Work function control of transparent ITO/Ag/ITO multilayer using nano-sized Ag and Al top layer

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We report on the effect of nano-sized Ag and Al layer on the electrical and optical properties of the ITO/Ag/ITO (IAI) multilayer films as well as a work function. With increasing the thickness of the Ag and Al layer, we investigated the change of electrical and optical properties of the IAI multilayer in detail. Regardless of thickness of the Ag and Al top layer, the IAI multilayer showed a constant sheet resistance of ~ 5 Ohm/square and a high transmittance of $\sim 87\%$. However, the surface morphology and microstructure of the IAI multilayer were affected by the nano-sized Al and Ag cover layer due to different oxidation behavior. The work function of the IAI multilayer with nano-sized Ag cover layer is constant (~ 4.95 eV) regardless of Ag thickness, while the work function of the IAI multilayer with Al layer decreased from 4.95 eV to 4.75 eV with increasing Al thickness. This indicates that the coating of the nano-sized Al is effective way to decrease the work function of the IAI multilayer films.

Key words: Nano-sized Ag and Al layer, ITO/Ag/ITO, Oxidation, Work function

1. Introduction

As a promising transparent electrode with a low resistivity and high optical transparency, a transparent oxide/metal/oxide (OMO) multilayer structure has been widely investigated in organic light emitting diodes (OLEDs) and organic solar cells (OSCs) because they provide better optical and electrical characteristics than those of attainable with a single-layer ITO film [1-5]. Until now, nano-sized Ag interlayer-based OMO schemes, such as ITO/Ag/ITO (IAI), IZO/Ag/IZO, IZTO/Ag/IZTO, GZO/Ag/GZO, AZO/Ag/AZO and ZTO/Ag/ZTO films, have been suggested due to their low resistivity comparable to those of metal films and high optical transmittance caused by the antireflection effect [6]. Although IAI multilayer can be prepared with a low resistivity, a high transparency, and a large area on a glass or flexible substrate using a batch-type sputtering or roll-to-roll sputtering, their integration into OLEDs and OPVs with a well-defined electronic energy level is critically affected by work function of the IAI multilayer. Therefore, engineering of the work function of the IAI multilayer is important to apply the IAI in high-efficient OLEDs and OPVs [7-9]. In general, the work function of the IAI multilayer significantly increased by plasma treatment or ozone treatment because the work function of top ITO layer in the IAI is easily affected by plasma or ozone treatment [10,11]. However, detailed investigation to decrease the work function of the IAI multilayer is still lack. Therefore, decreasing of the work function of IAI multilayer is one of the most important issues to apply the IAI multilayer as transparent cathode in OLEDs and OPVs.

In this work, we suggested a simple way to decrease the work function of IAI multilayer using a nano-sized Al

layer. The approach involves the evaporation of Ag and Al layer on the IAI multilayer, followed by measurement of the work function of the IAI multilayer using by ultra violet photoelectron spectroscopy (UPS). In addition, we investigated the effect of nano-sized Ag and Al layer on the electrical, optical, and morphological and structure properties of the IAI multilayer as a function of Ag and Al thickness.

2. Experiment

The ITO/Ag/ITO (IAI) multilayer films were prepared on glass substrate using a direct current (DC) magnetron sputtering with multi cathode guns at room temperature. Using tilted cathode guns, the bottom ITO, Ag, and top ITO layers were continuously deposited on glass substrate without breaking the vacuum. A commercial ITO target (10 wt.% SnO₂-doped In₂O₃) was used to sputter both bottom and top ITO layers. An optimized 35 nm-thick bottom ITO layer was sputtered at a constant DC power of 100 W, an Ar/O₂ flow ratio of 20/0.3 sccm, and a working pressure of 2 mTorr onto a 15×15 mm² glass substrate. After sputtering the bottom ITO layer, thin Ag interlayer was continuously sputtered on the bottom ITO layer using commercial Ag target at a constant DC power of 100 W. Finally, the top ITO layer was sputtered onto the Ag layer under same sputtering conditions to those used for the bottom ITO layer. After coating of IAI multilayer, Ag or Al layer was evaporated on the IAI multilayer as a function of thickness (0.3 and 0.5 nm) respectively. The electrical properties of the Ag or Al covered IAI multilayer were characterized using Hall measurements as a function of Ag or Al thickness. Using a UV/visible spectrometer, the optical transmittances of the Ag or Al covered IAI multilayer were measured at wavelengths between 300-

800 nm. The surface morphology and structure of the Ag or Al covered IAI multilayer was examined using a field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) as a function of Ag or Al thickness. UPS measurement was performed to investigate the change of work function of the IAI multilayer as a function of the thickness of nano-sized Ag or Al layer. The spectra were measured with a ESCALAB 210 system UV (He I) discharged sources, and the base pressure of the analysis chamber was 2×10^{-10} Torr. The spectra were measured with a sample bias of -10V (cutoff region) to accelerate the low energy secondary electrons.

3. Results and Discussion

Figure 1(a) and (b) show electrical properties of the IAI multilayer with Ag and Al layer as a function of thickness. In spite of evaporation of Ag and Al layer, the IAI multilayer showed similar sheet resistance and resistivity to those of as-deposited IAI multilayer. This indicates that evaporation of nano-sized Ag or Al layer cannot affect on the electrical properties of the IAI multilayer because the main conduction path of IAI multilayer is metal Ag interlayer between bottom and top ITO layers [12]. However, carrier mobility of the IAI multilayer with nano-sized Ag or Al layer slightly decreased due to scattering between Ag or Al layer and top ITO layer. The carrier concentration of the IAI multilayer slightly increased with evaporation of Ag or Al layer because the nano-size Ag or Al layer can provide electrons into the top ITO layer.

Figure 1 (c) and (d) show the optical transmittance of IAI multilayer with evaporated Ag or Al layer as a function of thickness. The identical optical transmittance ($\sim 87.9\%$) of the IAI multilayer with Ag or Al layer at a wavelength of 550 nm to that ($\sim 86.9\%$) of the bare-IAI multilayer indicates that the existence of nano-sized Ag or Al layer on the top ITO layer cannot affect the optical transmittance of the IAI multilayer.

Figure 2 (a) and (b) compared the surface morphology of IAI multilayer before and after evaporation of the Ag or Al layer. In case of the IAI multilayer with 0.3 and 0.5 nm thick Ag layer, they showed different surface morphology with that of bare-IAI multilayer as shown inset in Fig 2(a) due to agglomeration of Ag layer. However, it is noteworthy that the surface morphology of the IAI multilayer with 0.3 and 0.5 nm thick Al layer showed identical surface to that of bare-IAI multilayer. The similar surface morphology of the IAI multilayer with nano-sized Al layer to bare IAI multilayer could be attributed to the easy oxidation of Al layer on the top ITO layer [13]. Figure 2(c) and (d) show the XRD plots of IAI multilayer before and after Ag or Al evaporation. In case of bare IAI multilayer, it shows ITO (222), ITO (400), and Ag (111) peaks at $2\theta = 30, 33$ and 38° . The XRD plots of IAI multilayers with 0.3 and 0.5 nm thick Ag layer also show ITO (222) and Ag (111) peaks. Due to the overlap of Ag (111) peaks, it is difficult to distinguish the Ag interlayer peak and nano-sized Ag top layer peak.

Figure 1. Sheet resistance, resistivity, carrier mobility, and concentration of the IAI multilayer with evaporated (a) Ag and (b) Al layer as a function of thickness. Optical transmittance of the IAI multilayer with 0.3 and 0.5 nm thick (c) Ag and (d) Al evaporated layer.

However, there is no additional peak except crystalline ITO and Ag peak indicating no interfacial reaction between nano-sized Ag top layer and ITO layer. However, the IAI multilayer with 0.3 and 0.5 nm thick Al layer showed different XRD plot with the bare-IAI multilayer. Compared to XRD plot of bare IAI multilayer, it shows additional Al_2O_3 (104) peak at $2\theta = 35^\circ$ due to oxidation of evaporated Al layer on the top ITO layer.

Figure 3 shows the UPS spectra in the secondary electron cutoff region as a function of Ag or Al thickness on the IAI multilayer. As shown in Figure 3(a), similar the secondary electron cutoff indicate that evaporation of 0.3 and 0.5 nm thick Ag layer cannot change the work function of the IAI multilayer. However, the secondary electron cutoff of the IAI multilayer with Al layer shifts from 16.25 eV to 16.45 eV with increasing Al thickness. Compared to work function (4.95 eV) of the bare-IAI multilayer, the work function of IAI multilayer with 0.3 and 0.5 nm thick Al layer is 4.85 eV and 4.75 eV, respectively. The change of work function in IAI multilayer could be attributed to the oxidation of Al layer as expected from XRD results. In general, AlO_x exhibits a lower work function than clean Al layer [14]. Therefore, the oxidation of Al layer on ITO layer plays a important role in reducing the work function of the IAI multilayer.

Figure 2. Surface FESEM images of IAI multilayer with 0.3 and 0.5 nm thick (a) Ag and (b) Al layer with inset showing surface morphology of the bare-IAI multilayer. Comparison of XRD plots of the IAI multilayer with 0.3 and 0.5 nm thick (c) Ag and (d) Al layer.

Figure 3. The UPS spectra of the IAI multilayer with nano-sized (a) Ag and (b) Al layer as a function of Ag or Al thickness.

4. Conclusions

We developed a simple method for controlling the work function of transparent IAI multilayer using nano-sized Ag and Al layer. Regardless of thickness of the Ag and Al top layer, the IAI multilayer showed a constant sheet resistance of ~ 5 Ohm/square and a high transmittance of $\sim 87\%$. However, the surface morphology and microstructure of the IAI multilayer were affected by the nano-sized Al and Ag layer due to different oxidation behavior. The work function of the IAI multilayer with nano-sized Ag cover layer is constant (~ 4.9 eV) regardless of Ag thickness, while the work function of the IAI multilayer with Al layer decreased from 4.95 eV to 4.75 eV with increasing Al thickness. This indicates that the coating of the nano-sized Al is effective way to decrease the work function of the IAI multilayer films.

Acknowledgments

This work was supported by the Industrial Strategic technology development program (10042412).

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(Received January 31, 2015; Accepted June 1, 2015)