

Electrical properties of plastic/Cu_xS/Ni composites

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Thin electro-conductive Cu_xS films were deposited on plastic substrate from solutions containing copper chloride, thiourea (TU), sodium hydroxide, ethylenediaminetetraacetic acid disodium salt (EDTA), and polyethylene glycol (PEG) as surfactant. On the surface of Cu_xS film a layer of nickel was electrochemically deposited. The influence of etching treatment in acetone: water solutions and chromic mixture respectively on the electrical resistance of the obtained films was studied, as well as the influence of nickel deposition. After the deposition of nickel the electrical resistance of obtained multilayered composites decreased more than 5 times. The technique of deposition of an intermediate layer of copper sulphide in order to obtain a conducting plastic is preferable to classical technology, since the number of stages is reduced, and the necessity of using noble metals (Ag or Pd) is eliminated.

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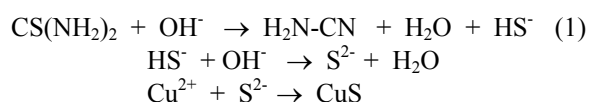
1. Introduction

Composite materials obtained by the deposition of a layer of copper sulphide on non-conducting substrates were intensively studied due to a large area of applications of those films, in solar control coating, photovoltaic cells, or as sensors.

The Cu_xS films can be obtained by chemical methods: Chemical Bath Deposition (CBD) [1-6], Spray Pyrolysis Deposition (SPD) [7-9]; electrochemical deposition [10,11], Successive Ionic Layer Adsorption and Reaction (SILAR) [12,13], photochemical deposition [14] or by Atomic Layer Deposition (ALE) [15,16].

Multilayered films consisting of Cu_xS and a metallic deposit were approached in a small number of studies. Zebrauskas et al. [17] described a method for obtaining copper sulphide films on the surface of polyethylene or plasticized polyvinyl chloride by a successive treatment with an aqueous solution containing sodium polysulphide and copper chloride. The sulphur is adsorbed by the polymer from the solution containing sodium polysulphide and by subsequent treatment with copper chloride, copper sulphide is formed. On the surface of the copper sulphide covered polymer a metal layer can be deposited by electrolysis. The intermediate layer of copper sulphide increases the adherence of metallic film from 0.005 kN/m, corresponding to a plastic – metallic film composite, to 1.2 kN/m (for polyethylene) or 10 kN/m (for polyvinyl chloride), in plastic/copper sulphide/metallic film composites.

Using solutions containing a copper salt and thiourea in alkaline environment, the formation of CuS occurs by the reactions:



In the deposition solutions chelating agents or/and surfactants are added, in order to lower the reaction rate. For example for the obtaining of Cu_xS (x = 1.83-1.85) films, EDTA [18] or EDTA and triethanol-amine [19] were used as chelating agents. The copper sulphides were obtained from the copper-EDTA and thiourea (TU) complexes.

The aim of this work is to obtain electro-conducting plastic materials using as substrate Acrylonitrile Butadiene Styrene (ABS) by a non-conventional method.

Usual methods involve a large number of stages: degreasing treatments; etching, sensitizing (with solutions containing Sn (II) salts), activation (with solutions containing noble metal salts), chemical deposition of Cu, and electrochemical deposition of Ni.

The deposition technique of an intermediate layer of copper sulphide in order to obtain a conducting plastic has important advantages as compared to classical technology, because the numbers of stages is reduced, and the necessity of using noble metals (Ag or Pd) is eliminated. For some applications, on the surface of Ni, Cr can be electrodeposited, using known methods.

The obtained composite materials can replace metal parts, leading to important saving of metals.

2. Experimental details

For the obtaining of plastic/Cu_xS/Ni, Acrylonitrile Butadiene Styrene (ABS) slides with the dimensions 25mmx25mmx2 mm were used as substrates. Before the deposition these substrates were cleaned in a detergent solution. In order to obtain highly adherent films the substrates were etched in aqueous solutions of acetone with the acetone: water ratios range between 1:1 to 3:1, at 20 °C, or in chromic mixture (H₂SO₄ and CrO₃) at 70 °C. At the surface of the etched substrate a layer of Cu_xS was deposited, by chemical bath deposition from a solution containing CuCl₂, thiourea, EDTA and NaOH. The

electrical resistance of the obtained film was measured and then a layer of nickel was deposited by electrolysis.

The square electrical resistance (sheet resistance) (R_{sq}) of the films was measured across pairs of silver paste electrodes of 5 mm length at 5 mm separation, printed on the surface of the films. A hand-held multimeter was used to measure the sheet resistance both for copper sulphide films and copper sulphide covered by a layer of Ni [20]. The used silver paste is highly conductive and strongly adheres to the substrate, avoiding the contact resistance.

Square electrical resistance (R_{sq}) is a frequently used parameter for film characterization, unanimously recognized by specialists in the field [20].

Assuming the film as parallelepiped strips with resistivity ρ , length l , width w and thickness h the relationship results:

$$R = \rho l / S = \rho l / wh \quad (1)$$

If $l=w$, for square resistance, the relationship for square resistance is obtained [21]:

$$R_{sq} = \rho / h \quad [\Omega / sq] \quad (2)$$

It can be observed that square resistance depends only on the resistivity and the thickness of the films [21]. R_{sq} vary inversely proportional to the thickness of the film.

3. Results and discussion

3.1. The influence of etching on the electrical resistance of Cu_xS films

In order to obtain highly adherent films, ABS samples were treated with solutions able to attack the surface of plastic. In this stage micro-cavities are formed on the treated surface. Those micro-cavities have the role to mechanical anchor the deposited Cu_xS layer. At the same time a diffusion of the formed Cu_xS deeply in the substrate takes places according to [22].

3.1.1. The influence of etching ABS substrates in acetone aqueous solutions

The ratio acetone: water varied from 1:1; to 3:1 for various treatment durations. After etching, the samples were washed in water and distilled water in order to remove the acetone from the surface of the substrate, and then a layer of Cu_xS was deposited from a solution containing $5 \times 10^{-2} M$ CuCl₂·2H₂O, 0.3M EDTA, 0.2M NaOH, 1% PEG, 0.1M TU at 50°C, with a deposition time of 2 hours.

The variation of electrical resistance as a function of treatment time in solutions of acetone: water 1:1 is presented in Fig. 1.

According to Zebrauskas [22], when a film of CuS is deposited on a plastic substrate, three layers are formed. The first layer, starting from the surface is a continuous thin one, followed by the second one which is formed in the microcavities resulted as a consequence of etching

treatment. The third one consists in dendrites placed at relatively great distance to each other, deeply penetrating the polymer substrate.

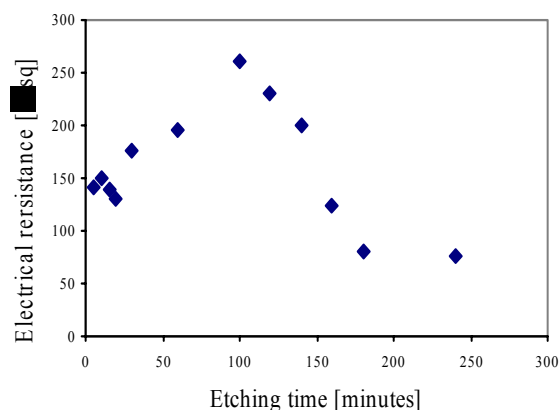


Fig. 1. The influence of etching time on the electrical resistance of Cu_xS films acetone: water 1:1.

Examining the data presented in figure 1, it can be seen that the values for electrical resistances are similar for similar treated from 5 to 20 minutes in solutions acetone: water 1:1, having an average value of 140 Ω/sq. The micro-cavities formed are small, and for this deposition time, layer no. 1 and 2 are preponderantly formed. As the etching treatment increased from 20 to 100 minutes the electrical resistances increased to, reaching the value of 260 Ω/sq. This behaviour can be correlated with the modification of the surface of the substrate. The Cu_xS is deposited in bigger micro-cavities and it is not enough to cover the whole surface of the plastic. Etching time higher than 120 minutes leads, probably to a general attack of the substrate surface, increasing the number of micro-cavities that are less deep. So, it is possible to ensure the conditions for the formation of a continuous layer at the surface of the substrate, if the treatment time is higher than 180 minutes.

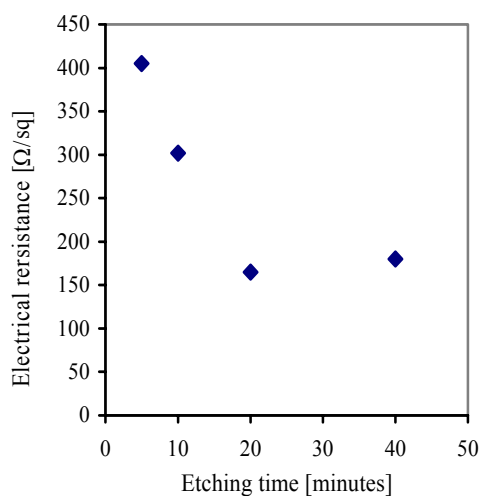


Fig. 2. The influence of etching duration on the electrical resistance of Cu_xS films acetone- water 2:1.

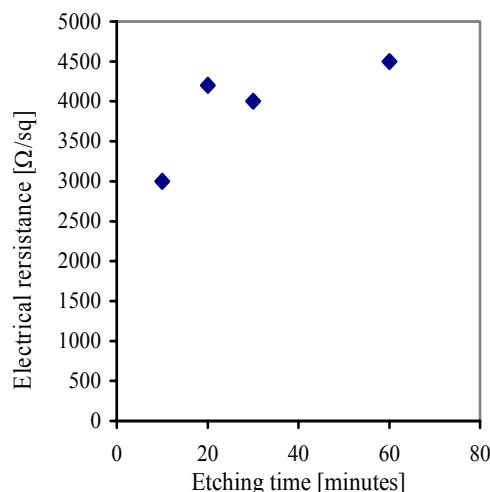


Fig. 3. The influence of duration time on the electrical resistance of Cu_xS films acetone- water 3:1.

At higher concentration of acetone for etching treatment, the electrical resistance of deposited Cu_xS increased. After etching for 5 min in acetone 2:1 (Fig. 2) the electrical resistance was about 3 times higher than that obtained for a more diluted acetone solution (acetone: water 1:1, see Fig.1). Probably the micro-cavities are deeper, and the first layer is discontinuous. By increasing the etching time from 10 to 40 minutes in solutions acetone- water 2:1, the electrical resistance decreased, because of the great number of micro-cavities, which lead to the formation of a continuous film.

In acetone-water 3:1 (Fig. 3) greater values of the studied parameter were obtained, which increased for a longer treatment time, due, probable, to the deeper micro-cavities.

In order to deposit a metallic film by electrolysis, the Cu_xS films must have electrical resistance under $150 \Omega/\text{sq}$. For that reason the treatments with those solutions do not present interest for our purpose.

3.1.2. The influence of etching ABS substrates in chromic mixture aqueous solutions

The most common procedure applied in order to assure the adherence of deposited films on butadiene (working also for ABS) is based on the treatment of the substrate with solutions containing sulphuric acid and Cr (VI) compounds, at high temperatures, for a sufficient long time.

The effectiveness of this kind of treatment applied to plastic materials can be explained by the mechanical mechanism of the adherence of the subsequently deposited film. According to this theory, during the etching treatment, the butadiene component of ABS is dissolved and in the formed cavities the deposited layer is mechanical anchored [23,24].

A study regarding etching treatment in chromic mixtures of ABS used as substrates for Cu, CuS , Cu_{2-x}S films was performed by Bikulcius [24], using solutions

with different concentrations, at temperatures of 20°C , 40°C , 70°C , for 10-240 seconds. Micrographs recorded for etched surfaces revealed the different grade of attack of ABS surface as a function of solution grade concentration, temperature and treatment duration. At 60°C even for a short treatment time (60 seconds), the micrographs revealed that the surface was attacked, but at room temperature after four minutes, the surface of ABS is almost identical with that of unattacked sample. During the treatment with chromic mixtures at the surface of ABS, compounds containing oxygen were formed. These compounds have a role in the formation of van der Waals and chemical bonds between copper sulphides and the substrate. In this case, the improved adherence of the formed films can be explained by the two ways of assuring the adherence, mechanical and chemical.

That was the reason why we chose as treatment temperature in chromic mixture the temperature of 75°C .

Our experiments related to the influence of the etching treatment using chromic mixtures were performed using solutions containing: CrO_3 370g/l, H_2SO_4 ($d = 1,84\text{g}/\text{cm}^3$) 225 ml/l and H_3PO_4 44%, at 75°C , varying the duration of the treatment. The solution for copper sulphide deposition was the same as that used for the deposition on the substrates etched with acetone solution. The films were deposited for 2 hours at 50°C . The obtained results are presented in figure 4.

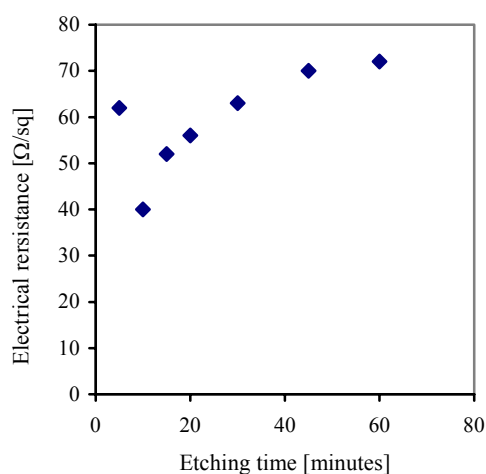


Fig. 4. The influence of etching treatment with chromic mixtures on the electrical resistance of Cu_xS films.

Comparing the electrical resistances of Cu_xS films obtained on ABS substrates, treated in solutions containing chromic mixtures, with those deposited on ABS treated with acetone solutions, it is evident that the values for electrical resistances are smaller, for all the durations of the treatments.

Electrical resistance of the deposited Cu_xS films varied against duration of the treatment in an interesting way. The minimum of the electrical resistance was obtained for a treatment time of 10 minutes. Increasing the treatment time the electrical resistance increased too. A total understanding of that dependence needs more investigation in order to determine the morphology of the

etched substrates. We suppose that for increased treatment time, the dimensions and the deepness of the micro-cavities increase too, leading to the formation of a discontinuous film.

3.2. The deposition of nickel on Cu_xS layers

In order to deposit Ni by electrolysis, on ABS substrates covered with a layer of Cu_xS, the electrical resistance of those layers must be as small as possible.

For Ni deposition the substrates covered with Cu_xS are subjected to a treatment in a solution containing 150 ml sulphuric acid in 1 liter of solution, for 15-30 seconds.

Using samples with electrical resistances from 270 to 300 Ω/sq as substrates for electrochemical deposition of Ni, films of Ni with the poor homogeneity were obtained. The formation of Ni islands suggests that the film of Cu_xS has an un-homogenous structure too. This phenomenon pleads for an island mechanism for the formation of Cu_xS film, a mechanism characteristic for the formation of semi-conducting films by Chemical Bath Deposition on conducting or non-conducting substrates. Islands effect is annihilated during the growth of the film, when the islands are joined, forming a continuous film.

When Cu_xS films with electrical resistance higher than 100 Ω/sq are used as substrates for Ni deposition, the “island phenomenon” can’t be observed at macroscopical level. That was the reason for using as substrates for Ni deposition samples having electrical resistances smaller than 100 Ω/sq.

The conditions for Ni electro-deposition on a two layered Cu_xS film, as well as the initial and final electrical resistance are presented in Table 1. Nickel films were deposited at room temperature.

Table 1. The conditions for Ni electro-deposition.

Sample	1	2	3
R _i (Ω/sq)	40	33-37	37-40
Current density Dc [A/dm ²]	10	10-18	22
Deposition duration [min]	2	5	4
R _f [Ω/sq]	7-8	6-7	6-7
Observations	Grey shiny compact adherent, films		
R _i - initial electrical resistance			
R _f - final electrical resistance			

From Table 1 it can be seen that working with current densities ranged between 10-22 A/dm², the deposition of nickel leads to the decreasing of electrical resistance of the obtained multilayered composite more than 5 times. The resulted layer has electrical resistances from 6-8 Ω/sq.

The adherence of the films on the substrate was evaluated semi-quantitatively by using “tape test”, both for ABS/Cu_xS and ABS/Cu_xS/Ni composites. In order to perform this test, a tape based on Polyethylene Terephthalate (PET) is pressed on the surface of an “as prepared” film, and than is suddenly removed. If the film totally remains on the substrate, it has an adherence higher

than 300-500 pounds per square. Generally the minimal demands related to the adherence of these kinds of films are accomplished if they pass “tape test”. The films prepared by us successfully passed this test.

4. Conclusions

Composite multilayered materials of ABS/Cu_xS/Ni were obtained. The etching treatment applied in order to obtain highly adherent films influences the electrical properties of the deposited Cu_xS film. Using mixtures containing acetone: water 1:1 solutions, the electrical resistance for the deposited copper sulphide varied between 76 Ω/sq, for a treatment time of 240 minutes to 260 Ω/sq, for a treatment time of 100 minutes. Using mixtures containing acetone: water 2:1 solutions, the electrical resistance varied between 165 Ω/sq, for a treatment time of 20 minutes to 405 Ω/sq, for a treatment time of 5 minutes. Increasing the concentration of acetone (acetone: water 3:1), leads to the obtaining of Cu_xS with higher electrical resistances: 4200 Ω/sq, for a treatment time of 10 minutes to 4500 Ω/sq, for a treatment time of 60 minutes. If chromic mixture was used for etching treatment, the electrical resistances were smaller: from 40 Ω/sq, for a treatment time of 10 minutes to 72 Ω/sq, for a treatment time of 60 minutes. In order to obtain copper sulphides with smaller resistance we deposited two layers of copper sulphide before the deposition of Ni.

For the deposition of Ni, samples with resistances of 33-40 Ω/sq were selected. After the deposition of nickel, the electrical resistance of obtained multilayered composites decreased more than 5 times.

The technique of deposition of an intermediate layer of copper sulphide in order to obtain a conducting plastic has an important advantage in comparison with classical technology, because the number of stages is reduced, and the necessity of using noble metals (Ag or Pd) is eliminated.

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