Solar Energy Materials & Solar Cells 128 (2014) 264–269

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Investigations on reduced graphene oxide film embedded with silver nanowire as a transparent conducting electrode

P. Meenakshi *, R. Karthick, M. Selvaraj, S. Ramu

CSIR – Network Institute of Solar Energy, CSIR – Central Electrochemical Research Institute, Karaikudi, India

ARTICLE INFO

Article history:
Received 25 January 2014
Received in revised form
7 May 2014
Accepted 9 May 2014
Available online 6 June 2014

Keywords:
Silver nanowire
Reduced graphene oxide
transparent conducting electrode
Dip-coating
Solution processable

ABSTRACT

A simple and effective transparent conducting electrodes (TCEs) based on reduced graphene oxide film embedded with silver nanowire- (AgNW-rGO) was developed. The AgNW-rGO hybrid electrode was fabricated by using a simple and scalable dip-coating method. This solution processed TCEs showed high electrical conductivity when compared with pristine AgNW. AgNW-rGO TCEs also exhibited better stability than the pristine AgNW film when exposed to the ambient atmosphere. The electrical conductivity is found to increase by 4-fold with increase in the number of dipping cycles of AgNW after coating the graphene oxide (GO). This increase in the observed conductivity is attributed to the gas-barrier property of GO. AgNW/rGO TCEs exhibited a sheet resistance of 27 Ω/□ with transparency = 72% at 550 nm.

1. Introduction

Transparent conducting electrodes (TCEs) are basic components for many optoelectronic devices such as liquid crystal displays [1], touch screens [2], plasma displays, Organic light emitting diodes (OLEDs) [3]and solar cells[4,5]. Tin doped indium oxide (ITO) has been widely used as a TCE due to its high transmittance ($T > 90\%$) and low sheet resistance ($R_s \sim 20\ \Omega/\square$). Although ITO has a wide range of applications as transparent conducting electrodes, it involves preparation by expensive physical vapour deposition and also fragile and prone to corrosion attack. Moreover, indium is a scarce and expensive resource. Therefore, alternatives to ITO are under continuous research. Such alternatives include carbon nanotubes (CNTs) [6–11], graphene-based materials [12–14], conducting polymers [15–20] and metal nanostructures [21–25]. Because of the high room temperature conductivity, metal nanostructures hold much promise as substitute for ITO. CNTs show high sheet resistance values of 150 Ω/□ for 80% transmittance (due to tube-tube contact resistance) [26] whereas graphene, prepared by expensive chemical vapour deposition shows 30 Ω/□ (Rs) at 90% transmittance [27]. To achieve high optical transparency and low sheet resistance values, metal-based nanostructures have to be used. Bulk metals cannot act as transparent electrodes due to their high reflection in the visible region. Optical transparency in metals can be achieved by decreasing their thickness to the nanometres range. In recent years, silver nanowires (AgNWs) are increasingly being used as transparent electrodes in optoelectronic devices. Although AgNWs match ITO in several key properties, a major drawback is the oxidation of silver. The resulting silver oxide increases the sheet resistance value due to junction–junction resistance between the nanowires. The success of AgNW transparent conducting electrode lies in overcoming the above problem. Two-dimensional carbon materials such as graphene and reduced graphene oxide (rGO) have been employed to circumvent the oxidation of AgNWs and to decrease NW–NW junction resistance of the AgNWs.

Among various methods for obtaining thin films of graphene (exfoliation, epitaxial growth, chemical vapour deposition) [28,29] and rGO, the solution process method reported hitherto has several advantages like low cost, ease of fabrication and large scale application. Many researchers adapt spin coating technique consuming lot of solution even for obtaining thin coating. In this study, AgNW/rGO TCE is developed through dip coating. Reduced graphene oxide serves as a protective top coat for the AgNW to prevent the oxide formation [30]. A reduction in the number of dipping cycles ensures consumption of a minimum amount of material and time.

2. Experimental

AgNWs were synthesised by polyol method and reported [31]. An ethylene glycol (EG) solution of 0.1 M polyvinylpyrrolidone (PVP) and 0.02 M sodium chloride (NaCl) were stirred thoroughly at 180 °C to obtain a homogeneous solution. To this solution, an EG

* Corresponding author. Tel.: +91 4565 227403; fax: +91 4565 227779.
E-mail address: meenachrist76@gmail.com (P. Meenakshi).

http://dx.doi.org/10.1016/j.solmat.2014.05.013
0927-0248/

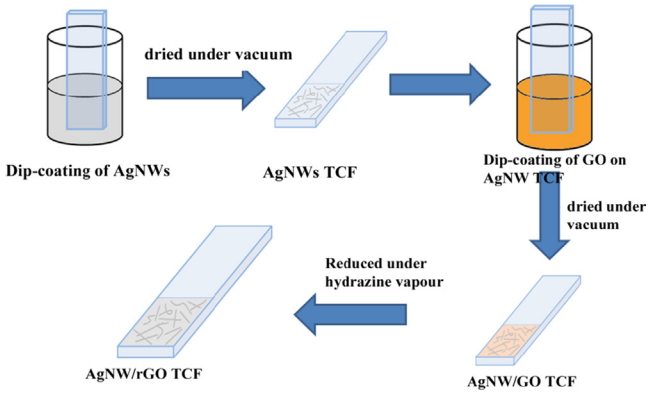

Fig. 1. The schematic representation of dip-coating of AgNW/rGO hybrid.

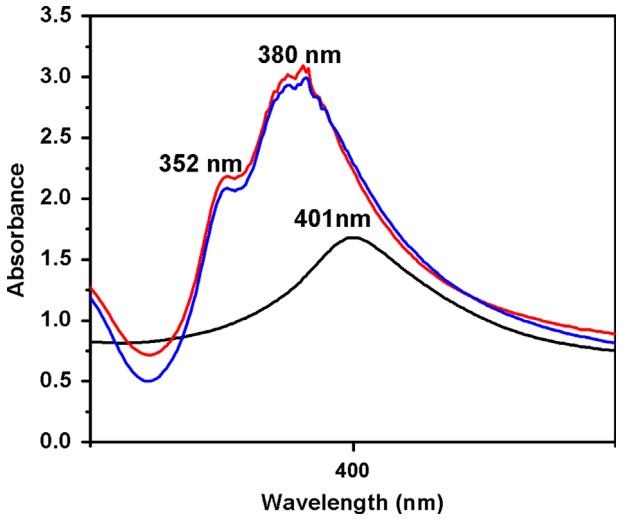

Fig. 2. UV–visible absorption peaks of silver nanoparticles and silver nanowires.

solution of 1 M $AgNO_3$ was added in drops till the colour of the reaction mixture became yellow, indicating the formation of silver nanoparticles. On stirring for 1 h, the reaction mixture turned grey due to the formation of AgNWs. The product was separated by centrifuging at 6000 rpm and subjected to repeated washing with acetone and milliporewater to remove excess PVP and EG. The purified product was stored in millipore water as dispersion. The graphene oxide (GO) was synthesised according to a modified Hummer's method [32]. The detailed description on synthesis of GO is given in supporting information S-1. Fig. 1 shows a schematic representation of simple dip-coating process for the fabrication of AgNW/rGO TCE. Prior to the dip-coating of AgNW, the surface of the glass slides were washed with detergent, distilled water and acetone to remove the impurities. The AgNW dispersion was dip-coated on the cleaned glass slides with low concentration of AgNWs (0.3 mg/ml) at varying dipping parameters (dipping speed=25 mm/min, lifting speed=75 mm/min, immersion time-=3 min, drying time=3 min). The AgNWs were coated by varying the number of dipping cycles. For simplicity, the dip-coated AgNW electrodes are referred to as "*N*-dip AgNW" where *N* denotes the number of dipping cycles. For example 5-dip AgNW means that the dipping of AgNW performed 5 times. After dipping, the AgNW film was dried at 100 °C to remove the solvent. Then the GO solution (0.2 mg/ml) was also dip-coated on the AgNW film at a dipping rate of 25 mm/min. The number of dipping cycles were kept constant for GO as 5. The GO over-coated film was also dried to remove the solvent. Then the AgNW/GO coated film was reduced under hydrazine vapours at 100 °C for 12 h.

The transmittance of the TCE was measured by UV–visible spectrometer and the sheet resistance of the AgNW/rGO conductive film was examined using four point probe technique. The surface morphology of AgNW/rGO was examined using Scanning electron microscope (SEM). The purity and the crystalline nature of AgNW were also studied using the X-ray diffraction (XRD) analysis. The high crystalline nature of AgNW and the microstructure of AgNW were also examined by transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM). The defects of rGO layer and over-coating of rGO layer on the AgNW film was studied by Laser-Raman spectroscopy.

3. Result and discussion

Fig. 2 shows a UV–visible spectrum of surface plasmon resonance (SPR) peaks at ~350 nm and ~380 nm and are assigned to the transverse SPR and longitudinal SPR of AgNWs. The silver nanowires were formed by the incorporation of silver nanoparticles [33]. Fig. S2 shows a SEM image depicting the step-wise growth of silver nanowires from silver nanoparticles. The SEM image of as synthesised AgNW shows a diameter of ~70 nm with a length of ~8 μm as evident from Fig. S2. The Figs. 3 and 4 show the sheet resistance and transmittance of AgNW/rGO TCE as a function of the number of dipping cycles of AgNW for constant rGO layer. Table 1shows the sheet resistance and transmittance values of AgNW and AgNW/rGO TCEs. The rGO layer shows a high sheet resistance, in the order of ~50 KΩ/□ and the single coated AgNW film shows a sheet resistance of ~1.2 KΩ/□. It is expected that a combination of conductive AgNWs with rGO layer can show a decrease in sheet resistance of AgNW/rGO TCE film due to the possibility of generating a strongly connected AgNW network which can act as an effective conducting path of AgNW/rGO TCE. Accordingly, the sheet resistance decreased from 305.2 Ω/□ to 27.3 Ω/□, which is ascribed to the increase in AgNW density and enhanced wire to wire contact with increasing number of dipping cycles. The stability of the TCE is also good as observed in Fig. 3. The sheet resistance value is constant for AgNW/rGO TCE whereas for AgNW TCE the sheet resistance value increased on exposing to the ambient atmosphere. This stability of AgNW/rGO is due to the over-coating of rGO layer on the AgNW film. This rGO layer covers the AgNW film from the atmospheric oxygen due to its gas-barrier property.

Fig. 5 shows that a figure of merit (FOM) value which is increasing with increase in the number of dipping cycles of AgNW. The FOM (σ_{DC}/σ_{Op}) is usually used to evaluate the performance of the transparent conductors, which depends both on the transmittance and sheet resistance of the film. The ratio of DC conductivity and optical conductivity (σ_{DC}/σ_{Op}) is calculated from the following equation [34]:

$$FOM = Z_o/2\,R_s(T^{-1/2}-1) \quad (1)$$

In this equation, Z_o is the impedance of the free space and has the value of 377 Ω, T is the transmittance and R_s is the sheet resistance. The FOM increases with increased AgNW density. The AgNW film shows a high FOM value of 34 while the AgNW/rGO film has a FOM value of 38. This slight increase in FOM value is attributed to the more intimate contact between the rGO layer and AgNWs as well as between the junctions in the AgNWs. Although the AgNW is more conductive than the rGO layer (high resistance), the hybrid film (AgNW/rGO) shows a high FOM value than the pristine AgNW. This increase in FOM is ascribed to the contact force exerted by the rGO layer on the AgNW to reduce the NW–NW junction resistance. In case of pristine AgNW film, the kind of intimate contact is not there owing to the presence of the quasi-3D stacking of the nanowires. But this quasi-3D stacking is almost