
Volume 65, No. 1, 15 January 2011
ISSN 0167-577X
ELSEVIER
materials letters
An interdisciplinary journal devoted to the rapid publication of short communications on the science, applications and processing of materials
Editor-in-Chief: Aldo R. Boccaccini
Editors: J. Hojo, T.G. Nieh, L.S. Shvindlerman, A.F.W. Willoughby
Available online at www.sciencedirect.com
ScienceDirect

Materials Letters 66 (2012) 233–235

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Characterization of transparent conducting oxide thin films deposited on ceramic substrates

Ramesh M. Krishna [a], Timothy C. Hayes [a], Daniel Krementz [b], George Weeks [b], Adrián Méndez Torres [b], Kyle Brinkman [b], Krishna C. Mandal [a,*]

[a] Department of Electrical Engineering, University of South Carolina, Columbia, SC 29208, USA
[b] Materials Science & Technology Division, Savannah River National Laboratory, Aiken, SC 29808, USA

ARTICLE INFO

Article history:
Received 17 May 2011
Accepted 18 August 2011
Available online xxxx

Keywords:
Transparent conducting oxides
Ceramic substrates
Atomic force microscopy
Electrical properties

ABSTRACT

In this work, we investigate the optical and electrical properties of various transparent conductive oxide (TCO) thin films deposited on insulating ceramics for emerging optoelectronic applications. Thin films investigated include indium tin oxide (ITO), ruthenium oxide (RuO_2), and iridium oxide (IrO_2) on Al_2O_3 ceramic substrates. The conducting films have been deposited by various techniques including RF magnetron sputtering and low-cost spray pyrolysis. The morphological characteristics of the films were carried out using high magnification optical microscopy and atomic force microscopy (AFM). Optical and electrical characterization was carried out by optical absorbance/transmittance, van der Pauw, current–voltage (I–V), and Hall effect measurements. The results are presented in this paper.

1. Introduction

Transparent conducing oxide (TCO) films are used extensively in a wide variety of applications, such as flat panel displays, photovoltaic solar cells, and light emitting diodes. Furthermore, emerging applications of TCO thin films require substrates capable of withstanding high temperature, harsh environmental conditions, or repeated stress cycles. The electrical properties of the TCO is very important for most applications; however these parameters change widely depending on substrate preparation conditions and thin film deposition methods [1].

This investigation provides insight on the use of TCO thin films on Al_2O_3 ceramic substrates for applications such as structural health monitoring in intrinsically tamper indicating ceramic seals [2]. Al_2O_3 ceramic substrates are able to withstand high temperature, various stresses, and extreme environmental conditions. However, it is unknown whether or not these ceramic substrates, when coated with a TCO layer, will be sensitive to cracks, cuts, or other structural tampering. Several TCO thin films were used for this investigation, one of which is ITO, and two less-extensively studied films, IrO_2 and RuO_2. The surface properties of these thin films on Al_2O_3 substrates are investigated. Furthermore, the effects of stressing the films are examined, specifically with an interest towards the changing electrical properties of the thin films. The changing electrical properties will determine the effectiveness of the thin films as a tamper indicating material.

2. Experiment

ITO, IrO_2, and RuO_2 conductive thin films deposited onto square (1×1 cm^2) Al_2O_3 substrates. ITO films of ~300 nm in thickness were deposited using RF magnetron sputtering [3], and were annealed in-situ at 250 °C in argon atmosphere. IrO_2 and RuO_2 thin films of ~500 nm in thickness were deposited using the spray pyrolysis technique [4]. $IrCl_3$ and $RuCl_3$ were sprayed at 50 psi using an airbrush onto ceramic substrates heated to 300 °C, and then annealed at

Table 1
Parameters of the studied IrO_2, RuO_2, and ITO thin films on Al_2O_3 substrates.

	ITO	RuO_2	IrO_2
Deposition method	Magnetron sputtering	Spray pyrolysis	Spray pyrolysis
Thickness (nm)	~300	~500	~500
Rms roughness (nm)	~330	~510	~685
Average grain size diameter (μm)	1.5	2.5	2
Conductivity type	n-type	–	–
Carrier mobility in as deposited film (cm^2/Vs)	~24	–	–
Sheet resistance of as-deposited film (Ω/□)	6.4	5.8	77
Resistivity of as-deposited film (Ω cm)	1.9×10^{-4}	2.9×10^{-4}	3.8×10^{-3}
Sheet resistance of scratched film (Ω/□)	10	7.5	79
Resistivity of scratched film (Ω cm)	3×10^{-4}	3.8×10^{-4}	4×10^{-4}

* Corresponding author. Tel.: +1 803 777 2722; fax: +1 803 777 8045.
E-mail address: mandalk@cec.sc.edu (K.C. Mandal).

0167-577X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2011.08.066

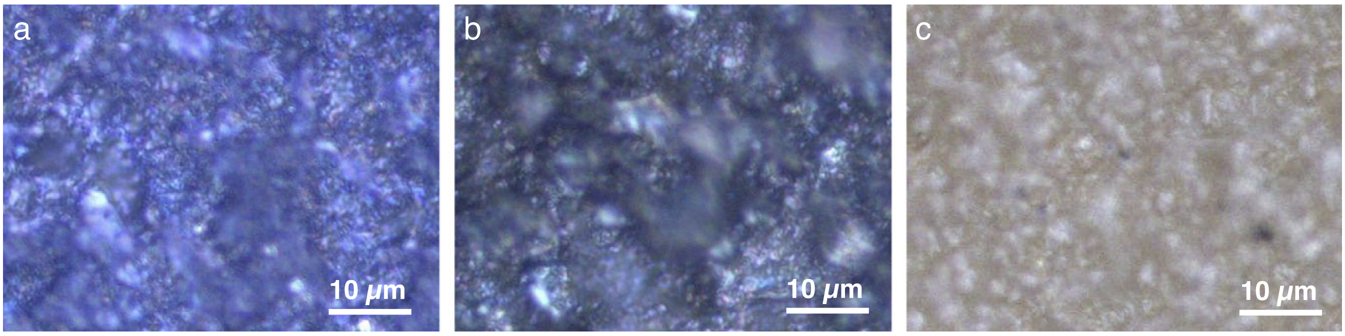

Fig. 1. Optical micrographs of (a) IrO_2, (b) RuO_2, (c) ITO thin films on Al_2O_3 substrate.

650 °C in air, to produce IrO_2 and RuO_2 thin films, respectively. During annealing the IrO_2 and RuO_2 are formed in accordance with the chemical reactions given by:

$$2IrCl_3 + 2O_2 \rightarrow 2IrO_2 + 3Cl_2\uparrow$$

$$2RuCl_3 + 2O_2 \rightarrow 2RuO_2 + 3Cl_2\uparrow$$

All films were matte looking and well adherent to the ceramic substrates without any cracks or holes. Nomarski optical micrographs of the film surfaces were taken using a Leica optical microscope, and grain sizes were measured by the methods described by Cottrell [5] and Jain et al. [6] and the values are given in Table 1. AFM images were taken using a Vecco Nanoscope IIIa AFM in tapping mode. Surface roughness data was obtained from AFM images using Nanoscope software by Vecco Inc.

Silver paint Ohmic contacts of ~1 mm in diameter were deposited in the corners of the samples for electrical characterization. Pin type probes were used to interconnect the samples with the measurement equipment. The resistivities and carrier mobilities of the films were measured using van der Pauw and Hall effect measurements. I-V measurements of the substrates were performed using Keithley 237 High Voltage Source Meter Unit using a pair of diagonal corner contacts.

The stressing of the films was performed by scratching the films using a diamond tipped blade. Scratch marks were made in one direction, from side to side on the surface of the thin films. A comparison of the electrical characteristics of the films before and after scratching was performed. Optical characterization was performed via UV–Vis absorbance/transmittance using Perkin Elmer Lambda 750 spectrophotometer.

3. Results and discussion

Optical and AFM images of the deposited films' surfaces are shown in Fig. 1 and Fig. 2 respectively. The images reveal irregular structure of the surface of the films with rms roughness of about 685 nm, 510 nm, and 330 nm for IrO_2, RuO_2, and ITO films respectively. Using Cottrell's [5] and Jain's method [6] on the optical micrographs, grain sizes for the IrO_2, RuO_2, and ITO thin films were calculated to be approximately 2 μm, 2.5 μm, and 1.5 μm respectively. The surface roughness is somewhat lower for ITO than RuO_2 and IrO_2 (Table 1), which we attribute to the difference in the methods used for film deposition. The optical transmission results for ITO film (Fig. 3a) yielded a band gap of 4.41 eV. The transmission is above 90% until the cutoff point, and remains above 95% in the infrared and above region, which indicates the high quality of the ITO thin film [7].

The resistivity measurements by van der Pauw technique show that the ITO film has the lowest and the IrO_2 film has the highest resistivity (Table 1). The carrier mobility ~24 cm^2/Vs of ITO film is high accounting for the good quality of the films. In contrast to the ITO film, we were unable to measure Hall mobility for the IrO_2 and RuO_2 films due to very small Hall voltage that was out of the measurement capability of our Hall effect system.

I–V characteristics (Fig. 3b) exhibited linear behavior showing Ohmic conduction of the contacts and the films. Although the ITO film had a lowest resistivity, the slope of its I–V characteristic is less than that for RuO_2 film, which is due to the higher contact resistance in case of the ITO film.

Stress testing results revealed an increase in the film resistivity and sheet resistance after scratching (Table 1). The most significant change in resistivity (~60%) was observed in the case of ITO film. Increases in the resistivity due to stress induced on ITO films have been reported in the literature [8]. The IrO_2 resistivity changed least, with

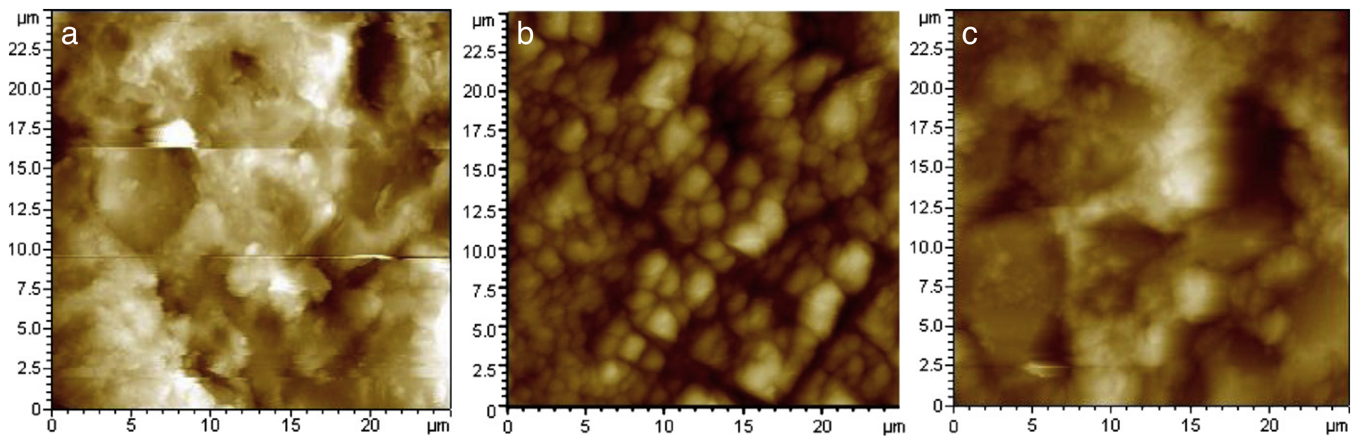

Fig. 2. AFM surface images of (a) IrO_2 (scale: 0 to 3000 nm), (b) RuO_2 (scale: 0 to 7000 nm), and (c) ITO (scale: 0 to 1500 nm) thin film layers deposited on Al_2O_3 substrates.

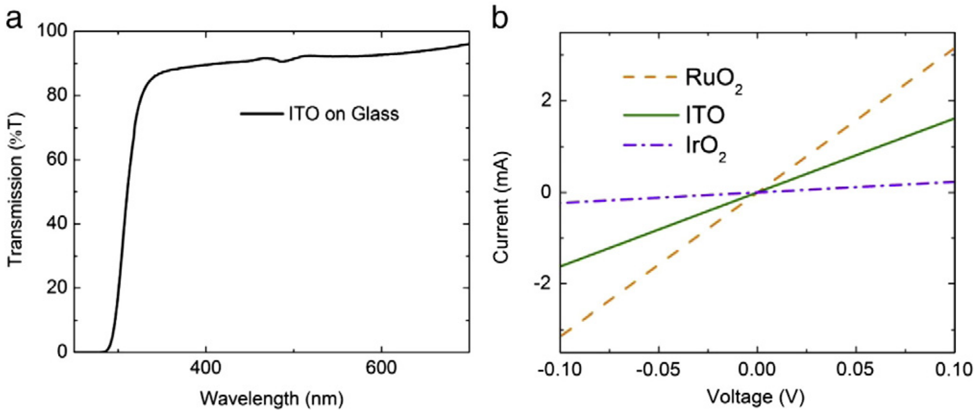

Fig. 3. (a) Optical transmission of 300 nm ITO film deposited on a glass "sister" sample. (b) Current–voltage characteristics of IrO_2, RuO_2, and ITO thin films on Al_2O_3 substrates.

only a 3% increase, while RuO_2 film showed ~30% increase of resistivity after scratch testing. Therefore ITO and RuO_2 films appear to be superior over IrO_2 film for structural health monitoring in terms of their electrical sensitivity to stressing.

4. Conclusions

We have investigated ITO, IrO_2, and RuO_2 conductive thin films deposited onto the Al_2O_3 ceramic substrates for structural health monitoring and intrinsically tamper indicating ceramic seals applications. The films were deposited by various techniques including RF magnetron sputtering and low-cost spray pyrolysis. AFM and optical microscopy revealed the granular structure of the films with rms surface roughness ~330 nm, 510 nm, and 685 nm for ITO, IrO_2, and RuO_2 films respectively. The resistivity of the ITO and RuO_2 films was ~2–3×10^{-4} Ohm cm, whereas IrO_2 film showed significantly higher resistivity ~4×10^{-3} Ohm cm. Stress testing revealed that the ITO and RuO_2 film with scratch-tampered surface had large increase in sheet resistance of 30%–60% compared to 3% increase in case of IrO_2 film. Therefore ITO and RuO_2 films are preferable as coatings applied for structural health monitoring and tamper indication over IrO_2 film in terms of their electrical sensitivity to stressing.

Acknowledgements

The authors would like to acknowledge the partial financial support of Savannah River National Laboratory (SCUREF Award # WEST181) for this investigation. The authors would also like to acknowledge Prof. Harry J. Ploehn, Dr. Hongsheng Gao, and Dr. Peter G. Muzykov for their assistance in providing AFM images and helpful discussions.

References

[1] Minami T. Transparent conducting oxide semiconductors for transparent electrodes. Semiconductor Sci Technol 2005;20:S35–44.
[2] Mendez-Torres A, Brinkman K, Lam PS, Krementz D, Weeks G, Krishna R, et al. Surface functionalization of insulating ceramics by conductive thin film deposition. INMM 52nd Annual Meeting, Palm Desert, CA; 2011. July 17–21.
[3] Joshi RN, Singh VP, McClure JC. Characteristics of indium tin oxide films deposited by R.F. magnetron sputtering. Thin Solid Films 1995;257:32–5.
[4] Gujar TP, Shinde VR, Lokhande CD, Kim WY, Jung KD, Joo OS. Spray deposited amorphous RuO_2 for an effective use in electrochemical supercapacitor. Electrochem Commun 2007;9:504–10.
[5] Cottrell AH. An introduction to metallurgy. London; 1985. p. 173.
[6] Jain GC, Chakravorty BC, Prasad A. Effect of annealing on resistivity and photoconductivity of solar-grade polycrystalline silicon and on solar-cell performance. J Appl Phys 1981;52:3700.
[7] Guillén C, Herrero J. Comparison study of ITO thin films deposited by sputtering at room temperature onto polymer and glass substrates. Thin Solid Films 2005;480–481:129–32.
[8] Carcia PF, McLean RS, Reilly MH, Li ZG, Pillione LJ, Messier RF. Influence of energetic bombardment on stress, resistivity, and microstructure of indium tin oxide films grown by radio frequency magnetron sputtering on flexible polyester substrates. J Vac Sci Technol 2003;21:745.