



Electrochemical Liquid-Liquid-Solid Deposition of Crystalline Gallium Antimonide



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ABSTRACT

Direct electrodeposition of phase-pure crystalline gallium antimonide (GaSb) films has been achieved at low processing temperatures from an aqueous electrolyte. A liquid gallium electrode was used to drive the electroreduction of Sb_2O_3 dissolved in 0.6M NaOH. The quality and purity of the resultant films produced depended strongly on the chosen conditions, including temperature, time, and concentration of dissolved Sb_2O_3 . Under select conditions, the direct production of polycrystalline films of GaSb was possible. Raman spectroscopy, powder X-ray diffraction, selected area electron diffraction, scanning electron microscopy, and transmission electron microscopy were separately used to analyze the identity and crystallinity of the electrodeposited films. The cumulative data showed that this electrodeposition process followed the features common both to conventional electrodeposition and melt crystal growth. Accordingly, this electrodeposition process could not be categorized as electrodeposition followed by annealing. Rather, the data implicate this method is akin to a hybrid electrodeposition solution-based crystal growth, where crystalline GaSb films could be grown up to thicknesses of 1 μm in 60 min.

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1. Introduction

Gallium antimonide (GaSb) thin films are attractive platforms for energy conversion technologies. For example, crystalline films of GaSb function as the absorber layers and/or substrate in the most efficient thermophotovoltaics [1–3], as deposition substrates for lattice matched ternary (AlGaSb, InAsSb) and quaternary (AlGaAsSb, InGaAsSb) alloys [4,5], as infrared-capturing cells in tandem solar cells [6] and as the lasing medium in low voltage diode lasers [7]. Unfortunately, the current methods (e.g. metal organic chemical vapor deposition and molecular beam epitaxy) for the production of crystalline GaSb are problematic at scale in several ways. Specifically, they rely on toxic gaseous precursors, require costly instrumentation, and do not allow high throughput [1,8]. Accordingly, a need exists to find alternative methods for the preparation of crystalline GaSb that retain quality but are better suited for rapid mass production.

In principle, conventional electrodeposition is a potential low cost route for crystalline GaSb thin films when performed in aqueous electrolytes at/near room temperature. However, the extant literature shows several issues with conventional

electrodeposition. Notably, electrodeposited GaSb is nonstoichiometric, amorphous, and contaminated with impurities from the electrolyte [9,10]. These factors individually are problematic and collectively are detrimental for electronic and optoelectronic application [11,12]. Non-stoichiometry is a direct consequence of unequal rates of incorporation of Ga and Sb in to the growing GaSb crystal. That is, the difference in the heterogeneous electroreduction rates of Ga- and Sb-containing precursors will lead to excesses/deficiencies of the constituent atoms in GaSb unless they are matched precisely. Further, electrodeposition of GaSb often results in films with high levels of impurities, both from the solvent and/or salts as well as metal contaminants in the electrolyte that were not removed prior to electrodeposition.

Alternatively, electrochemical liquid-liquid solid (ec-LLS) crystal growth is a new hybrid electrodeposition strategy amenable for the synthesis of crystalline semiconductor materials [13,14]. Briefly, in ec-LLS a liquid metal working electrode is used that functions both as a source of electrons for heterogeneous reductions and as a separate solvent for semiconductor crystal nucleation and growth [15]. In effect, ec-LLS couples conventional electrodeposition with melt crystal growth by using a liquid metal electrode with the ability to solubilize GaSb as the solvent to mediate crystal growth. Finite equilibrium solubilities of both $\text{Sb}^0(\text{s})$ and $\text{GaSb}(\text{s})$ in the liquid metal permits the formation of crystalline GaSb at low temperatures. Accordingly, this paper tests

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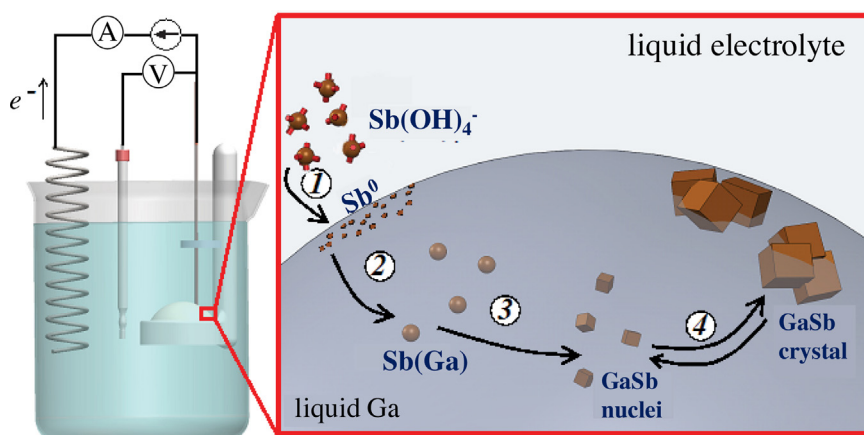


Fig. 1. Schematic depiction of GaSb ec-LLS. (1) The dissolved $\text{Sb}_2\text{O}_3(\text{aq})$ precursor is electroreduced to Sb^0 . (2) Dissolution of Sb^0 into the pool of $\text{Ga}(\text{l})$ and subsequent metallurgical alloying reaction with the liquid metal. (3) Supersaturation within the liquid metal phase leads to the formation of GaSb nuclei. (4) GaSb crystals grow and emerge from the liquid Ga pool.

the hypothesis that an ec-LLS process can be developed for crystalline GaSb using liquid gallium electrodes and Sb_2O_3 dissolved in aqueous electrolyte. Fig. 1 represents the ec-LLS tactic explored in this work. Through this method, we report the first demonstration of direct electrodeposition of crystalline GaSb at temperatures below the boiling point of water. Process conditions and experimental criteria for this method are identified and discussed herein.

2. Experimental

2.1. Materials

Antimony oxide (Sb_2O_3 , 99% Aldrich), sodium hydroxide (NaOH, >97%, Fisher), and Ga (99.999%, Alfa Aesar) were used as received. Water with a resistivity >18.2 $\text{M}\Omega \text{ cm}$ (Nanopure Barnstead Water Purification) was used throughout.

2.2. Electrochemical Experiments

CHI420A and CHI760C (CH Instruments) workstations and a Solartron 1286 (Solartron) potentiostat were used interchangeably for electrochemical experiments. All measurements were performed in a three-electrode Pyrex cell under ambient pressure. A liquid gallium pool housed within a glass bowl and contacted by a Pt wire that was isolated from the liquid electrolyte by a polytetrafluoroethylene (PTFE) coating was used as the working electrode, Pt-mesh was used as the counter electrode, and a Pt-wire was employed as a quasi-reference electrode. All potentials were then converted to the Ag/AgCl reference potential scale through the voltammetric response of the $[\text{Fe}(\text{CN})_6]^{3/4-}$ redox couple. Unless indicated otherwise, all potentials are reported relative to $E(\text{Ag}/\text{AgCl}/\text{Sat. KCl}(\text{aq}))$.

2.3. Materials Characterization

Raman spectra were taken using a Renishaw RM Series Raman microscope using a Nikon LU Plan 20x objective ($\text{NA}=0.4$), with edge filters for the 785 nm excitation line, in a backscatter geometry. A 785 nm diode laser was used as the incident excitation source with a total radiant power of 1.12 mW over a $20 \mu\text{m}^2$ spot which was collected for 20 seconds. The peak position of the TO mode for crystalline GaSb in the Raman spectra was obtained by fitting with a Voigt function using a max of 500 iterations with a tolerance of 10^{-15} . Scanning electron micrographs were obtained

from a FEI Nova Nanolab Dualbeam Focussed Ion Beam Workstation using a Schottky field emitter filament functioning at an acceleration voltage of 5 kV and a beam current 0.54 nA and a 1455 LEO scanning electron microscope using a tungsten filament source functioning at an acceleration voltage of 10 keV and a beam current of 20 pA. The secondary electrons were collected from an Everhart-Thornly Detector (ETD) or a through-the-lens detector (TLD). Powder X-Ray diffractograms were obtained from a Bruker D8 Advance X-ray diffractometer with a $\text{Cu K}\alpha$ X-ray source ($\lambda = 1.5406 \text{ \AA}$). The source slit was 0.6 mm using a data sampling interval of 0.040° for 0.7 seconds at each interval. Dark field and bright field transmission electron micrographs as well as the selected area electron diffraction pattern were collected with a JEOL 3011 TEM using a LaB_6 filament functioning at 300 kV. The TEM samples were prepared by freezing the liquid gallium ($\text{Ga}(\text{l})$) electrode directly after the deposition and removing the surface film with a razor blade. The razor blade was then placed in a scintillation vial containing about 1 mL of methanol (190 proof, ACS spectrophotometric grade, Aldrich) and the suspension was sonicated for approximately 45–60 min. A droplet of about 30 μL of the suspension was then cast onto a 400 mesh Cu TEM grid coated with an ultrathin carbon support (Ted Pella). The extensive sonication was needed due to the large particle size of the GaSb films. The SAED pattern for crystalline GaSb was simulated along the $\langle 111 \rangle$, space group F-43m, with the software Crystal Maker.

3. Results

Fig. 2 shows the current-potential response at the $\text{Ga}(\text{l})$ electrode immersed in electrolyte with and without dissolved Sb_2O_3 at a series of different concentrations. The maximum formal concentration attainable in this electrolyte was 0.6 mM. At the electrolyte pH of 12.3, the predominant species in solution is $\text{Sb}(\text{OH})_4^-$ [16,17]. In the blank electrolyte, the liquid gallium pool electrode readily oxidized at potentials less negative than -1.2 V but was stable at more negative potentials. These liquid gallium pool electrodes showed poor electrocatalytic activity for the H^+/H_2 redox couple ($\log(J_0/\text{mA cm}^{-2}) = -10.1$, $d \log(J)/dE = -6.1 \text{ V}^{-1}$). At this pH, the standard potential for the reduction of $\text{Sb}(\text{OH})_4^-$ is -0.720 V vs. Ag/AgCl [16,17]. Upon introducing Sb_2O_3 into solution, the cathodic current increased, indicating the liquid gallium electrode is active for the electroreduction of $\text{Sb}(\text{OH})_4^-$. However, a cathodic wave indicative of a diffusional limit for the reduction of $\text{Sb}(\text{OH})_4^-$ was not cleanly observed. Prolonged chronoamperometric experiments at potentials $\leq -1.27 \text{ V}$ resulted in the

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