

**Deposition of Electrically Conductive, Microwave Shielding,
and IR-Detecting Inorganic Coatings on Polymer Films**

Ivan GROZDANOV⁺

Arizona State University, Department of Chemical, Bio, and Materials Engineering,
Tempe, AZ 85287-6006, U.S.A.

A simple, inexpensive and pollution free electroless chemical deposition technique was used to deposit thin coatings of inorganic electrically conductive materials (Cu_xS , $x \sim 2$, CuS and Cu_2Se), microwave shielding materials (CuS and Cu_2Se) and IR-detecting materials (PbS and PbSe) on transparent polyester films. The technique is based on hydrolytic decomposition of thiosulfate and selenosulfate complexes of the corresponding metals in aqueous media.

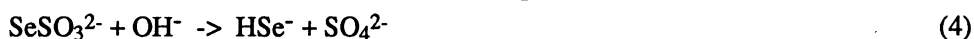
Coatings of conductive or semiconductive materials on the surface of organic polymers have potential utility for electrical and electrooptical devices of high elasticity and transparency. Although the deposition of metal chalcogenides on the surface of organic polymers would be of a great advantage, there have been only a few reports on the subject,¹⁻³⁾ mainly due to the unsuitableness of polymer films as substrates with commonly used deposition techniques, such as electrodeposition, vacuum deposition and spray pyrolysis. The difficulty in achieving stable contact between the inorganic layer and the polymer film surface seems to be an additional problem.

This paper reports a most simple, non-pollutive and inexpensive technique convenient for deposition of several metal chalcogenides on polyester transparency sheets, giving surface coatings of versatile electrical and optical characteristics. A fast and simple treatment of the polymer surface for deposition of inorganic layers is also reported.

The deposition of the metal chalcogenide coatings onto the polymer surface were carried out in a chemical bath in which the main components were a water soluble salt of the corresponding metal and aqueous solution of sodium thiosulfate or selenosulfate. The thiosulfate and selenosulfate ions form soluble complex compounds with most heavy metals. Some of these complexes undergo hydrolytic decomposition to finally give precipitates of the corresponding metal sulfides or selenides. In acidic media, sulfide ions are considered to be generated according to the following processes:⁴⁾



In alkaline media, selenide ions are considered to be produced,⁵⁾ according to:



⁺On Leave from the Institute of Chemistry, Skopje, Republic of Macedonia.



The metal ions then combine with the sulfide/selenide ions to give the corresponding non-soluble sulfide or selenide. These reactions were found convenient for chalcogenide coating depositions under appropriate experimental conditions to be described.

Pieces cut from clear polyester sheets, without any coating material, such as transparency films T2783 of Sigma Chemical Company were used as substrates. The substrates were first washed with soap in warm water, rinsed with distilled water and then soaked for 10 min in 0.03% aqueous solution of tin(II) chloride. This ensures a uniform wetting of the polymer surface and in a way activates it for the inorganic coating to be deposited. After being treated in tin(II) chloride, the substrates were rinsed with distilled water and dried in air before use.

Electrically conductive and microwave shielding coatings (Cu_xS , $x \sim 2$, CuS , and Cu_2Se) were deposited as follows. Typically, 10 cm³ 0.5 M aqueous solution of CuSO_4 were placed into a 100 cm³ beaker and 10 cm³ 0.5 M aqueous solution of sodium thiosulfate were added. The blue solution turned green at this point, due to the reduction of Cu(II) to Cu(I) by the thiosulfate ions. Distilled water was then added to make a total volume of 100 cm³, and the pre-treated substrates were vertically introduced into the bath. The temperature of the bath was brought and kept at 40-45 °C. In about 20-30 min, golden yellow to brown films were deposited onto the surface of the polymer substrates. The chemical analysis of the deposited material showed that it was Cu_xS , with x value of about 2. The thickness of the films deposited from a single bath was around 0.1 μm. Thicker films were obtained by re-introducing the initial films into a fresh bath.

Following a similar experimental procedure, but increasing the amount of sodium thiosulfate to 50 cm³ and the bath temperature to 70-80 °C, green color coatings were deposited onto the polymer surface. X-ray analysis of the as-deposited coatings revealed the material to be polycrystalline CuS .

To deposit Cu_2Se coatings onto the polymer surface, the following experimental procedure was employed. 10 cm³ of 0.5 M aqueous solution of CuSO_4 were introduced into a 100 cm³ beaker. Ammonia solution was then added until a clear blue solution was obtained. Then 10 cm³ of 0.5 M aqueous solution of selenosulfate were added and distilled water to make a total volume of 100 cm³. The pH of the bath was about 10. Then the pre-treated polymer substrates were vertically introduced into the bath and the temperature was raised and kept at 40-45 °C. In a few minutes, yellow-orange to brown films were deposited onto the polymer surface. X-ray diffraction showed that the as-deposited films were polycrystalline Cu_2Se . The surface resistivities of these films are presented in Table 1.

The optical spectra of these inorganic coatings were taken on a CARY 5 Spectrophotometer against a clear polyester film as a reference and are shown on Fig. 1, curves A, B and C. It can be seen that the transmittance of the CuS and Cu_2Se coatings in the NIR region is very low. Such coatings can therefore be used as microwave (infrared) shielding materials. All three films have peaked transmittances in the visible region between 550 nm and 750 nm. This suggests a potential use of these coatings for solar control architectural window application in regions with warm climates where just enough transmittance (10-30%) is required in the visible region and as little as possible infrared radiation in the interior.

IR-detecting coatings (PbS and PbSe) were also chemically deposited. The PbS coatings were deposited onto the polymer surface from a following bath. 30 cm³ 1.0 M aqueous solution of sodium thiosulfate were placed into a 100 cm³ beaker and 12 cm³ 0.5 M aqueous solution of lead(II) nitrate were slowly added to give a clear solution of lead(II) thiosulfate consecutive complexes. The pre-treated polyester substrates were then vertically introduced into the bath and the temperature of the bath was raised and kept at 75-80 °C. In about an hour, mirror-

Table 1. Surface resistivity of conductive inorganic coatings on polymer surface

Inorganic coating (about 0.1 μm)	Color	Surface resistivity (Ω/square)
Cu_xS , $x \sim 2$	brown	~ 300
CuS	green	~ 100
Cu_2Se	yellow-orange	~ 10

like, uniform, metallic grey coatings were deposited onto the polyester film surface. The as-deposited PbS was found to be a mixture of amorphous and polycrystalline phase and was semiconductive by nature.

The PbSe films were deposited as follows. 12 cm^3 0.5 M lead(II) nitrate were placed into a 100 cm^3 beaker and 2.0 M NaOH were added until a clear solution was obtained. Then 10 cm^3 of 0.5 M aqueous solution of sodium selenosulfate were added and distilled water to make a total volume of 100 cm^3 . The pH was about 10-11. The polyester substrates were introduced vertically and the temperature of the bath was brought and kept at 40-45 $^\circ\text{C}$.

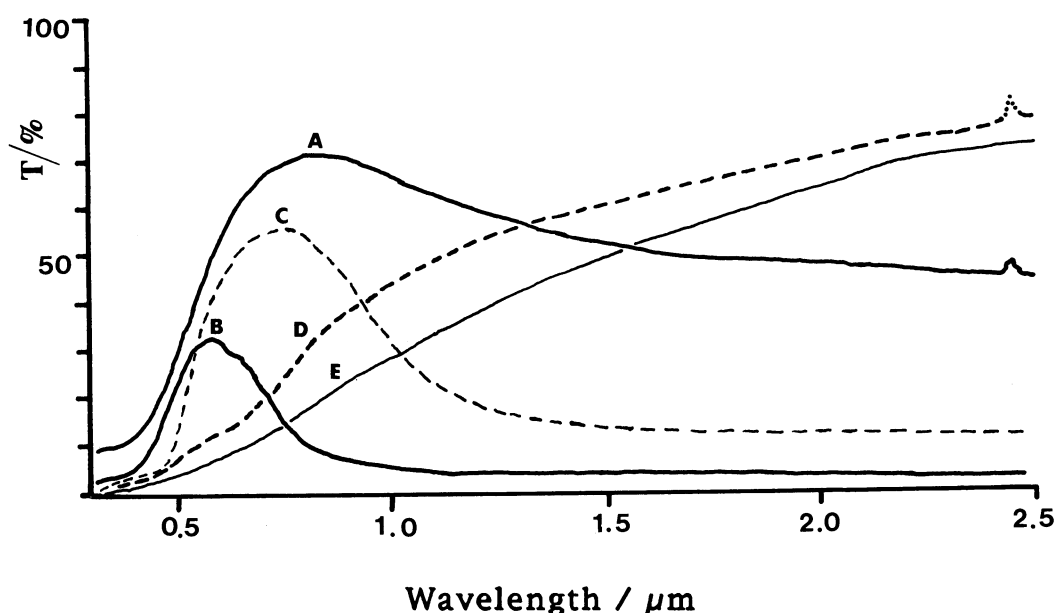


Fig. 1. Optical transmittance spectra of the inorganic coatings:
A, Cu_xS ; B, CuS ; C, Cu_2Se ; D, PbS ; E, PbSe .

Mirror-like, brown to grey films were thus deposited onto the polyester surface. The deposited films were found to be polycrystalline and semiconductive.

The optical spectra of PbS and PbSe films are presented in Fig. 1, curves D and E. The transmittance of both of these layers is continually increasing from the visible through the infrared region. PbS has been conventionally used in infrared detectors.⁶⁾ As obvious from Fig. 1, curve D, the PbSe coatings exhibit similar

optical characteristics to those of PbS coatings and can therefore be used for IR-detection.

The technique presented can also be applied to deposit multilayer coatings, to enhance particular characteristics. For example, CuS and PbS coatings can be combined to integrate the high reflectivity of PbS in the NIR region and the high absorptivity of CuS in the same region. Also, some preliminary experiments show that using the presented technique, many other chalcogenide coatings can be deposited on polymers, such as antimony, bismuth and silver sulfides and selenides as well as combinations of these. Furthermore, the technique is easily applicable to large area depositions and the bulk precipitates could be used either as mineral pigments or semiconducting powders.

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