250 °C. The substrate temperature mainly influences the migration and diffusion of the species on substrate. In general, the growth of amorphous film at low substrate temperature follows a two dimensional growth pattern, which has a tendency to form a more uniform structure. However, higher substrate temperature results in an increase of the surface mobility of the species on substrate, which benefits the phase separation and the formation of stable crystalline structures. The film is getting rougher and the particles getting bigger as the substrate temperature rising.

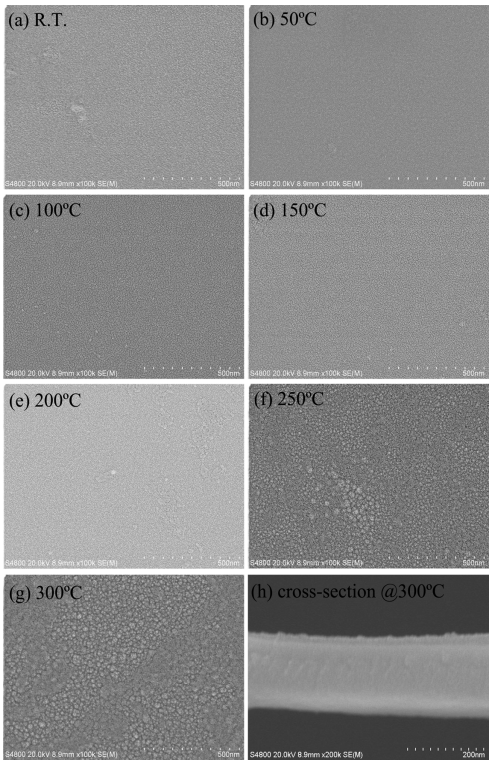

Fig. 2. SEM images of the IGZO films deposited at the growth temperature of (a) R.T., (b) 50 °C, (c) 100 °C, (d) 150 °C, (e) 200 °C, (f) 250 °C, (g) 300 °C, and (h) cross section of the IGZO film deposited at 300 °C.

The composition of the a-IGZO films deposited at R.T., 150 °C and 300 °C was determined by ICP-OES method. The atomic ratio of In:Ga:Zn is 2.0~2.3:1.9~2.2:0.9~1.1 respectively, which indicates that the atomic ratio of the a-IGZO films is consistent with that of the $In_2Ga_2ZnO_7$ target. This confirms that the influence of the structure and properties is due to growth temperature rather than composition. The electrical properties of the a-IGZO films were investigated by the Van der Pauw method at room temperature. In the present case, the as-deposited a-IGZO films show negative Hall coefficient, which confirms the n-

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type semiconductor behavior of the a-IGZO films. Figure 3 presents the dependence of the resistivity, carrier concentration, and Hall mobility of the a-IGZO films on the growth temperature. It can be seen from Fig. 3(a) that the resistivity of the a-IGZO films decreases when the growth temperature increases. The a-IGZO film deposited at R.T. shows low conductivity and has a resistivity of about 10^4 Ω·cm. However, the resistivity decreases drastically from 10^4 Ω·cm to 5.29×10^{-3} Ω·cm when the growth temperature increases.

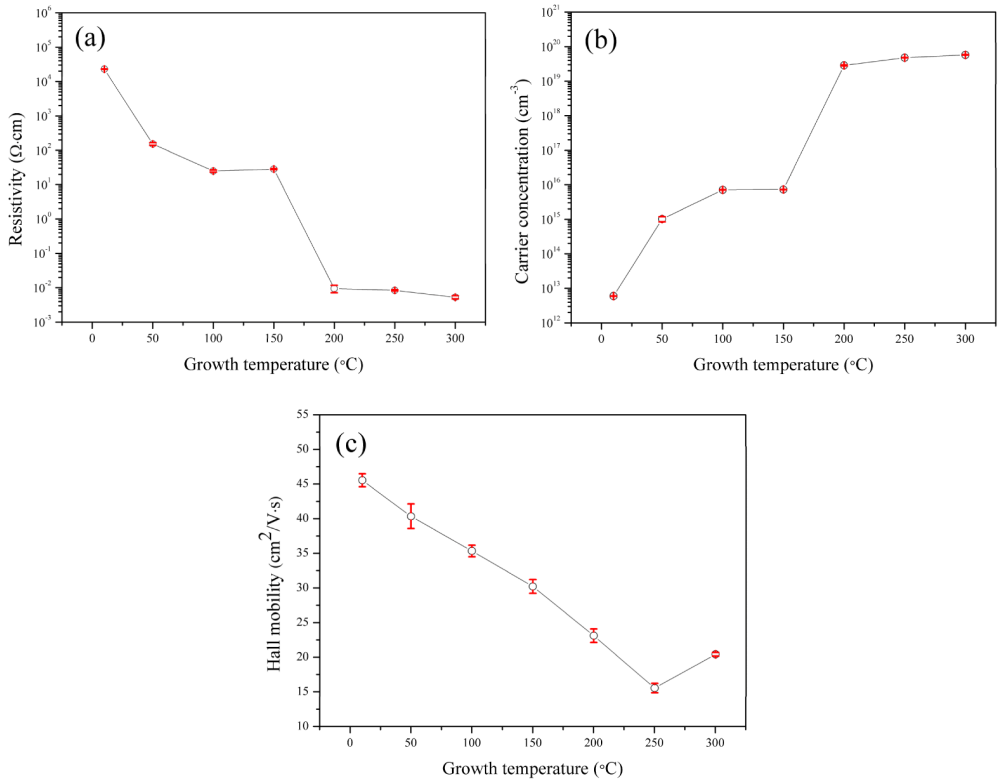

Fig. 3. (a) resistivity, (b) carrier concentration and (c) Hall mobility of the IGZO films deposited at the growth temperature range from R.T. to 300 °C.

The enhancement of conductivity could be mainly attributed to the increase of carrier concentration as shown in Fig. 3(b). It can be observed that the carrier concentration in the a-IGZO films increases from 10^{12} cm^{-3} to 10^{19} cm^{-3} when the growth temperature is increased from R.T. to 300 °C. In general, the crystallized transparent and conducting oxide (TCO) films, such as ITO or ZnO:Ga (GZO) films [20, 21], show an increase of Hall mobility with the increase of the growth temperature. However, Hall mobility of the a-IGZO films as shown in Fig. 3(c) decreases from 45 $cm^2/V·s$ to 15 $cm^2/V·s$ with the increase of the growth temperature. The decrease of Hall mobility was also observed in a-IGZO (In_2O_3:Ga_2O_3:ZnO = 1:9:90 wt.%) films prepared by r.f. magnetron sputtering [22]. The nonstoichiometry and doping of ITO, GZO or IGZO films is one of the important ways to improve their conductivity. It has been suggested that the oxygen vacancies originating from nonstoichiometry are the sources of free electrons in TCO materials. First-principles calculations indicated that the oxygen vacancies in TAOSs form defect levels within the band gap [23], and oxygen vacancies act as shallow donors and suppliers of conduction electrons in IGZO films, and that defect sites, meanwhile, can also act as scattering centers, reducing charge carrier conduction somewhat [4]. The decrease of resistivity of a-IGZO films deposited at high growth temperature could be explained as follows: thermally excited oxygen atoms may have higher probability to leave their original sites and induce vacancies

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with the remaining free electrons at those sites, and this has been verified for ZnO-based oxides [24]. Therefore, it could be concluded that the a-IGZO films are sensitive to oxygen. In order to confirm the influence of the oxygen vacancies on the electrical property of the a-IGZO films, the a-IGZO film was deposited under pure argon gas and at the growth temperature of 300 °C. The resistivity of the as-deposited a-IGZO film can be further decreased to 3.67×10^{-3} Ω·cm, which further proves the conductive role of the oxygen vacancies.

All the a-IGZO films were annealed in air ambience at 350 °C, 450 °C and 550 °C. The conductivity of all the a-IGZO films shows a huge decrease. The sheet resistance of all the a-IGZO films measured by four-point probe method is greater than 10^7 Ω/□ (the max measurement range of MCP-T610 four-point probe is 10^7 Ω/□). The sharp decline of the conductivity is due to the isolation of interstitial metal atoms in grain boundaries and the annihilation of oxygen vacancies. Therefore, the electrical stability of a-IGZO films at high temperature and oxygen ambience is lower than that of crystallized ITO films.

The optical analysis was used to determine the transmittance and band gap of the a-IGZO films. The transmission spectra (including the absorption of glass substrate) of the a-IGZO films as a function of the growth temperature are shown in Fig. 4.

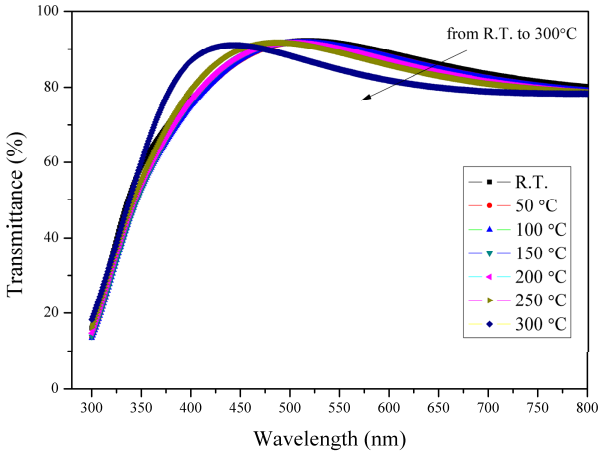

Fig. 4. Transmittance spectrum of the IGZO films deposited at the growth temperature range from R.T. to 300 °C.

It can be seen that the a-IGZO films are highly transparent in the visible light region of 380-800 nm, and the average transmittance in the visible light range exceeds 80%. The transmittance in the long wavelength region decreases as the growth temperature increases, which is due to the increase of carrier concentration originating from oxygen vacancies at high growth temperature. Higher carrier concentration results in higher reflection in long wavelength region.

The band gap (E_g) of the a-IGZO films which calculated from the Tauc plot as a function of the growth temperature is shown in Fig. 5. The Tauc gap was frequently used to characterize practical optical properties of amorphous materials [25]. The optical band gap can be determined by plotting $(\alpha hv)^2$ versus hv curve and extrapolating the straight line portion of the energy axis. The optical absorption coefficient is defined as,

$$I = I_0 e^{\alpha t} \tag{1}$$

Where I is the intensity of transmitted light, I_0 is the intensity of incident light, and t is the thickness of transparent film. The transmittance T is defined as I/I_0, so the absorption coefficient (α) is obtained from Eq. (1). The α and E_g are related by

$$(\alpha hv)^2 = \beta(hv - E_g) \tag{2}$$

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Where h is Planck's constant, v is the frequency of the incident photon, and β is a constant. The photon energy at the point where $(\alpha hv)^2$ is zero is E_g and can be determined by extrapolation of the curve. As shown in Fig. 5, the band gap shows a little red-shifting, and decreases from 3.82 eV to 3.77 eV when the growth temperature increases from R.T to 300 °C. Thakur [26] reported the similar band gap and red-shifting of the a-IGZO films deposited by r.f. magnetron sputtering using ceramic target with Ga_2O_3:In_2O_3:ZnO = 4:2:1 mol.% composition. Unlike the blue-shifting of TCO films, the red-shifting of the IGZO films may result from the increase of particle size of the a-IGZO films as shown in Fig. 2.

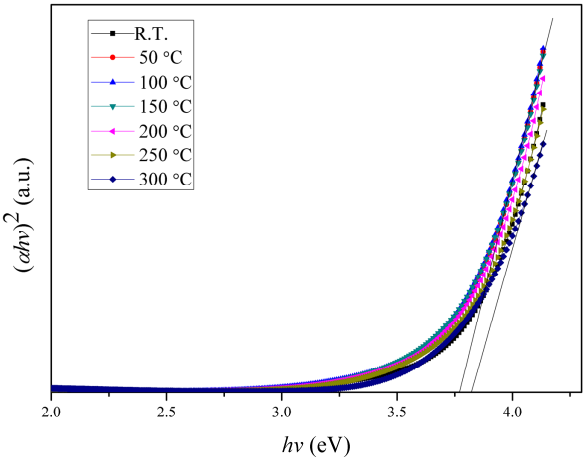

Fig. 5. Tauc plot of the IGZO films deposited at the growth temperature range from R.T. to 300 °C.

4. Conclusion

Transparent and conductive $In_2Ga_2ZnO_7$ films were deposited on glass substrate by d.c. magnetron sputtering using polycrystalline ceramic target at the growth temperature range from R.T. to 300 °C. The as-deposited IGZO films showed amorphous structure regardless of the growth temperature. The a-IGZO films were composed of a large number of nanoparticles, and showed considerable smooth surface. The a-IGZO films deposited at higher growth temperatures had lower optical band gap, lower resistivity and higher charge carrier concentration. The a-IGZO film deposited at 300 °C exhibited a minimum resistivity of 5.29×10^{-3} Ω·cm and Hall mobility of 20.4 $cm^2/V{\cdot}s$. The transmittance of the a-IGZO films in the visible light range showed high transparency of over 80%, and the corresponding band gap is about 3.8 eV.

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