博 士 論 文 の 内 容 の 要 旨

氏名	Elyas Ashenafi Abadi
学位名	博士（Doctor of Engineering）
学位授与年月日	2022 年 3 月 20 日
論文題目	Study of Sb doped SnS thin film and its heterojunctions Sb 添加 SnS 薄膜及びそのヘテロ接合に関する研究

（博士論文の内容の要旨）

In recent years, considerable attention has been directed towards studying tin mono-sulfide (SnS) as a possible earth-abundant with low toxic constituents (Sn, S) absorber material for thin-film solar cells. SnS has an excellent optical and electrical property for photovoltaic applications. However, the highest conversion efficiency of such a cell is still less than 5%, with an open-circuit voltage not more than 400 mV. Solar cell devices fabricated with CdS/SnS structure exhibited an efficiency of even lower than 1.3% with open-circuit voltage and a short-circuit current density of 260 mV and 9.6 $mAcm^{-2}$, respectively. A maximum photovoltage of 471 mV is reported with an alternative buffer layer of TiO_2 in SnS/TiO_2 solar cell structure, even though the efficiency (0.1 %) and a short-circuit current density (0.3 mA/cm^2) are still low. Some of the reasons for this low efficiency for SnS-based solar cells are the poor quality of the SnS layers, co-existence of impurity phases (Sn_2S_3 and SnS_2), and lack of proper band alignment between the SnS thin film and buffer layers. Besides searching for different buffer layers, researchers are employing an extrinsic dopant to control the carrier concentration and realize n-type conductive SnS for homojunction (n-SnS/p-SnS) solar cell application. Thus far, the influence of the SnS absorber layer post-treatment on material properties and the SnS/buffer band alignment has not been investigated theoretically and experimentally. This thesis, therefore, details the effect of post-growth annealing and Sb doping on SnS and its SnS/CdS junction properties.

The SnS thin films (~1 μm) were grown on the Soda-lime glass (SLG) substrates by a closed tube sulfurization of sputtered Sn precursor at a temperature of 200-400 °C for 30 min. Vacuum annealing of the as-grown samples was carried out in the evacuated (3×10^{-3} Pa) and sealed ampule. Sb-doping was done by the thermal diffusion method, where SnS was heated under Sb ambient at the temperature range of 350-550°C. Post-air-annealing was conducted for the single-phase SnS at 150 - 250 ℃ for 30 min at atmospheric pressure. Chemical bath deposition (CBD) and RF sputtering techniques were applied to deposit CdS and TiO_2, respectively, in the SnS/CdS and SnS/TiO_2 heterojunctions.

The RF sputtered Sn precursor was sulfurized at a temperature range of 200-400 ˚C for 30 mins under 1 atm sulfur pressure. A single-phase orthorhombic SnS could be grown at 250˚C. The formation of secondary phases (SnS_2 and Sn_2S_3) in addition to that of SnS phase were observed for sulfurization temperature higher than 300 ℃. Similar surface morphology was observed for samples grown at 200-300 ˚C, while platelet-like structure attributed to hexagonal type SnS_2 phase has appeared for a sample grown at 400 ˚C. An S/Sn ratio was increased from 1.03 to 1.50 for sulfurization temperatures of 250 ˚C and 300 ˚C, respectively. The carrier concentration of 1.3×10^{16} cm^{-3}, the electrical resistivity of 9.5×10^{1} Ω cm, and mobility of 5.01 $cm^2V^{-1}s^{-1}$ were obtained for the SnS grown at 250 ˚C. The carrier concentration was decreased to 4.1×10^{15} cm^{-3}, while resistivity and mobility were increased to 1.1×10^{2} Ω cm and 13.9 $cm^2V^{-1}s^{-1}$, respectively, for a sample grown at 300 ˚C. The optical band gap of grown samples was increased with sulfurization temperature and was varied in the range of 1.2 - 2.3 eV.

The samples grown at 250 ˚C and 300 ˚C were vacuum annealed at 400-500 ℃ for 30-120 mins. When the SnS thin film grown at 300 ℃ was vacuum annealed at 500 ℃ for 30 min, the secondary phases were decomposed, and a single-phase SnS thin film. No significant change in surface morphology was observed after vacuum annealing. The S/Sn ratio for the as-grown

SnS decreased from 1.28 to 1.08 after vacuum annealing at 500 ˚C. The carrier concentration of the vacuum annealed sample was increased from ~10^{15} cm^{-3} to ~10^{18} cm^{-3}, while the resistivity was decreased from ~10^{2} Ω cm to ~10^{1} Ω cm. The optical bandgap of the as-grown sample was reduced from 1.4 eV to 1.2 eV after vacuum annealing at 500 ˚C. When the sample grown at 250 ˚C was vacuum annealed at 400 ˚C for 30 min, no significant crystallinity change was observed. However, a dramatic increase in grain size with intense and sharp XRD peaks was observed for vacuum-annealed samples at 400 ˚C for 30 min. No secondary phases were detected for all as-grown and vacuum annealed samples by XRD. However, sulfur-rich secondary phases were observed on the surface of SnS thin film by XPS measurement. Elimination of sulfur-rich secondary phases was observed after vacuum annealing. The resistivity of annealed film was decreased to 7.0 Ω cm, while the carrier density and Hall mobility were increased to 1.2×10^{17} cm^{-3} and 17.06 $cm^2V^{-1}s^{-1}$, respectively. When annealing temperature was increased to 450 ˚C, there was no impact on the grain size of SnS, while a deterioration in crystallinity was observed for annealing temperature at 550 ˚C. There were no apparent changes in the crystallinity of post-air-annealed samples.

SnS thin films grown at 250 ˚C and 300 ˚C were Sb-doped at the temperature range of 350-550 ˚C for 30 mins. Sb doping of the SnS thin film, which was grown at 300 C, secondary phases such as SnS_2 and Sn_2S_3 were decomposed, and a single-phase SnS thin film was achieved. The formation of Sn defects at high higher doping temperature was observed due to the re-evaporation of S-rich phases. The amount of Sb diffused to the SnS thin film was increased as doping temperature was increased with a maximum value of 4.8% at 550 °C. The hole concentration of Sb-doped SnS thin films could be controlled between 4.1×10^{15} and 7.65×10^{12} cm^{-3} by adjusting the Sb content. The optical band gap of SnS thin films was changed between 1.2 – 1.3 eV with doping temperature. When the SnS thin film grown at 250 ˚C (single-phase SnS) was doped with Sb, the crystallinity of the thin films was improved, and the S/Sn ratio has remained close to the stoichiometry independent of doping temperature. Under the controlled S/Sn ratio, the effect of Sb concentration on the electrical and optical properties of SnS thin films was investigated. A maximum Sb concentration of 1.38% was observed at 550˚C. By Sb-doping a small amount of Sb, the resistivity was increased, while the carrier concentration was lowered due to the doping effect. A minimum hole concentration of 1.2×10^{14} cm^{-3} and maximum mobility of 12.75 $cm^2V^{-1}s^{-1}$ was observed at 0.55% Sb content. Low level (0.55%) Sb doping under controlled S/Sn ratio effectively fabricating Sb doped SnS thin films. However, the conductivity type of all grown films remained p-type. The optical bandgap was observed to be 1.2 eV independent of Sb content.

Finally, the heterojunction properties of SnS/TiO_2 and SnS/CdS were compared. The conduction band (ΔE_{CBO}) offsets values of 0.60 eV and 0.83 eV aligned in “spike-type” were obtained for the SnS/CdS and SnS/TiO_2 heterojunctions, respectively. A reverse saturation current of 8×10^{-3} A was observed for the device based on SnS/TiO_2, which is two times higher than that of the device based on SnS/CdS heterojunction. The effect of post-annealing and Sb doping on the properties of SnS/CdS heterojunction was also investigated.A “spike-type” SnS/CdS heterojunction was obtained for the device based on the as-grown, vacuum annealed, and Sb doped SnS absorber layer. The band alignment of SnS/CdS heterojunction could be adjusted between “spike” type and “cliff” type by post-annealing treatments. A change from “spike” to “cliff” type heterojunction was observed for the post-air-annealed samples at a temperature higher than 200 ˚C. The *I-V* characteristics of SnS/CdS heterojunction diode devices exhibited a rectification behavior, although no PV effect was observed due to improper band alignment. Our experimental results suggest that annealing at an optimal temperature under a suitable ambience could be a possible approach to achieving a proper SnS/CdS heterojunction alignment for PV applications.