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Optimized growth conditions of epitaxial SnSe films grown by pulsed laser deposition

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We have grown epitaxial tin monoselenide (SnSe) films on MgO or SrTiO₃ (STO) substrates by pulsed laser deposition (PLD) at $T_s = 473$ or 573 K, and investigated the optimized growth condition in terms of crystal orientation, crystallinity, and electrical resistivity. For the PLD procedure, a SnSe_x (x = 1.0-1.6) target containing excess Se was used to compensate for the vaporization of Se. The crystal orientation and crystallinity of the SnSe films changed depending on the growth conditions, and the magnitude of the electrical resistivity ρ of the films was closely related to the crystalline nature. The SnSe film grown on the MgO substrate at $T_s = 573$ K using the target with x = 1.4 was the most highly *a*-axis-oriented and highly crystalized among all of the films investigated in this study. However, the ρ of the film in the *bc*-plane was about one order of magnitude larger than those of the reported single crystal and the *a*-axis-oriented crystalline sample fabricated by spark plasma sintering. This larger ρ was suggested to result from the lattice mismatch and/or a small amount of nonstoichiometry in the film. © 2017 The Japan Society of Applied Physics

1. Introduction

Tin monoselenide (SnSe) is a p-type semiconductor with indirect transition, whose band gap is reported to be 0.9–1.0 eV.^{1–3} It has an orthorhombic crystal structure with the space group *Pnma* (No. 62) and it has a layered structure composed of alternate stacking of two [Sn²⁺Se^{2–}] layers along the *a*-axis. The orthorhombic distortion forms strong Se–Se bonds only along the *b*-direction. Because of the anisotropic layered structure, the carrier transport properties have a large anisotropy. Since the higher hole mobility can be realized in the *bc*-plane, *a*-axis-oriented films are usually advantageous for electronic devices such as memory switching devices⁴) and efficient solar materials^{5–8} because of the similarity of the energy gap to that of Si ($E_g = 1.12 \text{ eV}$).

SnSe single crystals have recently been investigated for applications related to thermoelectric conversion devices,⁹⁾ with which a higher thermoelectric performance has been achieved with dimensionless figure of merit [$ZT (= S^2T/\rho\kappa)$] values of 2.6 and 2.3 at 923 K along the *b*- and *c*-axes, respectively, owing to ultralow thermal conductivity κ , where *S* is the Seebeck coefficient, ρ is the electrical resistivity, and *T* is the absolute temperature. To enhance thermoelectric properties, the effects of doping with different materials such as Ag and Te have been investigated using SnSe polycrystals.^{10,11}

SnSe thin films are also fabricated by various methods such as flash evaporation,⁸⁾ reactive evaporation,¹²⁾ thermal evaporation,^{13,14)} and spray pyrolysis.¹⁵⁾ In almost all research studies, the polycrystalline films were fabricated mainly on glass substrates, in which the crystal orientation, absorption spectra, optical band gap, and electrical properties of the films were mainly investigated. However, there are only a few reports on the fabrication of epitaxial films on single-crystal substrates. Teghil et al. reported the SnSe epitaxial films grown on (001)-oriented MgO or SrTiO₃ (STO) substrates by pulsed laser deposition (PLD) at 293 and 473 K,¹⁶ but the characterization of the films was not detailed. The emission spectra of laser plume were also measured during the PLD of SnSe films.¹⁷⁾ Inoue et al. investigated the SnSe epitaxial films grown by PLD on various (001)-oriented single-crystal substrates (MgO, NaCl, and SrF₂) with different lattice parameters and on silica glass, particularly the fabrication condition dependences of the electrical and optical properties.¹⁸⁾ To realize the stoichiometry of SnSe thin films, they performed PLD using a SnSe_{1.2} target containing excess Se, which was the best target for realizing stoichiometric SnSe films. However, there are only a few investigations of the optimum growth conditions of the epitaxial SnSe films fabricated by PLD, except for investigations of the growth temperature T_s up to 823 K and of the laser fluence up to 10 J/cm^2 .

In this study, we performed PLD experiments on epitaxial SnSe films under various growth conditions such as the growth temperature T_s , the type of single-crystal substrate with a different lattice constant, and the target composition of SnSe_x. The optimum growth conditions were investigated in terms of crystallographic and electrical properties. The relationship between the crystallinity and electrical resistivity of the SnSe films was examined.

2. Experimental procedure

SnSe thin films were prepared by PLD using a fifth harmonic wave of an yttrium aluminum garnet (YAG) laser with $\lambda = 213$ nm and a repetition rate of 10 Hz. The laser pulse duration was 5 ns and the laser power density was 1.8 J/cm^2 . To fabricate $SnSe_x$ polycrystalline targets (x = 1.0, 1.2, 1.4,and 1.6), Sn shot (99.999%) and Se fine powder (99.9%) were used as starting materials. These were weighed at a stoichiometric ratio of Sn : Se = 1.0 : x, and then mixed in Ar atmosphere. After the mixed raw materials were evacuated and sealed in a quartz tube, they were heated at 1223 K for 6h and then furnace-cooled. The obtained precursor was pulverized and mixed in air for 0.5 h using an automatic mortar. The resulting powder samples were sintered using a spark plasma sintering (SPS) apparatus (NJS LABOX-110C) under a uniaxial pressure of 50 MPa at about 973 K for about 5 min in vacuum. The relative mass density of the obtained pellets (10 mm in diameter and 9 mm in thickness) was higher than 93% of the ideal density. In the $SnSe_x$ polycrystalline targets, the main phase was $SnSe_x$ and the amount of additional tin diselenide (SnSe₂) phase increased with increasing x for $x \ge 1.2$. This result is macroscopically consistent with the Sn-Se binary phase diagram.¹⁹⁾



Fig. 1. (Color online) Out-of-plane θ - 2θ XRD patterns of SnSe thin films grown on (a) MgO and (b) STO substrates at $T_s = 473$ and 573 K using the polycrystalline target SnSe_x with x = 1.0 and 1.4. (c) and (d) respectively show magnified plots of (800) XRD intensity of the SnSe films grown on MgO and STO substrates at $T_s = 473$ and 573 K. The XRD pattern of the SnSe powder is also shown in each figure.

The target and single-crystal substrates were mounted in the PLD vacuum chamber and counter-rotated at speeds of 7 and 3 rpm, respectively, to reduce non-uniform erosion and deposit the film uniformly. The deposition was carried out for 4 h in vacuum ($<10^{-7}$ Torr) at a substrate temperature of $T_s = 473$ or 573 K. The thickness of all the films was about 200 nm independent of the growth conditions, which was determined using a contact profiler. The PLD was also performed at $T_s = 673$ K, but the film was absent on the substrate owing to its revaporization from the substrate. The films were grown on (001)-oriented STO (a = 0.391 nm) and MgO (a = 0.421 nm) single-crystal substrates. The orthorhombic lattice parameters of the SnSe bulk are a = 1.150 nm, b =0.416 nm and c = 0.444 nm.⁹ On the basis of the relationship $\varepsilon = 100 \times (a_{\text{SnSe}} - a_{\text{sub}})/a_{\text{sub}}$, the lattice mismatches in the *bc*-plane are determined to be $\varepsilon = -1.4\%$ (tensile strain) along the *b*-direction and $\varepsilon = +5.2\%$ (compressive strain) along the *c*-direction for the film grown on MgO, and $\varepsilon =$ +6.4% (compressive strain) along the *b*-direction and $\varepsilon =$ +13.6% (compressive strain) along the *c*-direction for the film grown on STO. These results suggest that the lattice mismatch of the SnSe film on the MgO substrate is smaller than that on STO in the bc-plane. The MgO substrate was heated up to 600 °C for 30 min in vacuum to remove contaminants and improve the surface morphology, prior to PLD growth.

To clarify the crystalline quality of the grown films, X-ray diffraction (XRD) measurements of θ -2 θ and 2θ - ϕ scans were performed using Rigaku Ultima IV (40 kV, 40 mA), both of which identified the out-of-plane and in-plane alignments, respectively. 2θ - ω scans (out-of-plane XRD rocking

curve) were also measured to confirm the strain or tilting of the films, in which the crystalline quality in the films was assessed using $\Delta \omega$ measured from the full width at half maximum (FWHM) obtained from the rocking curve measurements. The microstructure and chemical composition of the films were analyzed by electron probe microanalysis using a field emission gun (FE-EPMA) and scanning electron microscopy (SEM). The electrical resistivity $\rho(T)$ was measured in the 10-300 K range by a standard four-probe method using a home-made measuring system.²⁰⁾ To determine the cause of the resistivity change in the SnSe films, the Hall effect was measured for the $SnSe_x$ polycrystalline bulk (0.97 $\leq x \leq 1.03$) fabricated by the SPS method under a magnetic field up to 5 T by a five-terminal method at room temperature. The carrier concentration p and the Hall mobility μ , which was calculated using $\mu = |R_{\rm H}|/\rho$ ($R_{\rm H}$: Hall coefficient), were determined.

3. Results

3.1 Optimization of epitaxial growth

Figures 1(a) and 1(b) respectively show typical out-of-plane XRD patterns of SnSe thin films grown on the MgO and STO substrates at $T_s = 473$ and 573 K using SnSe_x as the target with x = 1.0 and 1.4. On the MgO substrate shown in Fig. 1(a), *a*-axis-oriented epitaxial SnSe films can be fabricated at $T_s = 473$ and 573 K, but not in the film fabricated at $T_s = 473$ K using the x = 1.4 target, in which a weak (201) diffraction peak was observed. On the other hand, on the STO substrate shown in Fig. 1(b), the (210) and (321) diffraction peaks of the SnSe phase were seen for the film grown using the x = 1.0 target, and the (001) diffraction of the SnSe₂



Fig. 2. (Color online) XRD intensities of SnSe (400) peaks of the films grown on the MgO and STO substrates at $T_s = 473$ and 573 K as a function of composition *x* of SnSe_x target.

impurity phase was detected for the film grown using the x = 1.4 target, together with the (*l*00)-oriented diffractions of the SnSe phase. These results suggest differences in the orientation and the impurity phases between the films grown on the MgO and STO substrates.

Figures 1(c) and 1(d) show the magnified plots of the (800) diffraction intensity of the SnSe phase. The XRD pattern of $SnSe_x$ (x = 1.0) polycrystalline powder is also shown in each figure. In Fig. 1(c), the diffraction angle of the (800) peak for the films grown on MgO is lower than that for the polycrystalline powder. This result suggests that the unit cell in the SnSe films elongates along the a-axis direction and shrinks in the *bc*-plane. The diffraction angle of the films was independent of the target composition x and the growth temperature $T_{\rm s}$. Since the compressive lattice mismatch ε of the film on the MgO substrate is small within 5%, the films were restricted in the *bc*-plane by the MgO substrate, and as a result became elongated along the *a*-axis direction. On the other hand, the diffraction angle of the (800) peak of the films on the STO substrate is nearly the same as that of the polycrystalline powder. This result indicates that the lattice parameter a of the films is nearly the same as that of the polycrystalline powder. The films might be difficult to grow epitaxially, but might be grown under a weak strain on the STO substrate because the ε of the film grown on STO is fairly large (+6.4% along the *b*-direction and +13.6% along the *c*-direction).

Figure 2 shows the XRD intensity of the (400) peak of the SnSe films grown on the MgO and STO substrates at $T_s =$ 473 and 573 K, as a function of the SnSe_x target composition x. The XRD intensity depends not on the thickness of the film, but on crystallinity, because the film thickness was confirmed to be about 200 nm, which was independent of the growth conditions in this study. For each growth temperature, the XRD intensity of the film grown on the MgO substrate increases with increasing x, reaches a maximum at x = 1.4, and then decreases. The XRD intensity of the films grown at 573 K is higher than that at 473 K. On the other hand, for the films grown on the STO substrate, a similar behavior can be seen at $T_s = 573$ K. However, at $T_s = 473$ K, the (400) intensity is relatively low and reaches a maximum at x = 1.2and then steeply decreases with increasing x, which is closely related to the low *a*-axis orientation and the generation of the $SnSe_2$ impurity phase at higher *x* values.



Fig. 3. (Color online) In-plane XRD patterns $(2\theta - \phi \operatorname{scan})$ of the SnSe films grown on the MgO and STO substrates at 573 K using the target with x = 1.4. For the film grown on STO, the symbols + and * indicate two additional sets of four weak peaks with different angles.



Fig. 4. (Color online) Normalized out-of-plane X-ray rocking curves $(2\theta - \omega \text{ scan})$ of the (800) reflection for the films grown on MgO and STO substrates, at $T_s = 573$ K using a target with x = 1.4.

Figure 3 shows the in-plane XRD patterns $(2\theta - \phi \text{ scan})$ of the SnSe films grown on the MgO and STO substrates at $T_s = 573$ K using target with x = 1.4. For the films grown on the MgO and STO substrates, ϕ -scan was measured in the film plane at a fixed (511) reflection. For the film grown on MgO, four sharp peaks were observed every 90° and the in-plane alignment can be confirmed. On the other hand, for the film on STO, four weak peaks were observed every 90° with two sets of small fourfold symmetry peaks. These results suggest that the film was grown on the STO substrate like a mosaic with different angles.

Figure 4 shows the normalized out-of-plane X-ray rocking curves $(2\theta - \omega \text{ scan})$ of the (800) reflection for the films on the MgO and STO substrates, which were grown at $T_s = 573 \text{ K}$ using a target with x = 1.4. The FWHM values of the films grown on the MgO and STO substrates were 1.15 and 1.60°, respectively. Inoue et al. reported that the FWHM of SnSe epitaxial film depends on the laser power density and the growth temperature during PLD,¹⁸⁾ in which the FWHM of the film grown on MgO at 573 K was 1.0° at a laser power density of 1.0 J/cm^2 . In the present study, the FWHM of the film grown on MgO was 1.15° at a laser power density of 1.8 J/cm^2 , which indicates nearly the same crystalline quality as the film grown by Inoue et al. From the viewpoint of the crystallographic characteristics, high-quality a-axisoriented SnSe thin films can be fabricated at $T_s = 573 \text{ K}$ on the MgO substrate using a target with x = 1.4 in the present study.



Fig. 5. (Color online) Temperature dependences of the electrical resistivities $\rho(T)$ of the typical SnSe thin films grown on the (a) MgO and (b) STO substrates at $T_s = 473$ and 573 K using the SnSe_x target (x = 1.0 and 1.4).

3.2 Electrical properties of the SnSe thin films

Figures 5(a) and 5(b) show the temperature dependences of the electrical resistivities $\rho(T)$ of typical SnSe thin films grown on the MgO and STO substrates, respectively, at $T_s =$ 473 and 573 K using the SnSe_x target (x = 1.0 and 1.4). In each figure, $\rho(T)$ values in the *bc*-plane and along the *a*-axis of the SnSe bulk fabricated by the SPS method are also shown. The *a*-axis of the crystallites in the SPS bulk was fairly aligned along the uniaxial pressure, which was confirmed by XRD measurement. $\rho(T)$ in the *bc*-plane of the SPS bulk was smaller than that along the *a*-axis, which is reasonable and is consistent with the results of single crystal.⁹⁾ The $\rho(T)$ of the films changed depending on the growth conditions; in Fig. 5(a), the $\rho(T)$ of the film grown on MgO at $T_{\rm s} = 573 \,\rm K$ using the x = 1.4 target was lower than those of the other films. In the figure, the reported ρ value at 300 K for the SnSe film grown on the glass substrate at $T_s = 573 \text{ K}$ using the x = 1.2 target is also shown,¹⁸⁾ in which the film was highly *a*-axis-oriented and ρ was measured in the *bc*plane. The reported $\rho(300 \text{ K})$ was about five times larger than the present $\rho(300 \text{ K})$. The ρ of an epitaxial thin film changes, in general, depending on several factors such as epitaxial strain due to the lattice mismatch, the degree of crystal orientation, non-stoichiometry in the film, and the existence of impurity phases. In Fig. 5(b), the $\rho(T)$ of the film grown on STO at $T_s = 473$ K using the x = 1.4 target was somewhat lower and had a weaker temperature dependence than those of the other film grown on STO, in which the SnSe₂ impurity phase exists and the XRD intensity of the (l00) peak of the SnSe phase is very low. The low $\rho(T)$ of the film grown at $T_s = 473 \text{ K}$ using the x = 1.4 target may closely correlate



Fig. 6. (Color online) $\rho(300 \text{ K})$ values of the SnSe films grown on the MgO and STO substrates at $T_s = 473$ and 573 K, as a function of the composition *x* of the SnSe_x used. The reported $\rho(300 \text{ K})$ values of the single crystal along the *b*- and *c*-axes⁹⁾ and the measured $\rho(300 \text{ K})$ values of the SPS bulk sample in the *bc*-plane are also indicated.

with these characteristics. In both figures, the films grown at $T_{\rm s} = 473$ K using the x = 1.0 target show a larger $\rho(T)$, which may result from the low crystallinity due to the lower growth temperature and the Se deficiency in the film, as Inoue et al. pointed out.¹⁸⁾

Figure 6 shows the $\rho(300 \text{ K})$ values of the films grown on the MgO and STO substrates at $T_s = 473$ and 573 K as a function of the composition x of the SnSe_x target used. In the figure, the reported $\rho(300 \text{ K})$ values of the single crystal along the *b*- and *c*-axes⁹ and the $\rho(300 \text{ K})$ values in the bc-plane of the bulk sample fabricated by SPS shown in Fig. 5 are also indicated. Note that the $\rho(300 \text{ K})$ value of the SPS bulk is as low as that of the single crystal,⁹⁾ and that the $\rho(300 \text{ K})$ values of the films grown on STO at $T_s = 473 \text{ K}$ are fairly low. On the other hand, the $\rho(300 \text{ K})$ values of the other films grown under other conditions are relatively high, although the x, T_s , and substrate dependences are not clearly confirmed. These trends are quite similar to those of the (400) XRD intensity shown in Fig. 2. Taken together, $\rho(300 \text{ K})$ and the crystallinity confirmed by XRD measurements closely correlate with each other.

4. Discussion

In the previous section, the $\rho(T)$ values of the SnSe films change depending on the growth conditions, which are closely related to crystal alignment and crystallinity. However, the $\rho(T)$ values of the grown films are one or two orders of magnitude larger than those of the single crystal and oriented SPS bulk. Here, we discuss the causes of the change in the magnitude of the $\rho(T)$ of the SnSe films. Possible explanations for the larger $\rho(T)$ of the films are misalignment and low crystallinity, as shown in Sect. 3.1. Another explanation may be the nonstoichiometry of SnSe films, especially for the deficient films. In the reported Sn-Se equilibrium binary phase diagram, there is no other phase, except SnSe and SnSe₂.¹⁹⁾ However, a small amount of nonstoichiometry (Se deficient or excess Se) might exist in the SnSe film grown by nonequilibrium PLD, as suggested by Inoue et al.,18) which cannot be detected by elemental analysis method such as EPMA.

Figures 7(a) and 7(b) show the composition (COMP) images of the SnSe film surface grown on MgO at $T_s = 573$ K



Fig. 7. (Color online) Composition (COMP) image of the SnSe film surface grown on (a) MgO at $T_s = 573$ K using the x = 1.4 target and (b) on STO at $T_s = 473$ K using the x = 1.4 target. Atomic ratios Sn/Se of the films on MgO and STO substrates grown at $T_s = 473$ and 573 K using the x = 1.0 and 1.4 targets are shown in (c).

and on STO at $T_s = 473$ K using the x = 1.4 target, respectively. Figure 7(c) shows the Sn/Se atomic ratios of the films grown on MgO and STO at $T_s = 473$ and 573 K using the x = 1.0 and 1.4 targets, which were determined by EPMA. For the film grown on MgO at $T_s = 573$ K using the x = 1.4 target, as shown in Fig. 7(a), a smooth and homogeneous surface can be observed, in which the Sn/Se ratio was 1.003. On the other hand, for the film grown on STO at $T_s = 473$ K using the x = 1.4 target, as shown in Fig. 7(b), a fine mottled pattern can be seen, in which the Se/Sn ratio was 1.205. A small amount of SnSe₂ phase also exists in the main SnSe matrix, as shown in Fig. 1(b), which suggests that SnSe₂ exists in the film at a SnSe : SnSe₂ ratio of 8 : 2, and the mottled pattern may arise from the SnSe₂ phase.

We consider the effects of Se deficiency or Se excess in $[Sn^{2+}Se^{2-}]$ films on the generation of carriers on the basis of thermodynamics of nonstoichiometry, using the Kroger–Vink notation.²¹⁾ For Se deficiency and Se excess, the following charge compensation equations can be deduced:

$$Sn_{Sn}^{\times} + (1 - x)Se_{Se}^{\times} \rightarrow Sn_{Sn}^{\times} + (1 - x)Se_{Se}^{\times} + xV_{Se}^{\bullet\bullet} + 2xe', \qquad (1)$$
$$Sn_{Sn}^{\times} + (1 + x)Se_{Se}^{\times}$$

$$\rightarrow \operatorname{Sn}_{\operatorname{Sn}}^{\times} + \operatorname{Se}_{\operatorname{Se}}^{\times} + x\operatorname{Se}_{\operatorname{i}}'' + 2xh^{\bullet}, \qquad (2)$$

where $\text{Sn}_{\text{Sn}}^{\times}$ and $\text{Se}_{\text{Se}}^{\times}$ indicate the Sn and Se ions located in the normal lattice site, respectively. $V_{\text{Se}}^{\bullet\bullet}$ and $\text{Se}_{i}^{\prime\prime}$ indicate the Se vacancy and Se ion located in the interstitial site, respectively. e' and h^{\bullet} indicate the electron and hole, respectively. We supposed that the Se vacancy and the interstitial Se had changes of +2 and -2, respectively. According to Eq. (1), the Se deficiency in the SnSe layer introduces the Se vacancy. As a result, free electrons are introduced into the lattice, which compensates for intrinsic holes, and the number of free holes decreases with the increase in the number of Se deficiencies. On the other hand, according to Eq. (2), excess Se in the SnSe layer may exist as interstitial Se. As a result,



Fig. 8. (Color online) (a) Temperature dependence of the electrical resistivity $\rho(T)$ of the SnSe_x bulks with nominal compositions of x = 0.97, 0.985, 1.0, 1.015, and 1.03, fabricated by SPS. (b) Carrier concentration p and Hall mobility μ of the SnSe_x bulks at 300 K as a function of the nominal composition x.

additional free holes can be introduced into the lattice and the number of holes increases with the increase in the amount of excess Se, in addition to the intrinsic holes.

To confirm the above consideration, we fabricated $SnSe_x$ polycrystalline bulks with nominal compositions of x = 0.97, 0.985, 1.0, 1.015, and 1.03 by the SPS method and measured the electrical resistivity $\rho(T)$, carrier concentration p, and hall mobility μ . The bulks with x = 0.97 and 0.985 showed no impurity phase, as determined by XRD analysis, but the $SnSe_2$ phase was clearly observed for the bulks with x =1.015 and 1.03 and increased with increasing x. Figure 8(a)shows the temperature dependence of the electrical resistivity $\rho(T)$ of the SnSe_x bulks fabricated by SPS. The $\rho(T)$ of the x = 1.0 bulk is the same as that in the *bc*-plane, as shown in Fig. 5. The $\rho(T)$ of the SnSe_x bulks ($x \le 1.0$) increases with decreasing x from x = 1.0. For the SnSe_x bulks (x > 1.0), in which a small amount of $SnSe_2$ phase exists, $\rho(T)$ at T < 200 K decreased with increasing x from x = 1.0, although the relationship is reversed at approximately 300 K.

Figure 8(b) shows the carrier concentration p and Hall mobility μ of the SnSe_x bulks at 300 K as a function of the nominal composition x of the bulk. The carrier concentration p slightly increases with increasing x. The Hall mobility μ likely reaches its maximum at x = 1.0, which may be reasonable because a minimum number of defects exist in the stoichiometric bulk. As a result, $\rho(300 \text{ K})$ is minimum in the x = 1.0 bulk, as determined using the relation of $\rho = (ep\mu)^{-1}$. These results suggest that the change in the $\rho(T)$ of SnSe_x bulks can be roughly explained by the formalism in Eqs. (1) and (2).

We consider the reason why the magnitude of $\rho(300 \text{ K})$ in the SnSe films changes depending on the growth conditions, as shown in Figs. 5 and 6. The magnitude of $\rho(300 \text{ K})$ can be classified into three: 1) the lower $\rho(300 \text{ K})$ with $\sim 10^2 \text{ m}\Omega \text{ cm}$ such as the films grown on STO at $T_s = 473$ K using the x =1.2 and 1.4 targets, 2) the medium $\rho(300 \text{ K})$ with $\sim 10^3 \text{ m}\Omega \text{ cm}$ such as the film on MgO at $T_s = 573$ K using the x = 1.4target, and 3) the higher $\rho(300 \text{ K})$ with >10⁴ m Ω cm for other films. In the case of 1), excess Se in the film introduces hole carriers, similarly to the $SnSe_x$ bulk, as shown in Fig. 8(a), and shows a low resistivity. The existence of the SnSe₂ impurity phase, which is an n-type semiconductor,²²⁾ may not contribute to the generation of additional holes. In the case of 3), the Se deficiency of the films grown using the x = 1.0 and 1.2 targets, and the low crystallinity of the films at $T_s = 473 \text{ K}$ provide high ρ values. In the case of 2), the films grown on MgO at $T_s = 573$ K using the x = 1.4 target and those grown at $T_s = 473$ K using the x = 1.2 target have high degrees of crystal orientation and crystallinity as well as a stoichiometric composition. As a result, the $\rho(300 \text{ K})$ can be considered to be reasonable. These films in the case of 2) have similar $\rho(300 \text{ K})$ values to the reported film grown on fused silica at $T_s = 573$ K using the x = 1.2 target,¹⁸⁾ which was the best film among those in previous studies.

Finally, we comment on the ohmic contact for SnSe films. We first aimed to measure both the electrical resistivity $\rho(T)$ and Seebeck coefficient S(T) of the films for applications in thermoelectric devices. $\rho(T)$ was relatively easy to measure using the Ag paste as an ohmic electrode. However, the S(T) of the films cannot be measured stably using the Ag paste because of the existence of stray electromotive force. We also tried using sputtered Au and Pt to realize the fabrication of low-resistance ohmic contacts, but were unsuccessful. If a suitable ohmic contact material can be discovered for highly resistive SnSe films, further thermoelectric investigation can be carried out using the SnSe thin films such as single crystals and polycrystals.

5. Conclusions

We have grown epitaxial SnSe films on the MgO or STO single-crystal substrates by PLD at $T_s = 473$ or 573 K using SnSe_x (x = 1.0-1.6) as the target, and investigated the optimal growth conditions in terms of crystal orientation, crystallinity, and electrical resistivity. The important results and conclusions are summarized as follows.

(1) The crystal orientation and crystallinity of the SnSe films change depending on the growth conditions. The SnSe film grown on the MgO substrate at $T_s = 573$ K using the x = 1.4 target was highly *a*-axis-oriented without any other orientation or impurity phase owing to the small lattice mismatch between the SnSe film and the MgO substrate. On the other hand, the films grown on STO, which has a larger lattice mismatch, show crystal misalignment and low crystallinity.

(2) The electrical resistivity ρ of the film in the *bc*-plane changes depending on the growth conditions, which is closely related to crystal alignment and crystallinity. The lattice mismatch and/or the small amount of nonstoichiometry in the epitaxial film also affects ρ .

(3) The optimized SnSe film, which was grown on MgO at $T_s = 573$ K using the x = 1.4 target, shows a moderate resistivity of $\sim 10^2$ m Ω cm at 300 K. Although this value was about one order of magnitude larger than that of a single crystal, it was nearly on the same order as the previously reported SnSe epitaxial film grown on a glass substrate at $T_s = 573$ K using the x = 1.2 target.

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- 1) W. Albers, C. Haas, and F. van der Maesen, J. Phys. Chem. Solids 15, 306 (1960).
- J. Vidal, S. Lany, M. d'Avezac, A. Zunger, A. Zakutayev, J. Francis, and J. Tate, Appl. Phys. Lett. 100, 032104 (2012).
- F.-Y. Ran, Z. Xiao, H. Hiramatsu, H. Hosono, and T. Kamiya, Appl. Phys. Lett. 104, 072106 (2014).
- D. Chun, R. M. Walser, R. W. Bené, and T. H. Courtney, Appl. Phys. Lett. 24, 479 (1974).
- 5) J. J. Loferski, J. Appl. Phys. 27, 777 (1956).
- M. Rodot, Acta Electron. 18, 345 (1975).
 A. Bennouna, P. Y. Tessier, M. Priol, Q. D. Tran, and S. Robin, Phys.
- Status Solidi B 117, 51 (1983).8) G. H. Chandra, J. N. Kumar, N. M. Rao, and S. Uthanna, J. Cryst. Growth
- **306**, 68 (2007).
- L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, Nature 508, 373 (2014).
- 10) C.-L. Chen, H. Wang, Y.-Y. Chen, T. Day, and G. J. Snyder, J. Mater. Chem. A 2, 11171 (2014).
- 11) S. Sassi, C. Candolfi, J.-B. Vaney, V. Ohorodniichuk, P. Masschelein, A. Dauscher, and B. Lenoir, Appl. Phys. Lett. 104, 212105 (2014).
- K. J. John, B. Pradeep, and E. Mathai, J. Mater. Sci. 29, 1581 (1994).
 R. Indirajith, T. P. Srinivasan, K. Ramamurthi, and R. Gopalakrishnan,
- Curr. Appl. Phys. **10**, 1402 (2010). 14) R. Indirajith, M. Rajalakshmi, R. Gopalakrishnan, and K. Ramamurthi,
- Ferroelectrics **413**, 108 (2011).
- 15) D. Martínez-Escobar, M. Ramachandran, A. Sánchez-Juárez, and J. S. N. Rios, Thin Solid Films 535, 390 (2013).
- 16) R. Teghil, A. G. Guidoni, A. Mele, S. Piccirillo, G. Pizella, and V. Marotta, Thin Solid Films 241, 126 (1994).
- 17) R. Teghil, A. G. Guidoni, A. Mele, S. Piccirillo, M. Coreno, V. Marotta, and T. M. Di Palma, Surf. Int. Anal. 22, 181 (1994).
- 18) T. Inoue, H. Hiramatsu, H. Hosono, and T. Kamiya, J. Appl. Phys. 118, 205302 (2015).
- M. Hansen, in *Constitution of Binary Alloys*, ed. M. Hansen (McGraw-Hill, New York, 1958) p. 1187.
- 20) H. Fujishiro, M. Ikebe, T. Naito, K. Noto, S. Kobayashi, and S. Yoshizawa, Jpn. J. Appl. Phys. 33, 4965 (1994).
- 21) O. Johannesen, J. Mater. Educ. 8, 351 (1986).
- 22) L. Amalraj, M. Jayachandra, and C. Sanjeeviraja, Mater. Res. Bull. 39, 2193 (2004).