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Full Length Article

Effects of oblique angle deposition on structural, electrical and wettability properties of Bi thin films grown by thermal evaporation

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ABSTRACT

Oblique angle deposition is a promising technique for tuning the physical properties of thin films. Structural, surface morphology, electrical and wettability properties are strongly influenced by the angle of deposition. A comparison of these physical properties of normally and obliquely deposited Bi films is carried out in this study. X-ray diffraction studies show that films have highly oriented hexagonal crystal structure and crystallite size is smaller for obliquely deposited (70 nm) film as compared to that of normally deposited film (111 nm). Raman spectra of the films consist of peaks corresponding to E_g and A_{1g} first-order Raman modes of bismuth. The atomic force and scanning electron microscopy studies show that the surface roughness of obliquely deposited film is higher as compared to that of normally deposited film. Contact angle measurements reveal that both films are strongly hydrophobic in nature with the contact angles of $105 \pm 1^\circ$ and $119 \pm 1^\circ$ for normally and obliquely deposited films respectively. Oblique angle deposition enhances the hydrophobicity of the film. The electrical conductivity of the film is significantly reduced by oblique angle deposition. The activation energies for electrical conduction were determined by four-probe measurements and are 0.0166 ± 0.0003 eV and 0.0178 ± 0.0003 eV for normally and obliquely deposited films respectively.

1. Introduction

Bismuth is bestowed with special and very interesting properties such as high anisotropy, lower charge carrier concentration in comparison to the metals, low effective mass of charge carriers and high magnetoresistance [1]. Bi thin films have been reported to exhibit quantum confinement based phenomena such as bandgap originating from the confinement of electrons which produces semimetal-to-semiconductor transition for very low thicknesses owing to large mean free path for electron, large Fermi wavelength (~400 Å) and high electron mobility [2–5]. The oscillations in transport properties such as electrical conductivity, Hall coefficient etc., with film thickness have been reported in the literature and are attributed to the quantum size effect [2,3,6,7]. Although bismuth is not a good thermoelectric material [4], it is an important component of binary and ternary thermoelectric materials such as Bi_2Te_3, Sb_2Te_3 and $Bi_2(Se_yTe_{1-y})$ [8,9]. Bismuth compounds possess reasonably high values of efficiency of thermoelectric conversion that is given by the product of figure-of-merit, Z and temperature T (in Kelvin). The figure-of-merit is further given by $Z = S^2\sigma/k$, where S, σ and k are Seebeck coefficient, electrical conductivity and thermal conductivity respectively [8,9]. Therefore electrical properties of Bi play crucial role in determining the overall thermoelectric properties of the material. The fast growing field of nanoelectronics technology has generated great interest in the nanostructured materials such as nanoparticles and thin films whose, properties can be tailored compared to their traditional bulk counterparts [10]. For Bi, it has been reported that the thermoelectric efficiency enhances by reduction in size i.e. Bi nanostructures have enhanced Z-values as shown by Dresselhaus et al. [11,12]. Yang et al. have reported large values of magnetoresistance ratio, $[R(B)-R(B=0)]/R(B=0)$ of ~1500 at 5 K and 2.9 at 300 K and they reported decrease in this ratio with decrease in thickness of polycrystalline Bi thin films. This effect was found to be still larger for single crystal Bi films [7]. Besides the well-known interesting electrical properties of Bi films, Su et al. have reported very interesting switchable superhydrophobic and superhydrophilic properties of Bi thin films synthesized by chemical method and the switching was achieved by exposing the film to UV–Vis light for 50 min [13].

Hydrophobicity of the films is strongly influenced by the surface morphology, roughness and cleanliness of the sample [14,15]. The need of surfaces with low wettability has increased with the development of new technologies of micro- and nano- electromechanical systems [14].

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Hydrophobic thin films find applications in gas sensors [16] microfluidic devices [17] and chemical valves [18] etc. The hydrophobicity or hydrophilicity of the surface is evaluated by measuring the contact angle of a water droplet on the surface, if the contact angle is less than 90°, the surface is hydrophilic and if the contact angle is higher than 90°, the surface is hydrophobic. Surfaces with contact angles higher than 150° are superhydrophobic [14]. The surface properties of the film play an important role in determining its wettability properties. Bi thin films exhibit a variety of surface morphologies such as dendritic with multi-branch hierarchy, rod-like, strip-like and skeleton-like shapes [13,19]. This property of surface morphologies accomplishes the task of tailoring of various physical properties including magnetoresistance, hydrophobicity and electrical conductivity etc. The microstructure and surface morphologies of thin films are very much dependent upon the deposition technique. Variety of deposition methods have been employed for the synthesis of Bi thin films such as electrodeposition, magnetron sputtering, pulsed laser deposition, thermal evaporation, electron beam evaporation, molecular beam epitaxy and hydrothermal method [4–6,19–22]. Thermal evaporation is one of the most economical and simple methods of thin film synthesis and polycrystalline Bi thin films with good structural and surface morphological properties can be prepared by this technique. Further oblique angle deposition is a powerful and versatile tool for surface engineering to obtain desired physical properties for scientific and industrial applications [23]. The growth of film is governed by two contesting phenomena: surface diffusion and shadowing effect. In oblique angle deposition the shadowing effect becomes more pronounced which causes greater deposition on elevated portions resulting in microstructures that are significantly different from that of films fabricated by normal deposition [23,24]. Mukherjee et al. explained the role of substrate temperature for the determination of dominance of diffusion or shadowing effect. At low deposition temperatures i.e. for $T_s/T_m < \sim 0.24$, where T_s is the substrate temperature and T_m is the melting temperature of the depositing material, the diffusion is less hence the shadowing effect dominates and microstructures belonging to the Zone I of the structure zone model are produced [24]. The homologous temperature, $T_s/T_m > \sim 0.5$ forms equiaxed Zone III structures [24]. However, Torrisi et al. have reported that the homologous temperature is not the sole criterion for the determination of surface morphology [25]. Hawkeye et al. have reported that the shadowing effect quickly becomes dominant in glancing angle deposition at an early stage of film growth but still the surface diffusion remains the important factor and tends to neutralize the shadowing effect [26]. Thus oblique angle deposition results in notably different surface morphology which significantly influences the surface dependent properties such as hydrophobicity. Due to several unique properties, Bi films and nanostructures continue to be an exotic topic for experimental as well as theoretical research for many years.

In the present work, highly hydrophobic Bi thin films have been synthesized by thermal evaporation and it is found out that water repellent Bi films can be prepared by simple and economical thermal evaporation technique which is also more suitable as compared to chemical deposition technique for integrated device fabrication processes.

2. Experimental

Bi films were deposited on microscopy glass slides by thermal evaporation. No deliberate substrate heating was done during deposition. The substrates were cleaned ultrasonically prior to deposition. Thermal evaporation unit (Vacuum Technology, New Delhi, India) was used for thin film deposition. Base pressure of 5×10^{-6} mbar was achieved before deposition by an oil diffusion pump and liquid nitrogen trap. Rotary pump was used for backing of the diffusion pump. Two types of samples were prepared by evaporating Bi granules (Sigma Aldrich, 99.9%) in a Mo boat, first, by keeping the substrates parallel to the horizontal boat (0° with horizon) i.e. normally deposited film, and the second inclined (60° with horizon) i.e. obliquely deposited film. The condensation rate was 1–4 Å s^{-1}.

The structural properties of the films were studied by X-ray diffraction (Shimadzu Maxima 7000, Japan) in θ-θ scan (Bragg-Brenttano geometry) with a speed of 1 degree min^{-1}, step size of 0.02°, 40 kV accelerating voltage and 30 mA emission current.

Raman spectrometer (Renishaw, InVia Reflex, UK) with excitation laser of 514.5 nm from an Argon ion laser source was used for studying the short-range structure. FESEM (Zeiss, Supra 55, Germany) was used to analyze the surface morphology of the films. Thicknesses of the films were determined from the cross-sectional FESEM images. The surface of the films was also analyzed by atomic force microscopy (AFM, Nanosurf AG, Switzerland) in non-contact tapping mode. Si tip with radius of curvature < 10 nm and height 17 μm was used. The root mean squared values of surface roughness were obtained by using SPIP 6.7.4 image analysis software. The electrical properties of the films were studied by four-probe method (Scientific Equipment & Services (SES) Instruments Pvt. Ltd., Roorkee, India) as a function of temperature. The hydrophobicity of the films was measured by drop shape analyzer (Krüss, Easy drop, DSA25 E, Germany).

3. Results and discussion

3.1. Crystal structure and short range order

The XRD patterns (Fig. 1) confirm the formation of highly oriented Bi films with peaks at 22.4°, 45.8° and 71.4° corresponding to the (0 0 3), (0 0 6) and (0 0 9) planes respectively of the hexagonal crystal structure. Since XRD scans were performed in Bragg-Brenttano geometry, it is concluded that the crystallites are strongly oriented parallel to the substrate surface with the trigonal axis [0 0 1] perpendicular to it. The small peak at 27.5° is due to reflections of X-rays from (0 1 2) crystal plane. The observed growth of grains of (0 0 3), (0 0 6) and (0 0 9) orientation has also been reported by Das et al. [27]. Boffoue et al. have shown that Bi films grown by pulsed laser deposition (PLD) also exhibit the preferred growth of crystallites of (0 0 3) orientation as the thickness of the film is increased with slight initial growth of crystallites of (0 1 2) orientation [5].

The peak intensities in the XRD pattern of the film deposited at 60° is found to be less than that of the film deposited at 0° which is due to the reduced thickness and smaller crystallite size in the sample for oblique angle deposition [15]. The crystallite size was calculated from the Scherrer's formula (Eq. (1)) by considering the width of peak due to crystallites of (0 0 6) orientation.

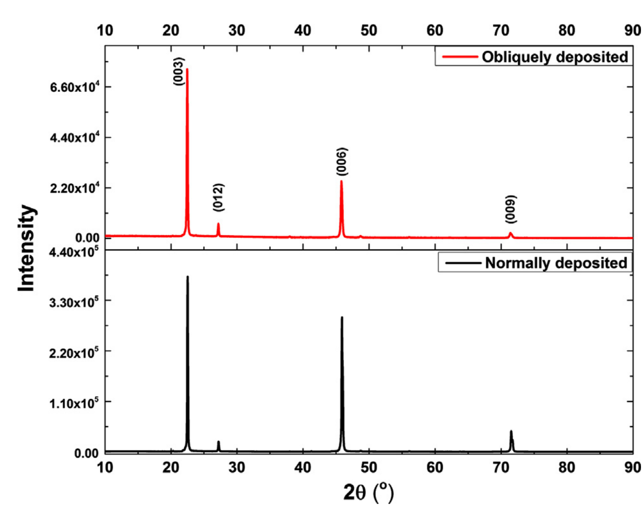

Fig. 1. XRD patterns of normally and obliquely deposited Bi thin films.