Thin Solid Films 598 (2016) 126–130

Contents lists available at ScienceDirect

Thin Solid Films

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

Improvement of the effective work function and transmittance of thick indium tin oxide/ultrathin ruthenium doped indium oxide bilayers as transparent conductive oxide

Kattareeya Taweesup [a], Ippei Yamamoto [b,c], Toyohiro Chikyow [b], Gobboon Lothongkum [a], Kazutoshi Tsukagoshi [b], Tomoji Ohishi [c], Sukkaneste Tungasmita [d], Patama Visuttipitukul [a], Kazuhiro Ito [e], Makoto Takahashi [e], Toshihide Nabatame [b,f,*]

[a] *Department of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[c] *Shibaura Institute of Technology, 3-7-5 Toyosu, Koto, Tokyo 135-8548, Japan*
[d] *Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[e] *Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[f] *CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form 24 November 2015
Accepted 26 November 2015
Available online 27 November 2015

Keywords:
Ruthenium
Doped indium oxide
Transparent conductive oxide
Effective work function
Indium tin oxide
Bilayers

ABSTRACT

Ruthenium doped indium oxide ($In_{1-x}Ru_xO_y$) films fabricated using DC magnetron co-sputtering with In_2O_3 and Ru targets were investigated for use as transparent conductive oxides. The $In_{1-x}Ru_xO_y$ films had an amorphous structure in the wide compositional range of $x = 0.3–0.8$ and had an extremely smooth surface. The transmittance and resistivity of the $In_{1-x}Ru_xO_y$ films increased as the Ru content increased. The transmittance of the $In_{0.38}Ru_{0.62}O_y$ film improved to over 80% when the film thickness was less than 5 nm, while the specific resistivity (ρ) was kept to a low value of 1.6×10^{-4} Ω cm. Based on these experimental data, we demonstrated that thick indium tin oxide ($In_{0.9}Sn_{0.1}O_y$, ITO) (150 nm)/ultrathin $In_{0.38}Ru_{0.62}O_y$ (3 nm) bilayers have a high effective work function of 5.3 eV, transmittance of 86%, and low ρ of 9.2×10^{-5} Ω cm. This ITO/$In_{0.38}Ru_{0.62}O_y$ bilayer is a candidate for use as an anode for organic electroluminescent devices.

1. Introduction

Transparent conductive oxides are commonly applied as anodes in organic electroluminescent (OEL) devices. The properties required in a perfect anode material are a low electrical resistivity, high transmittance in the visible range, excellent surface contact, and a high work function (Ø). Currently, indium tin oxide ($In_{0.9}Sn_{0.1}O_y$, ITO) is the most attractive anode material; however, ITO has a low Ø of 4.7 eV [1]. A Ø of over 5 eV is required for an anode because the highest occupied molecular orbital of a hole transport layer is usually over 5 eV. Additionally, an anode with a high Ø can reduce the potential barrier, allowing efficient hole injection, which can decrease the operating voltage of the device.

For these reasons, several approaches have been proposed to improve the Ø of ITO and to develop a new anode material. One approach is to introduce oxygen to replenish the oxygen deficiency of ITO films using surface treatment techniques such as oxygen plasma, oxidation annealing, and laser irradiation [2–4]. The work function increases as the oxygen concentration increases [3]. Another popular method is to dope with high work function elements such as Mo, Ni, W, and Pt in an In_2O_3 film to enhance the Ø [5–7]. This method is effective in increasing Ø and lowering the electrical resistivity. However, there is a trade-off between Ø and the transmittance because Ø increases and the transmittance reduces when the amount of the doping element increases.

We observed that ruthenium oxide (RuO_2) is an interesting material because of its high effective work function ($Ø_{m,eff}$) over 5 eV [8]. However, the low transmittance is a big issue when considering the use of RuO_2 as an anode. We expect that Ru-doped In_2O_3 ($In_{1-x}Ru_xO_y$) will affect the $Ø_{m,eff}$. The $Ø_{m,eff}$ value of an electrode is determined by the electrode/insulator interface rather than the top surface and bulk of the electrode [8–10]. Therefore, it is of great interest to determine if a bilayer of thick ITO and thin $In_{1-x}Ru_xO_y$ can carry enough current as an anode while the $Ø_{m,eff}$ value of the $In_{1-x}Ru_xO_y$ is maintained.

In this paper, the influence of Ru content on the electrical and physical characteristics of the $In_{1-x}Ru_xO_y$ films is reported. We

---

[*] Corresponding author at: International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
E-mail address: NABATAME.Toshihide@nims.go.jp (T. Nabatame).

http://dx.doi.org/10.1016/j.tsf.2015.11.070
0040-6090/

also discuss the usefulness of an ITO/$In_{1-x}Ru_xO_y$ bilayer as a transparent conductive oxide.

2. Experimental details

2.1. $In_{1-x}Ru_xO_y$ thin film preparation

P-type Si with a 100-nm-thick SiO_2 layer and synthetic quartz were used as substrates to evaluate the specific resistivity, transmittance, and surface roughness of the samples. The $In_{1-x}Ru_xO_y$ thin films were deposited on substrates at room temperature under a working pressure of 0.5 Pa in an Ar/O_2 (30/10) atmosphere by DC magnetron co-sputtering using In_2O_3 (99.99%) and pure Ru (99.90%) targets. The sputtering targets were 3 in. in diameter. The substrates were rotated at a rate of 18.5 rpm during sputtering. The composition of the $In_{1-x}Ru_xO_y$ thin films was varied by changing the sputtering power of each target as listed in Table 1.

2.2. Fabrication of SiO_2 MOS capacitors with an ITO/$In_{0.38}Ru_{0.62}O_y$ bilayer electrode

ITO/$In_{0.38}Ru_{0.62}O_y$-gated metal-oxide-semiconductor (MOS) capacitors were prepared to examine the $\text{Ø}_{m,eff}$ of the $In_{0.38}Ru_{0.62}O_y$ films. Thermal SiO_2 layers of different thicknesses from 6.9 to 12.0 nm were formed using a conventional furnace at 950 °C in an O_2 atmosphere. To fabricate an ITO/$In_{0.38}Ru_{0.62}O_y$ bilayer as a gate electrode, a 3-nm $In_{0.38}Ru_{0.62}O_y$ ultrathin film was deposited on the SiO_2 layers. Subsequently, a 150-nm-thick ITO film was deposited on an $In_{0.38}Ru_{0.62}O_y$ film at room temperature under a working pressure of 0.5 Pa in an Ar/O_2 (19.2/0.8) atmosphere with a deposition power of 200 W by radio frequency sputtering using an $In_{0.9}Sn_{0.1}O_y$ target. This bilayer electrode was patterned using photolithography and lift-off processes. The area of each square bilayer electrode was 6400 μm^2. Finally, post-metallization annealing (PMA) was performed at 300 °C for 10 min in N_2 to suppress the influence of fixed charge at the SiO_2/Si interface. ITO-gated SiO_2 MOS capacitors were also prepared by the same photolithography, lift-off and PMA processes as reference.

2.3. Characterization of the $In_{1-x}Ru_xO_y$ thin films

An X-ray diffractometer (XRD, Bruker D8 discover) using CuKα radiation was employed to examine the crystal structure and phase formation of the films. The morphology of the ITO/$In_{0.38}Ru_{0.62}O_y$/SiO_2/p-Si capacitor was observed by transmission electron microscopy (TEM, JEM-2100F) operating at 200 kV. Each elemental mapping of the capacitor was evaluated by energy dispersive X-ray spectroscopy (EDX) instrument combined with TEM. Surface morphology and roughness were observed using atomic force microscopy (AFM, SI-DF40P2). The transmittance of the oxide films was measured using a spectroscopic ellipsometer (M-2000™ XLS-100 D2) with a quartz tungsten halogen light source. The specific resistivity (ρ) of the oxide films was measured with a four-terminal specific resistance tester (four-point probe resistivity processor, Σ-5+). The electrical properties of the MOS capacitors were determined using capacitance–voltage (C–V) measurements performed with a semiconductor parameter analyzer (Keithley 4200 SCS). Flat-band voltage (V_{fb}) and the equivalent oxide thickness (EOT) were estimated from the C–V characteristics using MIRAI-ACCEPT software to determine $\text{Ø}_{m,eff}$.

Table 1
The co-sputtering conditions and $In_{1-x}Ru_xO_y$ composition estimated from the deposition rate.

Sputter power (W)		$In_{1-x}Ru_xO_y$ composition
In_2O_3	Ru	Deposition rate
200	0	In_2O_3
200	20	$In_{0.95}Ru_{0.05}O_y$
100	20	$In_{0.89}Ru_{0.11}O_y$
100	50	$In_{0.76}Ru_{0.24}O_y$
50	20	$In_{0.70}Ru_{0.30}O_y$
50	50	$In_{0.49}Ru_{0.51}O_y$
20	20	$In_{0.44}Ru_{0.56}O_y$
100	100	$In_{0.38}Ru_{0.62}O_y$
20	50	$In_{0.27}Ru_{0.73}O_y$
20	100	$In_{0.17}Ru_{0.83}O_y$
20	100	$In_{0.07}Ru_{0.93}O_y$
0	100	RuO_2

3. Results and discussion

3.1. Structure and surface morphology of $In_{1-x}Ru_xO_y$ thin films

The chemical composition of the $In_{1-x}Ru_xO_y$ thin films was estimated from the deposition rate summarized in Table 1. The twelve thin films were prepared by changing the sputtering power of In_2O_3 and Ru targets. Fig. 1 shows the XRD profiles of the $In_{1-x}Ru_xO_y$ thin films on SiO_2/Si substrates. The structure of the pure In_2O_3 and RuO_2 films is a result of the body-centered cubic (BCC) crystal structure of In_2O_3 and tetragonal crystal structure of RuO_2 [11–13]. The XRD peaks of the $In_{0.95}Ru_{0.05}O_y$ film are consistent with the (211), (222), and (332) planes of the BCC structure of In_2O_3. As the Ru content increased in the In_2O_3 films, the peaks from the BCC phase gradually decreased in intensity and eventually broadened. The XRD patterns revealed that increasing the content of Ru changed the phase structure of the films from BCC to amorphous. We found that the structure of the $In_{1-x}Ru_xO_y$ films could be divided into three regions: BCC structure of In_2O_3 with Ru

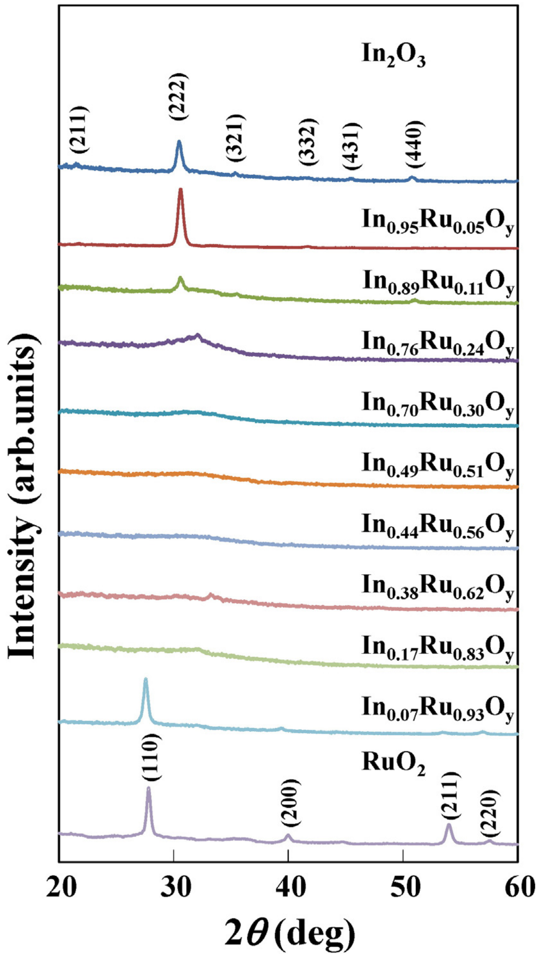

Fig. 1. XRD patterns of $In_{1-x}Ru_xO_y$ thin films on SiO_2/Si substrates. The Ru content was varied from 0 to 1.0.