

## Growth and characterization of $\text{SnS}_{2(1-x)}\text{Se}_{2x}$ alloys

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### Abstract

In this study, we present the growth of a series of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys layered crystals by using chemical vapor transport (CVT) method and adopting iodine as the transport agent. The crystal structure characterization has been substantiated by X-ray diffraction (XRD) and high resolution transmission electron microscope (HR-TEM) technologies. From each sample's XRD pattern, the peaks corresponds to (001), (002), (003), (004), and (005) which were found and used to determine the lattice constants. The band-gap energies modulated from 2.28 eV ( $\text{SnS}_2$ ) to 1.23 eV ( $\text{SnSe}_2$ ) with the increasing content of Se, which were verified by piezoreflectance spectroscopies (PzR) spectra and absorption spectra. By PzR spectra and absorption spectra, the empirical relation between band-gap energies and composition ratio, according to the extended Vegard's Law, has been predicted; accorded with a bowing parameter b of 0.56 eV and 0.54 eV, respectively.

### 1. Introduction

$\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys exhibit compositionally tunable optical properties and electronic structure. Thus, 2D ternary semiconductors attract lots of research interest due to their appreciable band-gap in optical and electrical properties. Recently, tin dichalcogenides ( $\text{SnS}_2$ ,  $\text{SnSe}_2$ ) [1,2] have driven considerable attention because of their high carrier mobility and good photo response. The multi-elemental single crystals are able to assist multiple degrees of freedom for dominant physical properties via ratio alteration. Furthermore, the properties of environmental friendly, earth abundant and low-cost make tin dichalcogenides desirable for sustainable optoelectronic devices.

$\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys have isostructural with the hexagonal close packed  $\text{CdI}_2$  type crystal structure which are similar to  $\text{SnS}_2$  and  $\text{SnSe}_2$ . It exhibits a unique crystal structure (S-Sn-Se strongly bonded covalently) with stacked layers, which act via weak Van Der Waals force between neighboring layers. This allows the creation of well balance in thin layers which thickness is under few atomic layers, and it will become a promising material platform.

In this study, the bulk  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  crystals with six different Se compositions ( $x = 0, 0.2, 0.6, 0.8$  and 1, respectively) have been grown by chemical vapor transport

(CVT). Consequently, we analyze the lattice structures of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys by X-ray diffraction (XRD) and transmission electron microscope (HR-TEM) technologies. The HR-TEM images reveal a random arrangement of the S and Se atoms in the 2D alloys. We also measure the optical properties of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  by piezoreflectance spectroscopies (PzR) spectra and absorption spectra.

### 2. Results and discussions

Figure 1(a) shows the XRD patterns for  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys with different Se contents. The top of figure 1(a) indicates that the lattice structure of our  $\text{SnSe}_2$  sample is consistent with hexagonal  $\text{SnSe}_2$  (JCPDS no. 89-2939); meanwhile, the bottom of figure 1(a) shows that our  $\text{SnS}_2$  sample can be indexed with hexagonal unit cells of the  $\text{CdI}_2$ -type (JCPDS no. 23-0677). Moreover, all of the peaks are derived from the direction of c-axis, which strongly suggests its single crystalline nature. The lattice constants of hexagonal  $\text{SnS}_2$  are  $a = b = 3.6486 \text{ \AA}$  and  $c = 5.8992 \text{ \AA}$  (JCPDS no. 23-0677), and the values of  $\text{SnSe}_2$  are  $a = b = 3.811 \text{ \AA}$  and  $c = 6.137 \text{ \AA}$  (JCPDS no. 89-2939) [3]. As expected, the main peak positions of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys gradually shift toward lower angles with increasing Se content in Figure 1(b).

HR-TEM images presented in figure 2(a) clearly reveals a naked view of hexagonal structured lattice, which with good consistency and the atomic model of  $\text{SnS}_{0.4}\text{Se}_{1.6}$  with hexagonal order of Sn, S and Se [4]. The obtained lattice plane spacing from figure 2(a) is 0.377 nm. Figure 2(b) shows the single-crystallinity of the  $\text{SnS}_{0.4}\text{Se}_{1.6}$  bulk investigated by selected area electron diffraction (SAED) oriented along the (001) and (110) direction. The diffraction pattern reveals a sixfold symmetry, which confirms the single crystallinity and high quality of  $\text{SnS}_{0.4}\text{Se}_{1.6}$ .

Figure 3(a) shows the PzR spectra [5] of the  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  crystals measured at 300 K. In the PzR spectra, one main resonance feature is observed in each spectrum. The band-gap energies can be discretely modulated from 2.28 eV ( $\text{SnS}_2$ ) to 1.23 eV ( $\text{SnSe}_2$ ) with the increase of Se content at 300 K. This result demonstrated that in the band-gap structure, which shows an obvious red shift behavior of the indirect transitions, is observed upon increasing the Se content, suggesting that the band-gaps are tuned with variation of Se composition.

Their band-gaps would change from 2.28 to 1.23 eV, which is in line with the extended Vegard's Law. Figure 3(b) presents the composition-dependent band-gaps of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys. The result is accorded with the conventional bowing, as described in eq. (1) :

$$E_g(x) = xE_g(\text{SnSe}_2) + (1-x)E_g(\text{SnS}_2) - bx(1-x) \quad (1)$$

where the band-gap bowing parameter  $b$  was calculated by PzR spectra and absorption spectra, with values of 0.56 eV and 0.54 eV, respectively.

Figure 4(a) shows the absorption spectra of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys with different Se contents. Obvious red shift behavior of the absorption edge is observed upon increasing the Se content, suggesting that band-gaps are tuned with variation of Se composition. The indirect band-gap semiconductor can be calculated from eq. (2). The calculated band-gaps of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys are shown in Table 1.

$$\alpha h\nu^{1/2} = A(h\nu - E_g) \quad (2)$$

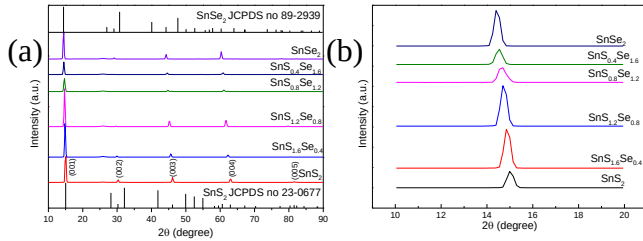


Figure 1 (a)  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys XRD with different Se contents, and (b) enlarged patterns of (a) from 10 to 20 degrees of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys.

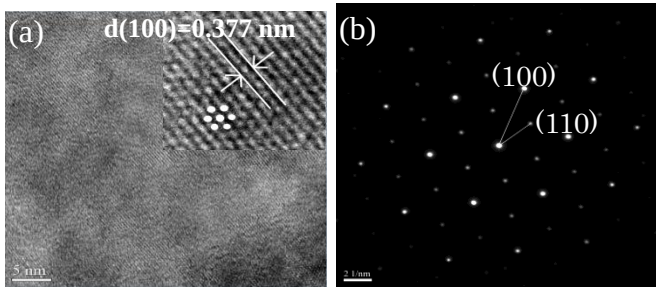


Figure 2 (a) HR-TEM image of bulk  $\text{SnS}_{0.4}\text{Se}_{1.6}$  (inset above shows the lattice constant calculated to be 0.377nm), and (b) SAED pattern (right) of bulk  $\text{SnS}_{0.4}\text{Se}_{1.6}$ .

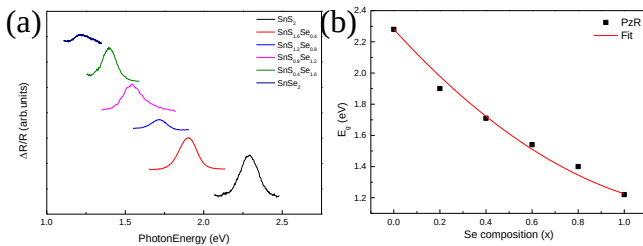


Figure 3 PzR spectra of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys with six different Se compositions ( $x = 0, 0.2, 0.6, 0.8$  and  $1$ ,

respectively), and (b) composition-dependent band-gaps and the corresponding fitting curve of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys.

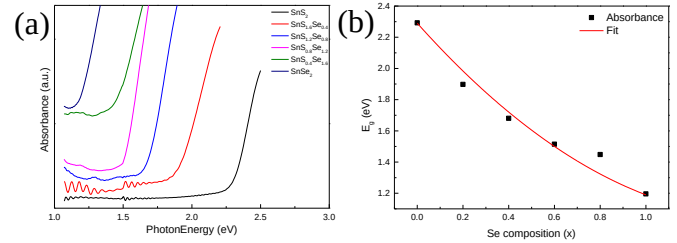


Figure 4 Absorption spectra of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys with six different Se compositions ( $x = 0, 0.2, 0.6, 0.8$  and  $1$ , respectively), and (b) composition-dependent band-gaps and the corresponding fitting curve of  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys.

Table 1 Compositions, band-gaps and lattice parameter  $c$  of

| $\text{SnS}_{2(1-x)}\text{Se}_{2x}$ alloys       |            |            |
|--------------------------------------------------|------------|------------|
| $x$ value in $\text{SnS}_{2(1-x)}\text{Se}_{2x}$ | PzR        | Absorption |
| predecessor                                      | $E_g$ (eV) | $E_g$ (eV) |
| 1                                                | 1.23       | 1.19       |
| 0.8                                              | 1.40       | 1.44       |
| 0.6                                              | 1.54       | 1.51       |
| 0.4                                              | 1.71       | 1.68       |
| 0.2                                              | 1.90       | 1.89       |
| 0                                                | 2.28       | 2.29       |

### 3. Conclusions

In conclusion, we have grown  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys crystals with six different Se compositions by adopting CVT and using iodine as the transport agent. The results from XRD and HR-TEM show the good quality of the sample. We performed a series of optical studies by using PzR and absorption measurements. The band-gap bowing parameter  $b$  was calculated by PzR spectra and absorption spectra, with values of 0.56 eV and 0.54 eV, respectively.  $\text{SnS}_{2(1-x)}\text{Se}_{2x}$  alloys exhibit compositionally tunable optical properties and electronic structure. Therefore, band-gap engineering by controllable doping provide a powerful approach to promote their physical and chemical properties.

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