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Vacancies ordered in screw form (VOSF) and layered indium selenide thin film deposition by laser back ablation

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ABSTRACT

Indium selenide thin films are important due to their applications in non-volatile memory and solar cells. In this work, we present an initial study of a new application of deposition-site selective laser back ablation (LBA) for making thin films of In_2Se_3. *In vacuo* annealing and subsequent characterization of the films by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) indicate that control of substrate temperature during deposition and post-deposition annealing temperature is critical in determining the phase and composition of the films. The initial laser fluence and target film thickness determine the amount of material deposited onto the substrate.

1. Introduction

Chalcogenide thin films have attracted much attention ever since they were proposed for phase change memory applications (i.e., Ovshinsky effect) [1] and now have become a commercial reality with $Ge_2Sb_2Te_5$ (GST) based optical recording media. Indium selenide (In_2Se_3) components have also found applications in photovoltaic cells. For example, the highest efficiency poly-crystalline thin film solar cell has been fabricated using $CuInSe_2$ [2]. In_2Se_3 has also been demonstrated to be a viable phase change memory constituent with resistive properties that could exceed those of GST [3,4]. In_2Se_3 device structures have also been fabricated with nanowires [5].

A variety of methods including vapor deposition molecular beam epitaxy and metal oxide CVD have been used to fabricate In_2Se_3 thin films [6]. Past research in our own collaborative group has been focused on understanding the heteroepitaxy of Group III-selenides on silicon for integration with microelectronics by MBE [7]. However, for device applications a faster synthetic technique is desirable. Pulsed laser deposition (PLD) has the unique advantage in offering faster processing, including target preparation and the ability to make multi-component combinatorial thin films relatively easily [8]. PLD has also been used for the deposition of various amorphous chalcogenides owing to their diverse applications, yet rarely applied to indium selenide thin films synthesis [9–11]. In this letter we report an initial study on the fabrication of crystalline In_2Se_3 thin films by laser back ablation (LBA) and their subsequent characterization by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM).

LBA has found use in the fabrication of patterned structures with feature sizes ranging from few microns to a few hundred nanometers (e.g., LIFT techniques) for metals, oxides and even polymers and other biological materials [12–14]. The LBA process is analogous to regular PLD but here, the focused laser beam interacts with the target from the 'back side' through a transparent media supporting the target material. This leads to the ablation of the target material and its subsequent transfer onto a substrate that is placed directly in front at a very short distance. When compared to regular PLD this leads to less waste of the starting target material and faster deposition rates. This is particularly important for both industrial

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applications and for environmental concerns about minimizing the use of toxic materials. The ability of PLD in making combinatorial films is reduced in this process (though we are working to overcome that difficulty) but it is believed that this technique could be a viable method for making thin films quickly from binary or ternary phases of uniform composition once the desired composition has already been selected.

2. Experimental

The capability for deposition-site selectivity is dependent first on the maximum spatial resolution of the laser ablation source. Utilizing a laser source with a spatial beam profile which can be described by a Gaussian function, the spot size at the focus of an optic in the beam path is suitably described as twice the beam radius (ω_0) at the Gaussian beam waist (z_0) where,

$$\omega_0 = \frac{z\lambda}{\omega(z)\pi} \quad \text{as } z \rightarrow \text{infinity} \tag{1}$$

To guarantee a well-characterized Gaussian laser source, we have selected to use a Nd:YAG laser operating on the 3rd harmonic of 355 nm and producing a dominant TEM_{00} single mode Gaussian spatial pulse of 5 ns temporal width. The Rayleigh criterion for spatial resolution is conveniently written as

$$d = \text{Diameter of spot size} = \frac{0.61\lambda}{\text{N.A.}} \tag{2}$$

where N.A. is the numeric aperture of the optic. In our case, we have used a Zeiss Fluar (20×, 0.75 N.A.) microscopic objective. Thus, the diffraction limit for our spot size using Eq. (2) is seen to be d = 289 nm.

We have been able to measure the produced near-diffraction limited laser spot. Fig. 1a displays our measurement of the laser spot, $2\omega(z)$, as it diverges from the objective at four extended distances, z, from the beam waist, z_0. In this way we have been able to estimate the effective average beam radius and spot size at the focus of our objective. This value of $2\omega_0$ = 414 nm is 30% larger than the diffraction limit for our configuration of optic and wavelength, and represents our maximum potential resolution for patterned structure deposition via LBA.

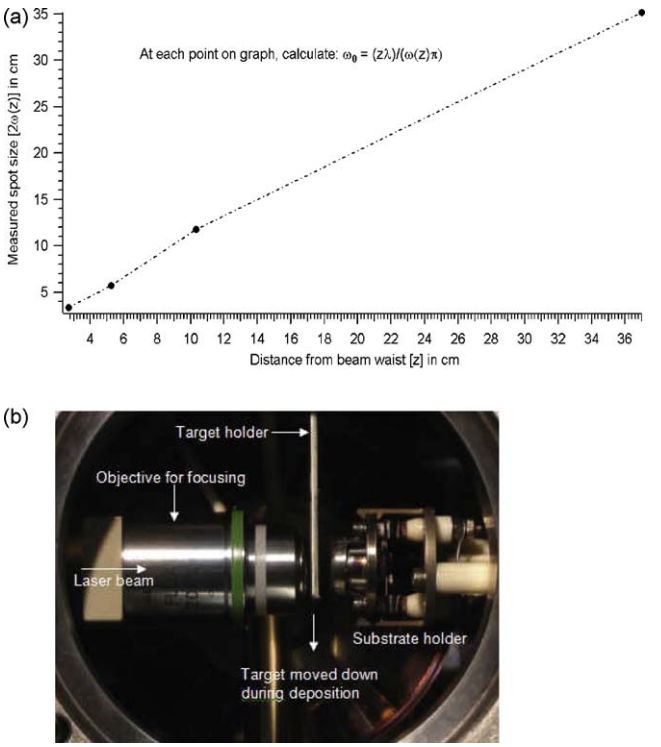

Fig. 1. (a) Displayed are data at four points, laser spot size versus distances from focus. Applying the Eq. (1), we determine the calculated beam radii at the given distances. Twice the average of these values gives us the effective laser spot size produced at the focus of our objective. (b) Side view of the experimental setup in the PLD chamber.

As the focal length at this wavelength is 0.5 mm, targets were made with 0.5 mm thick UV grade quartz slides onto which In_2Se_3 was coated via physical vapor deposition. The nominal depths of the target coatings were 200 nm. The schematic of the setup is shown in Fig. 1b. Thin film deposition was carried out on single crystal silicon substrates (0 0 1) in a chamber with a base pressure of 1×10^{-8} Torr. Initial runs were carried out with a tightly focused laser spot size conforming to our maximum spatial resolution at laser powers of 0.42 W and repetition rates of 20 Hz. Preferentially deposited, micron-scaled, thin film was visually observed on our substrate. In order to increase the coverage area and film uniformity in subsequent runs we further deposit thin film (herein reported) by selectively defocusing the laser. The target was moved in the vertical direction by a dc stepper motor as the deposition was being carried out so as to provide a fresh target region for the laser throughout the run.

The whole deposition process lasted less than 3 min once sufficient vacuum had been established in the system. Annealing of the deposited samples was done *in vacuo* following deposition. For the VOSF phase the sample was heated at 350 °C for 30 min and for the layered phase growth, the sample was heated to 550 °C for 2 min and allowed to cool slowly to room temperature before venting.

The XRD experiments were performed on a high resolution, double-crystal Philips X'Pert XRD system with a Cu anode. The experimental diffraction data were analyzed using JADE software (Materials Data, Inc., Livermore, CA) and compared with the Powder Diffraction File, PDF-2 database (International Centre for Diffraction Data, Newtown Square, PA). Secondary electron imaging was carried out using a field-emission environmental scanning electron microscope (Phillips Model XL30) (for both morphology of films and thickness) at 20 kV operating voltage. XPS was carried out in a Kratos Analytical AXIS-HS XPS system with an Al K_α anode operating at pass energy of 80 eV. Charge compensation was done by a focused electron gun operating at −1.0 eV. Data analysis was done using CasaXPS software and the peaks were offset by setting the adventitious C 1s peak to 285 eV.

3. Results and discussion

As-deposited thin films were amorphous in nature and covered the entire area exposed by the sample holder though the thickness

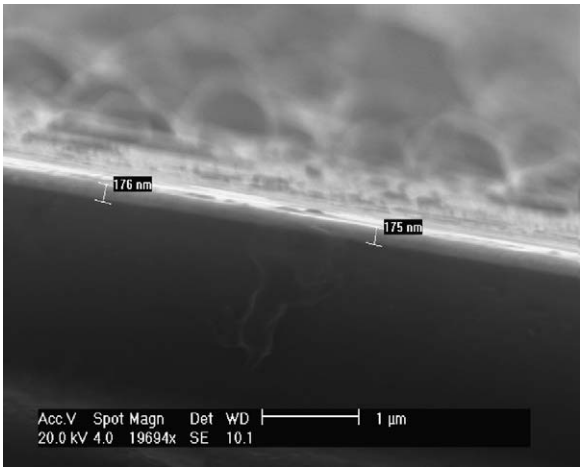

Fig. 2. SEM image of the film substrate interface clearly depicting the film thickness.