Conductive copper sulfide thin films on polyimide foils

J Cardoso[1,2], O GomezDaza[1], L Ixtlilco[1], M T S Nair[1] and P K Nair[1]

[1] Department of Solar Energy Materials, Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Temixco 62580, Morelos, Mexico
[2] UAM-I, CBI, Departamento de Física, Apartado Postal 55-534, CP 09340-México, DF, Mexico

E-mail: pkn@mazatl.cie.unam.mx and jcam@xanum.uam.mx

Abstract
Kapton polyimide is known for its high thermal stability, $>400\,°C$. Copper sulfide thin films of 75 and 100 nm thickness were coated on DuPont Kapton HN polyimide foils of 25 μm thickness by floating them on a chemical bath containing copper complexes and thiourea. The coated foils were annealed at 150–400 °C in nitrogen, converting the coating from CuS to $Cu_{1.8}S$. The sheet resistance of the annealed coatings (100 nm) is 10–50 $\Omega/\square$ and electrical conductivity, $2–10\times10^3\ \Omega^{-1}\ cm^{-1}$, which remain nearly constant even after the foils are immersed in 0.1–1 M HCl for 30–120 min. The coated polyimide has a transmittance (25–35%) peak located in the wavelength region 550–600 nm, with transmittance dropping to near zero below 450 nm and below 10% in the near-infrared spectral region. These characteristics are relevant in solar radiation control applications. The coated foils might also be used as conductive substrates for electrolytic deposition of metals and semiconductors and for optoelectronic device structures.

1. Introduction

Conventional polyimides are coloured (light amber to black) high-performance polymers with predominantly aromatic molecules [1]:
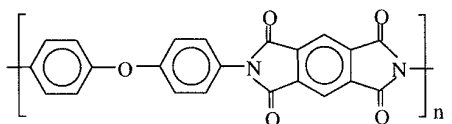
They are commercially known by brand names, Kapton, Kinel, Upilex, Upimol, Vespel etc, and are reputed for their high thermal stability, radiation resistance, inherently low flammability and smoke emission [2]. The properties of these polymers include high adhesion to copper coatings (peel resistance 10–20 N cm^{-1}) [3], high tensile modulus (2–4 GPa) and tensile strength (70–150 MPa), low water absorption (0.2–3% in 24 h), high hydrolytic stability in acid medium and high upper working temperatures (250–320 °C, depending on the number of aromatic groups) [2].

The initial development of aromatic polyimide films was driven by a market need for a thin insulating wrap (25–75 μm) on copper wires for traction motors and aircraft wiring

that would be thermally stable at an operating temperature of up to 220 °C [4]. Application in flexible printed circuit boards followed. Perspectives for application of polyimides as flexible solar radiation protectors, as orientation films in liquid crystal display devices, as optical waveguides and half wave-plates etc, have promoted interest in the development of optically transparent colourless polyimides [5].

In this paper we present the characteristics of electrically conductive copper sulfide coatings obtained on aromatic polyimide foils (Kapton HN, DuPont de Nemours, supplied by Goodfellow [2]) using a previously reported chemical bath formulation [6]. The coatings were annealed at different temperatures (150–400 °C) in a nitrogen atmosphere. As a result of this study, we found the coated polyimide foils to be stable at temperatures up to 400 °C with respect to optical and electrical properties. They show sheet resistance of 10–50 $\Omega/\square$ and electrical conductivity of $2–10\times10^3\ \Omega^{-1}\ cm^{-1}$ after annealing. It is well known that copper sulfide acquires this conductivity due to copper deficiency [7] and that a range of semiconductors in the Cu_xS system possessing different crystalline structures is possible [8]. Applications of Cu_xS coatings in solar radiation absorbers [9], solar cells [10] and solar radiation control coatings [11] have been previously

reported. We consider that the results presented here might be of general interest to researchers involved in the science and technology of polyimides, as well as in Cu_xS as a degenerate conductive coating. Applications as solar control coatings, as conductive substrates for the deposition of metal or semiconductor coatings by electrolytic deposition and as a conductive base for optoelectronic device structures are among the possibilities.

2. Experimental details

Deposition of the films

CuS was deposited from a chemical bath on a polyimide (Kapton) film of 25 μm thickness supplied by Goodfellow [2]. These foils are coloured yellow due to optical absorption associated with intra- and inter-molecular charge transfer complexes in the polyimide [5].

We used a chemical bath, prepared as reported in [6], for the deposition of CuS thin films. A 100 ml bath was prepared by mixing the following solutions in the given sequence with continuous stirring: 10 ml of a 0.5 M solution of Cu (II) chloride, 5 ml of 3.7 M triethanolamine, 8 ml of 15 M ammonia (aq.), 10 ml of 1 M sodium hydroxide, 6 ml of 1 M thiourea and the rest deionized water. Except thiourea, from Productos Químicos Monterrey, all other chemicals used were Baker analysed reagents. The solution was transferred to a shallow glass tray to a height of 5 mm and the polyimide foil was floated on it. The deposition proceeded at room temperature, 26 °C, for 4 and 8 h duration, after which the samples were removed, washed in running tap water and rinsed in deionized water and dried in hot air. It was not possible to determine the thickness by step measurement owing to the difficulty in creating a step on the film by etching with acid, so we estimated the thickness by comparing the interference colour produced by the coating in reflected daylight with that produced by the coatings on glass substrates. The estimate of thickness was 75 nm (4 h) and 100 nm (8 h).

In order to investigate the thermal stability of the coated foils, samples of small sizes were cut and placed between pairs of clean 3 mm sheet glass. These were held by pressure clips and introduced into a vacuum oven (T-M High Vacuum Products Inc., NJ). This arrangement would prevent corrugation of the coated foil when annealed at 400 °C. The annealing was carried out for 1 h at each desired temperature (150–400 °C) after evacuating the chamber to 20 mTorr and then introducing nitrogen into the chamber to maintain a pressure of 100 mTorr. This procedure was found to be successful in avoiding the presence of residual oxygen in the chamber [12], which would otherwise transform the copper sulfide coatings into sulfates and oxides at temperatures above 220 °C [13].

Characterization

X-ray diffraction (XRD) patterns of the coatings were obtained with a Rigaku system, using Cu Kα radiation. Optical transmittance (reference air) and near-normal specular reflectance spectra (reference aluminum mirror) of the coated foils were recorded on a Shimadzu PC3100 UV–VIS–NIR spectrophotometer in the wavelength range 200–2500 nm. In both measurements, the light beam was incident on the coated surface. The sheet resistance was directly measured with a multimeter using pairs of silver print electrodes (5 mm length at 5 mm separation) painted on the coating. The coatings subjected to different annealings were floated with the coating facing downward on 0.1 and 1 M HCl solution, to assess their stability to serve as conductive substrates for electrolytic deposition.

3. Results and discussion

Structure and composition

Figure 1 shows the XRD patterns of the coated foil before and after annealing at 400 °C. The patterns are dominated by the amorphous envelope and peaks due to some degree of crystallinity of the polyimide foil. There is no major change seen in the substrate foil subjected to annealing at 400 °C. The presence of the copper sulfide coating in the CuS form is detected from the presence of the (110) peak of covellite (CuS, JCPDS 6-464) with intensity 70% at $2\theta = 47.9°$. The (103) peak of covellite near $2\theta = 31.8°$ (100% intensity) is also seen. The coating annealed at 400 °C shows clearly the conversion of CuS to $Cu_{1.8}S$. The dominant (220) peak of digenite ($Cu_{1.8}S$, JCPDS 24-61) at $2\theta = 46°$, as well as the (200) and (311) peaks, are seen. The presence of other crystalline phases such as chalcocite is not ruled out. These results are in accordance with that reported before [12]—chemically deposited CuS thin films on glass substrates transformed to $Cu_{1.8}S$ (300 °C) and to a mixture of $Cu_{1.8}S$ and $Cu_{1.96}S$ (400 °C). We would like to mention here that annealing of CuS on polyester and acrylic substrates is not possible at such temperatures. The upper working temperature of polyester (polyethylene terephthalate, PET, PETP) is rated at 115–170 °C and that of acrylic (polymethyl methacrylate, PMMA) is 50–90 °C [2]. In an earlier paper on CuS coatings on PMMA, we reported that the coatings lost their specular reflectance when annealed at temperatures above 110 °C, thus limiting application as a solar radiation control glazing [14]. The thermal stability of polyimide foils permits such thermal processing without any adverse effect.

Electrical properties

Figure 2 shows the variation of the sheet resistance of copper sulfide coating of two different thicknesses with temperature of annealing for 1 h each. In general the behaviour matches the results reported in [2]. Initially the sheet resistance decreases because of an increase in the crystallinity of CuS. At 300 °C, the material has converted partially to $Cu_{1.8}S$, and has improved in crystallinity as well, taking the sheet resistance to nearly 10 $\Omega/\square$ for the 100 nm coatings. Assuming the thickness to remain of this order, the conductivity of the coating may be estimated (reciprocal of sheet resistance × thickness) as 10^4 Ω^{-1} cm^{-1}. This coating is a degenerate p-type semiconductor. Such high electrical conductivity of the Cu_xS system has been discussed in [7] for bulk materials and in [10, 15] for thin films. The general trend in the films is a decrease in conductivity or increase in sheet resistance with increase in x from 1.8 to 2.0. Annealing the coatings at 400 °C leads to loss of sulfur from the coatings and formation of
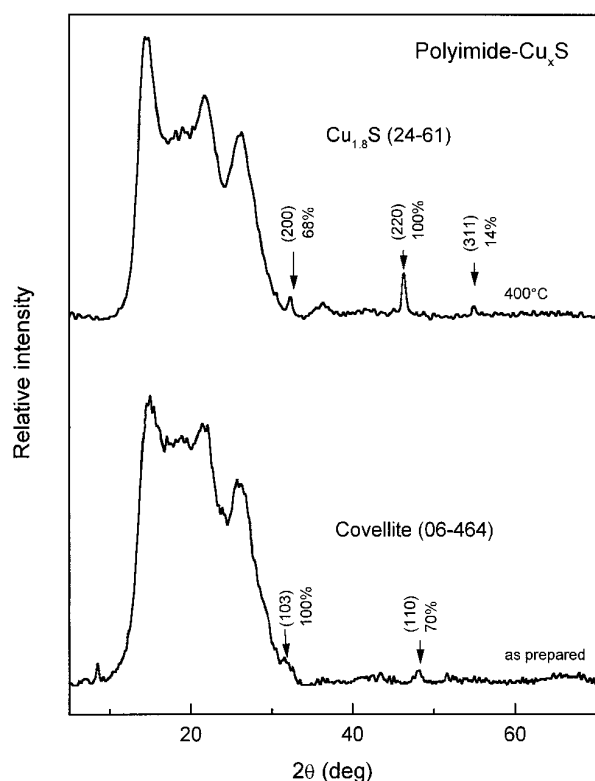
Figure 1. XRD patterns of polyimide foils coated with 100 nm copper sulfide coating, recorded before (as prepared) and after annealing at 400 °C for 1 h.

Figure 2. Sheet resistance of polyimide foils coated with copper sulfide thin films of 75 and 100 nm thickness, measured after annealing the coated foils for 1 h each at the different temperatures shown.

copper rich components, thus increasing the sheet resistance. Another contributing factor might be that the components of the coatings might diffuse into the interior of the polymer substrate, reducing the effective thickness of the coating. Both these lead to higher sheet resistance, as observed here.

We also note that, for partially conducting media of conductivity Φ, the optical reflection coefficient, R, for the air–medium interface at a wavelength λ is given by [16] $1-4(\pi c \epsilon_0 / \sigma \lambda)^{1/2}$, where c is the velocity of light and ϵ_0 is the permittivity of free space. At an electrical conductivity of 10^4 Ω^{-1} cm^{-1}, R would be 77% for $\lambda = 2500$ nm. However, this is when the medium is of sufficient thickness (higher than twice the skin depth), calculated as 130 nm for the above conductivity [16]. Since the film thickness (100 nm) is less than this, a reflectance of <77% is expected for the coating annealed at 300 °C.

The coated foils with sheet resistance of 10–50 $\Omega/\square$ may find application to serve as electrical contacts in optoelectronic device structures.

Optical properties

Figure 3 shows the optical transmittance, $T(\%)$, and specular reflectance, $R(\%)$, of the coatings. Also shown are the transmittance spectra of the DuPont Kapton HN polyimide foils of 25 μm thickness. The foils appear amber coloured in daylight due to electronic transitions in the charge transfer complex formed within and among the polymer chains [5], which produces strong optical absorption at wavelengths below
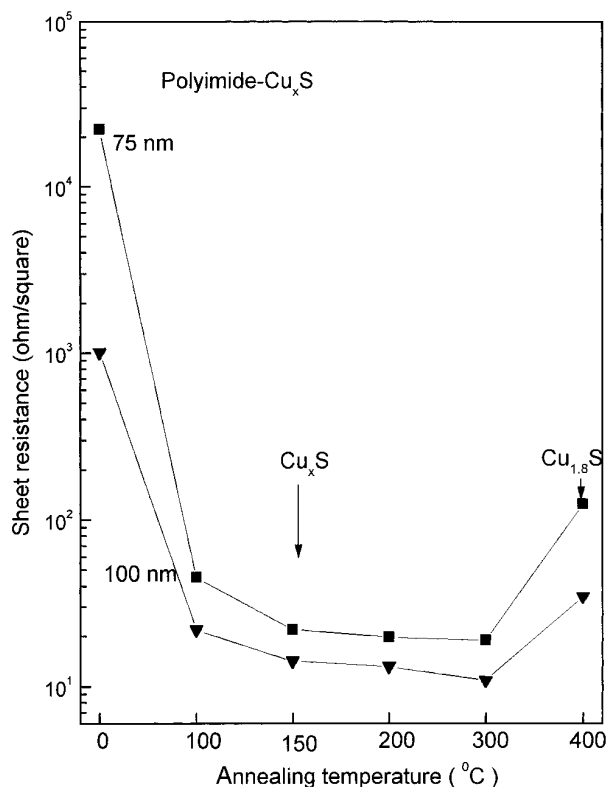
550 nm or at photon energies above 2.25 eV. Annealing at 400 °C does not alter the optical transmittance in the infrared and affects it only marginally in the visible region. This illustrates the high thermal stability of the charge transfer complex in polyimide.

In the case of the coated foils, the annealing at 300 °C that reduces the sheet resistance to nearly 10 $\Omega/\square$ leads to very low transmittance (<5%) in the near infrared. This arises predominantly as a consequence of a high reflectance of >60% at a wavelength of 2500 nm as mentioned above. The increase in the sheet resistance, or reduction in the conductivity, in the coating annealed at 400 °C has the effect of reduction in the reflectance and increase in the transmittance. The transmittance in the near-infrared region is also reduced due to the free carrier absorption process, which has been discussed before for the case of degenerate copper chalcogenide semiconductors [15, 17]. Overall, the band-to-band absorption, which is dominant in the visible–ultraviolet region, and the free carrier absorption and reflection in the infrared region of the spectrum, give rise to an asymmetric bell-type transmittance. The optical transmittance is peaked near the greenish yellow region at which the human eye has maximum sensitivity in daylight vision. This optical behaviour suggests the use of the present coatings in solar control glazings as discussed in [11].
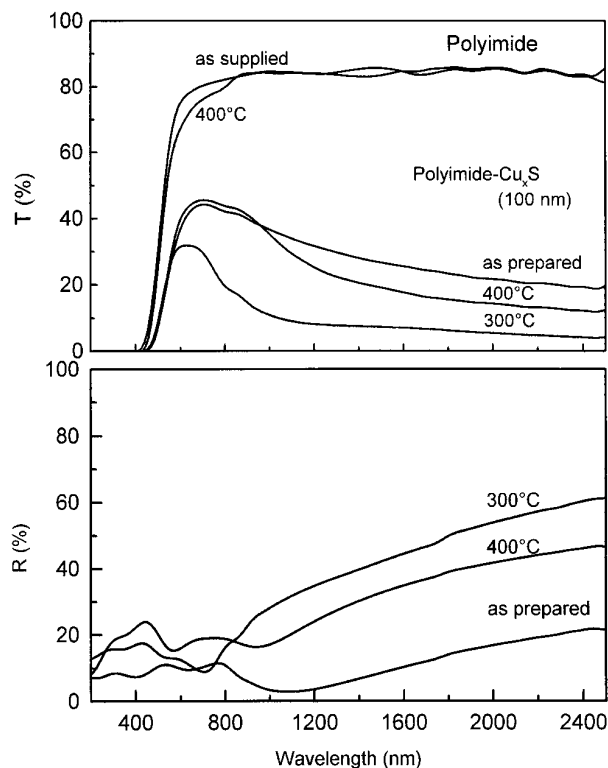
Figure 3. Transmittance, $T(\%)$, and specular reflectance, $R(\%)$, of polyimide foils and of those with Cu_xS coatings of 100 nm, before and after annealing for 1 h each at the temperature indicated.

Figure 4. Sheet resistance of annealed (1 h at 300 and 400 °C) polyimide foils with copper sulfide coatings of 100 nm after etching in 1 and 0.1 M solutions of HCl as a function of duration of immersion.

Stability of copper sulfide coatings on polyimide foils

The chemical structure of polyimide facilitates adhesion of CuS coating without pre-treatment because polyimide undergoes a partial hydrolysis to interact with copper in chemical bath deposition. We note here that a comprehensive pretreatment of polyimide surface has been prescribed prior to electroless and electrolytic deposition of copper [3]. In the present case, we achieved uniform copper sulfide coatings directly on as-supplied polyimide foils. The optical characteristics of these coatings (figure 3) are very similar to those of the coatings produced on glass substrates [12] subjected to similar annealing.

Figure 4 illustrates the stability of the coatings in dilute acids. This was done to examine the feasibility of using the electrically conductive coatings produced on polyimide to serve as electrical contacts in the electrolytic deposition of metals such as for light reflectors [3] or of semiconductor materials for solar cell applications [18]. It is seen that the coatings annealed at 300 °C remain stable in 0.1 and 1 M HCl for more than 30 min. The coatings remain reasonably stable for more than 90 min. According to the deposition procedure mentioned in [3], such chemical stability is appropriate for the purpose of electrolytic deposition. We would like to mention here that a CuS coating on many polymer substrates has been found to improve the adhesion of electrolytically deposited metal to polymer [19].

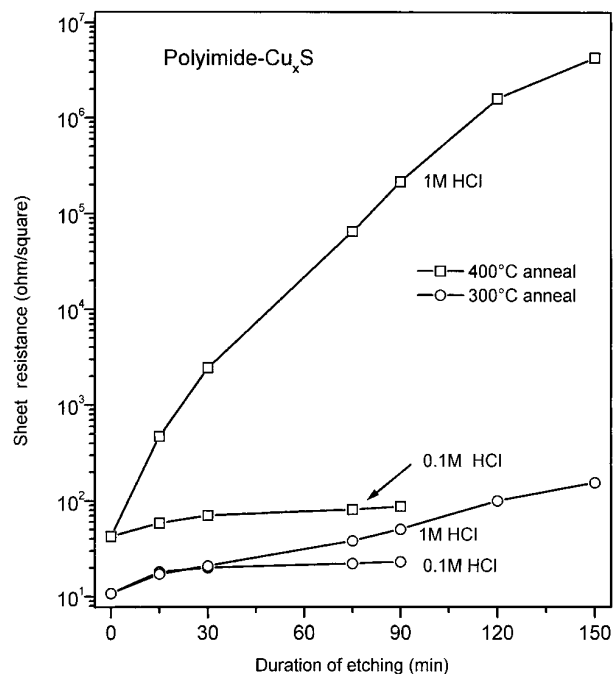All these open up new prospects for polyimides in the field of optical, electrical and optoelectronic applications by combining the excellent thermal and mechanical characteristics which they inherently possess with that of a stable conductive copper sulfide coating.

4. Conclusions

This work was basically inspired by the high thermal stability reported for polyimide and the ever-increasing interest in this polymer for optical applications other than its conventional role as an efficient electric insulator. One of the applications of polyimides might be as a thermally stable substrate for coatings to serve as reflectors for concentrating collectors, heat mirrors and solar control coatings. This is an area currently occupied by PET polyester (polyethylene terephthalate) foils and castings, which is thermally less stable than the present foils.

In this paper we have demonstrated that uniform copper sulfide coating may be obtained on polyimide foils by floatation in a chemical bath. The structure, composition and electrical and optical properties of the coatings were modified by annealing the coatings at temperatures up to 400 °C, without polyimide substrates exhibiting mechanical deformation. Some of the possible applications of the coated foils have been suggested.

References

[1] Licari J J and Hughes L A 1990 *Handbook of Polymer Coating for Electronics: Chemistry, Technology and Applications* 2nd edn (Park Ridge, NJ: Noyes) p 55

[2] Goodfellow Catalogue 1998–99 webpage www.goodfellow.com p 512

[3] Suchentrunk R (ed) 1993 *Metallizing of Plastics—a Handbook of Theory and Practice* (Finishing) p 181

[4] Kreuz J A and Edman J R 1998 *Adv. Mater.* **10** 1229

[5] Ando S, Matsuura T and Sasaki S 1997 *Polym. J.* **29** 69

[6] Nair P K, Garcia V M, Fernandez A M, Ruiz H S and Nair M T S 1991 *J. Phys. D: Appl. Phys.* **24** 441

[7] Okamoto K and Kawai S 1973 *Japan. J. Appl. Phys.* **12** 1130

[8] Loferski J J, Shewchun J, Mittleman S D, DeMeo E A, Arnott R, Huang H L, Beauliew R and Chapman G 1979 *Solar Energy Mater.* **1** 157

[9] Agnihotri O P and Gupta B K 1981 *Solar Selective Surfaces* (New York: Wiley) p 105

[10] Chopra K L and Das S R 1983 *Thin Film Solar Cells* (New York: Plenum) p 311

[11] Nair M T S and Nair P K 1989 *Semicond. Sci. Technol.* **4** 599

[12] Nair M T S, Guerrero Laura and Nair P K 1998 *Semicond. Sci. Technol.* **13** 1164

[13] Nair P K, Nair M T S, Pathirana H M K K, Zingaro R A and Meyers E A 1993 *J. Electrochem. Soc.* **140** 754

[14] Hu H and Nair P K 1996 *Surf. Coat. Technol.* **81** 183

[15] Nair M T S and Nair P K 1989 *Semicond. Sci. Technol.* **4** 191

[16] Pain H J 1979 *The Physics of Vibrations and Waves* 2nd edn (Bristol: Wiley) p 194

[17] Garcia V M, Nair P K and Nair M T S 1999 *J. Cryst. Growth* **203** 113

[18] Bhattacharya R N, Granata J E, Batchelor W, Hasson F, Wiesner H, Ramanathan K R, Kean J, Noufi R N and Sites J R 1997 *Proc. SPIE* **3138** 90

[19] Zebrauskas A, Spirikaviciene R and Baranauskas M 1990 *J. Adhes. Sci. Technol.* **4** 25