Microstructural characterization of unidirectionally frozen
in situ Sn-Se eutectic composites

K SHINOHARA, T SEO and S ISOMURA*

Department of Metallurgy, School of Engineering, Ehime University, Matsuyama 790, Japan
* Department of Electrical Engineering, School of Engineering, Ehime University, Matsuyama 790, Japan

Abstract. An array of lamellar SnSe-SnSe₂ structure is obtained by unidirectional solidification, in which SnSe and SnSe₂ are, respectively, p and n type semiconductors. Their structural morphology was examined with use of transmission and scanning electron microscopes. It was found that the ordering of the alternative layers of the phases could be accomplished by a suitable choice of freezing rates, although several kinds of structural defects such as terminations, misfit lamellae and colony structure were observed. The mechanisms of these defect formations were considered in terms of the constitutional supercooling. Furthermore, the crystallographic relationship between the two phases in the solidified state was determined.

Keywords. Sn-Se eutectic; composite semiconductor; constitutional supercooling; defect structure; crystallography.

1. Introduction

SnSe and SnSe₂ are, respectively, p and n type semiconducting compounds. The eutectic alloy of SnSe and SnSe₂ produces alternative layers of each phase and it may be considered a multi-layered p-n composite. The thickness of the layers can be controlled easily by varying solidification parameters. This enables the use of this alloy as a potential material having semiconducting properties. This investigation deals with the microstructural characterization and electrical properties of the eutectic SnSe-SnSe₂ composition.

2. Experimental method

2.1 Preparation of SnSe, SnSe₂ and their eutectic composite

The purity of Sn and Se elements used was 99.999%. Sn and Se are weighed to make Sn - 50.0 at.% Se for SnSe, Sn - 66.6 at.% Se for SnSe₂ and Sn - 61.0 at.% Se for eutectic
SnSe-SnSe$_2$ alloy. Each of the weighed elements was encapsulated in a quartz tube with an inner diameter of 8 mm which had been evacuated down to a pressure of approximately 0.01 Pa. Of them, SnSe$_2$ polycrystals and eutectic SnSe-SnSe$_2$ alloys were subsequently directionally solidified by the Bridgman technique under a temperature gradient of 1333 K/m.

Single crystals of SnSe were grown by the vapour transport technique in a closed tube (Yu et al 1981).

2.2 Microstructural examinations of the eutectic alloys

Eutectic alloys which had been directionally solidified were examined in a scanning electron microscope and a transmission electron microscope, which are respectively referred to as SEM and TEM hereafter. SEM observations were made both in the longitudinal and the lateral directions. In doing so, the specimens were cut out by a fine cutter, polished with emery paper, and finally cloth-polished in order to obtain a smooth surface. After successive polishings, it was etched for about 30 seconds in a solution consisting of one part of 50% HF and one part of 50% HNO$_3$ by volume (Yue & Yu 1982). In TEM observations, thin film specimens were peeled off from the cut surface of the eutectic mixture with the cleavage face parallel to the surface of the film.

2.3 Resistivity and Hall coefficient measurements of SnSe and SnSe$_2$

Resistivity and Hall coefficient were measured by Van der Pauw's method (1958). SnSe$_2$ polycrystalline specimens were cut into thin films 0.4 mm thick with faces parallel to the solidification direction and then polished to obtain a smooth surface. A SnSe wafer specimen of about the same thickness as the above was cut with the cleaved face parallel to (001) of the single crystal. The specimens were jointed with a platinum wire and pure In was evaporated onto them at $1.3 \times 10^{-3}$ Pa pressure, while silver paste was used in order to establish Ohmic contact. On measuring both resistivities and Hall coefficients, a constant current of 5 mA was passed through. In the case of Hall coefficient measurements, the magnetic field of 0.522 wb/m$^2$ was applied. The temperature was varied from 153 K to 593 K.

2.4 Preparation of single p-n junction

A single p-n junction was prepared by depositing SnSe$_2$ onto single crystalline SnSe within the reduced pressure of about $1.33 \times 10^{-3}$ Pa, wherein the temperature of the substrate, SnSe$_2$, was kept at 393 K.

3. Experimental results

3.1 Microstructure of eutectic SnSe-SnSe$_2$ alloy

Figures 1 and 2 show the SEM micrographs of the specimens grown at varying rates of 0.277 to 142 $\mu$m/s. It is clear that the greater the rate of solidification, the finer the interlamellar spacings, although the spacings of the lamellae are scattered in a considerable range of width. An array of the ordering and defect-free structure was favoured by the solidification rate of 4 $\mu$m/s under these conditions. Rates which are lower or greater than this value could cause an increase in the deterioration of the morphology of the layered structure. Identification of SnSe and SnSe$_2$ phases was made
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Figure 1. Scanning electron micrograph of SnSe-SnSe$_2$ eutectic at different growth velocities.

by the electron probe microanalyser, the results of which are illustrated in figure 3. In the figure, the phase designated as A corresponds to the phase rich in Sn and deficient in Se. Thus, the A-phase is identified as SnSe and similarly the B-phase as SnSe$_2$. Figure 4 illustrates the TEM micrograph of a film cleaved off from SnSe single crystals. The crystal structure of SnSe is orthorhombic with lattice parameters of $a = 0.446$, $b = 0.419$ and $c = 1.57$ nm. Figure 4 is the picture taken with the zone axis along the $c$-axis, i.e., [001] and from this it is clear that the cleavage planes are those containing the zone axes of $\langle 010 \rangle$ and $\langle 110 \rangle$.

Figure 5 shows the TEM picture of SnSe$_2$ single crystals having the hexagonal unit cell
Figure 2. Scanning electron micrograph of SnSe-SnSe₂ eutectic at different growth velocities.

with \( a = 0.38 \), \( c = 0.61 \) nm. The beam passes through the SnSe₂ crystal along the \( c \)-axis, showing that the cleavage planes are, one that contains the \( a \)-axis and the other that is normal to the \( c \)-axis. Furthermore, innumerable moiré fringes can be observed in this structure.

Figure 6 indicates the TEM structure of the longitudinal section of the specimen growth at the rate of 4.44 \( \mu m/s \). Obviously the following crystallographic orientations
**Figure 3.** Scanning electron micrograph and linear analysis in the unidirectionally grown SnSe-SnSe₂ eutectic.

**Figure 4.** Transmission electron micrograph of SnSe phase.
Cleaved SnSe$_2$ phase in SnSe-SnSe$_2$ eutectics.

Figure 5. Transition electron micrograph of SnSe$_2$ phase in SnSe-SnSe$_2$ eutectic.

Figure 6. Transmission electron micrograph of SnSe-SnSe$_2$ eutectic.
are seen to exist:

\[(001)_{\text{SnSe}} // (00\cdot1)_{\text{SnSe}_2}\]

\[[110]_{\text{SnSe}} // [11\cdot0]_{\text{SnSe}_2}\].

In figure 7 is plotted the average lamellar spacings of SnSe and SnSe\(_2\) vs. the unidirectional solidification rate on the logarithmic scale, from which the slope of the linear relationship is found to be 2.15. This suggests that the following Jackson-Hunt's relationship (Jackson & Hunt 1966) is approximately satisfied

\[\lambda^2 \cdot v = 2.8 \ (\mu \text{m/s})^3/\text{s}.\]  

1.2 Electrical properties of SnSe-SnSe\(_2\)

Figure 8 shows the temperature dependence of the resistivities of specimens which had been allowed to solidify at different rates. It is clear that in all the specimens at elevated temperatures, the resistivity decreases with increasing temperature and that at low temperatures it increases with decreasing temperature for SnSe\(_2\) and eutectic SnSe-SnSe\(_2\), whereas it decreases slightly with decreasing temperatures for SnSe.

Here, from the linear portion of figure 8 at an elevated temperature, the energy gap between the conduction band and the filled band is estimated to be 0.88 eV for SnSe single crystals, 1.0 eV both for SnSe\(_2\) polycrystals and SnSe-SnSe\(_2\) eutectic composites. Figure 9 demonstrates the temperature-dependence of the Hall coefficients measured from the same specimen shown in figure 8. The Hall coefficient of SnSe single crystals is essentially temperature-independent, whereas those of SnSe\(_2\) polycrystals and SnSe-SnSe\(_2\) eutectic mixtures fall rapidly with increasing temperature. Figure 10 shows the variation of mobilities at various temperatures. In all the specimens, the slope of the mobilities with respect to temperature are approximately the same. Figure 11 illustrates the current-voltage characteristic of a single p-n junction under illuminated or unilluminated conditions. It may be pointed out that the open circuit voltage of the specimens is 20 mV and the short circuit current is 0.4 mA.

4. Discussions

4.1 Directionally solidified SnSe-SnSe\(_2\) eutectics

In order for SnSe-SnSe\(_2\) eutectics to be used as potential material for semiconducting devices, it is required that each phase of SnSe and SnSe\(_2\) be free of structural defects in the aspect of ordering and morphology. For this, occurrence of constitutional supercooling must be avoided. Generally speaking, the morphology of the liquid-solid interface is determined by the supercooling from the equilibrium solidification temperature:

\[\Delta T = \Delta T_C + \Delta T_\sigma.\]  

The first term of (2) corresponds to the undercooling caused by the limited diffusivity at the planar front, which is given as:

\[\Delta T_C = m(C_E - C_x),\]  

where \(m\) is the slope of the liquidus temperature in the phase diagram and \(C_x\) the
composition at the solid-liquid interface. The second term on the right of (2) corresponds to the undercooling caused by the presence of the curvature of the front and it is given approximately by the Gibbs-Thomson equation (Ostwald 1901) as:

\[ \Delta T_s = aK_x = (T_E \sigma / L) (-d^2 z/dx^2) [1 + (dz/dx)]^{-3/2}, \]

where \( a \) is given by \( T_E \sigma / L \), \( T_E \) is the equilibrium temperature, \( \sigma \) the surface tension, \( L \) the latent heat, and \( K_x \) represents the radius of curvature of the front. Let us assume that both of these contributions are additive. Let SnSe and SnSe\(_2\) phases be referred to as \( \alpha \) and \( \beta \)-phases, respectively, for the sake of simplicity. The origin of the coordinate system is placed at the centre of \( \alpha \)-phase on the solid-liquid boundary. Jackson & Hunt (1966) obtained the relationship under the condition that the solidification proceeds so as to minimize the total supercooling, \( \Delta T \). The relationship they obtained is:

\[ \lambda^2 V = a^L / Q^L = \text{constant}, \]

where \( a^L \) and \( Q^L \) are, respectively, given by:

\[ a^L = 2(1 + \zeta) [(a_{L}^a/m_a) + (a_{L}^\beta/\zeta m_\beta)], \]

\[ Q^L = p(1 + \zeta^2) C_0 / \zeta D, \]

where \( \zeta \) is the relative thickness, \( S_\beta \) of the \( \beta \) layer divided by \( S_\alpha \) of the \( \alpha \) layer and \( S_\beta \) and \( S_\alpha \) each are half the thicknesses of its own phase. \( P \) is a parameter associated with \( \zeta \), \( D \) the diffusivity, \( C_0 \) the width of the miscibility gap between \( \alpha \) and \( \beta \)-phases,
$m_\alpha$ and $m_\beta$ the slope of the liquidus line of each phase and $a^L_\alpha$ or $a^L_\beta$ is the value of $\Delta T_e$ of the $\alpha$ or $\beta$-phase.

From the experimental measurements for the SnSe-SnSe$_2$ eutectic alloy, it was found that $\lambda^2 V = a^L_e/Q^L_e = 2.8$ (\(\mu m\))^3/s. This is a little smaller than the values found elsewhere for most other eutectic alloys. From the phase diagram of figure 12, we see that $C_0 = 0.166$ atomic fraction, $m_\alpha = 2000$ K and $m_\beta = 303$ K. All of these tend to reduce the value, $a^L_e/Q^L_e$, as tentatively compared with other eutectic alloy cases.

Adopting the previously given $m_\alpha$, $m_\beta$ and $C_0$, with the rest of the other parameters being assumed to be the same, rough estimate demands that in order for the value, $a^L_e/Q^L_e$, to be small, the value $a^L_e$ should be small, leading to a small value of $\sigma/L$. 

Figure 8. Temperature dependence of the resistivity for SnSe, SnSe$_2$ crystals and SnSe-SnSe$_2$ eutectic crystals.
Figure 9. Temperature dependence of Hall coefficients of SnSe, SnSe\textsubscript{2} and SnSe-SnSe\textsubscript{2} eutectics.

Figure 10. Temperature dependence of Hall mobilities in SnSe, SnSe\textsubscript{2} and SnSe-SnSe\textsubscript{2} eutectics.
Considering the interfacial energy between the \( \alpha \)-phase and the liquid to be approximately of the same order of magnitude as that between the \( \beta \)-phase and the liquid, the latent heat of the \( \beta \)-phase must be great.

Let us now consider the morphology of the boundary at the solidification front with the minimum undercooling principle. Jackson & Hunt (1966) derived the following expression of the curved front of the \( \alpha \)-phase i.e., in the region, \( 0 < x < S_\alpha \):

\[
\frac{dz}{dx} = \tan^{-1} \left\{ -\sin \theta \left[ \frac{x}{\lambda} \left( 1 + \frac{\zeta}{(1 + \zeta)^{1/2}} \right) \right] \right\}.
\]

\[
+ \left( \zeta + \eta \right) \left( \frac{2x}{\lambda} - \frac{2}{(1 + \zeta)^{1/2}} \int_0^x f(x') dx' \right), \tag{8}
\]

\[
\int_0^x f(x') dx' = \frac{x}{\zeta (1 + \zeta)^{1/2}}.
\]
and the curved front of the $\beta$-phase, i.e., in the region, $S_x < x < S_x + S_\beta$:

$$\frac{dz}{dx} = \tan \sin^{-1} \left\{ \sin \theta \left[ \left( \frac{\lambda - 2x}{\lambda} \right) \left( \frac{1 + \zeta}{\zeta} \right) \right.ight.
\left. + \left( \frac{1}{\zeta + \eta} \right) \left( \frac{\lambda - 2x}{\lambda} - \frac{2\zeta}{(1 + \zeta)P \lambda} \int_0^x f(x) \, dx \right) \right\} \right\}, \quad (9)$$

where

$$f(x) = \sum_{n=1}^\infty \frac{\sin \left[ \frac{n\pi}{1 + \zeta} \right] \cos \left( \frac{2n\pi x}{\lambda} \right)}{(n\pi)^2}.$$

Although $a_\beta$ and $a_x$ are unknown in the case of SnSe-SnSe$_2$ eutectics, it can be tacitly assumed that since $a_x$ or $a_\beta$ is given by $T_x \sigma/L$, $\sigma$ and $L$ for SnSe and SnSe$_2$ are of the same order of magnitude, and thus, $a_x = a_\beta$, then $\eta = 6.6$. Furthermore, $\zeta = 1.964$, $P = 0.025$ are obtained by computation (Jackson & Hunt 1966). When these values are inserted into (8) and (9), one obtains the expression for $dz/dx$ along the solid-liquid interface. It is now apparent that the curvature of the solid-liquid boundary in front of the $\alpha$-phase is convex toward the liquid whereas that in front of the $\beta$-phase is concave toward the liquid. This difference has arisen possibly because the value of $\eta$ is excessively large, that is, the difference in the slopes $m_x$ and $m_\beta$ is grossly different, giving rise to a big value of $\eta$ under the feasible assumption of $a_x = a_\beta$.

The supercooling required for the growth condition used here can be computed as follows:

$$\Delta T = 2ma^L/\lambda,$$

where

$$\frac{1}{m} = \frac{1}{m_x} + \frac{1}{m_\beta}, \quad a^L = 2(1 + \zeta) \left( \frac{a_x^L}{m_x} + \frac{a_\beta^L}{\zeta m_\beta} \right)$$

and, here, $m = 263$ K. Adopting the suitable value used for this growth experiment, the range of the undercooling for our growth conditions,

$$\Delta T = 0.016 - 0.27 \text{ K},$$

is obtained, from which it is clear that the supercooling at the solid-liquid interface may be seen to be small. Under growth conditions which are substantially close to the equilibrium, rupture of the regular lamellae takes place more often when the difference in the slopes of the liquidus lines are large than when the driving force for the solidification is small. The optimum condition of the unidirectional growth rate was observed at 4.44 $\mu$m/s in this investigation for SnSe-SnSe$_2$ eutectics.

### 4.2 Electrical properties of SnSe-SnSe$_2$ eutectics

Numata (1950) investigated the principal carrier of electrical conduction in SnSe$_x$ alloy with varying $x$. He found that when $x$ is greater than 1.5, the carrier is an electron while $x$ is less than 1.0, it is a positive hole. That is, when Sn is in excess, the alloy is a $p$-type semiconductor, and when Se is in excess, it is $n$-type. This indicates that SnSe-SnSe$_2$
eutectics having a regularly ordered lamellar structure have alternatively stacked multiple \( p-n \) junctions.

Figure 8 shows the variation of electrical resistivities as a function of the reciprocal of absolute temperature, indicating that the resistivity of SnSe\(_2\) polycrystals varies in a manner similar to that of SnSe-SnSe\(_2\) eutectics. Thus, it may be said that the resistivity of the eutectic is merely a contribution of the resistivity of a single phase of SnSe\(_2\). The same figure also shows that the resistivity change is influenced remarkably by the disorder of the lamellae at low temperatures, figure 9 demonstrates that the Hall mobility decreases with increasing temperature and it is seen from figure 10 that the mobility varies linearly with \( T^{-2} \). This result agrees with the observations made by Asanabe (1959). This result also indicates that the mobility is mainly determined by the contribution from lattice vibrations, leading to the conclusion that the resistivity variation of SnSe\(_2\) polycrystals and SnSe-SnSe\(_2\) eutectic samples depends to a great extent upon the conduction electrons, that is, the decrease of the Hall coefficient results from the increase in conduction electrons due to the increase in number of ionized atoms. The drop of the Hall coefficients at elevated temperatures corresponds to the intrinsic conduction region. The Hall coefficients of SnSe single crystals, on the other hand, show a slightly positive temperature dependence. This is considered to be due to the dissolved impurity atoms. As Asanabe (1959) pointed out, the variation of the electrical resistivity of SnSe-SnSe\(_2\) eutectics except in the intrinsic region is considered to be principally due to the single phase SnSe\(_2\), and, therefore, it may be said that the attendant property arises from the microstructural defects formed during the unidirectional freezing. Figure 4 proves that there is a considerable compositional fluctuation, since one can observe many Moiré fringes appearing in a single phase region. This may be another contributory factor for the increase in the electrical resistivities. Figure 11 shows the current-voltage characteristics for a single \( p-n \) junction made from SnSe and SnSe\(_2\), from which it turns out that the open circuit voltage is 20 mV and the short circuit current is 0.4 mA. These values are a little smaller than those found by Yue & Yu (1982). It may be said that the SnSe-SnSe\(_2\) eutectic alloy is one of the potentially useful materials for solar cells if it is allowed to solidify without defects and compositional fluctuations.

References

Numata T 1950 Bussei Kenkyu 27: 1
Ostwald W 1901 Analytische Chemi 3rd edn (Leipzig: Engelmann) 23