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Growth and thermal properties of various In_2Se_3 nanostructures prepared by single step PVD technique

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In_2Se_3 nanostructures have attracted much attention due to their potential applications in diverse areas, such as solar energy conversion, thermoelectric power generation, phase change random access memories, photodetectors, and optoelectronics in the visible region. In the present work, we have fabricated various In_2Se_3 nanostructures on SiO_2/Si substrate using a simple and single-step physical vapor deposition (PVD) method, without using metal seed layer on the substrates. Morphology, structure and phase of the as-grown In_2Se_3 nanostructures have been carried out using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, respectively. In addition, we have also explored thermal properties of In_2Se_3 nanostructures on SiO_2/Si substrate using temperature and power dependent Raman spectroscopy. Further, the thermal conductivity of nanoparticles, nanospheres, and rod like flowers at room temperature were found to be ~37.6, ~39.5, and ~15.6 W/m-K, respectively. This work suggests an effective way to form various novel nanostructures, opening up a new scenario to understand the vibrational properties and electron-phonon interactions of In_2Se_3 nanostructures.

1. Introduction

The III–VI semiconductors have been the focus of many investigations in recent years due to their high significance in electrical and optical properties as well as their potential applications in optoelectronic devices, such as solar cells, batteries, and photodetectors [1–7]. Among these III-VI semiconductors, Indium selenide (In_2Se_3) is a direct band gap semiconductor with band gap ranging from ~1.35 to 2 eV, which depends on existing crystal structure and phase [8–11]. Owing to the mismatch of valence electron numbers, indium selenides have various complex forms with different stoichiometric ratios, such as InSe, In_2Se_3, In_4Se_3, and In_6Se_7 [7,12,13]. Moreover, indium selenides are also available in different phases and crystal structures with the same stoichiometric ratio of In_2Se_3, such as, α-In_2Se_3, β-In_2Se_3, γ-In_2Se_3, κ-In_2Se_3, and δ-In_2Se_3 phases, in which polymorphic phases α, β and γ have been confirmed [11,13]. Due to this unique property of In_2Se_3, it has drawn tremendous research attention in the field of phase change random access memories and photovoltaic applications [6,14,15].

Several growth methods have been employed to prepare In_2Se_3 films/nanostructures, such as thermal evaporation [9], chemical vapor deposition (CVD) [16], molecular beam epitaxy (MBE) [17], vacuum evaporation [18], flash evaporation [19], sputtering [20], and solution-phase synthesis [21]. There are many challenges regarding the formation of indium selenide nanostructures due to firstly, indium ions are easy to hydrolyze in aqueous solution due to their deficient electron properties and secondly, several kinds of crystalline phases of In_2Se_3 nanostructures [21,22]. However, a very few research groups have been explored on In_2Se_3-nanostructures in growth direction by physical vapor deposition (PVD) method so far [9,23]. T. Zhai et al. [23] reported the synthesis of sulfur doped

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In_2Se_3 nanostructures such as, nanowire, ordered nanotree, and nanowire bundles by thermal evaporation of In_2Se_3 and graphite mixed powder as the source materials. Suryawanshi et al. [9] presented temperature and time dependent vapor phase growth of different In_2Se_3 nanoforms prepared by thermal evaporation. An alternatively, Chen et al. [24] have demonstrated that an efficient hetero junction photodiode formed by γ-In_2Se_3 nanoflower film by solution phase method. Li et al. [25] have reported an ambient pressure organic solution phase synthesis of amorphous In_2Se_3 nanoparticles and flower-like shaped β-In_2Se_3 nanocrystals, and 2D β-In_2Se_3 nanosheets. Nanostructures have become the focus of the worldwide research, due to their potential use as active materials in high performance nanoscale devices because of their high surface-to-volume ratios and rationally designed surfaces. In view of the properties and applications of In_2Se_3 nanostructures usually determined by their phase structures and morphologies, it is desirable and significant to fabricate pure phase In_2Se_3 with novel morphology by a simple method.

In this paper, we reported a simple and single step PVD method to grow the various In_2Se_3 nanostructures without using any metal coating as a seed layer, such as In_2Se_3 nanoparticles with different morphology and three-dimensional (3D) rod-like-flower shaped In_2Se_3 structures. Furthermore, we also described their phase and thermal properties of obtained nanostructures by Raman spectroscopy. To the best of our knowledge, there is no report on thermal conduction of In_2Se_3 nanostructures so far, performed using of micro-Raman spectroscopy. Such study is important for further understanding of the fine structure and properties of the material such as, nature of the atomic bonds, thermal expansion, specific heat, and thermal conductivity. In the view of In_2Se_3 nanostructures as a possible material for application in various optoelectronic devices, it is essential to know the electron-phonon (e-p) interaction and temperature dependent vibrational properties of nanostructures. In case of field-effect transistor (FET) based devices, by applying the bias voltage can results in the self-heating of the device which can affect the performance of In_2Se_3 based electronic device. Here, we also demonstrate a proof-of-concept for change in Raman peak position for In_2Se_3-nanostructures with a wide range of temperatures from 300 to 500 K.

2. Experimental details

High-quality In_2Se_3 powder was purchased from Smart Elements and used as a precursor. Silicon wafers with thermally grown SiO_2 layer (~300 nm) were used as substrates and is defined as SiO_2/Si. SiO_2/Si substrates were initially cleaned with organic solvents followed by RCA-1 ($NH_4OH:H_2O_2:H_2O$ – 1:1:2) treatment to remove organic impurities and small particles from the surface of the substrate and then ultrasonic cleaning with de-ionized water [26]. Finally, the substrates were blow dried under a stream of nitrogen gas, prior to use. The β-In_2Se_3 powder (0.2 g, 99.9% purity) was placed at the centre of a quartz tube. An Argon (Ar) gas flow of 100 sccm was maintained, and carried the vapor to deposit the In_2Se_3 nanostructures on the SiO_2/Si substrate, placed downstream about 20–25 cm away from the precursor as shown in Fig. 1(a). The growth temperature has been carried in the range of 650–950 °C at the rate of 15 °C/min. After 1 h deposition, the system was allowed to cool naturally under the constant Ar flow.

The surface morphology of the In_2Se_3 nanostructures was studied by a Hitachi SU 70 scanning electron microscope (SEM) at 10 kV. Micro-Raman spectroscopy was performed using a confocal Raman microprobe equipped with a 514 nm excitation wavelength of solid-state green laser. Temperature dependent Raman studies were carried out on different In_2Se_3 nanostructures in a temperature range from room temperature (RT) to 500 K then samples were allowed for five minutes thermal stabilization. The laser power was maintained at below 0.25 mW during the experiments in order to avoid the Raman shift introduced by laser heating. The Structure of the source material was obtained by X-ray diffraction (XRD, Bruker AXS D8 advance). Chemical composition of the In_2Se_3 nanostructures were studied by X-ray photoelectron spectroscopy (XPS), with a Thermo-Fisher Microlab 350 XPS system equipped with a

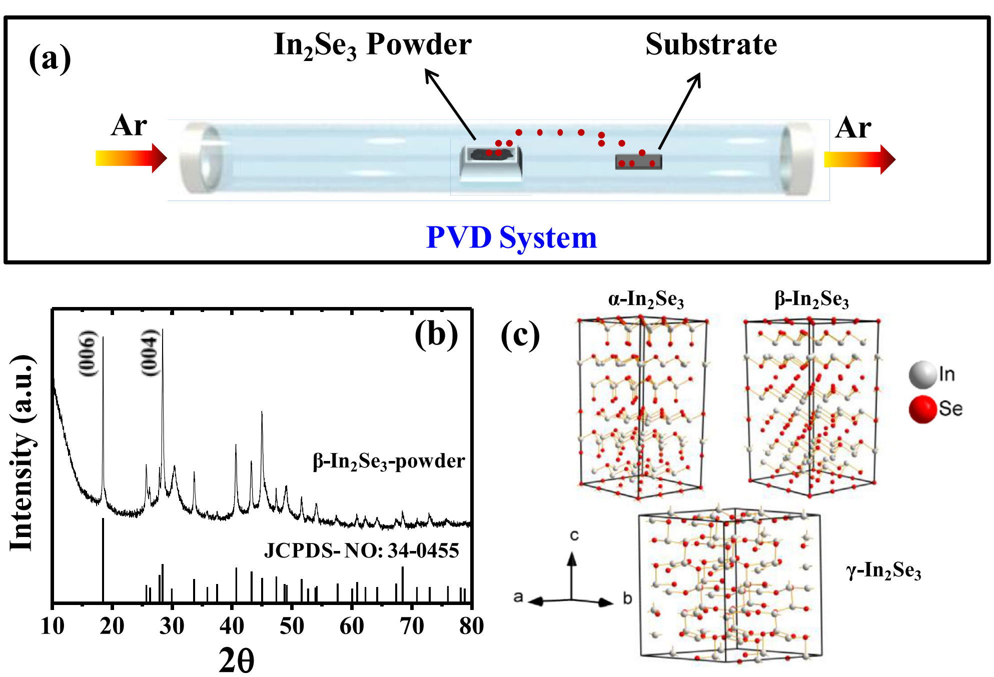

Fig. 1. (a) Schematic diagram of the physical vapor deposition for In_2Se_3 nanostructures growth, (b) XRD pattern of In_2Se_3 powder as precursors and (c) In_2Se_3 crystal structures at different phases.