MXenes are a large family of layered transition metal carbide/nitride materials that possess a number of desired properties such as flexible chemical composition, high mechanical strength, and excellent structural stability. Although MXene based semiconductors have attracted considerable recent research attention in the search of novel 2D electronic materials, accurate understanding of their electronic properties has not been established. In this work, we carry out fully converged GW quasiparticle calculations for M₂X₂ (M = Hf, Zr, and Ti) MXene based 2D semiconductors and alloys using newly developed accelerated GW methods. The quasiparticle band gaps of single-layer Hf₂CO₂, Zr₂CO₂, and Ti₂CO₂ are predicted to be 2.45, 2.13, and 1.15 eV, respectively. The narrow band gap of Ti₂CO₂ is attributed to the low energy of Ti 3d as compared with the Hf and Zr d states. Considering their chemical similarity, it is expected that Hf₂–xTi₂xCO₂ semiconductors can be synthesized without difficulties. We show that the quasiparticle band gap of Hf₂–xTi₂xCO₂ (0 ≤ x ≤ 1) semiconductor alloy can be continuously tuned from 2.45 to 1.15 eV, offering a unique 2D semiconductor with a moderate and tunable gap for future electronics applications.

1. Introduction

MXenes are a new family of layered transition metal carbide/nitride materials which have attracted considerable research interest since nanosheets of Ti₃C₂ MXene were first synthesized. MXenes can be synthesized by exfoliating the “A” laminar component from the MAX matrix phase in HF solution at low temperature. The MAX phase has a general chemical formula Mₙ₊₁AXₙ₋₁ (n = 1, 2, or 3), where M is an early transition metal (M = Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta or W), A is a Group IIIA or IVA element (A = Al, Ga, In, Si, Ge, Sn, Pb, P, As, S or Cd) and X is C and/or N. The strong M–X bonds have a mixed ionic, metallic and covalent character, while the M–A bond shows typical metallic nature. The disparate bonding strength among the M–A and M–X bonds in the MAX phase makes it possible to selectively etch out the A layers without disrupting the M–X framework. Since the as-synthesized MXenes are typically terminated by O, OH and/or F groups, they are usually denoted as Mₓ₁₋ₙXₙTₓ (n = 1, 2, and 3), with T standing for the terminating groups. MXenes combine the advantages of metals and ceramics, exhibiting high chemical stability, excellent electrical conductivity and exceptional mechanical properties. A number of potential applications have been proposed for these emerging layered materials, including Li-batteries, highly conductive optical coatings, high volumetric capacitors, and hydrogen storage.

Most MXenes are metallic, but there are also a number of MXene semiconductors reported. For example, Hf₂CO₂, Zr₂CO₂, V₂CF₂, V₂(OH)₂, Ti₂CO₂, Sc₂C(OH)₂, Sc₂CF₂ and Sc₂CO₂ are found to possess nonzero band gaps. These layered semiconductors may have some of the most sought-after properties such as having a moderate band gap and being highly stable, among others, opening a new avenue for fabricating next generation 2D electronic devices. For example, Hf₂CO₂ has been shown to have a higher thermal conductivity than that of the much studied phosphorene or MoS₂, and a high carrier mobility comparable to that of phosphorene. The reported band gap of single-layer (which consists of five atomic layers as shown in Fig. 1) Hf₂CO₂ MXene is 1.65 eV (ref. 14) using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional within density functional theory (DFT).

Although the HSE functional has been shown to be able to predict the band gap of a wide range of bulk semiconductors with reasonable accuracy, there are notable exceptions. For example, the measured band gap of FeS₂ is about 0.95 eV.
but the HSE functional predicts a band gap of FeS$_2$ of about 2.7 eV. In addition, straightforward applications of the HSE functional to predict the quasiparticle band gap of 2D materials deserve scrutiny since the dielectric screening properties in 2D materials are fundamentally different from those in bulk materials. A more rigorous approach for calculating the band gap, and more generally, the quasiparticle band structure, of semiconductors is the GW method.\textsuperscript{18} Therefore, it is imperative to carry out GW calculations for these emerging 2D semiconductors.

In this work, we have carried out first-principles quasiparticle calculations for Hf$_2$CO$_2$ within the GW approximation\textsuperscript{18} using a local version of the BERKELEYGW package.\textsuperscript{19} We find that the GW band gap of monolayer Hf$_2$CO$_2$ is about 2.45 eV. This value is significantly larger than the value (1.65 eV) predicted by the HSE functional. Since the optimal band gap of semiconductors varies significantly from applications to applications, for example, narrow gap semiconductors may be suitable for infrared or thermoelectric applications whereas power electronics requires wide-gap semiconductors, it is often desirable that the band gap of a class of materials (e.g., 2D MXenes in this work) be tunable to suit different applications. Considering the chemical flexibility of MXenes, it is likely that their band gap can be conveniently tuned through chemical substitutions of the metallic sites with isoelectronic elements. To this end, we have also carried out DFT and GW calculations for single-layer Zr$_2$CO$_2$, Ti$_2$CO$_2$ and Hf$_2$..."
3.265 Å, and the Hf–C and Hf–O bond lengths are 2.33 Å and 2.10 Å, respectively. Fig. 2 shows the PBE band structure superimposed with projections onto atomic orbitals. The valence band maximum (VBM) is placed at zero in Fig. 2. The lower group of valence states is mainly derived from O p states with some admixture of Hf d states, whereas the upper one has contributions from C p, Hf d, and O p states. The low energy conduction bands, on the other hand, consist mostly of Hf d states. The VBM states are located at the Γ point and are primarily composed of C px + pz orbitals hybridized with O px + py and Hf dxz + dyz. The conduction band minimum (CBM) is located at the M point of the hexagonal BZ, consisting mostly of Hf d states. Since the CBM of Hf2CO2 MXene is derived from the Hf d states, it is expected that substituting Hf with isoelectronic transition metals with lower d-state energy will result in a reduced band gap as we will discuss later.

Fig. 3 compares the PBE and GW band structures of single-layer Hf2CO2. The PBE functional predicts an indirect band gap of 0.99 eV, to be compared with the GW band gap of 2.45 eV. The minimum direct band gap at the M point is about 3.60 eV within the GW approximation. The valence bandwidth is also significantly enhanced with the GW correction. With a moderate band gap of 2.45 eV and other promising properties14 such as high thermal conductivity and carrier mobility, this MXene based 2D semiconductor holds great potential for future 2D electronics applications.

We now briefly discuss the convergence issue that is specific to GW calculations for 2D materials. In GW calculations, the BZ integration of the quasiparticle self-energy of state |nk⟩ near the Γ (q = 0) point is carried out using a uniform k-grid (for 2D systems, an N × N × 1 grid), i.e., Σnk = ∑q f(q)Σ(q). For bulk (3D) semiconductors, this summation converges quickly with increasing k-grid density. For example, for silicon (diamond structure with a 2-atom unit cell), a 6 × 6 × 6 k-grid is sufficient to converge the calculated GW band gap to within 0.01 eV. For 2D materials, however, the convergence is extremely slow27–29 due to the analytical behaviors of the 2D dielectric function and other relevant quantities as wave vector q approaches 0. Recently, we have successfully developed a combined subspace sampling and analytical integration technique25 that can drastically reduce the required 2D k-grid sampling density for achieving fully converged GW results. Our method is inspired by a recent work29 in which the authors proposed a nonuniform sampling scheme for GW calculations.

In our new method, the BZ integration of the self-energy of state |nk⟩ near the Γ (q = 0) point is replaced with an analyti-
cal integration over the mini-BZ (mBZ) enclosing the $\Gamma$ point, i.e., $\Sigma_{nk} = \sum_{\vec{q} \neq 0} f_{\vec{q}} \Sigma(\vec{q}) + \int_{mBZ} \Sigma(\vec{q}) d\vec{q}$. We first calculate $\Sigma(\vec{q})$ for a few small $\vec{q}$-points within the mini-BZ as shown with blue dots in Fig. 4. These results are then used to fit $\Sigma(\vec{q})$ with some analytical form as shown in Fig. 4 with the blue curve. Analytical integration within the mBZ is then carried out using this function. To illustrate the accuracy of the fitting function, we have also plotted in Fig. 4 $\Sigma(\vec{q})$ calculated at other $\vec{q}$-points (red squares), showing excellent agreement between the calculated results and the fitting function.

Using this method, we are able to carry out converged GW calculations for 2D materials using a $6 \times 6 \times 1$ coarse $k$-grid as shown in Fig. 5 in which we compare the performance of our new method with the conventional uniform $k$-point sampling approach. Using our new method, the calculated band gap converges to within 0.02 eV with a very coarse $k$-grid of $6 \times 6 \times 1$. In comparison, the band gap does not seem to converge even with a very fine $24 \times 24 \times 1$ grid using the conventional method. Note that the convergence behavior of the GW results calculated using the uniform sampling approach shown in Fig. 5 is consistent with previous work. For example, it has been shown that a $k$-grid of at least $24 \times 24 \times 1$ is needed to properly converge the GW band gap of MoS$_2$. Considering the fact that the computational cost of GW calculations (the calculation of the electron polarizability) scales as $O(N_k^2)$ where $N_k$ is the number of $k$-points used to sample the BZ, our method represents a speed-up factor of over two orders of magnitude compared with the conventional method. Combining this method with another method we developed in which the conventional band-by-band summation in the GW calculations is replaced with an energy integration, we can now carry out fully converged GW calculations for 2D materials with a speed-up factor of about three orders of magnitude.

### 3.2 M$_2$CO$_2$ (M = Hf, Zr, and Ti): structural and electronic properties

We now investigate the possibility of tuning the band gap of M$_2$CO$_2$ MXene based 2D semiconductors. As we have shown in Fig. 2, the CBM state of Hf$_2$CO$_2$ is mainly derived from Hf d states. Therefore, it is plausible the band gap of Hf$_2$CO$_2$ can be tuned by replacing Hf with isoelectronic transition metals such as Ti or Zr. In particular, since the 3d level of Ti atom is significantly lower than the Hf 5d level, replacing Hf with Ti may result in significantly lowered CBM thus reducing the band gap. In addition, due to their chemical similarity, it is
expected that semiconductor alloys of M₂CO₂ (M = Hf, Zr, and Ti) can be synthesized, providing a MXene based 2D material system with tunable band gap.

Before investigating their electronic structures, we first evaluate the stability of M₂CO₂ (M = Hf, Zr, and Ti) by calculating their formation energies. We define the formation energy as the difference in total energy between single-layer M₂CO₂ and stable competing subsystems, i.e., solid metal and CO₂ gas molecules, i.e., \( \Delta E = E_{\text{M}_2\text{CO}_2} - (E_{\text{metal}} + E_{\text{CO}_2}) \). Table 1 shows the calculated formation energies and lattice constants for the four single layer MXenes. Although the formation energy (absolute value) of Ti₂CO₂ is smaller than that of Hf₂CO₂, a formation energy of \(-6.67\) eV per formula unit (f.u.) still suggests that Ti₂CO₂ is thermodynamically stable and synthetically viable.

Fig. 6 shows the DFT-PBE band structures of Zr₂CO₂ and Ti₂CO₂. The DFT-PBE band gap of Ti₂CO₂ (0.26 eV) is indeed much smaller than that of Hf₂CO₂, a formation energy of \(-6.67\) eV per formula unit (f.u.) still suggests that Ti₂CO₂ is thermodynamically stable and synthetically viable.

Table 1: Formation energies (eV/f.u.), lattice constants (Å) and band gaps (eV) of single-layer Hf₂CO₂, Zr₂CO₂, Ti₂CO₂ and (HfTi)CO₂ MXene semiconductors

<table>
<thead>
<tr>
<th></th>
<th>Hf₂CO₂</th>
<th>Zr₂CO₂</th>
<th>Ti₂CO₂</th>
<th>(HfTi)CO₂</th>
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<tr>
<td>Formation energy</td>
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<td>-6.67</td>
<td>-7.20</td>
</tr>
<tr>
<td>Lattice constant</td>
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<tr>
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<td>0.55</td>
</tr>
<tr>
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<td>1.59</td>
<td>1.45</td>
<td>0.90</td>
<td>1.28</td>
</tr>
<tr>
<td>GW gap</td>
<td>2.45</td>
<td>2.13</td>
<td>1.15</td>
<td>1.80</td>
</tr>
</tbody>
</table>

Fig. 6 Atomic-orbital projected band structure of single-layer Ti₂CO₂ (upper) and Zr₂CO₂ (lower) calculated using the PBE functional.
share similar physical properties such as d level positions and atomic radii. Zr$_2$CO$_2$ has the largest lattice constant among the three systems. This is expected since Zr has the greatest ionic radius. We have also carried out GW calculations for the band gap of Zr$_2$CO$_2$ and Ti$_2$CO$_2$. Including GW self-energy corrections increases the band gap of Ti$_2$CO$_2$ to 1.15 eV and that of Zr$_2$CO$_2$ to 2.13 eV. These results suggest an interesting possibility of continuously tuning the band gap of these 2D semiconductors from 2.45 to 1.15 eV through alloying.

3.3 Continuous band gap tuning of Hf$_{2-x}$Ti$_x$CO$_2$ 2D semiconductor alloys

Isoelectronic substitution minimally disturbs the chemical bonding of a material while offering the possibility of significantly modifying the low-energy (near-edge) electronic states. The quasiparticle band gap of Hf$_2$CO$_2$ is predicted to be 2.45 eV whereas that of Ti$_2$CO$_2$ is about 1.15 eV. Therefore, alloying Hf$_2$CO$_2$ with Ti$_2$CO$_2$ may provide a material system with a widely tunable band gap. To this end, we have calculated the electronic properties of Hf$_{2-x}$Ti$_x$CO$_2$ (0 ≤ x ≤ 1) alloys. We create a 4 × 4 × 1 supercell containing 80 atoms for studying the alloy systems. Except for the end systems, for each Ti concentration x, several inequivalent structures are randomly created and their structures are fully optimized.

Fig. 7 shows a few structural models that we created for the HfTiCO$_2$ random alloy. We mention the special quasirandom structure (SQS) approach is a well-established approach for generating finite structural models that best mimic the radial correlation functions of perfectly random structures, and ideally one should adopt this approach for creating structural models for random alloys. Since we find that the calculated band gap does not depend sensitively on the specific structures (with a variation of about ±0.1 eV), we did not attempt to create SQS for these random alloys.

On the other hand, we have noticed that Wong and collaborators recently carried out a detailed study on the structural and thermodynamic properties of these random alloys. They concluded that Ti$_{2(1−x)}$Zr$_{x}$CO$_2$, Ti$_{2(1−x)}$Hf$_{x}$CO$_2$, and Zr$_{2(1−x)}$Hf$_{x}$CO$_2$ exist as disordered solid solutions. These results are expected since isoelectronic ions usually mix rather well as they have the same valency, especially when their ionic radii do not differ significantly as suggested by Hume–Rothery rules. Other MXene alloys have also been investigated theoretically. Admittedly, the stability of a material shall be ultimately determined by experiments. In recent years, experimentalists have been very successfully (and sometimes unexpectedly) in synthesizing metastable compounds. In particular, chemical vapor deposition (CVD) has been shown to be a powerful method for synthesizing 2D materials and heterostructures.

Fig. 7 A few structural models for the HfTiCO$_2$ 2D random alloy used in this work.

Fig. 8 Lattice constant (left) and band gap (right) of single-layer Hf$_{2-x}$Ti$_x$CO$_2$ alloy as functions of Ti concentration x. The band gaps are calculated within the DFT-PBE approach for all Ti concentrations and using the HSE and GW approaches for selected concentrations.
Fig. 8(a) shows that the lattice constant of Hf$_{2-x}$Ti$_x$CO$_2$ semiconductor alloy varies nearly linearly with Ti concentration $x$, obeying Vegard’s law. Interestingly, the calculated DFT-PBE band gap of Hf$_{2-x}$Ti$_x$CO$_2$ as a function of Ti concentration also shows a nearly linear dependence [Fig. 8(b)], suggesting a very small band gap bowing parameter for this system. For a given Ti concentration, different structures show slightly different band gap with a deviation of ±0.1 eV from their averaged values. The HSE and GW results for three Ti concentrations are also shown in Fig. 8(b) for comparison. Our results suggest that the quasiparticle band gap of Hf$_{2-x}$Ti$_x$CO$_2$ alloy can be continuously tuned from 2.45 eV to 1.15 eV.

Isoelectronic substitutions may be achieved beyond single pair of elements. Since the band gap of Zr$_2$CO$_2$ is just slightly smaller than that of Hf$_2$CO$_2$, alloys of these two semiconductors may not offer significant band gap tunability. However, considering the fact that Zr$_2$CO$_2$ has a larger lattice constant than Hf$_2$CO$_2$, whereas Ti$_2$CO$_2$ has the smallest lattice constant, it may be beneficial to synthesize ternary alloys Hf$_{2-x}$Ti$_x$Zr$_{2-x}$Ti$_x$CO$_2$ to minimize the lattice strain. In addition, co-doping with d$^4$ and d$^3$ pairs (e.g., Y and Nb, or Sc and Ta) may also be considered. We would like to mention that mechanical strain can also be used to tune the band gap of semiconductors. For example, we find that the band gap of Hf$_2$CO$_2$ reduces at a rate of about 0.1 eV per 1% compressive 2D lattice strain. It may be desirable to combine mechanical strain with chemical substitution to realize wide band gap tunability in certain applications.

4. Summary

M$_2$CO$_2$ (M = Hf, Zr, and Ti) MXene based tunable band gap 2D semiconductors are investigated using DFT and GW approaches. Recently developed accelerated GW methods are employed in this study. The quasiparticle band gap of single-layer Hf$_2$CO$_2$ is predicted to be 2.45 eV, which is significantly different from about 1.59 eV predicted using the HSE functional, suggesting the importance of accurate quasiparticle calculations for predicting the electronic properties of 2D semiconductors. The conduction bands of Hf$_2$CO$_2$ are mainly derived from Hf d states. This points to the possibility of tuning the band gap through Ti substitutions of Hf since Ti has lower d levels. Indeed, the calculated quasiparticle band gap of Ti$_2$CO$_2$ is about 1.15 eV, and we show that the quasiparticle band gap of Hf$_{2-x}$Ti$_x$CO$_2$ (0 ≤ $x$ ≤ 1) semiconductor alloy can be continuously tuned from 2.45 to 1.15 eV. Introducing Zr into the alloy system is expected to reduce the lattice strain while leaving the fundamental gap nearly unchanged. We believe that M$_2$CO$_2$ MXene based semiconductors and their alloys, which combine advantages such as structural stability, chemical flexibility, and electronic tunability, offer a unique material for future 2D electronics applications.

Conflicts of interest

There are no conflicts to declare.

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