

Structure, Morphology and Electrical Behaviors of Polymer (Polystyrene)-Metal (Copper) Composite Thin Films

Suman Sarkar^{a)} and Sarathi Kundu^{b)}

Soft Nano laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Vigyan Path, Paschim Boragaon, Garchuk, 781035, Assam, India.

^{a)}Corresponding author: suman.gu21@gmail.com

^{b)}sarathi.kundu@gmail.com

Abstract. Metal-polymer composite films are prepared by depositing copper over the polystyrene films. DC magnetron sputtering is used to deposit copper, whereas spin coating method is used to prepare polystyrene layer on glass substrate. The crystallinity of the composite samples is studied using X-ray diffraction (XRD) method. Surface morphologies of the composite films are obtained from Atomic Force Microscopy (AFM), while the optical absorption behaviors are analyzed using UV-Vis spectroscopy. The electrical behaviors of these composite films are measured as a function of the deposition time of the sputtered copper layer over the polystyrene films. Results obtained from the XRD, AFM and UV-Vis spectroscopy provide the evidence of copper nanocrystals formation and from the electrical measurements, it is observed that the conductance of the composite film increases with the increase of the amount of copper nanoparticles inside the composite films.

INTRODUCTION

Composite films consisting of insulating materials such as polymers, ceramics or glass with embedded nanostructured metallic particles or fillers have unique properties and are useful for electrical, optical and optoelectronic applications [1-4]. Different research works have been carried out in the field of polymer matrix based nanocomposites and among them, some are related with functional applications. Among the functional nanomaterials, nanocomposites consisting of metal nanoparticles distributed over a dielectric polymer matrix have particular interest due to their novel properties, which in turn offers some new achievements in application field [5]. The conductivity of the polymer composites containing dispersed metallic fillers depends on many factors such as the size and shape of the filler particles, their spatial distribution within the polymer matrix, the interactions between the polymer matrix and the filler surface, and the contact resistance between the adjoined particles [6,7]. These factors regulate the charge transport from one particle to another, i.e., the conductivity of the composite materials.

In this work, we have studied the structural, morphological and electrical behaviors of Cu layers deposited over polystyrene (PS) film, where Cu was deposited by DC magnetron sputtering method by varying the deposition time. A thin layer of polystyrene was first deposited on a glass substrate by spin coating method and then Cu layer was deposited. The crystallinity of the deposited copper-polystyrene (Cu-PS) composite samples is obtained from X-ray diffraction studies. The optical behaviors of the composite samples are studied using UV-Vis absorption spectroscopy, while the surface morphologies of the Cu-PS layers are investigated by atomic force microscopy (AFM). The electrical characteristics of the samples are studied using a Keithley source meter unit. Results show that Cu nanostructures are produced in Cu-PS composite thin films and the relatively bigger size nanoparticles combined together to form globule-like smaller nanoparticles on the surface of Cu layer with higher Cu deposition time and accordingly the optical absorption property changes. Current-voltage ($I-V$) characteristics show that the conductance of the Cu-PS composite film increases with increase in the amount of Cu deposited over the PS layer.

EXPERIMENTAL DETAILS

The polystyrene films were prepared over glass substrates using spin coating method (spin NXG2-APEX). The glass substrates were cleaned by boiling them in a mixed solution of ammonium hydroxide (NH_4OH , Merck, 30%), hydrogen peroxide (H_2O_2 , Merck, 30%) and Milli-Q water in a volume ratio of $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2 = 2:1:1$ for 5-10 min at 100°C , and dried at room temperature. A solution of polystyrene was prepared by dissolving it into toluene and then spread over the glass substrates using spin coating method at a rotational speed of 6000 rpm, followed by drying them overnight at room temperature. After the deposition of polystyrene on glass substrate, a layer of copper was deposited over the PS film using DC magnetron sputtering technique designed by Excel Instruments, India. A Cu target of 5 cm in diameter and 2.5 mm in thickness was used in the sputtering deposition technique for the deposition of Cu layer. The PS-coated glass substrates were clipped on the substrate holder at a constant distance of ≈ 6 cm from the target. Initially the sputtering chamber was evacuated to 2×10^{-6} Torr by using a turbo molecular pump which was backed by rotary pump. At the time of deposition, Argon gas with purity 99.99% was delivered to the vacuum chamber at 20 sccm flow rate. During deposition, the chamber pressure was maintained at 1.5×10^{-2} Torr, and a potential difference of .33KV and current 1.6 Amp was applied in between the electrodes. The deposition of Cu layer over PS-coated glass substrates were carried out for 30, 60 and 180 seconds and were marked as PS6000/Cu30, PS6000/Cu60, and PS6000/Cu180 respectively. UV-Vis absorption spectra of the samples were taken using Shimadzu UV-1800 spectrophotometer. For the structural information, X-ray diffraction (XRD) measurements were performed. X-ray diffraction measurements were carried out using D8 Advanced, Bruker, AXS setup. Surface morphologies of the samples were obtained through an atomic force microscopy (NTEGRA Prima, NT-MDT Technology). A Keithley 2635B source-meter unit (SMU) interfaced with a computer for automatic data collection was used for the electrical current measurements. These measurements were performed by four probe electrical measurement method. The SMU has a current and voltage range of 0.1 pA to 1.5 A and 100 nV to 200 V, respectively.

RESULTS AND DISCUSSION

X-ray diffraction spectra obtained from PS6000/Cu60 and PS6000/Cu180 films are shown in Fig. 1. Here a diffraction peak is observed nearly at $2\theta \approx 43.18^\circ$. This peak at that particular angle is due to the reflection of X-ray from (111) crystal planes of copper nanoparticles [8]. For both the films, the XRD peaks are observed nearly at the same position and slightly higher intensity is observed for the PS6000/Cu180 film than PS6000/Cu60. This implies the formation of more copper nanocrystals in the Cu-PS composite film with higher deposition time. However, the possibility of forming CuO layer surrounding the surface of Cu nanoparticles cannot be fully ignored.

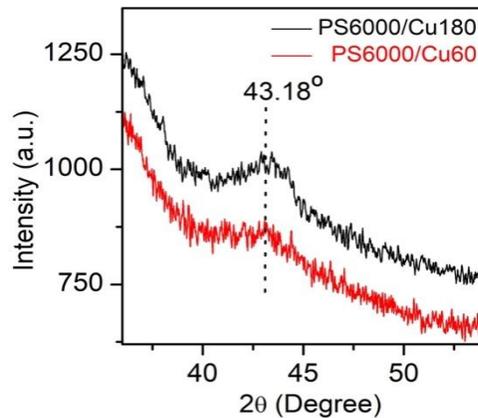


FIGURE 1. XRD spectra of PS6000/Cu60 and PS6000/Cu180 thin films.

The surface morphologies of the films PS6000/Cu60 and PS6000/Cu180 are shown in Fig. 2(a) and 2(b) respectively and the line profiles are shown in the corresponding insets. It is clear that large morphological modification has occurred after Cu deposition for longer time. Relatively bigger size particles formed due to shorter time deposition has become smaller globular like structure for longer time deposition. The average surface

roughness for the films PS6000/Cu60 and PS6000/Cu180 are found to be ≈ 1.65 and 2 nm, while the average heights are found to be ≈ 7.74 and ≈ 11 nm respectively.

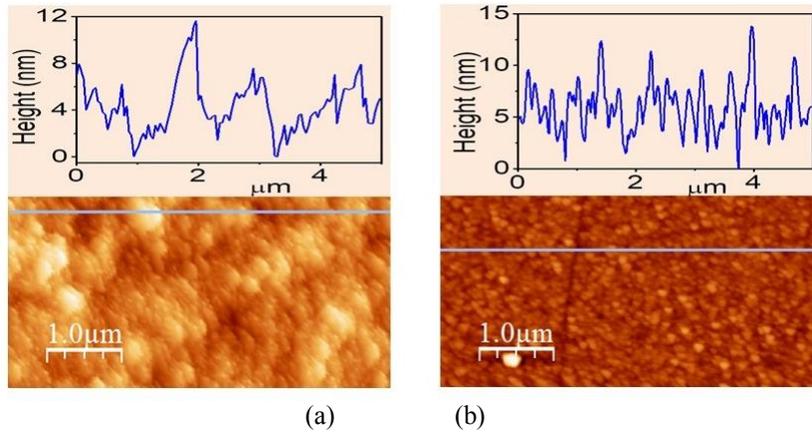


FIGURE 2. AFM image of (a) PS6000/Cu60 and (b) PS6000/Cu180. Insets: corresponding line profiles.

UV-Vis absorption spectra of PS6000/Cu30, PS6000/Cu60 and PS6000/Cu180 films are shown in Fig. 3. The intensity of the absorption peak is prominent for PS6000/Cu180 film, which is ≈ 0.94 and the position is found at ≈ 623.5 nm. The films PS6000/Cu30 and PS6000/Cu60 show the absorption peak at ≈ 639.0 nm with the absorption values of ≈ 0.38 and 0.55 respectively. It is clear from the UV-Vis absorption spectra that the absorption intensity of the peak due to Cu layer increases and a blue-shift is also visible in the absorption peak with increasing deposition time. This nearly matches with the AFM results as relatively bigger size particles become compact and on the top surface smaller size particles grow.

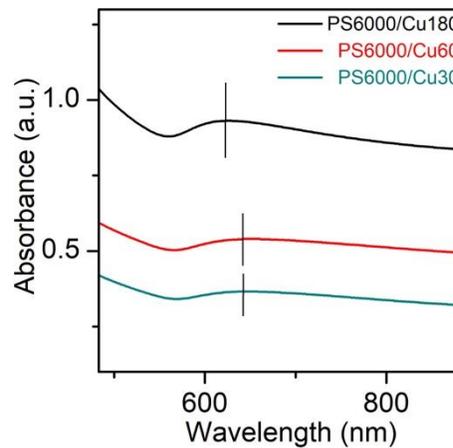


FIGURE 3. UV-Vis absorption spectra of PS6000/Cu30, PS6000/Cu60, and PS6000/Cu180 thin films.

Electrical measurements are performed on PS6000/Cu30, PS6000/Cu60 and PS6000/Cu180 films using four probe method. Fig. 4 shows the current-voltage (I - V) characteristics of the samples which are found to be Ohmic in nature. Here we applied $-1V$ to $+1V$ potential difference across the samples and the variation of the current was measured using the source meter. From the I - V curves, it is clear that for the same applied voltage the current gradually increases with increasing the Cu deposition time, i.e., relatively thicker layer of Cu gives higher electrical conductance. The maximum values of current obtained from I - V characteristics are ≈ 8.48 , 17.18 and 67.11 mA for PS6000/Cu30, PS6000/Cu60 and PS6000/Cu180 respectively, i.e., the corresponding film conductance becomes $\approx 8.48 \times 10^{-3}$,

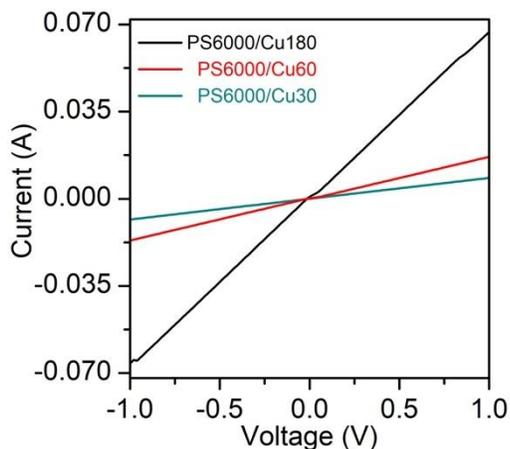


FIGURE 4. *I-V* characteristics of PS6000/Cu30, PS6000/Cu60, and PS6000/Cu180 thin films.

17.18×10^{-3} and 67.11×10^{-3} mho. It is clear that the conductance increases with increasing the deposition time for Cu over PS-coated glass substrates. Thus, by changing the sputtering time of Cu, the structure and morphology of the composite films can be modified and accordingly the optical absorption as well as electrical conductance can be varied.

CONCLUSION

Spin coating and DC magnetron sputtering methods are used to form copper-polystyrene composite films. The crystalline information of copper nanoparticles is obtained from XRD analysis while the surface morphologies of the composite films are found from AFM. The optical behaviors of composite films are obtained from UV-Vis absorption spectroscopy which shows that with the variation of the deposition time the initially formed bigger size Cu nanoparticles combined together to form globule-like smaller nanoparticles on the surface of the compact Cu layer. In addition, the electrical behaviors of these composite films are also studied, which show that the conductance of composite film increases with increasing the total amount of copper inside the composite films.

ACKNOWLEDGMENTS

Authors acknowledge Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), Govt. of India for the financial support.

REFERENCES

1. A. Biswas, O.C. Aktas, U. Schürmann, U. Saeed, V. Zaporjtchenko and F. Faupel, *Appl. Phys. Lett.* **84**, 2655-2657 (2004).
2. A. Kiesow, J.E. Morris, C. Radehaus and A. Heilmann, *J. Appl. Phys.*, **94**, 6988-6990 (2003).
3. J. Ouyang, C. W. Chu, R. Szmanda, L. Ma and Y. Yang, *Nat. Mater.* **3**, 918-922 (2004).
4. F. Faupel, V. Zaporjtchenko, T. Strunskus and M. Elbahri, *Adv. Eng. Mater.*, **12**, 1177-1190 (2010).
5. G. V. Ramesh, S. Porel and T. P. Radhakrishnan, *Chem. Soc. Rev.* **38**, 2646-2656 (2009).
6. S. Chunhui, P. Mu and Y. Runzhang, *Int. J. Hydrogen Energ.* **33**, 1035-1039 (2008).
7. L. Quercia, F. Loffredo and G. Di Francia, *Sens. Actuator B-Chem.* **109**, 153-158 (2005).
8. J. Ramyadevi, K. Jeyasubramanian, A. Marikani, G. Rajakumar and A. A. Rahuman, *Mater. Lett.* **71**, 114-116 (2012).