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Electrical and optical properties of $12CaO\cdot7Al_2O_3$ electride doped indium tin oxide thin film deposited by RF magnetron co-sputtering

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ABSTRACT

$12CaO\cdot7Al_2O_3$ electride (C12A7:e$^-$) doped indium tin oxide (ITO) (ITO:C12A7:e$^-$) thin films were fabricated on a glass substrate by an RF magnetron co-sputtering system with increasing number of C12A7:e$^-$ chips (from 1 to 7) and at various oxygen partial pressure ratios. The optical transmittance of the ITO:C12A7:e$^-$ thin film was higher than 70% in the visible wavelength region. In the electrical properties of the thin film, a decrease of the carrier concentration from 2.6×10^{20} cm^{-3} to 2.1×10^{18} cm^{-3} and increase of the resistivity from 1.4×10^{-1} Ω cm to 4.1×10^{-1} Ω cm were observed with increasing number of C12A7:e$^-$ chips and oxygen partial pressure ratios. It was also observed that the Hall mobility was decreased from 17.27 cm$^2\cdot$V$^{-1}\cdot$s^{-1} to 5.13 cm$^2\cdot$V$^{-1}\cdot$s^{-1}. The work function of the ITO thin film was reduced by doping it with C12A7:e$^-$.

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1. Introduction

Transparent conductive oxides (TCOs) are widely used in a variety of applications such as optoelectronics, flat panel displays (FPD), solar cells, and gas sensors [1–2]. Their combination of transparency and electrical conductivity is a useful property of TCOs. Indium tin oxide (ITO), an n-type semiconductor with a wide band gap, is one of the most frequently used TCOs due to its unique characteristics, such as its good conductivity, high optical transmittance over the visible wavelength region and excellent adhesion to substrates [3–5]. For top emission organic light emitting devices (TEOLEDs), the performance of the devices strongly depends on the electron injection efficiency of the transparent cathode [6–7]. ITO can be used as a transparent cathode in TEOLEDs due to its unique characteristics. However, the work function of ITO is quite high and limits the device performance. Therefore, the investigation of doped materials which can reduce the work function of ITO thin films for transparent cathodes is necessary to improve the performance of TEOLEDs. In previous reports, many materials with a low work function such as Mg, Ag and Ca were used as the cathode material, but they are unstable in a thermal or chemical environment and easily oxidized [8–10]. To overcome this problem, $[Ca_{24}Al_{28}O_{64}]^{4+}(4e^-)$ (C12A7:e$^-$) has been put forward as a new type of inorganic electride, as it is a stable metal in air with high conductivity and small work function (~2.4 eV), and so is suitable for fabricating transparent cathodes [11–13]. C12A7:e$^-$ originates from the crystal structure of its base material, $12CaO\cdot7Al_2O_3$ (C12A7). C12A7 has a cubic lattice ($d=1.199$ nm) with a unit cell composed of a positively charged lattice framework, $[Ca_{24}Al_{28}O_{64}]^{4+}$. This framework has 12 subnanometer-sized cages and two extraframework O_2-ions (free oxygen ions). Generally, C12A7 is a typical insulator, but it can be changed into a conductor by substituting the free oxygen ions with active monovalent anions or electrons. Their complete replacement with electrons leads to the formation of C12A7:e$^-$.

In this study, we investigated the work function of C12A7:e$^-$ doped ITO (ITO:C12A7:e$^-$) thin films as a function of the number of C12A7:e$^-$ chips and oxygen partial pressure ratios using an RF magnetron co-sputtering system for the purpose of increasing the electron injection efficiency.

2. Experimental details

C12A7:e$^-$ was fabricated by several steps. Firstly, C12A7 powder was synthesized by the solid-state reaction of a stoichiometric mixture of $CaCO_3$ and γ-Al_2O_3 at 1300 °C for 12 h, and the pellet of the pressed powder was sintered at 1400 °C for 2 h [14]. The sintered C12A7 ceramic target has dimensions of Ø10 mm × 2 mm thickness. Subsequently, C12A7:e$^-$ was prepared by the Ti-treatment method [12]. The C12A7 pellet was sealed in a silica glass tube in a vacuum (~1.3×10^{-5} Pa) together with metal titanium pellets and annealed at 1000 °C for 24 h. C12A7:e$^-$ and ITO were deposited on a glass substrate at the same time by RF magnetron co-sputtering with an ITO target ratios ($In_2O_3 : SnO_2 = 90 : 10$ wt.%, purity: 99.99%) and C12A7:e$^-$ chips in a gas mixture consisting of 4% $H_2\cdot$Ar and O_2 at 373 K. The vacuum chamber was evacuated down to a base pressure of ~2.7×10^{-4} Pa prior to deposition. When the reactive gases were introduced into the chamber, the required working pressure (0.1 Pa) was set and maintained during the deposition process. Before deposition, we cleaned the substrates by plasma treatment in 4% $H_2\cdot$Ar ambient

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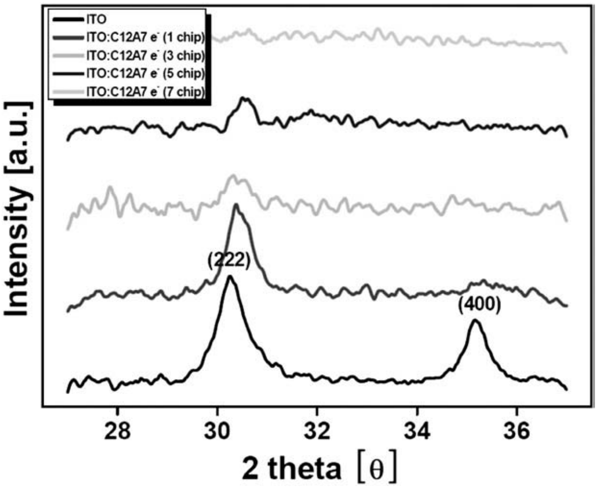

Fig. 1. X-ray diffraction patterns of ITO:C12A7:e$^-$ thin films deposited in a mixture of 4% H_2 Ar and O_2 (O_2/4% $H_2 \cdot Ar + O_2 = 1.2\%$).

plasma. The number of C12A7:e$^-$ chips was varied from 1 to 7 chips. The oxygen partial pressure ratio was varied from 1.0% to 1.6%. The RF power was maintained at 200 W for all of the experiments.

The crystal structure of the thin film was characterized by means of a high resolution X-ray diffractometer (HRXRD) with Cu Kα radiation (1.54 Å) (B8 Discover, Bruker AXS Ltd.). The carrier concentration and resistivity of the film were measured by a Hall Effect measurement system using the Van Der Pauw technique. The optical properties of the thin film were observed using a UV–VIS spectrophotometer (S-2100, Scinco). The chemical components of the ITO:C12A7:e$^-$ thin film were analyzed by an Electron Probe Micro-Analyzer (EPMA) (JXA-8900R). The work function was measured by a UV spectrometer (Riken Keiki, AC-2).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the ITO:C12A7:e$^-$ thin films with various numbers of C12A7:e$^-$ chips. These thin films fabricated at a fixed oxygen partial pressure ratio of 1.2% had a polycrystalline structure with slightly shifted (222) and (400) diffraction peaks compared with ITO thin film. However, these distinct diffraction peaks gradually decreased with increasing number of chips. Namely, the diffraction peak corresponding to (400) was disappeared and led to the loss of crystallinity in the thin films. Moreover, the disappearance of (222) peak was also observed and indicated that the films were amorphous above 5 chips. The loss of crystallinity can be explained by the crystal distortion caused by the extreme existence of C12A7:e$^-$ material in the film with increasing number of C12A7:e$^-$ chips. Furthermore, the loss of crystallinity caused to affect the electrical and optical properties of the ITO: C12A7:e$^-$ thin film.

The electrical properties of the ITO:C12A7:e$^-$ thin films are illustrated in Fig. 2. It was found that the carrier concentration, resistivity and Hall mobility were related to the number of C12A7:e$^-$ chips and oxygen partial pressure ratios. Fig. 2 (a) shows that the carrier concentration of the thin films was decreased from 2.6×10^{20} cm^{-3} to 2.1×10^{18} cm^{-3} as the number of C12A7:e$^-$ chips was increased from 1 to 7 and the oxygen partial pressure ratio was increased from 1.0% to 1.6%. In addition, the resistivity was increased from 1.4×10^{-3} Ω cm to 4.1×10^{-1} Ω cm as shown in Fig. 2 (b). Kim et al. suggested that the decrease of the carrier concentration and increase of the resistivity might be due to the increase in the disorder in the ITO films with increasing doping level and also correlated with the loss of crystallinity [4]. This is in agreement with our results. When the number of C12A7:e$^-$ chips was increased from 1 to 7, the loss of crystallinity in the films for higher dopant level as shown in Fig. 1 led to decrease in the carrier concentration and increase in the resistivity. In addition, the decrease of the carrier concentration and increase of the resistivity are also explained by the number of oxygen vacancies. The oxygen vacancies create free electrons and, consequently, an increase in the number of oxygen vacancies leads to an increase in the carrier concentration. As the oxygen partial pressure ratio was increased from 1.0% to 1.6%, the decrease in the carrier concentration and increase in

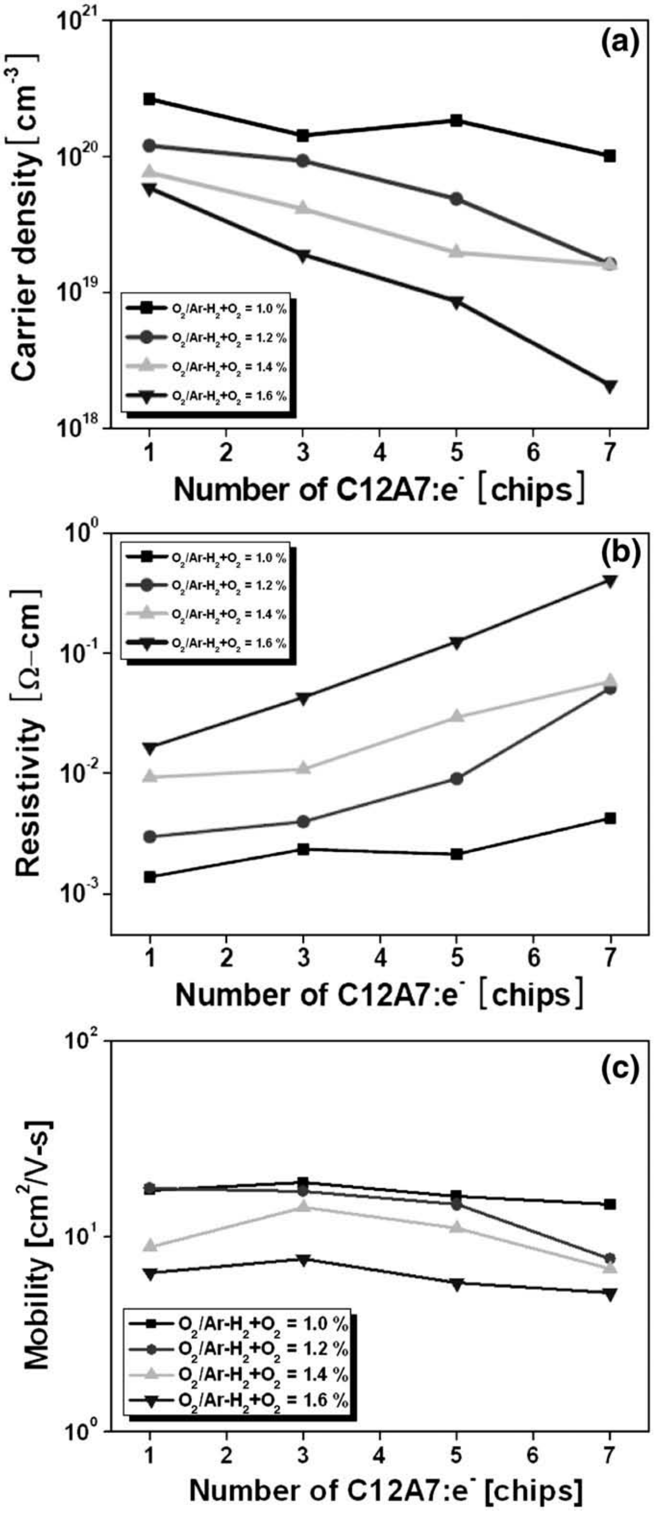

Fig. 2. The electrical properties of the ITO:C12A7:e$^-$ thin film as function of the number of C12A7:e$^-$ chips and oxygen partial pressure ratios: (a) carrier concentration, (b) resistivity, (c) hall mobility.

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