Electron-Doping Induced Semiconductor to Metal Transitions in ZrSe$_2$ Layers via Copper Atomic Intercalation

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**ABSTRACT:** Atomic intercalation in two dimensional (2D) layered materials can engineer the electronic structure at the atomic scale, bringing out tunable physical and chemical properties which are quite distinct in comparison with pristine one. Among them, electron-doped engineering induced by intercalation is an efficient route to modulate electronic states in 2D layers. Herein, we demonstrate a semiconducting to the metallic phase transition in zirconium diselenide (ZrSe$_2$) single crystal via controllable incorporation of copper (Cu) atoms. Combined with first-principles density functional theory (DFT) calculations, our angle resolved photoemission spectroscopy (ARPES) characterizations clearly revealed the emergence of conduction band dispersion at M/L point of Brillouin zone due to Cu-induced electron doping in ZrSe$_2$ interlayers. Moreover, the field-effect transistor (FET) fabricated on ZrSe$_2$ displayed a n-type semiconducting transport behavior, while the Cu-intercalated ZrSe$_2$ posed linear $I_{ds}$ vs $V_{ds}$ curves with metallic character shows n-type doping. The atomic intercalation approach has high potential for realizing transparent electron-doping systems for many specific 2D-based electronics.
Layered transition metal dichalcogenides (TMDCs) MX$_2$ (M = Mo, W, Zr, Hf; X = S, Se) semiconductors have captivated widespread interest due to their significant superior physical and electrical properties.\textsuperscript{1-6} The crystalline forms of 2D materials have been the subject of intense investigation owing to their unique physical properties\textsuperscript{7}, such as direct electronic bandgap in the single-layer limit\textsuperscript{8-12}, valence band (VB) splitting\textsuperscript{12-16}, valley degree of freedom\textsuperscript{17-21}, and excitonic nature of optical band spectra\textsuperscript{22-26}. Artem et al. recently observed the co-occurrence of exchange splitting and giant SOC in graphene at the same time with good magnetic characteristics\textsuperscript{27}. Thus, TMDCs are considered as an ideal materials for p–n junctions\textsuperscript{28}, field–effect transistors with high mobility of electrons\textsuperscript{29-31}, memory and switching devices\textsuperscript{32}, optoelectronics and photovoltaic applications\textsuperscript{33}. These layered materials can also be found in different forms of hybrid or in heterostructure forms.\textsuperscript{34-37} Particularly, the atomic phase engineering can result in observation of tremendous novel physical and electronic phenomena.\textsuperscript{38-42} Among them, the intercalation of electron-donating atoms has been an effective method to modulate intrinsic electronic properties, such as shifting the fermi level to higher or lower energy\textsuperscript{43}, changing band gap characteristics\textsuperscript{44-46} and inducing phase transitions.\textsuperscript{47,48} Morosan et al. reported that the phase transition arising at Fermi level in Cu-intercalated TiSe$_2$ could give rise to the new superconducting state in TiSe$_2$.\textsuperscript{49} Topological phase transition occurred in BiTl$\left(S_{1-x}Se_x\right)_2$ and Bi$_2$Se$_3$, as well as superconductivity in Cu$_x$ZrTe$_{2-y}$ with different doping ratio of Se, Co-phthalocyanine and Cu atoms respectively.\textsuperscript{50-52} Similarly, Tsipas et al. recently observed the semimetallic phase with massless Dirac Fermions is in ZrTe$_2$.\textsuperscript{53} The structure and electronic properties of the materials can be ascribes as a semiconductor or a semimetallic states with a small indirect or direct gap can be suppressed by intercalation or elemental doping.\textsuperscript{3, 16, 18-22, 31, 49} Likewise, the semiconductor to metal transition was witnessed MoTe$_2$ by strain or structural and
electronic phase transition by W substitution.\textsuperscript{54} In principle, the states of quantum matter: charge density waves, insulators, and superconductors can be ascribed from the spectral energy gap with different bandgap structures.\textsuperscript{55-57} Therefore, the fundamental changes in the band structure can provide vital information for considering and controlling physical and electronic properties.\textsuperscript{58}

In this particular work, we synthesized Cu-intercalated zirconium diselenide (ZrSe\textsubscript{2}) single crystals via chemical vapor transport technique (CVT), and investigated the change in electronic properties in comparison with pristine ZrSe\textsubscript{2} by combining synchrotron-based Angle Resolved Photoemission Spectroscopy (ARPES) with first-principles density functional theory (DFT) calculations. With the intercalation of Cu atoms, more electrons fill the bottom of conduction bands of ZrSe\textsubscript{2}, which change the electronic structure from semiconducting to metallic characters. Notably, this presented intercalation approach does not induce notable changes of crystal structure and overall band dispersions, indicating its high potentials for clean electron doping systems.

A high quality ZrSe\textsubscript{2} and Cu intercalated ZrSe\textsubscript{2} (Cu\textsubscript{x}ZrSe\textsubscript{2}, x = 0.07, x value was determined by ICP) single crystals were synthesized via an improved CVT method. The experimental detail of CVT synthesis is provided in the experimental part of the paper. The single crystal X-ray diffraction (XRD) patterns recorded on ZrSe\textsubscript{2} and Cu\textsubscript{0.07}ZrSe\textsubscript{2} samples at room temperature are shown in Fig. 1. The (001), (002), (003) and (004) peaks indicate the high quality single crystals of both samples. The diffraction peaks emerged at the same angles in both ZrSe\textsubscript{2} and Cu\textsubscript{0.07}ZrSe\textsubscript{2}, with a small change in the c-lattice constant from 6.1889Å to 6.2035Å after Cu-intercalation along (001) plane calculated from XRD. Similarly, the peak intensities of Cu\textsubscript{0.07}ZrSe\textsubscript{2} are enhanced, which is due to its increased crystallinity and other growth process. Highly crystalline large-sized single crystals of ZrSe\textsubscript{2} and Cu\textsubscript{0.07}ZrSe\textsubscript{2} can be seen inside the XRD figure having a typical lateral size of ~0.8-1cm with silver grey colour and hexagonal shape respectively.
To investigate the chemical compositions and elemental ratio in the grown crystals, X-ray photoelectron spectroscopy (XPS) was performed. Typical XPS spectra of ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ are shown in Fig. 2. For ZrSe$_2$, the obvious Zr 3d (Zr-3d$_{5/2}$, Zr-3d$_{3/2}$) peaks at 183.05 eV and 185 eV are displayed, along with clear Se 3d (Se-3d$_{5/2}$, Se-3d$_{3/2}$) peaks at 53.55 eV and 54.2 eV. These peak positions indicate the similar chemical bonding state for both ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$, with a small displacement of Zr-3d$_{3/2}$ to lower energy, while donating electron to Se atoms and Se-3d to higher energy due to the emergence of electrons from Zr and Cu atoms in case of Cu$_{0.07}$ZrSe$_2$. Moreover, Fig. 2(c) shows Cu 2p (Cu-2p$_{3/2}$ and Cu-2p$_{1/2}$) peaks at 932.2 eV and 952.2 eV. There is no satellite peak of Cu$^{2+}$ in the obtained Cu$_{0.07}$ZrSe$_2$ crystals, instead Cu$^{+1}$ peak is visible. This can be ascribed to the electron donation from the intercalated Cu$^0$ atoms to ZrSe$_2$ layers, resulting in Cu$^{+1}$ state that is consistent with previous Cu-substituted compounds.$^{59}$

In order to investigate the detailed local microstructure, compositions and topographical information with an atomic arrangement, we employed a high resolution scanning transmission electron microscopy (STEM) on Cu$_{0.07}$ZrSe$_2$. Fig. 3(a) is typical Z-contrast high resolution image recorded through STEM, showing the surface topography of atoms. It reveals a regular structure with perfect hexagonal atomic arrangement as indicated by inset red line frame. The microstructure of Cu$_{0.07}$ZrSe$_2$ is similar to that of pristine ZrSe$_2$ (see HRTEM image in Fig. S1). Fig. 3(b) shows a sketch of elemental configuration of ZrSe$_2$ with a hexagonal arrangements. The layered structure (Zr-Se) is indicating the hexagonal structure of Cu$_{0.07}$ZrSe$_2$ having two planes of Se atoms separated by Zr atoms with Cu ions randomly intercalated between the layers. Similarly, Fig. 3(c) shows a uniform structure of different layers with a d-spacing of about 2.29 Å that corresponds to (002) and Zr-Zr atom bond length of 1.73 Å corresponding to (003) lattice plane. From the d-spacing, it has been observed that Cu$_{0.07}$ZrSe$_2$ have the same layers spacing as that of ZrSe$_2$, with
a negligible enlargement. The Z-contrast intensity of lattices corresponds to the inset side view profile of the chemical structure in Fig. 3(e). The crystal orientation and diffraction pattern were measured by selected-area electron diffraction (SAED). The SAED pattern of Cu$_{0.07}$ZrSe$_2$ in Fig. 3(d) contains a set of diffraction spots along the rotational direction of superlattice (002) and (110) zone axes of a hexagon, which is consistent with XRD results and STEM images. The diffraction spots corresponding to the Cu$_{0.07}$ZrSe$_2$ are different from pristine sample in terms of the intensities and rational direction (see inset SAED image in Fig. S1). The diffraction spots of Cu$_{0.07}$ZrSe$_2$ are much brighter without 60° rotation in comparison with the lower brightness and have 60° rotation of diffraction spots in ZrSe$_2$. The elemental mapping images in Fig. 3(e) further confirm the homogeneous elemental distributions of Zr, Se and Cu atoms in the single crystal Cu$_{0.07}$ZrSe$_2$. Besides, that the energy dispersive X-ray spectroscopy (EDS) recorded for the samples also shows the existence adequate amount of Cu, Zr and Se elements in the single crystal (see Fig. S2, in supporting information). The stoichiometric ratio of Cu atoms is about 7wt%, as determined by inductively coupled plasma mass spectroscopy (ICP-MS) measurements as shown in Table S1. Combining the STEM analysis with XPS results, we can suggest that a small amount of Cu atoms have been randomly distributed into ZrSe$_2$ interlayers without any lattice changes.

To study the electronic properties, we performed DFT calculations to explore the band structures of pristine and Cu-intercalated ZrSe$_2$ single crystals. The computational details are given in the experimental section (supporting information). The structural model of bulk ZrSe$_2$ for calculations with a same hexagonal Brillouin zone (BZ) for both ZrSe$_2$ and Cu-intercalated ZrSe$_2$ of high-symmetry points is shown in Fig. 4(a, b) respectively. The calculated band structure results for ZrSe$_2$ are depicted in Fig. 4(c). The band structure of ZrSe$_2$ shows that the valance band maximum (VBM) appears at Γ point, which is mainly attributed by the p-orbitals of Se atoms. In
contrast, the conduction band minima (CBM) appeared at 0.29 eV above the Fermi level at L point, showing a semiconductor with an indirect band gap of 0.71 eV. After the intercalation of Cu atoms, the emergence of conduction band which crosses over the Fermi level at M/L points, indicates the excess electron doping donated from Cu, changing the system from semiconductor to metallic state as shown from the red line in Fig. 4(c), adopted from the calculated band structures of Cu-intercalated ZrSe$_2$ (Fig. S3(c)). The donated electron from the Cu 4s shell can make a stable closed-shell Cu$^+$ resulting in an increased charge distribution within ZrSe$_2$ layers. Notably, the intercalation of copper atom merely provides a change of carrier concentration without modifying band dispersions and the structural integrity of ZrSe$_2$ layers. From Fig. 4(c) we further confirmed that the emerging CB is composed of Zr-d$_{yz}$ and Zr-d$_{z^2}$ at M and L points, while the VB composed of Se-p$_x$ and Se-p$_y$ of high symmetry Γ point, (as we can see that from Fig. S3(c)). The Cu-p and Cu-d can only contribute in deeper energy (Fig. S3(d)), which can donate electrons to lift the Fermi level above the bottom of conduction band that is mainly composed of Zr-d orbitals. Based on band calculations, one can notice that a variation of doping can induce either hole or electron-type carriers, as dominated by different orbital characters from distinct elements as shown from Fig. 4(c). This can potentially provide additional freedom to manipulate electronic properties of charge carriers.

We further investigated the band structures through angle resolved photoemission spectroscopy (ARPES). According to previous ARPES investigation of ZrSe$_2^{60}$, we can determine the $k_z$ value accurately. Using the equation $k_{\perp} = \sqrt{(2m/\hbar^2) (E_{kin} \cos^2 \theta + |V_0|)}$ (where $k_{\perp}$ is the momentum value along $k_z$, $m$ is the electron mass, $E_{kin}$ is the kinetic energy of the photoelectron,
$V_0$ is the inner potential), in combination with the data in $^6$, we can determine $V_0 = 10.9$ eV, which gives 30 eV and 42 eV photon energies for $\Gamma$ and $A$, respectively.

Fig. 5 shows the ARPES intensity of ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ at various binding energies, measured in the first Brillouin zone at $T$=26 K. There is no spectral weight at the Fermi level in ZrSe$_2$ (Fig. 5(a1)), where one can notice electronic states around M at the Fermi level in Cu$_{0.07}$ZrSe$_2$ (Fig. 5(b1)), indicating that electrons are doped into the parent electronic system of ZrSe$_2$ after Cu intercalation. As shown in band calculations, these electronic states come from the bottom of conduction bands. While going into deeper binding energies, the spectral weight distributions are very similar in both ZrSe$_2$ (Fig. 5(a2-5)) and Cu$_{0.07}$ZrSe$_2$ (Fig. 5(b2-5)), showing a symmetry consistent with the lattice structure of ZrSe$_2$, though the pocket size changes slightly due to different electron doping level.

By comparing the band structure of Cu intercalated ZrSe$_2$ to that of pristine ZrSe$_2$, we can reveal how the electronic structures vary after the intercalation. Figs. 6(a, b) show the E vs k dispersions of ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ along the $\Gamma$->M direction, and Figs. 6(c, d) show data taken along the A->L direction. The pristine ZrSe$_2$ is a semiconductor, and our ARPES in Figs. 6(a, c) show that the Fermi level is within the band gap, and the top of the valence band is located at around -0.87 eV in binding energy. After the intercalation of Cu atoms, the band structures move to deeper binding energy by 70 meV, and the Fermi level cuts across the bottom of conduction bands around the zone boundary (see Figs. 6(b, d)), which gives rise to the electron pockets around M shown in Fig. 5(b1). Such a shift of Fermi level indicates that Cu atoms donate electrons into the pristine ZrSe$_2$ electronic systems, and changes it from a semiconductor to a conductor. There are no evident changes in the band dispersions with the Cu intercalation, suggesting that the electron correlation and the dimensionality of individual bands remain the same as pristine ZrSe$_2$. 
In Figs. 6(e, f), one can notice that the bottom of the conduction band is deeper at L, and this difference arises from the 3D characteristics of the conduction bands. The introduction of Cu induces an electron doping without the change of overall band dispersions, and this provides an opportunity to study the gap structure in the pristine ZrSe$_2$. In Figs. 6(b, d), we can clearly see that there is an indirect gap. The top of the valence band is at -0.94 eV, the bottom of conduction band is at -0.17 eV in Fig. 6(f), and these values yield an indirect band gap of 0.77 eV, which is highly consistent with the calculated band gap of 0.71 eV. The red lines in Figs. 6(e, f) show the calculated band structures adopted from Fig. S3(c) consist of Zr-$d_{yz}$ and Zr-$d_{z^2}$ orbitals, which are well matched with the experiment estimation data. In addition, both of Figs. 6(b, d) shows non-dispersive spectral weight at around -0.5 eV, which is absent in the pristine ZrSe$_2$. This feature can be attributed to some localized electronic states of Cu atoms intercalated in between the ZrSe$_2$ layers.

Furthermore, electrical properties were also investigated to confirm the metallic character of the as-synthesized Cu$_{0.07}$ZrSe$_2$ in comparison with the semiconducting ZrSe$_2$, the field effect transistors (FETs) were fabricated on ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ multilayers (in Fig. 7a) using Au/Ti as contact electrodes on SiO$_2$/Si substrate. Fig. 7(b) shows the channel length of the FETs with around 10 µm. Fig. 7(c, d) represents the output I$_{ds}$-V$_{ds}$ curves of the FET devices based on ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$. The forward and backward transport behaviour of ZrSe$_2$ displays gate tuneable I$_{ds}$-V$_{ds}$ properties under V$_{gs}$=0V, while the linear curve of the Cu$_{0.07}$ZrSe$_2$ shows metallic behaviour. In Fig. 7(d), the slope of I$_{ds}$-V$_{ds}$ curve of ZrSe$_2$ decreases with decreasing gate voltage from 30 to -30 V, showing n-type transport behaviour (the magnified image from V$_{ds}$ = 0-0.4V as shown in Fig. S4 with clear gate tuneable characteristics), whereas the linear I$_{ds}$-V$_{ds}$ curves of
Cu$_{0.07}$ZrSe$_2$ for all input gate voltages indicated Ohmic contact like behaviour between the metal electrodes with no tuneable character, strongly confirming the metallic behaviour.

In summary, we have controllably intercalated Cu atoms into layered ZrSe$_2$ single crystal via an improved CVT method, and comparatively studied the changes of microstructure and electronic structure of the ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ by using first-principles calculations and ARPES. Both our DFT calculations and experimental results clearly revealed the presence of the metallic state in Cu$_{0.07}$ZrSe$_2$ with an indirect bandgap nature that is very different from the semiconducting character in ZrSe$_2$. Similarly, the FET results further confirmed the semiconductor to metallic phase transition in ZrSe$_2$ after the intercalation of Cu atoms. These results are highlighting the significance of atomic intercalation-induced electron doping in 2D layered materials, which might be a vital trend for future valleytronic and electronics applications.
ASSOCIATED CONTENT

Supporting Information. Experimental section, CVT growth procedure, ARPES measurement, theoretical calculations, additional characterization and results.

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Author Contributions

+Z.M. and K.M. contributed equally to this work. L.S. and Z.S. supervised the project and designed the experiments. Z.M. carried out most of the experiments and analyzed the data. K.M. and Z.S. performed ARPES measurement and analysis. H.L. and X.W. performed the DFT calculations. C.W., Z.U.R. and M.H. partially contributed to experimental characterizations. Z.M., K.J.M., Z.S., X.W. and L.S. analyzed the data and co-wrote the paper. All authors discussed the results and commented on the manuscript.

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Notes

The authors declare no competing financial interests
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Figure 1. Single crystal XRD patterns of ZrSe₂ in comparison with Cu₀.₀₇ZrSe₂ depicting the enhancement of peaks and negligible enlargement.
Figure 2. XPS analysis of as-synthesized ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ single crystals. (a) Zirconium (Zr 3d). (b) Selenium, (Se 3d). (c) Copper (Cu 2p)
Figure 3. Microstructural characterizations of Cu$_{0.07}$ZrSe$_2$ single crystal through scanning transmission electron microscopy (STEM). (a) Typical STEM image with Z-contrast. (b) Structural configurations of bulk and side view of layered structure with Cu atom between the layers. (c) High resolution STEM image with specified layers identification and (d) SAED patterns of Cu$_{0.07}$ZrSe$_2$. (e) The elemental mapping image shows the uniform distribution of Zr, Se and Cu elements, respectively.
Figure 4. (a) Structural model of ZrSe$_2$. (b) Hexagonal Brillouin zone (BZ). (c) DFT orbital decomposed band structure calculations of bulk ZrSe$_2$ along the high symmetry k-points. After the intercalation of Cu atoms, the emergence of conduction band at M points indicates excess electrons donation that can change the system from semiconductor to metallic state as shown from the dash red line.
Figure 5. ARPES intensity of the pristine ZrSe$_2$ (upper panels, a$_1$-a$_5$) and Cu$_{0.07}$ZrSe$_2$ (lower panels, b$_1$-b$_5$) single crystals at various binding energies, taken with 30 eV photons. The black hexagonal boxes indicate the Brillouin zone.
Figure 6. (a, b) The photoemission intensity plots along $\Gamma \rightarrow M$ direction of pristine ZrSe$_2$ and Cu intercalated ZrSe$_2$ single crystals, respectively. The data were taken using 30 eV photons. (c, d) The photoemission intensity plots along $A \rightarrow L$ high direction of pristine ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$, respectively, taken using 42 eV photons. (e, f) The spectral weight of conduction bands around the zone boundary in panels b and d, respectively. The red dashed lines indicate the band dispersions from DFT calculations (adopted from Figure 4 (c)), consists of Zr $d_{yz}$ and $d_{z^2}$ orbitals.
Figure 7. Typical FET device fabricated on ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ exfoliated flakes. (a) Schematic of the device structure. (b) Optical image of the as-shaped nanodevice. The current-voltage curves at gate voltage = 0V showing (c) the forward and backward transport behavior indicate semiconducting and metallic behavior for ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$, respectively. (d) The output characteristics curves of ZrSe$_2$ and Cu$_{0.07}$ZrSe$_2$ at different gate voltages.
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**Single crystal ZrSe$_2$ and atomic Cu-intercalated ZrSe$_2$ layered structures** were synthesized in high crystalline quality by using chemical vapor transport method. Both theoretical DFT calculations and experimental ARPES results revealed a transition from semiconducting to metallic characteristics, indicating the emergence of conduction band dispersion at M/L point of Brillouin zone due to the electron doping of ZrSe$_2$ layers originated from additional atomic Cu intercalation.

*TOC Figure:*