Electrical and optical properties of ITO:Ca composite thin films for TEOLED cathode

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Abstract

ITO:Ca composite thin films were deposited on glass substrate by the rf magnetron co-sputtering method with various numbers of Ca chips and oxygen partial pressures. The carrier concentration of the ITO:Ca thin film was \(7 \times 10^{20} \text{ cm}^{-3}\) when the number of Ca chips was 4 at an oxygen partial pressure of 1.4%. The sheet resistance and optical transmittance of the ITO:Ca thin films were 68.2 Ω/sq. and 87%, respectively. The work function of the ITO:Ca thin films with 8 Ca chips was changed from 4.6 eV to 5.0 eV when the oxygen partial pressure was increased from 0.8% to 2.2%. When the oxygen partial pressure was 1.2%, a low work function of 4.6 eV was obtained for the ITO:Ca thin films.

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1. Introduction

Organic light-emitting devices (OLEDs) are attractive because of their promising application advantages, low driving voltage, low power consumption, high contrast, wide viewing angle, low cost, and fast response time[1,2]. The cathode materials used in top-emission organic light-emitting devices (TEOLEDs) need a low work function in order to have a high electron injection efficiency and high transparency [3,4]. The top-emission type of cathode material is used in the case of Mg/Ag and Al/Li metal thin films [5], Mg/Ag [6] and Al/Li [7] metal thin films have the advantage of a low work function, but they are highly reactive and oxidized in air, following which their optical transmittance is decreased to 50% [8,9]. Indium tin oxide (ITO) films are mainly used for transparent electrodes, because of their high transmittance in the visible region and low electrical resistivity [10–12]. However, their electron injection efficiency is low, because they have a high work function [13].

In this study, ITO:Ca composite thin films were deposited by rf magnetron co-sputtering using Ca chips and an ITO target to decrease the work function and electrical and optical properties of the ITO:Ca thin films in order to evaluate their potential for use as a top-emission cathode materials.

2. Experimental details

ITO:Ca composite thin films were deposited on glass substrates using rf magnetron co-sputtering with an ITO target.
and calcium (Ca) chips. The configuration of the deposition system is shown in Fig. 1. The purities of the ITO target and Ca chips were 99.99% and 99.9%, respectively. The sputtering system can supply rf bias power from both the substrates and the guns. Before the deposition of the ITO:Ca films, we cleaned the substrates by subjecting them to plasma treatment in 4% H₂ Ar balance ambient. Ca chips had been up to 8 form 4. The ITO:Ca thin films were deposited from gaseous mixtures of 4% H₂ Ar balance and O₂. The base pressure was around 2.7×10⁻⁴ Pa. The working pressure was maintained at 0.13 Pa and the substrate temperature was held at 373 K for all of the samples. The thickness of the samples under all of the deposition conditions was constant at 200 nm.

Hall effects measurements were conducted to observe the carrier concentration and hall mobility of the films. The optical transmission of the ITO:Ca thin films were measured using a UV–VIS spectrometer and their sheet resistance was measured by a four-point probe. The work functions of the samples were measured by means of a photoelectron spectrometer. The binding structure was measured by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

The electrical properties of the ITO:Ca thin films varied with the deposition parameters. Fig. 2 shows the electron concentration and electron mobility for various numbers of Ca chips and oxygen partial pressures. The carrier concentration of the ITO:Ca thin films decreased from 7×10²⁰ cm⁻³ to 5.5×10²⁰ cm⁻³ as the number of chip was increased from 4 to 8 at an oxygen partial pressure of 1.4%. It was assumed that the Ca ions play the role of free electrons in the ITO:Ca composite thin films. The decrease of the carrier concentration when the number of Ca chips was increased to 8, resulted from the increase in the amount of Ca oxide (CaO) contained in the ITO:Ca thin films, as a result of which the electron concentration was decreased. When the oxygen partial pressure was increased from 0.8% to 1.4%, the carrier concentration of ITO:Ca films was also increased. The increase of carrier concentration was explained as the number of oxygen vacancies in ITO:Ca films. The oxygen...
ITO:Ca thin films with 8 Ca chips was about 95%. We concluded that when the oxygen partial pressure was 1.6%, the optical transmittance of the films increased from 0.8% to 1.4%. When the number of Ca chips was both 4 and 8, the optical transmittance of the ITO:Ca thin films was 68.2 Ω/sq. The increase of the carrier concentration of the films was due to the scattering of the free electron. The electron mobility in the films increased from 1.6% to 2.2%, when the number of Ca chips was both 4 and 8. Ca ions make a role in free electron. The electron mobility in the films with increasing oxygen partial pressure was decreased at the ITO:Ca thin films.[12].

Fig. 3 shows the sheet resistance of the ITO:Ca thin films as a function of the number of Ca chips and oxygen partial pressure. The sheet resistance of the ITO:Ca thin films increased from 68.2 Ω/sq to 77.1 Ω/sq as the number of Ca chips increased from 4 to 8 at an oxygen partial pressure of 1.4%. We concluded that the increase of the sheet resistance of the films with 8 Ca chips was due to the decrease of the carrier concentration. The electron mobility of the films with increasing oxygen partial pressure was decreased at the ITO:Ca thin films.[12].

Fig. 4 shows the optical transmittance of the ITO:Ca thin films as a function of the number of Ca chips and oxygen partial pressure. When the number of Ca chips was 4, the optical transmittance of the ITO:Ca thin films increased as the oxygen partial pressure was increased from 0.8% to 1.6% and decreased thereafter. When the oxygen partial pressure was 1.6%, the optical transmittance of the ITO:Ca thin films was about 91%. The optical transmittance of the ITO:Ca thin films with 8 Ca chips increased when the oxygen partial pressure was increased from 0.8% to 1.4%. When the oxygen partial pressure was 1.6%, the optical transmittance of the ITO:Ca thin films with 8 Ca chips was about 95%. We concluded that the optical transmittance of the ITO:Ca thin films with 8 Ca chips was higher than that of the films with 4 Ca chips, because the deposition of ITO:Ca resulted in an increase of the grain size due to the increase in the number of Ca atoms in the lattice.

The work function of the ITO thin films deposited with an oxygen partial pressure of 1.4% was 4.8 eV. However, the work function of the ITO:Ca thin films with 8 Ca chips was 4.6 eV. This decrease of the work function resulted from the properties of Ca in the ITO:Ca thin films. Fig. 5 shows the work function of the ITO:Ca thin films for various oxygen partial pressures. The work function of the ITO:Ca thin films was 4.6 eV at oxygen partial pressure of 1.2%. However, when the oxygen partial pressure was increased from 0.8% to 2.2%, the work function of the ITO thin films was increased from 4.7 eV to 5.0 eV. These increase of the work function of ITO:Ca thin films was explained by changing the Fermi level. It is possible that these O– ions will repel the free electrons in the conduction band, and lead to a surface depletion region and consequently a shift in the Fermi level [14]. The Fermi level was decreased, because the increase of the sheet resistance was related to the decrease in the number of electron carriers. As a result, the increase of the work function resulted from the decrease in the number of electron carriers [15].

Fig. 6 shows the Ca 2p2/3 X-ray photoelectron spectroscopy (XPS) spectrum as a function of the number of Ca chips. The Ca and Ca–O peaks in the Ca 2p2/3 X-ray photoelectron spectroscopy (XPS) spectra for the ITO:Ca thin films were observed at 345.9 eV and 347.9 eV, respectively. In the comparison of the Ca 2p2/3 X-ray photoelectron spectroscopy (XPS) spectra for the ITO:Ca thin films with 4 and 8 Ca chips, the ratio of Ca bonds was found to be 3.56%, while the ratio of Ca–O bonds increased when the number of Ca chips was increased from 4 to 8.

4. Conclusion

The electrical and optical properties of ITO:Ca composite thin films were investigated as a function of the oxygen partial pressure and the number of Ca chips. The sheet resistance of the ITO:Ca thin films deposited at an oxygen partial pressure of 0.8% was 68.2 Ω/sq. The increase of the carrier concentration of the ITO:Ca thin films resulted from the decrease of the sheet resistance, because the Ca atoms played the role of free electrons. The transmittance of the ITO:Ca thin films deposited at oxygen partial pressure of 1.4% with 4 Ca chips was 87%. An ITO:Ca composite thin film cathode with a high optical transparency (87%) and low work function (4.6 eV) was obtained by rf sputtering at an oxygen partial pressure of 1.4%. The work function of the ITO:Ca composite thin film could be decreased to 4.6 eV without any decrease of the optical transparency and electrical conductivity.

References