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

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Abstract: Ruthenium doped indium oxide ($\text{In}_{1-x}\text{Ru}_x\text{O}_y$) films fabricated using DC magnetron co-sputtering with In_2O_3 and Ru targets were investigated for use as transparent conductive oxides. The $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films had an amorphous structure in the wide compositional range of $x = 0.3\text{--}0.8$ and had an extremely smooth surface. The transmittance and resistivity of the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films increased as the Ru content increased. The transmittance of the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ 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 $1.6 \times 10^{-4} \Omega \text{ cm}$. Based on these experimental data, we demonstrated that thick indium tin oxide ($\text{In}_{0.9}\text{Sn}_{0.1}\text{O}_y$, ITO) (150 nm)/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm) bilayers have a high effective work function of 5.3 eV, transmittance of 86%, and low ρ of $9.2 \times 10^{-5} \Omega \text{ cm}$. This ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer is a candidate for use as an anode for organic electroluminescent devices.

Keywords: Ru-doped In_2O_3 ; Transparent conductive oxide; Effective work function; ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer

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 (ϕ). Currently, indium tin oxide ($\text{In}_{0.9}\text{Sn}_{0.1}\text{O}_y$, ITO) is the most attractive anode material; however, ITO has a low ϕ of 4.7 eV [1]. A ϕ 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 ϕ 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 ϕ 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 ϕ [5–7]. This method is effective in increasing ϕ and lowering the electrical resistivity. However, there is a trade-off between ϕ and the transmittance because ϕ 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 ($\phi_{\text{m,eff}}$) over 5 eV [8]. However, the low transmittance is a big issue when considering using RuO_2 as an anode. We expect that Ru-doped In_2O_3 ($\text{In}_{1-x}\text{Ru}_x\text{O}_y$) will affect the $\phi_{\text{m,eff}}$. The $\phi_{\text{m,eff}}$ 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 $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ can carry enough current as an anode while the $\phi_{\text{m,eff}}$ value of the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ is maintained.

In this paper, the influence of Ru content on the electrical and physical characteristics of the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films is reported. We also discuss the usefulness of an ITO/ $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ bilayer as a transparent conductive oxide.

2. Experimental Details

2.1 $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ thin film preparation

P-type Si with a 100-nm-thick SiO₂ 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/O₂ (30/10) atmosphere by DC magnetron co-sputtering using In₂O₃ (99.99%) and pure Ru (99.90%) targets. The sputtering targets were 3 inches 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 SiO₂ MOS capacitors with a 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 $\phi_{m,eff}$ of the In_{0.38}Ru_{0.62}O_y films. Thermal SiO₂ layers of different thicknesses from 6.9 to 12.0 nm were formed using a conventional furnace at 950 °C in an O₂ 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 SiO₂ layers. Subsequently, a 150-nm-thick ITO film was deposited on a In_{0.38}Ru_{0.62}O_y film at room temperature under a working pressure of 0.5 Pa in an Ar/O₂ (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 μm². Finally, post-metallization annealing (PMA) was performed at 300 °C for 10 min in N₂ to suppress the influence of fixed charge at the SiO₂/Si interface. ITO-gated SiO₂ 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/SiO₂/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-2000TM 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 $\phi_{m,eff}$.

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. Figure 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 content of 0.0–0.24, amorphous structure with Ru content of 0.30–0.83, and tetragonal structure with Ru content of 0.93–1.0.

The reason of amorphous structure formation is thought to be due to the difference of crystal structure and volume of unit cell between pure In_2O_3 and RuO_2 . In_2O_3 has a cubic structure with $a = 10.12 \text{ \AA}$ [14] and RuO_2 has a tetragonal structure with $a = 4.50$ and $c = 3.11 \text{ \AA}$ [15]. Furthermore, we noticed that the valence numbers of In and Ru are +3 and +4, respectively. Doping Ru into In_2O_3 , Ru and In atoms may complete each other to form their oxide compounds, and results in disorder of their oxide crystalline structures. Therefore, the amorphous structure is formed easily.

The surface morphology of the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ thin films was examined using AFM as shown in Figure 2. The crystalline In_2O_3 , $\text{In}_{0.95}\text{Ru}_{0.05}\text{O}_y$, and RuO_2 films had large root mean square (RMS) roughnesses of 4.83, 2.88, and 1.66 nm, respectively. In contrast, the surface roughness of the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ film was much lower (0.69 nm) because of its amorphous structure. The smooth surface of the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ film should increase the contact area with any overlayer to result in improved electroluminescence and current injection [16-18]. Therefore, surface roughness is an important factor influencing the performance of the anode.

3.2 Transmittance and resistivity of $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ thin films

Figure 3(a) shows the optical transmittance of 150-nm-thick In_2O_3 , $\text{In}_{0.95}\text{Ru}_{0.05}\text{O}_y$, $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$, $\text{In}_{0.17}\text{Ru}_{0.83}\text{O}_y$, and RuO_2 films on synthetic quartz substrates measured over a wavelength range of 250–1000 nm. The In_2O_3 film had a maximum transmittance of approximately 92% at a wavelength of 600 nm because of its large bandgap (3.75 eV) [19, 20]. The maximum transmittance of the $\text{In}_{0.95}\text{Ru}_{0.05}\text{O}_y$ film was slightly lower than the In_2O_3 film and was about 80% at 600 nm. The $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$, $\text{In}_{0.17}\text{Ru}_{0.83}\text{O}_y$, and RuO_2 films had a much lower transmittance of 8, 2, and 2%, respectively. Considering their potential use as an anode in OEL devices, the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ film has the advantage of possessing a smooth surface, although higher transmittance would be desirable.

Next, we examined the thickness dependence of the transmittance of the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ film, as shown in Fig. 3(b). The thickness of $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ films was varied from 1 to 10 nm. The transmittance increased as the film thickness decreased. For thicknesses less than 5 nm, the maximum transmittance was more than 80%. The transmittance of a 150-nm-thick ITO film and a thick ITO (150 nm)/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm) bilayer are also plotted in Figure 3(b). The ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer had a transmittance of 86%, which is nearly as good as that of the ITO film at 600 nm. These results indicate that the transmittance of an amorphous $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ film can be improved by using a thick ITO/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer.

Figure 4 shows the changes in ρ and the transmittance as a function of Ru content in 150 nm $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films. The ρ values of the In_2O_3 , $\text{In}_{0.95}\text{Ru}_{0.05}\text{O}_y$, and $\text{In}_{0.89}\text{Ru}_{0.11}\text{O}_y$ films were too high to measure, which indicated that these films are insulating. It is clear that ρ and the transmittance of the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films decreases as the Ru content increases. The $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films with Ru content over 0.62 had significantly low ρ values of around $10^{-4} \Omega \text{ cm}$. However, the transmittance decreases to less than 10% with Ru content over 0.51. These results indicate that the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ film satisfies the trade-off between ρ and the transmittance. We found that the low transmittance can be solved by decreasing the thickness to 5 nm or less. Also, the thick ITO (150 nm)/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm) bilayer had a low ρ value of $9.2 \times 10^{-5} \Omega \text{ cm}$. This suggests that there is a clear interface between the ITO and $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ layers because there is the same dominant element of indium and because of the amorphous structure of the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ layer. Therefore, the thick ITO and ultrathin $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ bilayer is expected to be a good anode electrode because of the low ρ and high transmittance.

3.3 Effective work function of ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer

We next examined the C-V characteristics of ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ -gated SiO_2 MOS capacitors to estimate $\phi_{m,\text{eff}}$ of the ITO/ $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ bilayer. Fig. 5 (a) shows a cross sectional TEM image of a ITO (150 nm)/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm)/ SiO_2 (10.5 nm)/p-Si capacitor. The ITO

layer had a rhombohedral crystal structure from XRD pattern (not shown). The $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ layer had an amorphous structure because no halo ring and spotty electron diffraction pattern except ITO were not observed (not shown). To examine the elements distribution, the EDX elemental mapping of Si, O, In, Sn, and Ru are represented in Fig. 5(b). The corresponding EDX maps indicate that ruthenium is only located in the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ layer. There were no severe reactions in any of the layers because the individual layers and interface are distinct.

Figure 6(a) shows the C-V curves of ITO (150 nm)/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm)-gated MOS capacitors with different SiO_2 thicknesses from 6.9 to 12.0 nm. The maximum capacitance decreases as the thicknesses of the SiO_2 increases. The inset in Fig. 6(a) shows experimental data and an ideal simulation line without some charges for SiO_2 (6.9 nm) capacitor. The simulation is closely fixed to the experimental data, indicating that the fixed charges of this capacitor is negligible small. Figure 6(b) shows the relationship between the V_{fb} and the EOT of the capacitors with ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ and ITO gates. There is a linear relationship between V_{fb} and EOT for ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ capacitors, indicating that the charge in the SiO_2 film was negligible as explained in Fig. 6(a). Then, $\phi_{m,eff}$ values were determined by extrapolating the plots of V_{fb} versus EOT using the following equation [21]:

$$V_{fb} = (\phi_{m,eff} - \phi_{si}) - Q_{ox} / (\epsilon_0 \epsilon_{ox}) \times \text{EOT}, \quad (1)$$

where ϕ_{si} , Q_{ox} , ϵ_0 , and ϵ_{ox} are the Fermi level of the silicon substrate, a fixed charges of SiO_2 , the permittivity, and the dielectric constant of SiO_2 , respectively. The $\phi_{m,eff}$ of the ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer was estimated to be 5.3 eV. Moreover, the $\phi_{m,eff}$ of the ITO was determined to be 4.8 eV. This $\phi_{m,eff}$ value of the ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayer is almost equal to that of pure RuO_2 (5.5 eV) [8] and much higher than that of ITO. The $\phi_{m,eff}$ value of an electrode is determined only at electrode/insulator interface [8-10]. Therefore, the characteristic

of the ultrathin (3 nm) $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ led to this high $\phi_{\text{m,eff}}$ value. Considering the requirements for anode materials for OEL devices, we suggest that thick ITO/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayers show potential for use as anode materials.

4. Conclusion

The electrical and physical properties of the $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films can be strongly modified by the Ru content. The 150-nm-thick $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ films had an amorphous structure in the wide compositional range of $x = 0.3\text{--}0.8$, a low resistivity in the $x = 0.62\text{--}1.0$, and high transmittance in the narrow range of $x = 0.0\text{--}0.11$. The transmittance of the $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ film was improved to over 80% when the film thickness was less than 5 nm. We found that thick ITO (150-nm)/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm) bilayers had an effective work function of 5.3 eV, high transmittance of 86%, and low ρ of $9.2 \times 10^{-5} \Omega \text{ cm}$. These data indicate that the amorphous thick ITO/ultrathin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ bilayers are useful for an anode of OEL devices.

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Figure captions

Figure 1. XRD patterns of $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ thin films on SiO_2/Si substrates. The Ru content was varied from 0 to 1.0.

Figure 2. AFM images of (a) In_2O_3 , (b) RuO_2 , (c) $\text{In}_{0.95}\text{Ru}_{0.05}\text{O}_y$, and (d) $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ thin films.

Figure 3. (a) The transmittance of 150-nm-thick In_2O_3 , $\text{In}_{0.95}\text{Ru}_{0.05}\text{O}_y$, $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$, $\text{In}_{0.17}\text{Ru}_{0.83}\text{O}_y$, RuO_2 and glass substrate. (b) The transmittance of $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ films with different thicknesses from 1 to 10 nm, a 150-nm-thick ITO film, and an ITO (150-nm)/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3-nm) bilayer.

Figure 4. The specific resistivity and transmittance as a function of Ru content in the 150-nm $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ thin films.

Figure 5. (a) a cross sectional TEM image and (b) EDX elemental mapping of the Si, O, In, Sn, and Ru of a ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ /SiO₂/p-Si MOS capacitor

Figure 6. (a) The C-V curves of thick ITO (150 nm)/ultra-thin $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ (3 nm)-gated MOS capacitors with SiO₂ layers of different thicknesses. An inset graph is comparison between experimental and simulation of capacitor with a SiO₂ 6.9 nm. (b) The relationship between V_{fb} and EOT of the ITO/ $\text{In}_{0.38}\text{Ru}_{0.62}\text{O}_y$ and ITO-gated capacitors.

Table caption

Table 1. The co-sputtering conditions and $\text{In}_{1-x}\text{Ru}_x\text{O}_y$ composition estimated from the deposition rate.

Table 1

Sputter power (W)		In _{1-x} Ru _x O _y composition
In ₂ O ₃	Ru	Deposition rate
200	0	In ₂ O 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

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

(a)

(b)

Figure 6