Journal of Ceramic Processing Research. Vol. 13, Special. 2, pp. s181~s185 (2012)

JOURNAL OF
Ceramic
Processing Research

Characteristics of p-type gallium tin oxide (GTO) thin films prepared by RF magnetron sputtering

Ferdyano Finanda, Damisih, Hong Chan Ma and Hee Young Lee*
School of Materials Science and Engineering, Yeungnam University, Gyeongsan, 712-749, Korea

Transparent p-type gallium-doped tin oxide (GTO) thin films with 20 at% Ga doping were successfully prepared on fused silica glass substrates by RF magnetron sputtering. GTO films were deposited under different processing variables such as RF power from 125 to 175 W, working pressures from 5 to 8 mtorr and annealing in pure oxygen ambient at various temperatures from 400 to 700 °C. The electrical properties determined by Hall effect measurements showed that the processing variables for GTO deposition played a strong influence on the conductivity type where it changed from n-type to p-type as variables adjusted.

Key words: Gallium tin oxide (GTO), RF magnetron sputtering, P-type oxide semiconductor, Transparent conducting oxide (TCO)

Introduction

Transparent conductive oxides (TCOs) are unique materials which possess low resistivity characteristics while maintaining high optical transparency. Because of these properties, there have been many possibilities of applying them in the field of solar cell, flat-panel display, organic light emitting diode (OLED) and other optoelectronic devices [1-4]. However, suitable p-type TCO has not been well-established compared to n-type TCO, which became an obstacle in forming oxide p-n junctions. Therefore, many attempts to obtain applicable p-type TCO with both low resistivity and high optical transparency have been made, but much improvement is still needed [5, 6]. One of the most widely investigated material for p-type TCO is ZnO, but both resistivity and transmittance properties should be improved to the levels of n-type TCOs before it can be used in any practical devices [7].

On the other hand, SnO_2 is another promising material for transparent electronics and optoelectronic devices due to its good conductivity, high optical transparency, thermal-chemical-mechanical stability and low cost. SnO_2 is known as a wide band-gap semiconducting material with E_g = 3.6-4.0 eV [8-10].

There are only a few reports on p-type transparent conducting tin oxide films which prepared by DC and RF magnetron sputtering [11, 12], spray pyrolysis [13, 14], and MOCVD [15]. Among these deposition methods, RF magnetron sputtering method is widely used because of high deposition rate, good adhesion, and easy control of the electrical properties of the films by controlling processing parameters such as sputtering power, pressure and temperature.

In this work, we investigated the effect of processing variables, i.e. RF power and working pressure, which could have great influence on the conductivity type of gallium-doped tin oxide (GTO) thin films. The effect of post-deposition annealing is also discussed in some detail.

Experimental Procedure

P-type GTO thin films were prepared on fused silica glass substrates by RF magnetron sputtering using a target with chemical composition of 80 at% tin (SnO_2) and 20 at% gallium (MTI Corporation, 99.99% pure). Initially, the glass substrates were cleaned in ultrasonic bath using acetone, ethanol and de-ionized water for 15 minutes each. The target to sample distance was fixed at around 10 cm. In order to obtain homogenous films, the substrates were rotated with constant speed of 75 rpm. Before sputtering, the base pressure in the vacuum chamber was reduced to below 10^{-6} torr or 1.33×10^{-4} Pa, and then applied Ar working pressures from 5 to 8 mtorr or 0.67-1.07 Pa, and RF powers from 125 to 175 W. The films were deposited at room temperature for 30 minutes and the gas flow rate was controlled using the mass flow controller (MFC) using high purity Ar gas (99.999%) at 20 sccm as a plasma source. Each deposition began with 10 minute pre-sputtering to clean the target surface. After deposition, the GTO films were annealed at various temperatures from 400 to 700 °C for 30 minutes in pure oxygen ambient (99.995%).

The thickness of the films was measured using a stylus profilometer (Dektak 3). Film resistivity was measured at room temperature using the four-point probe method. A Hall measurement system (Ecopia HMS-5000) was used to measure carrier concentration and mobility, which operated at room temperature. The

*Corresponding author:
Tel : +82-53-810-2562
Fax: +82-53-810-4628
E-mail: hyulee@yu.ac.kr

structure of GTO films was studied by using an X-ray diffractometer (Rigaku D500) operated at 40 kV and 30 mA with Cu Kα radiation. Field emission scanning electron microscope (FE-SEM, Hitachi S-4800) was utilized to examine the surface morphology of the films. The optical transmittance was measured in the wavelength range from 200 to 1000 nm using UV-VIS-NIR spectrophotometer (Cary 500).

Results and Discussion

Fig. 1 gives the structural characteristics of GTO films deposited under various processing variables. All the films deposited on glass substrate were polycrystalline and remained rutile structure without revealing any secondary phases. It was noted in Fig. 1(a), with changing RF powers, while working pressure and annealing temperature are fixed, the peak intensity of GTO films were enhanced with the increase of RF power due to higher kinetic energy of atoms and clusters arriving at the substrate [16]. At 125 W and 150 W, the films showed only (110), (101), (200), and (211) reflections. Further increase of sputtering power to 175 W revealed the additional (301) reflection peak which indicated improved crystallization and larger grain size. The grain size of the films was calculated from full width at half maximum of the (101) peak using Debye-Scherrer equation.

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{1}$$

where λ is x-ray wavelength (0.154 nm), β is full width half maximum (FWHM) intensity of the peaks in radians, and θ is Bragg angle. The grain size of the films increased from 19 to 28 nm as the RF power increased from 125 to 175 W.

It was noticed by the increase of working pressure the intensity was slightly reduced as seen in Fig. 1(b). This result implies that at lower working pressure, fewer molecular collisions in the plasma and longer plasma throw distance resulting in better crystallinity [17, 18]. From Fig. 1(c), it is noticeable that the films gradually changed from amorphous to polycrystalline structure with the increase of annealing temperature from 400 to 700 °C. The films started to crystallize at about 500 °C marked by the appearance of (101) peak. Obviously, post-deposition heat treatment may reduce point defects and/or dislocation density by increased grain size and the overall microstructure improvement [14, 19].

The transmittance versus wavelength across the visible spectrum is shown in Fig. 2. Aside from the film annealed at 400 °C, the average transmittance of all films in the visible range (390-750 nm) exceeds 85%. The oscillation in the spectrum is related to the interference of the reflection from the surface of the film and the interface between the film and the substrate which is well known as Fabry-Perot oscillation [20]. It was found that the transmittance value slightly increased and the threshold wavelength decreased as the RF power decreased (Fig. 2(a)). This result might also be attributable to improved crystallization [16], which was evident from XRD profile shown in Fig. 1(a). No significant differences in the transmittance spectra were found by working pressure change (Fig. 2(b)). Upon annealing, the average transmittance value increased due to better crystallinity corresponding to the XRD pattern in Fig. 1(c). It was observed that the transmittance spectra shift toward the shorter wavelengths with the

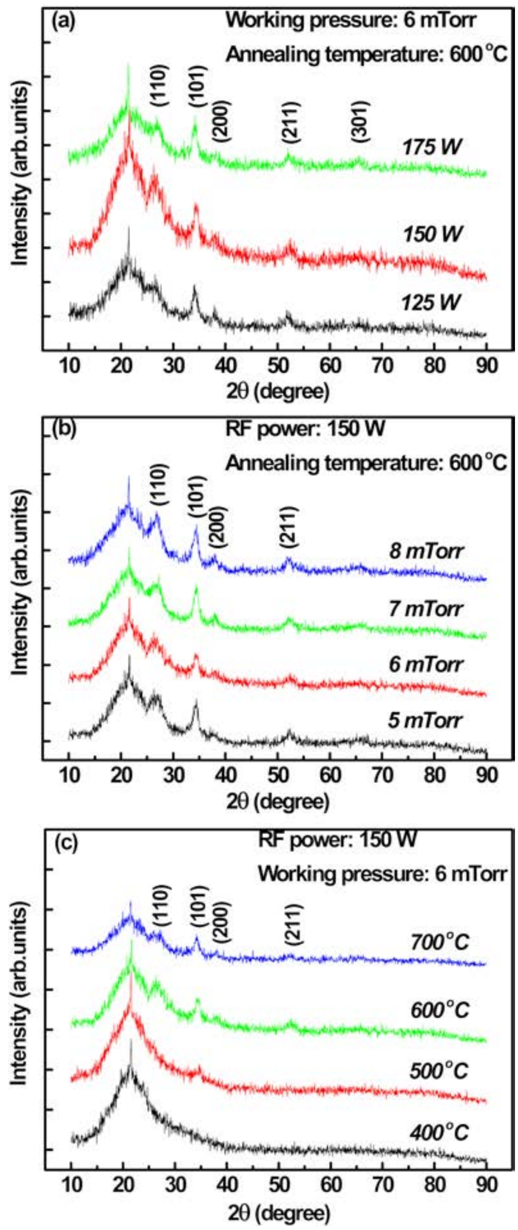

Fig. 1. XRD patterns of GTO films deposited with keeping all the other processing variables fixed and only changing (a) RF powers (working pressure: 6 mtorr, annealing temperature: 600 °C), (b) working pressures (RF power: 150 W, annealing temperature: 600 °C), and (c) annealing temperatures (RF power: 150 W, working pressure: 6 mtorr), respectively.

annealing temperature increase was caused by the increase of carrier concentration, which is known as Burstein-Moss effect [19].

The optical band-gap energy (E_g) of GTO films was estimated from so-called Tauc plots, where the linear portion was extrapolated to the photon energy axis. The optical band-gap energy for gallium-doped tin oxide is around 3.7 - 4.1 eV, which coincides with previous research results [11, 15]. Fig. 3(a) demonstrates that band-gap energy gradually decreased as the RF power increased. It was caused by the creation of oxygen vacancies which was filled by electrons and acted as donor impurities with an energy level close to the conduction band [16]. From Fig. 3(c), the optical band-gap was increased from 3.70 to 4.10 eV as the increased of annealing temperature from 400 to 700 °C which was attributed to the crystallization [21].

The electrical properties of GTO thin films grown under different processing variables are shown in Fig. 4. According to RF power dependence (Fig. 4(a)), the lowest resistivity was achieved at 150 W, which corresponds to the highest carrier concentration (2.6×10^{19} cm^{-3}). Another remarkable point observed was that the film showed p-type characteristic only when the RF power was 150 W.

The electrical properties of GTO thin films deposited at various working pressure and followed by annealing at 600 °C in pure oxygen ambient are shown in Fig. 4(b). The conductivity type of the films tends to change from p-type to n-type along with the increase of working pressure. This result is in good agreement with the report by Hwang *et al.* [22] where donor concentration might be decreased with the decrease of

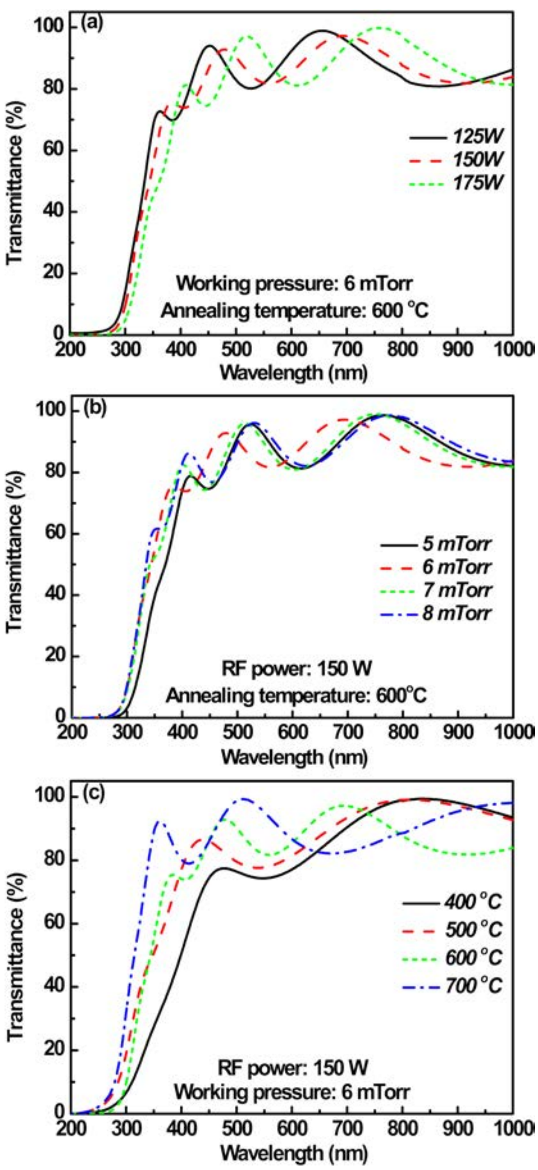

Fig. 2. The transmittance spectra of GTO films deposited under various processing variables as shown in Fig 1.

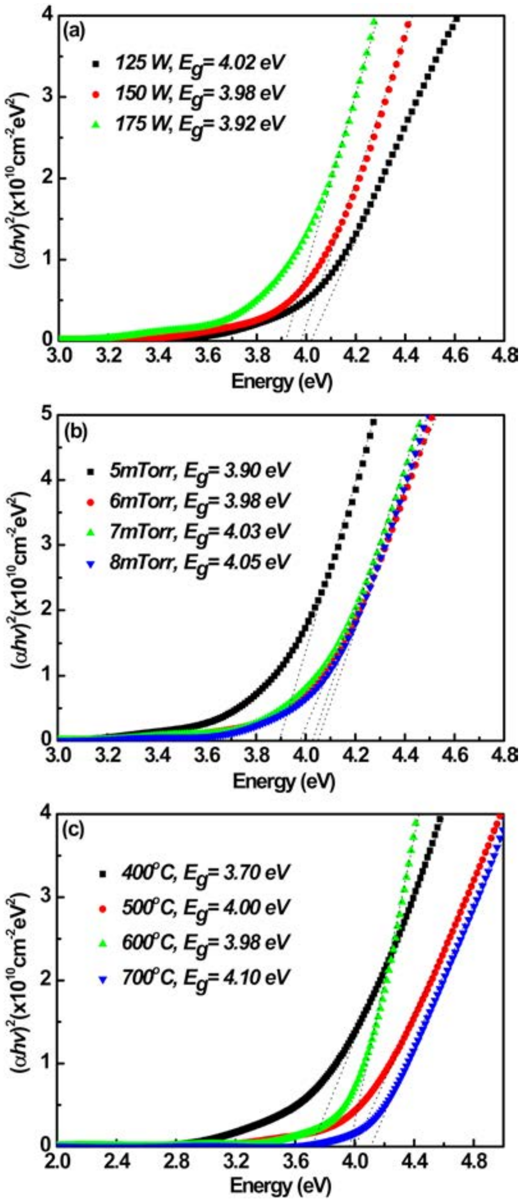

Fig. 3. The optical band-gap energy of GTO films deposited under various processing variables as shown in Fig 1.

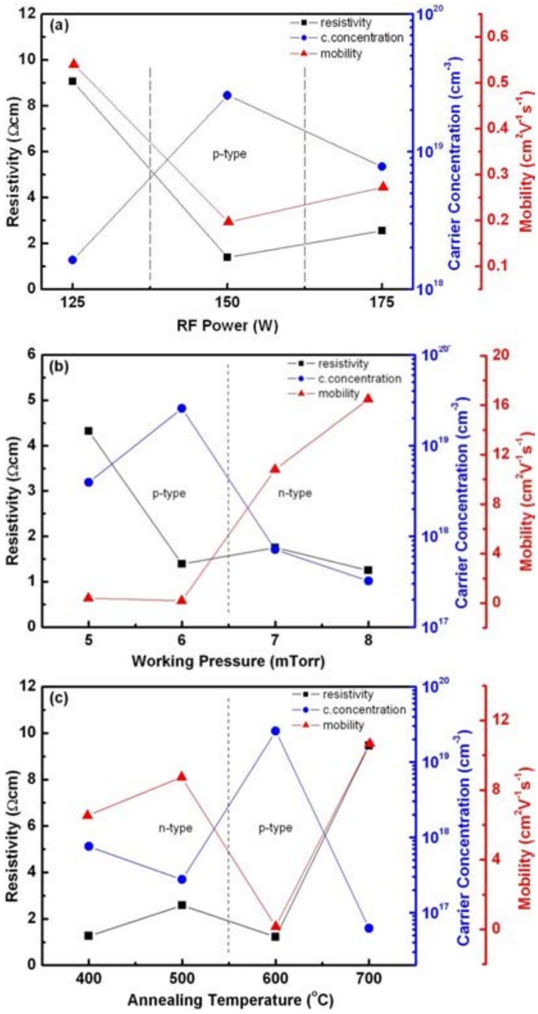

Fig. 4. The electrical properties of GTO films deposited under processing variables as in Fig 1.

working pressure due to the improvement of the crystal quality and fewer native donor-like defects. The mobility of the film increased which is well known to be proportional to the reciprocal of the product of the change in carrier concentration [18].

From the graph in Fig. 4(c), annealing temperatures seems to have a significant effect in controlling the conductivity type of the film. As the annealing temperature increased, GTO film changed from n-type to p-type. According to Hall effect measurements at room temperature, the annealing temperature could activate gallium as effective acceptor and mainly fill Sn lattice sites [11, 12]. However, higher annealing temperature also produces more intrinsic point defects which act as a donor in the films resulting in higher resistivity. Thus, there exists an optimum temperature for p-type GTO thin films which is around 600 °C confirmed with the maximum carrier concentration of 2.6×10^{19} cm^{-3} in this study.

To investigate the surface morphology of the GTO films deposited at different annealing temperature, FE-SEM was utilized and the results are given in Fig. 5. It was observed that the grain size became larger with the increase of annealing temperature. This fact is in line with the XRD patterns which are attributed for improving the crystallinity [17, 19]. Indeed, the film deposited at 600 °C exhibited a homogenous grain which was related to the optimum electrical properties.

Conclusions

This work shows that the structural, optical and electrical properties of p-type gallium-doped tin oxide was strongly dependent upon the processing variables

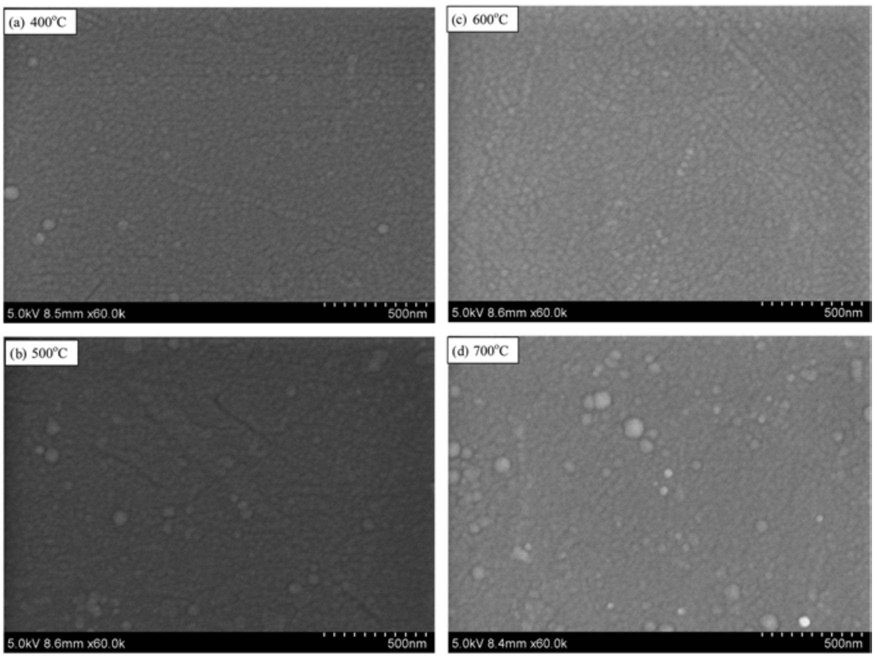

Fig. 5. SEM surface morphology of GTO films annealed at various temperatures: (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C (RF power: 150 W, working pressure: 6 mtorr).

such as sputtering power, working pressure, and annealing temperature. The crystallinity was improved by carefully adjusting the processing variables. Hall effect measurements suggested that by lowering working pressure, there could be a better chance to have p-type gallium-doped tin oxide (GTO) thin films. The conductivity type might change from n-type to p-type as temperature increased over 500 °C while maintaining high transparency. The optimum condition of p-type GTO thin films was achieved at the sputtering power 150 W and working pressure 6 mtorr followed by annealing in pure oxygen ambient at 600 °C. The minimum resistivity for p-type conduction was approximately 1.2 Ωcm and the average transmittance in the visible range was higher than 85%.

Acknowledgements

This research was supported by the Yeungnam University research grants in 2012.

References

1. J.K. Rath, Y. Liu, M.M. de Jong, J. de Wild, J.A. Schuttauf, M. Brinza, R.E.I. Schropp, Thin Solid Films 518 (2010) e129-e135.
2. H.Y. Lee, J.-H. Lee, J.-J. Kim, D.J. Lichtenwalner, and A.I. Kingon, J. Ceram. Process. Res. 10 (2009) s116-s119.
3. J. Ouerfelli, S.O. Djobo, J.C. Berne`de, L. Cattin, M. Morsli, and Y. Berredjem, Mater. Chem. Phys. 112 (2008) 198-201.
4. H. Liu, V. Avrutin, N. Izyumskaya, Ü. Özgür, and H. Morkoç, Superlattices Microstruct. 48 (2010) 458-484.
5. A.N. Banerjee and K.K. Chattopadhyay, Prog. Cryst. Growth Charact. Mater. 50 (2005) 52-105.
6. Z. Ji, Z. He, Y. Song, K. Liu, and Z. Ye, J. Cryst. Growth 259 (2003) 282-285.
7. G. Xiong, J. Wilkinson, B. Mischuck, S. Tüzemen, K. B. Ucer, and R. T. Williams, Appl. Phys. Lett. 80 (2002) 1195-1197.
8. H. Hosono, Thin Solid Films 515 (2007) 6000-6014.
9. Damisih, H.C. Ma, J.-J. Kim, and H.Y. Lee, Thin Solid Films 520 (2012) 3741-3745.
10. M. Batzill and U. Diebold, Prog. Surf. Sci. 79 (2005) 47-154.
11. Y. Huang, Z. Ji, and C. Chen, Appl. Surf. Sci. 253 (2007) 4819-4822.
12. T. Yang, X. Qin, H.-H. Wang, Q. Jia, R. Yu, B. Wang, J. Wang, K. Ibrahim, X. Jiang, and Q. He, Thin Solid Films 518 (2010) 5542-5545.
13. Z. Ji, L. Zhao, Z. He, Q. Zhou, and C. Chen, Mater. Lett. 60 (2006) 1387-1389.
14. Q. Mao, Z. Ji, and L. Zhao, Phys. Status Solidi B 247 (2010) 299-302.
15. X. Pei, F. Ji, J. Ma, T. Ning, Z. Song, Y. Tan, and C. Luan, J. Lumin. 130 (2010) 1189-1193.
16. V. Nirupama and S. Uthanna, J. Mater. Sci. 21 (2010) 45-52.
17. S.T. Hwang, C.B. Park, and G.C. Hoang, Trans. Electr. Electron. Mater. 11 [6] (2010) 279-284.
18. V. Assuncao, E. Fortunato, A. Marques, H. Aguas, I. Ferreira, M.E.V. Costa, and R. Martins, Thin Solid Films 427 (2003) 401-405.
19. C.-H. Yang, S.-C. Lee, S.-C. Chen, and T.-C. Lin, Mater. Sci. Eng. B 129 (2006) 154-160.
20. B. Šantiæ, Thin Solid Films 518 (2010) 3619-3624.
21. L. Wong, M. Milosavljevic, M.A. Lourenc, G. Shao, R. Valizadeh, J.S. Colligon, and K.P. Homewood, Semicond. Sci. Technol. 23 (2008) 035007.
22. D.-K. Hwang, M.-S. Oh, Y.-S. Choi, and S.-J. Park, Appl. Phys. Lett. 92 (2008) 161109.