PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 1 (2017) P. 69-74
DOI: 10.15330/pcss.18.1.69-74

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 1 (2017) С. 69-74

PACS: 61.05.cp 78.66.-w, 73.61.-r

ISSN 1729-4428

Leandro Voisin[1], Makoto Ohtsuka[2], Svitlana Petrovska[3],Bogdan Ilkiv[3], Ruslan Sergiienko[4], Takashi Nakamura[2]

Indium Saving Indium Tin Oxide Thin Films Deposited by Sputtering at Room Temperature

[1]AMTC, Advanced Mining Technology Center and DIMin, Mining Engineering Department, University of Chile, Chile.
[2]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan
[3]National Academy of Science of Ukraine, Frantsevich Institute for Problems of Materials Science, 3 Krzhyzhanivsky Str., Kyiv 03680, Ukraine, sw.piotrowska@gmail.com
[4]Physico-Technological Institute of Metals and Alloys NAS of Ukraine, 34/1 Vernadsky Ave., Kyiv-142 03680, Ukraine

Indium saving indium tin oxide ITO thin films have been deposited using a sputtering deposition technique in pure Ar and in mixed argon-oxygen atmosphere at room temperature**.** A transmittance value of more than 85 % in the visible region of the spectrum and a resistivity of 2420 μΩcm has been obtained for the thin films deposited in pure Ar and subsequently heat treated at 923 K. The structure of the as-deposited indium saving indium-tin oxide films was amorphous and the crystallinity was improved with increasing heat treatment temperature. An increase in the heat treatment temperature does not enhance the transmittance of the films at oxygen flow rate higher than 0.4 cm^3/min.

Keywords: indium saving indium tin oxide; sputtering; electrical properties; optical properties

Стаття поступила до редакції 22.11.2016; прийнята до друку 05.03.2017.

Introduction

Tin-doped indium oxide (ITO) is extensively used as transparent and conductive electrode in flat panel displays and solar cells due to its low resistivity and high optical transmittance in the visible region. Many works is devoted to production of low-resistivity ITO films at low temperatures using different deposition methods, such as sputtering [1-3], evaporation [4], and pulsed laser deposition [5, 6].

Among these methods, sputter deposition has the advantage of being able to control deposition process and results in uniform films with good quality deposited on the large substrates. There is a need in high quality ITO thin films synthesized at low temperatures. However recent changes in demand and supply of indium have resulted in high prices. Therefore transparent conducting oxides that contain a reduced amount or no indium have recently attracted much attention as substitute materials for ITO transparent electrode applications.

Details on the various deposition methods and characterization studies of indium saving ITO thin films have been reported [7-9]. In the reference [9] ITO thin films with different SnO_2 content (0-44.5 mass%) were obtained by direct current magnetron sputtering method. Authors [9] showed that only ITO thin films with 5 mass% of SnO_2 are useful for solar cell while those with 10-15 mass% of SnO_2 are suitable for heat reflection films. In present work, we choose to deposit thin films containing 50 mass. % of indium oxide by DC sputtering method from oxide target, because this method allows achieving a high deposition rate associated with good film properties. Since in the fabrication of ITO films with oxide targets, the oxygen flow rate is very important for determining the electrical and optical properties of ITO films hence in this study these properties of ITO films were examined at various oxygen flow rates. Post-deposition heat treatment is effective to promote grain growth or crystallinity of ITO thin films improving their properties. Therefore it is important to investigate the optical and electrical characteristics of the ITO50 coatings depending on heat treatment temperature T_{HT}.

I. Experiment

ITO50 thin films were deposited onto glass substrates (Corning EAGLE 2000, surface: 50 mm×50 mm, thickness: 0.7 mm) at room temperature by a sputtering method using a ceramic ITO50 target

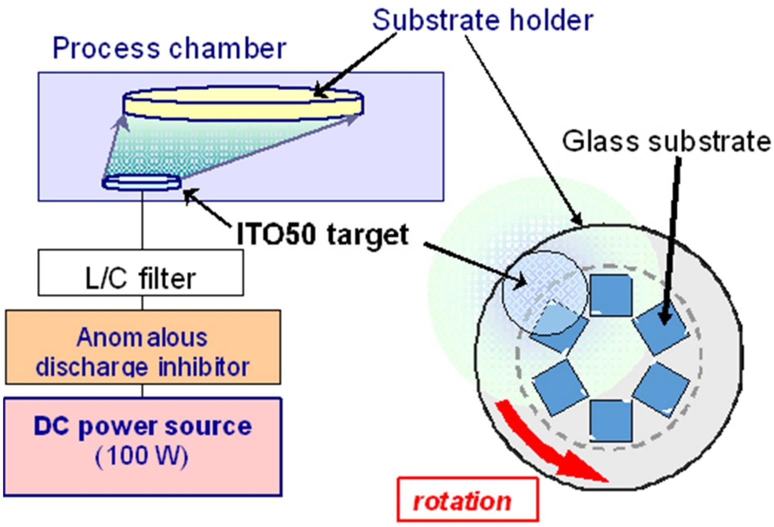

Fig. 1. Schematic diagram of the sputtering apparatus.

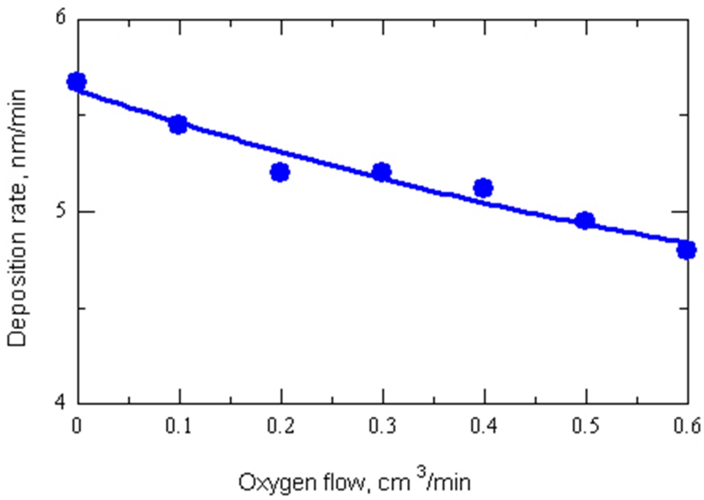

Fig. 2. ITO50 film deposition rate at different $Q(O_2)$.

(Mitsui Mining & Smelting, 50 mass% In_2O_3 and 50 mass% SnO_2). A schematic diagram of the sputtering apparatus (ULVAC, CS-200) used in the present study is shown in Fig. 1.

Process chamber was vacuumed at 10^{-5} Pa for its base pressure. The rotation of the substrate holder (40 rpm) was applied in order to obtain a homogeneous deposition of composition. Typical film-preparation conditions are listed in Table 1.

Thickness of sputtered thin films was measured using a scanning probe microscope (SPM, SII L-trace II), under dynamic force mode (DFM) applying technique described elsewhere [10].

Table 1

Film-preparation conditions

Target	ITO50
Substrate	Glass (t = 0.7 mm) Corning EAGLE 2000
Sputter power	DC 100 W
Gas flow rate	Q(Ar)=50 cm^3/min $Q(O_2)$=0 ~ 0.6 cm^3/min
Pressure	0.67~0.68 Pa
Substrate temperature	Room temperature
Sputter time	30 min

The deposited films were heat treated in air at 523-923 K for 60 min and cooled at room temperature. Using the obtained thickness information, their optical and electrical properties were determined for both as deposited (as-depo.) and heat treated (HT) conditions. The volume resistivity ρ_v was determined by a resistivity meter (Mitsubishi chemical analytech, Loresta GP Model MCP-T610) using a 4-terminal method. Optical transmittance τ was measured into the 200~900 nm range of wavelength using a Spectrophotometer (Hitachi High-Tech, U-3900H) taking the glass substrate τ (92 % in the range of wavelength between 350 and 1000 nm) as reference.

The effects of the oxygen flow and heat treatment temperature, T_{HT}, on the optical and electrical properties for the ITO50 thin films were investigated and compared against those previously obtained by the authors [11] for the ITO90 thin film produced under the gas flow ratio condition of argon to oxygen, $Q(Ar)/Q(O_2)$ = 50/0.2 cm^3/min, which resulted to be the best condition

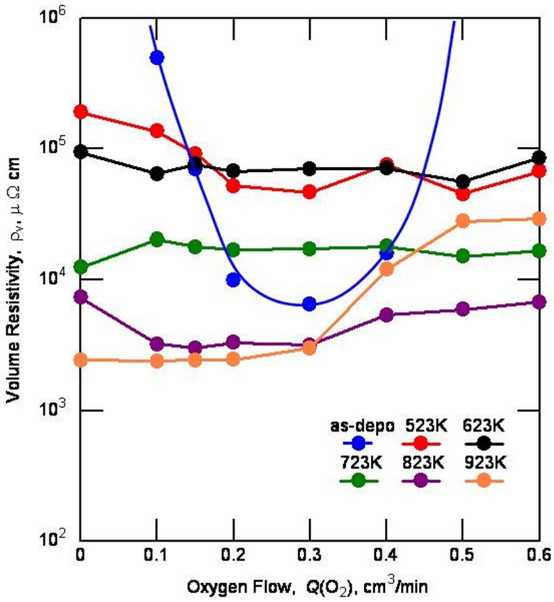

Fig. 3. Effects of $Q(O_2)$ and T_{HT} on the volume resistivity of ITO50 thin films.

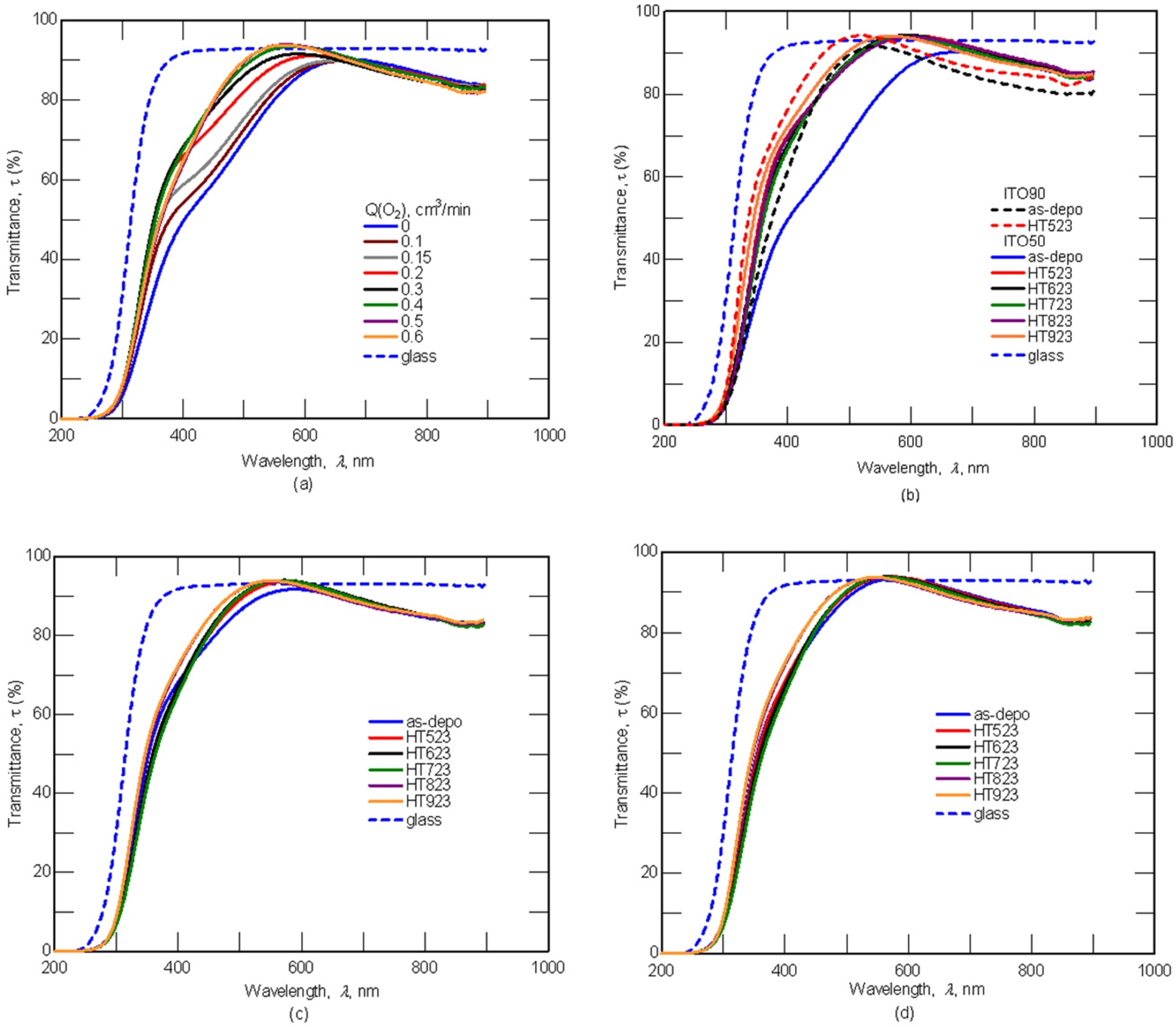

Fig. 4. Effects of $Q(O_2)$ on the transmittance of as-depo. ITO50 (*a*) and T_{HT} on the transmittance of ITO50 deposited in pure Ar and comparison with τ curves of as-depo. and HT523 ITO90 obtained at $Q(O_2)$=0.2 cm^3/min (*b*) and T_{HT} on the transmittance of ITO50 deposited at $Q(O_2)$=0.3 cm^3/min (*c*) and T_{HT} on the transmittance of ITO50 deposited at $Q(O_2)$=0.4 cm^3/min (*d*).

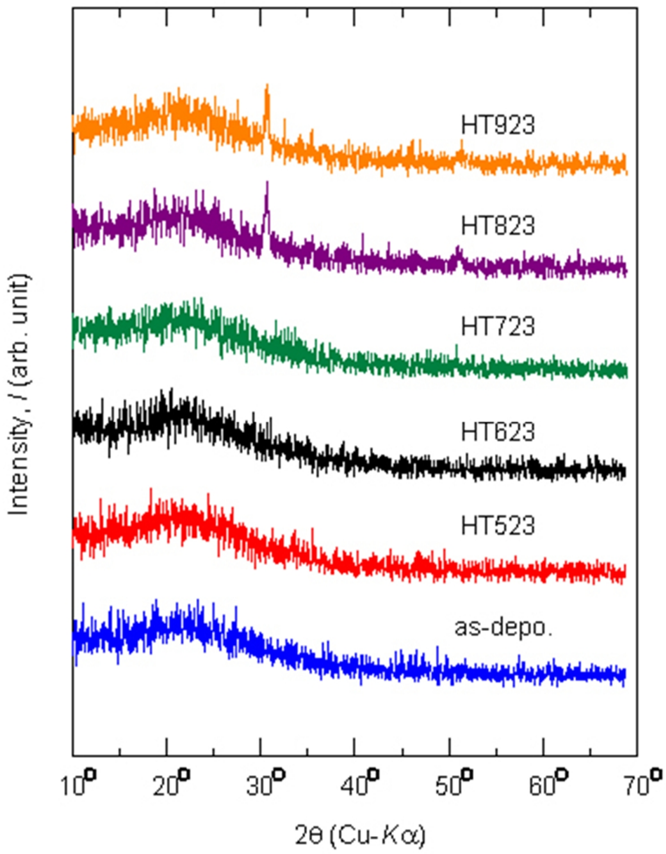

Fig. 5. XRD results for ITO50 films deposited at $Q(Ar)/Q(O_2)$ = 50/0.3 cm^3/min.

for that material.

Structural changes in the films caused by different heat treatment temperatures (523-923 K) were determined from their X-ray diffraction measurements using an X-ray difractometer (Bruker, D2 phaser) with Cu*K*α (wavelength: 0.15418 nm) radiation.

II. Results and discussion

2.1. Deposition rate.

Fig. 2 shows the deposition rate of ITO thin film as a function of oxygen flow rate. The deposition rate continuously decreased from 5.7 to 4.8 nm/min when $Q(O_2)$ increased in the range from 0 to 0.6 cm^3/min.

Such behaviour could be connected with the decrease in the mean free path of the atoms [12].

2.2. Electrical properties.

Fig. 3 shows the variations of the resistivity of ITO50 films as a function of oxygen flow rate for various heat treatment temperatures.

It is shown that the resistivity reveals strong dependence on the $Q(O_2)$ and T_{HT}. The as-depo. ITO50 films exhibit a decrease in the resistivity to 6500 µΩcm when increasing oxygen flow rate to $Q(O_2)$=0.3 cm^3/min. It is also shown that the as-depo. ITO50 films reveal an increase in the resistivity with rise in oxygen flow rate from 0.3 to 0.6 cm^3/min since vacancy-like oxygen defects were substituted by oxygen atoms and the additional oxygen atoms in the films function as carrier traps [13]. Thin films with minimal volume resistivity (2420 µΩcm) were obtained by sputtering in pure Ar and heat treated at 923 K. This value is lower than that obtained from as-depo. ITO90 thin films deposited onto unheated substrates (2851 µΩcm) [11].

2.3. Optical properties.

Fig. 4(*a*) shows the transmittance of ITO50 thin films deposited in pure Ar and at different oxygen flow rates.

As can be seen from Fig. 4(*a*) transmittance increases with increasing oxygen flow rate to 0.4 cm^3/min and further increase of oxygen flow rate does not affect so much on transmittance. It should be noted that the ITO films deposited at different oxygen flow rates showed different colour, that clearly yield the various transmittance.

The results in Fig. 4(*b*) reveal that transmittance of ITO50 thin film deposited in pure Ar increases to 92.6 % at λ=550 nm with increasing heat treatment temperature to 523 K and keeps almost the same value with increasing T_{HT}. Such value is commensurable with that of HT523 ITO90 obtained at $Q(O_2)$=0.2 cm^3/min (93.6 %). Transmittance of ITO50 thin film deposited in pure Ar and heat treated at 923 K reaches 93.9 %.

It is shown in Fig. 4(*c*) that transmittance of ITO50 thin film deposited at $Q(O_2)$=0.3 cm^3/min that showed minimum resistivity in as-depo. state slightly increases with increasing heat treatment temperature to 523 K and than does not change significantly. The as-depo. ITO50 thin film obtained at $Q(O_2)$=0.3 cm^3/min showed high transmittance (90.7 % at λ=550 nm).

As can be seen from Fig. 4(*d*) the transmittance of the films deposited at $Q(O_2)$=0.4 cm^3/min does not change with increasing heat treatment temperature.

Increase of transmittance with increasing oxygen flow rate can be explained by oxidation of sub-oxides such as InO_x and SnO_x. However, when $Q(O_2)$ is over 0.4 cm^3/min, the redundant oxygen can be absorbed in the defect such as grain boundaries [14].

2.4. Structural properties.

The XRD patterns of the ITO50 thin film deposited at $Q(O_2)$ = 0.3 cm^3/min and heat treated at 523-923 K are shown in Fig. 5.

It is shown that there is no diffraction peak present in pattern of as-depo. thin film This indicates that the as-depo. ITO films is entirely amorphous. The hump between 2θ = 20° and 30° is owing to the background of the glass substrates. Films heat treated at temperatures at 823 K showed an improvement of the crystallinity.

Conclusions

Indium saving ITO thin films were deposited onto glass substrates at room temperature by sputtering method at different oxygen flow rates and subsequently heat treated.

In order to reduce indium usage in ITO films, an amount of indium oxide in the target was decreased from 90 mass% to 50 mass%.

It is shown that the oxygen flow rate as well as the heat treatment temperature play major role in controlling the electrical properties of the ITO50 thin films. The best obtained values of volume resistivity 2420 μΩcm for the ITO50 films was derived at HT923 and $Q(O_2)$=0 cm^3/min. ITO50 thin films deposited at room temperature under optimum condition satisfied the required transmittance of > 85% in the visible region of the spectrum. It should be noted that at oxygen flow rate higher than 0.4 cm^3/min an increase in the heat treatment temperature does not enhance the transmittance of the films.

Voicin L. – Professor, Head of Lab.;
Otsuka M. – Ass. Prof., Dr.;
Petrovska S. – researcher, Ph.D.;
Ilkiv B. –researcher, Ph.D.;
Sergienko R – senior researcher, Ph.D.;
Nakamura T. – Professor.

[1] S. Ishibashi, Y. Higuchi, Y. Ota, K. Nakamura, J.V ac. Sci. Technol.A 8(3), 1403 (1990).
[2] Y.Hoshi, R. Ohki, Electrochimica Acta 44, 3927 (1999).
[3] C. Guillén, J. Herrero, Thin Solid Films 480–481, 129 (2005).
[4] J. Ma, D. Zhang, S. Li, J. Zhao, H. Ma, Jpn.J. Appl.Phys. 37, 5614 (1998).
[5] F.O. Aduodija, H. Izumi, T. Ishihara, H. Yoshioka, M. Motoyama, K. Murai, Jpn.J.Appl.Phys.39, L377 (2000).
[6] H. Kim, C.M. Gilmore, A. Pique, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, and D. B. Chrisey, J. Appl. Phys.86, 6451 (1999).
[7] P.K. Biswas, A. De, K. Ortner, S. Korder, Materials Letters 58, 1540 (2004).
[8] P.K. Biswas, A. De, N.C. Pramanika, P.K. Chakraborty, K. Ortner, V. Hock, S. Korder, Materials Letters 57, 2326 (2003).
[9] K. Utsumi, H. Iigusa, R. Tokumaru, P.K. Song, Y. Shigesato, Thin Solid Films 445, 229 (2003).
[10] L. Voisin, M. Ohtsuka, T. Nakamura, Mater. Trans. 51(3), 503 (2010).
[11] L. Voisin, M. Ohtsuka and T. Nakamura, ICCE-17 International Conference, (Hawaii, USA, 2009).
[12] L. Kerkache, A.Layadi, A. Mosser, Journal of Alloys and Compounds 485, 46 (2009).
[13] K.-H. Kim, Journal of Ceramic Processing Research. 8, 19 (2007).
[14] S. Li, X. Qiao, J. Chen, Materials Chemistry and Physics 98, 144 (2006).

Леандро Воісін[1], Макото Отсука[2], С. Петровська[3], Б. Ільків[3],
Р. Сергієнко[4], Такаші Накамура[2]

Індійзберігаючі тонкі плівки оксиду індію-олова, нанесенні методом магнетронного напилення при кімнатній температурі

[1]AMTC, Advanced Mining Technology Center and DIMin, Mining Engineering Department, University of Chile, Chile
[2]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan
[3]Національна академія наук України, Інститут проблем матеріалознавства ім. І.М. Францевича, вул. Кржижанівського, 3, Київ 03680, Україна, sw.piotrowska@gmail.com
[4]Національна академія наук України, Фізико-технологічний інститут металів та сплавів, бульвар Вернадського, 34/1, Київ-142 03680, Україна

Індійзберігаючі тонкі плівки оксиду індію-олова нанесені за допомогою магнетронного напилення в чистому аргоні та в змішаній атмосфері аргон-кисень при кімнатній температурі. Для плівок, нанесених в чистому аргоні та підданих термообробці при 923 К величина пропускання плівки у видимій області спектра перевищувала 85 % , а питомий опір становив 2420 мкОм·см. Індійзберігаючі тонкі плівки оксиду індію-олова безпосередньо після напилення аморфні, та їх кристалічність покращується з підвищенням температури термообробки. Було встановлено, що зростання температури термообробки не підвищує пропускання плівок при швидкості потоку кисню, що перевищував 0,4 $см^3$/хв.

Ключові слова: індійзберігаючі плівки оксиду індію-олова; магнетронне напилення; електричні властивості; оптичні властивості.