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Metallic conduction induced by direct anion site doping in layered SnSe₂

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The emergence of metallic conduction in layered dichalcogenide semiconductor materials by chemical doping is one of key issues for two-dimensional (2D) materials engineering. At present, doping methods for layered dichalcogenide materials have been limited to an ion intercalation between layer units or electrostatic carrier doping by electrical bias owing to the absence of appropriate substitutional dopant for increasing the carrier concentration. Here, we report the occurrence of metallic conduction in the layered dichalcogenide of SnSe₂ by the direct Se-site doping with Cl as a shallow electron donor. The total carrier concentration up to $\sim 10^{20} \text{ cm}^{-3}$ is achieved by Cl substitutional doping, resulting in the improved conductivity value of $\sim 170 \text{ S} \cdot \text{cm}^{-1}$ from $\sim 1.7 \text{ S} \cdot \text{cm}^{-1}$ for non-doped SnSe₂. When the carrier concentration exceeds $\sim 10^{19} \text{ cm}^{-3}$, the conduction mechanism is changed from hopping to degenerate conduction, exhibiting metal-insulator transition behavior. Detailed band structure calculation reveals that the hybridized *s-p* orbital from Sn 5*s* and Se 4*p* states is responsible for the degenerate metallic conduction in electron-doped SnSe₂.

Two dimensional (2D) materials have recently been intensively investigated due to its unique electronic and/or optical properties^{1–7}. Since the remarkable properties of graphene have initiated the research, other 2D materials with layered structure are also emerged as new counterparts to exhibit striking physical properties under the 2D confined systems^{1–3}. Layered dichalcogenides are one of the representative materials drawing great attention from the fact that they can be easily prepared as a form of high quality nanosheet by mechanical and/or chemical exfoliation techniques as graphene did^{2,4}.

As a practical engineering method to modulate 2D material properties, doping is an important technique especially for controlling electrical characteristics. Until now, the doping methods for 2D materials have been tried mainly by electrostatic carrier doping introduced by the electrical bias through an dielectric barrier^{5,6}, or insertion of interstitial intercalants between the layer units which are weakly bonded each other by Van der Waals interaction^{7–9}. In particular, for the case of layered dichalcogenides, striking carrier transport characteristics can be provoked by effective carrier doping^{5,6,8,9}, but direct substitutional doping has been rarely reported due to the absence of adequate substitutional dopant to the best of our knowledge¹⁰.

In this study, we report the emergence of metallic conduction in layered dichalcogenide of SnSe₂ achieved by direct Se-site doping with Cl atoms. Substitutional Cl dopant on Se-site worked well as a shallow electron donor to increase carrier concentration (n_e) up to $\sim 10^{20} \text{ cm}^{-3}$, and the transition from semiconductor to metallic state was observed when n_e exceeded critical limit ($\sim 10^{19} \text{ cm}^{-3}$). Based on the electronic structure calculation, it was clarified that the hybridization between largely spread Sn 5*s* and Se 4*p* orbital is the origin of degenerate conduction in Cl-doped SnSe₂.

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Figure 1. Structural characterizations of Cl-doped SnSe_2 . (a) Schematics of crystal structure of Cl-doped SnSe_2 along b- (upper) and c-axis (lower). (b) The patterns of powder X-ray diffraction from various amount of Cl-doped SnSe_2 samples [A: undoped ($n_e = 7.2 \times 10^{17} \text{ cm}^{-3}$), B–H: doped samples with increasing Cl doping ratio from B ($n_e = 5.1 \times 10^{18} \text{ cm}^{-3}$) to H ($n_e = 8.6 \times 10^{19} \text{ cm}^{-3}$)]. Reference peak positions of SnSe_2 are displayed at the bottom of the graph. Representative lattice planes are indicated and SnSe impurity phase is marked with arrows and asterisk, respectively.

sample	Nominal amount of Cl content	Lattice parameter	
	(x)	a (Å)	c (Å)
A	0	3.81043 (35)	6.13279 (37)
B	0.002	3.81085 (20)	6.13322 (20)
C	0.004	3.81086 (20)	6.13408 (30)
D	0.006	3.81126 (18)	6.13321 (23)
E	0.010	3.81097 (20)	6.13392 (29)
F	0.020	3.81055 (28)	6.13306 (32)
G	0.030	3.80848 (33)	6.13364 (59)
H	0.040	3.80934 (34)	6.13173 (36)

Table 1. Nominal amount of Cl contents and lattice parameters extracted from PXRD patterns of respective Cl-doped SnSe_2 samples.

Results and Discussion

Figure 1(a) schematically illustrates the crystalline structure of SnSe_2 as characterized by the powder X-ray diffraction (PXRD) results in figure 1(b). SnSe_2 has a hexagonal layered structure ($P-3m1$ space group) with lattice parameters of $a = 3.81 \text{ Å}$ and $c = 6.13 \text{ Å}$, which agree well with those reported in literature¹¹. Fig. 1(b) shows the PXRD results with increasing Cl dopant ratio introduced during SnSe_2 synthesis. The doped samples were named from A to H with increasing dopant content as listed in Table 1. No observable impurity compound associated with Cl dopant was detected except for small amount of SnSe phase in the sample F. The lattice parameters of the samples were calculated from the PXRD patterns and also listed in Table 1. They are almost identical within 0.1% variation for all samples. Similar lattice parameters of the samples are attributed to the fact that Se^{2-} (1.98 Å) has similar ionic radius to Cl^- (1.81 Å), supporting that Cl dopants are not located on the inter-layer space as intercalants, but on the Se site as substitutional atoms for Se^{2-} to minimize the lattice deformation¹². The theoretical prediction for formation energies of probable defect states also indicates that Cl substitution to Se-site is the most stable compared to other defect candidates. (Figure S1 in the supplementary information).

Figure 2. XPS and Raman spectroscopy. (a) X-ray photoemission and (b) Raman spectroscopy results for sample A ($x = 0$, non-doped SnSe_2) and sample H ($x = 0.04$). Dashed line in Fig. 2(a) remarks the characteristic Cl^- peak position.

To more strongly reveal the Cl dopant substitution on Se-site in SnSe_2 samples, we performed X-ray photoemission spectroscopy (XPS) as well as Raman spectroscopy with non-doped (A of $x = 0$) and the most heavily doped sample (H of $x = 0.04$). As shown in figure 2(a), characteristic Cl 2p core level peak at 199.05 eV was observed with sample H while sample A did not show any Cl related one. From the fact that the measured core level corresponds well with Cl^- state which is almost identical to the Cl 2p position in the form of CdCl_2^{13} , it indicates that the Cl dopant exists as Cl^- state which could serve well as an electron donor if it substitutes on Se^{2-} site. Figure 2(b) displays the Raman spectroscopy results with the same samples. With sample H, we could observe not only the downshift but also the peak broadening occurred for A_{1g} mode compared to those from sample A¹⁴. It strongly evidences that Cl dopant well substitutes on Se-site as decreasing the force constant in SnSe_2 as reported in other substitutionally doped materials^{15–17}.

Figure 3(a–c) shows the temperature (T) dependence of conductivity (σ), n_e , and mobility (μ), respectively for Cl-doped SnSe_2 samples, extracted from the measurement of four point-probe resistivity and Hall coefficient. As shown in Fig. 3(a), σ exhibits thermally activated behavior from A to C sample, while the trend changes to degenerate conduction for sample D to H. Hall-effect measurement reveals that all SnSe_2 samples are n-type and their n_e value increases up to $8.6 \times 10^{19} \text{ cm}^{-3}$ (H sample with nominal Cl content, x of 0.04) with the maximum σ value of $\sim 170 \text{ S}\cdot\text{cm}^{-1}$ at 300 K as Cl doping ratio increases as shown in Fig. 3(b). (The n_e values of the sample E, F and G are located in-between those of the sample D and H (refer to Fig. 4), showing same electrical behavior and removed for brevity). It proves that Cl dopants act as electron donors to SnSe_2 and that Cl^- is successfully substituted on Se^{2-} site simultaneously supported by XPS and Raman results. (See Fig. 2) It should be noted that n_e becomes T independent when degenerate conduction occurs as is the case with sample D and H. It indicates that the Fermi level (E_F) exceeds the conduction band edge of SnSe_2 as n_e increases over 10^{19} cm^{-3} ¹⁸. T dependence of μ was deduced from the relation of $\sigma = en_e\mu$, where e is the charge of electron and presented in Fig. 3(c)¹⁹. When n_e is less than 10^{19} cm^{-3} , μ is limited by lattice vibration scattering at high T region, while limiting scattering mechanism changes to ionized impurity scattering at low T region as also displayed in figure S2(b) in supplementary information²⁰. (The transition point is observed at about 100 K.) With the samples with high n_e over 10^{19} cm^{-3} , μ value keeps increasing as T decreases and saturates at specific values, indicating that μ of the samples is governed dominantly by lattice vibration scattering in whole T region, as is the case with typical metals¹⁹. Experimental results of electrical transport strongly support the emergence of metallic states from layered SnSe_2 semiconductor by Cl substitutional doping on Se-site.

Figure 3. Electron transport properties of Cl-doped SnSe₂. Temperature dependence of (a) electrical conductivity, (b) carrier concentration and (c) mobility of Cl-doped SnSe₂ samples.

To investigate the origin of semiconductor to metal transition in Cl-doped SnSe₂, we estimate the disorder parameter, $k_F l_e$, based on the Ioffe-Regel criterion, which can be determined by^{6,21–23},

$$k_F l_e = (3\pi^2)^{2/3} \frac{\hbar \sigma}{e^2 n_e^{1/3}} \quad (1)$$

where k_F is Fermi wave number, l_e is electron mean free path, and $\hbar$ is Planck's constant divided by 2π . In figure 4(a), the relation between $k_F l_e$ and n_e at 300K is plotted based on equation (1). From the fact that degenerate conduction occurs when n_e exceeds $1.13 \times 10^{19} \text{ cm}^{-3}$ as observed in Fig. 3, we can obtain the critical value of $(k_F l_e)_c$ as 0.71 where the metal-insulator transition occurs. (Note that the metal-insulator transition point can also be confirmed by estimating $w(0)$ from the mathematical function of $w(T) = d(\ln \sigma)/d(\ln T)$ as shown in figure S3²⁴). As shown in figure 4(b), μ increases with increasing $k_F l_e$ when $k_F l_e < (k_F l_e)_c$, while it starts decreasing when $k_F l_e > (k_F l_e)_c$. As Pearson and Bardeen have proposed, donor ionization energy (E_d) should decrease with increasing n_e for the doped semiconductor with a substitutional dopant atom due to the decrease of average potential energy of electrons²⁵. E_d can be calculated from the slope of $\ln(n_e)$ versus $1/T$ plot (Refer to figure S2(a) in supplementary information) for the case of $k_F l_e < (k_F l_e)_c$ based on the relation below¹⁹,

$$n_e = \left(\frac{1}{2} N_c N_d \right)^{1/2} \exp \left(-\frac{E_d}{2k_B T} \right) \quad (2)$$

where N_c is the effective density of states at conduction band edge, N_d is donor concentration, and k_B is the Boltzmann constant. The values are estimated as 13.97, 6.95, and 3.77 meV for n_e of 7×10^{17} , 5×10^{18} , and $9 \times 10^{18} \text{ cm}^{-3}$ at 300 K, respectively. It strongly suggests that the increase of μ with n_e increment (for $k_F l_e < (k_F l_e)_c$) mainly originates from enhanced l_e with reduced E_d which is deeply associated with trap energy levels of the scatterers in the semiconductor regime²⁵. On the other hand, when n_e exceeds the critical value, $(k_F l_e)_c$, Cl dopants start to act as scattering centers, then μ starts decreasing due to ionized impurity scattering. As a consequence, it can be concluded that metallic transition of conduction mechanism for SnSe₂ is primarily due to sufficient electron concentration and long electron mean free path achieved from shallow E_d level.

Figure 4. Disorder parameters of Cl-doped SnSe₂. Disorder parameter ($k_F l_e$) dependences of (a) carrier concentration and (b) mobility of Cl-doped SnSe₂ samples at 300 K. Dashed line points out the critical point [$(k_F l_e)_c = 0.71$] where metal-insulator transition occurs.

Figure 5(a)–(d) describe the calculated band structure and density of states (DOS) profiles of un-doped SnSe₂ based on density functional theory (DFT). As shown in Fig. 5(a), E_F is set to be zero in the energy scale. The conduction band minimum (CBM) and valence band maximum (VBM) are located at L-M and H- Γ path, respectively, indicating the indirect band-gap semiconductor nature which agrees well with our experimental results for non-doped SnSe₂. Since the structural parameters are almost identical regardless of Cl doping ratio as confirmed by PXRD results (see Table 1), it is reasonable to assume the rigid band behavior with raised E_F upon CBM for an electron-doped SnSe₂ system. As n_e increases, E_F shifts upward until it meets CBM, and degenerate conduction should occur based on the CBM state, as are the case with typical heavily doped degenerate semiconductors^{18,26}. As observed from the results of total and projected DOS in Fig. 5(b)–(d), the total DOS mainly consists of Sn 5s and Se 4p orbitals with similar contributions, indicating that the metallic conduction of electron-doped SnSe₂ originates from the hybridized orbital states between Sn 5s and Se 4p orbital. It is worthwhile to note that $(k_F l_e)_c$ value of 0.71 for electron-doped SnSe₂ is close to those of conducting oxide materials showing largely spread orbital conduction such as In 5s ($(k_F l_e)_c = 0.1 \sim 0.3$ for In₂O₃, In-Ga-Zn-O and In-Zn-O), but much smaller than the reported value of other layered transition metal dichalcogenide. ($(k_F l_e)_c = 2.5$ for electron-doped MoS₂)^{6,22,23}. It strongly suggests that electron pathways in SnSe₂ would be dispersed well, compared to localized electrons in other layered chalcogenide materials, due to effective overlap of delocalized large Sn 5s orbital as observed in In-based conducting oxide group. Therefore, metallic conduction of Cl-doped SnSe₂ could be attributed to a large number of electrons supplied by efficient substitutional doping and their de-localization behavior originated from Sn 5s orbital.

Conclusions

In summary, we successfully synthesized metallic layered SnSe₂ from original semiconducting state by direct substitutional doping of Cl atoms. Doped Cl atoms on Se-site acted well as shallow donors to introduce high n_e up to $\sim 10^{20} \text{ cm}^{-3}$, changing conduction mechanism to degenerate conduction from thermally activated conduction of undoped SnSe₂. Detailed analysis of carrier transport mechanism and calculation of band structure confirm that metallic transport in electron-doped SnSe₂ originates from highly dispersive Sn 5s orbital which is hybridized with Se 4p state. We anticipate that the engineering of conductivity from semiconducting to metallic states by direct chemical doping can be used as key technology for practical applications of 2D layered dichalcogenide materials, as has been proven for Si-based technology.

Figure 5. Electronic structure of SnSe₂. (a) Calculated band structure of SnSe₂. Fermi energy level is taken as origin. (b–d) Density of states profiles from total, Sn and Se contribution, respectively.

Methods

Sample synthesis. To synthesize polycrystalline SnSe₂ samples doped with Cl, we mixed stoichiometric amount of Sn and anhydrous SnCl₂ powders: $(2-x)\text{Sn} + x\text{SnCl}_2 \rightarrow 2\text{SnCl}_x$, and then melted the mixtures in fused silica tubes at 250 °C for 24 hrs. (Detailed nominal x's are listed in Table 1.) After the first reaction was finished, stoichiometric Se grains were added to synthesize the final compound of Cl-doped SnSe₂: $2\text{SnCl}_x + 2(2-x)\text{Se} \rightarrow 2\text{SnSe}_{2-x}\text{Cl}_x$, followed by the second annealing process in fused silica tubes at 600 °C for 48 hrs. To improve homogeneity, the synthesized samples were ground into powder form in an agate mortar and re-annealed by repetition of the process described above. Densification of all synthesized samples was conducted with spark plasma sintering (SPS) equipment at 500 °C for 10 min under a pressure of 70 MPa, which resulted in higher densities than 95% of theoretical values.

Structural and electrical analysis. The crystalline phases of the fabricated samples were identified by PXRD using a Bruker diffractometer model D8 ADVANCE (Cu K_α). To measure the electrical properties of polycrystalline Cl-doped SnSe₂ pellets, electrical contacts in the four point-probe and Hall bar geometries were made by applying Ag paste onto the samples. The four point-probe resistivity and Hall coefficient were measured in the temperature range of 6–300 K using Physical Property Measurement System (PPMS, Quantum Design).

Spectroscopic analysis. The XPS was carried out using focused monochromatized Al K_α radiation (1486.6 eV). Raman spectra were measured by confocal Raman spectrometer with 488 nm wavelength excitation.

Electronic structure calculations. To investigate electronic structure of SnSe₂, first principle calculations implemented in the Vienna ab initio simulation program (VASP) code were performed. The generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) functional form and the projected augmented plane-wave (PAW) method were employed, which is distinct from previous calculation methods^{27–29}. The plane-wave basis-sets with 240 eV cut-off were used. And valence electron states of $4d^{10}5s^25p^2$ and $4s^24p^4$ were considered for Sn and Se atoms, respectively. The convergence threshold was set to be $10^{-2}\text{ eV}\cdot\text{\AA}^{-1}$ and 10^{-4} eV for force and energy minimization, respectively. The experimental lattice constants of $a = 3.81\text{ \AA}$ and $c = 6.13\text{ \AA}$ for SnSe₂ were used.

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Author Contributions

K.L., I.H. and Y.S. conceived the study. K.L. designed the experiments. S.I.K., S.H., S.Y.K., D.W.J., K.S.M., H.J.P. and K.L. synthesized the samples. J.H.K. performed and analysed the PXRD experiments. D.J.Y. carried out the XPS measurement. S.I.K. and K.L. analysed the Raman spectroscopy results. Y.J.C. and K.L. measured the electrical transport properties. W.J.L. and Y.H.C. performed and analysed the DFT calculations. S.I.K., S.H., S.Y.K., K.L. and Y.S. co-wrote the manuscript. All the authors discussed the results and commented on the manuscript.

Additional Information

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