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# Crystal orientation, crystallinity, and thermoelectric properties of $Bi_{0.9}Sr_{0.1}CuSeO$ epitaxial films grown by pulsed laser deposition

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## Crystal orientation, crystallinity, and thermoelectric properties of Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO epitaxial films grown by pulsed laser deposition

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We have grown Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO epitaxial thin films on MgO and SrTiO<sub>3</sub> (STO) single-crystal substrates by pulsed laser deposition (PLD) under various growth conditions, and investigated the crystal orientation, crystallinity, chemical composition, and thermoelectric properties of the films. The optimization of the growth conditions was realized in the film grown on MgO at the temperature  $T_s = 573$  K and Ar pressure  $P_{Ar} = 0.01$  Torr in this study, in which there was no misalignment apart from the *c*-axis and no impurity phase. It was clearly found that the higher crystal orientation of the epitaxial film grown at a higher temperature under a lower Ar pressure mainly enhanced the thermoelectric power factor  $P (= S^2/\rho)$ , where S is the Seebeck coefficient and  $\rho$  is the electrical resistivity. However, the thermoelectric properties of the films were lower than those of polycrystalline bulk because of lattice distortion from lattice mismatch, a low crystallinity caused by a lower  $T_s$ , and Bi and Cu deficiencies in the films. © 2018 The Japan Society of Applied Physics

#### 1. Introduction

The thermoelectric technology that converts thermal energy directly to electricity using waste heat has been revived because of the recent energy crisis together with other renewable energy sources. The performance of thermoelectric materials can be evaluated using the dimensionless figure of merit  $ZT = S^2 T / \rho \kappa$  and the thermoelectric power factor P  $(=S^2/\rho)$ , where S is the Seebeck coefficient,  $\rho$  is the electrical resistivity,  $\kappa$  is the thermal conductivity, and T is the absolute temperature. Most conventional thermoelectric materials with high ZT values, such as Bi<sub>2</sub>Te<sub>3</sub> and PbTe, however, exhibit thermal and chemical instabilities in air at high temperatures, and contain toxic, scarce, or expensive elements.<sup>1-3)</sup> Oxides can be used to overcome these problems and therefore are attracting increasing interest from researchers. Recently, oxyselenide, BiCuSeO, with p-type conduction has been paid considerable attention for its relatively high thermoelectric performance from 700 to 1000 K.<sup>4-16</sup>) This material crystallizes in a layered structure that is composed of conductive [Cu<sub>2</sub>Se<sub>2</sub>]<sup>2-</sup> layers constituting a conduction pathway for carrier transport alternately stacked with insulating  $[Bi_2O_2]^{2+}$ layers acting as a charge reservoir along the *c*-axis of the tetragonal unit cell (P4/nmm).<sup>5,6)</sup> The BiCuSeO system has a low Hall mobility ( $\mu \sim 2-20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and a relatively high carrier concentration  $(p \sim 10^{18} \text{ cm}^{-3})$ .<sup>12)</sup> The presence of Bi, which is known to exhibit strong anharmonic vibrations as it is a heavy element, is detrimental for heat transfer, leading to low thermal conductivity  $\kappa$  (= 4.6 mW cm<sup>-1</sup> K<sup>-1</sup> at 873 K).<sup>11)</sup> The BiCuSeO system showed excellent charge transport and thermoelectric behaviors owing to the introduction of hole carriers by replacing Bi3+ with divalent alkaline-earth ions such as Sr<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, and Pb<sup>2+</sup> in the insulating  $[Bi_2O_2]^{2+}$  layer.<sup>11,12,16)</sup> In the  $[Cu_2Se_2]^{2-}$  layer, the  $Se^{2-}$  site is replaced with the isovalent  $Te^{2-}$  to open a small gap in the electronic structure.<sup>17)</sup> The deficiency of Cu<sup>+</sup> was also investigated for the BiCu<sub>1-x</sub>SeO system, which introduces hole carriers.<sup>18)</sup> Hole doping also induces point defect scattering and reduces the thermal conductivity. To date, the highest ZT of 1.4 has been achieved at 923 K for a Bi<sub>0.875</sub>Ba<sub>0.125</sub>CuSeO bulk sample.<sup>19)</sup> We have investigated the ball milling effects for  $\text{Bi}_{1-x}\text{Sr}_x\text{CuSeO}$  (x = 0, 0.1) bulk materials fabricated by a spark plasma sintering (SPS) method, in which thermoelectric properties were enhanced by the use of ball-milled powder, mainly owing to the induced carriers, rather than the reduction in thermal conductivity.<sup>20</sup>

A thin film of a thermoelectric material is preferably used to realize a fully *c*-axis texture and to tremendously enhance ZT via the quantum confinement effect and interface engineering. However, there are few reports on thin films of the BiCuSeO system. Epitaxial thin films of this system were first reported by Tate et al.;<sup>21)</sup> such films grown on a SrTiO<sub>3</sub> (STO) substrate by pulsed laser deposition (PLD) were determined to exhibit strong 00l peaks by X-ray diffraction (XRD). XRD rocking curves indicate that the alignment of the textured film is in good agreement with a full width at half maximum (FWHM) of about 1°. The electrical resistivity decreases with increasing Ca concentration for the Bi site, reaching  $\rho = 5.6 \text{ m}\Omega \text{ cm}$  at 300 K for the Bi<sub>0.85</sub>Ca<sub>0.15</sub>CuSeO film, in which the carrier concentration is  $p = 7 \times 10^{20} \text{ cm}^{-3}$  and the Hall mobility is  $\mu = 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Zakutayev et al. investigated the thermoelectric properties of Bi0.9Ca0.1CuSeO films on STO fabricated by PLD,<sup>22)</sup> in which  $\rho$  decreased with increasing Ca content, but the Seebeck coefficient S remained almost the same around room temperature. As a result, the power factor P was enhanced by Ca substitution and was larger than that of polycrystals. The largest P of about 1.2 mW m<sup>-1</sup> K<sup>-2</sup> has been achieved in Bi<sub>0.96</sub>Pb<sub>0.04</sub>CuSeO epitaxial thin films grown at 673 K;<sup>23)</sup> such a value is much larger than that of polycrystal ceramics with random orientation, suggesting that *c*-axis oriented BiCuSeO-based single crystal thin films might have great potential for application in thermoelectric thin-film devices. The transverse thermoelectric (TE) effect was investigated using a Pb-doped thin film grown by PLD.<sup>24,25)</sup> The thin films on quartz and Si wafers were also investigated.<sup>26)</sup> However, there are only a few systematic investigations on the crystallinity and stoichiometry of the metal elements for the epitaxial BiCuSeO films grown by PLD on single-crystal substrates with different lattice constants, and no investigations on Sr-doped BiCuSeO thin films. In this study, we fabricated epitaxial  $Bi_{1-x}Sr_xCuSeO$  thin

films (x = 0.1) by PLD under various growth conditions such

as the growth temperature  $T_s$ , the Ar pressure  $P_{Ar}$ , and the type of single-crystal substrate differing in lattice constant. The effects of lattice mismatch between the substrate and the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO material, and the chemical composition and microstructure of the films on thermoelectric properties were systematically investigated. The thermoelectric properties of Sr-doped BiCuSeO thin films were compared with those of the reported Pb- and Ca-doped BiCuSeO thin films.

#### 2. Experimental procedure

Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films were grown by PLD using a fifthharmonic wave of a yttrium aluminum garnet (YAG) laser with  $\lambda = 213$  nm and a repetition rate of 10 Hz.<sup>27</sup>) The pulse duration was 5 ns and the laser power density was  $1.8 \text{ J/cm}^2$ . To fabricate the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO polycrystalline target for PLD, Bi (99.9%), Bi<sub>2</sub>O<sub>3</sub> (99.9%), SrO (99.5%), Cu (99.9%), and Se (99.9%) fine powders were used as raw materials. These were weighed with a stoichiometric ratio of Bi : Sr : Cu : Se = 0.9 : 0.1 : 1.0 : 1.0 and mixed in Ar atmosphere. After the mixed raw materials were evacuated and sealed in a quartz tube, they were heated at 973 K for 12h and then furnace-cooled. The obtained precursor was pulverized and mixed in air for 0.5 h using an automatic mortar. The powders were sintered using SPS apparatus (NJS LABOX-110C) under a uniaxial pressure of 40 MPa at about 973 K for 10 min in vacuum. The mass density of the obtained pellets (10 mm in diameter and 9 mm in thickness) was higher than 93% of the ideal density.

The target and substrate were mounted in the PLD vacuum chamber and rotated at speeds of 7 and 3 rpm, respectively, to reduce nonuniform erosion and deposit the film uniformly. The distance between the target and the substrate was 60 mm. The deposition was carried out for 4 h in Ar atmosphere from  $P_{\rm Ar} = 0.001$  to 0.1 Torr at substrate temperatures of  $T_{\rm s} = 473$ and 573 K. The films were grown on (001)-oriented MgO (a = 0.421 nm) and STO (a = 0.391 nm) single-crystal substrates. The tetragonal lattice parameters of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>-CuSeO bulk were a = b = 0.393 nm and  $c = 0.894 \text{ nm}.^{17}$ Using the relation  $\varepsilon = (a_{sub} - a_{BiCuSeO})/a_{sub}$ , the in-plane lattice mismatch  $\varepsilon$  was measured to be +6.8% for MgO and -0.6% for STO, in which a large in-plane tensile stress was assumed to be applied to the film grown on MgO and a small compressive stress was applied to the film on STO. The film thickness was determined by observing the cross section by transmission electron microscopy (TEM; JEOL JEM-2100) and by the optical absorption coefficient using a spectrophotometer (Shimadzu UV-3100PC). The average film thickness was about 70-120 nm for each film, which was measured and averaged by the TEM observation of the cross section of the films at several points.

To clarify the crystal orientation and crystalline quality of the grown films, XRD analyses of  $\theta$ -2 $\theta$  and  $2\theta$ - $\phi$  scans were performed, which identified the out-of-plane and in-plane alignments, respectively. The crystalline quality was assessed using  $\Delta \omega$  measured using the FWHM from the  $\omega$  rocking curve ( $2\theta$ - $\omega$  scan) measurements in the films. The chemical composition and microstructure of the films were analyzed by electron probe microanalysis using a field emission gun (FE-EPMA) and scanning electron microscopy (SEM). The electrical resistivity  $\rho(T)$  and Seebeck coefficient S(T) were measured in the temperature range from 300 to 10 K by a standard four-probe method and a steady-state heat flow method, respectively, using a laboratory-built measurement system.<sup>28)</sup> The thermoelectric power factor  $P = S^2/\rho$  was calculated using these measured values.

#### 3. Results and discussion

#### 3.1 Optimization of epitaxial growth

Figure 1 shows the XRD  $\theta$ -2 $\theta$  patterns of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>-CuSeO thin films grown on MgO or STO at 473 or 573 K for various Ar pressure  $P_{Ar}$  values. All the films are generally *c*-axis oriented. However, a small number of (110) and (106) diffraction peaks can be observed in the films on MgO at  $T_s = 473 \text{ K}$  [Fig. 1(a)], on STO at  $T_s = 473 \text{ K}$  [Fig. 1(c)], and on STO at  $T_s = 573 \text{ K}$  [Fig. 1(d)]. The Cu<sub>2</sub>Se impurity peak was also observed in the film on STO at  $T_s = 473 \text{ K}$ [Fig. 1(c)]. On the other hand, the films grown on MgO at  $T_{\rm s} = 573$  K, in the  $P_{\rm Ar} = 0.001$  and 0.01 Torr cases [Fig. 1(b)] are fully *c*-axis oriented without any impurity phases. The c-axis lattice constants of the films grown on MgO and STO at  $T_s = 573$  K, determined using the (006) diffraction angle, are in the range of 0.890-0.892 nm and independent of the type of substrate used and slightly smaller than that of the target bulk (c = 0.894 nm), although the lattice mismatch  $\varepsilon$ values of the film are different. These results suggest that the present epitaxial films are loosely fixed to MgO and STO, but are generally oriented along the *c*-axis. The smaller *c*-axis lattice constant may result from the expanded in-plane lattice constants owing to the Bi and Cu deficiencies in the films, as shown later.

Figure 2 shows the XRD intensity ratio I(110)/I(003) values of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films grown on MgO and STO at  $T_s = 473$  and 573 K as a function of the Ar pressure  $P_{Ar}$ , which show the relative amount of off-axis alignment against the *c*-axis orientation. The I(110)/I(003) value of the films grown at  $T_s = 573$  K is fairly small, except for the film grown on STO at  $P_{Ar} = 0.1$  Torr, and is the smallest for the films grown on MgO at  $P_{Ar} = 0.001$  and 0.01 Torr, which is in clear contrast to that of the films grown at  $T_s = 473$  K. These results suggest that the *c*-axis orientation is promoted by the increase in  $T_s$  and that films on MgO are more likely to be *c*-axis-oriented than those on STO, although the lattice mismatch  $\varepsilon$  of the film on MgO (= +6.8%) is larger than that on STO (= -0.6%).

Figure 3 presents the  $2\theta - \phi$  azimuth scan for the Bi<sub>0.9</sub>Sr<sub>0.1</sub>-CuSeO thin films grown on MgO and STO at  $T_s = 573$  K in the  $P_{Ar} = 0.01$  Torr case. Four sharp peaks of the (111) reflections ( $2\theta = 33.65^\circ$ ) were observed every 90° and the in-plane alignment was confirmed. The fourfold symmetry was also confirmed for the films grown under the other conditions, regardless of the type of substrate used,  $T_s$ , and  $P_{Ar}$ . The Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO films grown under the present growth conditions were confirmed to be epitaxial.

Figure 4 shows  $\Delta \omega$  of the (006) diffraction for the films grown on MgO and STO at  $T_s = 473$  and 573 K as a function of  $P_{Ar}$ . The  $P_{Ar}$  dependence of  $\Delta \omega$  changes, depending on the growth condition. The inset shows an example of the rocking curve for the film grown on MgO at  $T_s = 573$  K in the  $P_{Ar} =$ 0.01 Torr case. In this sample,  $\Delta \omega$  was 1.8°, which was markedly larger than those reported for the nondoped BiCuSeO films:  $\Delta \omega = 0.56^{\circ}$  on the Si wafer<sup>26)</sup> and 0.2° on STO.<sup>23)</sup> The larger  $\Delta \omega$  of the present films may originate



**Fig. 1.** (Color online) XRD  $\theta$ -2 $\theta$  patterns of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films (a) on MgO at  $T_s = 473$  K, (b) on MgO at  $T_s = 573$  K, (c) on STO at  $T_s = 473$  K, and (d) on STO at  $T_s = 573$  K for various Ar pressures  $P_{Ar}$ .



**Fig. 2.** (Color online) XRD intensity ratio I(110)/I(003) values of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films grown on MgO and STO at  $T_s = 473$  and 573 K as a function of the Ar pressure  $P_{Ar}$ .



**Fig. 3.** (Color online) In-plane XRD patterns  $(2\theta - \phi \text{ scan})$  of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films grown on MgO and STO at  $T_s = 573$  K in  $P_{Ar} = 0.01$  Torr case.

from the Bi-site substitution for the Sr and/or lower growth temperature or nonstoichiometry of the Bi and Cu elements in the films. These possibilities are discussed later.



**Fig. 4.** (Color online)  $\Delta\omega$  values of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films grown on MgO and STO at  $T_s = 473$  and 573 K as a function of Ar pressure  $P_{Ar}$ . The inset shows the normalized X-ray rocking curve ( $2\theta - \omega$  scan) of the (006) reflection for the film grown on MgO at  $T_s = 573$  K in the  $P_{Ar} = 0.01$  Torr case.

Figure 5 shows the SEM images of the film surfaces grown on MgO at  $T_s = 473$  and 573 K for various Ar pressures ( $P_{Ar}$ ). At  $T_s = 473$  K, as shown in Figs. 5(a)–5(c), small crystal particles, which may be directly ablated from the target as droplets, were deposited on the film surface, and the number of particles decreases with increasing  $P_{Ar}$ . On the other hand, at  $T_s = 573$  K, as shown in Figs. 5(d)–5(f), the particle size on the film increases owing to the increased migration energy and rectangular crystals can be clearly observed at  $P_{Ar} = 0.001$ and 0.01 Torr, which show the *ab*-plane of the crystallites. The crystallites are connected to each other and the film surface becomes smooth at the higher Ar pressure of 0.1 Torr.

Figure 6 presents the SEM images of the film surfaces grown on STO at  $T_s = 473$  and 573 K for various Ar pressures ( $P_{Ar}$ ). Such SEM images show similar  $P_{Ar}$  and  $T_s$ dependences to those of the film surfaces grown on MgO as shown in Fig. 5, suggesting that the surface morphology does



Fig. 5. SEM images of the  $Bi_{0.9}Sr_{0.1}CuSeO$  films grown on MgO at  $T_s = 473$  K [(a)–(c)] and 573 K [(d)–(f)] for various Ar pressures ( $P_{Ar}$ ).



Fig. 6. SEM images of the  $Bi_{0.9}Sr_{0.1}CuSeO$  films grown on STO at  $T_s = 473 \text{ K} [(a)-(c)]$  and 573 K [(d)-(f)] for various Ar pressures ( $P_{Ar}$ ).

not depend on the type of substrate used but on  $P_{\text{Ar}}$  and  $T_{\text{s}}$ . In Figs. 6(d) and 6(e) at  $T_{\text{s}} = 573$  K, the rectangular crystals can clearly be observed, similarly to Figs. 5(d) and 5(e).

Figure 7(a) shows the TEM cross-sectional image of the film grown on MgO at  $T_s = 573$  K in the  $P_{Ar} = 0.01$  Torr case, which is the optimum growth condition in this study. A well-ordered layered structure along the *c*-axis can be clearly observed in the image, which is consistent with the XRD pattern shown in Fig. 1(b). The distance of the lattice plane, which is about 0.88 nm, is nearly consistent with the *c*-axis lattice parameter (= 0.891 nm) determined by XRD. Figure 7(b) shows the TEM cross-sectional image of the film grown on STO at  $T_s = 473$  K in the  $P_{Ar} = 0.001$  Torr case, which is not the optimum growth condition. The lattice plane inclined about  $45^{\circ}$  away from the substrate surface can be observed, together with the layered structure stacked along

the *c*-axis. These results are consistent with the XRD pattern shown in Fig. 1(c).

To investigate the deviation from the stoichiometric composition of the metallic elements, EPMA was performed. The results of the element analysis for the films grown on MgO are shown in Table I, in which the measurements were performed at 15 points for each sample and averaged. The deviation of the results in each film was within 5%. The result of the target bulk is also shown. The atomic ratios of (Bi+Sr): Cu : Se and Bi : Sr were normalized as (Bi+Sr) + Cu + Se = 3.0 and Bi + Sr = 1.0, respectively. The oxygen contents in Bi<sub>0.9</sub>Sr<sub>0.1</sub>-CuSeO thin films are not shown in the table, because the oxygen contents measured by FE-EPMA also include those from MgO owing to the thin film. The atomic ratios of (Bi+Sr): Cu : Se and Bi : Sr change depending on the growth temperature  $T_s$  and Ar pressure  $P_{Ar}$ . Compared with



**Fig. 7.** TEM cross-sectional images of the films grown (a) on MgO at  $T_{\rm s} = 573$  K in  $P_{\rm Ar} = 0.01$  Torr case and (b) on STO at  $T_{\rm s} = 473$  K in  $P_{\rm Ar} = 0.001$  Torr case.

the measured ratios of the target bulk [(Bi+Sr) : Cu : Se =0.99 : 1.07 : 0.94 and Bi : Sr = 0.91 : 0.09], the ratios of the films grown at  $T_s = 473$  K and at a high  $P_{Ar}$  are nearly the same as those for the target bulk. On the other hand, for the films grown at  $T_s = 573$  K, the number of Bi+Sr atoms decreases and that of Cu atoms also decreases, compared with that of Se atoms, and the atomic ratio of Bi : Sr shifts to 0.8 : 0.2. These results suggest that Bi and Cu deficiencies exist in the films grown, especially at 573 K, although the films show the best crystalline orientation without any impurity phases in this study, as shown in the previous figures. The deficiency of Cu atoms has been investigated for the BiCu<sub>1-x</sub>SeO,  $^{18,29)}$  LaCu<sub>1-x</sub>SO,  $^{30,31)}$  and BaCuChF (Ch: chalcogen) systems,<sup>32)</sup> which introduces hole carriers and decreases the resistivity. The calculated formation energies of Cu and Bi vacancies were reported to be 0.219 and 0.238 meV per formula unit under ambient pressure, respectively, and these values increased with increasing pressure.<sup>29)</sup> These calculated results indicate that the Cu and Bi deficiencies from the stoichiometric composition are easy to create during PLD under lower pressures. The exhausted Bi and Cu atoms might vaporize with increasing  $T_s$ . The results of the element analysis for the films grown on STO are nearly the same as those for the films on MgO, regardless of the lattice mismatch between the film and the substrate.

### 3.2 Thermoelectric properties of Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO films

In the previous subsection, the film grown on MgO at  $T_s = 573$  K and  $P_{Ar} = 0.01$  Torr was the best epitaxial film in this study from the viewpoint of crystal orientation and crystallinity. We investigated the thermoelectric properties of the

**Table I.** EPMA estimates of atomic ratios for  $Bi_{0.9}Sr_{0.1}CuSeO$  thin films grown on MgO at  $T_s = 473$  and 573 K under various Ar pressures ( $P_{Ar}$ ). The nominal atomic ratios of the target bulk are (Bi+Sr) : Cu : Se = 1.00 : 1.00 : 1.00 and Bi : Sr = 0.90 : 0.10.

<i>T</i> <sub>s</sub> (K)	$P_{\rm Ar}$ (Torr)	(Bi+Sr) : Cu : Se	Bi : Sr
Target bulk (nominal)		1.00 : 1.00 : 1.00	0.90:0.10
Target bulk (measured)		0.99:1.07:0.94	0.91:0.09
473	0.001	0.98:0.84:1.18	0.85:0.15
	0.01	0.93:1.01:1.06	0.88:0.12
	0.1	1.05 : 0.97 : 0.98	0.90:0.10
573	0.001	0.77:1.06:1.17	0.81:0.19
	0.01	0.87:0.97:1.16	0.82:0.18
	0.1	0.88:0.97:1.14	0.81:0.19

Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO films grown on MgO and STO. Figures 8(a) and 8(b) respectively show the temperature dependences of the electrical resistivity  $\rho(T)$  and Seebeck coefficient S(T) of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO films grown on MgO at  $T_s = 573$  K at various  $P_{\rm Ar}$  values. For comparison, the values of the target bulk fabricated by SPS, which were independent of the direction of the applied pressure during SPS,<sup>20)</sup> are also shown. The  $\rho(T)$  and S(T) values of the films at 300 K are smaller than those of the SPS bulk, which change independent of  $P_{\rm Ar}$ , and suggest that the hole carriers are introduced into the films during PLD. Figure 8(c) shows the thermoelectric power factor  $P(T) = S^2/\rho$ . P(T) of the films is smaller than that of the SPS bulk, mainly owing to the smaller S(T) of the films, although  $\rho(T)$  is lower.

Table II shows the electrical resistivity  $\rho(300 \text{ K})$ , Seebeck coefficient S(300 K), and power factor P(300 K) of the  $Bi_{0.9}Sr_{0.1}CuSeO$  films grown on MgO and STO at  $T_s$  (473) and 573 K) and PAr from 0.001 to 0.1 Torr. The XRD intensity ratio I(110)/I(003) is also shown for each film. Roughly,  $\rho(300 \text{ K})$  decreases with decreasing I(110)/I(003). The PLD process at 573 K reduces  $\rho(300 \text{ K})$  and, at the same time, the optimum  $P_{Ar}$  may exist around 0.01 Torr, although the Bi and Cu deficiencies exist in the films. The decrease in  $\rho(300 \text{ K})$  is closely related to the higher c-axis orientation. The S(300 K)values of the films grown at  $T_s = 573$  K and  $P_{Ar} = 0.01$  Torr are enhanced in spite of the decrease in  $\rho(300 \text{ K})$ . This tendency is in contrast to a classical wide-gap semiconductor model, in which the Seebeck coefficient is inversely proportional to  $\log p$  (p: hole concentration) and S(T) might be decreased by the enhanced carrier concentration. The S(T)enhancement may originate from the confinement effect of the carriers in the epitaxial films.

Figure 9(a) shows the power factor P(300 K) values of the films grown on MgO and STO at  $T_s = 473$  and 573 K as a function of  $P_{\text{Ar}}$ . The value of the SPS bulk,  $P(300 \text{ K}) = 5.0 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ , is also shown. At  $P_{\text{Ar}}$  lower than 0.01 Torr, it was found that P(300 K) is mainly determined by the growth temperature  $T_s$ . P(300 K) takes a maximum for the films grown at  $T_s = 573 \text{ K}$  and  $P_{\text{Ar}} = 0.01$  Torr mainly owing to the increase in S(300 K). However, the maximum P(300 K) of the films is lower than that of the SPS bulk mainly because of the smaller S(300 K). Figure 9(b) shows the P(300 K) values of the thin films as a function of I(110)/I(003). P(300 K) is closely related to I(110)/I(003), which suggests that the highly *c*-axis oriented (Bi,Sr)CuSeO film shows better thermoelectric properties.



**Fig. 8.** (Color online) Temperature dependences of (a) electrical resistivity  $\rho(T)$ , (b) Seebeck coefficient S(T), and power factor P(T) of Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films grown on MgO at  $T_s = 573$  K under various Ar pressures ( $P_{AT}$ ). Those of the bulk are also shown for comparison.

**Table II.** Electrical resistivity  $\rho(300 \text{ K})$ , Seebeck coefficient *S*(300 K), and power factor *P*(300 K) of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO films grown on (a) MgO and (b) STO at *T*<sub>s</sub> (473 and 573 K) and *P*<sub>Ar</sub> from 0.001 to 0.1 Torr.

I(110)/I(003)
1(110)/1(003)
1.16
0.42
0.15
0
0
0.16
<i>I</i> (110)/ <i>I</i> (003)
0.51
0.30
0.19
0.10
0.04
1.22

Finally, we compare the thermoelectric properties of the present Sr-doped BiCuSeO thin films with those of the Pband Ca-doped BiCuSeO thin films. Table III shows a summary of the growth conditions and thermoelectric properties of the present Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin film grown on MgO at  $T_s = 573$  K and  $P_{Ar} = 0.01$  Torr, and SPS bulk and reported films.<sup>22,23</sup>  $\rho(300 \text{ K})$  of the present Sr-doped film, in which a small amount of Bi deficiency existed and hole carriers were created, was smaller.<sup>20)</sup> S(300 K) of the present Sr-doped film is the smallest, among those of other materials. The main difference observed in the films is the growth temperature  $T_s$ ,



**Fig. 9.** (Color online) (a) Power factor P(300 K) at 300 K of the Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO thin films grown on MgO and STO at  $T_s = 473$  and 573 K as a function of Ar pressure  $P_{\text{Ar}}$ . P(300 K) of the SPS bulk is also shown. (b) P(300 K) of the thin films as a function of the XRD intensity ratio I(110)/I(003).

which is 573 K for the present film and is lower than 773 K for the Ca-doped film  $(x = 0.1)^{22}$  and 673 K for the Pb-doped film (x = 0.06).<sup>23)</sup> It is better to grow films at higher temperatures for PLD. We attempted to grow films at temperatures higher than 573 K. However, we could not successfully realize epitaxial films using our apparatus owing to the vaporization of elements. If Sr-doped films are grown at

**Table III.** Growth conditions and thermoelectric properties of the present  $Bi_{1-x}Sr_xCuSeO$  thin film (x = 0.1) grown on MgO at  $T_s = 573$  K and  $P_{Ar} = 0.01$  Torr, compared with those of the reported Ca- and Pb-doped  $Bi_{1-x}Sr_xCuSeO$  films.<sup>22,23)</sup> Those of Sr-doped bulk (x = 0.1) fabricated by the SPS method are also shown as a reference.

Growth conditions and physical properties	Sr-doped bulk $(x = 0.1)$	Sr-doped film $(x = 0.1)$	Ca-doped film $(x = 0.1)$	Pb-doped film $(x = 0.06)$
T <sub>s</sub> (K)	_	573	773	673
$P_{\rm Ar}$ (Torr)	_	$1.0 \times 10^{-2}$	$1.0 \times 10^{-1}$	$7.5 \times 10^{-4}$
Substrate	_	MgO	STO	STO
Wavelength of laser, $\lambda$ (nm)	_	213	248	308
$\rho(300 \mathrm{K}) (\mathrm{m}\Omega \mathrm{cm})$	4.1	2.45	3.0	1.3
$S(300  \text{K}) \; (\mu \text{V}/\text{K})$	145	85.1	130	110
$P(300 \text{ K}) (\times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2})$	5.0	2.95	5.6	9.3
Reference	This work	This work	22	23

higher  $T_{\rm s}$  values, similar crystallographic and thermoelectric properties to those of the reported Pb- and Ca-doped BiCuSeO thin films can be achieved. The shorter wavelength  $\lambda$  used in the present study, which is expected to reduce the local heating on the target, may also affect the crystallographic and thermoelectric characteristics of the BiCuSeO epitaxial films.

#### 4. Conclusions

We have grown Bi<sub>0.9</sub>Sr<sub>0.1</sub>CuSeO epitaxial thin films on MgO and STO single-crystal substrates by PLD at  $T_s = 473$  and 573 K in the Ar pressure  $P_{\rm Ar}$  range from 0.001 to 0.1 Torr, and investigated their crystal orientation, crystallinity, chemical composition, and thermoelectric properties. The optimization of the growth conditions was realized in the film grown on MgO at the growth temperature  $T_s = 573$  K and Ar pressure  $P_{\rm Ar} = 0.01$  Torr in this study, in which there was no misalignment apart from the *c*-axis and no impurity phase. However, the FWHM value,  $\Delta \omega$ , was larger than the reported value. The higher crystal orientation of the epitaxial film grown at a higher temperature under a lower Ar pressure mainly enhanced the thermoelectric power factor  $P (= S^2/\rho)$ . However, the thermoelectric properties of the films were lower than those of polycrystalline bulk, mainly because of the lattice distortion from the lattice mismatch and low crystallinity caused by lower  $T_s$  and Bi and Cu deficiencies in the films. If the present Sr-doped films are grown at  $T_s$  higher than 573 K, their crystallographic and thermoelectric properties could be improved, which are as high as those of the reported Pb- and Ca-doped BiCuSeO thin films.

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