

Electroconductive copper selenide films on transparent polyester sheets

Ivan Grozdanov*

Department of Chemical, Bio and Materials Engineering, Arizona State University, Tempe, AZ 85287-6006 (USA)

(Received November 17, 1993; accepted January 14, 1994)

Abstract

Electroconductive thin films of copper selenide (Cu_2Se) were deposited on transparent polyester sheets by a simple electroless deposition technique based on hydrolytic decomposition of selenosulfate in alkaline aqueous solutions. X-ray analysis confirmed that the deposited material is polycrystalline Cu_2Se . Surface resistivities of the films are about 50–500 ohms/square, depending on the experimental conditions. Optical spectra revealed that the Cu_2Se films obtained are fairly transparent in the visible region, while the transmittance drops substantially in the near-infrared region. This suggests a possible use of these films as microwave (infrared) shielding coatings. The deposited films are p-type semiconductors with an optical energy bandgap of 2.33 eV.

1. Introduction

Electroconductive coating of non-conductive organic polymers has recently received considerable attention [1–5]. Such conductive coatings deposited on flexible substrates have numerous technological applications, such as opto-electronic devices [6], display devices [7] or active electrode material in energy storage [8] and a prospective application for the control of electromagnetic radiation and dissipation of electrostatic charge [3]. The effectiveness of these devices is largely a function of the surface conductivity of the deposited material.

Although there are numerous inorganic materials that would be of interest as surface coatings on polymer substrates, there have only been a few reports on the subject, mainly because organic polymers are inconvenient substrates with the most frequently used deposition techniques, such as electrodeposition and vacuum deposition. Also, the difficulty in achieving good adherence of the inorganic layer onto the polymer surface has been an additional discouragement.

Among the inorganic electroconductive coatings deposited on an organic polymer, CuS has received considerable attention, due to its metal-like behavior, useful in the fabrication of electronic devices [1, 2, 9].

Electroless chemical deposition of inorganic materials at near-room temperatures is a promising technique

which can be explored for coating organic polymer surfaces with electroconductive thin film.

This paper reports a simple electroless chemical deposition technique for coating transparent polyester sheets with an electroconductive Cu_2Se thin layer. A quick way of activating the polyester surface for uniform deposition is also proposed. Some of the electrical and optical characteristics of the deposited films are also reported.

2. Experimental

The experimental set-up required no special equipment or instrumentation. A 50 ml laboratory beaker can be used for small-sized substrates or a large bath container for large-area deposition. Glass or plastic bath containers can be used, since the temperature required does not exceed 45 °C. No stirring is necessary and the substrate can be of virtually any size or shape.

2.1. Preparation of the substrates

In this work, transparent polyester films were used as substrates, such as those of the Sigma Chemical Company, T2783, commonly used for overhead projections. Pieces of different size were cut and soaked for 15 min in warm water in which some oxygen bleach cleanser (such as Ajax of the Colgate-Palmolive Company, USA) was dissolved. This provides a uniform wetting of the polyester surface. The substrates were then rinsed with distilled water and immersed in a 0.03% aqueous solution of tin(II) chloride for 15 min

*On leave from the Institute of Chemistry, Skopje, Macedonia.

(or 3 min in an ultrasound bath). This further improves the uniform wetting of the polyester surface and in a way activates it for the inorganic layer to be deposited. The substrates were then taken out, rinsed with distilled water and dried in air before use.

2.2. Deposition of Cu_2Se films

For small-sized substrates (50 mm × 25 mm), a 100 ml beaker was used. Typically, 10 ml 0.5 M aqueous solution of CuSO_4 was placed into a beaker and diluted (1:3) ammonia solution was introduced with constant stirring until a clear blue solution was obtained (tetraamino complex of copper). Then 10 ml aqueous solution of 1.0 M sodium selenosulfate was added and distilled water to make a total volume of 80–90 ml. The pH of the bath should be about 10–10.5. The previously cleaned and activated polyester substrates were then vertically introduced into the bath and the temperature was adjusted and kept at 40–45 °C. Alternatively, warm distilled water can be added to make up the total volume, in which case no further heating of the bath is necessary. After a few minutes, a brown precipitate began to form in the bath and transparent yellow–brown coatings deposited onto the polyester surfaces. Some 20–40 min later, the substrates with the deposited films were taken out, rinsed with distilled water and soaked in distilled water for several hours to ensure complete removal of poorly adhered particles and potential water-soluble contaminants. The coated polyester substrates were then taken out and dried in air before examining their physical properties. The as-deposited films were uniform, mirror-like and had excellent adherence to the substrate.

2.3. Physical measurements

The thicknesses of the films were estimated by ellipsometry. The surface resistivity was determined by a standard two-probe method.

The identity of the deposited material was determined by X-ray diffractometry (XRD). For this purpose, a fairly thick film was deposited onto a glass substrate. The obtained XRD pattern was then compared against the standard JCPDS-ICDD diffraction powder data, PDF-2 sets, 1-42 Database (1992).

The optical spectra were taken by a CARY 5 spectrophotometer in the Vis–NIR spectral region.

3. Results and discussion

3.1. Chemistry of the technique

Uniform, transparent and electroconductive Cu_2Se thin films were deposited onto polyester sheets, according to the following overall reaction:

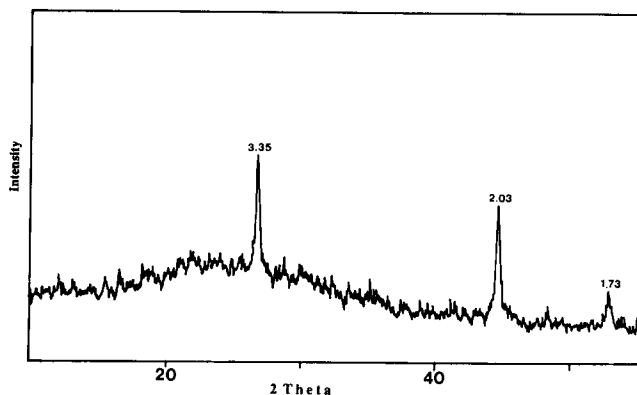


Fig. 1. X-ray diffraction pattern of a Cu_2Se thin film.

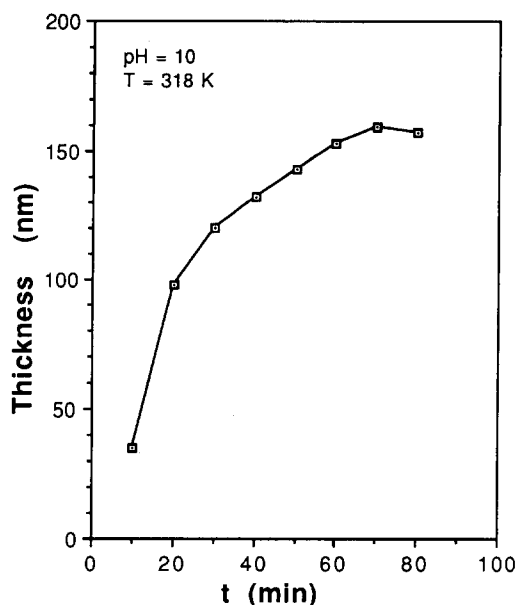
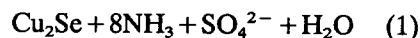
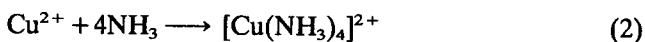


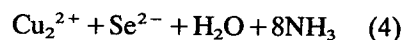
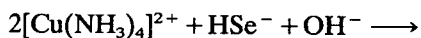
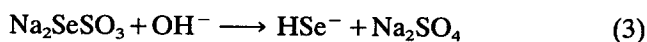
Fig. 2. Thickness vs. deposition time for Cu_2Se films.



First, the copper(II) ions form a tetraamine complex with NH_3 :



Sodium selenosulfate hydrolyzes in alkaline solutions, producing selenide ions and reducing the $\text{Cu}(\text{II})$ into $\text{Cu}(\text{I})$; the latter then combine with the selenide ions to give insoluble Cu_2Se precipitate:



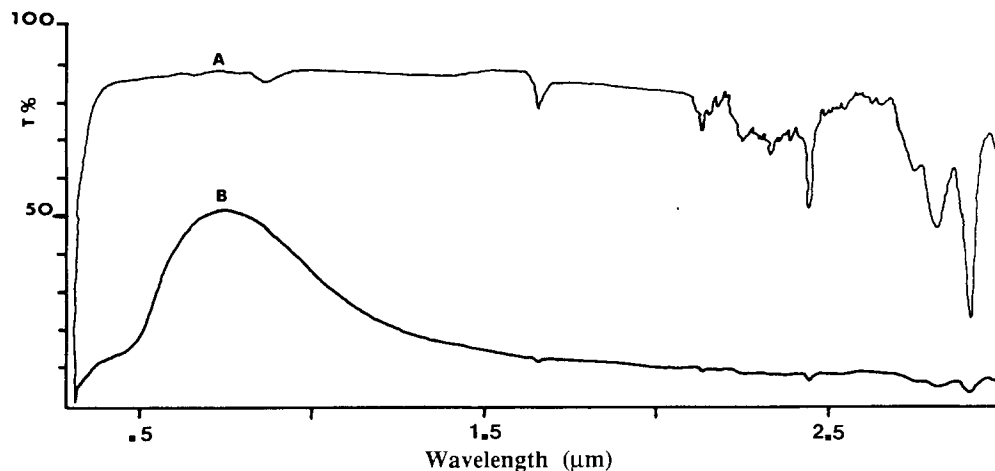


Fig. 3. Optical transmittance spectrum of 0.12 μm thick Cu_2Se film on polyester substrate: A, clear polyester substrate; B, Cu_2Se film.

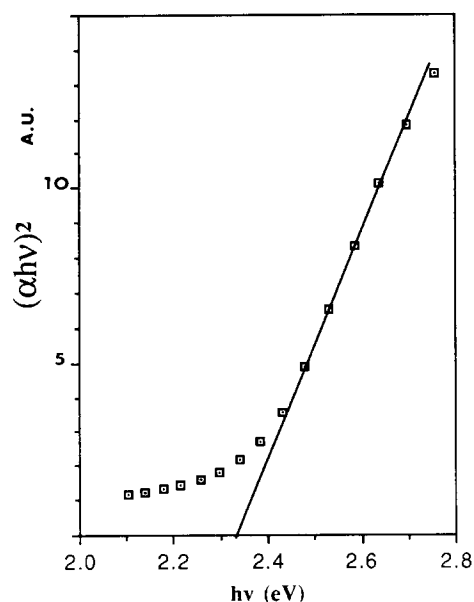


Fig. 4. Graphical determination of the optical energy bandgap for Cu_2Se films.

This electroless deposition technique is therefore based on hydrolytical decomposition of selenosulfate in alkaline solutions and its ability to reduce copper(II) to copper(I) under appropriate experimental conditions.

The optimal concentrations of both copper and selenosulfate ions were found to be as stated in the Experimental section. At lower concentrations, ultrathin but uniform films (<50 nm) are deposited. At higher concentrations than those specified, non-uniform films are formed in the midst of heavy precipitate in the bath and precipitate particles are randomly attached and trapped within the film.

The pH of the chemical bath should be in the range 9–11. At lower pH values the solution in the bath becomes turbid, due to copper hydroxide formation;

excess ammonia is needed to dissolve the precipitate and form the soluble tetraamine complex of copper. At higher pH values, the precipitated Cu_2Se has larger grains resulting in non-uniform film formation, although thicker films could generally be obtained at higher pH.

3.2. Characterization of the deposited Cu_2Se films

The XRD pattern of the deposited material is shown in Fig. 1. The deposited material was found to be polycrystalline and the d values (in angstroms) are stated above the peaks rather than the hkl values because the three peaks observed turned out to be common for several Cu_2Se species listed with the JCPDS-ICDD diffraction patterns, such as the cubic Cu_2Se , #4-839, monoclinic, #27-1131, and tetragonal, #29-575.

The thickness of the films at specified concentrations and temperature is a function of the depositing time (Fig. 2). Terminal thickness of about 160 nm was achieved from a single bath in about an hour at 45 °C. Thicker films could be obtained by re-immersing the initial films into a fresh bath. The surface resistivity of the films was 50–500 ohms/square, depending on the copper-to-selenosulfate molar ratio used in the chemical bath. Least conductive films were obtained at a molar ratio 1:1, while more conductive films were obtained at higher concentrations of selenosulfate. X-ray studies showed that at copper-to-selenosulfate molar ratios higher than 1:4, CuSe was precipitated rather than Cu_2Se . However, the adherence of CuSe onto the polyester substrate was poor. At molar ratios between 1:1 and 1:4, a mixture of Cu_2Se and CuSe was deposited as observed in the change of color from brown to bright yellow to yellow-green accompanied by decrease in surface resistivity.

The optical transmittance spectrum of a Cu_2Se film deposited onto a polyester substrate is presented in Fig. 3. The spectrum shows that a peaked transmittance

of the Cu₂Se film is observed in the visible region around 0.7 μm while a substantial decrease in transmittance is observed throughout the infrared region (1.0–3.0 μm). This suggests a potential application of these films as microwave (infrared) shielding coatings.

A calculation of the absorption coefficient α at different wavelengths and a construction of a plot $(\alpha h\nu)^2$ versus $h\nu$ shown in Fig. 4 reveals that Cu₂Se is of a semiconductive nature with an optical energy bandgap of 2.33 eV. Thermoelectric probe testing showed p-type conductivity.

4. Conclusions

Electroconductive Cu₂Se films were successfully deposited onto transparent polyester substrates by a simple electroless chemical deposition technique based on hydrolytic decomposition of selenosulfate. The films obtained were uniform and had excellent adherence to the substrate. This was achieved by a special treatment of the substrates in a 0.03% tin(II) chloride aqueous solution. The technique and experimental conditions are easily applicable for large-area deposition and fabrication of electroconductive coatings on polyester sheets.

These films can be used in a variety of electro-optical devices where conductive coatings on a flexible substrate are desired or required. The optical spectrum of Cu₂Se

also reveals that this material can be used as a microwave shielding coating.

Acknowledgements

Part of this work has been carried out under a US Government Fulbright Grant. The author is also indebted to Dr S.K. Dey for providing lab facilities and chemicals, and to Dr Jim Allen for use of his Cary 5 UV-Vis-NIR spectrophotometer.

References

- 1 T. Yamamoto, K. Tanaka, E. Kubota and K. Osakada, *Chem. Mater.*, 5 (1993) 1352.
- 2 M. Inoue, C. Cruz-Vazquez, M.B. Inoue, K.W. Nebesny and Q. Fernando, *Synth. Met.*, 55–57 (1993) 3748.
- 3 D.C. Trivedi and S.K. Dhawan, *Synth. Met.*, 59 (1993) 267.
- 4 S. Yanagida, T. Enokida, A. Shindo, T. Shiragami, T. Ogata, T. Fukumi, T. Sagakami, H. Mori and T. Sakata, *Chem. Lett.*, (1990) 1773.
- 5 D.C. Trivedi and S. Srihivasan, *J. Mater. Sci. Lett.*, 8 (1989) 709.
- 6 G. Gustaffson, Y. Cao, G.M. Treacy, F. Clavetter, N. Colaneri and A.J. Heeger, *Nature*, 357 (1992) 477.
- 7 S.K. Dhawan and D.C. Trivedi, *J. Appl. Electrochem.*, 22 (1992) 563.
- 8 C. Gasgrande, S. Ponero, P. Prospero and B. Scrosati, *J. Appl. Electrochem.*, 22 (1992) 195.
- 9 E. Ramli, T.B. Rauchfuss and C.L. Stern, *J. Am. Chem. Soc.*, 112 (1990) 4043.