Defect engineering in Sb_2Se_3 via post-growth thermal treatments: a photoluminescence study

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***Abstract* — Sb_2Se_3 is an emerging inorganic quasi-one-dimensional (Q1D) semiconductor absorber material for sustainable thin film photovoltaics. The efficiency of Sb_2Se_3 solar cells is mainly limited by the strong recombination of light-induced charge carriers resulting in low open circuit voltage of the devices. A route to suppress the formation of harmful deep defects in Sb_2Se_3 limiting the carrier lifetime, mobility and concentration via post-growth thermal treatment is presented in this study. The defects in the as-grown and post-growth heat - treated Sb_2Se_3 polycrystals are investigated by detailed photoluminescence spectroscopy.**

I. Introduction

Sb_2Se_3 is an inorganic quasi-one-dimensional (Q1D) semiconductor compound, which in recent years has been extensively studied aiming for thin film photovoltaic (PV) applications. Sb_2Se_3 has many advantages over the alternative chalcogenide absorbers for thin film solar cells, such as simple binary composition with high elemental abundance, single-phase orthorhombic crystal structure, a high absorption coefficient ($>10^5$ cm^{-1}) in the visible spectral region, a long minority carrier lifetime ($\approx$ 60 ns), and an optimal band gap of 1.2 eV for solar energy conversion [1],[2],[3]. Currently, Sb_2Se_3-based thin film solar cells have demonstrated device efficiencies close to 11% [1].

The efficiency of Sb_2Se_3 solar cells remains low compared to conventional photovoltaics, primarily due to a significant open-circuit voltage (V_{oc}) deficit, which is attributed to complex intrinsic defects in Sb_2Se_3. Although consisting of only two elements, low symmetry configuration of atoms in the crystal lattice of Sb_2Se_3 leads to a large variety of point defects and complicated defect chemistry [4],[5]. Intrinsic defects include point defects on non-equivalent atomic sites of Se and Sb in Sb_2Se_3 dominated by the cation-replacing-anion (Sb_{Se}) and anion-replacing-cation (Se_{Sb}) antisite defects with mid-gap energy levels. These deep defects can act as recombination centers for the light-induced charge carriers, leading to a reduced carrier lifetime and reduction in the solar energy conversion efficiency of the PV device.

To improve the power conversion efficiency of Sb_2Se_3 solar cells, it is critical to understand the defect structure of the absorber material and its complex behavior, and to suppress the formation of harmful defects that limit the charge carrier density and lifetime. This study presents a route to suppress the formation of deep defects in Sb_2Se_3 polycrystals via post-growth thermal treatment. Different annealing conditions, including various temperatures and annealing environments, were implemented. The resulting changes in the defect structure were studied by temperature and excitation power dependent photoluminescence spectroscopy.

II. Experimental Details

Sb_2Se_3 polycrystals were synthesized from 5 N purity Sb and Se elemental precursors, which were handled in a glove box under an inert atmosphere to prevent oxidation. The Sb and Se precursor powders were weighted according to the stoichiometric Sb_2Se_3 composition, mixed in an agate mortar and milled to achieve homogeneous composition of the polycrystals. The resulting precursor mixture was transferred into quartz ampoule, which was then sealed under vacuum to avoid contamination and unwanted reactions. A stepwise annealing process was implemented. Within the next 3 hours, the temperature was raised to 200 °C, where the ampoule was maintained for 24 hours. Following this, the furnace was gradually heated to 550 °C over 3-hour period and the material was annealed at this temperature for 300 hours. After the annealing process, the ampoule was taken out of the furnace and cooled down naturally to room temperature. This as-grown Sb_2Se_3 polycrystalline material was then subjected to post-growth thermal treatment under following conditions.

The as-grown polycrystals were divided into two equal portions. The first portion of Sb_2Se_3 as-grown polycrystals was inserted into quartz ampoule together with elemental selenium and vacuum sealed. The second portion of as-grown Sb_2Se_3 polycrystals was inserted into quartz ampoule filled with argon gas (200 Torr) and sealed. Both ampoules were containing elemental Se and Sb_2Se_3 polycrystals positioned on opposite ends of the ampoule. The ampoules were annealed in a two-zone furnace.

For both sets of as-grown Sb_2Se_3 polycrystals, same annealing conditions were applied to identify the role of argon atmosphere to the changes in the defect structure of Sb_2Se_3. During the annealing, the Sb_2Se_3 polycrystal side of the ampoule was at 500 °C and the Se component side at 440 °C.

The elemental composition of the polycrystals were determined by Energy Dispersive X-ray Spectroscopy using a Bruker Esprit 1.8 system on Zeiss Merlin high-resolution Scanning Electron Microscope, which revealed the slightly Sb-rich composition of the as-grown Sb_2Se_3 polycrystals and slightly Se-rich composition of the heat-treated polycrystals. The phase analysis was studied by using room-temperature micro-Raman analysis with Horiba's LabRam HR800 spectrometer with a 532 nm line of the YAG:Nd laser. For the PL measurements the polycrystals were mounted on the cold finger of a closed-cycle helium cryostat Janis CCS-150 of Lake Shore Cryotronics and the measurements were carried out in the temperature region of 8–300 K. A LakeShore Model 335 temperature controller was used to control the temperature. A pulsed CryLaS FQSS266-Q2 laser with 532 nm line with a maximum average power P_{max}=7.5 mW, peak energy 1.1 μJ, and peak width <1 ns at 10 kHz was employed as an excitation source. Neutral density filters were used to vary the incident laser beam's power density.

III. RESULTS AND DISCUSSION

Raman scattering analysis revealed single phase Sb_2Se_3 composition of the as-grown as well as the annealed polycrystals with the dominating A_g^2 mode slightly shifting to higher wavenumbers after thermal treatments. Secondary phases were not detected.

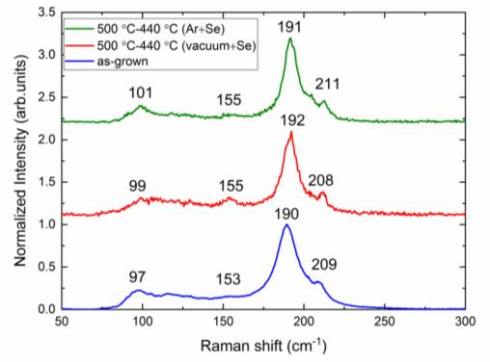

Fig. 1. Raman scattering spectra of as-grown and selenized Sb_2Se_3 polycrystals using annealing in argon atmosphere and vacuum annealing.

Defect structure of the synthesized Sb_2Se_3 polycrystals was studied by photoluminescence spectroscopy, which is one of the most sensitive methods to detect defects in semiconductors. The low-temperature PL spectra of as-grown as well as selenized Sb_2Se_3 polycrystals are presented in Fig.2, revealing that by heat-treatment in an argon atmosphere in a two-zone furnace using 500 °C at the Sb_2Se_3 polycrystal side and 440 °C at the Se component side resulted only in the edge PL emission at 1.3 eV. This means it is possible to get rid of the deep defects related radiative recombination at around 0.9 eV in Sb_2Se_3 by using the developed post-growth heat-treatment, which should enable higher Sb_2Se_3 solar cell device efficiencies.

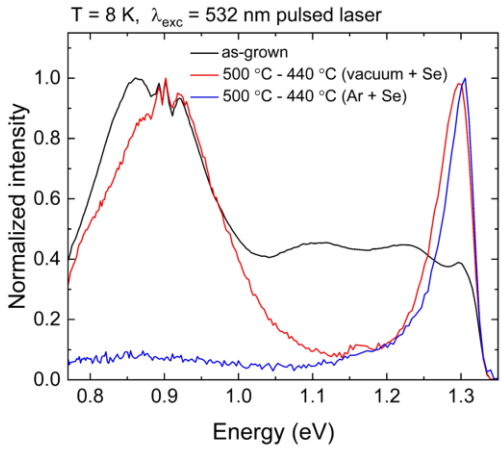

Fig. 2. Low-temperature (T = 8 K) PL spectra of as-grown and selenized Sb_2Se_3 polycrystals using annealing in argon atmosphere and vacuum annealing.

Detailed PL study using different measurement temperatures in the temperature region of 8–300 K and varying laser power densities were used to determine the radiative recombination mechanisms in the as-grown as well as selenized Sb_2Se_3 polycrystals, for which the low-temperature PL spectra are presented in Fig.2. For the as-grown Sb_2Se_3 polycrystals, the temperature and laser power dependent PL spectra are presented in Fig.3 and Fig.4. The as-grown Sb_2Se_3 revealed the radiative recombination mechanisms previously detected by us for slightly Se-rich Sb_2Se_3 and involving donor-acceptor pairs, deep donor-deep acceptor pairs as well as excitonic and band-to-band emission [6], [7]. The PL from the post-growth thermally treated Sb_2Se_3 polycrystals revealing only the edge PL emission will be presented in detail at the conference.

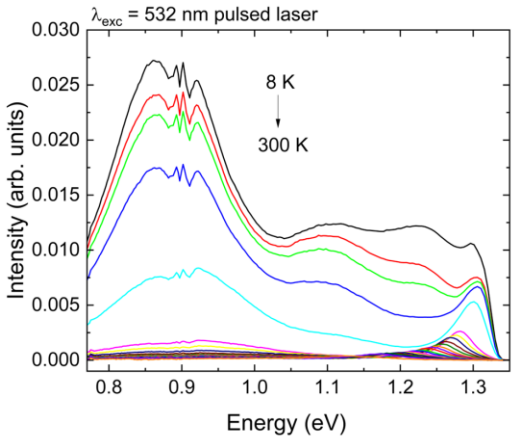

Fig. 3. Temperature dependent PL spectra of as-grown Sb_2Se_3 polycrystals revealing the deep PL emission as well as the edge emission.

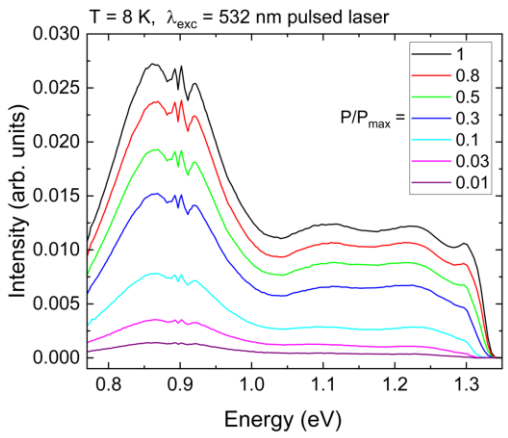

Fig. 4. Laser power dependent PL spectra at T = 8 K of as-grown Sb_2Se_3 polycrystals revealing the deep PL emission as well as the edge emission.

IV. SUMMARY

A route to suppress the formation of deep defects in Sb_2Se_3 polycrystals via post-growth thermal treatment is presented. A detailed photoluminescence study showed that heat-treatment in an argon atmosphere in a two-zone furnace using 500 °C at the Sb_2Se_3 polycrystal side and 440 °C at the Se component side resulted only in the edge PL emission at 1.3 eV as deep PL emission has been detected in the corresponding as-grown Sb_2Se_3. This development provides a route to suppress deep defects in Sb_2Se_3 possibly enhance the power conversion efficiency of Sb_2Se_3 thin film solar cells.

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