# Controlling carrier concentration of SnS by Sb doping

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## 1. Introduction

SnS, which has native p-type conduction is one of the promising material for low-cost thin-film solar cells due to its bandgap of 1.3 eV and a fundamental absorption coefficient larger than  $10^4$  cm<sup>-1</sup> <sup>[1]</sup>. However, SnS based heterojunction solar cells have efficiency record of <5% <sup>[1]</sup>. Unfavorable band offset and rapid carrier recombination near the interface could be some of the main reasons. In this aspect, synthesis of n-type layer for fabrication of SnS homojunction could give better performance. There are researches for realizing n-type SnS using group V elements such as Sb <sup>[1]</sup> and Bi <sup>[2]</sup>. Among them Sb is one of the promising n-type dopant because of its similarity in ionic radius with group IV Sn. In this paper, we are focusing on the effect of Sb doing on the electrical and crystal-line properties of SnS thin-films.

## 2. Experimental method

SnS was prepared by closed tube sulfurization of sputtered Sn precursor at 300 °C <sup>[3]</sup>. Doping was done by thermal diffusion method where SnS was heated under Sb ambient at the temperature range of 400-550 °C. Structural and compositional analyses were done by XRD and EPMA, respectively. Electrical properties of the films such as resistivity, carrier concentration, and carrier mobility were characterized by Van der Pauw's technique and AC Hall measurement.

#### 3. Results and discussion

Fig. 1 depictes the X-ray diffraction patterns of grown thin-films. In the as-grown SnS film, there are mixed phases of SnS,  $Sn_2S_3$ , and  $SnS_2$ . After vacuum (1 x 10<sup>-3</sup> Pa) annealing at 500 °C, hexagonal SnS<sub>2</sub> phase is vanished whereas hexagonal Sn<sub>3</sub>S<sub>4</sub> is formed, which could be due to the re-evaporation during the thermal decomposition of SnS<sub>2</sub>. For the samples doped with Sb, a major orthorhombic SnS is achieved. However, the existence of Sn<sub>2</sub>S<sub>3</sub> is undistinguished by XRD alone.

By EPMA analysis, the S/Sn ratio in the as-grown thin-film is 1.28, while that of the annealed film is decreased to 1.08, which is close to the stochiometric composition of SnS. This result shows that the sulfur excess phases such as  $Sn_2S_3$ ,  $Sn_3S_4$ , and  $SnS_2$  are reducing to SnS phase after annealing. In the case of Sb doped samples, the amount of Sb diffused is increased with doping temperature. The S/(Sn+Sb) ratio of the samples doped at 400, 500, and 550 °C is 1.18, 1.16, and 1.15, respectively. In comparing the samples doped at 400 and 500°C, it is found that the S/Sn ratio is converged near 1.2. However, in the case of sample doped at 500 °C, S/Sn ratio is increased to 1.28, which is the same to that of undoped film. This indicates that the formation of Sn defects, which are the origin of hole carriers, is also favours at higher Sb content due to crystal distortion.

Hall-effect measurement of all doped and undoped films showed p-type conductivity. Fig. 2 shows the electrical resistivity and carrier density of as-grown and Sb doped SnS. The resistivity is increased from  $1.10 \times 10^2$  to  $4.43 \times 10^5 \Omega$ - cm for the sample with 1.2% Sb content, while the carrier density decreases from  $4.1 \times 10^{15}$  to  $7.65 \times 10^{12}$  cm<sup>-3</sup>. A drastic decrease in hole density and increase in resistivity of the films grown at 1.2% Sb doped SnS could be due to the carrier compensation. However, in the case of samples with Sb content larger than 2.7%, the hole density (resistivity) is increased (decreased) again, which could be due to formation of Sn defects.

# 4. Conclusions

By vacuum annealing of as-grown SnS film, it is possible to reduce the secondary phase such as  $SnS_2$ . Formation of Sn defects at high Sb content was observed. The hole concentration of SnS could be controlled between  $4.1 \times 10^{15}$  to  $7.65 \times 10^{12}$  cm<sup>-3</sup> by adjusting the Sb content.







Figure 2: Carrier concentration and resistivity at various Sb Contents.

#### References

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