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Analysis and effect of chemically deposited cadmium sulphide (CdS) thin films on solar absorptance and thermal emittance of stainless steel AISI 304 BA 2B

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ABSTRACT

Thin films of cadmium sulphide (CdS) were deposited on 24 polished sample plates of stainless steel AISI 304 BA 2B using chemical bath deposition technique for different molar concentrations of CdS in bath solution at a fixed deposition time and also for a fixed concentration of CdS at different deposition times. The average thermal emittance values of the polished and coated sample plates were determined before and after the deposition of thin films, respectively. The average thermal emittance and average solar absorptance value of the uncoated polished sample plate is 0.15 ± 0.01 and 0.47 ± 0.01 while average thermal emittance values of the coated sample plates is 0.15 ± 0.01 for those done with varying concentrations of CdS in bath solution and a fixed deposition time and for those done with fixed concentration of CdS in bath solution and varying deposition times. Average solar absorptance values for various and fixed CdS concentrations of the coated sample plates in bath solution, fixed and various deposition times gave 0.47 ± 0.01 and 0.64 ± 0.01, respectively. The film thickness of the coated sample plates varied from 0.21 to 0.61 ± 0.01 μm. These low thermal emittance values compare well with those obtained for oxidized stainless steel selective surfaces. The coated sample plates with most favourable conditions of thermal emittance 0.19 ± 0.01, solar absorptance 0.64 ± 0.01 and film thickness 0.44 ± 0.01 μm could find applications in photothermal conversion of solar energy. The results indicate that the chemical bath deposition technique could be employed to fabricate selective surfaces for use in solar energy applications.

Keywords: Thermal emittance, cadmium sulphide (CdS), solar absorptance, thin films, chemical bath deposition technique.

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INTRODUCTION

Energy plays a vital role in the sustenance of life and man's existence. In other words, energy is the life wire of every human activity. Present civilization cannot be without energy. The quality of life depends to a great extent on the availability of energy. The global energy crisis made it clear to man that energy from nature is fast depleting and can no longer sustain the world energy needs (Hayes, 1978). As a result, attention is focused on alternative sources of energy which cannot be depleted that is, solar energy. Many researchers are now working on semiconductor thin films to find out which of them have good enough characteristics to achieve required results for fabrication of selective absorbers using stainless steel to overcome degradation at elevated temperatures and humidity. Examples of such research include chemical and thermal oxidation of 300 series stainless steel (Sharma and Hutchins, 1979), chemical oxidation of stainless steels AISI 321 (Sharma et al.,

1988), coloration of stainless steel by aluminium andodizers using hot chronic and sulphuric acid (Granziera, 1977) and solution growth (Ilenikhena and Mordi, 2005; Ilenikhena, 2008).

Chemical bath deposition technique has been used extensively for the deposition of thin films of sulphides and selenides (Eze and Okeke, 1997; Ndukwe, 1992), oxides (Ezema and Okeke, 2003; Chopra and Das, 1983) and ternary compounds (Ezekoye and Okeke, 2005; Okoli et al., 2006). The films produced by this technique have comparable structural and photoelectric properties to those produced by other techniques and has been applied in producing emerging material for solar cells, solar collectors among others and is now being adopted by some industries (Ilenikhena and Okeke, 2002, 2004; Ezema and Okeke, 2003; Ilenikhena and Mordi, 2005). Also, the choice of this method arises from its low cost, ease of handling, and possibility of application on a large surface; hence it is most suitable for adaptation in developing countries where faculties for other highly expensive and technically advanced techniques such as Chemical Vapour Deposition, Spray Pyrolysis, Electro-Chemical Deposition, Molecular Beam Epitaxy, RF Sputterings etc are not easy to come by. Its technology is also based on slow release or controlled precipitation of the desired compound from its ions in a reaction bath. A complexing agent or catalyst is employed to control the reaction in a suitable medium to obtain crystal growth, otherwise spontaneous reaction and sedimentation of materials will occur. A compound is deposited when its ionic product is greater than the solubility product K_{sp} (Chopra and Das, 1983; Lange, 1992). The complexing agent of the metal in solution forms fairly stable complex ions of the metal and provides a controlled number of free ions according to an equilibrium reaction as follows:

$$M(A)^{2+} \longleftrightarrow M^{2+} + A, \tag{1}$$

Where, M^{2+} is the metal ion and A is the complexing agent.

The concentration of an ion at any temperature is given by:

$$\frac{[M^{2+}][A]}{M(A)^{2+}} = K_d \tag{2}$$

Where, K_d is dissociation or instability constant of a complex ion. The negative ions required for the precipitation can be slowly generated by suitable complex compounds bearing them (Chopra and Das, 1983).

This paper investigates the effect of solution grown cadmium sulphide thin films on solar absorptance (α_s) and thermal emittance (ε_h) of stainless steel AISI 304 BA 2B. The values of the thermal emittance and absorptance were determined and compared with those obtained for oxidized selective absorbers.

EXPERIMENTAL

Preparation of sample plates

Twenty-four flat sheets of stainless steel AISI 304 BA 2B sample plates (7.7 cm × 7.7 cm × 0.57 cm) were polished with three abrasive papers of progressive grit numbers 100, 150 and 310 respectively with progressively decreasing grain size and a grade B-gamma polishing Alumina of particle grain size of 0.05 micron using cotton wool soaked with distilled water until the required mirror finishing was obtained. The polished plates were re-washed with distilled water, allowed to dry at room temperature and marked with numbers for identification.

Preparation of solution

Reagents used for the deposition of cadmium sulphide thin films were 1.0 M NaCl, 4 M ammonia (NH_3), 2.5 M sodium hydroxide (NaOH) and 1.0 M thourea. Distilled water was added to each reaction bath consistently to raise the volume to the required level. The mass of each reagent was calculated with a weighing device of 0.01 g resolution and obtained as follows:
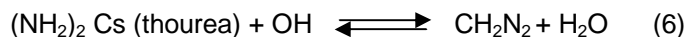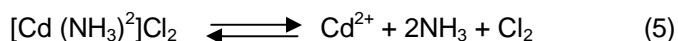
$$m = \frac{M \times W \times V}{1000} \tag{3}$$

Where, M is the required molar concentration, W is the molar mass of the chemical reagent and V is the volume of distilled water.

Deposition of cadmium sulphide thin films

The prepared solutions were measured into a 500 ml glass beaker for the deposition of cadmium sulphide thin films which were aqueous solution of 1 M cadmium sulphide, 4 M ammonia, 2.5 M sodium hydroxide and 1 M thourea as the complexing agent constitute in the bath solution were used. Pre-test runs were carried out to ensure optimum deposition conditions. Different volumes for the prepared solution were measured into the deposition bath to obtain the required molar concentration of cadmium sulphide. Twenty four polished plates, 4 each, at a time were coated with thin films. This was done using 0.04, 0.08, 0.12, 0.16, 0.20 and 0.24 molar concentration of cadmium sulphide in different bath solution for a deposition time of 24 h. The experiment was repeated for 0.24 molar concentrations of cadmium sulphide in bath solution for varying deposition times. After deposition, the as-grown CdS thin films on the sample plates were rinsed with distilled water and drip dried. The deposited thin films result from the dissociation reaction and controlled release of ions according to the
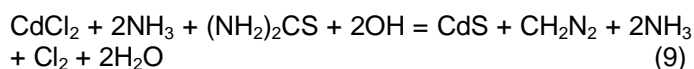
equation:

$$CdCl_2 + 2NH_3 = [Cd (NH_3)_2] \, Cl_2 \qquad (4)$$

$$[Cd (NH_3)^2]Cl_2 \; \rightleftharpoons \; Cd^{2+} + 2NH_3 + Cl_2 \qquad (5)$$

$$(NH_2)_2 Cs \, (thourea) + OH \; \rightleftharpoons \; CH_2N_2 + H_2O \qquad (6)$$

$$H_5 + OH \; \rightleftharpoons \; H_2O + 5O \qquad (7)$$

The source of the S_2 ions is thourea

$$Cd^{2+} + S_2 + CdS \qquad (8)$$

The overall equation for the chemical reaction is:

$$CdCl_2 + 2NH_3 + (NH_2)_2CS + 2OH = CdS + CH_2N_2 + 2NH_3 + Cl_2 + 2H_2O \qquad (9)$$

Measurement of thermal emittance and solar absorptance

The thermal emittance (ε_h) measurement of the polished stainless steel AISI 304 BA 2B sample plates with the deposited CdS thin films was determined by an emission meter (emissiometer) consisting of a radiation detector and heat sink. The emissiometer output was obtained in millivolts and calibrated by a black standard sample plate of polished aluminium (ε_{al}) and black standard plate ($\varepsilon_h = 0.93$). Values for each thermal emittance of the sample plates were calculated from the following formula:

$$\varepsilon_h \text{ of sample plate} = \frac{V_{sample}}{V_{standard \, plate}} \times 0.93 \qquad (10)$$

Where 0.93 is the thermal emittance of a standard black surface.

Also for the solar absorptance (α_s), several pairs of reading were taken and the reflectance, r, of the stainless steel AISI 304 BA2B was calculated using an Alphatometer with a digital volt meter. The output again was obtained in millivolts and was calculated from each pair of readings using:

$$R = \frac{\text{Reflected voltage reading (R)}}{\text{Incident voltage reading (I)}} \qquad (11)$$

The solar absorptance (α_s) was then calculated from:

$$\alpha_s = 1 - r \qquad (12)$$

The measurements were repeated and the mean values

of thermal emittance and solar absorptance were obtained, before and after deposition of thin films. As can be seen from Tables 1 and 2, the emittance and absorptance quoted accuracies are the standard deviations of the mean and are within the error limits of the instruments.

Measurement of film thickness

The film thickness of the deposited thin films was calculated using:

$$T = \frac{m}{2A\rho} \qquad (13)$$

Where, m is the mass of the thin film deposited on the polished sample plate, obtained from the difference in mass of each sample plates before and after film deposition. A is the film area on the sample plate and $\rho = 4.82$ g/cm^3 is the density of cadmium sulphide (CdS).

RESULTS AND DISCUSSION

Table 1 shows the average emittance and solar aborptance of polished and cadmium sulphide (CdS) films deposited on sample plates at different molar concentrations of CdS in bath solution at a deposition time of 24 h with corresponding film thickness readings. While Table 2 shows the emittance, absorptance and films thickness readings for deposition of CdS thin films at 0.24 molar concentrations of CdS in bath solution at different deposition times.

Figure 1 shows the graph of thermal emittance and solar absorptance as a function of molar concentration, while Figure 2 shows the graph of film thickness of deposited CdS thin films as a function of molar concentration. Figure 3 shows the graph of the thermal emittance and solar absorptance as a function of deposition time while Figure 4 shows the graph of the film thickness of deposited CdS thin films as a function of deposition time.
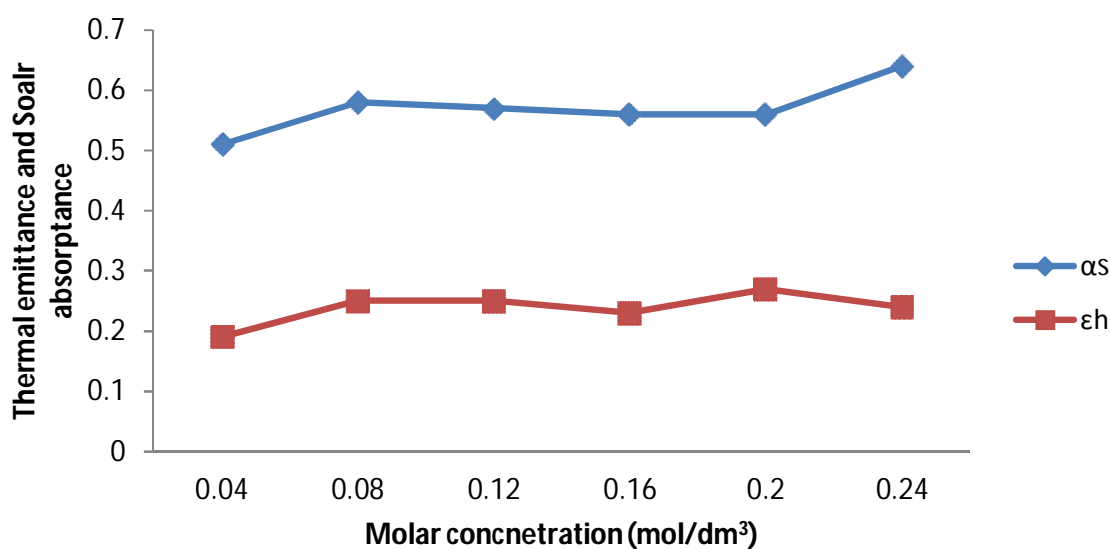
The average thermal emittance and solar absorptance for uncoated polished stainless steel of AISI 304 BA 2B sample plates for different molar concentrations of CdS in deposition bath for deposition time of 24 h is 0.15 ± 0.01 and 0.47 ± 0.01, respectively. While that for uncoated sample plates of stainless steel 304 BA 2B for 0.24 molar concentrations of CdS in deposition bath for different deposition times is 0.15 ± 0.01 and 0.47 ± 0.01. This thermal emittance result compares well with the thermal emittance value of 0.13 to 0.17 ± 0.01 for polished stainless steel AISI 321 using abrasives of different grain sizes (Sharma, 1982) and thermal emittance value of 0.15 ± 0.01 for polished stainless steel 430 (Damisa and

Table 1. Solar absorptance (α_s), thermal emittance (ε_h), film colour and film thickness (t) for coated sample plates of stainless steel 304 BA 2B for different molar concentrations of CdS in deposition bath for deposition time of 24 h.

Sample plate no.	Surface treatment	Molar conc. of CdS in solution (mol/dm³)	Film colour	Film thickness (µm) ± 0.01	Solar absorptance (α_s ± 0.01)	Thermal emittance (ε_h ± 0.01)	Deposition time (h)
-	Polished and uncoated	-	Malt silver	-	0.47	0.15	-
1-4	Polished and coated	0.04	Dull yellow	0.25	0.51	0.19	24.00
5-8	Polished and coated	0.08	Yellow	0.45	0.58	0.25	24.00
9-12	Polished and coated	0.12	Light deep yellow	0.61	0.57	0.25	24.00
13-16	Polished and coated	0.16	Deep yellow	0.53	0.56	0.23	24.00
17-20	Polished and coated	0.20	Deep yellow	0.60	0.56	0.27	24.00
21-24	Polished and coated	0.24	Deep yellow	0.44	0.64	0.24	24.00

Table 2. Solar absorptance (α_s), thermal emittance (ε_h), film colour and film thickness (t) for coated sample plates of stainless steel 304 BA 2B for 0.24 molar concentrations of CdS in deposition bath for different deposition times.

Sample plate no.	Surface treatment	Molar conc. of CdS in solution (mol/dm³)	Film colour	Film thickness (µm) ± 0.01	Solar absorptance (α_s ± 0.01)	Thermal emittance (ε_h ± 0.01)	Deposition time (h)
-	Polished and uncoated	-	Malt silver	-	0.47	0.15	-
1-4	Polished and coated	0.24	Yellow	0.21	0.48	0.19	12.00
5-8	Polished and coated	0.24	Yellow	0.31	0.55	0.24	16.00
9-12	Polished and coated	0.24	Yellow	0.20	0.57	0.23	20.00
13-16	Polished and coated	0.24	Yellow	0.20	0.50	0.22	24.00
17-20	Polished and coated	0.24	Deep yellow	0.23	0.55	0.21	28.00
21-24	Polished and coated	0.24	Deep yellow	0.21	0.54	0.25	32.00

Figure 1. Variation of thermal emittance and solar absorptance of CdS film with molar concentration.

Ilenikhena, 2013; Ilenikhena and Mordi, 2005; Ilenikhena, 2008; Igbinovia and Ilenikhena, 2010). Table 1 and

Figure 1 show the thermal emittance values of the coated sample plates increased slightly from 0.15 to 0.27 ± 0.01
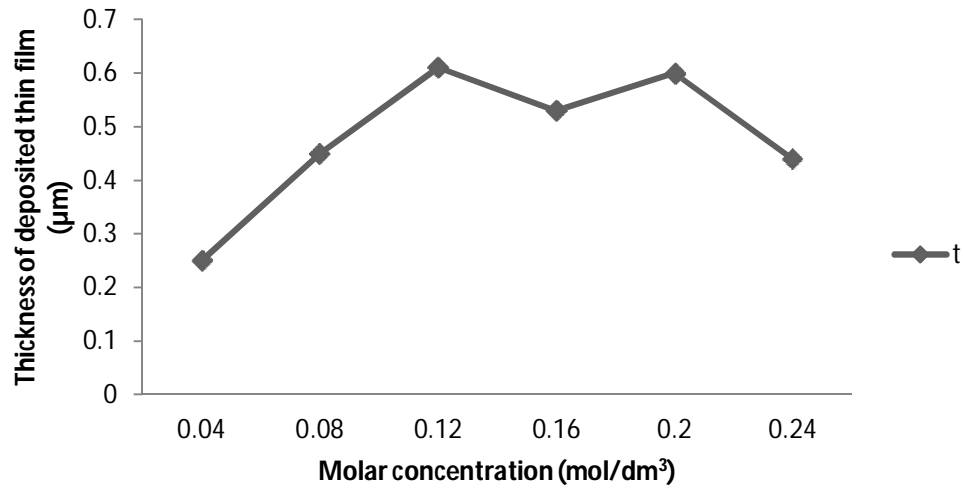
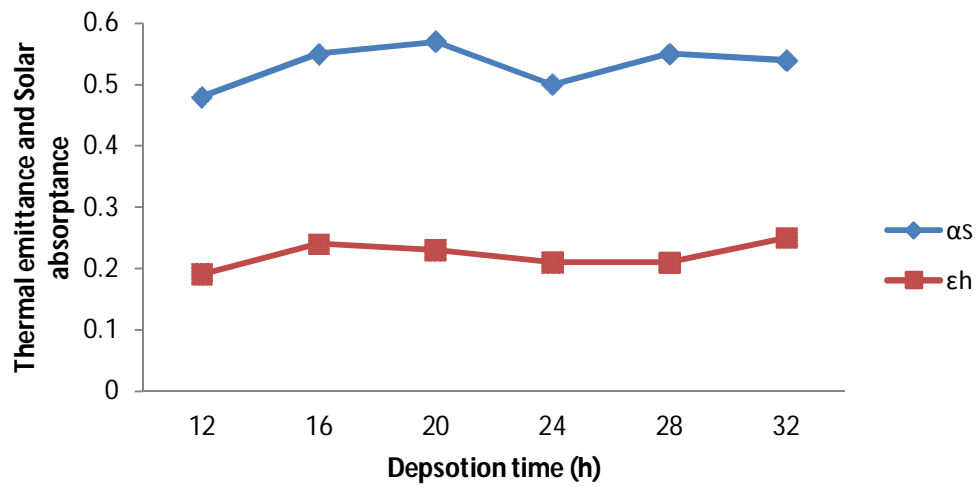**Figure 2.** Variation of thickness of deposited CdS thin film molar concentration.

Figure 3. Variation of thermal emittance and solar absorptance of CdS film with deposition time.
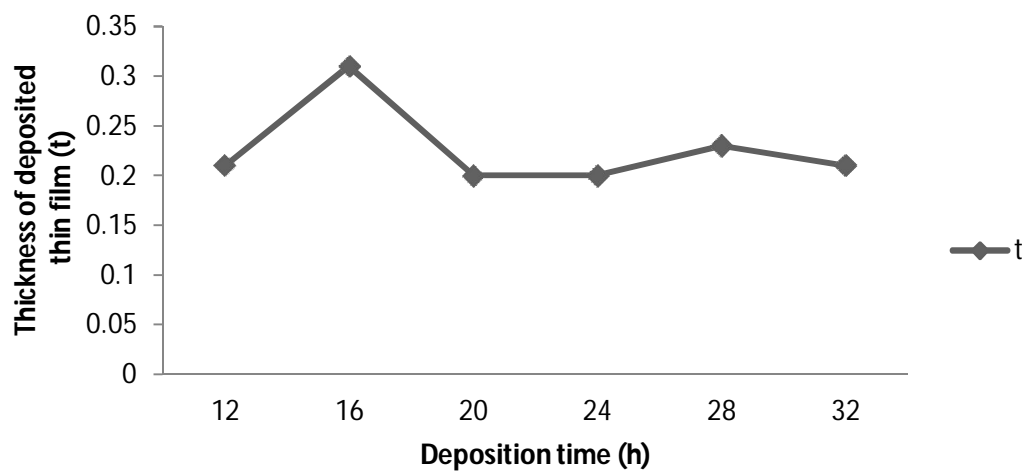

Figure 4. Variation of thickness of deposited thin film with deposition time.

and solar absorptance values also increased greatly from 0.47 to 0.64 ± 0.01 for increased molar concentration of CdS in bath solution at 24 h deposition time. Also there was a gradual increase in film thickness from 0.27 to 0.61 ± 0.01 µm for molar concentration of 0.04 to 0.12 and a slight decrease in thickness of 0.60 to 0.44 ± 0.01 µm for molar concentration rise of 0.20 to 0.24 as shown in Figure 2.

Table 2 and Figure 3 show the thermal emittance values of the coated sample plates that increased slightly from 0.15 to 0.25 ± 0.01 and solar absorptance values also increased greatly from 0.47 to 0.57 ± 0.01 for 0.24 molar concentrations of CdS in bath solution at different deposition times. Figure 4 shows a great increase of deposited thin film thickness of 0.21 to 0.31 ± 0.01 µm for deposition time of 12 to 16 h and a gradual decrease and almost stable gradient of thin film thickness from 20 to 32 h. These results show that thermal emittance values of deposited CdS thin films on stainless steel 304 BA 2B are low and can be compared to thermal emittance values of oxidized stainless steel selective surfaces which are used for photothermal conversion of solar energy. The most favourable thermal emittance values of 0.19 ± 0.01 compare to 0.18 ± 0.01 for oxidized stainless steel selective surfaces (Sharma, 1982; Sharma et al., 1988) and also the solar absorptance of 0.64 ± 0.01 were obtained with film thickness of 0.44µm ± 0.01 with 0.24 molar concentration of CdS in bath solution at deposition time of 24 h.

The coatings help to modify the micro structure and composition of the absorber plate so as to provide higher absorbance for the wavelength range of 0.3 to 2.5 µm (Sharma et al., 1988). The thickness of the thin film deposited could be hardened to withstand adverse weather condition and degradation thus prolonging the lifespan of the absorber surface.

CONCLUSION

CdS thin films were deposited on polished stainless steel of AISI 304 BA 2B sample plates using solution growth method at different molar concentration of CdS in bath solution for deposition time of 24 h and also at a fixed molar concentration and different deposition times. An emissiometer was used to determine the thermal emittance values of the sample plates before and after thin film deposition. Also, an alphatometer was used to determine the solar absorptance values of the sample plates before and after thin film deposition. The average thermal emittance of the polished sample plates is 0.15 ± 0.01 and the average solar absorptance value for polished sample plate is 0.47 ± 0.01. Thin film deposition was done under condition of varying molar concentration and fixed deposition time, the values of thermal emittance of the coated plates varied from 0.19 to 0.27 ± 0.01 and the absorptance from 0.51 to 0.64 ± 0.01. Their corresponding film thicknesses varied from 0.25 to 0.60 ±

0.01 µm. Thin films deposited with 0.24 molar concentrations at varying deposition times had thermal emittance value of coated plate vary from 0.19 to 0.25 ± 0.01 and solar absorptance value of 0.48 to 0.57 ± 0.01 with film thickness of 0.21 to 0.31 ± 0.01 µm.

The coated sample plates with most favourable condition which could be employed for solar thermal devices had thermal emittance value of 0.24 ± 0.01, solar absorptance value of 0.64 ± 0.01 and thin film thickness of 0.12 ± 0.01 µm for 0.24 molar concentration of CdS in solution bath at deposition time of 24 h.

Consequently, the solution growth method could be used for deposition of thin films at various concentration and deposition times to fabricate the selective absorbers which could be used for applications in photothermal conversion of solar energy.

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