Journal of Non-Crystalline Solids 356 (2010) 911–916

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Indium tin oxide thin films for silicon-based electro-luminescence devices prepared by electron beam evaporation method

Neng Wan, Tao Wang, Hongcheng Sun, Guran Chen, Lei Geng, Xinhui Gan, Sihua Guo, Jun Xu *, Ling Xu, Kunji Chen

Nanjing National Laboratory of Microstructures, Jiangsu Provincial Key Laboratory of Photonic and Electronic Materials Sciences and Technology, School of Physics and School of Electronic Science and Technology, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 26 March 2009
Received in revised form 17 December 2009
Available online 18 January 2010

Keywords:
Electrical and electronic properties
Films and coatings
Electroluminescence
Indium tin oxide and other transparent conductors

ABSTRACT

Tin doped indium oxide thin films were deposited by electron beam evaporation (EBE) method. The influences of deposition atmosphere, film thickness and post-annealing temperature on the optical and electrical properties are studied. It is found that depositing films in oxygen atmosphere is helpful for improving the electrical and optical performance due to the improvement of the film microstructure. The sheet resistance is increased obviously in ITO films with reducing the film thickness, which is caused by the enhanced surface scattering towards the carriers. The obtained ITO thin films deposited under optimized conditions have good electrical and optical properties with typical resistivity of $4.5 \times 10^{-4}\ \Omega$ cm and the optical transmittance of about 85% (at 550 nm). Furthermore, the EBE deposited ITO thin film can be applied as the top electrode in the Si-based electro-luminescence devices and a strong electro-luminescence (EL) is observed.

1. Introduction

Tin doped indium oxide (ITO) has been used in many kinds of advanced opto-electronic devices due to its unique properties [1–3]. The un-doped indium oxide is n-type semiconductor with a fundamental band-gap of 3.65 eV. By doping with tin, the density of the carrier can be increased up to the Mott critical ($\sim10^{20}/cm^3$), and the highly degenerated semiconductor is formed [1]. This highly doped semiconductor is characterized as high transparency in visible light region, high reflection in infrared region, strong absorption in UV region and high conductivity at room temperature. ITO films can be used in many fields, such as smart windows for energy saving due to its high reflection in the infrared region and high transmission in visual region [1], and transparent conduction oxide (TCO) electrode in solar cells and electro-luminescence (EL) devices due to its high conductance and transmission in wide optical range [2,3].

So far, many methods have been used to deposit ITO thin films, such as pulsed laser deposition (PLD) [4,5], sputtering [6], e-beam evaporation (EBE) [7], sol–gel technique [8], and spray pyrolysis [9,10]. Among all these methods, e-beam evaporation has the advantages of low cost, low temperature, high purity and high deposition rate [1,7]. Motivated by the need of high transparency and high conduction of the ITO thin films in EL devices, it is interesting to study the influences of deposition parameters on the film properties in order to further understand the fundamental deposition process of ITO films. In this work, the e-beam evaporation method was used to deposit ITO thin films with low resistance and high transparency. The effect of oxygen pressure, substrate temperature, and annealing temperature on the electrical and optical properties were studied and correlated with each other. The optimized deposition parameters were discussed and concluded. ITO thin films deposited under the optimized deposition conditions show the good electrical and optical properties which is comparable with the best results of ITO films prepared by other different techniques. The performance of EL devices with the ITO top electrode on the Si/SiO_2 multilayer is experimentally demonstrated.

2. Experiments

ITO pellets of In/Sn = 95/5 filled in a copper crucible were used as evaporation sources. The electron beam source is the heated tungsten filament under an accelerating voltage of 6 kV. Glass slide with the dimension of 1 cm × 2 cm was used as substrate which is placed on a substrate holder. The substrate temperature is controlled by a heater attaching on the back of the substrate holder, and the distance from the substrate holder to the evaporation source is about 40 cm. During all the experiments the base pressure is lower than 5×10^{-4} Pa. In some of the deposition process, oxygen gas is introduced into the evaporation chamber by using a needle valve. The deposition rate and the thickness of the film

* Corresponding author.
E-mail address: junxu@nju.edu.cn (J. Xu).

0022-3093/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2009.12.026

is monitored and controlled through a quartz crystal probe assembled at the center of the substrate holder. The as-deposited films were annealed in a quartz tube furnace under N_2 atmosphere at different temperatures for half an hour in order to promote the crystallization and elevate the carrier concentration [8].

Various kinds of methods were used to characterize the microstructures and physical properties of ITO films. X-ray diffraction (XRD, Rigaku, D/Max-RA) method was employed for studying the crystal structure of the ITO films. Field emission scanning electron microscopy (FESEM, LEO 1530VP, Zeiss) was adopted for observing the surface morphology and measuring the thickness of the films. The In/Sn ratio in the film is determined by using the X-ray photoelectron spectroscopy (XPS, ESCALB MK-II) with the systematic error of 10% for determining the compositions in the film. UV/VIS/NIR transmission (T) and reflection (R) spectra were obtained by using Shimazu UV-3600 photospectrometer with the transmission measurement error less than 0.01%T and wavelength precision of 0.1 nm. The transmission spectra were obtained with air as reference in the normal incidence geometry, the reflection spectra were obtained with aluminum mirror as reference using a 5° reflection geometry, and the absorption (A) of the thin film is deduced by using the relationship of $A = 1 - R - T$. The resistance of the ITO films was measured by using the four probe method. The EL signals from ITO coated Si quantum dots-based devices were collected by using JY Fluromax-2 spectrometer at room temperature.

3. Results

It is well known that the deposition atmosphere has an important effect on the EBE process especially for depositing metal oxide materials and oxygen deficiency species will result in low transparency and poor optical and electric performance in the deposited ITO films [11,12]. Fig. 1(a) and (b) shows the FESEM micrographs of the ITO films deposited without oxygen and with the oxygen pressure of 2.7×10^{-2} Pa, respectively. The substrate temperature is kept at 150 °C during the deposition, and the thickness of the films is around 180 nm. It is found from the figures that the microstructure of the thin films is affected greatly by the oxygen gas. Films deposited without oxygen have porous structures. Some nanostructures with different sizes could be seen in the figure. Some of them are as large as 100 nm, while most of them are several tens of nanometers. A very different picture of surface morphology is observed with films deposited in oxygen rich atmosphere, which shows a condensed and flat surface. A lot of small grains could be observed in the figure, and the average grain size is about 30 nm with quite a good uniform size distribution. It is noted that the films annealed at different temperatures show similar microstructure with the as-deposited films, which could also be confirmed by the following XRD results.

The XRD patterns of the films deposited in oxygen atmosphere and post-annealed at different temperatures in N_2 are presented in Fig. 2. As seen in the figure, the as-deposited thin film shows relatively weaker XRD peaks indicating poor crystallization, while all the annealed ITO films are well crystallized into the BCC structure [6]. The intensity of diffraction peaks increases with elevating the annealing temperature, indicating that the crystallization of the thin film is improved after high temperature annealing. The full width at half maximum of the diffraction peaks decrease with elevating the annealing temperature, indicating the grain size increases with higher annealing temperature, which can be ascribed to the low crystallization temperature of ITO films.

Fig. 3(a)–(f) gives the optical transmission, reflection and absorption spectra of the film deposited without and with oxygen, respectively. As shown in the figures, the as-deposited films have low transmission during the whole range of the spectrum. Comparing with the films deposited without oxygen atmosphere, the films deposited in oxygen atmosphere show higher transmission, suggesting that the oxygen deficiency could be one of the sources for the low optical transmission. High temperature annealing is efficient for enhancing the transmission. As seen in the transmission spectra, the film annealed above 350 °C shows good transparency in the visual light region both for films deposited with (about 85% at 550 nm) or without oxygen gas (about 80% at 550 nm). We ascribe the improved optical transmission to the improvement of the film microstructure and elimination of the defects after high temperature annealing. The sharp falling-down in the transmission spectra below 400 nm is caused by the strong absorption of the glass substrate and ITO itself, because the band-gap of ITO is about 3.65 eV (~340 nm) and the glass substrate show strong absorption below 350 nm. This can also be easily interpreted from the absorption spectra shown in Fig. 3(c) and (f). A decrease in the infrared region (above 1600 nm) is observed in all of the transmission spectra, and this is mainly due to the high infrared reflection of the ITO films [1], which can be directly observed in Fig. 3(b) and (e). The reflection in the near infrared region can be ascribed to the carrier plasma generated by the high degeneration of the ITO thin films. According to the XPS results (not shown here) the films always have the stoichiometry ratio of In/Sn = 8–9, so the ITO thin film must be highly doped with tin and high degeneration can be realized, which is the origin of the carrier in the films. According to previous reports [1], the reflection in the infrared region is realized to be related with the carrier density in the ITO thin films.

The absorption spectra shown in Fig. 3(c) and (f) give useful information about the property of the thin films. As shown in the figures, the as-deposited films have much higher absorption than the high temperature annealed films. This could be the source of the low transparency of the as-deposited films. Comparing the films deposited with and without oxygen atmosphere, the former ones show relatively lower absorption in the whole spectral region.

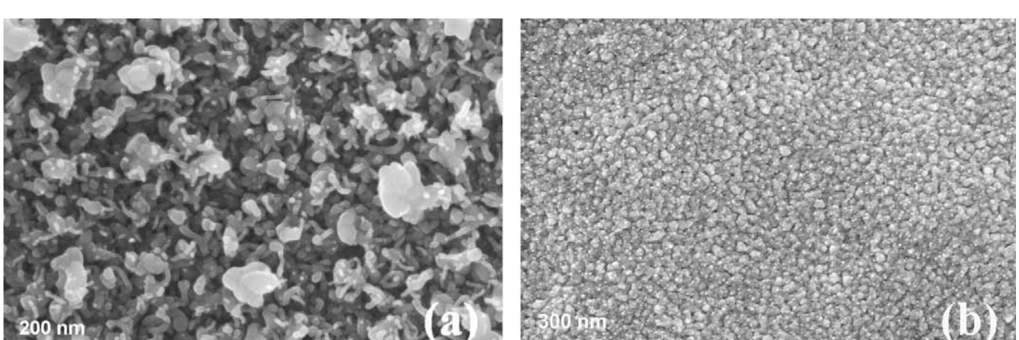

Fig. 1. FESEM images of the ITO thin film deposited without oxygen atmosphere (a), and with the oxygen pressure of 2.7×10^{-2} Pa (b).