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Transparent conductive Sb-doped SnO_2/Ag multilayer films fabricated by magnetron sputtering for flexible electronics

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Abstract

The effects of an embedded silver layer and substrate temperature on the electrical and optical properties of Sb-doped SnO_2 (ATO)/silver (Ag) layered composite structures on polyethylene naphthalate substrates have been investigated. The highest conductivity of ATO/Ag multilayer films was obtained with a carrier concentration of 1.5×10^{22} cm^{-3} and a resistivity of 2.4×10^{-5} Ω cm at the optimum Ag layer thickness and substrate temperature. The photopic averaged transmittance and Haacke figure of merit are 81.7%, and 21.7×10^{-3} Ω^{-1}, respectively. In addition, a conduction mechanism is proposed to elucidate the mobility variation with increased Ag thickness. We also describe the influence of substrate temperature on the structural, electrical and optical properties of the ATO/Ag multilayer films, and propose a mechanism for the changes in electrical and optical properties at different substrate temperatures.

Keywords: Semiconductors; Multilayer thin films; Electrical properties; Growth temperature; Mechanism

1. Introduction

Transparent conducting oxide (TCO) films have been widely used as transparent conducting electrodes in many optoelectronic and electro-optical devices such as solar cells and flat panel displays [1–5]. Sn-doped In_2O_3 (ITO) thin film is the most widely used TCO film due to its low resistivity, high transparency and high work function [6,7]. However, the conductivity of ITO thin film is limited by its semiconductor mechanism, these materials are expensive due to the cost of indium. Therefore, it is important to develop cheap and high-performance TCO thin films. Impurity-doped tin oxide (SnO_2) thin films have received much attention as TCO films [8–13] because they are nontoxic, and use cheap and abundant elements. Sb and F are the most commonly used dopants for photovoltaic devices. Sb has been shown to be effective and low cost, and hence is an attractive material [13]. However, inherent limitations in the conductivity need to be further improved by using multilayer structures.

Although three-layer structures have been widely reported, there are to date few reports about double-layer structures, despite the latter being cheaper to produce. Many papers on multilayer films on glass substrates have been reported [14–18]. However, there is little in the literature about multilayer coatings on flexible substrates, and no Sb-doped SnO_2 (ATO)/metal multilayer films on polymer substrates have yet been reported. In this work, we used polyethylene naphthalate (PEN) as a flexible substrate, due to its superior optical properties compare to other materials [19,20]. We selected Ag as the metal layer because of its low resistivity.

In this work, magnetron sputtering was used to deposit ATO/Ag multilayer films by radiofrequency (RF) sputtering of ATO and direct current (DC) sputtering of Ag on

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PEN substrates. These multilayer films had the highest conductivity yet reported in the literature, while retaining transmittance values acceptable for optoelectronic applications. We investigated the conduction mechanism and optical properties of the multilayer films deposited at various thicknesses of Ag layers. The role of substrate temperature on the structural, electrical and transmission properties of the films are also investigated.

2. Experimental

First, Ag thin films were deposited onto PEN substrates using a metal Ag target by DC magnetron sputtering. Then, ATO thin films were directly deposited on the Ag layer using a Sb-doped SnO_2 ceramic target by RF magnetron sputtering. Bulk Sb-doped SnO_2 ceramic targets were prepared using a solid-state reaction method from SnO_2 powder (99.5% purity) and Sb_2O_3 powder (99.9% purity). The powders were pressed to form pellets with a molar mixture ratio of Sb_2O_3:$SnO_2 = 0.1$:0.8, which were sintered at 1400 °C for 5 h in air. The Ag target was 99.99% pure. The targets were 5.0 cm in diameter and 0.4 cm thick. The PEN substrates were ultrasonically cleaned in acetone for 30 min, rinsed in absolute ethyl alcohol and subsequently dried before the deposition. The base pressure of the sputter system before each deposition was approximately 3×10^{-4} Pa. An ATO layer was deposited by RF magnetron sputtering at 50 W, at a deposition rate of about 12.5 nm min^{-1}. The ATO layer was approximately 40 nm thick. High-purity (99.999%) Ar and O_2 were introduced through separate mass flow controllers. The total pressure during sputtering was maintained at 0.5 Pa, and the Ar/O_2 ratio was 14:1. The Ag layer was deposited by DC magnetron sputtering at 40 W, using a deposition rate 1 nm s^{-1}, at a pressure of 0.5 Pa in a pure Ar atmosphere. There was no break in the vacuum at any stage during the preparation of the films. The thickness of the Ag layer was varied between 3 and 13 nm and that of the substrate temperature was varied between room temperature and 200 °C. The thickness of the ATO and Ag layers was estimated based on the deposition time and deposition rate. The substrate temperature was measured using a thermocouple gauge and a hot cathode gauge. The variation of substrate temperature during deposition was maintained within ±1 °C.

X-ray diffraction (XRD) patterns were collected on a DX-2500 diffractometer with Cu K_α radiation ($\lambda =$ 1.5418 Å). The surface morphologies were investigated by scanning electron microscopy (JEOL JSM-7600F, Akishima, Tokyo, Japan). Hall measurements by the van der Pauw technique were done using an Ecopia HMS 3000. The four-point probe technique was used for sheet resistance measurements. Optical transmittance spectra and absorption spectra were obtained on an ultraviolet–visible–near infrared (UV–Vis-NIR) spectrophotometer (Varian Cary 5000) in the wavelength range 300–800 nm.

3. Results and discussions

3.1. Effect of the Ag layer thickness on the properties of ATO/Ag multilayer films

3.1.1. Optical properties

Fig. 1 shows the transmission spectra in the wavelength range 300–800 nm for the ATO/Ag multilayer films on PEN substrate with different Ag film thicknesses deposited at room temperature (~25 °C). The average optical transmittance T_{av} can be computed as follows:

$$T_{av} = \frac{\int V(\lambda)T(\lambda)d\lambda}{\int V(\lambda)d\lambda}, \quad (1)$$

where $T(\lambda)$ is the transmittance and $V(\lambda)$ is the standard photopic luminous efficiency function [21]. As can be seen, the optical transmittance of ATO thin film without any Ag layer is above 90% in the visible wavelength range (400–800 nm). After insertion of the 3 nm Ag layer, the transmittance of the multilayer films drops to 81%, and then increases slightly to 84% as the Ag layer thickness increases from 3 to 7 nm, and noticeably decreases to 65% with a further increase in Ag layer thickness to 13 nm. The initial increase in transmission spectra is attributed to a decrease in the scattering of the aggregated Ag islands. When the Ag layer thickness is thin (<7 nm), the Ag islands are discontinuous, and the low transmittance is attributed to light scattering at the ATO/Ag interface in isolated islands of Ag. However, increasing Ag thickness leads to an improvement in the transmittance because the near-continuous Ag layer has lower scattering loss. As the Ag layer thickness increases further, the Ag layer becomes continuous, resulting in an increase in its plasmon absorption and reflectivity [22], and therefore, the transmittance decreases.

The change in photon energy ($h\nu$) and optical absorption coefficient (α) for the ATO/Ag multilayer films with different Ag film thicknesses deposited at room tempera-

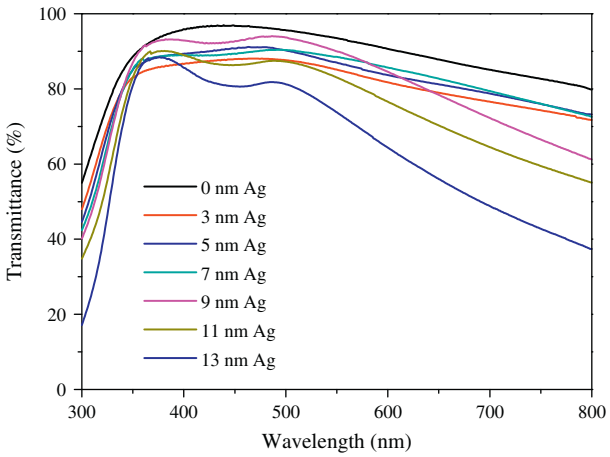

Fig. 1. Optical transmittance spectra of ATO/Ag multilayer films deposited at room temperature (~25 °C) as a function of Ag layer thickness.