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Chemical deposition and characterization of thorium-alloyed lead sulfide thin films

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ABSTRACT

We present a chemical bath deposition process for alloying PbS thin films with ^{232}Th, a stable isotope of thorium, to provide a model system for radiation damage studies. Variation of deposition parameters such as temperature, reagent concentrations and time allows controlling the properties of the resulting films. Small amounts of incorporated thorium (0.5%) strongly affected the surface topography and the orientation of the films and slowed down the growth rate. The Th appears to be incorporated as substitutional ions in the PbS lattice.

1. Introduction

Lead chalcogenide semiconductor thin films have been a subject of considerable research due to their technological importance in monocrystalline and polycrystalline forms as infrared radiation detectors, infrared emitters and solar control coatings. A variety of chemical and physical methods have been developed to prepare thin metal chalcogenide films [1–3]. Among the different thin film fabrication methods, the chemical bath deposition (CBD) from aqueous solution offers a simple and cost-effective route for the fabrication of high quality semiconductor thin films, without the need for high deposition temperatures, stringent vacuum or plasma generators compared to other sophisticated techniques [4–7]. Lead sulfide (PbS), being the most studied material among the lead chalcogenides, is a narrow, direct band gap semiconductor [8]. The interest in PbS is due to its useful optoelectronic properties for infrared detection and emission [9]. Recently, the interest in nanocrystalline PbS has been dramatically increased due to its potential use in solar cells and visible light sensors [10]. Nanocrystalline films and quantum dots of the IV–VI semiconductors PbS, PbSe and PbTe exhibit unique properties and investigations of effects of strong confinement of electrons and phonons are underway [11,12]. CBD of PbS and PbSe can provide a range of controlled microstructure from isolated nanocrystalline particles to compact, dense polycrystalline layers by varying the deposition parameters such as deposition time, temperature, precursor and complexant ratios, pH and intermediate lead chalcogenide layers [5,13–15].

Several cases of epitaxial CBD of PbS films in different systems have been reported [7]. Osherov et al. reported epitaxial CBD PbS films on GaAs(100) substrates from alkaline solution containing lead nitrate, thiourea, and sodium hydroxide [15]. Cross-sectional transmission electron microscopy (TEM) and selected area electron diffraction (SAED) revealed a non-conventional $(011)_{PbS}||(100)_{GaAs}$ and $\left[0\bar{1}1\right]_{PbS}\left\|\left[01\bar{1}\right]_{GaAs}\right.$ orientation relationship between the film and the substrate.

Moreover, it was shown that the morphology evolution of thin lead chalcogenide films on GaAs substrate is strongly affected by the active deposition mechanism during the deposition process. By controlling the deposition conditions it is possible to control the active deposition mechanism, and thus the resulting film morphology and thickness [4–6,8,13–16]. Most recent CBD PbS studies were carried out on various semiconductor substrates such as monocrystal GaAs substrates, while others used glass substrates mostly due to their cost effectiveness and transparency in the visible range [17,18]. The CBD PbS thin film on GaAs(100) is a well-known system. Osherov and Golan have reported on the continuous, adherent single phase PbS films on GaAs(100) and showed a good chemical compatibility between the two materials [17].

The properties of irradiated materials are of scientific interest and practical importance in nuclear and space applications. Studies of radiation damage are focused on the understanding of the changes in physical properties due to the microscopic evolution of the accumulated damage to the lattice. This is usually achieved by irradiating the samples externally in accelerators or reactors. A different branch of radiation damage studies focuses on the change in properties of materials that are subject to self-irradiation due to their radioactive nature, e.g., metals of the actinide series. The study of the actinides is complicated due to

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their radioactive and chemical toxicity which require special care and equipment [19]. The possibility to carefully control the growth of lead-based thin films such as PbS and alloying them with radioactive thorium, makes these materials excellent candidates to become model systems for the study of processes that are similar to self-irradiation damage.

In the present work, we developed an alloying procedure for the incorporation of ^{232}Th ($t_{1/2} \sim 10^6$ years) in chemically deposited PbS films and explored the effect of thorium on the deposition of PbS thin films and their microstructure. Subsequent incorporation of radioactive α-emitting ^{228}Th ($t_{1/2} = 1.9$ years) presents a noteworthy concept for studies of self-irradiation in (otherwise non-radioactive) semiconductor thin films. In order to develop the desired alloying process we had to overcome several challenges, such as the lack of an existing phase diagram of the Th–PbS system and the lack of similar processes for Th alloying on record, set aside protocols for using CBD. Moreover, there are generally very few works dealing with alloying by CBD [10,20]. In this work, we show incorporation of thorium ions in chemically deposited PbS thin film and report on their notable effect on the deposition kinetics and on the film properties.

2. Experimental

2.1. Materials and chemicals

Sodium hydroxide (Gadot, AR), lead (Pb^{2+}) nitrate (Aldrich, analytical 99.99+ %), thiourea (Aldrich, ACS ≥ 99.0%), and tetravalent thorium cations (Aldrich, 1000 ppm of Th^{4+} in 5.1 wt.% HNO_3) were used without further purification for deposition of PbS. Single crystal GaAs(100) substrates were purchased from AXT (epi-polished, undoped, ±0.1° miscut). Distilled water was obtained using a Millipore Direct Q3. The films were deposited from a solution with a final composition of 9 mM $Pb(NO_3)_2$, 51 mM $CS(NH2)_2$ and various concentrations of Th solution at pH 12.6 according to a protocol reported by Osherov and Golan [17]. Prior to deposition, the solution contained in a Pyrex beaker was purged with pure N_2 for 60 min in order to reduce levels of dissolved O_2 and CO_2 and placed in the dark in a thermostatic bath to reach the desired temperature. Growth of PbS films on GaAs was carried out at different temperatures and different times. Single crystal GaAs(100) wafer substrates were cleaved into 1 × 3 cm^2 rectangles and cleaned with distilled water, then with analytical ethanol and dried. Films were deposited on the bottom face of the substrates in order to prevent large particles from adhering to the growing film. Therefore, the substrates were placed epi-side down in the solution, mounted on a custom-designed Teflon stage at an angle of ca. 70° with respect to the air–solution interface.

The influence of the thorium salt addition on film growth and resulting morphology was studied and compared to deposition of PbS in the absence of thorium. Reference PbS films were deposited from solutions that were adjusted to the exact same pH at the same temperature and time as the thorium containing films. Since the thorium is provided as a nitrate salt in HNO_3, control experiments were carried out in the presence of nitrate anions and at the same pH as the thorium alloying experiments — in order to isolate the effect of thorium addition on the deposition process.

2.2. Characterization methods

2.2.1. X-ray diffraction (XRD)

The structure and orientation of the films were studied by XRD. A Panalytical Empyrean powder diffractometer equipped with PIXcel linear detector and monochromator on diffracted beam was used. Data were collected in the 2θ/θ geometry using Cu Kα radiation (λ = 1.5405 Å) at 40 kV and 30 mA. Scans were run during 8 min in a 2θ range of 20–65° with steps of ~0.039°.

2.2.2. High resolution scanning electron microscopy (HR SEM)

The morphology of the films was observed using a JEOL JSM-7400F field emission gun HR-SEM without coating of the surface. Acceleration voltages ranged from 1 to 5 kV. Film thickness was measured from cross sections while surface topography was observed in plan-view.

2.2.3. X-ray photoelectron spectroscopy (XPS)

Spectra were measured using a Thermo ESCALAB 250 spectrometer with monochromatic Al X-ray source (excitation energy 1486.6 eV) at base pressure of 1 × 10^{-7} Pa. General elemental survey and high-resolution spectra of selected elements were recorded.

2.2.4. Analytical transition electron microscopy (ATEM)

ATEM investigations including Energy Dispersive Spectroscopy (EDS) analysis in the scanning TEM (STEM) mode were carried out by using a JEOL JEM-2100F analytical TEM operating at 200 kV. Cross sections were prepared by cutting the sample into slices normal to the interface and gluing them together face-to-face using M-Bond 610 adhesive (Allied HighTech Ltd.). The samples were polished with a precision small-angle tripod holder on a series of diamond polishing papers (Allied HighTech Ltd) until a thin wedge was formed, glued to a Mo slot grid (1 × 2 mm^2) and final thinning was done by Ar ion milling using a Gatan model 691 precision ion polishing system.

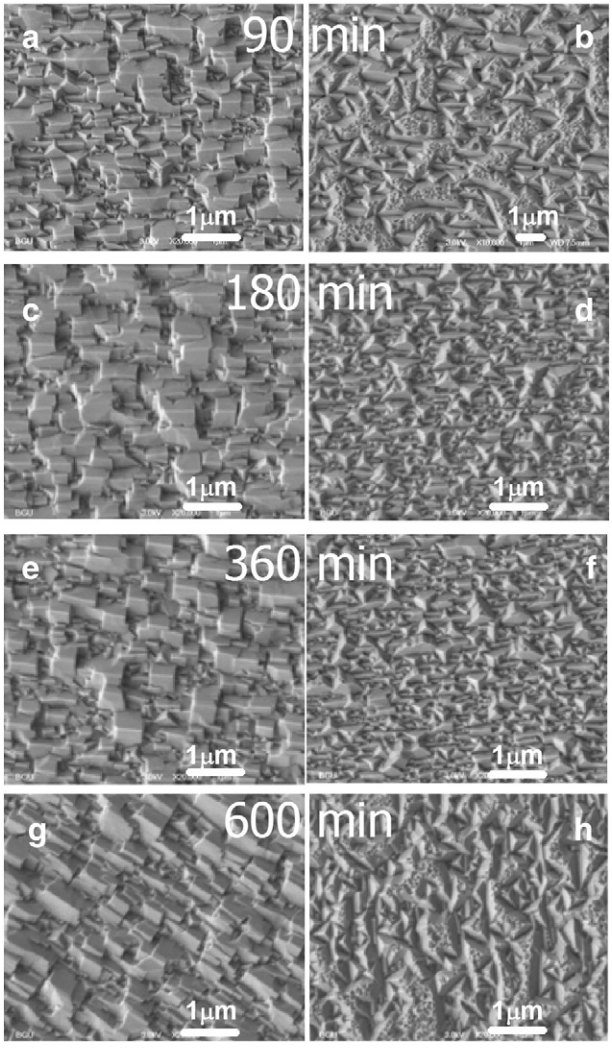

Fig. 1. The effect of deposition time. Secondary electron HR-SEM images of (a, c, e, g) PbS thin films (without thorium); (b, d, f, h) PbS(Th) thin films prepared with 0.438 mM thorium concentration in the solution and deposited on GaAs(100) at 30 °C for 90, 180, 360 and 600 min.