

Low Temperature Crystallization of Indium-tin-oxide

Kuo-Lung Fang, Han-Tu Lin, Feng-Yuan Gan, and Hsin-Chih Chiu

Array Technology Division, AUO Technology Center

AU Optronics Corporation

No. 1 Li-Hsin Rd. 2, HsinChu Science Park HsinChu 300, Taiwan

Hardy.Fang@auo.com

Abstract: Indium-tin-oxide (ITO) thin films were deposited at different temperatures via physical vapor deposition. Amorphous ITO annealing process was proceeded to study the crystallization under low temperature of 180 °C. Effects of both sputtering temperature and post-annealing temperature on the resistivity and optical transparency were investigated. It is observed that sputter-deposited ITO films at 110 °C requires lower crystallization temperature to reduce bulk ITO resistivity. Meanwhile, room temperature sputter-deposited ITO films need higher anneal temperature to achieve lower resistivity and increase transparency. It is believed that as-deposited ITO films 110 °C were inherently formed with very small nucleus grain, and hence requiring lower post-anneal temperature than the room-temperature deposited one to have better crystalline structures.

Keywords: low temperature; ITO; crystallization; resistivity

Introduction

Thin film of indium-tin-oxide (ITO) has been widely used for transparent conducting layer in various optoelectronic devices, such as liquid crystal displays (LCD), plasma display, and solar cells. Within the flat panel display applications, ITO thin films were typically deposited with DC sputtering at low substrate temperature in order to be in amorphous structure state. Though non-crystallized ITO is with higher resistivity and lower transparency, it could be easily patterned via oxalic acid wet-etching. Thus patterned ITO thin films with high transparency and low resistivity after post-crystallization annealing are suitable for flat panel display (FPD) applications such as, mobile phones and personal digital assistants. ITO films were normally crystallized by annealing at about 250 °C to gain low resistivity and high transparency [1-2]. Nowadays, FPD devices were typically processed on plastic substrate that does not support high temperatures. Therefore low temperature process technology has drawn more and more attention recently.

In this work, we focus on the low temperature annealing process (below 200 °C) of sputter-deposited ITO films. ITO thin films were firstly deposited at different substrate temperature and followed with different anneal temperature blow 200 °C.

Experimental

ITO thin films were deposited on glass substrate by physical vapor sputtering using an ITO ceramic target. Two glass substrate temperatures were chosen for ITO deposition. Sample-A was deposited of 42nm at 110 °C,

and Sample-B was deposited of 70nm at room temperature 23 °C. The total gas pressure was kept at 0.67Pa. The Ar gas flow was kept constant with 1 sccm H₂O introduction with power density of 15KW/m². Post annealing of the films at temperature 130 °C, 150 °C and 180 °C for different period of time were carried out in N₂ gas ambient to clarify the relationships between the microstructure and the various properties of the ITO films. X-ray diffraction (XRD) analysis was carried out in 2θ scan mode by using Cu radiation to study ITO structure. Transmission spectra in the visible 400-800 nm were measured with a UV-VIS spectrophotometer (Lamda-800). Resistivity of the ITO films was analyzed by four-point probe method.

Results and Discussion

Fig. 1 reveals the resistivity measurements of Sample-A after post-annealing in nitrogen gas (N₂). It was observed that Sample-A's resistance can be reduced apparently after long time annealing at 150 °C and its resistance tends to saturate after 4 hours annealing. Nevertheless, annealing at 130 °C did not have any strong effect on Sample-A's bulk resistivity until reaching 4 hours annealing. The slightly reduction of resistance after first hour annealing at both conditions results from the condensation effect ITO film structure instead of ITO crystallization.

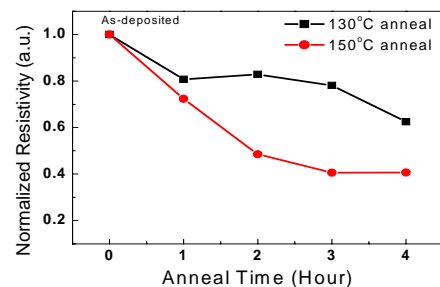


Figure 1. Resistance measurement of sample-A with different anneal temperature and time.

Fig. 2(a) and 2(b) are the measured results of transmittance in Sample-A after oven annealing. There is no obvious improvement in transmittance at 130 °C condition; meanwhile, annealing at 150 °C can have higher transparency. As for Sample-B, the N₂-annealing at 150 °C had little influence on ITO resistivity. Fig. 3 exhibits the annealing results of resistance and transmittance corresponding to Sample-B under different temperatures. It is noted that annealing at 180°C help to reduce sample-B's resistivity but the trend can not be

found for annealing at 150 °C. Besides, there was little impact of Sample-B's transparency measurement after 150 °C 4 hours annealing. Only longer time N₂-annealing with 180 °C could improve Sample-B's transparency. Both transmittance results of annealed Sample-B were shown in Fig. 4(a) and 4(b).

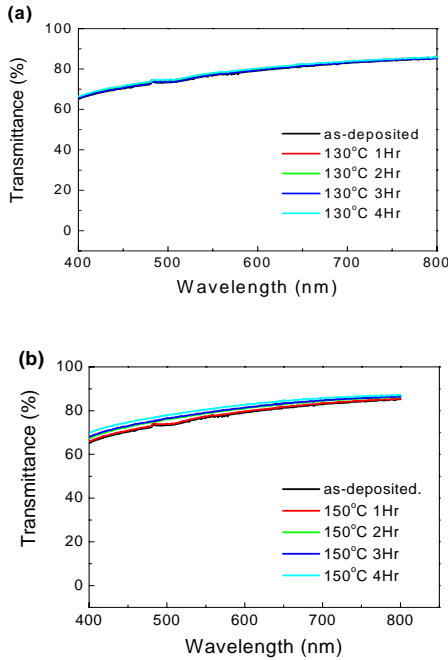


Figure 2. Transmittance measure of Sample-A after (a) 130 °C annealing and (b) 150 °C annealing.

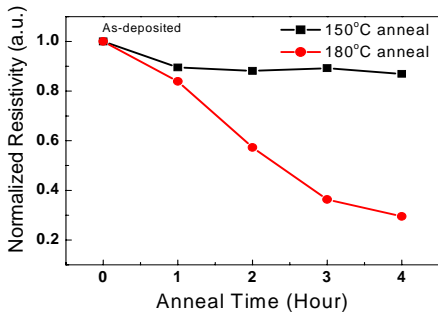


Figure 3. Resistance change of Sample-B with different anneal temperature and time.

To understand the difference between both samples in the above discussion, XRD measurement results were analyzed. The results were displayed in Fig. 5(a) and 5(b). All samples have one broaden amorphous peak profile at 2θ angle about 23 °, this might result from glass substrate. There was one (2,2,2) orientation peak at 2θ angle 30.5 ° of Sample-A after 150 °C 4 hours annealing. It is understood that 150 °C long time annealing help

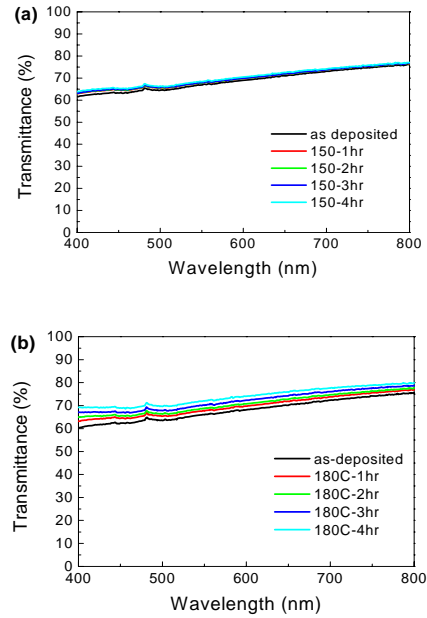


Figure 4. Transmittance measure of Sample-B after (a) 150 °C annealing and (b) 180 °C annealing.

Sample - A crystallize into poly-type with grain growth (Fig. 5(a)). But there were not any change of Sample-B after the same annealing condition (Fig. 5(b)). Sample-B kept amorphous without any growth of orientation peak. Slightly (2,2,2) orientation peak can be found at 2θ angle 30.5 ° after 2 hours annealing at 180 °C and became even stronger after 4 hours annealing. It is now understood that the reduction of resistance for both Sample-A and Sample-B were contributed by annealing the amorphous ITO phase into polycrystalline structure.

There is one unclarified question about the difference on the magnitude of ITO crystallization temperature between two samples. Thus the TEM measurement and transmission electron diffraction (TED) of both ITO films were analyzed. Fig. 6(a) and Fig. 6(b) show the thickness of both samples, in which Sample-A is with thickness of 42.2 nm, while Sample-B is with thickness of 70 nm. From the TED results of Sample-A (Fig. 7(a)), we could understand that as-deposited ITO film at 110 °C can show stronger diffraction pattern, which can explain that as-deposited Sample-A was in slightly crystalline state. Small nucleus grains may be formed during ITO sputtering under 110 °C with power density 15KW/m². The following 150 °C annealing could help Sample-A nucleus grains to grow larger and thus reducing its resistivity.

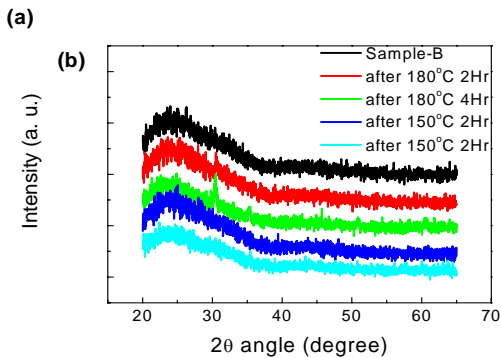
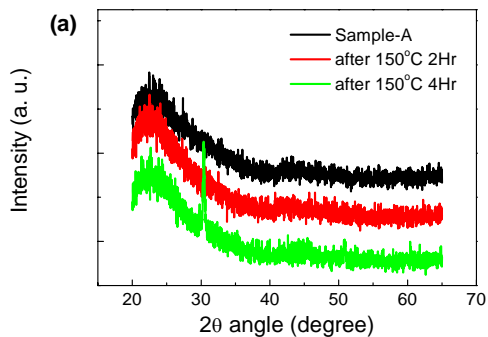


Figure 5. XRD measurements of (a) Sample-A and (b) Sample-B after thermal annealing

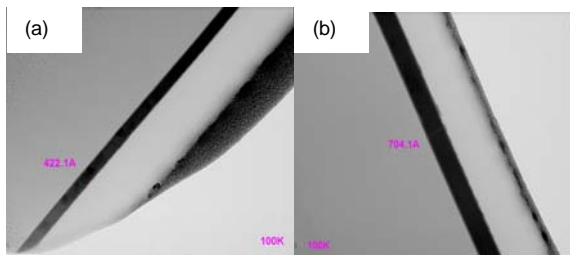


Figure 6. TEM thickness measurement of (a) sample-A and (b) sample-B

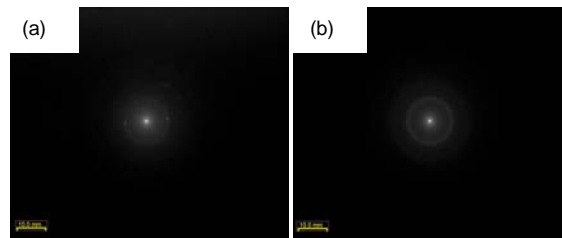


Figure 7. Transmission electron diffraction pattern of as-deposited (a) Sample-A and (b) Sample-B

But as shown in Fig. 7(b), as-deposited Sample-B did not have any diffraction pattern. It means that ITO deposited at room temperature with power density 15KW/m² could not help amorphous ITO to form nucleus grains. And Sample-B need more higher temperature, 180 °C, to form initial nucleus grains and then grow into larger grains by heat energy.

Conclusions

We have investigated the kinetics of the crystallization of amorphous ITO by using sputtering system at room temperature and 110 °C temperature and its effect to the electrical behavior of the material during and after low temperature annealing. It was found that the resistivity of ITO is changed via two different thermally activated temperatures. ITO deposited at 110 °C was formed intrinsically with nucleus grains under power density 15KW/m². Thus lower temperature annealing at 150 °C could help to decrease its resistivity. ITO deposited at room temperature was fully amorphous structure, and needed higher temperature annealing to form nucleus grains to migrate into crystalline state. This provides us one alternative way to fit the demands of low temperature and short thermal annealing process between sputter deposition temperature and post annealing temperature.

References

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