Journal of Ceramic Processing Research. Vol. 12, No. 5, pp. 578~582 (2011)

JOURNAL OF
Ceramic Processing Research

Surface and electrical properties of rhombohedral In_2O_3 thin films prepared by an O_2 plasma process

S. Shanmugan* and D. Mutharasu
Nano Optoelectronics Research Laboratory, School of Physics, Universiti Sains Malaysia (USM),11800, Minden, Pulau Penang, Malaysia

Rhombohedral In_2O_3 (rh-In_2O_3) thin films were synthesized by O_2 plasma processed indium thin films prepared by RF sputtering. The as-prepared and processed thin films were characterized to know the influence of the plasma power, O_2 gas flow rate and also process time on the surface morphology and electrical properties. SEM images showed the film quality as uniform, well adherent and completely free of pin-holes and creaks. All processed films showed indium clusters as islands over the surface. The resistivity of the as-prepared films was drastically decreased by the O_2 plasma process. Plasma power and O_2 flow rate influenced the change in resistivity of the rh-In_2O_3 thin films. I-V characteristics showed the conductivity behavior of rh-In_2O_3 thin film for various process conditions. The observed particle size of rh-In_2O_3 lie in between 75 and 105 nm and were confirmed by AFM analysis. A noticeable change in surface roughness was also confirmed with respect to plasma process conditions using AFM images.

Key words: rh-In_2O_3, Morphology, Surface roughness, Electrical resitivity.

Introduction

Indium oxide (In_2O_3) is a potential material for use in solar cells, for ultraviolet lasers and sensor applications [1]. Therefore, there have been many investigations of their growth conditions and the optimization of their properties in depending on the synthesis method ranging from evaporation, sputtering, a sol-gel process and chemical pyrolysis to metal organic chemical vapour deposition. In_2O_3 thin films have a good adherence to the substrate surface and high chemical inertness [2]. In_2O_3 can appears in two stable modifications as body-centered (bcc) cubic (a = 10.118 Å) and rhombohedral (rh) (a = 5.478 Å and c = 14.51 Å) (crystallographic data are taken from [3]). Nowadays In_2O_3 has became a very interesting material for gas sensor applications being the best material which allows detection of ozone in the ppb range [4, 5]. The literature also shows that indium oxide can be used to detect NO_x [6, 7], and that it presents high selectivity detection for CO in the presence of H_2 [8]. Its properties such as high transparency in the visible region and high electrical conductivity make In_2O_3 an interesting material also for other applications such as: solar cells [9, 10], optoelectronic devices [11], liquid crystal displays [12], etc.

In_2O_3 is also a typical transparent oxide semiconductor (TOS) material with a direct wide band gap of about 3.6 eV. A high performance, a high transparency and a low processing temperature enable the realization of transparent circuits on cheap, flexible substrates, although much work is still needed under these prospects. Indium oxide can exhibit considerable non-stoichiometry [13-15], and shows extremely good n-type dopability [16], the origin of which is still under debate. The functional properties of these oxides are, to a large extent, controlled by the presence of native point defects and impurities.

In the case of rh-In_2O_3, there are only a few reports concerning the growth and characterization of rh-In_2O_3 in the literature using hydrothermal processing [17] and MOCVD [18], because rh-In_2O_3 can only be synthesized through high pressure and high temperature processes[19, 20]. However, the electrical and surface characteristics of rh-In_2O_3 thin films prepared at room temperature (using an O_2 plasma) have not been reported in the literature so far. Thus, further research on the properties and applications of this material is hindered due to lack of appropriate deposition methods. In this paper, the electrical, surface and IV characteristics of rh-In_2O_3 thin film prepared by an O_2 plasma are reported in detail. The observed results are compared with those in the published literature.

Experimental Technique

Indium (In) films were deposited on soda lime glass substrates in an Ar atmosphere at ambient temperature by RF magnetron sputtering (Edwards make, Model-Auto 500). Pure In (99.999%) and high purity argon gas were used as the sputtering target and the work gas, respectively. The base pressure of the chamber was $\sim 2 \times 10^{-7}$ torr (26.66 μPa). During the deposition, a gas flow rate of

*Corresponding author:
Tel : +60-04-6533672
Fax: +60-04-6579150
E-mail: subashanmugan@gmail.com

14 sccm and a gas pressure P_{Ar} of 1.4×10^{-2} torr (18.66×10^5 μPa) were employed. An RF power of 40 W was used for all In coatings. To get a uniform thickness, a rotary drive system was used and 25 rpm was fixed for all the In film coatings. The sputtering duration was adjusted to yield In thicknesses of about 100 nm. All indium films were coated at 0.09 nm S^{-1}. The sputtered In films were then subjected to an oxygen plasma in an inductive coupled plasma and reactive ion etching system (ICP-RIE, Oxford Plasmalab 80 Plus) for various plasma powers (100 W and 200 W), gas flow rates (15 and 20 sccm) and various process times (5 and 10 minutes). The samples name are identified for the different process conditions throughout this text as follows: S1- as grown, S2-100W; 15 sccm; 5 min, S3- 100 W; 15 sccm; 10 minutes, S4- 200 W; 15 sccm; 5 minutes, S5- 200 W; 15 sccm; 10 minutes, S6- 100 W; 20 sccm; 5 minutes, S7- 100 W; 20 sccm; 10 minutes, S8- 200 W; 20 sccm; 5 minutes, S9- 200 W; 20 sccm; 10 minutes. The process pressure for In films was fixed at 80 mtorr (10.66×10^6 μPa).

The crystal structure of the plasma processed In thin film is confirmed as rhombohedral In_2O_3 (see Fig. 1) by using a high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). A CuKα (k = 1.54056 Å) source was used and the scanning range was between $2\theta = 20°$ and $80°$. The surface morphology of the plasma processed samples was characterized using a scanning electron microscope (Model-JSM-6460 LV). The topography of these films was characterized by a commercially available atomic force microscope system (model: ULTRA Objective, Surface Imaging Systems, GmbH) in the non-contact mode. The sheet resistance of all the processed samples was measured using a four probe resistivity measurement system (Model: Changmin Tech CMT-SR2000N). To obtain a current-voltage (I-V) plot of the film, the substrate was cut into a 4-mm wide strip. Two strips of conductive paste were put on the cut substrate as contacting electrodes with a 4-mm gap.

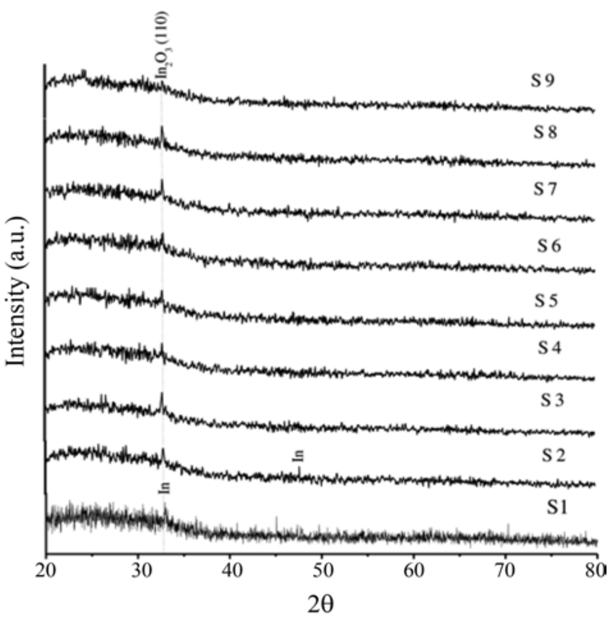

Fig. 1. XRD spectra of O_2 plasma processed In thin film shows the (110) rh-In_2O_3 phase.

Results and Discussion

SEM analysis

Scanning electron micrographs of Indium thin films before (Fig. 2(e)) and after processed with various plasma conditions are shown in Fig. 2(a)-(d). The film growth is found perpendicular to the substrate surface. Fig. 2(e) shows an as-grown In thin film. After the O_2 plasma process, the surface morphology of the film changes significantly and shows that the films are uniform, well adherent and completely devoid of pin holes and cracks. This indicates that the process mechanism in the reactive ion etching plasma technique is controlled by the two-dimensional (2D) layer-by-layer mode (Frank-van der Merwe mode)[21].

The images revealed that the film processed in the presence of the O_2 plasma consisted of loosely populated islands with smaller grains (Fig. 2(b)-(d)). Similar results have been reported for In_2O_3 film preparation at a low substrate temperature (ie 250 °C) [2]. This may be due to the presence of free-standing indium nanoclusters showed better electrical conducting properties (see I-V characteristics section) [22].

Electrical studies

Fig. 3 shows the variation of resistivity of O_2 plasma processed indium thin films for samples S1-S9. The as-

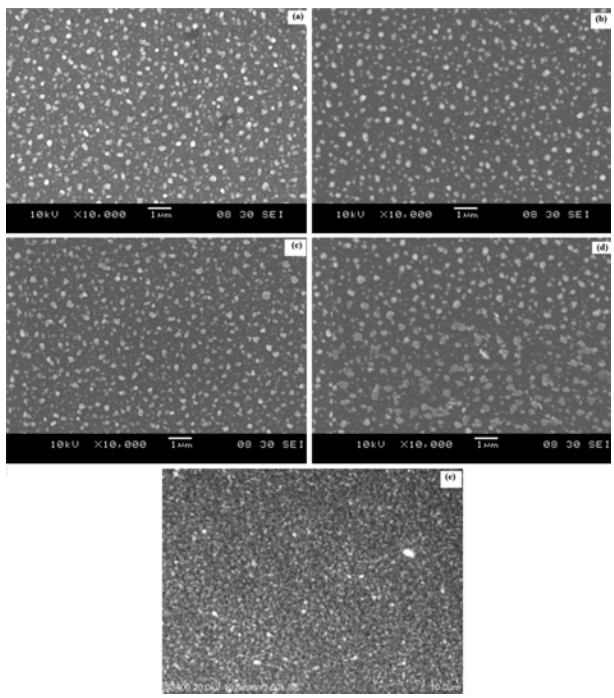

Fig. 2. SEM images of rh-In_2O_3 thin films prepared at (a) 100 W-15 sccm-5 minutes, (b) 200 W-15 sccm-10 minutes, (c) 100 W-20 sccm-5 minutes, (d) 200 W-15 sccm-10 minutes and (e) RF sputtered In metal film.

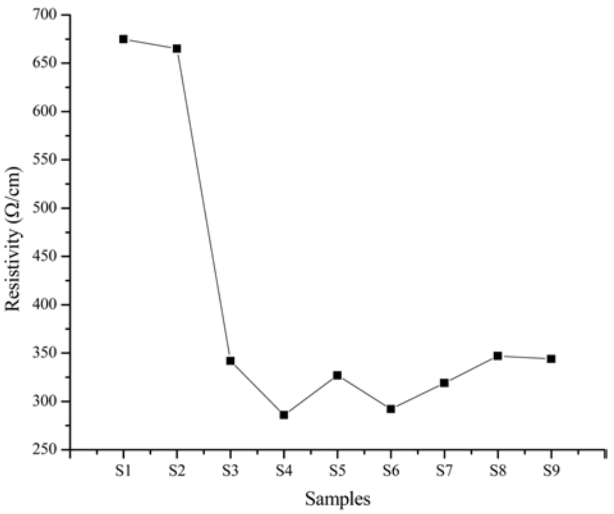

Fig. 3. Resistivity of rh-In_2O_3 thin films prepared with various O_2 plasma process conditions.

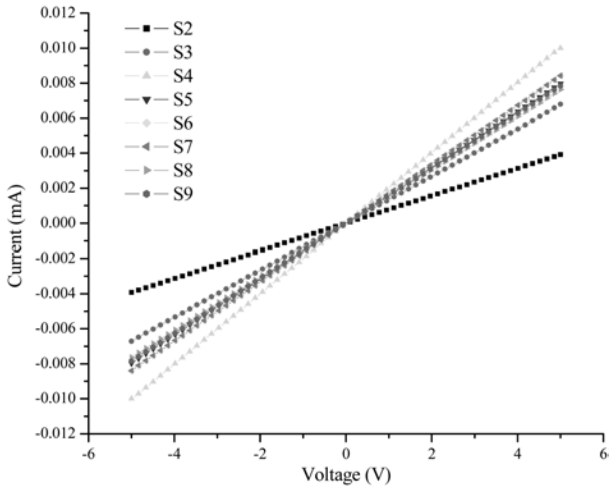

Fig. 4. I-V characteristics of rh-In_2O_3 thin films prepared at various O_2 plasma process conditions.

grown sample showed a higher resistivity of about 675 Ω/cm but this decreased as the plasma power and O_2 gas flow rate were increased. From Fig. 3, it is observed that the resistivity of the S2 sample is nearer to the as-grown. An increase in the O_2 flow rate from 15 sccm to 20 sccm does not show any improvement in the resistivity when processed at 100 W. It is also found that a drastic reduction in resistivity is observed with an increase in plasma power from 100 to 200 W at an O_2 flow rate of 15 sccm with a 5 minutes duration whereas the resistivity increases for the 20 sccm O_2 flow rate at the same plasma power increase.

I-V Characteristics

Fig. 4 displays the I-V characteristics of the rh-In_2O_3 thin films prepared from the O_2 plasma processed indium thin film deposited by RF sputtering at room temperature. The electric current increased linearly up to 4 V; at every applied voltage, the current could be measured without fluctuation by a digital multimeter. This is evidence of the good electrical behavior of the rh-In_2O_3 thin films prepared. This reveals that the In film processed at 200 W plasma power with 15 sccm O_2 flow rate shows a better conductive nature than indium films processed with other parameters. It is also found that a change in O_2 flow rate from 15 sccm to 20 sccm reveals an improvement in the conductive behavior with respective to plasma power. The O_2 flow rate does not show any improvement on the I-V curve for samples when the indium films were processed at 200 W.

AFM analysis

In order to study the influence of the O_2 plasma in detail, the surface topography of all processed films is captured using AFM and presented in Fig. 5(a)-(e). Fig. 5(a)

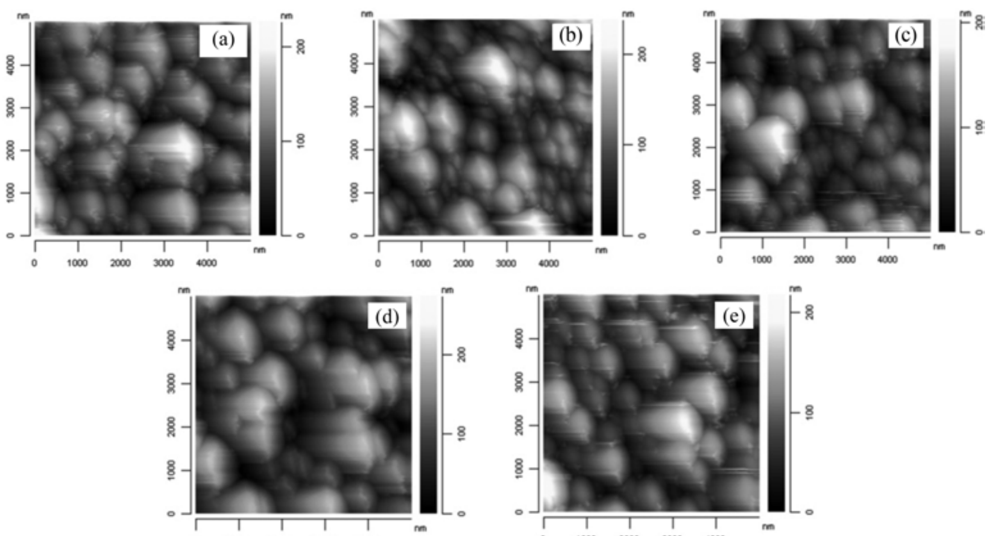

Fig. 5. AFM images of (a) RF sputtered indium metal film and rh-In_2O_3 thin films prepared at (b) 100 W-15 sccm-5 minutes, (c) 200 W-15 sccm-10 minutes,(d) 100 W-20 sccm-5 minutes, & (e) 200 W-15 sccm-10 minutes.

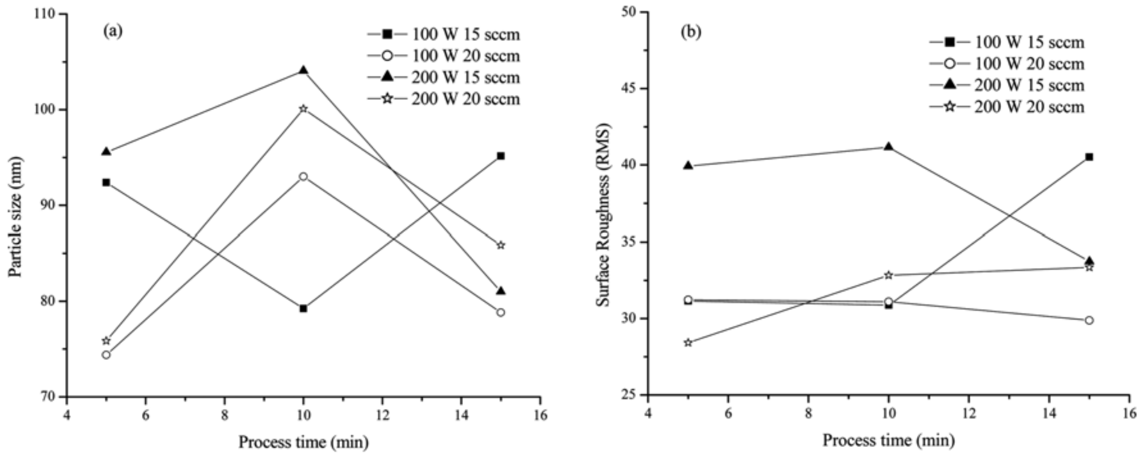

Fig. 6. Change in particle size (a) and surface roughness (b) of rh-In_2O_3 thin films prepared at various process time durations for different plasma powers and O_2 flow rates.

shows the topography of the pure indium metal film. Fig. 5(b)-(e) show the surface morphology of plasma processed indium metal films with various process conditions. From the AFM images, it is observed that the grain growth of a processed film is clearly noticed for the S6 sample. It seems that the O_2 gas flow rate modifies the grain size. It is also noticed that the surface morphology is modified when the as-grown film is processed at 100 W with the 15 sccm O_2 flow rate (Fig. 5b). In order to understand the influence of the plasma power, O_2 flow rate and time on the particle size and surface roughness, the particles size and surface roughness of all processed film at various time durations were studied.

The variation of particle size for different process times is plotted in Fig. 6(a). This shows the variation of particle size with respect to process time duration for various process conditions. From Fig. 6(a), it is observed that the particle size for all films lies in between 75 and 105 nm. It also shows that the sample processed at 100 W with 20 sccm shows an inverse effect when compared with the sample processed at 100 W with 15 sccm. A considerable decrease in particle size is observed when the sample is processed at a high plasma power (200 W) with a 20 sccm O_2 gas flow rate for 5 minutes duration. It is also noticed that an increase in particle size is observed for 15 sccm O_2 flow rate with a high plasma power (200 W) when samples are processed for 10 minutes duration. Overall, the figure shows that the films processed at a high O_2 flow rate (20 sccm) show a low particle size irrespective of the plasma power.

The variation of surface roughness for different process times is plotted in Fig. 6(b). It is observed that the surface roughness of an indium film processed at a high plasma power with a 20 sccm O_2 flow rate shows a low value compared to the other samples. But it increases as with process time increases. Meanwhile, a high surface roughness is observed with a 15 sccm gas flow rate at a high plasma power in 10 minutes duration. This is decreased by increasing the process time to 15 minutes. From Fig. 6(b), it is also observed that the process time is one of the main criteria in changing the surface roughness of O_2 plasma processed indium films.

This is evidenced by measuring a high surface roughness for the sample processed at 100 W with a 15 sccm O_2 gas flow rate for 15 minutes process duration. The same behavior is also observed with the film processed at 200 W with a 15 sccm O_2 gas flow rate for a 15 minutes process duration.

Conclusions

RF sputtered indium films were processed under an O_2 plasma at various process conditions. The processed films were confirmed as rhomboheadral In_2O_3 by XRD analysis. The prepared films were characterized for the influence of plasma power, O_2 flow rate and process time on the surface properties and electrical properties using SEM, AFM and I-V characteristics respectively. The processed films were uniform, well adherent and creak free with pin hole free surfaces. In resistivity measurements, a noticeable decrease and small increases in electrical resistivity were observed for an increase in plasma power from 100 to 200 W at 15 sccm and at 20 sccm respectively. I-V analysis proved the good electrical conductivity of the rh-In_2O_3 thin films prepared. The observed particle size of rh-In_2O_3 thin films was lie in between 75 and 105 nm. A noticeable change in surface roughness was observed with respect to plasma power, O_2 flow rate and process time.

References

1. J. Xu and Y. Chen, J. Shen, Mater. Lett. 62 (2008) 1363-1365.
2. P. Prathap, G. Gowri Devi, Y.P.V. Subbaiah, K.T. Ramakrishna Reddy and V. Ganesan, Curr. Appl. Phys. 8 (2008) 120-127.
3. ICDD PDF-2 Data base, JCPDS-Int. Center for Diffraction Data, Pennsylvania, 1994.
4. M.Z. Atashbar, B. Gong, H.T. Sun, W. Wlodarski and R. Lamb, Thin Solid Films 354 (1999) 222-226.
5. T. Takada, K. Suzuki and M. Nakane, Sens.Actuators B 13 (1993) 404-407.

6. T.K.H. Starke, G.S.V. Coles and H. Ferkel, Sens. Actuators B 85 (2002) 239-245.
7. H. Steffes, C. Imawan, F. Solzbacher and E. Obermeier, Sens. Actuators B 68 (2000) 249-253.
8. H. Yamaura, T. Jinkawa, J. Tamaki, K. Moriya, N. Miura and N. Yamazoe, Sens. Actuators B 36 (1996) 325-332.
9. K. Hara, K. Sayama and H. Arakawa, Sol. Energy Mater. Sol. Cells 62 (2000) 441-447.
10. D.E. Schafer, Sol. Cells 21 (1987) 454.
11. Y. Meng, X.L. Yang, H.X. Chen, J. Shen, Y.M. Jiang, Z.J. Zhang and Z.Y Hua, Thin Solid Films 394 (2001) 218-222.
12. J.F. Smith, A.J. Aronson, D. Chen and W.H. Class, Thin Solid Films 72 (1980) 469-474.
13. I. Hamberg and C.G. Granqvist, J. Appl. Phys. 60 (1986) R123-R159.
14. H.L. Hartnagel, A.K.J. Dawar and C. Jagadish in "Semiconducting Transparent Thin Films" (Institute of Physics Publishing, Bristol, 1995).
15. J.H.W. de Wit, J. Solid State Chem. 13 (1975) 192-200.
16. G. Frank and G. Kostlin, Appl. Phys. A 27 (1982) 197-206.
17. M. Sorescu, L. Diamandescu, D. Tarabasanu-Mihaila and V.S. Teodorescu, J. Mater. Sci. 39 (2004) 675-677.
18. Ch. Y. Wang, Y. Dai, J. Pezoldt, B. Lu, Th. Kups, V. Cimalla and O. Ambacher, Crystal Growth & Design, 8 (2008) 1257-1260.
19. R.D. Shannon, Solid State Commun. 4 (1966) 629-630.
20. A.N. Christensen, N.C. Broch, O. Heidenstam and A. Nilson, Acta Chem. Scand. 21 (1967) 1046-1056.
21. J.A. Venables, G.D.T. Dpiller and M. Hanbuecken, Rep. Prog. Phys. 47 (1984) 399-459
22. F.F Shi, M. Bulkowski and K.C. Hsieh, Nanotechnology 18 (2007) 265301 (6pp).