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Highly transparent and conducting ITO/Ag/ITO multilayer thin films on FEP substrates for flexible electronics applications

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ABSTRACT

Transparent and conducting ITO/Ag/ITO (IAI) multilayer coatings were deposited on glass and flexible fluorinated ethylene propylene (FEP) substrates by reactive sputtering using metallic In:Sn (90%:10%) and Ag targets at room temperature. Middle Ag layer thickness was optimized to obtain maximum figure of merit (ϕ) and the optimum Ag layer thickness was found to be ~13 nm. The optimized IAI multilayer on glass substrate showed transmittance of ~88.6% and sheet resistance of ~7.1 Ω/sq. The transmittance increased to ~91.4% for the IAI multilayer deposited on one side etched glass. The optimized IAI multilayer coating was also deposited on flexible FEP substrates. The electrical, optical, structural and morphological properties of IAI deposited on glass and FEP substrates were compared. IAI deposited on FEP substrate showed transmittance of ~90.2% at λ = 550 nm, sheet resistance of ~6.9 Ω/sq. and figure of merit of $\sim 52 \times 10^{-3}\,\Omega^{-1}$. Bending test of IAI deposited FEP proved the high flexibility of IAI multilayer for the flexible transparent electrode applications. Solar selectivity study of IAI on FEP substrate showed it can effectively reflect the higher wavelength region of solar spectrum and can be used as a flexible solar spectrum segregator. Optical haze measurements of IAI coated glass and FEP show that high haze value can be achieved by increasing the roughness on non-coated side of the FEP substrate.

1. Introduction

Transparent conductor is one of the key materials for high performing devices in energy (smart windows, transparent heat mirror, solar cells, etc.), information (display, OLED, etc.), and automobile sectors [1]. Recent research is being directed towards flexible solar cells, OLEDs, displays, and wearable electronics, etc. [2–4]. The light weight, low cost, easy for storing and transport makes flexible devices more adapted to day to day life. But two mutually opposing properties like optical transparency and electrical conductance combining in one material is the most challenging task for making these transparent conducting devices. Materials such as indium tin oxide (ITO), fluorine doped tin oxide (FTO), aluminium zinc oxide (AZO), silver nano-wires, carbon nanotubes, graphene, graphene oxide, metal networks, etc. are the important materials in this area of research [1,5]. However, ITO is one of the most successful transparent conducting materials, which is widely used in commercially available devices because of its very low sheet resistance (~10 Ω/sq.), high optical transmittance (> 90%) and large area uniformity. However, due to the brittle nature of ITO films it has limitation in high performing flexible electronic devices because cracks can develop during the bending which increase the electrical resistance and hence the performance of the device will come down [2,4]. Moreover, low sheet resistant ITO film requires high processing temperature (> 300 °C), which is not favorable for many plastic substrates with low melting temperature [6]. Even though extensive research is being carried out on silver, carbon and metal network based transparent electrodes, they could not come over the hurdles like low processing temperature, uniform sheet resistance, high transmittance and mass production.

Many researchers have reported ITO-metal-ITO (IMI) multilayer as an effective alternate for single ITO electrode. The middle ductile metal layer can improve the flexibility of ITO film. Moreover, very low sheet resistance (< 10 Ω/sq.) can be achieved for IMI coating deposited even at room temperature with almost same transmittance of ITO film [2]. Ag, Au, Cu, Al, etc. were used as the intermediate metallic layers by different researchers [6–8]. However, Ag is found to be the best

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candidate for this application due to its lowest absorption coefficient and lowest refractive index (n ~ 0.05-i2.90) in the visible region of the solar spectrum [9]. Many researchers have studied the electrical, optical and mechanical (flexible) properties of ITO/Ag/ITO (IAI) multilayer as a transparent electrode in applications such as solar cells, displays, OLEDs, electrochromic devices, etc. [3,4,6,7,10,11]. IAI multilayer is also used as a solar spectrum splitter in hybrid solar energy conversion system and as heat mirror in energy efficient windows because of its high transmittance in the visible region and high reflection in the NIR and IR regions [12,13]. In our previous work we described the optical properties of IAI coating and optimized the layer thicknesses on glass substrate for getting maximum efficiency for hybrid solar cell application [13]. We have reported that nano-meter range difference in the thicknesses of ITO and Ag layers can drastically alter the optical properties of IAI multilayer system.

In the present work we report the electrical and optical properties of reactive sputtered IAI multilayer on rigid glass and flexible fluorinated ethylene propylene (FEP) substrates. FEP is a commercially available flexible transparent film. FEP shows very good mechanical and thermal insulating properties. FEP is used in many applications such as thermal control in satellite, solar mirrors, cover plate for the solar cells, as a capillary material in biological applications, etc. [14–17]. It has been reported that FEP substrates have very good durability for solar radiation. Even after the exposure of 1 sun solar radiation for 27 years there was no much change in the optical properties of FEP substrate [14,15]. However, there are no data available for the IAI transparent electrode coated FEP substrate in the literature. Substrates like highly transparent and flexible FEP with good chemical stability and mechanical properties can be useful in many flexible electronic applications in future. Therefore, the study of highly transparent and conducting IAI coated FEP substrate will have great potential for the future optoelectronic devices.

2. Experimental details

Transparent and conducting IAI multilayer was deposited on glass and FEP substrates by a multi-target balanced DC magnetron sputtering system. Borosilicate glass (n ~ 1.53) of thickness 1 mm and FEP film (n ~ 1.34) of thickness 127 µm were used as the substrates. Prior to the deposition, the glass substrate was cleaned with acetone and iso-propylene alcohol (IPA) in ultrasonic agitator and blown dried with nitrogen gas. FEP was cleaned in IPA and dried with nitrogen gas. After loading glass or FEP substrate into the chamber, ultimate vacuum of 5.0×10^{-4} Pa was created by using a turbomolecular pump, backed with a rotary pump. Bottom and top ITO layers were reactively sputtered using a metal alloy In:Sn (90%:10%) target of purity 99.99% in oxygen and argon atmosphere at 60 W pulsed DC power (frequency = 100 kHz and pulse width = 2976 ns). Flow rates of argon and oxygen gases were controlled by mass flow controllers. Without breaking vacuum, the middle Ag layer, was deposited on top of the ITO layer using an Ag metal target (purity 99.99%) in argon environment at 5 W DC power. On top of the Ag layer final ITO layer was deposited at identical conditions that of the bottom ITO layer. ITO and Ag layer thicknesses were optimized on glass substrate for optimum optical transmittance and sheet resistance to achieve maximum figure of merit. Hereafter, the optimized ITO and Ag layers were deposited on FEP substrate. All the depositions, even on the glass substrates, were carried out at room temperature. To enhance the optical transmittance of IAI multilayer, the transmittance was enhanced by etching one side of the glass substrate. IAI multilayer was deposited on non-etched side of the glass substrate. Etching of the glass substrate was done using hydrogen fluoride (HF) vapours. Details of the HF vapour phase etching process can be found elsewhere [18]. IAI multilayer was also deposited on one side plasma etched FEP substrate to study the effect of etching on the optical and haze properties of multilayer system. FEP etching was carried out using a plasma etching instrument, Plasma Matrix (BDISCOM) at RF power 100 W in argon atmosphere at room temperature. Etching was done for different durations to increase the roughness of FEP substrate.

Total, specular and diffuse optical transmittance, and haze of the IAI multilayer on glass and FEP substrates were measured using UV/Vis/NIR spectrophotometer (PerkinElmer, Lambda 950). Haze measurement was carried out as per the ASTM 1003-92 standard, using an integrating sphere attached with the spectrophotometer [19]. Sheet resistance of IAI multilayer on both glass and FEP substrate was measured using four point probe setup (JANDEL, Model- RM 3000). The crystal structure of IAI multilayer was investigated by X-ray diffractometer (XRD, Bruker- D8 Advance) with a Cu K_α source (λ = 0.15406 nm) in thin film mode. The surface morphology of IAI multilayer was investigated using field emission electron microscopy (FESEM, Supra 40 VP Carl Zeiss) and atomic force microscopy (AFM, Bruker). Roughness of IAI coatings and substrates was obtained from AFM.

3. Results and discussion

3.1. Optimization of ITO/Ag/ITO on glass substrate (IAI/Glass)

To obtain high transmittance and low resistance usually thick ITO film needs to be deposited at an elevated temperature of 250 °C with post annealing > 300 °C. But, when a thin Ag layer is inserted between two thin ITO layers, high optical transmittance similar to that of ITO along with very low sheet resistance (lesser than that of ITO) can be achieved. The high transmittance of IAI multilayer in the visible region is due to the antireflection effect from the two finite thickness dielectric layers which cancel the reflection from the Ag layer [13]. Solar spectrum transmittance and reflectance of the IAI multilayer can be adapted by carefully varying the thicknesses of ITO and Ag layers. Nanometer range changes in the thicknesses of Ag and ITO layers significantly affect the optical properties of IAI coating. However, for the applications like transparent conductors, along with optical transmittance, the sheet resistance is also an important factor to be considered. So the highest optical transmittance has to be achieved with the lowest electrical resistance.

Fig. 1(a) shows the total transmittance of IAI/Glass of different Ag layer thicknesses and Fig. 1(b) shows the transmittance at λ = 550 nm ($T_{550\ nm}$) and average transmittance ($T_{avg.}$) in the visible region of the solar spectrum (calculated for wavelength range from 400 to 800 nm) as a function of Ag layer thickness. We can observe from the figure that at the lowest thickness of Ag layer (i.e, ~5 nm) the transmittance was low. Many previous studies have reported that at lower thickness Ag layer shows island like structure (Volmer-Weber growth mode) instead of continuous film, which affects the optical and electrical properties of multilayer adversely [19]. While increasing the thickness of Ag layer, transmittance increased. Maximum transmittance of ~88.6% at λ = 550 nm was achieved when the Ag layer thickness was ~13 nm, and after that, the transmittance started to decline. At the same time average transmittance was maximum (~83%) when Ag layer thickness was 9 nm; then it started to decrease.

The sheet resistance of IAI multilayer mainly depends on the sheet resistance of middle Ag layer when it is beyond the critical thickness needed for a continuous film [20–22]. Fig. 2(a) shows the measured sheet resistance and resistivity of IAI multilayer as a function of Ag layer thickness. When the Ag layer thickness is too low (i.e., ~5 nm) the sheet resistance and resistivity were on the higher side (~42.9 Ω/sq. and $\sim5.37\times10^{-4}$ Ω-cm, respectively), while increasing the Ag layer thickness both were decreased. Jeong and Kim (2009) have reported that, at lower thickness, the agglomerated island like growth of Ag films will not provide conducting path for electrons and the resistance will be high for IAI multilayer structure [22]. Lowest sheet resistance ~4.8 Ω/sq. and resistivity $\sim7.0\times10^{-5}$ Ω-cm were achieved when the Ag layer thickness was ~25 nm.

If we consider each layer in IAI structure as a parallel connection of