Fabrication of Graphene/Silver Nanowire Based Transparent Conductive Solar Cell Electrodes via LBL Deposition

B. Tuğba Camic[1,3,4], Faruk Oytun[2], Meltem Sezen[1], M. Hasan Aslan[3], Fevzihan Başarır[4]

[1]Sabanci University Nanotechnology Research and Application Center (SUNUM), Istanbul, Turkey
[2]Department of Chemistry, Istanbul Technical University, Istanbul, Turkey
[3]Department of Physics, Gebze Technical University, Kocaeli, Turkey
[4]Materials Institute, TUBITAK Marmara Research Center (MRC), Kocaeli, Turkey

Abstract

In this study, solution-processed transparent conductive electrodes were fabricated from graphene oxide (GO) and silver nanowires (Ag NWs) by means of layer-by-layer (LBL) deposition technique. Oppositely-charged GO and AgNWs were sequentially coated on a modified glass substrate via LBL deposition, which provided highly controllable thin films in terms of optical transmittance and sheet resistance. The resulting Graphene/Ag NWs multilayer film was characterized by a UV–Vis spectrometer and sheet resistance was measured using four-point probe system. The samples were then cross-sectioned and imaged at the high resolution using a Focused Ion Beam - Scanning Electron Microscope (FIB-SEM) dual-beam platform.

1. Introduction

Transparent conductive electrodes (TCE) have been widely used in photovoltaic and optoelectronic devices, such as solar cells, flat displays, touch panels and light emitting diodes [1,2]. Commonly, indium tin oxide (ITO) has been used as TCE due to its high optical transparency and low sheet resistance. However, it has several drawbacks including high material cost, need for complex processing and fragility under stress [2]. Therefore, new materials such as carbon nanotubes (CNT) [3], graphene (G) [3] and silver nanowires (AgNW) [4] have been considered as alternative materials to ITO. Among these, silver nanowires (AgNW) demonstrate have optical and electrical properties comparable to ITO. However, the mesh structure of AgNW film promotes the surface roughness, which in turn lead to shor-circuit of devices. Combinations of AgNW and graphene can be used effectively to overcome these problems [5].

In this study, G/Ag NWs hybrid transparent electrodes were prepared as an ITO alternative. 2- and 3-bilayer G/Ag NWs films exhibited good electrical conductivity and optical transparency, which are comparable to those of ITO.

2. Experimental Procedure

In this work, Graphene/AgNWs hybrid electrodes were fabricated using solution based layer by layer (LBL) coating technique, which makes it possible to control the thickness, optical transmittance and sheet resistance. First, graphene oxide (GO) samples were synthesized by Hummers method. Next, amine moiety was introduced onto AgNWs via ligand exchange reaction. Then, negatively charged graphene oxide (GO) and positively charged AgNW were coated alternatively via LBL deposition on APTES (aminopropyltriethoxysilane) treated glass substrate. This was followed by reduction process with sodium borohydride ($NaBH_4$). The transmittance of Graphene/Ag NWs hybrid electrodes were measured by UV–Vis spectrometry, whereas sheet resistance was analyzed using four-point probe method.

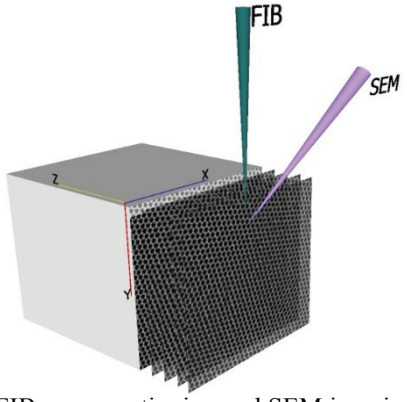

Figure 1. FIB cross-sectioning and SEM imaging process.

Moreover, nanostructuring applications, such as serial slicing and simultaneous imaging were performed at Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) platforms for revealing the morphology in the cross-sections of the multilayered materials (Fig. 1).

2.1. Preparation of G/Ag NWs hybrid conducting films

The LBL coating of GO and Ag NWs-NH_2 was performed for preparation of TCE. First, the glass substrates were functionalized by immersing in a 3% APTES solution for 3 h, followed by rinsing with excess methanol and drying under N_2 flow. The substrates were then annealed at 100 °C for 1 h to enable crosslinking of the APTES molecules on the surface. The GO solution (1 mg/mL, 150 µL) was spin-coated (2500 rpm and 25 s) on the APTES modified substrate, washed with DI water vigorously, and dried at 50 °C for 30 min. Next, the substrates were dipped into the Ag NWs-NH_2 dispersion (0.5 mg/ml) for 20 min, followed by rinsing with DI water and drying at 50 °C for 30 min. Multilayer films were obtained by repeating these processes. Consequently, the films were dipped in the 150 mM $NaBH_4$ solution at room temperature for 2 h to reduce the GO and then washed with excess DI water. Finally, the films were annealed in a tube furnace at 230 °C for 30 min under an air atmosphere.

2.2. Nanostructuring and Characterization

The sheet resistances of the TCEs were measured with a four-point probe technique (RM3000, Jandel) while the optical properties were examined using an ultraviolet visible spectrometer (UV–Vis,Lambda 750, Perkin-Elmer, USA). The surface morphology of the TCEs was analyzed by and field emission scanning electron microscope (FE-SEM, JEOL 63335F JSM) and FIB-SEM Multibeam System (JIB 4601F). For FIB slice&view experiments, the surface of the sample was first locally carbon deposited via gas injection system (GIS) at the FIB-SEM. Then the cross-section was ion milled using gallium source at 30 keV ion energy and 1-10 nA ion currents. Then the SEM images of the cross-sections were taken simultaneously with the ion processing.

3. Results and Discussion

The morphology of the GO/Ag NWs films was influenced by the number of GO/Ag NWs bilayers. As shown in Fig. 2, the density of the Ag NWs on the substrate was increased with an increasing number of bilayers, which demonstrates the success of successful LBL deposition.

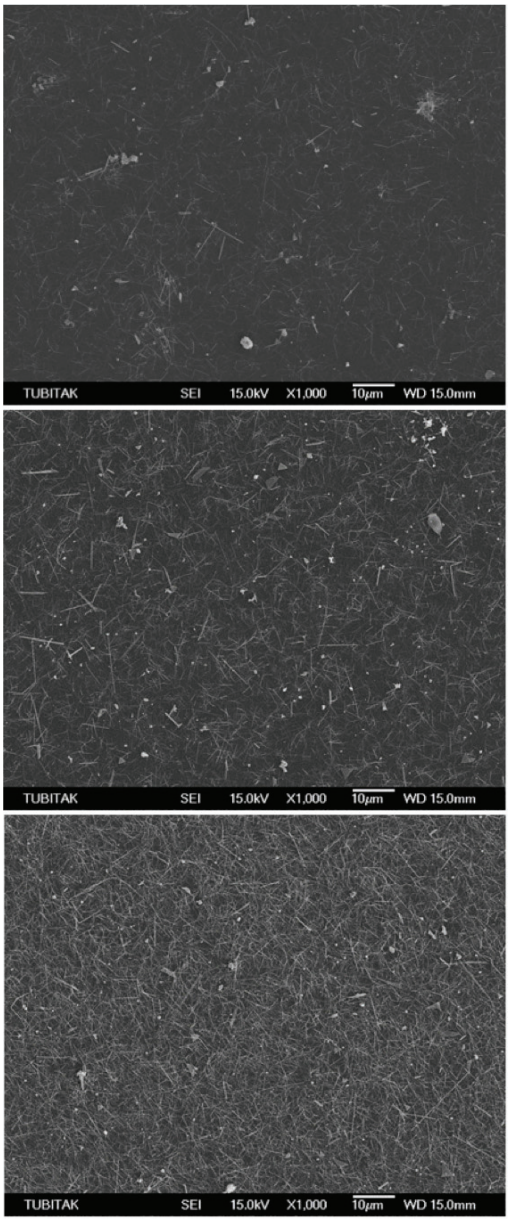

Figure 2. SEM images of 1, 2 and 3 bilayer GO/Ag NWs films. The scale bar is 10 µm.

As shown in Fig. 3, the optical transmittance of hybrid films decreased with increasing the number of layers. The transmittance values of 1-, 2- and 3-bilayer TCEs were 89.1%, 78.3% and 67.5%, respectively.

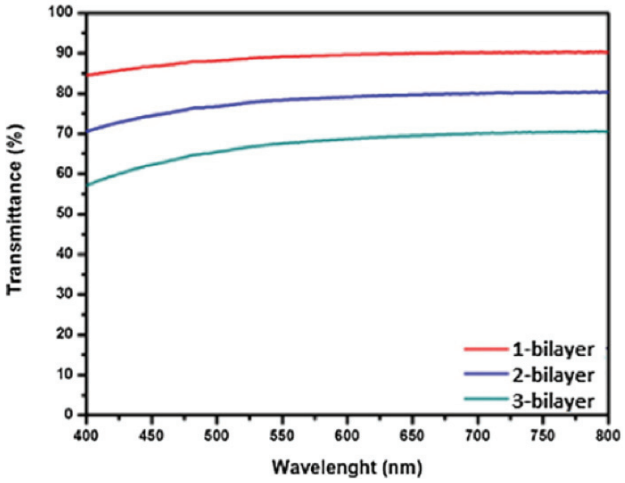

Figure 3. Transmittance of G/Ag NWs multilayer films.

Moreover, serial slicing and simultaneous imaging of the multilayered material were performed via FIB-SEM platforms. Tilted-view SEM images of GO/AgNWs/GO multilayered structure were revealed in Fig. 4. The cross-sectional Secondary Electron (SE) images showed the lateral surfaces of the graphene/nanowires that are adhering to the glass substrates (Fig. 6.).

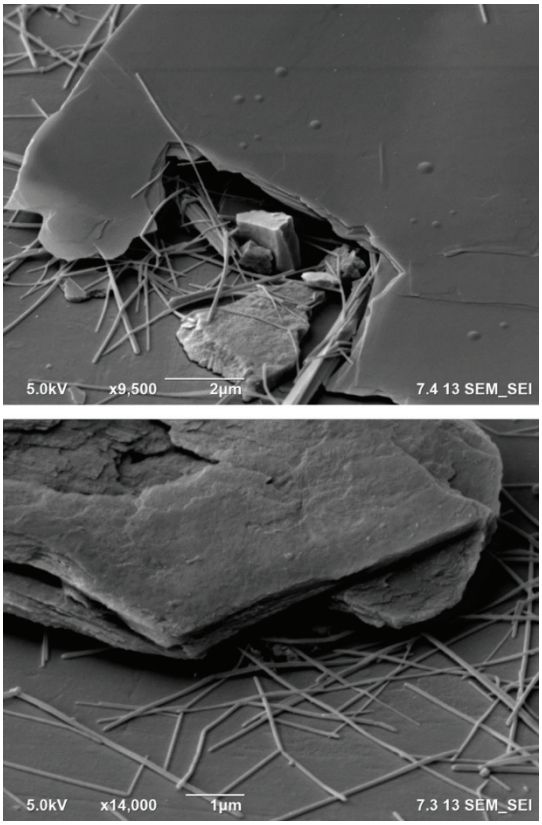

Figure 4. Tilted SEM images of GO/AgNWs/GO multilayered structures.

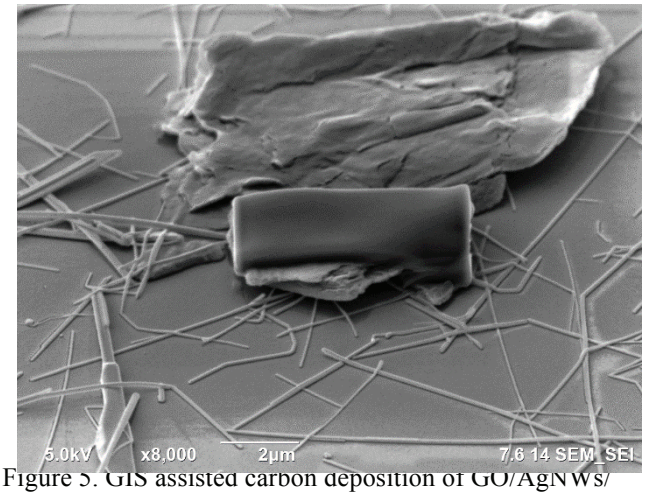

Figure 5. GIS assisted carbon deposition of GO/AgNWs/GO multilayered structures before FIB processing.

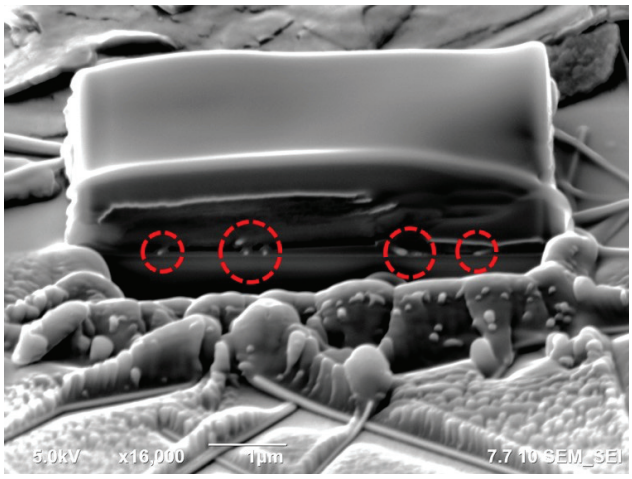

Figure 6. FIB cross-sectioning and SEM imaging of GO/AgNWs/GO multilayered structures. The marked regions correspond to the cross-sections of the nanowires.

Table 1 shows the sheet resistance and transmittance values of the 2-,3-bilayer G/Ag NWs hybrid films. The sheet resistances of 2- and 3-bilayer G/Ag NWs films were 6.5 and 4 Ω sq^{-1}, which are comparable to those of commercial ITO.

Table 1. Sheet resistance and transmittance of hybrid TCEs.

TCE	T (%)	R_s (Ω sq^{-1})
2-Bilayer G/Ag NWs	76.1	20
2-Bilayer G/Ag NWs (anneal.)[a]	78.2	6.5
3-Bilayer G/Ag NWs	65.3	5.7
3-Bilayer G/Ag NWs (anneal.)[a]	67.3	4

[a] Anneal.: Thermal annealing.

These results proved that GO and Ag NWs were successfully coated on glass substrates using LBL coating method.

4. Conclusion

A high performance G/Ag NWs transparent electrode was fabricated as an alternative to an ITO transparent electrode via the LBL method. We controlled sheet resistance and optical transmittance by varying the number of G/AgNWs layer. Finally, the best result was achieved with a 2-bilayer film with sheet resistance of 6.5 Ω sq^{-1} and an optical transmittance of 78.2% at 550 nm, which values are comparable to those of comercial ITO electrodes. Electron microscopy analysis by imaging on the surfaces and at the cross-section confirmed that the nanowires and graphene were succesfully coated on the glass substrates. These results indicating that G/Ag NWs films prepared by LBL deposition can be a promising candidate for TCEs in organic photovoltaics.

References

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