Structural and Optical Properties of AgIn₅S₈ Films Grown by Pulsed Laser Deposition

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Abstract—Thin AgIn₅S₈ films are grown on glass substrates by pulsed laser deposition using bulk crystals as targets, and their structure, chemical composition, surface morphology, and optical properties (transmission and reflection spectra in the range 0.5–2.5 μm) are investigated. The transmission and reflection data are used to evaluate the absorption coefficient of the films and the energies of direct and indirect interband transitions. The results obtained for laser-deposited AgIn₅S₈ films agree well with those for bulk crystals.

INTRODUCTION

A₁BᵢᴵCᵥᴵ (A = Cu, Ag; B = Al, In, Ga; C = S, Se, Te) compound semiconductors are being used increasingly in producing nonlinear optical devices and high-efficiency (η = 19%) thin-film solar cells [1–3]. The parameters of such materials can be tuned by varying their composition, typically via the formation of solid solutions [1]. At the same time, the Aᴵ–Bᵢᴵ–Cᵥᴵ systems in question contain, along with the AᴵBᵢᴵCᵥᴵ compounds, ordered phases with the general formula AᴵBᵢᴵCᵥᴵ [4, 5], which also can be used in producing materials with tailored properties. The physical properties of such phases have not yet been studied in sufficient detail, and their potential for practical application is not yet fully understood. The ternary compound AgIn₅S₈ is a defect-rich semiconductor in which ~25% of the cation sites are vacant. Impurities and irradiation have little effect on the transport properties of AgIn₅S₈, which makes it an attractive material for semiconductor and quantum electronics.

A major technical problem in producing compound semiconductor films arises from deviations from stoichiometry due to material dissociation in the course of evaporation. In connection with this, conventional techniques for growing thin films (thermal evaporation, cathode sputtering, and others) are of limited utility in some systems. Pulsed laser deposition is widely used to grow thin layers of refractory and multicomponent materials and is believed to have a number of advantages over conventional deposition techniques [6, 7].

In this work, we report the structural and optical properties of thin AgIn₅S₈ films grown by pulsed laser deposition.

EXPERIMENTAL

As targets, we used Bridgman-grown AgIn₅S₈ crystals. Stoichiometric mixtures (25 g) of V₄ silver, V₄ indium, and V₅ sulfur were loaded into short-conical-bottom silica ampules precleaned by chemical etching in a 1:3 mixture of HNO₃ and HCl, followed by rinsing with distilled water and heat treatment at 400 K. To the bottom of each ampule, we fused a quartz rod, which was used as a holder and was connected to a vibrator. After pumping down to ~10⁻³ Pa, the ampule was sealed off and mounted in a vertical single-zone furnace with a preset temperature gradient. The mixture was heated to 1370 K at a rate of ~50 K/h, with isothermal holds and vibration stirring, and held there for ~3 h with constant stirring. Then, stirring was stopped and the melt was solidified by cooling at ~2 K/h to 1000 K, followed by isothermal annealing for 200 h. Next, the temperature was lowered to 700 K, and the ingot was furnace-cooled. The resultant ingots were 14 mm in diameter and ~50 mm in length.

In pulsed laser deposition experiments, we used a free-running commercial laser (λ = 1.06 μm, 1-ms pulses). The laser output was focused onto the AgIn₅S₈ target surface by a glass lens (f = 500 mm). The angle of incidence of the laser beam was 45°. The pulse repetition rate was 0.03 Hz, and the pulse energy was 150–180 J. The process was run in a vacuum chamber at a residual pressure of 2 × 10⁻⁵ Pa. The deposition rate was ~20–40 μm/s. The films were deposited onto chemically cleaned Corning Code 7059 glass substrates main-
tained at 750–790 K. The uniform portions of the films (2 cm²) ranged in thickness from 0.7 to 1.5 μm.

The structure and phase composition of the crystals and films were determined by x-ray diffraction (XRD) analysis (2θ = 15°–100°, CuKα radiation, λ = 1.5405 Å, incident-beam graphite monochromator). The phases present in the films were identified using JCPDS Powder Diffraction File data. Surface morphology and cross-sectional specimens were examined on a Hitachi H-800 scanning electron microscope (SEM). The elemental composition of the crystals and films was deter-

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**Fig. 1.** Typical XRD patterns of AgIn₅S₈ (1) crystals and (2) films.

**Fig. 2.** SEM micrographs of AgIn₅S₈ films: (a) film surface, (b) cross-sectional specimen.