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Fabrication of Spectrally Selective Multinary Thin Nanofilms on Glass as Infra-Red Reflectors for Heat Control Inside Buildings

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Abstract: ***We have fabricated spectrally selective multinary thin nanofilms as good infra-red reflectors for heat control application in buildings and car cabins in both hot and cold climates. Crystalline thin films of Sb-SnO_2/SiO_2 were grown on plane glass substrates using chemical bath deposition (CBD) techniques. Two CBD baths were used, one to grow silica on glass and the other to grow antimony-doped stannic oxide on top of the silica to form composite multinary and stack heterojunction glass coating that is highly infra-red reflecting. Simple chemicals were used which included $SiCl_4$, NaOH, $SnCl_4$, triethanolamine and distilled water. Thin film formation was a slow pyrolysis precipitation and coalescence of crystal grains into a continuous polycrystalline deposits on glass which were specifically identified by x-ray diffraction done on the films. The elemental, and optical characterization done on the films deciphered film elements in their percentages and showed that the films are high in transmittance (60 - 80 %) in the visible spectrum and also high, up to 80 % in reflectance, in the infra-red ranges thus making our fabrication good candidates for heat controls inside buildings and car cabins.***

Keywords: Infra-red, Reflectors, Chemical bath technique, optical analysis, selective surfaces

1. Introduction

The characteristics of heterojunction multinary thin films have been very useful in recent times for application where binary thin semiconducting films are not very successful regarding their optical properties. In modern architecture, glass window coating has attracted most research interest especially on how to apply thin film coatings as infra-red reflectors in buildings and car cabins. Solar control coatings in hot climate involves windows of spectrally selective high transmittance, T, low reflectance, R and low absorbance, A in visible spectrum, VIS and high R, low T as well as low A in the infra-red (IR) ranges. The best reflectors comprise shinny metals like Au, Ag and especially Al that each has up to 90 % IR reflectivity but unfortunately cannot be a good window coating candidate due to its very poor transmittance in the visible electromagnetic waves.

For long, semiconductors have been significant as candidate materials for fabrication of selective surfaces [1 – 3] and transparent windows [4, 5]. Well crafted heterojunction semiconductors can have such energy gaps and molecular arrangements that favour their vibration and rotational modes that redshift energy in favour of high IR reflectance. In this work, we targeted multinary films that, whilst thus highly reflecting in IR, still selectively and highly transmit VIS waves. We have, in this research, fabricated spectrally selective multinary thin nanofilms on glass surface as IR reflectors that can control heat inside buildings and car cabins in hot climates. The thin film (TF) is SiO_2/Sb-SnO_2, that is, a composite of silicon oxide/antimony doped thin oxide thin films deposited on plane glass surfaces.

Good quality crystalline films of SiO_2 and SnO_2, that offer effective transparent windows, have been variously separately grown using various popular technologies [6−13] that are too expensive and not applicable for large area architectural applications. We have found a way of using chemical baths deposition (CBD) technique which is an electroless technique that is particularly applicable for uniform crystal growth coverage of irregular and large surface area such as in usually large area vehicle and architectural windows [14−16]. This chemical bath deposition method, though versatile in growing binary thin films [17, 18], has however difficult challenges in growing multinary heterojunction films of meaningful optical qualities. Our two-step chemical baths technique [19] of achieving ordered two dimensional growth of composite film of nano thickness is herein reported.

2. Experimental Details

Chemical Bath Deposition technique was used to fabricate SiO_2 and Sb-doped SnO_2 on plane glass slides of 75x25x1mm dimension. The slides were previously degreased in concentrated hydrochloric acid, washed in detergent solutions, rinsed with distilled water and left to dry in dust-free environment. Two chemical baths were used: bath A was used to deposit SiO_2 while bath B was used to deposit Sb-doped SnO_2 (ATO). In bath A was introduced 3.0 ml of 1.2 M $SnCl_4$ + 10 ml of 0.5 M NaOH and 2.0 M of triethanolamine (TEA) all stirred vigorously while still adding distilled water to make the volume of reactants up to 40 ml in the 50 ml beaker used. The bath was raised to 80 ℃ before the substrates, pre-heated to a temperature of 140 ℃ were vertically inserted in the solution and suspended from synthetic foam which rests on top of the beaker. Sb-doping was achieved by adding small quantity $SbCl_3$ to the bath. This set up was left at this 80 ℃ temperature for 30 min after which the substrates, now covered with Antimony

Tin Oxide (ATO), was removed, rinsed in distilled water and drip dried in dust free environment.

Bath B was prepared following the growth pattern of bath A by mixing into it 4.2 ml of 1.0 M $SiCl_4$, 12.5 ml of 0.85 M NaOH and 1.0 M triethanolamine in 50ml beaker that contained 40 ml distilled water. The growth temperature was kept at 90 ℃. The (prepared) glass slides recovered from bath A (with Sb-SnO_2 deposit) were similarly loaded at room temperature and after 25 min, the work now covered with transparent orderly deposit of SiO_2 were removed and similarly drip dried. In baths A and B were triethanolamine-complexed reactions that enabled slow and orderly growth (of otherwise rapid precipitations) of ATO (first bath) and stack SiO_2/ATO (second bath). Consideration of sticking coefficient affinity favoured the given order of deposition since ATO bonding with glass is far stronger than SiO_2-glass bond. Thin film formations were basically oxidation processes complexed by triethanolamine as follows:

SnO_4 + TEA → $[Sn(TEA)]^{4+} + 4Cl^-$
$[Sn(TEA)]^{4+}$ → Sn^{4+} + TEA
$2NaOH + 4OH^-$ → $2Na^+ + 3O^{2-} + 3H_2O$
$Sn^{4+} + 2O^{2-}$ → SnO_2
And:
SiO_4 + TEA → $[Si(TEA)]^{4+} + 4Cl^-$
$[Si(TEA)]^{4+}$ → Si^{4+} + TEA
$2NaOH + 4OH^-$ → $2Na^+ + 3O^{2-} + 3H_2O$
$Si^{4+} + 2O^{2-}$ → SiO_2

Crystal film growth success depended critically on growth variables that included the concentration of reagents, deposition period, annealing temperatures, doping impurity levels, *et cetera*, and the optimum values, in this exercise, are only reported. Although the as-deposited composite film on glass, as given above and labeled A, has the requisite IR reflection qualities, it was not very commercially effective since it is not stable for long term use. It is also not scratch resistant and degrades rapidly with time. The works were therefore quickly annealed, after removal from bath B, for 2 hrs each time to improve film stability, sticking coefficient and scratch resistivity. Our annealing temperature were 200 ℃, 250 ℃, 300 ℃, and 350 ℃ and films so annealed were labeled A, B, C, D respectively.

Successfully grown films were subjected to Rutherford backscattering (RBS) using proton-induced x-ray emission (PIXE) scans from a Tandem accelerator model 55DH by National Electrostatic Corporation (NEC) which deciphered the elements in both deposits and substrates. The RBS also deciphered the thicknesses of the deposit as well as the substrates.

We ran an X'Pert-Pro diffractions on the films using CuK_α radiator of λ = 0.15406 nm to scan films continuously as 2θ varied from 0 – 100° at a step size of 0.02 ° and at a scan step time of 0.2 s. This enabled us determine the film diffraction patterns and hence decipher the precipitation product of the baths. We also did two spectroscopic analysis to determine the film optical characteristics especially the reflectance R, and transmittance T in:

(i) UV-VIS-NIR in the range 300 – 840 nm and

(ii) IR in the range 840 – 4300 nm.

Both R and T are related to film absorbance A as:

$$A+T+R = 1 \quad (1)$$

and T is related to R as [16]:

$$T = (1 - R)^2 e^{-\alpha t} \quad (2)$$

where α is the absorption coefficient of the thin film given as [20] :

$$\alpha = \frac{ln\,(I_o/I)}{t} \quad (3)$$

$$= \frac{ln\,(1/T)}{t} \quad (4)$$

Here, I_0 is the electromagnetic wave intensity incident on the thin film and I is the intensity after traversing the film of thickness t,

3. Results and Discussion

3.1 X-Ray Diffraction Results

The results of X-ray diffraction scans done on the as-deposited and on optimized (annealed stack film, D) are as shown in Fig. 1a and Fig. 1b. respectively. They show that the as-deposited film is almost completely amorphous while the annealed sample exhibited polycrystalline order the pattern of which manifest at 2θ = 26.7 ° and 29.8 ° with the more prominent peak appearing at crystal plane (111) as depicted in JCPDS data 03-065-61623. This identification was antimony tin oxide/silica composite, a heterogeneous structure that has good sticking coefficient to glass surfaces. The average grain size was 29.97 nm. The pre-heating of prepared substrate (before insertion to bath) was to enable initial rapid pyrolysis growth of seed crystals on it such that these seeds enabled growth patterns in the subsequent but complexant-controlled slow precipitations and seeds coalescence at the chemical bath growth temperatures. This control was engendered by the chemical complexation occasioned with the triethanolamine used.

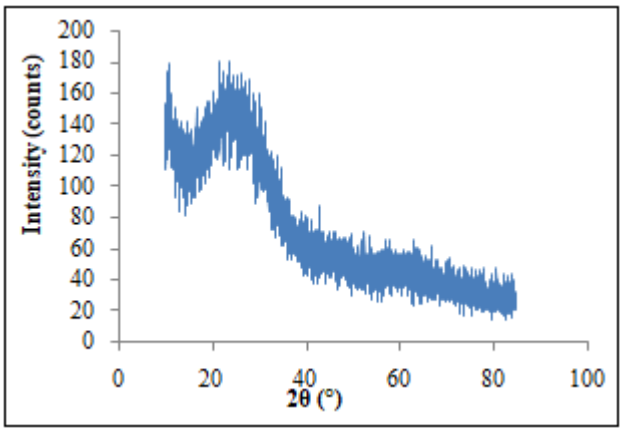

Figure 1(a): XRD pattern for as-deposited thin film

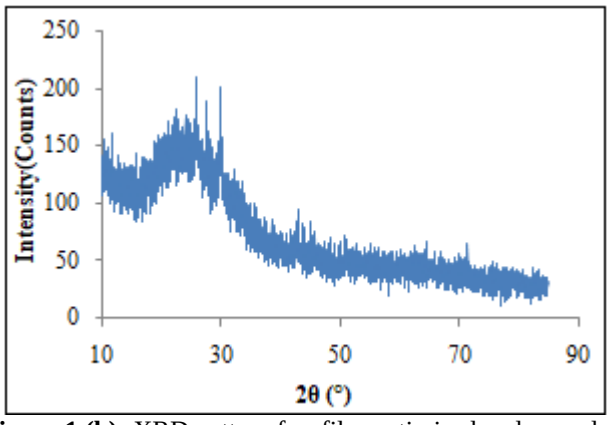

Figure 1 (b): XRD pattern for film optimised and annealed at 200 ºC

3.1 Rutherford Backscattering Results

The result of Rutherford backscattering analysis for annealed and optimized film D was as shown in Fig. 2 which presented film of thickness 385 nm and composition Sn, O, Sn, Sb and Si grown on top of glass substrate of thickness 954740 nm and composition given hereunder. The elements percentage abundances were also deciphered as shown which revealed that antimony atoms were very low (0.54 %). They were impurity atoms which exact roles in IR reflectivity, film affinity (to substrate) and precipitation dynamics is still being studied. RBS result for as-deposited film (not shown) revealed higher percentage oxygen content which the heat treatment reduced.

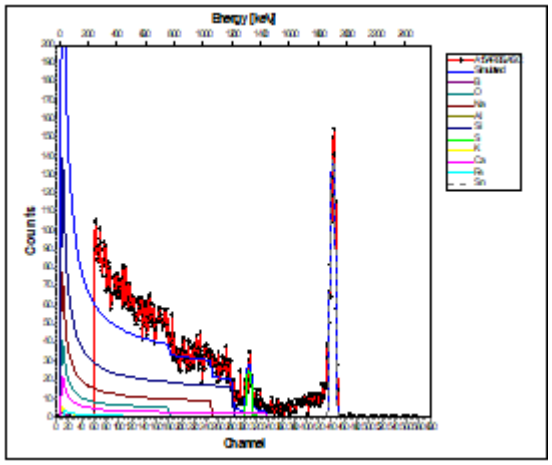

Figure 2: RBS micrograph of Film sample B Sb-SnO_2/SiO_2 annealed at layer 1: Thickness**:** 385 nm; Compo: Sn 32.0 %, Si 24.1 %, Sb 0.54 %, O 43.40 % . Layer 2: Thickness: 677894 nm; Compo: Si 31.97 %, O 32.89 %, Na 25.85 %, Ca 1.64 %, Al 0.25 %, K 1.05 %, Fe 0.38 %, B 5.89 %

3.3 Optical Results

(i) Optical Results in UV-VIS-NIR

Fig. 3 and Fig. 4 show the optical absorption and transmission results respectively for UV-VIS-NIR in the range 300 – 840nm. It can be seen that the absorbance in VIS of samples B and D annealed at 250 ℃ and 350 ℃ respectively are lowest at 13.7 % and 23.8 % respectively. All samples absorb highly (60 – 80 %) in the UV ranges ($\lambda <$ 400 nm). Highest transmittance for sample B was 80 % and for sample D was 60 % in the VIS and NIR ranges. Other samples A and E were not transparent enough (T < 51 %) in the VIS to be useful window materials and were not to be further considered in the infra red reflectivity analysis that followed. The as-deposited film was not also considered because of its low functional stability. The reflectance values for the four samples were as presented in Fig. 5 which shows acceptably low reflectance for all four films.

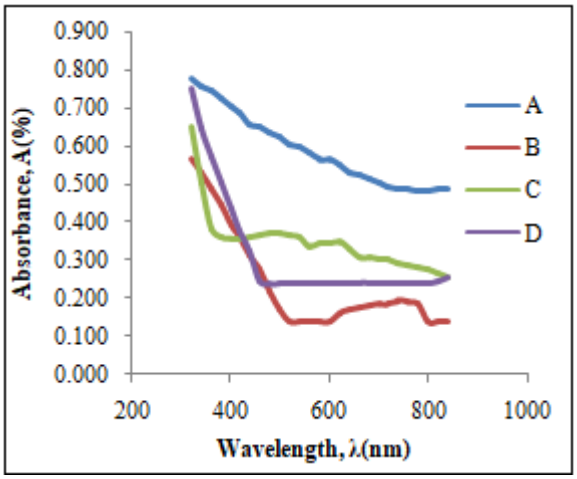

Figure 3: Spectral absorbance of thin films in the UV-VIS-NIR ranges

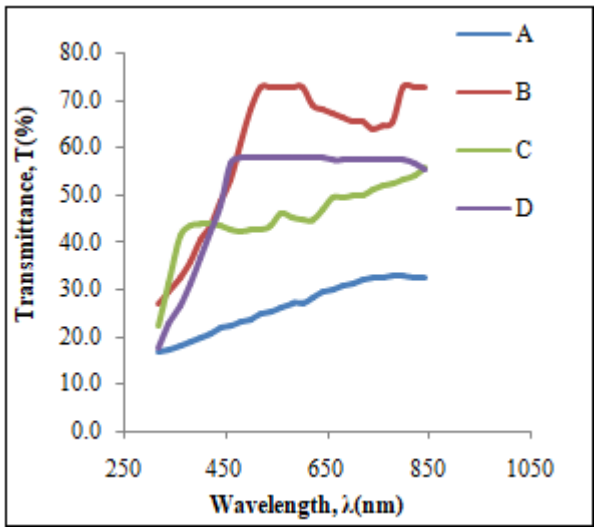

Figure 4: Spectral transmittance of thin films in the UV-VIS-NIR ranges

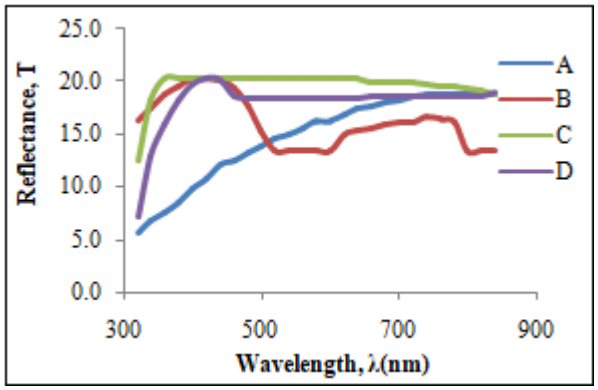

Figure 5: Spectral Reflectance of thin films in the UV-VIS-NIR ranges

(ii) Optical Results in Infra-red Ranges

The IR reflectance rose rapidly as wavelength increased from NIR to reach a maximum of 77 % for sample B and 67 % for sample D as shown in Fig. 6. These peaks remained fairly steady for short wave infra-red, SWIR (1400 – 3000 nm) and most MID IR covered ($\lambda > 3000$ nm). At $\lambda = 3300$ nm, the IR reflectance of sample D overtook that of B to level off at impressive 61 % as against B (58 %) for the rest of wavelength considered.

Transmission of IR, as shown in Fig. 7 was as low as 9.0 % for sample B and 23.5 % for D in some of the wavelengths considered. This rose, though slowly, to values of 31 % (for B) and 25 % (for D) and hereafter remaining constant for most far infra-red (FIR) energies ($\lambda > 4000$ nm). The rather smooth curves were however truncated by the usual kicks in reflectance that is usual in IR spectrometry. The kicks represent characteristic absorption by deposit as well as substrate molecules due to their changing vibration and rotation modes resulting from varying molecular dipole moments. The corresponding wavelengths of such kicks become fingerprints of the thin film composition.

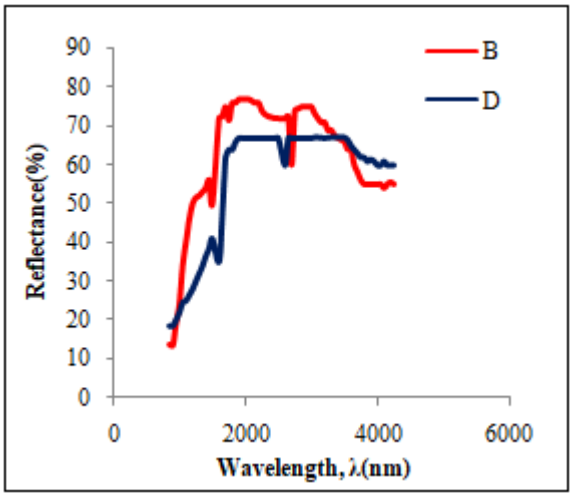

Figure 6: Infra-red reflectance of thin films

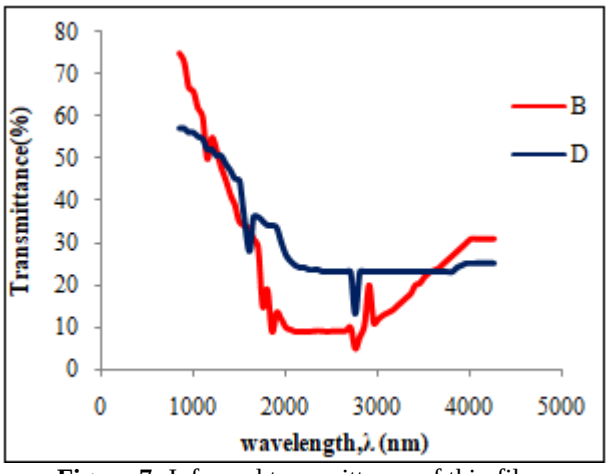

Figure 7: Infra-red transmittance of thin films

4. Conclusion and Future Scope.

We have successfully coated SiO_2/Sb-SnO_2 multinary films of nanosizes (~380 nm thick) on glass to serve as good infra-red reflecting window. We could get IR reflectance of between 67 % and 77 % for silicon oxide/stannic oxide composite film that was doped with little quantity antimony atoms. These coated plane glass could however highly transmit (60 – 80 %) visible light and absorb highly (~ 75 %) in the ultra violet ranges ($\lambda < 400$ nm). The IR reflectivity of this spectral selective coating compares favorably with that of commercial and well known metal films like aluminum, silver and gold (80 – 90 %) [21] but which cannot be used as IR reflectors in car or architectural windows since all metals have very low transmittance for visible spectrum. Annealing the composite films at various temperatures between 200 and 350 ℃ tremendously increased the sticking coefficient to glass and hence expected to enhance the stability of the selective window in long term usage. Effort is thus being made by our team to determine and improve this sticking coefficient and scratch resistance of the fabricated films. Such film on window glasses could screen out (reflect) heat waves entering offices, in hot weather, while transmitting visible light almost completely. Hot weather can be caused by climate or factory emissions and other local environment. Cost of air-conditioning in such offices can thus be reduced using our fabrication. Such window will as well find uses in offices and vehicles in cold environment where it reflects back to rooms/cabins the IR heat already delivered by domestic heaters thus saving heating cost.

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