Full Length Research Paper

Improved chemical deposition and thermal emittance of tin (iv) oxide (SnO$_2$) thin films for photothermal conversion of solar energy and possible applications

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Thin films of tin (iv) oxide (SnO$_2$) were deposited on six polished sample plates of stainless steel 430 using improved chemical bath deposition (CBD) method at 302 K and pH value of 12.4 for different deposition time of 16 to 36 h at 4 h interval, respectively. Ethylenediamine tetra acetate (EDTA) was used to stabilize the deposition at the required pH value. The thermal emittance values of the polished and coated sample plates were determined before and after the deposition of films, respectively, using thermocouple potentiometer. The average thermal emittance value of the uncoated polished sample plate is 0.15 ± 0.01 while thermal emittance values of the coated sample plates vary from 0.15 to 0.19 ± 0.01. The film thickness of the coated sample plates varies from 33.73 to 77.59 μm. These low thermal emittance values compare well with those obtained for oxidized stainless steel selective surfaces. The coated sample plates with most favorable conditions of thermal emittance 0.17 to 0.18 ± 0.01 and film thickness 45.70 to 69.18 μm could find applications in photothermal conversion of solar energy. The improved chemical bath deposition technique could be employed at different pH values with suitable deposition time to fabricate selective surfaces for use in solar energy applications.

Key words: Improved chemical bath deposition (CBD) method, thermal emittance of tin (iv) oxide (SnO$_2$), thin films and possible applications in solar thermal devices.

INTRODUCTION

The application of solar energy are numerous and environment friendly when it is converted to heat, electricity or biomass. The devices for the conversion of solar energy into heat and electricity are photothermal (solar thermal) devices and photovoltaic or solar cells, respectively. An efficient photothermal device requires the presence of a spectral selective absorber. A spectral selective absorber is a surface that has maximum absorption of solar wavelengths (0.3 to 2.5 μm) and a minimum emittance of thermal wavelengths (3.0 to 30.0 μm) (Sharma et al, 1988). Advantages of using spectral selective absorbers in solar energy collectors were first introduced by Tabor (1956; 1959); Gier and Dunkle (1955). Several methods have been used to fabricate

selective surfaces on metallic substrate such as copper, galvanized iron, steel and aluminum substrates. Most of the selective absorbers are found to suffer atmospheric degradation and corrosion at elevated temperatures (Daletsiki et al., 1979, Smith and Ignatiev, 1980; Choudhury and Sehgal, 1983). Currently, there is a widespread research on the fabrication of selective absorbers using stainless steel to overcome the atmospheric degradation at elevated temperatures. Examples of such research include chemical and thermal oxidation of 300 series stainless steels (Sharma and Hutchins, 1979), chemical oxidation of stainless steels AISI 321 (Sharma et al., 1988), coloration of stainless steel by aluminum anodizers using hot chronic and sulphuric acid (Granziera, 1977) and solution growth (Ilenikhena and Mordi, 2005; Ilenikhena, 2008).

The chemical bath deposition (CBD) technique was predominantly employed in production of silver mirrors. It

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is a simple, cost effective and reproducible method of producing compound semiconductor metal halides and chalcogenide thin films on both metallic and non-metallic substrates (Chopra and Das, 1983; Chandra et al., 1980; Brinker and Harrington, 1981; Cho et al., 1998; Okujagu and Okeke, 1997). The films produced by this technique have comparable structural and photoelectric properties to those produced using other sophisticated thin film deposition techniques such as chemical vapor deposition, sputtering etc. It has also been applied in producing emerging materials for solar cells, solar collectors among others and is now being adopted by some industries (Ilenikhena and Okeke, 2002; 2004; Ezema and Okeke, 2003; Osuji, 2003; Ilenikhena and Mordi, 2005). Its technology is based on slow release or controlled precipitation of the desired compound from its ions in a reaction bath. A complexing agent acting as a catalyst is employed to control the reaction in a suitable medium as indicated by the pH to obtain crystal growth. Otherwise, spontaneous reaction and sedimentation of materials will result. A compound is deposited when its ionic product I.P. 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 of the form:

$M (A)^{2+} \leftrightarrow M^{2+} + A,$
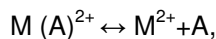
Where, M^{2+} is the metal ion and A is the complexing agent.

The concentration of an ion at any temperature is given by

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

Where, K_d is dissociation or instability constant of the complex ion. The negative ions required for the precipitation can be slowly generated by suitable complex compounds bearing them (Chopra and Das, 1983). The chemical bath deposition method could be improved by controlled addition of a second complexing agent with pH oppose to that of deposition bath constituents to enhance variation of deposition conditions at different pH values (Ilenikhena and Okeke, 2005; Ilenikhena, 2007; 2008). This paper reports the thermal emittance of stainless steel 430 before and after deposition of tin (iv) oxide (SnO_2) thin films using improved chemical bath deposition (CBD) method at 302 K and pH value 12.4 for different deposition times. Controlled addition of ethylenediamine tetra acetate (EDTA) was used to stabilize the deposition at the required pH values. The values of thermal emittance were determined and compared with those obtained for oxidized selective

absorbers. Possible applications of deposited tin (iv) oxide thin films for photothermal energy conversion were also discussed.

EXPERIMENTAL

Sample plate preparation

Six flat stainless steel 430 plates ($75 \times 75 \times 1$ mm^3) were polished using three different emery papers of progressively decreasing grain sizes and a grade B polishing alumina until the required mirror finishing was obtained. The polished plates were washed with distilled water, degreased with methylated spirit, rewashed with distilled water and dried.
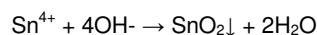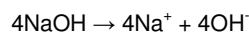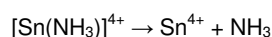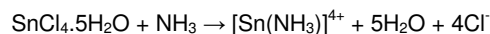
Preparation of solution

Reagent used for the deposition of tin (iv) oxide (SnO_2) thin films were freshly prepared solutions of 0.36 M tin (iv) chloride pentahydrate ($SnCl_4.5H_2O$) as source of tin (iv) ions (Sn^{4+}), 5.0 M ammonia (NH_3aq) as complexing agent and 2.5 M sodium hydroxide (NaOH) as source of hydroxyl ions (OH^-). 0.2 M ethylenediamine tetra acetate (EDTA), another complexing agent with pH opposed to that of both constituents was used to stabilize the deposition at pH value of 12.4. The mass m of the various chemical reagents were calculated from the formula

$$m = \frac{M \times W \times V}{1000},$$

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

Film deposition

The prepared solutions measured into 400 ml glass beakers for the deposition of tin (iv) oxide thin films were 25 mls, 0.36 M $SnCl_4$ $5H_2O$, 15 mls, 5.0 M NH_3(aq) and 24 mls, 2.5 M NaOH solution. 20 mls of H_2O was added to raise the volume of the mixture to a certain level. A controlled addition of ethylenediamine tetra acetate (EDTA) was used to enhance the deposition condition at a pH value of 12.4. Pre-test runs were carried out to ensure optimum deposition conditions and eliminate the incorporation of solid phase $Sn(OH)_4$ into the films. Six polished sample plates were suspended vertically, one in each reaction bath at 302 K for different deposition times ranging from 16 to 36 h at 4 h interval, respectively. After deposition, the as-grown SnO_2 thin films on the sample plates were rinsed with distilled water and dried. The deposition of tin (iv) oxide (SnO_2) thin films result from dissociation reaction and controlled release of ions according to the equation

$SnCl_4.5H_2O + NH_3 \rightarrow [Sn(NH_3)]^{4+} + 5H_2O + 4Cl^-$

$[Sn(NH_3)]^{4+} \rightarrow Sn^{4+} + NH_3$

$4NaOH \rightarrow 4Na^+ + 4OH^-$

$Sn^{4+} + 4OH^- \rightarrow SnO_2\downarrow + 2H_2O$

The overall equation for the chemical reaction is:

$SnCl_4.5H_2O + NH_3 + 4NaOH \rightarrow SnO_2\downarrow + 4NaCl + NH_3 + 7H_2O$
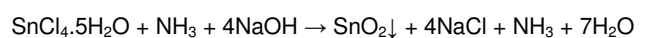
Table 1. Thermal emittance of polished stainless steel 430 sample plates and tin (iv) oxide (SnO_2) thin films produced on the sample plate at a pH value of 12.4 and 302 K for deposition time of 16 to 36 h.

Sample plate no.	Surface treatment	Deposition time (h)	Thermocouple reading		Thermal emittance $\varepsilon \pm 0.01$
			Black surface V_b(mV) ± 0.01	Sample surface V_s(mV) ± 0.01	
−	Polished and uncoated	−	59.30	49.60	0.15
1	Polished and coated	16.00	90.00	77.10	0.15
2	Polished and coated	20.00	98.00	81.00	0.16
3	Polished and coated	24.00	96.00	91.20	0.17
4	Polished and coated	28.00	97.00	92.10	0.17
5	Polished and coated	32.00	101.00	99.20	0.18
6	Polished and coated	36.00	80.06	84.90	0.19

Table 2. Thickness of tin (iv) oxide (SnO_2) thin films deposited on stainless steel 430 sample plates at pH of 12.4 and 302 K for deposition time of 16 to 36 h.

Sample plate number	Surface treatment	Deposition Time (h)	Mass of deposited film m(g) ± 0.01	Area of deposited film A(cm^2) ± 0.01	Thickness of Film t(µm) ± 0.01
1	Polished and coated	16.00	1.00	21.33	33.73
2	Polished and coated	20.00	1.00	18.02	39.53
3	Polished and coated	24.00	1.40	22.04	45.70
4	Polished and coated	28.00	1.60	21.60	53.29
5	Polished and coated	32.00	2.00	20.80	69.18
6	Polished and coated	36.00	2.20	20.40	77.59

Measurement

The measurement of the thermal emittance ($\in$) of the polished stainless steel of 430 sample plate and tin (iv) oxide (SnO_2) films deposited on the sample plate was determined by a thermocouple potentiometer. The potentiometer output was obtained in millivolts and calibrated by a black standard surface heated to the same temperature as the sample surfaces. Values of the thermal emittance ($\in$) were calculated from the formula;

$$\in = \frac{V_s}{V_b} \times 0.18$$

Where, V_b and V_s were potentiometer readings for black standard surface and sample surface, respectively. The measurements were repeated and their mean values of $\in$ obtained. The quoted accuracies of the thermal emittance are the standard deviations of the mean and are within the error limits of the instruments used as shown in Tables 1 and 2.

Measurement of film thickness

Film thickness was calculated from the formula:

$$t = \frac{m}{2 \ dA}$$

Where, m is the mass of the tin (iv) oxide (SnO_2) film deposited on a sample plate, obtained from the difference in mass of each sample plate before and after film deposition. A is the area of film on the sample plate and d = 6.95g/cm^3 is the density of tin (iv) oxide (SnO_2).

RESULTS

Table1 shows average emittance of polished and tin (iv) oxide (SnO_2) films deposited on sample plates at pH value 12.4 and 302 K between 16 to 36 h while Table 2 shows the corresponding film thickness of coated sample plates at the same pH value for the different deposition times.

DISCUSSION

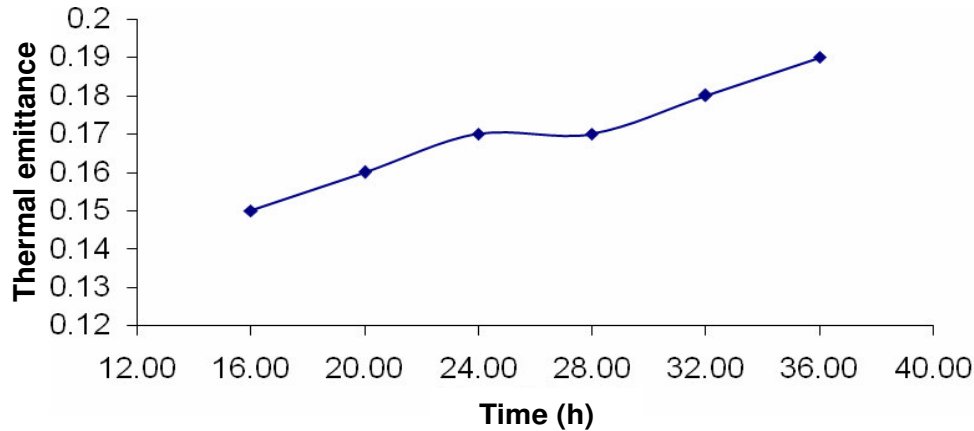The average thermal emittance value for uncoated

Figure 1. Variation of thermal emittance of tin (iv) oxide film with deposition time.
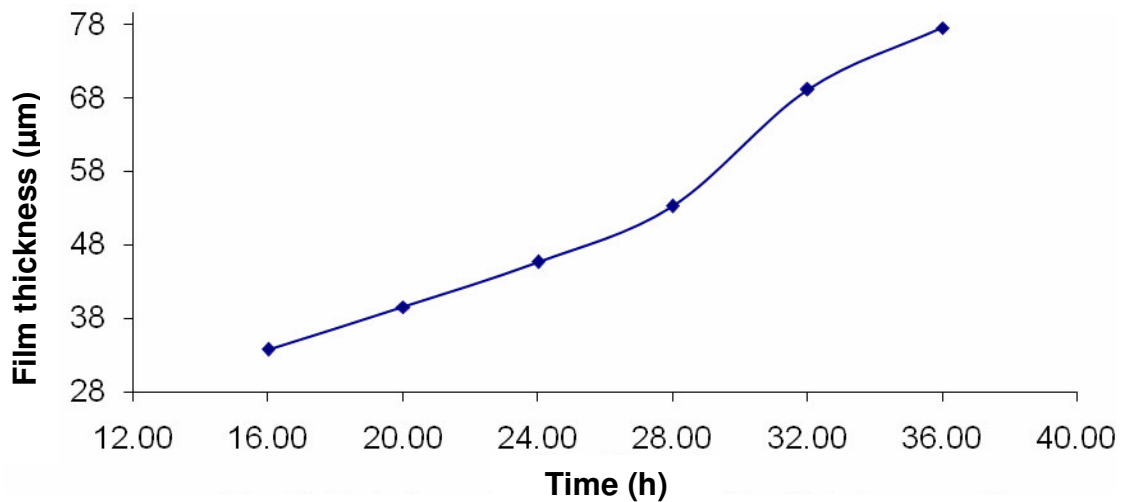

Figure 2. Variation of tin (iv) oxide film thickness with deposition time.

polished stainless steel of 430 sample plates is 0.15 ± 0.01 in Table 1. This compares well with the thermal emittance values of 0.13 to 0.17 ± 0.01 for polished stainless steel AISI 321 using abrasives of different grain sizes (Sharma, 1982). Table 1 and Figure 1 show that the thermal emittance values of the coated sample plates increased slowly from 0.15 to 0.19 ± 0.01 with deposition time of 16 to 36 h. Table 2 and Figure 2 also show that the film thickness increased slowly from 33.73 to 77.59 µm with the same deposition time. Figure 3 shows that the thermal emittance of the coated sample plates increased with the film thickness and vice versa. These results show that the thermal emittance values of deposited tin (iv) oxide thin films on stainless steel of 430 are low and compare favourable with thermal emittance values of oxidized stainless steel selective surfaces for photothermal conversion of solar energy. The most favourable thermal emittance values of 0.17 to 0.18 ±

0.01 compare well to 0.18 ± 0.01 for oxidized stainless steel selective surfaces (Sharma, 1982; Sharma et al., 1988). The thermal emittance values of 0.17 to 0.18 ± 0.01 were obtained with film thickness values of 45.70 to 69.18 ± 0.01 µm for deposition time of 24 to 32 h at pH value of 12.4 and 302 K. The increase in thermal emittance values for the coated sample plates is due to increase in deposition of the thin films. The coatings help to modify the microstructure and composition of the absorber so as to provide high solar absorbance for the wavelengths range 0.3 -2.5 µm (Sharma et al., 1988). The thickness of the film could be hardened to withstand adverse weather condition. The coated surfaces with lower thermal emittance and film thickness cannot withstand adverse weather conditions for photothermal conversion of solar energy (Sharma et al., 1988).

The improved chemical bath deposition method could be used at different pH values and with suitable
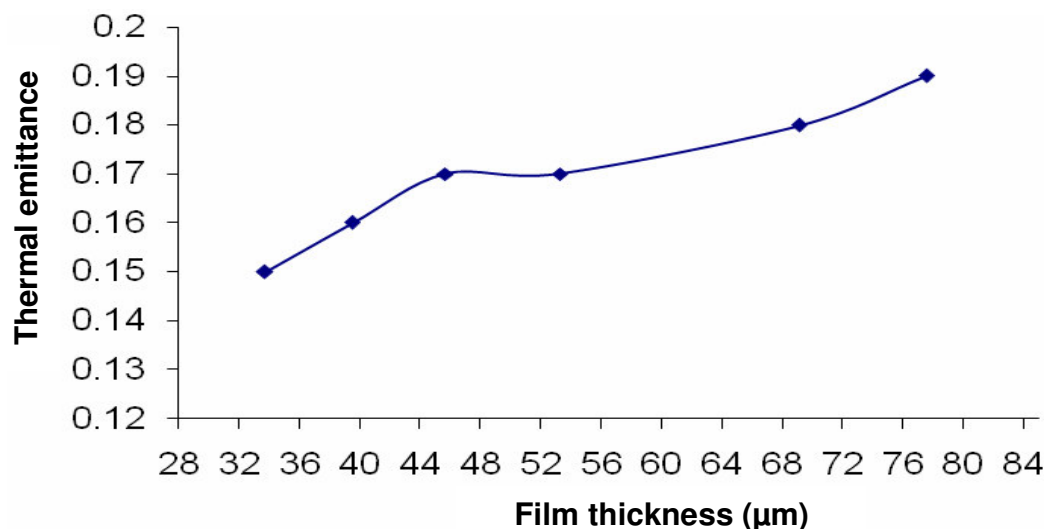
Figure 3. Variation of thermal emittance with deposited tin (iv) oxide film thickness.

deposition time to produce selective absorbers of low emittance and good film thickness for use in solar thermal devices. Such selective absorbers could retain enough heat to find applications in solar collectors, solar water heaters, solar distillation, solar thermal refrigeration, solar cookers, solar dryers, poultry production, egg incubation, etc. (Ileoje, 1997; Ilenikhena, 2007; 2008; Oladipo, 1999; Okonkwo et al., 1992) and solar thermal electric converters.

Conclusion

Tin (iv) oxide thin films were deposited on the polished stainless steel of 430 sample plates using improved chemical bath deposition method at 300 K and pH value of 12.4 for deposition time between the hours 16 and 36 at 4 h interval respectively. A thermocouple potentiometer was used to determine the thermal emittance values of the sample plates before and after film deposition. The average thermal emittance of the polished sample plates is 0.15 ± 0.01. Values of thermal emittance of the coated sample plates vary from 0.15 to 0.19 ± 0.01. Their corresponding film thicknesses vary from 33.73 to 77.59 ± 0.01μm. The values of thermal emittance of the coated sample plates were low, compared well with those obtained for oxidized stainless steel selective surfaces and increased with film thickness. The coated sample plates with most favourable thermal emittance values of 0.17 to 0.18 ± 0.01 and film thickness 45.70 to 69.18 ± 0.01 μm could be employed in solar thermal devices. The improved chemical bath deposition (CBD) could be used at different pH values with suitable deposition time to fabricate selective absorbers for applications in photo-thermal conversion of solar energy in solar still among a lot of other things.

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