Solar Energy Materials & Solar Cells 92 (2008) 938–941

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

ITO/metal/ITO multilayer structures based on Ag and Cu metal films for high-performance transparent electrodes

C. Guillén *, J. Herrero

Departamento de Energía (Edif. 42), CIEMAT, Avda. Complutense 22, Madrid 28040, Spain

ARTICLE INFO

Article history:
Received 22 February 2008
Accepted 26 February 2008
Available online 14 April 2008

Keywords:
Transparent conductive oxide
Metal
Multilayer
Optical properties
Electrical resistivity

ABSTRACT

Transparent conductive indium tin oxide (ITO)/metal/ITO multilayer electrodes have been prepared by sputtering at room temperature. Ag and Cu thin films with thickness ranging from 5 to 35 nm have been used as intermediate metal layer, between ITO coatings of about 30 nm thickness. Evolution of the optical and electrical characteristics of the multilayers as a function of each metal film thickness has been analyzed. High-quality transparent electrodes have been obtained, with sheet resistance below 6 Ω/sq for Ag film thickness above 10 nm or Cu film thickness above 16 nm. These multilayers also showed high transmittance in the visible spectral range, above 90% by discounting the glass substrate, with a maximum that is located at lower wavelength for Ag-based electrodes than for the Cu-based ones. After heating at 350 °C in flowing nitrogen, some improvement in the optoelectronical characteristics of the multilayer electrodes has been achieved that is related to the structural improvement of the ITO components.

1. Introduction

Indium tin oxide (ITO) thin films have shown low electrical resistance and high transmittance in the visible range of the spectrum; and so are widely used as transparent conductive electrodes in flat panel displays, electrochromic devices or photovoltaic solar cells [1–3]. High-quality ITO layers are commonly obtained by annealing at high temperature (>300 °C) during or after the deposition process, because heating promotes material crystallization and reduces the crystalline structure defects, allowing to achieve more transparent and conductive films [4–7]. In these conditions, ITO electrical resistivity as low as $2–3\times10^{-4}\,\Omega$cm and optical transmittance in the visible wavelength range above 90% have been reported for typical thickness around 300 nm [4–6]. Nevertheless such resistivity is rather high in some cases for improved practical applications, and methods to enhance the conductivity of transparent electrodes are being investigated in order to accommodate the increasing technological demand for large area devices with improved performance. In this sense, inclusion of a thin metal film in combination with ITO or other metal oxides has been shown effective to obtain transparent and conductive electrodes more adjusted to the required specifications [8–11]. Ag is the first choice because has the lowest resistivity of all metals, and Cu has an only slightly higher value, that in both cases are below $2\times10^{-6}\,\Omega$cm for the bulk materials [12]. However, it should be taken into account that optical and electrical properties of very thin metal films, as are required to keep high visible transmittance, depend considerably on the film thickness and other specific deposition conditions [13–16].

In this work, ITO, Ag and Cu thin films have been deposited onto conventional soda-lime glass (SLG) substrates by sputtering at room temperature. Structural, optical and electrical characteristics of metal/ITO/SLG and ITO/metal/ITO/SLG samples have been analyzed as a function of the metal film thickness. Effect of post-deposition heating in nitrogen at 350 °C has also been investigated. The objective is to determine the interdependence between optical and electrical parameters for each metal-based multilayer system in order to achieve high-performance transparent and conductive electrodes.

2. Experimental details

Electrodes based on metal/ITO and ITO/metal/ITO thin films have been prepared onto 2-mm-thick SLG substrates by means of an in-line sputtering system. The system has a ceramic ITO target of In_2O_3/SnO_2 (90/10 wt%), metallic Ag and Cu targets (99.99% purity) and a carrier for the substrates which can be moved in front of the targets with a speed up to 10 cm/min. Sputtering process has been performed at room temperature in argon atmosphere, that is adjusted during ITO and metal deposition

* Corresponding author. Tel.: +34 91 346 6669; fax: +34 91 346 6037.
E-mail address: c.guillen@ciemat.es (C. Guillén).

0927-0248/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2008.02.038

with varying sputtering parameters such as substrate speed or deposition time and sputtering power. By means of these parameters, the thickness of the ITO layers has been adjusted around 30 nm and the thickness of the metal layer has been extended from 5 to 35 nm, as was verified by subsequent profilometric measurements. Post-deposition annealing of the samples was carried out in a tubular furnace at 350 °C, 15 min, in flowing nitrogen.

Optical measurements were done with unpolarized light at normal incidence in the wavelength range from 300 to 1500 nm, with a double-beam spectrophotometer Perkin-Elmer Lambda 9. Electrical sheet resistance of the coatings was determined from the four-point probe method. Crystalline structure of the as-grown and annealed samples was analyzed by X-ray diffraction (XRD) by using the nickel-filtered Kα1 emission line of copper ($\lambda = 1.5405$ Å) in a Philips X'pert instrument.

3. Results and discussion

Optical transmittance spectra and sheet resistance values of metal/ITO electrodes on SLG substrates have been measured as a function of the metal film thickness and are represented in Figs. 1 and 2 for Ag and Cu layers, respectively. Minimum metal thickness that enables to decrease the sheet resistance with respect to that of the ITO single layer is found to be 8 nm for both Ag and Cu films in the present experimental conditions. For metal film thickness increasing beyond 8 nm, sheet resistance decreases sharply and transmittance becomes lower in the near infrared, but transmission remains above 50% in the visible spectral region for a wide range of metal thicknesses. Maximum transmittance is observed around 600 nm, and extends towards lower wavelengths for the Ag than for the Cu layers. Metal resistivity calculated from the sheet resistance and film thickness values is found decreasing with increasing thickness, as expected for such very thin films. When the metal film thickness grows from 8 to 20 nm, resistivity decreases from 21 to 4 $\mu\Omega$ cm for the Ag layers and from 24 to 8 $\mu\Omega$ cm for the Cu ones. These resistivity values are according to those reported for other Ag and Cu layers within analogous thickness ranges [13–15], where it has been established that specific resistivity is strongly dependent on the deposition conditions. Although thin film resistivity tends to decrease for increasing layer thicknesses, usually remains above that corresponding to the bulk material, owing to the particular characteristics of metallic nanofilms [17,18].

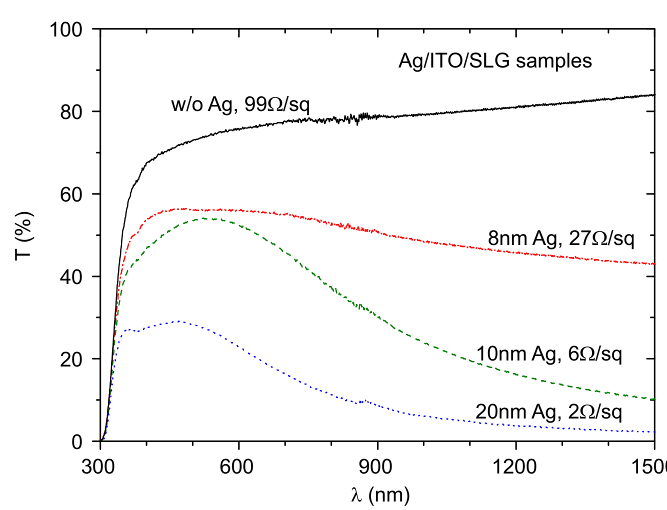

Fig. 1. Transmittance spectrum and sheet resistance value for Ag/ITO/SLG samples with various silver film thicknesses.

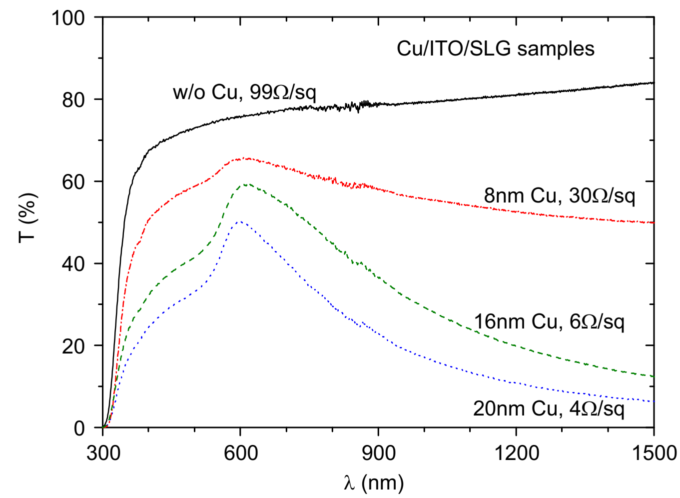

Fig. 2. Transmittance spectrum and sheet resistance value for Cu/ITO/SLG samples with various copper film thicknesses.

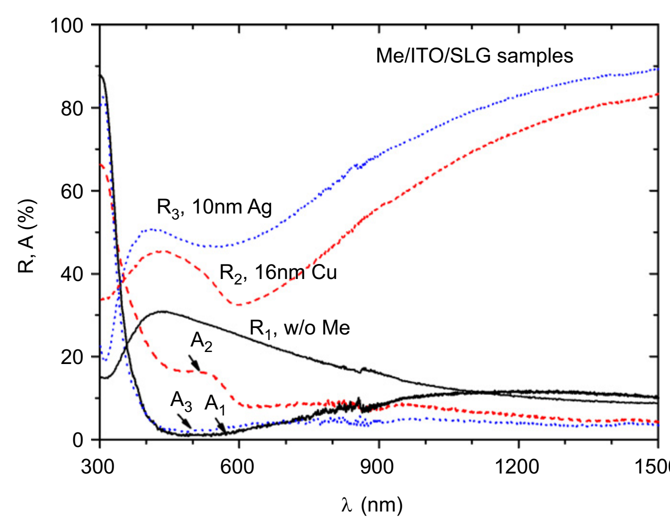

Fig. 3. Reflectance and absorbance spectra for metal/ITO/SLG samples before and after coating with Cu or Ag metal film.

Reflectance and absorbance spectra have also been analyzed for the different metal/ITO/SLG samples, and the main data obtained before and after coating with Cu or Ag metal films are compared in Fig. 3. Absorbance spectrum of the ITO/SLG before metal deposition shows the characteristic band absorption edge in the ultraviolet spectral region at a wavelength around 335 nm corresponding to the ITO band gap energy of ~3.7 eV [19,20]. For these ITO layers, electron density is in the range of 10^{20}–10^{21} cm^{-3} [7,20] and the plasma absorption wavelength lies in the infrared spectrum at wavelengths above 1200 nm [21]. Thus, no significant absorption is detected for the ITO/SLG sample in the visible spectral region. Fig. 3 shows that no additional absorption occurs in the visible range after Ag film deposition, but some absorption increment around 500 nm wavelengths is observed for Cu thin film. In general, metals have high electron densities in the 10^{22}–10^{23} cm^{-3} order, which correspond to plasma absorption in the 100–400 nm wavelength region [22]. However, it should be taken into account that specific values for metallic nanofilms can differ from those of the bulk material [23]. Thus, optical