Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Spectroscopic ellipsometry characterization of ZnO:Sn thin films with various Sn composition deposited by remote-plasma reactive sputtering

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ARTICLE INFO

Article history:
Received 29 July 2016
Received in revised form 19 October 2016
Accepted 25 October 2016
Available online xxx

Keywords:
Spectroscopic ellipsometry
Remote-plasma reactive sputtering
ZnO:Sn
Optical properties

ABSTRACT

ZnO:Sn thin films were deposited onto thermally oxidized silicon substrates using a remote plasma reactive sputtering. Their optical constants (refractive index n and extinction coefficient k) were determined from ellipsometric data recorded over a wide spectral range (0.05–6 eV). Parametrization of ZnO:Sn complex dielectric permittivity consists of a parameterized semiconductor oscillator function describing the short wavelength absorption edge, a Drude oscillator describing free carrier absorption in near-infrared part of spectra and a Lorentz oscillator describing the long wavelength absorption edge and intra-band absorption in the ultra-violet part of the spectra. Using a Mott-Davis model, the increase in local disorder with increasing Sn doping is quantified from the short wavelength absorption edge onset. Using the Wemple-DiDomenico single oscillator model for the transparent part of the optical constants spectra, an increase in the centroid distance of the valence and conduction bands with increasing Sn doping is shown and only slight increase in intensity of the inter-band optical transition due to Sn doping occurs. The Drude model applied in the near-infrared part of the spectra revealed the free carrier concentration and mobility of ZnO:Sn. Results show that the range of transparency of prepared ZnO:Sn layers is not dramatically affected by Sn doping whereas electrical conductivity could be controlled by Sn doping. Refractive index in the transparent part is comparable with amorphous Indium Gallium Zinc Oxide allowing utilization of prepared ZnO:Sn layers as an indium-free alternative.

1. Introduction

Transparent conductive oxides (TCOs), which are derived from wide band-gap semiconductors with low resistivity and high transparency in the visible spectrum, have been used in flat panel displays for many decades. The most widely used material is indium tin oxide (ITO) [1]. However, due to the concerns over the shortage of supply and high cost of indium, aluminium- or gallium- doped zinc oxides (AZO or GZO) have been intensively investigated as alternatives to ITO. Both the electrical and optical properties of these materials have been reported. In particular, spectroscopic ellipsometry has been widely used to investigate the dielectric functions of ZnO in a broad spectral range [2–6].

Amorphous oxide semiconductors (AOSs) such as doped ZnO are also used as channel layers in thin film transistors (TFTs). The requirement for this is different from TCOs. A resistive film with a well-controlled carrier concentration, high carrier mobility and preferably amorphous microstructure for better uniformity over large area are required. Various multi-component AOSs have been incorporated in TFTs [7], and the leading material, amorphous indium gallium zinc oxide (a-IGZO) has been demonstrated in displays [8]. Amorphous zinc tin oxide (a-ZTO) is an important indium-free alternative to the a-IGZO, and TFTs incorporating this material show high carrier mobility [9]. While the electrical properties of these materials have been well investigated, there are fewer reports on their optical properties [10–12].

Ellipsometric studies on high quality, single crystalline ZnO that have been epitaxially grown on sapphire substrates have shown

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http://dx.doi.org/10.1016/j.apsusc.2016.10.169

that the band edge transition occurs at 3.3 eV [5] and that the surface roughness needs to be accounted for to achieve the best fitting of the measured data [3]. A shift in the absorption edge has also been reported when ZnO is doped with either aluminum or gallium in TCOs [4]. Similarly, AZO deposited by direct current magnetron sputtering shows an increase in the optical bandgap with the efficiency of aluminum doping in the film [13]. A Tauc-Lorentz model with a Lorentz-type oscillator is applied on the optical absorption spectra of crystalline (c-IGZO) and a-IGZO, which is further divided into high or low quality films depending on their Hall mobilities [10]. While an optical transition ~3.7 eV is determined for all the films, significant differences in the dielectric functions are observed which are attributed to the cation content, the crystallinity and the quality of the films [10].

In this paper, spectroscopic ellipsometry was used to study the optical properties of ZnO:Sn with various tin doping produced by remote-plasma reactive sputtering. The effect of tin doping on the complex dielectric functions of the ZTO are investigated over a broad spectral range from 0.05 to 6 eV. In the vicinity of the absorption edge ($3.0 < E < 4.0$ eV) a Mott-Davis model, in the semi-transparent spectrum ($0.5 < E < 2.5$ eV) a Wemple-DiDomenico single oscillator dispersion, and in the mid-infra-red (MIR) ($0.2 < E < 0.5$ eV) a Drude model were employed as this analysis provide physical meaning of the extracted parameters.

2. Experimental details

ZnO:Sn thin films were deposited onto thermally oxidized silicon substrates using a remote plasma reactive sputtering without intentional substrate heating. Zinc: tin metal alloy targets with tin compositions of 10, 33 and 50 atomic% were used. For reference, undoped ZnO were also deposited from a 100% zinc targets using the same sputtering conditions. The details of the system and the deposition conditions can be found elsewhere [14], and are simply summarized here. Films were deposited for times between 10 and 15 min with an optimized flow of argon and oxygen (60 sccm and 35 sccm respectively) at a pressure $\sim 6 \times 10^{-3}$ mbar during sputtering. The deposited films were highly resistive which are suitable as channel layers in TFTs [14]. Moreover, it has been confirmed that the as-deposited ZnO:Sn thin films are amorphous while the as-deposited ZnO thin film is polycrystalline [14].

Chemical compositions were determined using energy dispersive X-ray spectroscopy (EDS) (Aztec X-Max 20, Oxford Instruments) attached to the scanning electron microscope (LYRA 3, Tescan) where each sample was analyzed at two spots (100×100 μm size) and the data were averaged. The ratio of tin compositions in the ZnO:Sn films were determined to be ~33, 50 and 65 atomic%. Therefore, the undoped ZnO and doped ZnO samples are denoted as ZT0, ZT33, ZT50 and ZT65. No post-deposition annealing had been performed. Surface topography was also studied using atomic force microscopy (Solver NEXT, NT-MDT). Two measurements (spot size 10×10 μm) were performed on each sample and the average root mean square (RMS) of the surface roughness was determined according to the ISO 4287/1.

Optical characterizations were performed using two variable angle spectroscopic ellipsometers (VASE and IR-VASE, J. A. Woollam Co.). The first, rotating analyzer ellipsometer, operates in the spectral range 190 nm–1700 nm (ultra-violet (UV)–vis (VIS)-near-infrared (NIR)). Measurements with 30 analyzer revolutions with photon energy steps of 0.05 eV at three selected angles of incidence (AOI) at 50°, 60° and 70° were performed for each sample. The second, rotating compensator ellipsometer, covers the spectral range 1.7 μm–22 μm (NIR-MIR). Spectra for AOI of 50°, 60° and 70° were recorded (measuring 25 scans, 15 spectra per revolution, with wavenumber steps 8 cm^{-1}). Near normal incidence optical reflectance was measured by the same instruments. WVASE32 software was used for modeling of the measured data.

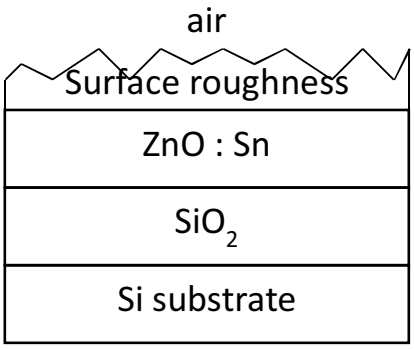

Fig. 1. Sketch of the optical model used to fit the ellipsometry data.

3. Results and discussion

3.1. Structure model and material optical constants

As shown in Fig. 1, a sample model used to analyze the raw ellipsometry data consists of i) a semi-infinite crystalline silicon substrate, ii) a SiO_2 layer, iii) a homogenous, isotropic layer representing the ZnO:Sn layer, iv) surface roughness and v) air as the ambient medium.

Optical constants of Si and SiO_2 in the NIR-VIS-UV ranges were taken from the literature [15]. Optical constants of Si and SiO_2 layer in the MIR part of spectra was obtained by measurement of an uncoated SiO_2/Si substrate.

In the literature different models describing mostly the transparent part of the spectra for ZnO, such as Cauchy or Sellmeier have been reported [16]. Mammadov et al. have applied the parameterized semiconductor oscillator function (PSEMI) model for describing the dielectric function of ZnO over a wide spectral range [6]. The PSEMI model analytically describes the dielectric functions as the summation of several energy-bounded Gaussian-broadened polynomials and poles accounting for index effects due to absorption occurring outside the region being modeled [17–19].

In this work, the model dielectric function used for the ZnO:Sn layer consists of several contributions:

$$\tilde{\varepsilon} = \tilde{\varepsilon}_{PSEMI} + \sum \tilde{\varepsilon}_{Lorentz} + \tilde{\varepsilon}_{Drude} \quad (1)$$

The above mentioned PSEMI oscillator functions sufficiently describes the short wavelength absorption edge of amorphous doped ZnO:Sn samples and polycrystalline undoped ZnO samples as well. In addition, a Lorentz oscillator is further applied to model inter band transitions in the UV [20]. In the MIR region ($0.05 < E < 0.5$ eV), Lorentz oscillator functions are used to model the long wavelength absorption edge and a Drude oscillator to model free carrier absorption [21]. Surface roughness is modeled by a Bruggeman type effective medium approximation [22] with 50% of voids and 50% of ZnO:Sn.

3.2. Figure of merit and quality of the fit

The measured spectroscopic ellipsometry parameters, ψ^{exp} and Δ^{exp}, are fitted against the designed model in the spectral range

Please cite this article in press as: P. Janicek, et al., Spectroscopic ellipsometry characterization of ZnO:Sn thin films with various Sn composition deposited by remote-plasma reactive sputtering, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2016.10.169