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Influence of Oxidation in Starting Material Sn on Electric Transport Properties of SnSe Single Crystals

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We found that the electronic transport property of SnSe single crystals was sensitively affected by oxidation in raw Sn. Semiconducting SnSe single crystals were obtained by

using Sn of grain form as a starting material while powder Sn resulted in metallic SnSe. X-ray photoelectron spectroscopy analysis revealed that the surfaces of raw Sn were oxidized, which volume fraction is lower in grain Sn. This indicates that the amount of oxygen in raw Sn is the key factor for the electronic transport property of SnSe.

SnSe is well-known as a p-type semiconductor for a long time [1-3]. Recently, Zhao et al. reported that SnSe single crystal shows ultrahigh dimensionless figure-of-merit (*ZT*) values of 2.6 and 2.3 at 923 K in the *b* and *c* directions [4]. These high *ZT* values are achieved with high power factor and extremely low thermal conductivity. After the report in 2014, intense investigations have been conducted by many groups [5-22]. More recently, the *ZT* values around 2.0 have been reported with Bi-doped n-type and Na-doped p-type SnSe single crystals [5, 16, 17]. However, the reproducibility of the exceptionally high thermoelectric performance has not been obtained to date. Different thermoelectric properties, especially in electrical conductivity, have been reported from several groups for both of single crystalline and poly crystalline samples. Some groups reported metallic behavior in electrical conductivity [16-18]. On the other hand, others reported semiconducting behavior [19-23] and consistent results have not been obtained so far.

Motivated to figure out the reason of these different results, we focused on the possible influence of oxygen content in the starting materials of Sn. Herein, we report on the electrical conductivity measurements along the *bc* plane for SnSe single crystals in a temperature range from 2 to 390 K. It was found that the electrical conductivity was controlled by changing the oxygen content during the synthesis. The electrical conducting behavior changed from semiconducting to metallic with increase of the oxygen content

41 in the raw Sn.

42 Single crystals of SnSe were grown from the congruent melt. Starting materials were
43 Se chips and two different forms of Sn. Grain form Sn (diameter: ~ 3.0 mm) and powder
44 form Sn (diameter: ~ 0.15 mm) with the same purity of 99.99 % were used. To examine
45 the form dependence on electric transport property of grown single crystals, the ratio of
46 grain and powder form Sn was systematically varied (grain Sn : powder Sn = 100 : 0, 90 :
47 10, 70 : 30, 0 : 100). These Sn grains and/or Sn powders and Se chips were loaded into
48 quartz tubes in stoichiometric composition. The tubes were then evacuated and sealed.
49 They were slowly heated to 600ºC and kept for 12 hours followed by furnace cooling. As
50 a result, poly crystalline ingot of SnSe was obtained. The obtained ingot was ground and
51 heated to 1000ºC and kept for 10 hours in the double sealed evacuated quartz tubes. These
52 double quartz tubes are necessary to avoid the enters of the oxygen by the breaks of inner
53 quartz tube due to stress from the structural transition during furnace cooling. They were
54 cooled down to 840ºC in 8 hours followed by furnace cooling. Finally, SnSe single
55 crystals with typical size of $10 \times 5 \times 3$ mm^3 were obtained.

56 Powder X-ray diffraction (XRD) patterns were measured by using Mini Flex 600
57 (Rigaku) with Cu-Kα radiation. For the measurements, single crystals were ground into
58 powder. Chemical states of raw Sn were examined by X-ray photoelectron spectroscopy

(XPS) analysis using an AXIS-ULTRA DLD (Shimadzu/Kratos) with an Al-Kα X-ray radiation ($h\nu$ = 1486.6 eV), operating at a pressure of 9×10^{-9} Torr. The analyzed area was approximately 1×1 mm^2. Electrical conductivity was measured using a Physical Properties Measurements System (PPMS, Quantum Design) in the temperature range of 2–390 K.

XPS analysis was carried out to examine the chemical states of raw Sn in the both grain (red line) and powder (blue line) forms (Fig.1). There is a well-defined peak at 487.5 eV in the XPS spectrum of the Sn 3d, which is associated with the Sn $3d_{5/2}$ state. This is a characteristic feature of a tetravalent Sn ion (Sn^{4+}) [24], implying the presence of SnO_2 in both grain and powder Sn. Most likely, it could be on the surfaces. The smaller peak at around 485 eV arises from the Sn^0 state [24], indicating the presence of the non-oxidized metal Sn. The thickness of SnO_2 layer should be less than few nm that is the value of the penetration depth of XPS measurement. These results indicate that by using the powder Sn the larger amount of oxygen content would be included during the synthesis due to larger volume fraction of SnO_2 coming from the larger surface area.

Figure 2 shows the X-ray diffraction patterns of pulverized SnSe single crystals grown from grain and powder Sn. Inset shows the enlargement of the (400) reflection. The diffraction patterns of both samples can be indexed with an orthorhombic system of the

77 space group *Pnma*. The lattice constants of *a*, *b* and *c* axes were determined to be *a* =
78 11.48(7) Å, *b* = 4.44(2) Å and *c* = 4.15(1) Å for both samples comparable to the literature.
79 Note that there are no peaks related to SnO_2, indicating that the oxygen content is quite
80 low.

81 Figure 3 shows the temperature dependence of the electrical conductivity of SnSe single
82 crystals along the *bc* plane. The electrical conductivity strongly depends on the ratio of
83 grain and powder form Sn used as starting materials. The sample from grain Sn 100%,
84 which may contain the smallest amount of oxygen content, showed semiconducting
85 behavior. The conductivity sharply decreased with decreasing temperature. The small
86 electrical conductivity indicates a low hole concentration ensuring the purity of the
87 sample that has small deviation from the ideal stoichiometry. On the other hand, the
88 electrical conductivities increased and their behaviors became metal like with decreasing
89 the ratio of grain Sn and increasing the amount of oxygen content. The electrical
90 conductivity of SnSe grown by 100% powder Sn showed good agreement with that of the
91 reported ones by Zhao et al. [4]. The present results indicate that transport properties of
92 SnSe single crystal can be controlled from semiconductor to metal by varying the ratio of
93 grain and powder form of Sn used as a starting material. This can be due to the difference
94 of the oxygen volume fraction presenting on the surface of both raw Sn. In fact, pure SnSe

is known as a p-type semiconductor [1-3], which is in good agreement with our semiconducting SnSe single crystals with the lowest amount of oxygen content. Hole carrier can be doped by the lack of Sn [1]. Our metallic SnSe could also be explained by the increase of hole carrier with increasing the Sn deficiency, which can be caused by the deviation from the stoichiometry due to the oxidization of the surface of raw Sn. In any case the existence of oxygen plays the important role to change the electronic state of SnSe, possibly by interacting with a lone pair or existing in an interstitial site, and so on. Further investigation on the mechanism of oxygen effect for electrical conduction would be important for the comprehension of intrinsic properties of SnSe.

We found that the different electrical conductivity reported by several groups could be intrinsically related to the amount of oxygen content during the synthesis. We succeeded in controlling the transport properties of SnSe single crystals by changing the oxygen amount presented in raw Sn as a surface oxidization. The electrical conducting behavior varied from semiconductor to metal with increase of oxygen amount.

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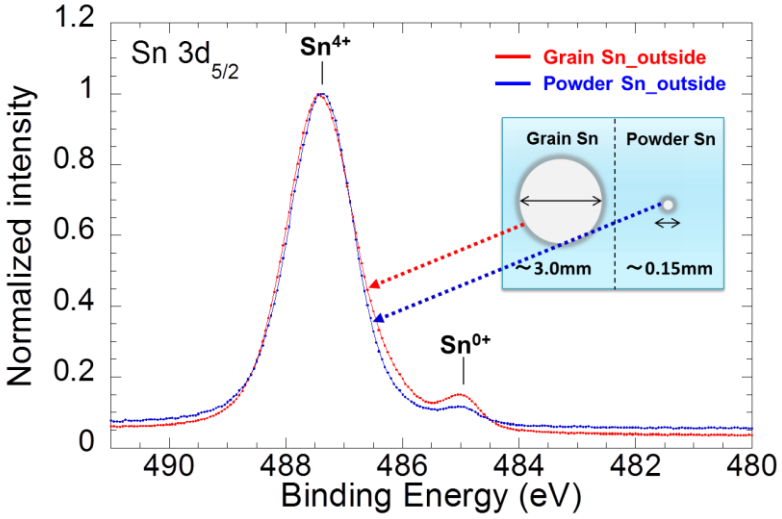
Fig. 1 (Color online) Sn $3d_{5/2}$ XPS spectrum for the surface of grain and powder Sn.

Fig. 2 (Color online) XRD patterns of the pulverized SnSe single crystals synthesized from grain and powder Sn.

Fig. 3 (Color online) Temperature dependence of the electrical conductivity of SnSe single crystals along the *bc*-plane grown by using different ratio of grain and powder form Sn as a starting material.



181

182 Fig.1

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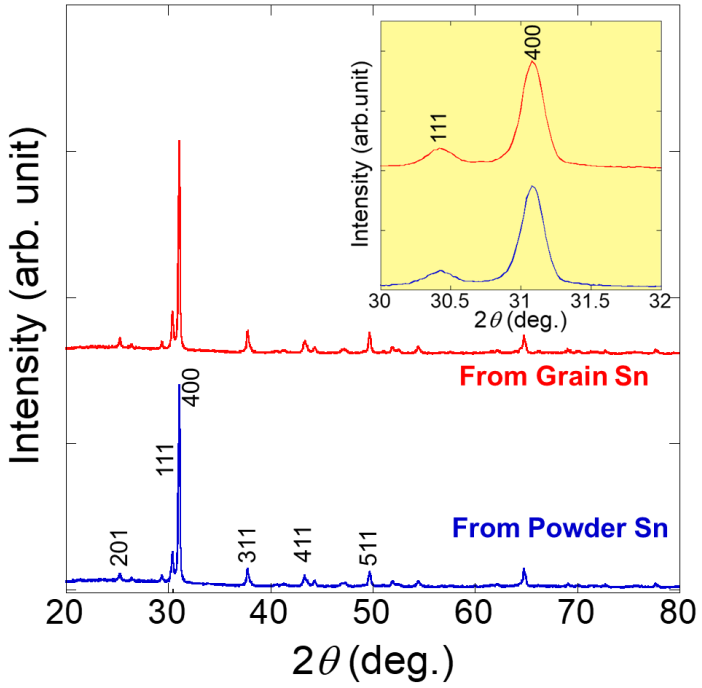

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185 Fig.2

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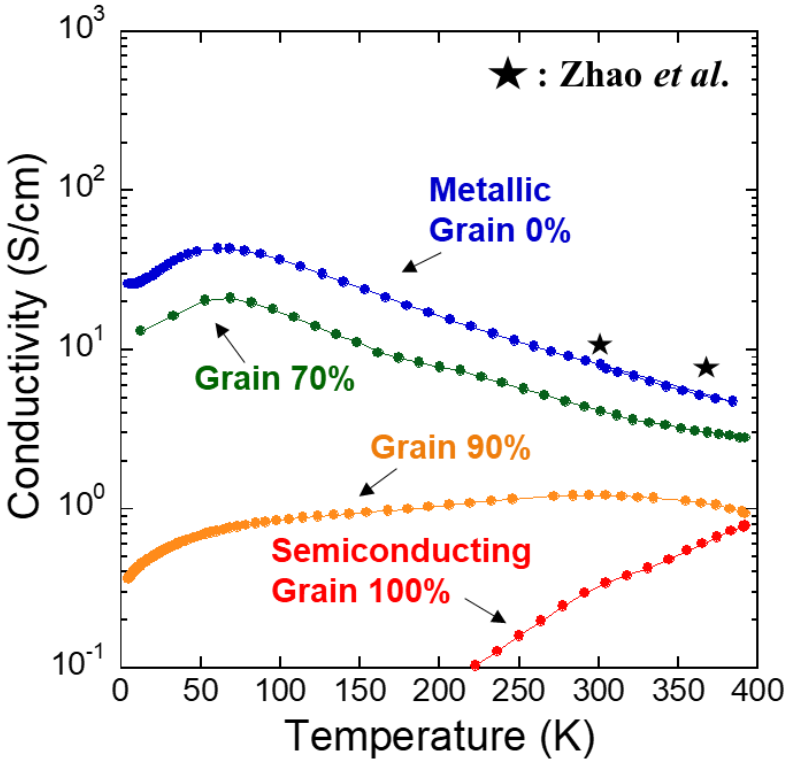

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190 Fig.3