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Bismuth Sulfide Thin Film Deposited by AACVD using Single Molecular Precursors

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Abstract

Single-molecular precursors, Bis-N, N-(Diethyldithiocarbamato) bismuth (III) **(SM-1)** and Bis-N, N-(Dicyclohexyldithiocarbamato) bismuth (III) **(SM-2)** for Bi_2S_3 thin films were synthesized by reacting secondary amine and CS2 with bismuth chloride in acetonitrile as a solvent. These precursors were characterized by FTIR. SM-1 and SM-2 complexes undergo thermal decomposition at temperature range from 310 °C to 330 °C to give Bi_2S_3 residue. Thin films of bismuth sulphide were deposited on glass substrate using aero-sol assisted chemical vapor deposition (AACVD) at temperature suggested from TGA studies of SM-1 and SM-2. Surface chemistry including phase purity, particle size, and elemental composition of thin films were determined using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) techniques. Thin films were found to have flakes and fiber like morphologies.

Keywords: Chemical vapor deposition, Thin films, Single molecular precursors.

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Introduction

In recently years, inorganic semiconductors have gained attention due to their wide range of physical and chemical properties make them suitable for solution process able optoelectronic devices.[1-6] However, these materials have toxic elements such as lead or cadmium, which have adverse effect on environment. Among these semiconductors, bismuth sulphide have low toxicity and have been emerged as potential semiconducting material due to its applications in photovoltaic, photodiode, thermo-electrics, memory devices and gas sensors.[7-10] Bi_2S_3 have shown properties like high absorption coefficient, direct band gap in the range of 1.25–1.70 eV, [11, 12] low processing cost, ease in fabrication even on flexible substrates and enhanced stability.[5, 9, 13, 14] Various chemical and physical deposition methods have been adopted for bismuth sulphide thin films fabrication including reactive evaporation,[15] thermal evaporation,[16] hot wall method,[17] molecular layer epitaxy,[18] successive ion later adsorption and reaction,[19] spray pyrolysis,[20] sol gel,[21] electro deposition,[22] chemical bath deposition [23] and chemical vapour deposition.[24] Among these methods, aerosol assisted chemical vapour deposition is a simple and attractive technique with good potential for scale up.[25]

In this study, we reported the synthesis of two bismuth di-thio carbamate complexes (SM-1 and SM-2) as single source precursors for the deposition of thin films of Bi_2S_3 using AACVD technique. The single source precursors were found volatile enough at normal pressure and decompose on the surface of substrate at elevated temperature. High temperature ensures the decomposition of organic part of precursor compounds leaving behind thin film of bismuth sulphide on the surface of the glass substrate. The as-deposited thin films of Bi_2S_3 were then characterized by XRD, SEM and EDX to determine the crystallinity, composition and morphologies obtained by using SM-1 and SM-2 complexes.

Experimental

Materials

Carbon disulphide, potassium hydroxide, bismuth chloride, diethyl amine, di cyclo hexyl amine, toluene and ethanol were purchased from Sigma Aldrich and were used without further purification.

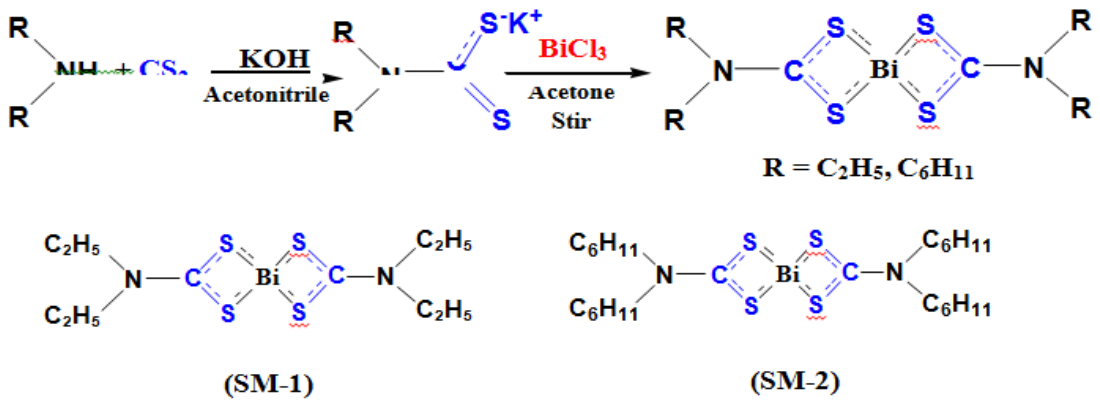
Characterizations

Phase purity was determined by using X-Ray powered diffraction (XRD) on Panalytical, X- Ray Diffracto meter, Model 3040/60 X-pert Pro. The samples were scanned in the range 20- 70°. Thin films were coated with carbon before taking their SEM and EDX images on Field Emission Scanning Electron Microscope (FE-SEM), TESCAN, Czech Republic. Infrared spectra were taken on Varian 640-IR using KBR palettes techniques. Thermal Gravimetric Analysis (TGA) was performed by using TGA/DSC1 STARe-System, of Model No. D- 09123, Mettler Toledo, Switzerland. 2-3mg of the samples were analysed in alumina crucibles

using N_2 as a flushing gas at the flow rate of 60.0 ml per minute. The scan speed was set at 10°C per minute.

Procedure for the synthesis of single molecular precursors

Single molecular precursors (SM-1 and SM-2) were synthesized according to the method reported in literature.[26] Briefly, secondary amine (diethyl amine and di cyclo hexyl amine) (20 mmol) was dissolved in acetonitrile (30 ml) followed by the addition of 24 mmol KOH aqueous solution. Carbon disulphide (24 mmol) was then added under stirring for one hour at room temperature. The solution of $BiCl_3$ (10 mmol) in acetone was then added to the reaction mixture under stirring for 1 hour. The as-obtained precipitates were filtered and washed with ethanol three times.



Scheme 1: Synthesis of single source precursors for the fabrication of Bi2S3 thin films by AACVD.

Deposition of thin films by AACVD

Bismuth sulfide thin films were deposited on glass substrates by AACVD technique using single source precursors. The glass substrates were cleaned in isopropanol, distilled water and acetone. In the typical procedure, 500 mg of bismuth complex was dissolved in 20ml toluene. The aerosols of precursor solution were generated at room temperature using ultrasonic humidifier operating at 50Hz frequency. The aerosol generated was then transported to reaction chamber (350°C) under argon flow rate of 100 sccm. Thin film deposition was carried out at 350°C for 2 hours.

Results and Discussion

The synthesis of Dithiocarbamate bismuth complexes was confirmed by using FTIR spectroscopy are presented in figure 1 (a-b). The C-H, C=S and C-S stretching vibration peak were observed in the range 2922-2927 cm^{-1}, 1000-1250 cm^{-1} and 747- 963 cm^{-1} respectively. The peak in between 1250 to 1350 cm^{-1} was due C-N stretch while the absorption peak of C=N lies in between 1446-1513 cm^{-1} showing the partial double bond nature of the C-N bond. All these observations were according to literature and are evidence of dithiocarbamate complex formation.[27, 28]

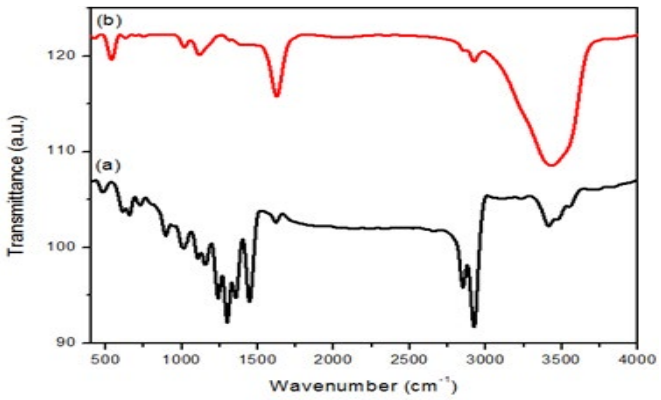


Figure 1: FT-IR graphs of single molecular precursors (a) complexes SM-1, and (b), complex SM-2.

Meanwhile, thermogravimetric analysis (TGA) was performed to find out suitable temperature for the deposition of complexes SM-1 and SM-2 to deposit thin films using AACVD. Figure 2 shows that the SM-1 complex was stable up to 240°C. A major weight loss event was observed between 275°C-300°C which indicates a single step degradation to reduce the total solid residue to 35% of the initial weight of the complex. The residual weight (35%) was very close to calculated value (35.64%) and it remains constant from 3100C to 600°C indicating thermal stability of Bi_2S_3.

The complex SM-2 was stable up to 280°C and in the temperature ranges from 280°C to 300°C, major decrease in the weight (43%) of initial mass was observed. This loss of mass indicates complete breakages of complex leaving only bismuth sulphide. The residual weight (57%) was very close to calculated Bi_2S_3 weight (57.24%). Further heating brings no considerable change in weight of residue showing its thermal stability.

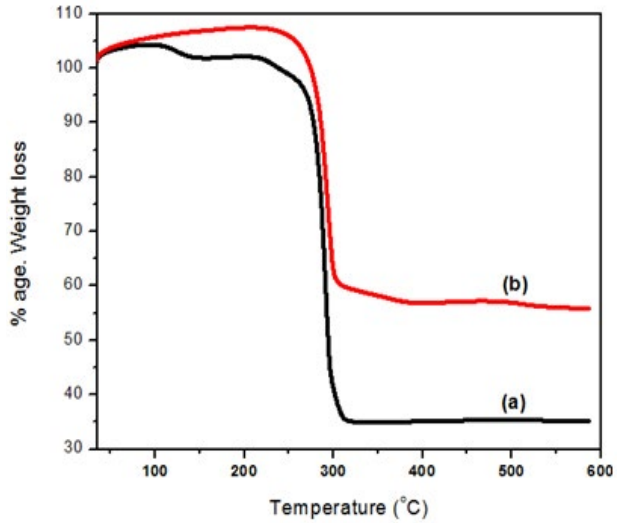


Figure 2: TGA spectra of dithiocarbamate complexes (a) SM-1 and (b) SM-2

AACVD of the as-synthesize complexes (SM-1 and SM-2) gives uniform and well adhered dark brown films deposited onto glass substrates at 350°C. The as-deposited bismuth sulphide thin films by AACVD were characterized by XRD as shown in figure 3. The SM-2 shows the major diffraction peaks at 23.69, 24.97, 27.33, 28.57, 30.51, 31.82, 38.50, 41.56 and 45.5° which corresponds to the orthorhombic phase of Bi_2S_3 [ICDD: 00-017-0320]. The SM-1 shows the XRD diffraction peaks at 24.78, 27.10, 28.47, 30.85, 33.77, 41.89 and 45.35 which belongs to the orthorhombic phase of Bi_2S_3 [ICDD: 00-017-0320].

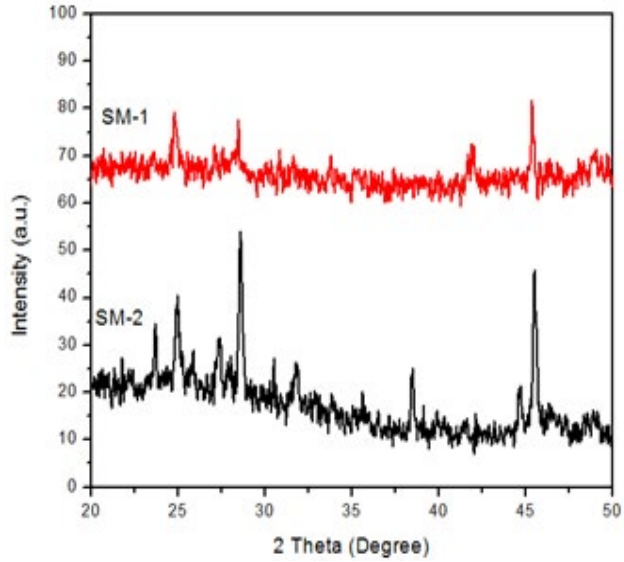


Figure 3: XRD spectra of thin films deposited by AAVD using complex (a) SM-1 and (b) SM-2.

Morphology of as-deposited thin films was determined by scanning electron microscopy. Figure 4 (a-f) shows the SEM images of Bi2S3 thin film deposited by AACVD using bismuth dithiocarbamate complexes SM-1 and SM-2. It can be observed that regular flakes like morphologies were appeared when SM-1 was deposited at 350°C (figure 4 (a-c). The shape of these flakes was very precise and regular with well-defined boundaries. However, the nanofibers were appeared when the deposition was carried out using SM-2 complex under same condition as show in figure 4 (d-f). The formation of two different morphologies under same condition using AACVD is due to the different decomposition pathway of the precursors. It can be observed that cyclohexyl group promotes the formation of fibres which may be due to the bulky nature of cyclohexyl group. On the other hand, the absence of bulky nature in ethyl group based SM-1 complexes facilitates the formation of flake morphologies. Energy dispersive X-ray (EDX) results of thin films deposited by using complexes SM-1 and SM-2 showed elemental composition which almost matches the expected stoichiometry for Bi_2S_3.

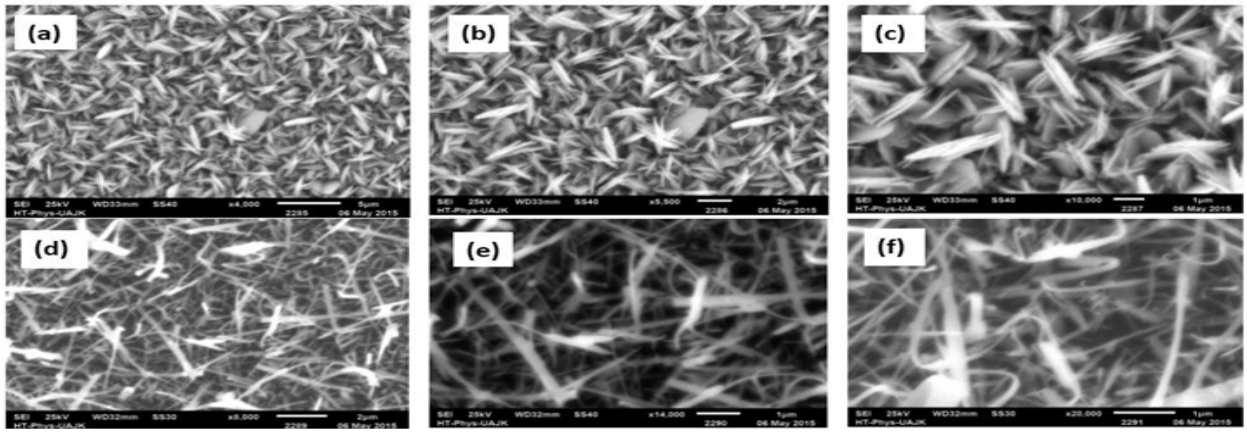


Figure 4: SEM images of Bismuth oxide from complex (a-c) SM-1 and (d-f) SM-2 deposited on glass substrate at 350 °C using ACCVD

Conclusion

Bismuth complexes with dithiocarbamate ligands were successfully synthesised and characterized by FT-IR spectroscopy and thermal gravimetric analysis (TGA). Thin films of Bi_2S_3 from these complexes were deposited by AACVD at temperatures of 350 °C. XRD confirmed the nano-crystallinity of Bi_2S_3 thin films having orthorhombic phase. Ethyl and cyclohexyl based dithiocarbamate bismuth complexes have shown flakes and thread like morphologies of Bi_2S_3, respectively which suggest that dithiocarbamate derivates could affect the thin film morphologies.

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