

# Formation of SnS/BaSi<sub>2</sub> Heterojunction by Sequential Thermal Evaporation toward Solar Cell Applications

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## Abstract

The p-type SnS/n-type BaSi<sub>2</sub> heterojunction is a promising structure for thin-film solar cells with a potential high efficiency. We attempted to fabricate the SnS/BaSi<sub>2</sub> heterojunction by thermal evaporation and postannealing. It has been found that the SnS/BaSi<sub>2</sub> interface is oxidized by the residual gas in vacuum when adopting proper substrate temperatures for single BaSi<sub>2</sub> and SnS films. By low-temperature sequential deposition of BaSi<sub>2</sub> and SnS followed by annealing, interface O concentration was reduced, and the SnS/BaSi<sub>2</sub> heterojunction was successfully formed. Moreover, the SnS layer was dense owing to the annealing.

## 1. Introduction

Tin monosulfide (SnS) and barium disilicide (BaSi<sub>2</sub>) have attractive properties as earth-abundant absorber layer materials for thin-film solar cells. For example, the band gaps are 1.1–1.3 eV [1,2], matching the solar spectrum. Optical absorption coefficients are high ( $> 10^4 \text{ cm}^{-1}$  above the absorption edges [1,2]). In particular, BaSi<sub>2</sub> can have a long minority-carrier lifetime ( $\sim 10 \text{ }\mu\text{m}$  [3]), which suggests a potential high conversion efficiency when a suitable solar cell structure is employed. The heterojunction of p-type SnS and n-type BaSi<sub>2</sub> is a promising solar cell structure, the efficiency of which can be over 24.1% under 1 sun according to device simulation [4]. This is because the electron affinities of SnS and BaSi<sub>2</sub> are similar, leading to a similar band alignment to a pn homojunction with small band offsets [4]. This SnS/BaSi<sub>2</sub> heterojunction has, however, not been realized yet. One obstacle is a thick native oxide layer on BaSi<sub>2</sub> ( $\sim 8 \text{ nm}$  [5]), which prevents the formation of the junction between SnS and BaSi<sub>2</sub>.

In this study, we attempted to form the SnS/BaSi<sub>2</sub> heterojunction by suppressing the oxidation of the BaSi<sub>2</sub> surface by means of sequential thermal evaporation and following annealing. It is shown that the low-temperature deposition and post-annealing is useful for avoiding the interface oxidation and the densification of the SnS layer.

## 2. Experimental method

BaSi<sub>2</sub> and SnS films were sequentially deposited on n-type Si(100) substrates by thermal evaporation in a high vacuum chamber with a base pressure of  $2 \times 10^{-4} \text{ Pa}$ . The substrates were cleaned by acetone, methanol, and HF solution before loading. Commercial BaSi<sub>2</sub> lumps and SnS powder were used as

evaporation sources. They were evaporated by resistive heating of tungsten boats. Before the deposition of BaSi<sub>2</sub> films, source premelting was performed to suppress the deposition of Ba-rich vapor [6]. The substrate temperature ( $T_{\text{sub}}$ ) for BaSi<sub>2</sub> deposition is 150 and 650 °C while that for SnS is 150–300 °C. After film deposition, a 150 °C-deposited sample was lamp-annealed at 400 °C for 10 min under Ar flow. We placed another sample upside down on top of the sample subjected to annealing to suppress the evaporation of SnS. The films were analyzed by grazing-incidence X-ray diffraction (XRD), scanning electron microscopy (SEM), and Auger electron spectroscopy (AES).

## 3. Results and discussion

Figure 1 shows the grazing-incidence XRD patterns of deposited films. When proper  $T_{\text{sub}}$ 's for single BaSi<sub>2</sub> and SnS films, namely 650 and 250–300 °C, respectively, were adopted [Figs. 1(a) and 1(b)], all observed peaks are attributed to BaSi<sub>2</sub> and SnS, indicating that SnS/BaSi<sub>2</sub> stacked structures are formed. On the other hand, when  $T_{\text{sub}}$  is low (150 °C) and postannealing was performed at 400 °C for 10 min (c), the peaks from  $\beta$ -Sn (tetragonal) are detected in addition to BaSi<sub>2</sub> and SnS. This is possibly because of the segregation of Sn through the evaporation loss of S or through the reaction between S and BaSi<sub>2</sub> during postannealing.

The cross-sectional SEM images of the films are compared in Fig. 2. A two-layer structure is observed in Fig. 2(a) for the BaSi<sub>2</sub> and SnS films deposited at  $T_{\text{sub}} = 650$  and 250 °C. Considering the XRD result which detected BaSi<sub>2</sub> and SnS, this is presumably the SnS/BaSi<sub>2</sub> stacked structure. When  $T_{\text{sub}}$  is low (150 °C) and postannealing was performed (b), particles with a diameter of hundreds nanometers are observed on a two-layer structure. These particles are probably  $\beta$ -Sn while the two layers are presumably SnS and BaSi<sub>2</sub>. In the BaSi<sub>2</sub> layer, voids are observed, which maybe formed by the Kirkendall effect during BaSi<sub>2</sub> formation through the mutual diffusion of Ba and Si. Although the formation of Sn particles and voids in BaSi<sub>2</sub> is not preferable for applications, it should be noted that the SnS layer is denser than that formed without postannealing (a). This result demonstrates the benefit of postannealing for the dense SnS film formation.

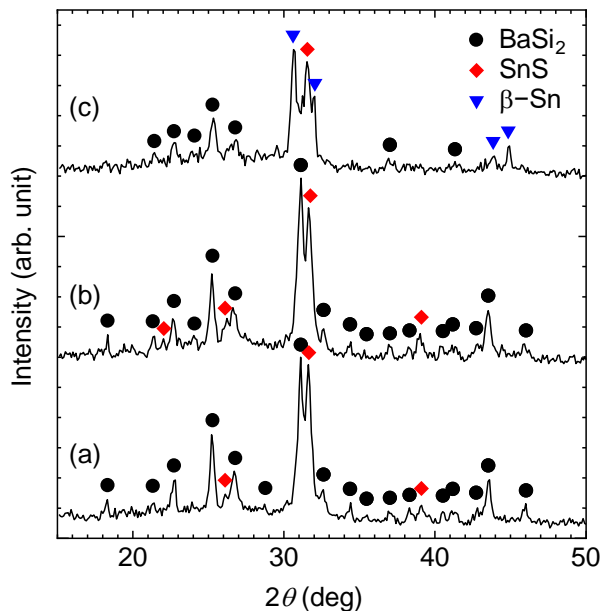


Fig. 1 XRD patterns of the deposited films measured at a fixed X-ray incident angle of  $3.8^\circ$ . (a)  $T_{\text{sub}}$ 's are 650 and 250  $^\circ\text{C}$  for  $\text{BaSi}_2$  and  $\text{SnS}$ , respectively. (b)  $T_{\text{sub}}$ 's are 650 and 300  $^\circ\text{C}$  for  $\text{BaSi}_2$  and  $\text{SnS}$ , respectively. (c)  $T_{\text{sub}}$  is 150  $^\circ\text{C}$  for both  $\text{BaSi}_2$  and  $\text{SnS}$ , and postannealing was performed at 400  $^\circ\text{C}$ .

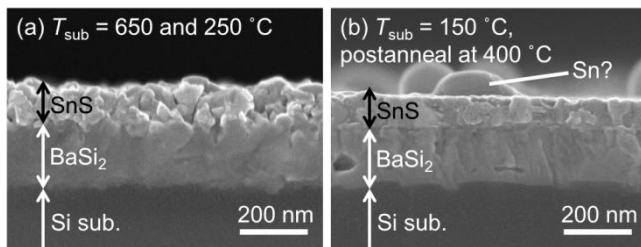


Fig. 2 Cross-sectional SEM images of the deposited films. (a)  $T_{\text{sub}}$ 's are 650 and 250  $^\circ\text{C}$  for  $\text{BaSi}_2$  and  $\text{SnS}$ , respectively. (b)  $T_{\text{sub}}$  is 150  $^\circ\text{C}$  for both  $\text{BaSi}_2$  and  $\text{SnS}$ , and postannealing was performed at 400  $^\circ\text{C}$ .

AES composition depth profiles of the films are shown in Fig. 3. The profiles of the films deposited at 650 and 250  $^\circ\text{C}$  (a) confirm the  $\text{SnS}/\text{BaSi}_2$  stacked structure, although the reason of a significantly higher  $\text{Sn}/\text{S}$  ratio than the stoichiometric one needs more investigations. It is noted, however, that the  $\text{O}$  concentration is high at the  $\text{SnS}/\text{BaSi}_2$  interface. This is presumably due to the oxidation of  $\text{BaSi}_2$  surface during cooling from 650 to 250  $^\circ\text{C}$  (44 min) by the residual gas in vacuum. To reduce oxygen concentration at the interface, the base pressure of the chamber or a cooling period should be drastically reduced.

On the other hand, when  $T_{\text{sub}}$  is low (150  $^\circ\text{C}$ ) and postannealing was performed (b),  $\text{O}$  concentration at the  $\text{SnS}/\text{BaSi}_2$  interface is significantly low, presumably be-

cause of the immediate capping of the  $\text{BaSi}_2$  surface with  $\text{SnS}$ . The mutual diffusion of  $\text{S}$  and  $\text{Ba}$  is also observed, which should be suppressed by optimizing the annealing condition.

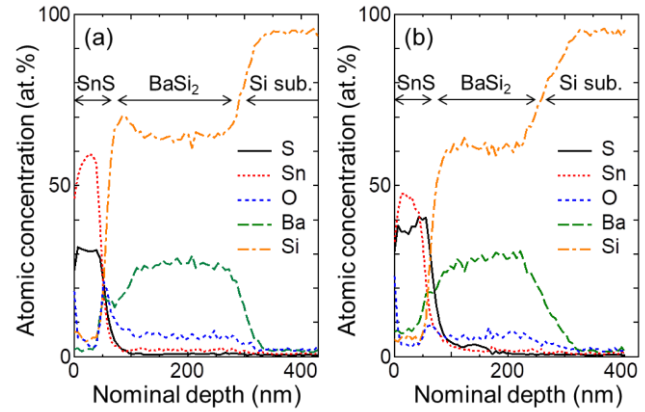


Fig. 3 AES composition depth profiles of the deposited films. (a)  $T_{\text{sub}}$ 's are 650 and 250  $^\circ\text{C}$  for  $\text{BaSi}_2$  and  $\text{SnS}$ , respectively. (b)  $T_{\text{sub}}$  is 150  $^\circ\text{C}$  for both  $\text{BaSi}_2$  and  $\text{SnS}$ , and postannealing was performed at 400  $^\circ\text{C}$ .

#### 4. Conclusions

Fabrication of  $\text{SnS}/\text{BaSi}_2$  heterojunction has been attempted by sequential thermal evaporation at different  $T_{\text{sub}}$ 's with and without postannealing. It has been found that when  $\text{BaSi}_2$  and  $\text{SnS}$  are deposited at proper  $T_{\text{sub}}$ 's for single films,  $\text{SnS}/\text{BaSi}_2$  stacked structures are successfully formed. However, the  $\text{SnS}$  layer can be porous, and  $\text{O}$  impurity is incorporated into the interface. On the other hand, when  $\text{SnS}$  and  $\text{BaSi}_2$  are deposited at low  $T_{\text{sub}}$  (150  $^\circ\text{C}$ ) and postannealed at 400  $^\circ\text{C}$  for 10 min, a  $\text{SnS}/\text{BaSi}_2$  heterojunction was successfully formed with a dense  $\text{SnS}$  layer and low  $\text{O}$  concentration at the interface, demonstrating the potential availability of the low  $T_{\text{sub}}$  deposition followed by postannealing.

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