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PROSPECTS OF CHEMICALLY DEPOSITED CoS-Cu_2S COATINGS FOR SOLAR CONTROL APPLICATIONS

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ABSTRACT

Good quality thin films of Cu_2S were successfully deposited on CoS-precoated glass substrates by the chemical bath deposition process using triethanolamine (TEA) and aqueous ammonia NH_3(aq) as complexing agents and Copper II nitrate and thiourea as precursors. The thin films of Cu_2S deposited on CoS-precoated glass substrates from chemical baths and annealed at 100°C were found to have desirable solar control characteristics superior to commercial tinted glass and magnetron sputtered multilayer metallic solar control coatings. These include: transmission spectra in the visible region similar to photopic vision spectra, with an integrated transmittance in the range of about 23-28% and an integrated reflectance of about 10-15%, coupled with a range of colours in transmitted and reflected daylight. Moreover, the coating of the glass substrates with a thin layer of CoS prior to Cu_2S film deposition was found to improve the mechanical stability of the Cu_2S thin films, offering the choice of different shades of colours for the same integrated transmittance in the visible region in solar control applications. The possibility therefore exists for multiple-dip deposition of Cu_2S films to enhance the film thickness, enabling the realisation of solar absorber coatings.

Key Words: CoS – Cu_2S Thin Films, Solar Control Coatings, Chemical Deposition

INTRODUCTION

The applications of suitable thin film coatings directly deposited onto glazings as adhesive coatings can be used to save a considerable amount of energy, which provides an acceptable comfort level inside buildings. This can be in the form of solar control coatings or selective solar radiation filters required for glazing applications in warm climate and heat mirror coatings required for applications in cold climate (Lampert, 1981; Ritchie and Wilfred, 1987). Solar control coatings are required for architectural glazing applications in locations with a warm climate. Their use is particularly vital for energy conservation in buildings when conventional ideas in passive architecture are not acceptable - such as in tower-type edifices in urban set-up and when windows are required to face east or west in search of scenic beauty. In ideal situations the solar control coatings must enable controlled optical transmittance within the visible range ($T^*(vis) \sim 10\text{-}50\%$) and low reflectance ($R^*(vis) < 10\%$) in the visible region (0.40-0.70μm) and high reflectance ($R^*(ir) \sim 90\%$) for longer wavelength (> 0.70μm) radiations. These characteristics are capable of providing an adequate natural illumination of the interior of the buildings while a cut-off of much of the incident radiations which might cause an undesirable increase in the interior temperature of the building is achieved. This will consequently lead to a great reduction in cooling cost in areas with warm climate (Nair et al., 1989). In contrast, the ideal heat mirror coatings must possess a high transmittance (~ 90%) in the entire solar spectrum (up to ~ 2.50μm). It also possesses a high reflectance (~ 90%) for thermal radiations. This causes temperatures to rise inside buildings in colder regions thereby reducing heating costs.

Generally the effects of optical absorption are quite different in solar control and heat mirror coatings. Primarily, absorption is unwanted since it reduces the transmission. However, the absorbed radiation is converted into heat which is unwanted in solar control applications, but of value in the case of heat mirror coatings. A solar control film should therefore be applied on the inner surface of the outer glass, while a heat mirror coating is most useful on the outer surface of the inner glass. Commercial solar control glazings usually employ metallic coatings obtained by capital-intensive high vacuum techniques (Lampert, 1981; Ritchie and Wilfred, 1987).

Solar control characteristics of chemically deposited Cu_2S thin films using various precursors and complexing agents have been extensively reported (Nair et al., 1989; Nair and Nair 1989a; Nair et al., 1987; Bhattacharya and Pramanik 1981; Nair and Nair 1989b; Nair and

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Nair 1992). The films however, suffer from poor adhesion on glass substrates. It has been demonstrated that pre-coating the glass substrates with suitable metal sulphide films prior to the deposition of Cu_2S thin films solves the problem of poor adhesion to a great extent, while offering optical characteristics desirable for various applications (Nair and Nair, 1992). Chemical deposition of Cobalt sulphide thin films and their strong adhesion on glass substrates have been reported previously (Eze and Okeke 1997; Eze 2001). In this paper we report on the use of chemically deposited CoS thin films as a substrate film on glass for the chemical deposition of Cu_2S thin films. We also evaluate the solar control characteristics of the films in the glass-CoS-Cu_2S structure.

EXPERIMENTAL DETAILS

DEPOSITION OF THE FILMS

CoS Thin Films

The chemical bath composition found suitable for the deposition of CoS thin films on glass substrates at room temperature for durations up to forty eight hours is as follows: 15 ml of 0.5M cobalt sulphate solution, 5ml of 0.2M EDTA, 15 ml of 13.36M aqueous ammonia and 15ml of 0.5M thiourea $(NH_2)_2CS$. Various chemical baths were set up by changing the Co:TU mole ratios.

The conditions of deposition for CoS thin films used in the present work are listed in table 1. The test samples of CoS as well as CoS-Cu_2S thin films were deposited on 76mm x 26mm x 1mm glass slides for optical transmittance and absorbance measurements. Prior to the film deposition the glass slides were thoroughly cleaned in cold solution of detergent and rinsed with distilled water. They were subsequently soaked in aquaregia for 12 hours, re-washed with distilled water and then dried in air. The cleaned substrates were supported vertically on the wall of the 50ml beakers containing the above solution for deposition.

The CoS coated substrates were removed from the bath, washed well with distilled water, and dried in air. The films appeared uniformly brown in reflected daylight and rusty orange in transmitted daylight. Some of these films were used as substrate films for the deposition of Cu_2S thin films.

Cu_2S Thin Films

The chemical bath deposition of Cu_2S film is possible from a wide range of bath compositions (Nair and Nair, 1987). In the present case the chemical baths were constituted from 10ml of 0.5M copper II nitrate solution, 5ml of 7.5M triethanolamine (TEA), 10ml of 13.36M

TABLE 1: Details of the Chemical Deposition of CoS, Cu_2S and CoS- Cu_2S thin Films

	Thin Film Deposition					Thickness (nm)		Substrate side
Sample Label	Substrate	Material	Duration H, min	Molar Ratio Co: EDTA: NH_3: TU Cu: TEA: NH_3: TU:	Bath Temp (°C)	Substrate CoS	top Film	Daylight Appearance
A	Glass	CoS	24	0.5: 0.2: 13.36: 0.5	29	0.09	-	Silvery brown
B	Glass	CoS	48	0.3: 0.2: 13.36: 0.5	29	0.14	-	Brown
C	Glass	CoS	72	0,3: 0.2: 13.36: 0.3	29	0.17	-	Brassy brown
D	Glass	Cu_2S	7	0.5: 7.5: 13.36: 0.5	29	-	282	Greenish-blue
E	Glass	Cu_2S	6	0.5: 7.5: 13.36: 0.3	29	-	271	Bluish-purple
F	Glass	Cu_2S	4	0.3: 7.5: 13.36: 0,3	29	-	266	Greenish-yellow
G	CoS	Cu_2S	4	-	29	0,09	300	Brownish-blue
H	CoS	Cu_2S	4	-	29	0.16	298	Purple-blue
I	CoS	Cu_2S	4	-	29	0.12	291	Brownish-blue
K	CoS	Cu_2S	4	-	29	0.17	326	Brownish-blue

NH_3(aq) and 10ml of 0.5M of thiourea (TU). Various chemical baths were obtained by varying the Cu:TU mole ratio. Deposition conditions stated for samples G-K in table I show that the presence of CoS substrate film provides the necessary mechanical stability to the Cu_2S films for longer deposition periods and multiple dip depositions so that higher film thickness may be obtained. All the samples have been annealed at 100°C for l h to obtain improved solar control characteristics.

Characterization

The film thickness was measured using an Alpha Step instrument and values up to about 350nm were obtained. The film deposited on the side of the substrate facing the wall of the beaker was retained for the various measurements. The film on the other side of the substrate was removed with cotton swabs moistened in dilute acids. The optical absorbance A and transmittance T were measured using a DR–200 UV–VIS double beam spectrophotometer in the wavelength range 350 – 900nm. The spectra were recorded for glass substrate-side incidence of the light beam, bearing the intended application in mind. The reflectance R of the film was deduced from the relation, T + R + A = I.

Evaluation of Solar Control Characteristics

For the comparison of the solar control characteristics of the films, we define the integrated transmitted intensity (I_T) and integrated reflected intensity (I_R) for the appropriate solar spectrum (Holzman 1989):

$$I_{T,\lambda_1\text{-}\lambda_2} = \frac{1}{100}\int_{\lambda_1}^{\lambda_2} E_\lambda T_\lambda d\lambda \quad \text{and} \quad I_{R,\lambda_{-1}\lambda_2} = \frac{1}{100}\int_{\lambda_1}^{\lambda_2} E_\lambda T_\lambda d\lambda \qquad \text{.....(1)}$$

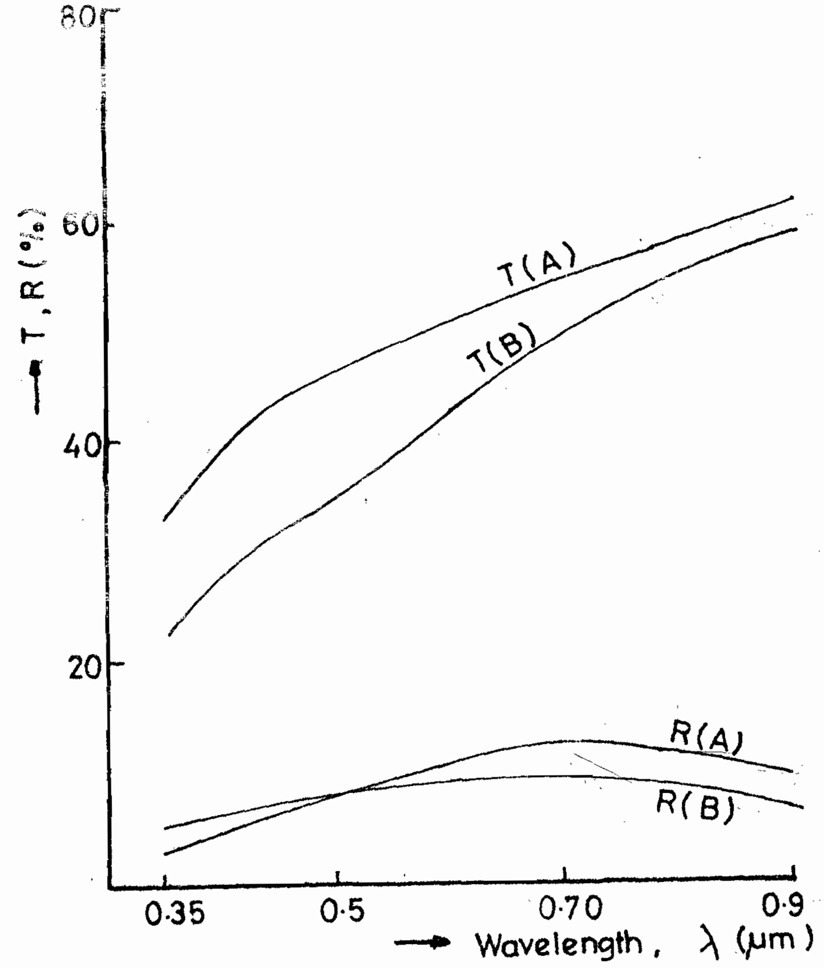

Figure 1: Optical transmission T(A), and T(B) reflection R(A), R(B) spectra of the CoS thin films.

where the incident intensity in the spectral range $\lambda_1 - \lambda_2$ is

$$I_{\lambda_1-\lambda_2} = \int_{\lambda_1}^{\lambda_2} E_{\lambda}\, d\lambda \qquad \text{.........} \ (2)$$

The integrated transmittance (T*) and the integrated specular reflectance (R*) for the spectral range $\lambda_1 - \lambda_2$ are:

$$R^*_{\lambda_1-\lambda_2} = \frac{100\ I_{T,\lambda_1-\lambda_2}}{I_{T,\lambda_1-\lambda_2}} \quad \text{and} \quad R^*_{\lambda_1-\lambda_2} = \frac{100\ I_{R,\lambda_1-\lambda_2}}{I_{T,\lambda_1-\lambda_2}} \qquad \text{..........} \ (3)$$

The integrations are carried out in the spectral range 400 – 700nm for the visible (VIS) region of the electromagnetic spectrum, 700 – 2500nm range for the infrared (IR) region and for the solar spectrum (SOL) in the entire 350 –2500nm region. Spectral irradiance (E_λ) values corresponding to AM2 solar spectrum are generally chosen for all the calculations to represent the case in tropical locations. The E_λ values are available from sources such as (Chopra and Das, 1983).

The distribution of the incident intensity among the various components of the reflected and transmitted radiation can be expressed as percentage of the intensity of AM2 radiation (745Wm^{-2}), i.e. as I_T (VIS), I_R (VIS), I_T(IR) and I_R(IR) where,

$$I_T\,(\text{VIS}) = \frac{\int_{400\text{nm}}^{700\text{nm}} E_\lambda T_\lambda\, d\lambda}{745\text{Wm}^{-2}} \ ; \quad I_T\,(\text{IR}) = \frac{\int_{700\text{nm}}^{2500\text{nm}} E_\lambda T_\lambda\, d\lambda}{745\text{Wm}^{-2}} \qquad \text{.......} \ (4)$$

$$I_R\,(\text{VIS}) = \frac{\int_{400\text{nm}}^{700\text{nm}} E_\lambda R_\lambda\, d\lambda}{745\text{Wm}^{-2}} \ ; \quad I_R(1R) = \frac{\int_{700\text{nm}}^{2500\text{nm}} E_\lambda R_\lambda\, d\lambda}{745\text{Wm}^{-2}} \qquad \text{......} \ (5)$$

Thus the percentage of absorbed solar radiation can be expressed as

$$A^*(\%) = 100 - [I_T(\text{VIS}) + I_R(\text{VIS}) + I_T(\text{IR}) + I_R(\text{IR})] \qquad \text{........} \ (6)$$

However, limitations on our spectrophotometer could not allow us to extend the wavelength range of our measurements beyond 900nm. Thus, our calculations were limited only to the visible region of the electromagnetic spectrum.

RESULTS AND DISCUSSION

Deposition Characteristics

The solution composition found suitable for the deposition of CoS thin films on glass substrates used in the present work, (samples A-C) are listed in table 1. We consider that optimization of the deposition bath and temperature may make possible good quality CoS films of thickness greater than 200nm. In the present work, where our intention has been to illustrate the application of these films as substrates for the chemical deposition of other metal sulphide films, thicknesses less than 200nm corresponding to samples A–C have been found to be sufficient. The CoS thin films deposited on glass substrates appeared pale-brown in transmitted daylight

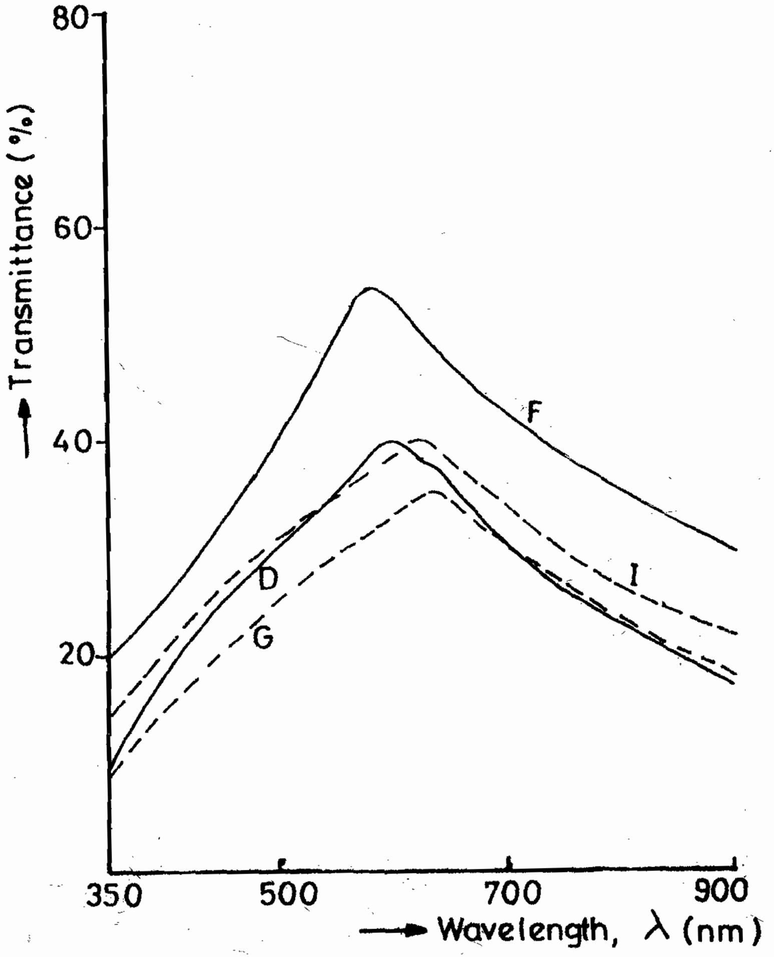

Figure 2: Optical transmission spectra of the various Cu_2S and CoS-Cu_2S thin films: D, F – Cu_2S; G, I – CoS-Cu_2S.
The specifications are given in table 1.

and silvery brown in reflected daylight. They showed remarkable adhesion to the glass substrates as demonstrated by a Scotch tape test. This showed excellent agreement with previous results (Eze and Okeke 1997; Eze, 2001).

Details of the chemical deposition of Cu_2S thin films from aqueous solution of Cu II nitrate, TEA, NH_3 (aq. 30%), NaOH and thiourea (TU) are given in table 1 (Samples D-F). The detachment of the Cu_2S films from glass substrates at longer durations of deposition has prevented us from achieving film thicknesses greater than about 300nm. Moreover, the use of a protective polymer coating over the film, as required in the solar control and solar absorber coating applications of the films, has been found to transfer the films on to the polymer foil in peeling tests (Nair and Nair, 1992). The deposition conditions stated for samples G–K in table1 show that the presence of the CoS substrate film provides the necessary mechanical stability to the Cu_2S films for longer deposition periods and multiple dip deposition so that higher film thicknesses may be obtained as may be required for solar absorber coatings. The samples have been annealed in air at 100°C for it to improve the optical properties of the films.

OPTICAL AND SOLAR CONTROL CHARACTERISTICS

The optical transmission and reflection spectra of the 100°C air annealed CoS thin films (samples A-B), are shown in fig. 1. The average transmittance of the 100°C annealed CoS films is about 43% in the visible region of the electromagnetic spectrum and about 57% in the 750 – 900nm wavelength range. The reflectance, on the other hand, shows rather broad peaks toward the end of the visible region. The transmission spectra for the 100°C air annealed Cu_2S and CoS-Cu_2S thin films show well defined peaks in the middle of the visible region of the electromagnetic spectrum as shown in fig. 2. The reflection spectra of the 100°C air annealed Cu_2S and CoS–Cu_2S thin films are shown in fig. 3 (samples D-F and G-I). The optical reflectance of the films shows a minimum in the middle of the visible region. The transmittance and reflectance spectra of the Cu_2S and CoS-Cu_2S thin films illustrate the following:

(i) Cu_2S films exhibiting nearly the same optical transmittance but different shades of colours in reflected daylight can be produced using CoS substrate films of different thicknesses in the 90-170nm range (e.g. samples G-K of table 1). The solar control characteristics of the films indicate integrated visible transmittance T*(VIS) of about 49, 29, and 23%, respectively for the CoS, Cu_2S and CoS-Cu_2S coatings, which provide adequate greenish-yellow, brownish-blue and greenish-blue illumination levels in the interior of the building-acceptable for much of indoor activities.

(ii) It can be observed from Fig.2 that the optical transmittance spectra of the Cu_2S and CoS–Cu_2S coatings are strongly peaked in the spectral region approximately corresponding to the maximum sensitivity of photopic vision of about 560nm wavelength (Pritchard 1978). Thus any T*(VIS) value for Cu_2S or CoS-Cu_2S coatings provides a higher lighting sensation than metallic solar control coatings with the same T*(VIS) value. More importantly such a glazing is capable of creating the sensation of a particular illumination level at an integrated visible transmittance, T*(VIS) that is lower than at that for the glazing with panchromatic transmittance (Nair and Nair 1989b), thereby improving the energy efficiency of the building.

(iii) Solar control coatings of chemically deposited CoS and Cu_2S thin films in the glass-CoS-Cu_2S structures have the advantage that by controlling the thicknesses of the individual films a range of combinations of T*(VIS), R*(VIS), T*(IR), R*(IR) and colours in reflected daylight, are achievable. This makes them very versatile for architectural glazing applications to suit different space conditioning, illumination level and cosmetic requirements.

(iv) The transmittance of both CoS and Cu_2S thin films in the UV region is very low (less than 10%). This means that polymer protective coatings could be applied to the films without the usual UV degradation of polymers upon prolonged operation under sunlight.

(v) Chemically deposited thin films of glass–CoS-Cu_2S structure can be obtained on the inside or outside of planar or curved surfaces or inside double –walled surfaces. R*(VIS) values

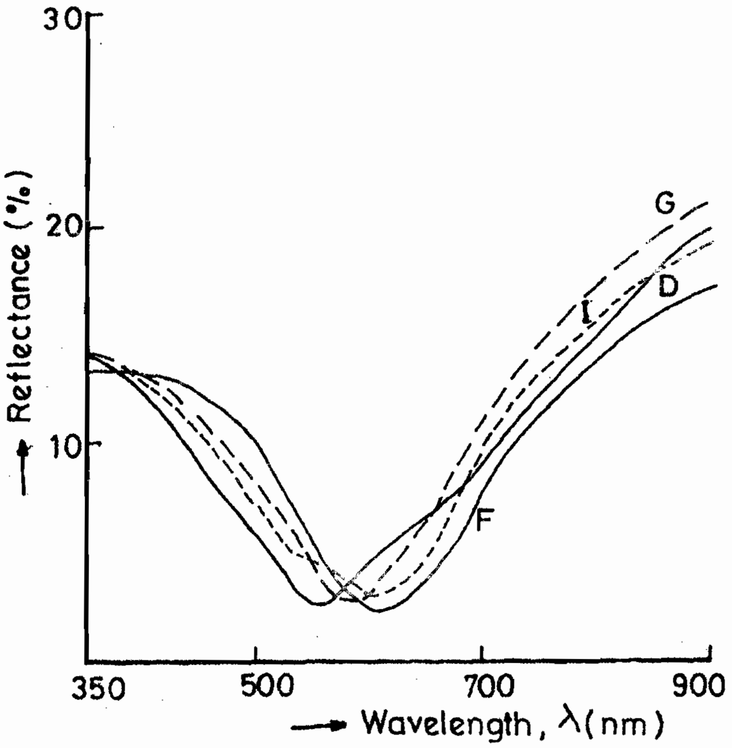

Figure 3: Optical reflectance spectra of the various Cu_2S and CoS-Cu_2S thin films as specified in table 1

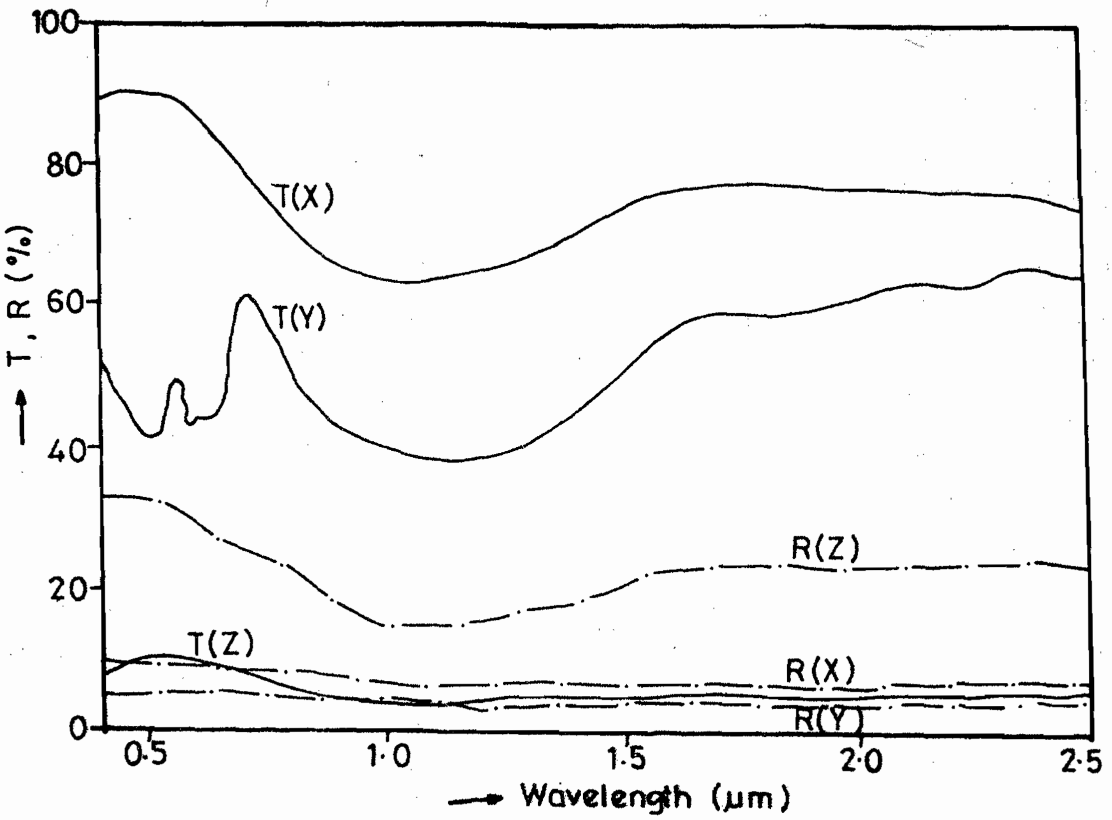

Figure 4: Transmittance T and reflectance R characteristics of commercial glazings, (Ref. 14). X – 6nm clear sheet glass;
Y – 6nm tinted glazings; Z –stainless steel/copper coating on 6nm sheet glass.

of the coatings are in the 10-15% range, with a choice of mildly or brightly coloured shades of golden, purple, bluish, greenish, brownish, yellowish, etc., and the intermediate shades, depending on the thin film combinations. Thus, there is immense potential for these coatings as decorative coatings such as for chandliers, flower vases and glassware.

(vi) For comparison, fig. 4 shows the optical transmission and reflection spectra of commercially available clear sheet glass (X), tinted sheet glass (Y) and the glazing employing magnetron-sputtered multilayer coatings such as copper/stainless steel (Z) (Ritchie and Wilfred, 1987). The tinted glazings exhibit a high infrared transmitted, T*(IR) of about 50%, combined with a low integrated infrared reflectance R*(IR) of about 4%, which is the reverse of what is required. The glazing with the metallic coatings offer acceptable infrared characteristics, e.g. T*(IR) of about 6% and R*(IR) of about 20% but its high integrated reflectance in the visible region, R*(VIS) of about 30% may produce strong glare problems in the neighbourhood.

(vii) Although optical measurements could not be made beyond a wavelength of 900nm, the transmission and reflection spectra in the wavelength range 350-900nm indicate that the CoS-Cu_2S thin films, as reported here, have desirable optical properties that make them suitable as excellent coatings, for solar control applications.

CONCLUSIONS

We have shown in this paper that CoS thin films deposited on glass substrates from chemical baths can be used as a substrate for chemically deposited Cu_2S thin films. The CoS-Cu_2S configuration offers definite advantages over tinted glazings, magnetron sputtered metallic glazings and single- layer chemically deposited glazings in solar control and solar absorber applications. Further work on the characteristics of the films for other possible applications will be reported subsequently.

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