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Corrosion behavior in simulated environments of ITZO films prepared by two targets co-sputtering

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Abstract

Indium tin zirconium oxide (ITZO) films were deposited by a co-sputtering technique with ITO and zirconium targets. The stability and corrosion behavior of films in simulated environments were studied on account of microstructure and optical–electrical properties. The results show that ITZO films possess a better crystalline structure and optical–electrical properties. Zirconium-doping changes the preferred orientation of ITO films, and ITZO films under the optimum parameters have sheet resistance of 10 Ω/sq and transmittance of above 85%. According to the polarization measurements and the relative resistance change of the films in simulated environments such as acidic climate, oceanic climate and industrial climate, the doping films show better chemical and thermal stabilities than ITO films. Besides the influence of crystal structure, the better stability of zirconium oxide can improve the chemical and thermal stabilities. ITZO films have better electrical stability and chemical antcaustic properties, and the films could find more extensive applications.
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1. Introduction

Since the 1990s, flat panel display and solar photovoltaic technology have greatly promoted the development of the optical–electrical films. Due to the high carrier concentration and wide optical band gap, transparent conductive oxide films show good optical–electrical properties, such as low resistivity and high visible light transmittance. Indium tin oxide (ITO) films have good optical properties and are widely used for transparent electrode. ITO films, which have more excellent comprehensive performance than other transparent conductive oxide films [1,2], are a highly degenerate n-type semiconductor and the semiconducting mechanism is attributed to oxygen vacancies and doping with Sn^{4+}. But at present the chemical and thermal non-stabilities and low surface energy limit the extensive application of ITO films. The enhancement of optical–electrical properties and the comprehensive performance of ITO films is always an important direction of current research [3,4]. ITO films are currently focused on improving the conductivity of films without sacrificing its transparency, while increasing its stability in harsh environments. Although some other binary oxides such as ZnO and SnO_2 can partially solve some problems [5–7], these oxides cannot fully resolve the problem of maintaining better optical–electrical performance, while improving its related physical and chemical properties.

According to the fact that it is difficult to achieve better optical–electrical properties as well as physical and chemical properties with ternary compounds, recently, some studies on the improvement of properties of ITO films were carried out by using multi-component oxide [8–10]. As we all know, the characteristics of ITO films strongly depend on its oxidation state and the content of impurities. Carrier concentration can be modified by the dopant activation state, which is due to a donor atom to substitute the lattice site of indium oxide and produce some free electrons to increase carrier concentration. Some high-valence metal elements such as zirconium element can be regarded as the donor, which replaces indium of the In_2O_3 matrix. The ionic radius of Zr^{4+} is lower than that of In^{3+}, which implies that a limited solid solution can be formed. The optical–electrical properties of films are closely

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related to the degree of crystallinity. The presence of high melting Zr oxide crystals may be used as the initial particle of heterogeneous nucleation, which can promote crystallization of the films. The Zr dopant can also improve the activation of Sn dopant.

The study of ITO films both at home and abroad mainly focused on the optical–electrical properties, and the chemical stability, as well as electrochemical corrosion tests and surface state has not been reported. In this paper, ITZO films were deposited on glass substrates by co-sputtering with ITO target and zirconium target. The electrical and electrochemical stabilities of ITZO films are investigated in various simulated environments.

2. Experimental details

Dual sputtering sources in a two targets sputtering system, including DC power and RF power, were used for co-sputtering with an ITO target and a zirconium target (99.995%). ITO and ITZO films were all deposited on glass substrates. DC sputtering power of ITO target was 45 W, and RF sputtering power of zirconium target was 10 W. ITO target was hot-pressed In_2O_3 target containing 10 wt% SnO_2. The target-to-substrate distance was 65 mm. Typically, the base vacuum was about 1.0×10^{-4} Pa, and during the deposition processing the total pressure can be constantly kept at 0.5 Pa by controlling argon gas flow. Oxygen flow rate was kept at 0.3 sccm by a mass flow controller. After chemical cleaning and etching, the float glass substrates were placed into the vacuum chamber. The substrates temperature was 400 °C. All sputtering processes were dynamic with the substrate rotating in front of the target. After 30 min deposition, the film thicknesses of about 240 nm were achieved. The averaged metal atomic ratios of ITO and ITZO films were In:Sn=9:1 and In:Sn:Zr=9:1:0.2, respectively. ITO and ITZO films showed about the same thicknesses under the similar deposition processing.

The method of relative electrical resistance change was used for evaluation of the corrosion behavior. According to the relative resistance change ($\Delta R/R$) in per area of the films, it not only determined the corrosion properties but also predicted the long-term behavior of the films in field tests or in applications. The present paper mainly investigated the environmental effects on the stability of electrical properties and long-term reliability of the films in 3.5% NaCl, 0.5 M Na_2SO_4 and 0.5 M HCl solutions at 25 °C, which separately simulated marine, industrial and acidic environments.

Electrochemical experiments were performed using an IM6e electrochemical interface controlled by a personal computer. The measurements of potentiodynamic polarization curves were carried out at a scanning rate of 1 mV/s from −1000 mV to 2000 mV with regard to the free corrosion potential (E_{corr}). The potential of the working electrode was measured against a saturated calomel electrode (SCE). A platinum electrode was employed as the counter electrode. The luggin capillary was placed close to the working electrode. All the potentials mentioned in this paper were with reference to SCE. The films deposited on glass substrates were used as the working electrode. An electrochemical measurement meter adopted horizontal, and leaved a hole as the contact area between films and solution, and 0.8 cm^2 area was exposed in the corrosion medium. The films were coated with a piece of metal aluminum foil to wrap the upper part of the films both front and rear so that positive and negative areas of samples could be conductive. The films were pressed at the hole with a conductive sheet metal, which was regarded as the working electrode.

The film thicknesses were measured with an alpha-step profilometer (Dektak 6M). The sheet resistance was determined using a four-point probe system (SDY-5). The crystal structures were examined by an X-ray diffractometer (XRD; D/max 2550V) using Cu-Kα radiation. The surface morphology of films were evaluated by atomic force microscopy (AFM; AJ-III) and transmission electron microscopy (TEM; JEM-100CX), respectively. Optical transmittance and reflectance spectra of ITO/Glass structure were measured with a UV–vis–NIR Scanning Spectrophotometer (Lamda950). The morphology of films was examined with scanning electron microscopy (SEM; S-520) after corrosion. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Microstructural and optical–electrical properties

Fig. 1 shows the XRD patterns of ITO and ITZO films. All the films are well crystallized and show clear XRD peaks. The films are crystallized in the cubic bixbyite structure of indium oxide, and there are no second phases corresponding to either Zr or its oxides. Zr-doping leads to the preferred orientation change from (2 2 2) to (4 0 0) plane. The oxidation of the growing film is in competition with the oxygen removal phenomenon, and the competition has an impact on the modification of the preferred orientation growth from (2 2 2) to (4 0 0) plane. In the case of Zr addition to the sputtering system, Zr-doping leads to oxygen deficiency in the In_2O_3 matrix, which favors the preferred orientation along the (4 0 0)

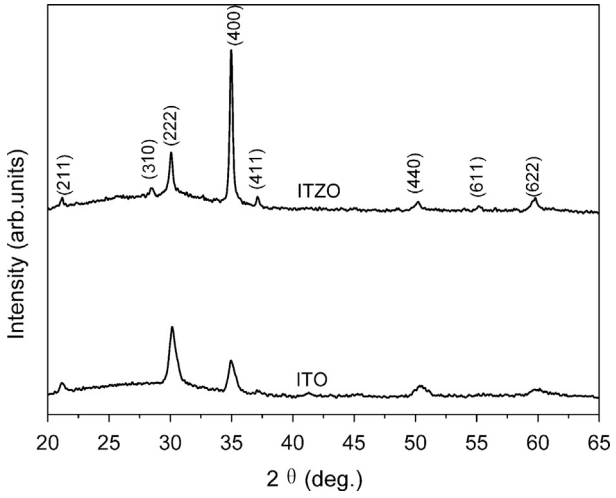

Fig. 1. XRD patterns of ITO and ITZO films.

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