Indirect-direct band gap transition driven by strain in semiconducting Cu$_2$Se monolayer

Renjun Du$^1$, Liming Liu$^1$, Wei Shangguan$^1$, Jinming Cai$^1$, Jianqing Dai$^1$, Lei Gao$^2$ and Cuixia Yan$^1$*  

$^1$ Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, People’s Republic of China  
$^2$ Faculty of College of Science, Kunming University of Science and Technology, Kunming 650050, People’s Republic of China  
* Authors to whom any correspondence should be addressed.  
E-mail: cuixiayan@kust.edu.cn and lgao@kust.edu.cn  

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Abstract  
Cu$_2$Se monolayer (ML) synthesized experimentally is a member of transition metal chalcogenides materials, which has attracted significant attention due to its diversity and unique properties. However, the feature of an indirect band gap of Cu$_2$Se ML in the low-temperature phase limits its’ application in electronics devices. Our study results based on the first principle calculations show that indirect-direct band gap transitions can occur in Cu$_2$Se ML under appropriate uniaxial or biaxial strains. The band gap of Cu$_2$Se ML is controllable due to the different responses of the edge-states near the Fermi level to the strain. The phonon dispersion suggests that the semiconducting Cu$_2$Se ML can maintain dynamic stability in a wide range of strains. With the tunable electronic structure, semiconducting Cu$_2$Se ML would become a promising candidate for electronic devices.

1. Introduction

Transition metal chalcogenides (TMCs) have attracted much attention due to their diversity and unique properties [1–5]. Copper selenium compounds are important members of TMCs materials. In 2018, a graphene-like CuSe ML with special topological, transport, and optical properties was realized experimentally [6, 7]. However, the strong interaction with the substrate prevents the formation of independent CuSe ML. In 2020, Cu$_2$Se ML was successfully synthesized on bilayer graphene (BLG), which solves the problem mentioned above well [8]. But Cu$_2$Se ML has an indirect band gap in the low-temperature state, which limits its’ applications in electronic devices.

A variety of methods have been developed to modify the band gap of nanomaterials, including control of layers number [9], heterostructure [10], strain engineering [11], alloying [12], substrate engineering [13, 14], external electric field [15], and so on. The band gap of PdSe$_2$ can be tuned from 1.37 eV (monolayer) to 0.5 eV (bulk) [16]. Black phosphorus can be changed from semiconductor to metal under the applied electric field [17]. Moreover, MoS$_2$ has direct-indirect band gap transition under the biaxial tensile strain of 1% [18]. Strain engineering is a common and feasible method to adjust the band gap due to nanomaterials allowing a wide range of stresses to existing [19, 20]. The effect of uniaxial and biaxial strains on the band gaps of TMCs materials has been proved in various works [21, 22]. In addition, in practical applications, lattice mismatches between nanomaterials and the substrate may generate and maintain strains [23].

In this paper, based on first-principles calculations, the electronic properties of the low-temperature phase of Cu$_2$Se ML and the influence of uniaxial and biaxial strains on the electronic properties have been studied. The band gap can be effectively adjusted by applying uniaxial or biaxial strains. An indirect-direct band gap transition has been achieved. Furthermore, the dynamic stability of Cu$_2$Se ML under strains has also been calculated. Our finding provides essential physical significance into the application of Cu$_2$Se ML in electronic devices.
2. Computational details

All the first-principles calculations in this work were performed within the density functional theory framework by using the Vienna *ab initio* Simulation Package (VASP) [24, 25]. The exchange–correlation functional was treated using the projector-augmented wave (PAW) method and the local-density approximation (LDA) [26, 27]. The rotationally invariant LDA + U formalism proposed by Dudarev *et al* [28] was adopted with $U_{\text{eff}} = 6.52$ eV for Cu [8]. In order to avoid interaction under periodic boundary conditions, the vacuum distance was kept to 20 Å in the z-direction. The energy cutoff of 450 eV was set for the plane-wave basis. The structure parameters were fully relaxed until the energy was less than $10^{-6}$ eV and the force convergence criteria were less than 0.01 eV Å$^{-1}$ for each atom. The Monkhorst-Pack scheme of $15 \times 27 \times 1$ k-points mesh was applied for the self-consistent calculation. The PHONOPY code [29] was utilized using the density functional perturbation theory (DFPT) to verify the dynamic stability of Cu$_2$Se ML under strain engineering. Herein, a series of uniaxial or biaxial strains were applied to the Cu$_2$Se ML. The strain ($\varepsilon$) was defined as $\varepsilon = (l - l_0)/l_0 = \Delta l/l_0$, where $l_0$ and $l$ were the unstrained and strained lattice parameters of Cu$_2$Se ML, respectively. The negative and positive values represented compressive and tensile strains.

3. Results and discussion

3.1. Geometric properties of the Cu$_2$Se monolayer

The top and side views of the geometric structure of the Cu$_2$Se ML are shown in figures 1(a) and (b), respectively. The geometric structure of the rectangular unit cells of Cu$_2$Se ML, with $P2_1/c$ (No. 14) space group, is indicated by the black dashed rectangle that containing eight copper (Cu) and four selenium (Se) atoms. The lattice parameters of the optimized Cu$_2$Se ML (a = 0.41 nm and b = 0.67 nm) agree with the previous ones [8]. The average Cu-Se bond length is 2.43 Å. Each Cu atom is tricoordinated with three Se atoms. The chemical bonding between atoms in the monolayer can be explained by the electron localization function (ELF) [30] (as shown in figure 1(c)). The ELF diagram in figure 1(c) shows the electron accumulation of Se atoms and the absence of electrons around Cu atoms. It is considered that transition metal Cu provides electrons to nonmetal Se, and nonmetal atoms transfer a part of electrons to the gap region, which results in a small amount of charge density in the gap region. It is a typical feature of metal bonding.

3.2. Effect of strain on the electronic structures of the Cu$_2$Se monolayer

In order to research the electronic states, the electronic band structure and partial density of states (PDOS) have been calculated, as shown in figure 2. The results show that Cu$_2$Se ML is an indirect semiconductor with the band gap of 0.76 eV, in which the valence band maximum (VBM) is located at $\Gamma$ point and the conduction band minimum (CBM) is on the $\Gamma Y$ path away from the $\Gamma$ point (figure 2(a)). From the PDOS of Cu$_2$Se ML, it is found
that the VBM is mainly originated from Se-p_z + p_y and Cu-d_x^2-y^2 + d_xy orbital states. The CBM is primarily derived from Se-p orbital states, and small part of contributions originate from the orbital states of Cu atoms.

Since external strain can effectively engineer the band structures of 2D nanomaterials [31, 32], the effect of strain on the electronic properties of Cu_2Se ML materials has been systematically explored. Due to the rectangular lattice of Cu_2Se ML, the effects of the uniaxial strains along the x (ε_x) and y directions (ε_y) and biaxial strain (ε_xy) effects have been investigated. The simulated strains ε_x, ε_y, or ε_xy are varied from −5% to 5%, in which positive/negative values impose extension/compression formation. The evolutions of the Cu_2Se ML band structures under various strains (ε_x, ε_y, and ε_xy) are demonstrated in figures 3(a)–(c)–3(a)–(c). For simplicity, the three bands near the Fermi level are carefully observed, namely the highest valence band and the two lowest conduction bands. The points A, B, C, and D, in figures 3(a)–(c)–3(a)–(c) are band edge states. The
energy shifts of states A–D are shown in figures 3(d)–5(d). The variation of the band gaps under strain is demonstrated in figures 3(e)–5(e).

Firstly, the effect of uniaxial strain $\varepsilon_x$ on the electronic structure of Cu2Se ML is presented in figure 3. It can be found that the CBM and the VBM of Cu2Se ML under 5% compression strain (figure 3(a)) are still located at state A and state D, respectively, compared with the band structure of the original monolayer (figure 3(b)). However, the CBM of Cu2Se ML with $\varepsilon_x = 4\%$ is in state B, making it a direct band gap in figure 3(c). Figure 3(d) shows the change curves of the states A–D. It can be clearly seen that with the decrease of compression strain and increase of tensile strain, the energy of state A increases, while state B decreases almost linearly, which makes state B shift below state A. In general, with the reduction of states D and B, the enhancement of state A, the band gaps of Cu2Se ML increase. Due to the curve of state C being above the ones of the states A and B, it does not affect the band gap of Cu2Se ML. The evolution of the band gap can be seen in figure 3(e), which increases almost monotonically with the increase of the strain. It is noteworthy that the critical strain for indirect-direct band gap transition is tensile of 3%. Figure S1 (available online at stacks.iop.org/MRX/8/045003/mmedia) shows the band gaps of Cu2Se ML under $-5\%$ to 5% strain, from which it can be seen obviously the value of each band gap and the indirect–direct transition of the band gap.

Then, the effect of the strain in the y direction on the band gap has been studied. As displayed in figure 4(a), Cu2Se ML has a larger band gap under compression strain ($\varepsilon_y = -4\%$), but it is still an indirect band gap. Under strain $\varepsilon_y = 3\%$, state C shifts down near state B, as seen in figure 4(b). When the strain is increased to $\varepsilon_y = 5\%$, state C continues to move down below state B, which changes it to a direct band gap, as shown in figure 4(c). From figure 4(d), it is shown that state A is almost unchanged, states B and D rise up first and then go down. However, the eigenvalue of state C largely decreases after a slight increase. Therefore, with the rise of the tensile strain, state A remains nearly constant, and the states B and C decrease at different rates, resulting in the transition of the indirect–direct band gap. The critical strain is at $\varepsilon_y = 5\%$, as shown in figure 4(d). Besides, under uniaxial strain along the Y axis, the band gaps of Cu2Se ML are fluctuating greatly, which can be seen in figure 4(e). It is observed obviously that the band gap decreases from 0.9 eV ($\varepsilon_y = -5\%$) to 0.76 eV ($\varepsilon_y = -1\%$), then increases to 0.84 eV ($\varepsilon_y = 4\%$), and finally decreases to 0.78 eV under 5% tensile strain.

Under biaxial strain $\varepsilon_{xy}$, the strain also affects the band gap vastly, as seen in figure 5. For the case of $\varepsilon_{xy} = -5\%$, namely, the compression strain being 5%, the eigenvalues of state A of D are almost equal, which
imposes the indirect band gap is virtually zero. When \( \varepsilon_{xy} = 1\% \), the eigenvalue of state B decreases, and the eigenvalue of state A increases above B point (figure 5(b)). In this state, Cu\(_2\)Se ML becomes a direct band gap semiconductor, which is more convenient for practical application. For \( \varepsilon_{xy} = 5\% \), it is observed that the band gap is still direct in figure 5(c). In fact, with the increase of the strain from 1% to 5%, the states B and D both decrease, and state A rises, as can be seen in figure 5(d). In the evolution, the band gap is always direct, as seen in figure S3. The size change and indirect-direct transformation of the band gap can be seen directly in figure 5(e).

When biaxial tensile strain exceeds 1%, the indirect band gap changes to a direct band gap.

3.3. Stability of the Cu\(_2\)Se monolayer

A critical factor in strain engineering is the dynamic stability of the materials. The instability of phonons can lead to materials failure. Herein, the phonon spectra of Cu\(_2\)Se ML under the uniaxial and biaxial strains have been studied, as shown in figure 6. For the cases of \( \varepsilon_x = 5\% \) and \( \varepsilon_y = -5\% \), the phonon dispersions of Cu\(_2\)Se ML exhibit imaginary frequency (figures S4 and S5), which implies Cu\(_2\)Se ML is unstable under the two strains. Except those, there are no imaginary vibrational frequencies in the entire Brillouin zone (as seen in figure 6). It indicates that the Cu\(_2\)Se ML is dynamically stable over most of the applied strain ranges.

3.4. Electronic structures of high-temperature phase of Cu\(_2\)Se monolayer

Considered that strain may induce structural phase transition in two-dimensional materials [33, 34], the band structure of high-temperature phase of Cu\(_2\)Se ML has also been studied under the same calculation method. The optimized structure and band structure are shown in the figure S7. The lattice parameters of the optimized Cu\(_2\)Se ML (a = b = 0.40 nm) agree with the previous ones [8]. Figure S7(c) shows that it is a direct band-gap semiconductor. It implies that the result is still desired, even if the phase transition is induced under strain. The discussion on the effect of strain on phase structure could be another topic for the future work.
4. Conclusion

In summary, we systematically study the effects of uniaxial and biaxial strains on the electronic structures of Cu$_2$Se ML by means of the first-principles calculations. The band gap of Cu$_2$Se ML can be continuously adjusted by the application of strains. Since the near-edge states near the Fermi level have different responses to the strain, Cu$_2$Se ML undergoes a transition from the indirect band gap to the direct band gap after applying appropriate uniaxial or biaxial strains. In addition, the semiconductor Cu$_2$Se ML can sustain structural stability under a wide range of tensile or compressive strains. Our research demonstrates that the electronic structures of Cu$_2$Se ML is tunable by applying strain, which provides promise applications for controllable electronic devices.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Jinming Cai https://orcid.org/0000-0003-0869-1515
Jianqing Dai https://orcid.org/0000-0003-4352-0789
Cuixia Yan https://orcid.org/0000-0001-5766-1254

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