1 Introduction

Superconductivity, one of the macroscopic quantum phenomena, is old but still a new field in condensed-matter physics. The discovery of graphene together with its unique properties immediately motivated both theoretical and experimental research efforts, including regarding its potential superconductivity. Although pristine graphene is not a superconductor owing to its small density of states (DOS) around the Fermi level and its symmetrical restriction in the electron-phonon coupling (EPC), superconductivity can be introduced into this system through metal decorating/intercalating, carrier doping, strain, and magic angle twisting, which opens the door for two-dimensional (2D) superconductivity. Beyond graphene, lots of studies have demonstrated that superconductivity can be induced by the metallization of other monolayer materials, such as strained silicene, Li-intercalated h-BN bilayers, strained phosphorene, electron-doped arsenene, electron-doped phosphorene, Li-intercalated bilayer phosphorene, single-layer MoS$_2$, Li-intercalated bilayer MoS$_2$, strained MoX$_2$ (X = S or Se), and metal-intercalated blue phosphorus bilayers. However, until now, intrinsic 2D superconductors are still rather scarce in real planar monolayer systems.

Superconductors with one atomic thickness have been continuously filled with numerous interests due to their interplay with the quantum effects at the 2D limit, which are important for realizing next-generation quantum information techniques. However, to the best of our knowledge, few real planar monolayer systems have been reported to be intrinsic superconductors. Several examples are as follows: single layer B$_3$C, which is slightly corrugated with the boron and carbon layers separated in the vertical direction by only 0.032 Å, has been predicted to be a 2D intrinsic Bardeen–Cooper–Schrieffer (BCS) superconductor; single-atomic-layer Cu-benzenehexahedral (Cu-BHT), a 2D metal–organic framework, has been predicted by first-principles calculations and later experimentally verified as a BCS superconductor; $\lambda_3$ and $\beta_{12}$ borophenes ($\lambda_3$-B and $\beta_{12}$-B), fabricated on a Ag(111) surface, have been demonstrated to be phonon-mediated superconductors.

In the present work, we focus on a Cu$_2$Si monolayer (see Fig. 1) which was firstly predicted by a combination of first-principles calculations and the particle-swarm optimization method and then was successfully synthesized by directly evaporating atomic Si on a Cu(111) surface or Cu deposition on a Si(111) surface in an ultrahigh vacuum chamber. This 2D system is a nonmagnetic metal with excellent stability and has been identified as a 2D nodal-line semimetal. It has potential for gas sensing, electrode materials and high-speed...
low-dissipation devices, etc. Here, we investigate carefully the superconductivity and other exotic properties that may exist in this real planar monolayer system. On the basis of first-principles calculations, we prove that the 2D Cu2Si is an intrinsic BCS superconductor with \( T_c = 4.1 \) K, and demonstrate that the partial mechanism of its superconductivity is from Fermi surface (FS) nesting. Moreover, we study the effects of carrier doping and biaxial strain on its superconductivity. Unfortunately, the superconductivity of 2D Cu2Si is sensitive to these external conditions, resulting in smaller \( T_c \) than its pristine form. This explains to some extent why this system has never been measured as a superconductor, although it has been synthesized for years. Our results indicate that a high quality Cu2Si monolayer synthesized on substrates with negligible lattice mismatch is urgent for exploring its superconductivity in experiments.

2 Computational methods

The first-principles electronic structure calculations are performed using the Perdew–Burke–Ernzerhof form of the generalized gradient approximation (GGA), as implemented in the Vienna \textit{ab initio} simulation package (VASP). The cutoff energy of 500 eV and a \( 32 \times 32 \times 1 \) Monkhorst–Pack \( k \)-point mesh are used in the calculations. The length of the unit cell of 20 Å along the \( z \) direction is used to get rid of the interaction between adjacent images. All geometry structures are fully relaxed until the residual forces on each atom are less than 0.01 eV Å\(^{-1}\).

The EPC and superconductivity are calculated utilizing the density functional perturbation theory (DFPT) through the Quantum-ESPRESSO code. The PBESol form of GGA from the Standard Solid State Pseudopotentials (SSSP) library is employed in the phonon calculations. The kinetic energy cutoff and the charge density cutoff of the plane wave basis are chosen to be 80 and 800 Ry, respectively. Self-consistent electron density is evaluated by employing \( 32 \times 32 \times 1 \) \( k \) mesh. Both phonon and EPC are calculated by using a \( 4 \times 4 \times 1 \) \( q \) mesh.

Here, the magnitude of the EPC \( \lambda_{q\nu} \) is calculated according to the Migdal–Eliashberg theory by

\[
\lambda_{q\nu} = \frac{\gamma_{q\nu}}{\pi \hbar N(E_F) \omega_{q\nu}},
\]

where \( \gamma_{q\nu} \) is the phonon linewidth, \( \omega_{q\nu} \) is the phonon frequency, and \( N(E_F) \) is the electronic DOS at the Fermi level. The \( \gamma_{q\nu} \) can be estimated by

\[
\gamma_{q\nu} = \frac{2\pi \alpha_{q\nu}}{\Omega_{BZ}} \sum_{k,n,m} |g_{k,n,k+qm}^T|^2 \delta(\varepsilon_k - \varepsilon_F) \delta(\varepsilon_{k+qm} - \varepsilon_F),
\]

where \( \Omega_{BZ} \) is the volume of the Brillouin zone (BZ), \( \varepsilon_k \) and \( \varepsilon_{k+qm} \) denote the Kohn–Sham energy, and \( g_{k,n,k+qm}^T \) represents the EPC matrix element. The \( g_{k,n,k+qm}^T \) can be determined self-consistently by the linear response theory. The Eliashberg electron–phonon spectral function \( z^2 F(\omega) \) and the cumulative frequency-dependent EPC \( \lambda(\omega) \) can be calculated by

\[
z^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}} \delta(\omega - \omega_{q\nu})
\]

and

\[
\lambda(\omega) = 2 \int_0^{\omega} \frac{z^2 F(\omega)}{\omega} d\omega,
\]

respectively.

Using a typical value of the effective screened Coulomb repulsion constant \( \alpha^* = 0.140,42,62–64 \) as well as the Eliashberg spectral function \( z^2 F(\omega) \) and \( \lambda \), one can calculate the logarithmic average frequency \( \omega_{\text{log}} \) and the superconducting transition temperature \( T_c \) by

\[
\omega_{\text{log}} = \exp \left[ 2 \int_0^{\omega} \frac{d\omega}{\omega} z^2 F(\omega) \log \omega \right]
\]

and

\[
T_c = \frac{\omega_{\text{log}}}{1.2} \exp \left[ - \frac{1.04(1 + \lambda)}{1 - \alpha^*(1 + 0.62)} \right].
\]

According to eqn (2), we find that the phonon linewidth has two major contributions: the EPC matrix elements and the FS nesting factor \( \tilde{\zeta}(q) \). This factor is in the form of

\[
\tilde{\zeta}(q) = \sum_{k,n,m} \delta(\varepsilon_k - \varepsilon_F) \delta(\varepsilon_{k+qm} - \varepsilon_F).
\]

3 Results and discussion

3.1 Atomic structure and electronic properties

The atomic structure of the freestanding form of a Cu2Si monolayer, along with the electron localization function, is shown in Fig. 1. The structure of the Cu2Si monolayer is truly a planar structure without buckling, featuring planar hexacoordinate copper and planar hexacoordinate silicon. The optimized lattice constants along the \( a \) and \( b \) axes are both 4.10 Å. The calculated Cu–Si and Cu–Cu bond lengths are both 2.33 Å. Dominant ionic bonds form between Cu and Si atoms. Meanwhile, neighboring Cu atoms are connected via metallic bonds.

The band structure and FS are plotted in Fig. 2. Clearly, the Cu2Si monolayer is metallic with three bands crossing the Fermi level. As illustrated by the FS, there are three bands contributing to the three closed contours around the \( \Gamma \) center: a hexagon, a hexagram, and a circle. These results accord well with the
To measure the contributions of the three bands to the intrinsic metallic feature for the Cu$_2$Si monolayer, we calculate the charge density at each cross-over point of these bands and the Fermi level (see Fig. 3), corresponding to the a–f points in Fig. 2(a). In Fig. 3(b) and (f), we can see that there are massive electron transfers at the b and f points, formed by the second band crossing the Fermi level. As shown by Fig. 3(f), the electrons transfer in the line channels. While at the c and d points, there are few charges [see Fig. 3(c) and (d)], indicating weak electron transfer. As shown by the projected electronic density of states (PDOSs) in Fig. 4, there is apparent hybridization between the Si-3p and Cu-3d$_{4p}$ states near the Fermi level. The dominant contributions to the electronic states at the Fermi level are from d$_{xy}$, d$_{xz}$, d$_{yz}$, and p$_x$, p$_y$ states of Cu, followed by some contributions from p$_x$, p$_y$ and p$_z$ states of Si. Thus, the metallic nature of the Cu$_2$Si monolayer is mainly controlled by its Cu-3d orbitals.

### 3.2 EPC and superconductivity

After analyzing the electronic structures, we now focus on the vibration properties and EPC. The phonon dispersions of 2D Cu$_2$Si are shown in Fig. 5. The real frequencies of all modes in the BZ indicate that this 2D crystal is dynamically stable, consistent with previous results from first-principles calculations.

To gain deep insights into the phonon vibrations, the phonon $k$-p theorem is used to sort the phonon branches according to the continuity of their eigenvectors:

$$
\sum e_{k_0,\sigma}^{*}(j) \cdot e_{k_0,A_2^z}(j) = |\delta_{\sigma_1,\sigma_2} - 0(A)|. \quad (8)
$$

where $e_{k_0,\sigma}^{*}(j)$ is the displacement of the atom $j$ in the eigenvector of $(k,\sigma)$ vibrational modes, and $A$ is a small wave vector. As indicated in Fig. 5(a), three acoustic branches, including the out-of-plane (ZA), in-plane transverse (TA) and in-plane longitudinal (LA) modes, cross the two low-frequency optical branches. This kind of crossing indicates a strong optical-acoustic phonon coupling.

From the decomposition of the phonon spectrum with respect to the vibrations of Cu and Si atoms [see Fig. 5(b)], we find that the main contributions below 100 cm$^{-1}$ are from out-of-plane modes of Cu-$z$, including the ZA and the lowest optical branch (LOB). The interactions between in-plane modes of Cu-$xy$ and out-of-plane of Si-$z$ contribute to the intermediate-frequency region from 100 to 350 cm$^{-1}$. Meanwhile, the in-plane modes of Si-$xy$ occupy the high frequencies above 150 cm$^{-1}$ mostly. The highest mode frequency, 421 cm$^{-1}$, is much smaller than those of $\gamma_{12}$-B (1200 cm$^{-1}$), $\gamma_{12}$-B (1290 cm$^{-1}$), and B$_2$C (1243 cm$^{-1}$), indicating weak bonding (ionic and metallic bonds) interactions between its component atoms. From the projected phonon density of states (PhDOS), as shown in Fig. 6(b), we can also draw these conclusions.

To explore the superconductivity of a Cu$_2$Si monolayer, we calculate the Eliashberg spectral function [eqn (3)], the EPC constant $\lambda$ [eqn (4)], the logarithmic average frequency $\omega_{\log}$ [eqn (5)] and $T_c$ [eqn (6)] and present them in Fig. 6. The Eliashberg spectral function exhibits three major peaks, at 35.8, 62.1 and 153.7 cm$^{-1}$, in the whole frequency region.
that phonons in the low-frequency region (0–100 cm\(^{-1}\)) contribute mainly to the EPC, as they account for 81.5% of the total EPC (\(\lambda = 0.81\)). The first and the second peaks of \(\xi^2F(\omega)\) are responsible for this part. We can also see from Fig. 5(c) that the large values of the \(\lambda_q\) are around the \(M\) point in a frequency range of 19.7–69.6 cm\(^{-1}\), mainly on the softened ZA branch. They are responsible for the first peak of \(\xi^2F(\omega)\). Besides, some medium values of the \(\lambda_q\) are on the flat LOB, which results in the second peak. The middle-frequency region (100–350 cm\(^{-1}\)), in which the TA and the second-lowest optical branches interact tightly, expand flat in BZ, and result in the third peak of \(\xi^2F(\omega)\). In this medium, the high-frequency phonons (350–420 cm\(^{-1}\)) contribute to the remaining weight (3.7%) of the EPC. Similar to the \(\lambda_q\) of borophene\(^{42,43}\) and single layer Cu-BHT\(^{40}\), the EPC induced by high-frequency phonons is almost negligible. With a typical value of 0.1 for \(\mu^*\), we obtain the frequency-dependent superconducting transition temperature \(T_c(\omega)\) [see Fig. 6(c)]. Its derivative also exhibits three big peaks corresponding to those of \(\xi^2F(\omega)\). The total \(T_c\) is calculated to be 4.1 K, which is comparable to those of the Ca-intercalated bilayer graphene \(\text{Ca}_x\text{CaC}_6\) (4.0 K)\(^{6,69}\), 2D tri-Mo\(_2\text{B}_2\) (3.9 K)\(^{70}\) and 2D AlB\(_2\) (4.7 K)\(^ {71}\).

Overall, the Cu\(_2\)Si monolayer is a weak BCS-type superconductor with \(\lambda = 0.81\).

In Table 1, we list the superconductive parameters of \(\mu^*, N(E_F)\), \(\omega_{\text{log}}\) and \(\lambda\) for some realistic 2D superconductors with a flat geometry synthesized in experiments. These systems are or may be intrinsic 2D superconductors without external conditions, such as carrier doping, high pressure, metal decorations/intercalations and/or functional groups. Among them, the Cu-BHT was firstly predicted by the BCS theory\(^{40}\) as a superconductor and then has been verified by experiments.\(^{41}\) This fact clearly indicates that the combination of the first-principles calculations and the BCS theory is reliable and also powerful in predicting 2D superconductors. Compared with the two forms of borophene (\(\chi_{12}\)B and \(\beta_{12}\)B),\(^{42}\) the \(T_c\) of Cu\(_2\)Si is fundamentally small, although their values of \(\lambda\) are comparable. This fact is mainly due to the small value of \(\omega_{\text{log}}\) that Cu\(_2\)Si possesses. After all, the atomic masses of Cu and Si are largely heavier than that of boron, constraining the phonon vibrations.

### Table 1

<table>
<thead>
<tr>
<th>Comp.</th>
<th>(\mu^*)</th>
<th>(N(E_F))</th>
<th>(\omega_{\text{log}})</th>
<th>(\lambda)</th>
<th>(T_c)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_{12})B</td>
<td>0.1</td>
<td>323.43</td>
<td>0.95</td>
<td>24.7</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>(\beta_{12})B</td>
<td>0.1</td>
<td>384.16</td>
<td>0.89</td>
<td>18.7</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Cu-BHT</td>
<td>0.1</td>
<td>51.8</td>
<td>1.16</td>
<td>4.43(3)</td>
<td>40 and 41</td>
<td></td>
</tr>
<tr>
<td>Cu(_2)Si</td>
<td>0.1</td>
<td>83.594</td>
<td>0.81</td>
<td>4.03</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3 FS nesting

As discussed above, the large values of the EPC \(\lambda_q\) are mainly in the low-frequency region, in which the soft ZA phonon mode is along the \(K-M\) and \(M-G\) directions. To clearly understand the phonon softening, we investigate the FS nesting in the Cu\(_2\)Si monolayer by calculating the nesting function [eqn (7)]. The results of \(\xi(q)\) along the high-symmetry paths are shown in
the regions of the phonon softening [see Fig. 5(c)] correspond to strong FS nesting occurs along these directions. Not coincidentally, almost unchanged. As expected, $N$ induced by the FS nesting. Besides, we display the distribution of superconductivity of 2D Cu$_2$Si, but electrons transferring from carrier doing, we provide theory clues for future experimental investigations (Fig. 8).

Since the Cu$_2$Si monolayer is synthesized on Cu(111) or Si(111) substrates, the estimation of a freestanding sample is not enough to reflect real samples. Therefore, we study the superconductivity of strained Cu$_2$Si by biaxial strains ($\zeta$) (−2% < $\zeta$ < 2%) to simulate the real samples grown on substrates with different lattice constants. The $\zeta$ is calculated by $\zeta = \frac{a - a_0}{a_0} \times 100\%$ (positive value means tensile strain while negative one means compressive strain), atomic coordinates are fully relaxed in each case. The calculated superconductive parameters are presented in Fig. 9. Obviously, the $\lambda$ and $T_c$ decrease with applied both tensile and compressive strains, and even under tensile strains the $\omega_{\text{log}}$ and $N(E_F)$ have been increased. When compressing 2%, the $\lambda$ and $T_c$ reach the minimum values about 0.39 and 0.2 K, respectively. Thus, biaxial strains can suppress the superconductivity of 2D Cu$_2$Si. We further estimate the lattice mismatch between Cu$_2$Si and Cu(111)/Si(111) surface to reflect the practical situation of experimental synthesis. The result of lattice mismatch between the Cu$_2$Si and Cu(111) surface is −15.9% and the lattice mismatch

3.4 Effects of doping and strain

5w? Inspired by former successes in controlling the electronic properties as well as the superconductivity of 2D systems by carrier doing, here we also want to investigate its effects on the Cu$_2$Si monolayer. Within a compensating uniform charge background of opposite sign to maintain charge neutrality, the carrier doping is simulated by directly adding electrons into or removing electrons from the system. For each doping concentration, we fully relax the plane lattice constants and atomic coordinates. We apply both hole and electron dopings ranging from 0.2 h per cell to 0.2 e per cell. The changes in the superconductive parameters of $\lambda$, $\omega_{\text{log}}$, $N(E_F)$ and $T_c$ are shown in Fig. 8(a)–(d), respectively. Increasing hole doping concentration, although $\lambda$ and $\omega_{\text{log}}$ change to some extent, $N(E_F)$ and $T_c$ are almost unchanged. As expected, $N(E_F)$ increases with the electron doping concentration but the $\lambda$ and $T_c$ decrease. Thus, we can conclude that the hole doping has almost no impact on the superconductivity of 2D Cu$_2$Si, but electrons transferring from the Cu(111) substrate to the Cu$_2$Si monolayer can suppress its superconductivity. Although we fail to modulate the $T_c$ higher by

Fig. 9 The related superconductive parameters of (a) $\lambda$, (b) $\omega_{\text{log}}$, (c) $N(E_F)$ and (d) $T_c$ under different strains.
between the Cu$_2$Si and Si(111) surface is 6.1%. Based on our calculated results [see Fig. 9(d)], such large lattice mismatches would result in the absence of superconductivity in 2D Cu$_2$Si.

As already mentioned above, the electron doping and biaxial strains usually have negative effects on the superconductivity of 2D Cu$_2$Si. This supplies theoretical evidence for why the superconductivity in the Cu$_2$Si monolayer has never been reported experimentally, though it has been synthesized for years. This problem has also been found in probing superconductivity in substrate-supported $\beta$-$\text{Bi}_2$.64,78 In order to preserve or even enhance the $T_c$ of 2D Cu$_2$Si, according to our calculated results, it’s urgent to avoid interference from external conditions.

4 Conclusions

In conclusion, we systematically explore the electron structures, phonon vibrations and superconductivity of one recent experimentally synthesised real planar monolayer Cu$_2$Si system, combining first-principles calculations and the BCS theory. Our results clearly indicate that 2D Cu$_2$Si is not only a Dirac nodal-line semimetal, but also a BCS superconductor with its urgent to avoid interference from external conditions.

Conflicts of interest

There are no conflicts to declare.

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