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Exploring the photoluminescence emission behaviour of vacuum deposited Sb_2O_3 thin film having randomly oriented thorn like structures

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ABSTRACT

An intense UV–visible photoluminescence of vacuum deposited Sb_2O_3 thin film surface crowded with randomly oriented thorn like structures have been studied using photoluminescence (PL) spectroscopy. The resulting UV emissions are near band edge (NBE) emissions. All the visible deep level emissions (DLE) are due to oxygen defect states. The thorn like structures is achieved by the inclined arrangement of substrates with respect to the source in the vacuum chamber. Some distorted polygonal shapes also emerge among the randomly oriented thorns giving an impression of a hybrid formation upon annealing. This formation of various structures leads to decreased UV NBE and defect level PL emission. The excitation wavelength dependence of PL emission has also been studied. The optical band gap energy of the film is found to be varying from 3.64 to 3.42 eV on annealing. The prepared films are of Sb_2O_3 cubic structure with polycrystalline nature as confirmed from XRD results. The emergence of thorn like morphology is clearly demonstrated with the aid of FE-SEM and TEM analyses. EDS verifies the elemental composition of Sb_2O_3. This paper provides an insight into the influence of confinement directions or film surface morphology on the PL emission intensities and PL emission ranges of Sb_2O_3.

1. Introduction

The quality of modern world devices is highly reliable on thin films prepared through vacuum based synthesis techniques. Vacuum pressure plays an important role in modifying thin film parameters like adhesion, purity, homogeneity, film thickness etc. [1]. High vacuum of nearly $\sim 10^{-5}$ Torr and more is used in various vacuum deposition techniques such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), Molecular Beam Epitaxy (MBE), Sputtering etc. A major significance of PVD method is that a large variety of substrates can be coated with unlimited number of materials including metals, alloys, semiconductors, organic and inorganic compounds etc. The thin films produced are of various microstructures with excellent adhesion. Such thin films are widely used in optical, opto-electronic and microelectronic systems [2,3]. The greatest advantages of vacuum thermal evaporation are faster evaporation rate, better step coverage and substrate damage prevention in comparison with other PVD techniques like sputtering, CVD etc. In addition, film purity and thickness can be controlled using suitable vacuum condition and by varying the deposition rates [4].

Antimony Trioxide (Sb_2O_3) is a semi-metal oxide semiconductor with wide and direct band gap of 3.3 eV [5,6]. This V – VI group compound has got many applications in optoelectronics and industrial chemistry. Antimony Trioxide is an excellent flame retardant synergist in plastic and polymer industry [7,8] and can even act as a good catalyst in organic synthesis and photochemistry [9–13]. Like any other metal oxide semiconductors, Antimony Trioxide also got applications in optoelectronic devices such as solar cell and UV LED. It is also used as a part in heat mirrors and spectrally selective coatings [14]. Sb_2O_3 exist in two polymorphic phases: the low-temperature senarmontite phase with cubic shape and the high-temperature valentinite phase with orthorhombic shape [15–17].

Recently, synthesis and characterization of micro and nanostructures of Sb_2O_3 have been intensively studied by many authors. For examples, Jamal et al. studied the photocatalytic degradation of acridine orange and chloroform sensing using as grown Sb_2O_3 microstructures [13]. Cebriano and coworkers studied the photoluminescence and optical resonances in Sb_2O_3 micro and nanotriangles [18]. Besides, they studied the self-assembly phenomena, luminescence and phase transitions in Sb_2O_3 micro-rods [19]. Zhengtao and coworkers synthesized Sb_2O_3 single-crystalline nanobelts with elliptical cross section and studied its emission properties [20]. They as well investigated the emission properties of single crystalline Sb_2O_3 nanowires with rectangular cross section [21]. Several studies have been

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focused on structural and optoelectronic properties of vacuum deposited Sb_2O_3 thin films [22–24]. N. Tigau discussed the surface morphology, optical transmission and optical band gap studies of vacuum deposited Sb_2O_3 thin films in his work [22]. Tigau et al. studied the influence of heat treatment on the electrical conductivity of vacuum deposited Sb_2O_3 thin films [23]. Tigau et al. analyzed the effect of substrate temperature on the optical properties of polycrystalline Sb_2O_3 thin films synthesized from vacuum thermal evaporation [24]. They also investigated the effect of thickness on the structural, optical and electrical properties of Sb_2O_3 thin films [25]. In previous studies, it was proved that Sb_2O_3 thin films exhibit high refractive index in the range of 1.85–2.3, excellent transmission at infrared wavelengths and large absorption in the UV region [23,24]. M. Haj Lakhdar et al. studied the structural, dielectric and a. c. conductivity behaviour of Sb_2O_3 thin films synthesized by three steps of evaporation process in high vacuum through the formation of Sb_2S_3 using Sb powder and sulfur grains [26]. Though, luminescence studies on micro and nanostructures of Sb_2O_3 were reported earlier [18–20], to the best of our knowledge this is the first ever made report on the photoluminescence properties of vacuum deposited Sb_2O_3 thin films having surface crowded with randomly oriented thorn like structures.

In the present work, we prepared Sb_2O_3 thin films having surface crowded with randomly oriented thorn like structures using high vacuum thermal evaporation technique with the inclined arrangement of substrate with respect to the source. Its structural, morphological, molecular and optical characterization have been carried out using XRD, EDS, FE-SEM, TEM, FTIR, Raman spectroscopy, UV–Visible absorption spectroscopy and Photoluminescence analysis. The influence of the film surface morphology on the PL emission intensities and emission ranges of Sb_2O_3 thin film has also been investigated.

2. Experimental details

The Sb_2O_3 thin films are prepared through vacuum thermal evaporation of polycrystalline Sb_2O_3 powder (99.99% purity from Merck India Ltd) under a high vacuum of about 2×10^{-5} m bar onto chemically cleaned glass substrates using high vacuum coating apparatus Model 12A4D HHV. The glass substrates have been maintained at room temperature and kept above the evaporation source. The arrangement of the substrates with respect to the source is in such a way that the evaporated flux may fall on it at an inclined angle as depicted in Fig. 1. The evaporation source consists of a molybdenum boat resistively heated by two electrodes. The dome of the coating chamber is water cooled to avoid heating of substrate and other parts. A few of the thin film samples are annealed in air at 200 °C, 300 °C, 400 °C and 500 °C for 30 min.

The structure of as-deposited and annealed films are studied by room temperature X-ray diffraction technique using Cu K_α radiation ($\lambda = 0.15406$ nm) of Bruker AXS D8 Advance diffractometer. The FTIR spectra of the samples are recorded in the range 300–4000 cm^{-1} using Perkin-Elmer spectrum 2 Spectrometer. Raman studies are carried out using the Confocal Raman microscope WITec Alpha 300 RA. Energy Dispersive Spectrum (EDS) analysis is done by EDS analyzer attached to JEOL JSM-6490 LA scanning electron microscope. ZAF standardless quantitative analysis is used for obtaining EDS spectrum. The FE-SEM analysis is conducted with NOVA NANO SEM 450. The detailed structural analyses are performed with the help of high resolution transmission electron microscopy (HR-TEM) using FEI TECNAI F20 G2 transmission electron microscope. For TEM specimen preparation, the film is cleaved from the substrate using a sharp edged surgical blade and the slices obtained are dissolved in acetone using sonication for 15 min. The solution is then diluted well and one drop is placed on the copper grid of dimension 3 mm using a micropipette. This grid is dried at room temperature and used for analysis. The EDS spectrum is attained during TEM analysis and the quantitation method used is Cliff Lorimer thin ratio section. The UV–Vis absorption spectra in the wavelength range 200–700 nm are recorded using Cary 300 spectrophotometer and Photoluminescence measurements are made with Horiba scientific Fluromax-4 spectro-fluorometer.

3. Result and discussion

3.1. Material characterization

3.1.1. X-ray diffraction

X-ray diffraction peaks of a crystal usually include three types of information -structural, geometrical and physical. The structural information is related to the XRD peak position and intensity. The crystallinity and phase of the products have been investigated with XRD measurements. The XRD patterns obtained for the samples are shown in Fig. 2. which reveals that the synthesized films are polycrystalline in nature. The sharp intense peaks point out how well the samples are crystallized. As deposited samples and all annealed samples except 500 °C annealed samples are cubic phase of Sb_2O_3 (or Senarmontite: JCPDS card no: 721334). The 500 °C annealed sample contains both cubic Sb_2O_3 and cubic Sb_2O_4 (JCPDS card no: 731735) phases. During

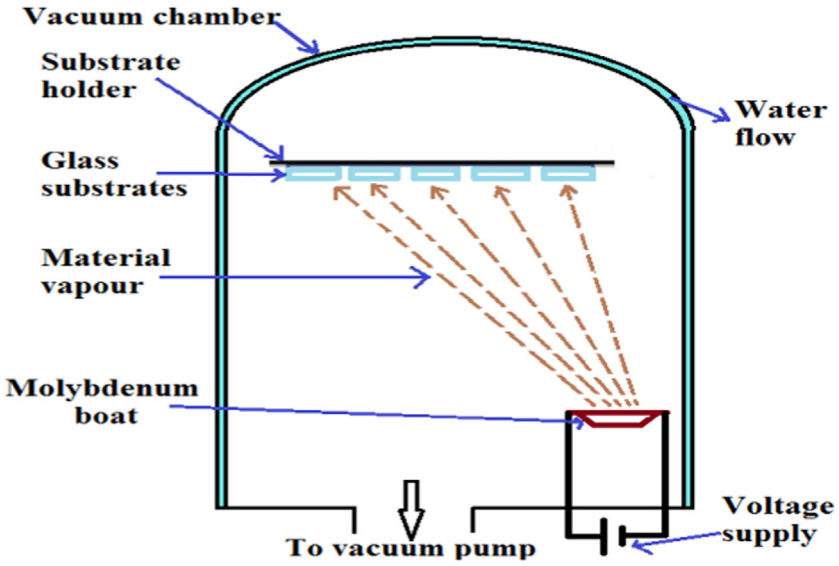

Fig. 1. Arrangement of glass substrates with respect to the source in the vacuum chamber.