Effects of thermal treatment on the electrical and optical properties of silver-based indium tin oxide/metal/indium tin oxide structures

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Effects of thermal treatment on the electrical and optical properties of silver-based indium tin oxide/metal/indium tin oxide structures

Yeon Sik Jung*, Yong Won Choi, Ho Chul Lee, Dong Wook Lee

Research and Development Center, Samsung Corning, 644, Jinpyoung-dong, Gumi, Kyoung-buk 730-725, South Korea

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Abstract

In this article, we report the results of the study of thermal treatment effects on the electrical and optical properties of silver-based indium tin oxide/metal/indium tin oxide (IMI) multilayer films. Heat treatment conditions such as temperature and gaseous atmosphere was varied to obtain better electrical and optical properties. We obtained improved electrical properties and observed considerable shift in the transmittance curves after heat treatment. Several analytical tools such as X-ray diffraction, spectroscopic ellipsometer and spectrophotometer were used to explore the causes of the changes in electrical and optical properties. The sheet resistance of the structure was severely influenced by deposition conditions of the indium tin oxide (ITO) layer at the top. Moreover, the shift of optical transmittance could be explained on the basis of the change in refractive indices of ITO layers during heat treatment. The properties of Ag-alloy-based IMI films were compared with those of pure Ag-based ones. Some defects originating from Ag layer corrosion were observed on the surface of ITO-pure Ag–ITO structures, however, their number decreased significantly in the cases of Ag-alloys containing Pd, Au and Cu, though the resistivity values of Ag-alloys were slightly higher than those of silver. Atomic force microscopy measurement results revealed that the surface of the IMI multilayer was so smooth that it meets the required qualifications as the bottom electrode of organic light emitting diodes.

PACS: 68.55.-a; 73.61.-r; 78.66.-w

Keywords: Indium tin oxide; Silver; Electrical properties and measurements; Optical properties

1. Introduction

Many kinds of transparent conducting oxide (TCO) films such as impurity-doped indium oxides, tin oxides and zinc oxides systems have been most widely used as the transparent conductors for numerous opto-electronic applications [1–3]. Nowadays, the TCOs for high performance flat panel displays, e.g. liquid–crystal display (LCD), organic light-emitting diode (OLED) and plasma display panel require much lower resistivity for higher response rate, lower power consumption and driving voltage. Recently, some researchers proposed silver-based indium tin oxide/metal/ indium tin oxide (IMI) multilayer structures with much lower resistance as a good candidate for transparent conducting electrodes [4–7]. Several advantages of IMI structures have been reported, which have very low sheet resistance, high optical transparency in the visible range, relatively lower thickness than single-layered TCO films and better durability than single-layered metal films [4–7].

We investigated the effects of thermal treatment on the electrical and optical properties of silver-based IMI multilayers. Heat treatment conditions such as temperature and gaseous atmosphere were varied to obtain better electrical and optical properties. There have been controversial reports about the effects of heat treatment. Hence, we have performed more in-depth experiments to examine them. We found improved electrical properties and the shift phenomenon of transmittance spectra after the heat treatment, which should be considered seriously for designing color display devices.

Several analytical tools such as X-ray diffraction (XRD), atomic-force microscopy (AFM), spectroscopic

*Corresponding author. Tel.: +82-54-470-7494; fax: +82-54-470-7814.

E-mail address: ysjung@samsung.com (Y.S. Jung).

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ellipsometer and spectrophotometer were used for the characterization of the prepared samples.

2. Experiments

The thin films of indium tin oxide/(silver or silver alloy)/indium tin oxide structures were sputter-deposited using an indium tin oxide (ITO) and silver or silver-alloy targets in an in-line magnetron sputter deposition system equipped with DC power suppliers. The chamber, which was equipped with a load-lock system and diffusion pumps, had a base pressure of 5×10^{-6} torr. The targets (128×450 mm) used were sintered ITO containing 10 wt.% SnO_2, pure Ag (99.99%), AP (98 at.%Ag, 2 at.%Pd) and ACA (98 at.%Ag, 1 wt.%Cu, 1 at.%Au). The sputtering was carried out at a pressure of $1\sim2\times10^{-3}$ torr in a pure Ar or Ar/O_2 gas mixture with varying sputtering parameters such as oxygen flow rate and deposition temperature. The films were deposited on glass substrates (Corning 1737), which was placed 50 mm apart and parallel from the target surface, after the target was pre-sputtered for 3 min. The thickness of the ITO layer was 42 nm, and those of Ag or Ag-alloy were 15 nm, which was optimized by optical calculations.

Heat treatment was carried out under vacuum ($5\times10^{-6}\sim5\times10^{-5}$ torr)/O_2 (10^{-3} torr)/N_2 (10^{-3} torr)/air (1 atm) atmosphere, respectively, and the temperature was varied from 200 to 500 °C. Conventional θ–2θ XRD studies on the films were carried out in a Philips PW1710 diffractometer using Cu Kα radiation. Surface roughness was determined and surface images were taken by AFM (Auto-probe M5, PSIA company), and the scan area was 5×5 μm^2. Sheet resistance was measured using 4-point probe method. The indices of refraction as well as the extinction coefficients of the films were determined in the wavelength range of 300–1000 nm by using a spectroscopic ellipsometer (VASE, J.A. Woollam Co., Inc.), and optical transmittance was measured in the range of 350–800 nm by UV/VIS/NIR spectrophotometer (Lambda19, PERKIN–ELMER). Optical calculations were carried out using simulation software. (The Essential Macleod, Thin Film Center Inc.)

3. Results and discussions

3.1. Electrical properties

Fig. 1a shows the change of sheet resistance of ITO–Ag–ITO multilayer depending upon the deposition temperature. The three layers of each sample were deposited at the same temperature. Sheet resistance was lowest when the films were deposited at 100 °C, and increased very sharply at above 200 °C. Choi et al. reported the sharp rise of sheet resistance as the deposition temperature increased from 25 to 200 °C, which was due to the agglomeration of Ag layer [6]. However, Klöppel et al. presented a quite different result, which was the monotonous decrease of sheet resistance from RT to 150 °C [5]. In this study, the enhancement of Ag layer crystallinity might result in the decrease of sheet resistance of the sample deposited at 100 °C. The resistivity of ITO layer also decreased during thermal treatment, however, its influence on the total resistance of the

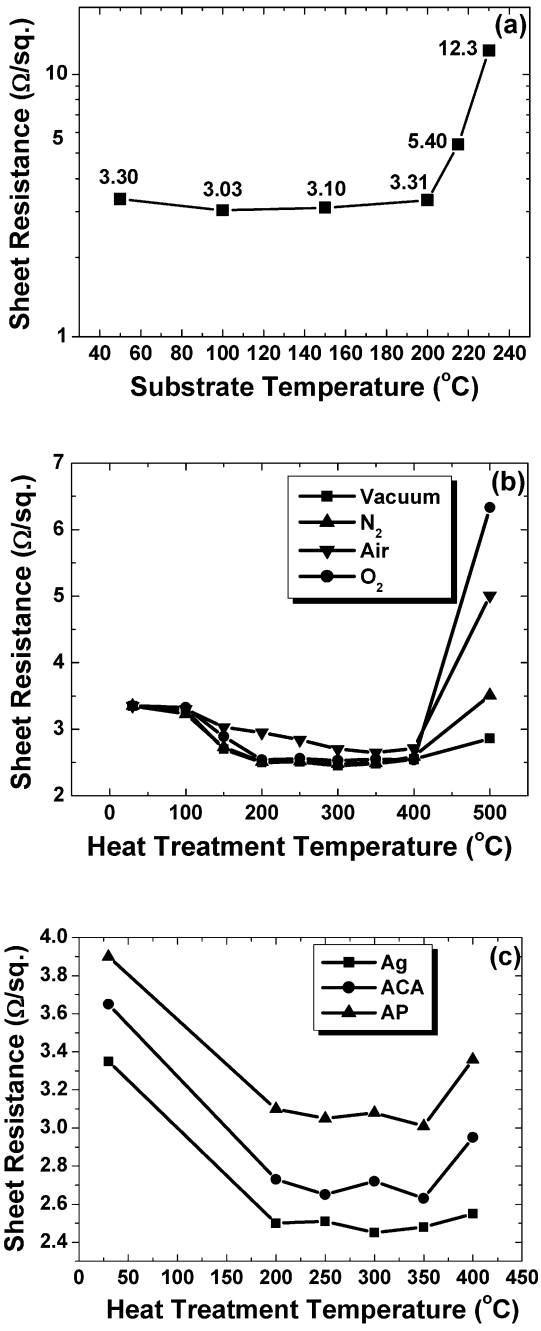

Fig. 1. Changes of sheet resistance depending upon (a) deposition temperature, (b) temperature of heat treatment with varying atmosphere and (c) temperature of heat treatment with varying metal layer.

multilayers is insignificant because of much higher resistivity of ITO than that of Ag. Meanwhile, as the deposition temperature increased from 100 °C, the surface scattering effect of electrons due to the agglomeration of silver and the degree of oxidation on the surface of Ag thin film seemed to increase, which might bring about the significant rise of resistivity. Fig. 1b shows the change of sheet resistance depending upon the temperature of thermal treatment. The heat treatment was carried out under vacuum, O_2, N_2 and air atmosphere, respectively. In the cases of vacuum, oxygen and nitrogen atmospheres, the sheet resistance was 2.45–2.53 Ω/sq when annealed at 300 °C, which was approximately 25% lower than that of untreated sample. Klöppel et al. presented similar results too [4]. Some researchers also reported that crystallinity was improved when Ag thin films with protective layers were heat-treated [4,8]. However, sheet resistance increased slowly as the temperature increased from 300 °C and very sharply at above 400 °C.

The change of X-ray diffraction profiles of ITO–Ag–ITO structures depending upon the annealing temperature is shown in Fig. 2a. The thickness of Ag layer was 30 nm. Ag(111) peak increased considerably after the treatment and Fig. 2b shows the increase of grain size, which was calculated using the obtained FWHM of Ag(111) peak and Scherrer's formula [9]. The grain size of the samples increased doubly after treatment. Therefore, the reduction of grain boundary scattering seems to lead to decreased resistivity. However, if the annealing temperature was above 400 °C, severe interdiffusion of atoms at the Ag/ITO interfaces seemed to occurr [4]. Thus, Ag atoms diffuse through ITO layers and O atoms diffuse through Ag layers, which cause the oxidation of the metal layers. Because of the small atomic radius of Ag, active interdiffusion through other film layers has been reported [10]. Moreover, the resistivity of Ag is closely related to the oxygen content in the Ag layer [4]. When being heat-treated under air atmosphere, the sheet resistance was slightly higher than those of other conditions. Because of high partial pressure of oxygen in the air, oxygen atoms diffused through the ITO layer and oxidized the Ag layer partly. A relatively sharper increase of sheet resistance at above 400 °C in the case of oxygen atmosphere supports this idea. Thermal treatment at 200–400 °C under vacuum condition seems to be the best for electrical properties. Fig. 1c shows the changes in sheet resistance with different metal layers. The tendency of change in sheet resistance was similar, however, sheet resistance was higher for ACA or AP layers due to the increase of resistivity. The free electron model proposes that the resistivity of a metal is proportional to the concentration of impurities [11]. The purity of Ag was 98 at.% for AP and ACA. Meanwhile, it was reported that the Ag-alloy containing 0.9 at.%Pd + 1.7 at.%Cu exhibited better resistance to hillock formation and agglomeration upon annealing in the air [12]. However, in this research, the metal layers have protection films at the top, so even the pure Ag films were not agglomerated during heat treatment. If we consider only the electrical properties of IMI structures, then pure Ag seems to be a better choice than Ag-alloys.

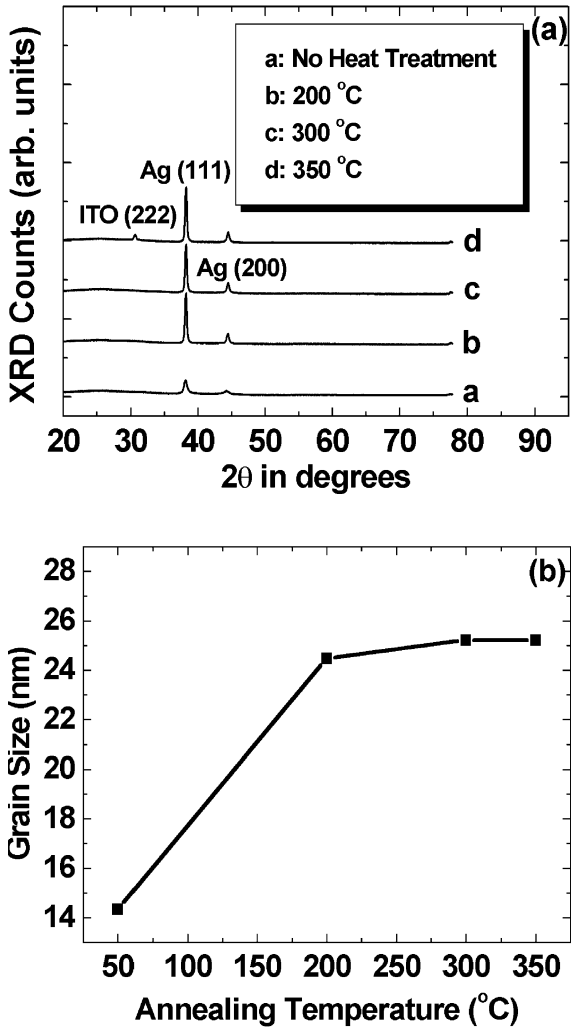

Fig. 2. (a) XRD spectra taken from IMI films deposited on glass substrates depending upon deposition temperature and (b) calculated grain size.

Fig. 3a and b presents the variation of sheet resistance of the ITO–Ag–ITO structure as the oxygen flow rate increases when depositing the top and the bottom ITO layers, respectively. The lowest sheet resistance was obtained when the oxygen flow rate was 2 sccm for the two kinds of ITO layers. Sheet resistance increased sharply by more oxygen supply than 2 sccm during the deposition of the top ITO layer (Fig. 3a), whereas it increased just slightly in the case of the bottom ITO layer (Fig. 3b). The single ITO thin film deposited with the oxygen flow rate of 2 sccm showed minimum

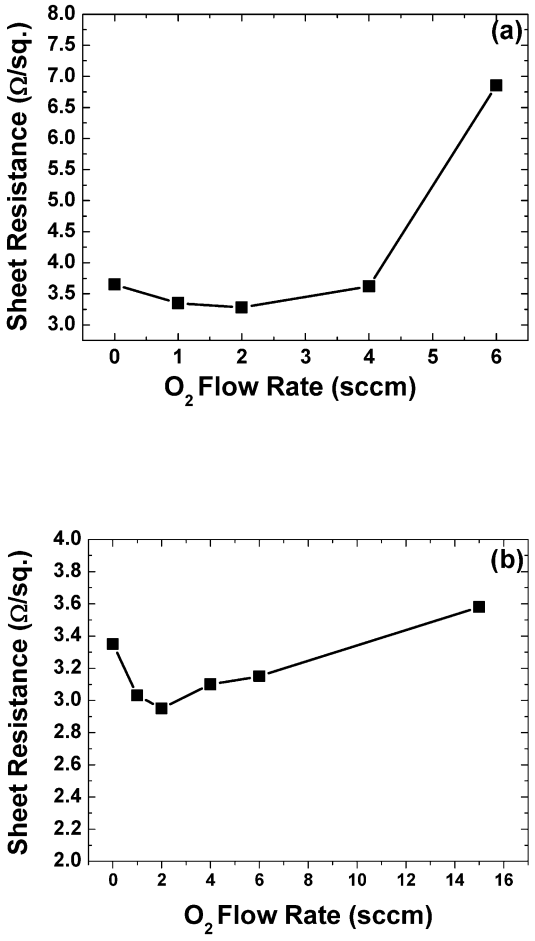

Fig. 3. Variation of sheet resistance of IMI films as the oxygen flow rate increases when depositing (a) the top and (b) the bottom ITO layers, respectively.

resistivity, and the oxygen flow rate of 15 sccm made the film non-conducting in the range of our measurement. Klöppel et al. reported that the minimum sheet resistance of IMI multilayer was obtained with an optimum oxygen flow rate during ITO deposition [4]. Our results seem to be good evidence in which the deposition conditions of top ITO layer mainly influenced resistivity of the Ag layer, if the deposition parameters of Ag were fixed. The existence of the optimum oxygen condition means that there were two or more factors affecting the sheet resistance of IMI structures depending upon the oxygen flow rate. Firstly, supplying more oxygen gas when depositing the top ITO layer, which further oxidizes the Ag layer, would result in an increased resistivity. Secondly, the supplied oxygen atoms reduce the oxygen vacancies and improve the stoichiometry of ITO films, therefore, suppressing the interdiffusion of atoms and oxidation of the Ag layer, which might prevent the increase of resistance [4]. These opposite effects might lead to the U-shaped curve of sheet resistance shown in Fig. 3a. In the case of the bottom ITO layer, the additional oxygen flow does not influence the degree of oxidization of the Ag layer as much as the top ITO layer, and the lowest sheet resistance at 2 sccm seems to be due to the lowest resistivity of ITO.

3.2. Optical properties

Fig. 4a shows the change of transmittance depending upon the deposition temperature. Transmittance

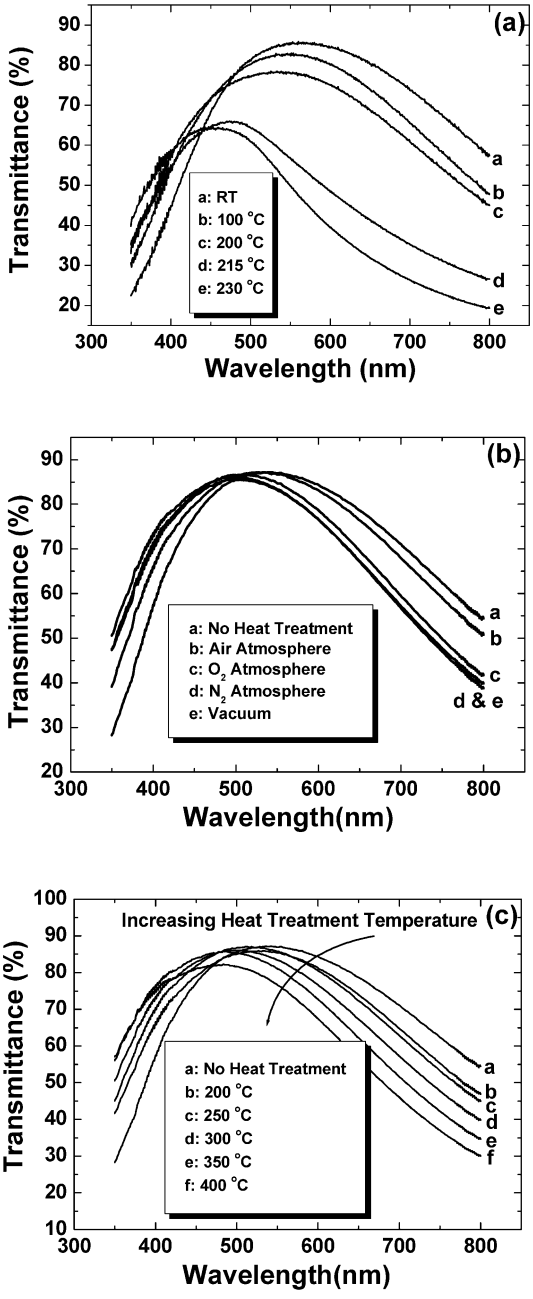

Fig. 4. Transmittance curves depending upon (a) deposition temperature, (b) heat treatment atmosphere and (c) the temperature of heat treatment.

decreased as the deposition temperature increased, and transmittance curves shifted towards the direction of shorter wavelength and lower transmittance. Transmittance decreased especially rapidly at above 200 °C. Choi et al. presented similar results [6], but Klöppel et al. reported that transmittance increased with the deposition temperature, and saturated from 100 until 150 °C [5]. Choi et al. proposed that the surface of Ag layer became rough as the deposition temperature increased, which resulted in the decrease of transmittance [6]. The transmittance curves of samples heat-treated at 300 °C under different atmospheres are shown in Fig. 4b. The curves shifted toward shorter wavelengths, and the amount of shift was less for the sample of air atmosphere than vacuum or N_2 atmosphere. Most LCD panels experience the temperatures of 200–300 °C during fabrication processes, so these transmittance shift phenomena may happen, which would result in the deviation of color coordinates from original designs. Accordingly, if we want to obtain a maximum transmittance at 550 nm after thermal treatment, then we need to slightly increase the thickness of ITO layers. The fact that transmittance curves shifted less for the sample of air atmosphere might be due to the influence of oxygen. Fig. 4c presents the change of transmittance as the heat treatment temperature increases. As the heat treatment temperature increased, the amount of shift of the curves increased, and the maximum transmittance was not changed considerably. However, at 400 °C, the maximum transmittance decreased, which might due to the diffused Ag atoms into ITO layer. That result is in accordance with the change of sheet resistance. To verify whether the shift of the transmittance curves is because of the changes of refractive index (n) or extinction coefficients (k), spectroscopic ellipsometry measurements were performed applying a model combining Drude and Lorentz terms (Fig. 5). The refractive indices (n) of the heat-treated samples decreased, and those of the samples annealed under vacuum and N_2 atmosphere decreased more significantly. Some researchers reported that the indices of refraction of SiO_2 or TiO_2 thin films decreased after heat treatment [13,14]. Poelman et al. proposed that the decrease of refractive indices was due to lower packing densities, resulting from the microstructural changes in the layer by thermal treatment [13]. Massoud et al. also found that the index of refraction of SiO_2 thin film increased with compressive stress and explained that the decrease of index of refraction is due to stress relaxation during heat treatment [14]. These explanations can also be applied to our results, the decrease of refractive indices of ITO films after heat treatment. Furthermore, study about the densities of ITO thin films after thermal treatment need to be performed to account for these results more clearly. The extinction coefficients of the heat-treated samples decreased, and those of the samples annealed under Air or O_2 atmospheres decreased more significantly. When the TCOs of

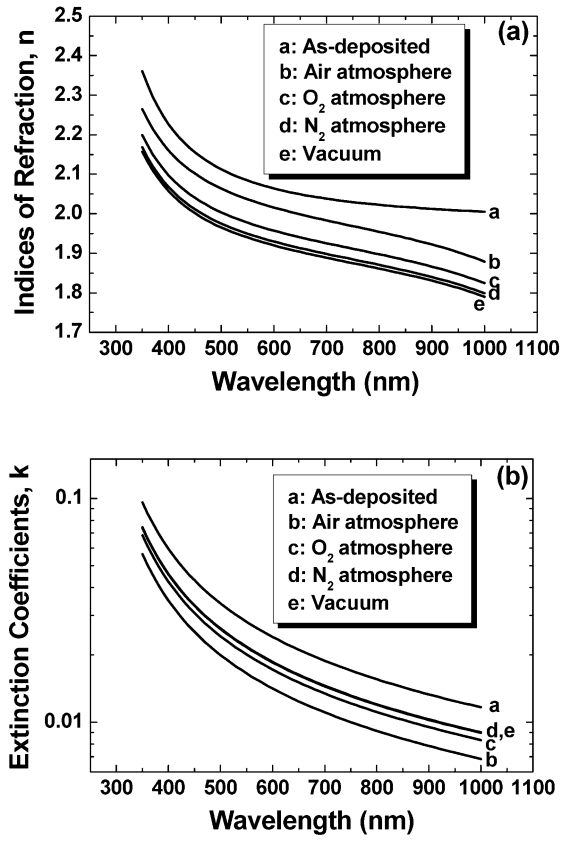

Fig. 5. Variations of (a) the refraction indices and (b) the extinction coefficients of ITO thin films depending upon heat treatment atmosphere.

In_2O_3 systems are deposited at low temperatures, suboxide phases such as InO_x or SnO_x act as optical scattering centers [15]. With thermal treatment, the suboxide phases are transformed to In_2O_{3-x} and SnO_{2-x}, and their composition approaches to stoichiometry when annealed under oxygen pressure, which leads to reduction of the number of optical scattering centers. The shift of transmittance after heat treatment seems to be closely related to the change of refractive indices. The calculated transmittance curves of the as-deposited and heat-treated samples were shown in Fig. 6. The calculation was carried out using a simulation software and the measured n, k values by spectroscopic ellipsometry. The n, k values of the sample heat-treated under vacuum condition were used for those of bottom ITO layers except the as-deposited case, because the bottom ITO layers were not exposed to gas atmospheres during heat treatment. Fig. 6 also presents the shift of the transmittance curves after heat treatment, which is consistent with the results of Fig. 4b.

3.3. Morphological property and defects

The two-dimensional AFM image of an IMI sample is shown in Fig. 7. The sample was heat-treated at 350

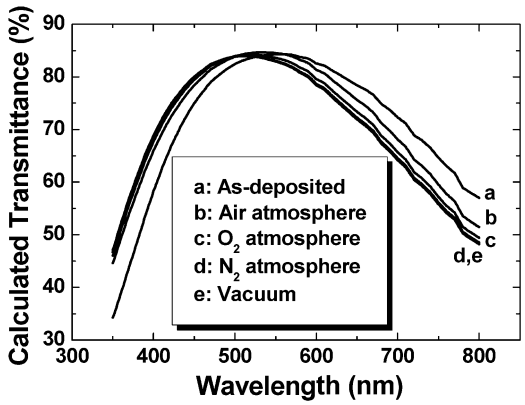

Fig. 6. Calculated transmittance curves of as-deposited and heat-treated IMI samples.

°C under vacuum condition for 60 min. The R_{p-v} of 50 Å and R_{rms} of 4.4 Å reveal that the surface of the sample was very smooth. The smooth surface of the amorphous ITO layer on the top seems to be maintained after heat treatment. These low roughness values satisfy the requirements of general OLEDs sufficiently. Heat-treated single ITO films, which are crystallized after being deposited as amorphous phase, also have very smooth surfaces; nevertheless, their resistivity values are relatively higher than those of the other ITO films grown at high temperature. However, the ITO–Ag–ITO multilayer structure has low sheet resistance as well as a very smooth surface, therefore, it could be used as a promising bottom electrode for OLED.

Fig. 8a and b are the optical microscope images taken immediately and after 3 months, respectively. More white spots were observed as time passed, and some of the spots grew to become very large. Fig. 8c shows an image of the grown spots. It was reported that generation of the defects is related with the corrosion of Ag [16]. Meanwhile, very few spots were observed for the samples where AP or ACA is used instead of Ag, which means better durability against corrosion.

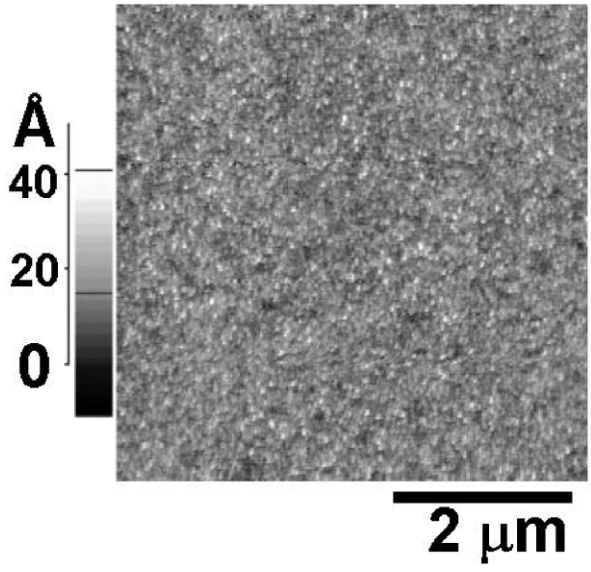

Fig. 7. Two-dimensional AFM image.

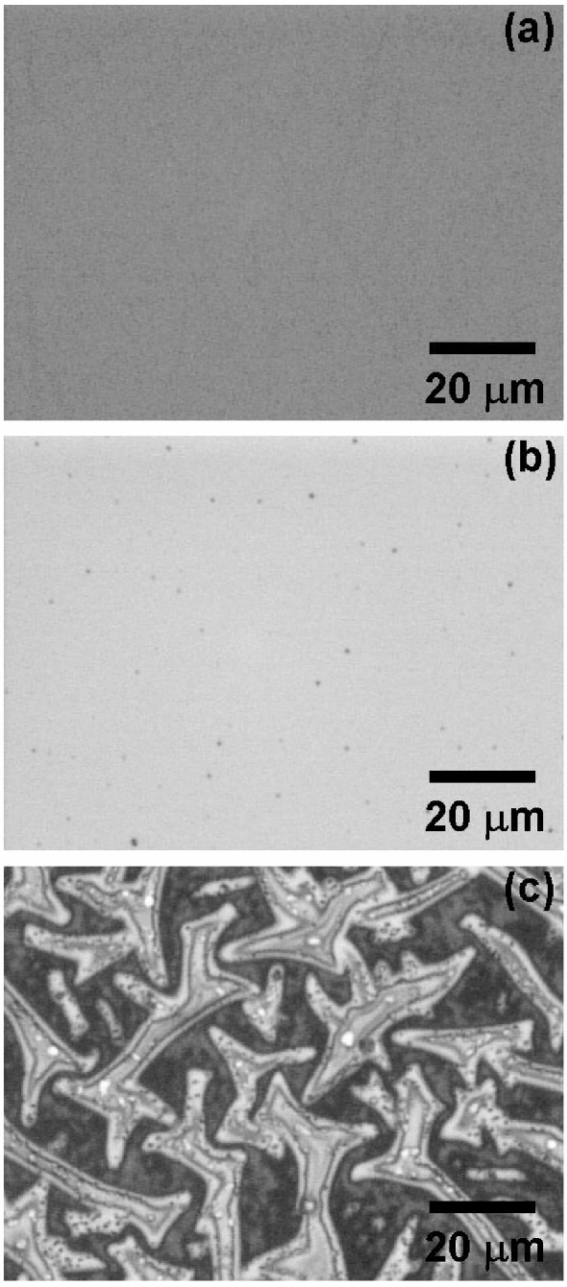

Fig. 8. Optical microscope images taken (a) immediately and (b) 3 months after fabrication, and (c) an image of a grown spot.

4. Conclusion

Transparent and conducting ITO–Ag–ITO multilayer films were deposited on glass substrate. By heat treatment, the sheet resistance was reduced as much as 25%, which was due to the increased grain size of Ag film.

The samples heat-treated at 200–400 °C under vacuum or nitrogen atmosphere showed the best electrical properties. As in other researches about IMI films, when depositing ITO layers, the optimum oxygen flow rate existed for the lowest sheet resistance of the multilayer, which was mainly influenced by the deposition condition of top ITO layer. The shift of the transmittance curves after thermal treatment was observed, and spectroscopic ellipsometry and optical calculations showed that the shift was caused by decreased refractive indices of ITO layer during heat treatment. The surface of the IMI multilayer was so smooth that it meets the requirements as the bottom electrode for OLED. When AP or ACA was deposited instead of pure Ag, the number of the defects-like white spots decreased, though sheet resistance was relatively higher.

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