Currently, most two-dimensional (2D) materials that are of interest to emergent applications have focused on van der Waals-layered materials (VLMs) because of the ease with which the layers can be separated (e.g., graphene). Strong interlayer-bonding-layered materials (SLMs) in general have not been thoroughly explored, and one of the most critical present issues is the huge challenge of their preparation, although their physicochemical property transformation should be richer than VLMs and deserves greater attention. MAX phases are a classical kind of SLM. However, limited to the strong interlayer bonding, their corresponding 2D counterparts have never been obtained, nor has there been investigation of their fundamental properties in the 2D limitation. Here, the authors develop a controllable bottom-up synthesis strategy for obtaining 2D SLMs single crystal through the design of a molecular scaffold with Mo$_2$GaC, which is a typical kind of MAX phase, as an example. The superconducting transitions of Mo$_2$GaC at the 2D limit are clearly inherited from the bulk, which is consistent with Berezinskii-Kosterlitz-Thouless behavior. The authors believe that their molecular scaffold strategy will allow the fabrication of other high-quality 2D SLMs single crystals, which will further expand the family of 2D materials and promote their future application.

**Keywords:** 2D MAX phase crystals, strong interlayer bonding, molecular scaffold, chemical vapor deposition
**Introduction**

Graphene provided humankind the first exposure to materials with a two-dimensional (2D) extended structure and transformed the landscape of condensed-matter physics.\(^1\)–\(^3\) In the past 10 years, graphene analogues, such as hexagonal boron nitride, transition metal dichalcogenides, and black phosphorus, have been continually investigated and have brought about various unique transport properties.\(^4\)–\(^8\) These 2D films are all van der Waals-layered materials (VLMs), where the bonding within a layer is covalent whereas the interlayer bonding occurs through weak noncovalent (van der Waals) interactions, thus allowing individual layers to be easily separated and to be thinned to atomic thickness. Meanwhile, there exists another kind of layered materials where their interlayer bonding belongs to strong interaction, such as covalent bonding. We call them strong interlayer-bonding-layered materials (SLMs). At first glance, they will be prohibited from existing as an atomic layer. Exfoliation strategies that are applicable for producing few layer or even monolayer VLMs are ineffective for obtaining 2D SLMs, while their direct synthesis usually leads to bulk material formation. Considering that 2D-layered materials with stronger interlayer coupling exhibit higher sensitivity to layer number,\(^9,10\) the transformation of SLMs to 2D systems should be more exciting and deserves an in-depth investigation because the surficial unsaturated dangling bonds will lead to the enhanced surface states or surface relaxation or reconstruction\(^11,12\) and even improved performance.\(^13\)–\(^16\) Providing the establishment of a controllable strategy for fabricating SLMs is found, the discovery of such materials in the 2D limit will certainly redefine the landscape of 2D-layered materials in general.

MAX phases (\(\text{M}_n\text{AX}_n\); \(\text{M}\) is the \(p\)-block element, and \(\text{A}\) is the \(\text{C}\) or \(\text{N}\)) are typical SLMs.\(^16\)–\(^18\) The layered structure and the mixed metallic-covalent nature of the \(\text{M}–\text{X}\) bonds, which are exceptionally strong, together with \(\text{M}–\text{A}\) bonds allow MAX phases to exhibit many excellent properties.\(^19,20\) MAX phases combine the property of metal and ceramic, such as being electrically and thermally conductive, exceptionally damage tolerant, lightweight, and able to maintain strength at high temperature.\(^16,21\)–\(^23\) This provides a broad array of applications of this material family, such as magnetism transport\(^24\) and new optoelectronic devices;\(^25\) as well as ohmic contacts for semiconductor electronics\(^26\) and as a heterogeneous catalyst for dehydrogenation of alkanes\(^27\) in harsh high-temperature environments. Some MAX phases also display self-healing behavior\(^28\) and reversible deformation.\(^29\) However, the metallic or covalent bonds between the layers in the MAX phases are too strong to be broken by shear or any similar mechanical means,\(^20,30\) which is a great barrier to realize their two-dimensionalization. The top-down chemical exfoliating or etching methods can only produce its derivatives, MXenes.\(^31\) The bottom-up synthesis also has not realized the fabrication of 2D MAX phase single crystals with high quality.\(^18,26,27,32–36\) Thus far, the fabrication of 2D MAX phase single crystals has never been achieved, which significantly hampers the further exploitation of their fundamental properties and the promotion of their application in the 2D limit.

Here, we present a precise bottom-up synthesis strategy for obtaining 2D ultrathin SLM single crystals via the design of a molecular scaffold. We took \(\text{Mo}_2\text{GaC}\), a typical kind of MAX phase, as an example. We preset a precise molecular scaffold—an ultrathin crystalline \(\text{Ga}_2\text{O}_3\) layer—to achieve a confined chemical reaction. Based on a designed molecular scaffold, the chemical reaction will occur at the scaffold during a chemical vapor deposition (CVD) process. For the first time, we obtained \(\text{Mo}_2\text{GaC}\) single crystals with a thickness comparable to that of the unit cell, and these flakes showed very high quality as indicated by transmission electron microscopy (TEM) structural investigations. In addition, the superconducting transport properties of the ultrathin \(\text{Mo}_2\text{GaC}\)-layered single crystal in the 2D limit were clearly observed, such as Berezinskii–Kosterlitz–Thouless (BKT) behavior and strong anisotropy with magnetic field orientation. What’s more, our as-obtained 2D \(\text{Mo}_2\text{GaC}\) is the first CVD-grown high-quality superconducting single crystal with strong interlayer interaction, which will offer an ideal platform for the exploration of the unprecedented physical properties, such as localization of electrons or Cooper pairs, transition-temperature oscillations caused by quantum size effects, excess conductivity originating from superconducting fluctuations, and quantum phase transitions at zero temperature.\(^37\) We believe such a design through the use of a scaffold will allow the fabrication of other high-quality 2D SLM single crystals, which will further expand the family of 2D materials and promote their future application.

**Molecular scaffold growth of 2D, strong interlayer-bonding \(\text{Mo}_2\text{GaC}\) single crystal**

We design a precise molecular scaffold, an ultrathin \(\text{Ga}_2\text{O}_3\) layer, to construct the \(\text{Mo}_2\text{GaC}\) crystals, as shown in Figure 1. The design of the molecular scaffold is the key. Main group III metals, such as gallium (Ga), naturally form a thin surface metal oxide layer on contact with oxygen in the atmosphere, which creates a physical barrier to corrosion or further oxidation in most environments. Ga is an active metal with an ultralow melting point and tends to be oxidized easily with time under ambient atmospheric conditions.\(^38\) The oxidized layer of Ga is initially one-unit-cell thick and reaches a saturation state, leading to the formation of an intimate self-passivated oxidation layer.
The thickness of the oxidation layer is just a few nanometers and does not increase over time.\textsuperscript{39,40} At temperatures above 300°C, the as-formed amorphous or poorly crystallized oxide layer at room temperature is transformed into a crystalline $\beta$-Ga$_2$O$_3$ layer as a molecular scaffold to build the Mo$_2$GaC crystals with unit cell thickness (Supplementary Figure S1). The existence of the ultrathin Ga$_2$O$_3$ layer on the metallic Ga surface is identified by an X-ray photoelectron spectroscopy (XPS) depth analysis. The Ga 3p signal attributed to the formation of Ga$_2$O$_3$ could only be detected on the surface and disappeared after a $\sim$150 s Ar-ion sputtering to remove the superficial metal oxide (Supplementary Figure S2).

With such an ultrathin Ga$_2$O$_3$ layer serving as the molecular scaffold and with methane (CH$_4$) as the carbon source, large-area ultrathin Mo$_2$GaC crystals embedded in the Ga$_2$O$_3$ molecular scaffold were obtained at 1000°C. The high temperature allows the Ga underneath the ultrathin Ga$_2$O$_3$ layer to stay in a liquid state, and a Mo–Ga alloy forms simultaneously, ensuring decomposition of the CH$_4$. Subsequently, some Mo atoms diffuse from the Ga–Mo liquid alloy bulk to the surface of the liquid Ga, which react with the ultrathin Ga$_2$O$_3$ film and adsorbed C atoms (from decomposed CH$_4$) to form Mo$_2$GaC crystals, as shown in the schematic diagram (Figure 1).

The ultrathin crystalline Ga$_2$O$_3$ layer acts as a molecular scaffold to enable the bottom-up synthesis of 2D Mo$_2$GaC single crystals. Traditional synthesis requires Mo and C powders to react with liquid Ga over a period of up to 4 weeks,\textsuperscript{41} which is inefficient. To confirm the important role of the Ga$_2$O$_3$ molecular scaffold in the growth of Mo$_2$GaC, contrast experiments were conducted. It was found that Mo$_2$GaC would not form without the Ga$_2$O$_3$ layer (Supplementary Figure S3). Accurate Auger electronic spectroscopy (AES) further helps to confirm the as-proposed growth process. When not reacting with the Mo and C atoms, the Ga$_2$O$_3$ film remains well preserved (Supplementary Figure S4). We ascribe this to its compactness and passivation nature. The compactness of the atomically thin Ga$_2$O$_3$ molecular scaffold not only allows an extremely low amount of Mo diffusing across the defect site to be involved in the reaction, but also ensures an effective reaction to form the high-quality 2D Mo$_2$GaC crystals with few defects and high phase purity.

Because the as-formed Mo$_2$GaC crystals are highly related to the Ga$_2$O$_3$ molecular scaffold, the thickness of Mo$_2$GaC crystals can be tuned by adjusting the thickness of the Ga$_2$O$_3$ layer. The Ga$_2$O$_3$ layers with different thickness are obtained by altering the duration of preoxidization of the liquid Ga. We conducted the preoxidization process at a temperature of 50°C for different durations and subsequently performed the growth process under the same conditions. The thickness of the oxide layer was identified by detecting the signal of O1s peak using an XPS depth analysis (Supplementary Figure S5). The statistics of the relationship between etching duration and the peroxidation duration is also given in the supplementary information (Supplementary Figure S6). When the preoxidization duration was increased to 10 min, the Ga$_2$O$_3$ layer stopped growing, verifying the self-passivation behavior of Ga. The relationship between the thickness of the as-derived Mo$_2$GaC and the peroxidation duration also demonstrated the self-passivating growth behavior (Supplementary Figure S7).

The as-grown crystals were initially examined using a scanning electron microscopy (SEM) as shown in Figure 2a. Large-scale distributed Mo$_2$GaC crystals with lateral sizes of over 10 $\mu$m can be successfully obtained from our designed molecular scaffold synthesis approach. Figure 2b shows the typical circular shape of the Mo$_2$GaC crystals due to the growth happening on an isotropic liquid growth substrate.\textsuperscript{42} Figure 2c shows the corresponding atomic force microscope (AFM) image. The thickness of the flake is around 2.2 nm, which is consistent with the value of the Mo$_2$GaC unit cell. In addition, XPS spectra of the as-synthesized Mo$_2$GaC crystals that were transferred onto 300 nm SiO$_2$/Si were collected to confirm the chemical composition of the as-obtained ultrathin crystal. Figure 2d shows a typical
XPS spectrum of the Mo 3d edge, which exhibits the primary spin-orbital components 3d5/2 and 3d3/2 located at 227.9 and 231.1 eV, respectively. The Ga 3p3/2 and 3p1/2 components show dominant peaks at the binding energies of 104.0 and 107.1 eV, respectively (Figure 2e). Ga2O3 is also indicated by shoulder peaks at the high binding energy side of the Ga 3p1/2 peak, which we attribute to an unreacted ultrathin Ga2O3 molecular scaffold. The characteristic carbide carbon peak from a Mo2GaC crystal is observed at 283.3 eV, as shown in Figure 2f. A C 1s peak at 284.8 eV is also observed, which probably originates from carbon adsorbates from the atmosphere. All these peaks are in accordance with the literature.43,44 In addition, the AES mapping further confirms the uniform elemental distribution from an individual Mo2GaC (Supplementary Figure S8).

Characterization of 2D, strong interlayer-bonding Mo2GaC single crystals

High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), energy-dispersive spectrometry (EDS), and electron diffraction were used to evaluate the quality and crystal structure of these ultrathin Mo2GaC crystals.

Figure 3a shows a low-magnification TEM image of a Mo2GaC crystal. We recorded the selected area electron diffraction (SAED) pattern and convergent beam electron diffraction (CBED) pattern. The inset in Figure 3a shows the SAED pattern and the derived in-plane lattice parameters of the crystal, a and b are equal and their value is about 2.97 Å. The lattice parameter c is derived from the CBED pattern (Figure 3b) and its value is 13.18 Å, according to the equation, $r^2 + (\lambda - 1 - c)^2 = \lambda^2$, where $\lambda = 0.00197$ nm is the electron wavelength in a 300 kV TEM, and $r = 27.78$ nm is the radius of the first-order Laue ring. These lattice parameters are consistent with those of a hexagonal Mo2GaC crystal. The EDS spectrum extracted from the crystal indicates that the crystal was composed of Mo, Ga, and C with an atomic ratio of $\sim 2:1:1$, as seen in Figure 3c.

The aberration-corrected atomic resolution, high-angle, annular dark-field STEM (HAADF-STEM) image further reveals the atomic structure of the 2D, strong interlayer-bonding Mo2GaC single crystal. Mo2GaC is a typical superconducting MAX phase with two formula units per unit cell.45 In this compound, the hexagonal close-packed lattice is formed by six Mo atoms. The C and Mo atoms form an orthorhombic structure [Mo6C], with C atoms located at the octahedral sites surrounded by six Mo atoms. It is worth noting that the contrast between Ga and Mo sites is not obvious because there
are always two Mo atoms overlapping with one Ga atom, which makes the intensity of six atoms around C atoms similar in intensity within the STEM image. C atoms are not visible due to their low element number compared with surrounded heavier atoms of Ga and Mo in the crystal. Here, the simulated Mo$\textsubscript{2}$GaC structure is consistent with the experimental results. It is assumed that the electron beam irradiates the crystal from the Ga atom side, as shown in Figure 3f. Details of the image simulation are shown in the supplementary information (Supplementary Figure S9). The line scanning profiles taken directly from the experimental (solid green line) and simulated (brown dashed line) images are in good agreement. In addition, the near close-packed Mo atoms are interleaved with a single layer of pure Ga element. Figure 3g shows a high-magnification HAADF-STEM atomically resolved cross-section view of the flakes. The inset shows the SAED pattern. Figure 3h shows the cross-sectional structure of the lamella. The inset corresponds to the atomic structure models indicating the aligning positions of the Ga, Mo, and C atoms in the stacking sequence. Figure 3i Schematic of the unit cell of a Mo$\textsubscript{2}$GaC crystal.
consistent with the analysis described previously. The STEM image in Figure 3h acquired at a higher magnification clearly shows the sequential ordering of the close-packed layers, which agrees well with the simulated structure shown in Figure 3h. To validate the single crystal structure, a series of SAED patterns were acquired from different sample regions, and all of them showed the same sixfold symmetry with a consistent orientation (Supplementary Figure S10). Moreover, EDS mapping shows C–K, Mo–L, and Ga–L signals, indicating that the crystal is comprised of uniformly distributed C, Mo, and Ga (Supplementary Figure S10).

**Superconductivity of 2D, strong interlayer-bonding Mo$_2$GaC single crystals**

The high-quality ultrathin Mo$_2$GaC crystals provide an ideal system to probe the intrinsic transport properties in the 2D limit. In this work, a four terminal device was fabricated based on a Mo$_2$GaC single crystal with a thickness of 12.4 nm for superconducting property measurements, as shown in Supplementary Figure S11. The collected normalized resistance versus temperature $R/R_{\text{in}}(T)$ curve in the superconducting transition regime is shown in Figure 4a. The resistance displays a decline at 4.06 K and decreases to zero at 3.1 K. This provides convincing evidence for the existence of superconductivity. The transport properties of Mo$_2$GaC single crystals with different thicknesses are also exhibited. When the thickness is down to 11.2 or 8.9 nm, the superconductive transitions can still be observed and the corresponding transition temperatures ($T_c$) are 2.75 and 2.33 K, respectively.

To clarify why the superconducting $T_c$ decreases with the thickness, first principles calculations of electron-phonon coupling for the ultrathin film and the bulk phases have been conducted according to the Allen-Dynes formula, which is modified from BCS theory. Based on the experimentally observed Mo-terminated surface of the thin Mo$_2$GaC single crystal, an ultrathin film with a minimal thickness represented by a seven atomic-layer MoCMo–Ga–MoCMo slab model was studied and compared with the bulk phase. According to the calculations, $T_c$ will decrease with the thickness of the Mo$_2$GaC due to the weaker electron-phonon coupling in the slab, which can be attributed to the Ga deficiency and structural relaxation within the slab. The slab is Ga deficient compared with the bulk because it is terminated by Mo$_2$C at both the front and the back surfaces. Compared with the strong Mo–C bonds, Ga is weakly bonded to the adjacent Mo$_2$C layers. As such, the Ga-related phonons are soft. The reduction in Ga-related soft phonons in the Ga-deficient Mo-terminated slab contributes strongly to the reduction of the electron-phonon coupling and the $T_c$ in the slab. Further analyses of the structures of the bulk and the slab reveal that the Mo–C bond length on the surfaces of the slab (2.08 Å) is shorter than that in the bulk (2.12 Å) as a result of the relaxation of the surfaces and the in-plane crystal lattice. From the SAED patterns (the inset of Figure 3a,g), we can derive the in-plane lattice constant to be 2.97 Å, which is close to the calculated value (3.03 Å) corresponding to the 2D Mo$_2$GaC. This leads to stronger Mo-related phonons, which contribute to the weaker electron-phonon coupling in the slab. The Ga deficiency and the enhanced Mo–C bonding on the surface of the slab and their influence on the electron-phonon coupling should become less significant with increasing film thickness. The detailed calculations are shown in Supplementary Figures S12–S15. The foregoing analysis also suggests that it should be possible to raise the superconducting $T_c$ substantially by terminating the structure with a Ga end layer, which would induce soft Ga-related phonons and thereby more Eliashberg spectral weight at low energy, raising the electron-phonon coupling constant $\lambda$.

Temperature-dependent resistance under different magnetic fields with the direction perpendicular to the crystal surface was also probed. As shown in Supplementary Figure S16, the transition temperature would drop as the applied magnetic field increases and the superconducting transition region broadens. When the magnetic field increases to 0.5 T, the superconducting transition behavior disappears. To reveal the dimensionality of the intrinsic superconductivity in our crystals, the relationship between the superconducting transition and the angle of the applied magnetic field on the crystals is further investigated.

We recorded the upper critical field for superconductivity ($H_{c2}$) at selected angles ($\theta$) at 1.9 K for a 12.4 nm thick Mo$_2$GaC crystal, where $\theta$ is the angle between the crystal plane and the applied magnetic field, as indicated in the inset of Figure 4c. As shown in Supplementary Figure S17, the superconductivity transition shifts to higher fields with a decreasing angle. When the rotated magnetic field direction is parallel to the sample plane ($\theta = 0^\circ$), $H_{c2}$ is obviously enhanced, from which the existence of strong anisotropy is confirmed.

Furthermore, the Ginzburg–Landau (GL) coherence length ($\xi_{\text{GL}}$) and effective superconducting thickness ($d_{\text{SC}}$) of the Mo$_2$GaC crystals can be used to analyze the character of the 2D superconductor. They can be derived from the temperature-dependent upper critical fields in the directions perpendicular ($H_{c2}$) and parallel to the plane. The superconducting critical transition field in the perpendicular direction or in the parallel direction under different temperatures ($H_{c2}$) (which is defined as the field at which the resistance drops to 10% of the normal state value just above the onset) is extracted from the magnetic-field-dependent resistance characteristics at different temperatures (Supplementary Figures S18 and S19). The corresponding temperature-dependent upper
Critical field \( (H_{c2}(T)) \) values are provided in Figure 4b. For the perpendicular magnetic field condition, \( H_{c2,\perp} \) a linear dependence to \( T \) is observed, which is in agreement with the standard linearized GL theory for 2D superconductors:

\[
H_{c2,\perp}(T) = \frac{\Phi_0}{2\pi\xi_{GL}(T)} \left(1 - \frac{T}{T_c}\right)
\]

where \( \Phi_0 \) is the magnetic flux quantum and \( \xi_{GL}(T) \) is the GL in-plane coherence length at a temperature of 0 K. The value of \( \xi_{GL}(T) \) is calculated to be 18.0 ± 0.3 nm from the fitted curve of \( H_{c2,\perp}(T) \), whereas for the parallel field condition, the temperature-dependent \( H_{c2,\parallel} \) relationship fits the following formula

\[
H_{c2,\parallel}(T) = \frac{\Phi_0 \sqrt{12}}{2\pi\xi_{GL}(0)d_{SC}} \left(1 - \frac{T}{T_c}\right)^{1/2}
\]

where \( d_{SC} \) is the effective superconducting thickness. The value of \( d_{SC} \) is extracted to be 12.4 ± 0.1 nm from the analysis and fittings of \( (T) \) curve. Notably, this value is in excellent agreement with the measured thickness of our test sample. The value of \( d_{SC} \) is smaller than that of \( \xi_{GL}(0) \), demonstrating good agreement with 2D superconducting behavior. Moreover, the function relationship between \( H_{c2}(\theta) \) and \( \theta \) at a temperature of 1.9 K is described in Figure 4c. When the applied field is parallel to the crystal surface, the upper critical field exhibits a maximum. Careful fitting of the \( H_{c2}(\theta) \) data is consistent with the Tinkham formula, namely,

\[
\frac{|H_{c2}(\theta)\sin\theta|}{H_{c2,\perp}} + \left(\frac{H_{c2}(\theta)\cos\theta}{H_{c2,\parallel}}\right)^2 = 1
\]

The corresponding fit (red dashed line in Figure 4c) matches well, which further confirms the 2D superconducting nature of the systems (\( d_{SC} < \xi \)).
Current–voltage (I–V) measurements in the superconducting transition region were also conducted so as to explore the superconductivity in 2D Mo2GaC crystals. The I–V curves were implemented at temperatures ranging from 1.9 to 5.0 K as shown in Figure 4d (log–log scale). The relationship between the measured V and I values exhibits a power-law dependence, that is, \( V \propto I^\alpha \). As the temperature decreases, the expected relationship is increasingly non-linear, which follows the theoretical model of the BKT transition for a 2D superconductor. At a high temperature, ohmic behavior is clearly observed, as seen from the blue dashed line in Figure 4d. As plotted in Figure 4e, the temperature-dependent exponent \( \alpha \) monotonously grows and increases rapidly below 2.9 K. It is noteworthy that when the exponent \( \alpha \) ascends to a value of 3 (\( V \propto I^3 \), as the solid blue line describes), we can deem the temperature of 2.93 K as the BKT transition temperature (\( T_{\text{BKT}} \)), below which a phase transition leading to a 2D topological order occurs.51–53 When the temperature reaches a value just above \( T_{\text{BKT}} \), the temperature dependence of the resistance \( R(T) \) can be described as the following:

\[
R = R_0 \exp(-bt^{1/2})
\]

where the relevant \( R_0 \) and \( b \) are regarded as the material parameters with respect to 2D superconductors and \( t = T/T_{\text{BKT}} - 1 \) is the declined temperature.55–57 As shown in Figure 4f, the fitted \( T_{\text{BKT}} \) is 2.87 K from the BKT equation, which is consistent with the data derived from the \( V(t) \) curves. Thus, our analysis on BKT transitions in atomically thin Mo2GaC crystals provides strong evidence for the 2D nature of the observed superconductivity.

In summary, for the first time, the bottom-up synthesis of high-quality 2D SLMs single crystals via the precise design of a molecular scaffold has been achieved with 2D Mo2GaC, which is a typical kind of MAX phase as an example. Various elemental and structural characterizations confirm its formation. In addition, the superconducting transitions of Mo2GaC at the 2D limit are clearly observed, which is consistent with BKT behavior. Moreover, the influence of anisotropy and thickness of the 2D single crystal on its superconducting transition was also systematically studied. We believe the presented work on ultrathin MAX phases will open up new developments for the 2D SLMs family. In addition, the presented molecular scaffold design is suitable for the synthesis of other new 2D materials far beyond current traditional 2D materials.

**Methods**

**Molecular scaffold growth of 2D, strong interlayer-bonding Mo2GaC single crystals**

A commercial Ga pellet was divided into small droplets in hot ethanol and then frozen into tiny Ga balls. The Mo foils were ultrasonicated and rinsed with acetone, ethanol, and deionized water before being dried under a nitrogen (N2) stream. The Ga pellets with a purity of 99.999 wt % and the Mo foils with a purity of 99.95 wt % were purchased from Alfa Aesar China (Tianjin Co. Ltd.) and Shanghai Minor Metals Co. Ltd. A Ga (25–30 mg) was placed on a Mo foil (cut into 1 x 1 cm squares) and then melted on a heating stage at 50°C for different times, in an ambient atmosphere, leading to the formation of a superficial oxidized layer with different thickness. The growth of 2D, strong interlayer-bonding Mo2GaC single crystals was performed in a quartz tube furnace (HTF 55322C Lindberg/Blue M) under ambient pressure. The growth process consisted of the following four steps: (1) placing the Ga–Mo substrates in the center region of the quartz tube; (2) heating the Ga–Mo substrates to 1000°C at a rate of 30°C/min under the flow of Ar and H2; (3) exposing the substrates to a carbon source at 1000°C for 20 min under 300 sccm Ar and 1 sccm CH4; and (4) turning off the CH4 and cooling the substrates to room temperature rapidly under Ar. Notably, the original amorphous or poorly crystallized oxidized layer formed at room temperature can be transformed into a crystalline \( \beta \)-Ga2O3 layer at a temperature above 300°C, which provides a molecular scaffold to construct the Mo2GaC crystals with unit cell thickness.

**Transport measurements**

The transport measurements were performed in a standard four-terminal configuration from room temperature to 1.85 K with a physical property measurement system (Quantum Design). The magnetic field was always applied perpendicular to the 2D Mo2GaC crystal plane.
except for the angular-dependence measurements of the anisotropic superconducting transition.

**Characterization**

The X-ray diffraction characterizations were taken with a Rigaku MiniFlex600. SEM images were obtained on a Hitachi-S4800 and a ZEISS Merlin Compact SEM. The XPS measurements were conducted using a Thermo Scientific ESCALAB 250Xi. The measuring spot size was 500 μm, and the binding energies were calibrated by referencing the C 1s peak (284.8 eV). The XPS depth profiling was performed by Ar ionic bombardment to gradually remove the surface layers. The AFM images were taken with a NT-MDT Ntegra Spectra with samples transferred onto the 300 nm SiO2/Si. The AES was performed using a PHI-700 system in an ultrahigh vacuum system under a base pressure below 3.9×10−9 Torr. The HRTEM images, SAED measurements, and EDS measurements were conducted by an aberration-corrected high-resolution TEM system (FEI Titan 3, Zeiss Libra 200 MC) using an operating voltage of 80 kV. CBED measurement was conducted at an operating voltage of 300 kV. A Nion UltraSTEM 100 operated at 60 kV and equipped with a probe spherical aberration corrector was used to acquire HAADF-STEM images along the c axis. The samples were transferred onto a copper TEM grid for characterization.

**Calculation**

Quantum-Espresso package was employed for the electron-phonon coupling calculations using a linear-response density functional theory. Norm-converging pseudopotentials generated with PHI98PP code from the Quantum Espresso website were adopted, and semiconductor states of Mo and Ga were also included in this version of pseudopotentials. The Perdew–Burke–Ernzerhof functional was used to approximate the exchange-correlation functional. A kinetic energy-off of 80 Ry were used for wave function expansion with plane-wave basis. K-meshes of 1×16×8 and 16×16×1 were used for the bulk and the slab, respectively, in electronic calculations. Q-mesh of 4×4×1 was used in phonon calculations. The formula for the electron-phonon calculation is as follows:

\[ \alpha^2 F(\omega) = \frac{1}{N(\omega)} \sum_{q} \frac{g_{n,m,n'}^{q}}{2} \delta(\omega - \omega_{n,m}) \times \sum_{k/m/n} \delta(\omega - \omega_{k/m/n}) \]

\[ \lambda(\omega) = \frac{2}{\omega} \int_{0}^{\omega} \frac{\alpha^2 F(\omega)}{\omega} \, d\omega' \]

\[ \omega_{\log} = \exp \left[ \frac{2}{\lambda} \int_{0}^{\omega_{\max}} \alpha^2 F(\omega) \, d\omega \right] \]

Here, \( N_{\omega} \) and \( N_{m} \) are the total number of \( q \) and \( k \) points used. \( g_{n,m,n'}^{q} \) is the electron-phonon interaction matrix element, and \( m \) and \( n \) are electron band indexes.

**Conflicts of Interest**

The authors declare no competing financial interests.

**Supporting Information**

Supporting information is available.

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**References**

1. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, *438*, 197–200.

2. Zhang, Y.; Tan, Y. W.; Stormer, H. L.; Kim, P. Experimental Observation of the Quantum Hall Effect and Berry’s Phase in Graphene. *Nature* **2005**, *438*, 201–204.

3. Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.

4. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

5. Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun’ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite. *Nat. Nanotechnol.* **2008**, *3*, 563–568.

6. Paton, K. R.; Varrella, E.; Backes, C.; Smith, R. J.; Khan, U.; O’Neill, A.; Boland, C.; Lotya, M.; Istrate, O. M.; King, P.; Higgins, T.; Barwich, S.; May, P.; Puczkar, P.; Ahmad, I.; Moebius, M.; Pettersson, H.; Long, E.; Coelho, J.; O’Brien, S. E.; McGuire, E. K.; Sanchez, B. M.; Duesberg, G. S.; McEvoy, N.; Pennycook, T. J.; Downing, C.; Crossley, A.; Nicolosi, V.; Coleman, J. N. Scalable Production of Large Quantities of
Defect-Free Few-Layer Graphene by Shear Exfoliation in Liquids. Nat. Mater. 2014, 13, 624–630.

7. Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L. J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. Nat. Chem. 2013, 5, 263–275.

8. Cunningham, G.; Lotya, M.; Cucinotta, C. S.; Sanvito, S.; Bergin, S. D.; Menzel, R.; Shaffer, M. S.; Coleman, J. N. Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. ACS Nano 2012, 6, 3468–3480.

9. Tongay, S.; Sahin, H.; Ko, C.; Luce, A.; Fan, W.; Liu, K.; Zhou, J.; Huang, Y.-S.; Ho, C.-H.; Yan, J.; Ogletree, D. F.; Aloni, S.; Ji, J.; Li, S.; Li, J.; Peeters, F. M.; Wu, J. Monolayer Behaviour in Bulk ReS2 Due to Electronic and Vibrational Decoupling. Nat. Commun. 2014, 5, 3252.

10. Zhao, Y.; Qiao, J.; Yu, Z.; Yu, P.; Xu, K.; Lau, S. P.; Zhou, W.; Liu, Z.; Wang, X.; Ji, W.; Chai, Y. High-Electron-Mobility and Air-Stable 2D Layered PTSe2 FETs. Adv. Mater. 2017, 29, 1604230.

11. Al Balushi, Z. Y.; Wang, K.; Ghosh, R. K.; Vila, R. A.; Eichfeld, S. M.; Caldwell, J. D.; Qin, X.; Lin, Y. C.; DeSario, P. A.; Stone, G.; Subramanian, S.; Paul, D. F.; Wallace, R. M.; Datta, S.; Redwing, J. M.; Robinson, J. A. Two-Dimensional Gallium Nitride Realized through Graphene Encapsulation. Nat. Mater. 2016, 15, 1166–1171.

12. Wang, F.; Wang, Z.; Shifa, T. A.; Wen, Y.; Wang, F.; Zhan, X.; Wang, Q.; Xu, K.; Huang, Y.; Yin, L.; Jiang, C.; He, J. Two-Dimensional Non-Layered Materials: Synthesis, Properties and Applications. Adv. Funct. Mater. 2017, 27, 1603254.

13. Yin, H.; Zhao, S.; Zhao, K.; Muqits, A.; Tang, H.; Chang, L.; Zhao, H.; Gao, Y.; Tang, Z. Ultrathin Platinum Nanowires Grown on Single-Layered Nickel Hydroxide with High Hydrogen Evolution Activity. Nat. Commun. 2015, 6, 6430.

14. Zhao, S.; Wang, Y.; Dong, J.; He, C.-T.; Yin, H.; An, P.; Zhao, K.; Zhang, X.; Gao, C.; Zhang, L.; Lv, J.; Wang, J.; Zhang, J.; Khattak, A. M.; Khan, N. A.; Wei, Z.; Zhang, J.; Liu, S.; Zhao, H.; Tang, Z. Ultrathin Metal–Organic Framework Nanosheets for Electrocatalytic Oxygen Evolution. Nat. Energy 2016, 1, 16184.

15. Guo, J.; Zhang, Y.; Zhu, Y.; Long, C.; Zhao, M.; He, M.; Zhang, X.; Lv, J.; Han, B.; Tang, Z. Ultrathin Chiral Metal–Organic-Framework Nanosheets for Efficient Enantioselective Separation. Angew. Chem. Int. Ed. 2018, 57, 6873–6877.

16. Eklund, P.; Beckers, M.; Jansson, U.; Högborg, H.; Hultman, L. The Mn+1xsXn Phases: Materials Science and Thin-film Processing. Thin Solid Films 2010, 518, 1851–1878.

17. Sun, Z. M. Progress in Research and Development on Max Phases: A Family of Layered Ternary Compounds. Int. Mater. Rev. 2013, 56, 143–166.

18. Dahlqvist, M.; Lu, J.; Meshkian, R.; Tao, Q.; Hultman, L.; Rosen, J. Prediction and Synthesis of a Family of Atomic Lamine Phases with Kagome-Like and in-Plane Chemical Ordering. Sci. Adv. 2017, 3, e1700642.

19. Barsoum, M. W. The M$_{68}$M$_{3}$Sc$_{2}$ Phases: A New Class of Solids. Prog. Solid State Chem. 2000, 28, 201–281.
34. Palmquist, J. P.; Li, S.; Persson, P. O. A.; Emmerich, J.; Wilhelmsson, O.; Hogberg, H.; Katsnelson, M. I.; Johansson, B.; Ahuja, R.; Eriksson, O.; Hultman, L.; Jansson, U. Mnn,Axn Phases in the Ti-Si-C System Studied by Thin-Film Synthesis and ab Initio Calculations. Phys. Rev. B 2004, 70, 165401.

35. Phani, A.; Krzanowski, J. E.; Nainaparampil, J. Structural and Mechanical Properties of TiC and Ti-Si-C Films Deposited by Pulsed Laser Deposition. J. Vac. Sci. Technol. A 2001, 19, 2252–2258.

36. Hu, J.; Bultman, J.; Patton, S.; Zabinski, J. Pulsed Laser Deposition and Properties of Mn

37. Saito, Y.; Nojima, T.; Iwasa, Y. Highly Crystalline 2D Superconductors. Nat. Rev. Mater. 2016, 2, 16094.

38. Plech, A.; Klemradt, U.; Metzger, H.; Peisl, J. In Situ X-ray Reflectivity Study of the Oxidation Kinetics of Liquid Gallium and the Liquid Alloy Ga0.93Hg0.07. J. Phys.: Condens. Matter 1998, 10, 971.

39. Downs, A.J. (Ed.). Chemistry of Aluminium, Gallium, Indium and Thallium. Springer Netherlands: Berlin, 2009.

40. Regan, M. J.; Tostmann, H.; Pershan, P. S.; Magnusson, O. M.; DiMasi, E.; Ocko, B. M.; Deutsch, M. X-ray Study of the Oxidation of Liquid-Gallium Surfaces. Phys. Rev. B 1997, 55, 10786–10790.

41. Toth, L. High Superconducting Transition Temperatures in the Molybdenum Carbide Family of Compounds. J. Less-Common Met. 1967, 13, 129–131.

42. Zeng, M.; Tan, L.; Wang, L.; Mendes, R. G.; Qin, Z.; Huang, Y.; Zhang, T.; Fang, L.; Zhang, Y.; Yue, S.; Rummeli, M. H.; Peng, L.; Liu, Z.; Chen, S.; Fu, L. Isotropic Growth of Graphene toward Smoothing Stitching. ACS Nano 2016, 10, 7189–7196.

43. Lai, C. C.; Meshkian, R.; Dahlqvist, M.; Lu, J.; Nåslund, L. Å.; Rivin, O.; Caspi, E. N.; Ozeri, O.; Hultman, L.; Eklund, P.; Barsoum, M. W.; Rosen, J. Structural and Chemical Determination of the New Nanolaminated Carbide Mo2Ga2Cf from First Principles and Materials Analysis. Acta Mater. 2015, 99, 157–164.

44. Zeng, M.; Chen, Y.; Li, J.; Xue, H.; Mendes, R. G.; Liu, J.; Zhang, T.; Rümmeli, M. H.; Fu, L. 2D WC Single Crystal Embedded in Graphene for Enhancing Hydrogen Evolution Reaction. Nano Energy 2017, 33, 356–362.

45. Jeitschko, W.; Nowotny, H. T.; Benesovsky, F. Carbides of Formula T2MC. J. Less-Common Metals 1967, 7, 133–138.

46. Allen, P. B.; Dynes, R. C. Transition Temperature of Strong-Coupled Superconductors Reanalyzed. Phys. Rev. B 1975, 12, 905–922.

47. Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. Theory of Superconductivity. Phys. Rev. 1957, 108, 1175–1204.

48. Kozuka, Y.; Kim, M.; Bell, C.; Kim, B. G.; Hikita, Y.; Hwang, H. Two-Dimensional Normal-State Quantum Oscillations in a Superconducting Heterostructure. Nature 2009, 462, 487–490.

49. Reyren, N.; Garigli, S.; Caviglia, A.; Jaccard, D.; Schneider, T.; Triscone, J.-M. Anisotropy of the Superconducting Transport Properties of the LaAlO3/SrTiO3 Interface. Appl. Phys. Lett. 2009, 94, 112506.

50. Tinkham, M. Introduction to Superconductivity. McGraw-Hill Incorporation: North Chelmsford, Massachusetts, 1996.

51. Reyren, N.; Thiel, S.; Caviglia, A.; Kourkoutis, L. F.; Hammerl, G.; Richter, C.; Schneider, C.; Kopf, T.; Rüetschi, A.-S.; Jaccard, D. Superconducting Interfaces between Insulating Oxides. Science 2007, 317, 1196–1199.

52. Yuli, O.; Asulin, I.; Millo, O.; Orgad, D.; Iomin, L.; Koren, G. Enhancement of the Superconducting Transition Temperature of La2–x Srx Cuo 4 Bilayers: Role of Pairing and Phase Stiffness. Phys. Rev. Lett. 2008, 101, 057005.

53. Kosterlitz, J. M.; Thouless, D. J. Ordering, Metastability and Phase Transitions in Two-Dimensional Systems. J. Phys. C: Solid State Phys. 1973, 6, 1181.

54. Kosterlitz, J. The Critical Properties of the Two-Dimensional XY Model. J. Phys. C: Solid State Phys. 1974, 7, 1046.

55. Halperin, B.; Nelson, D. R. Resistive Transition in Superconducting Films. J. Low Temp. Phys. 1979, 36, 599–616.

56. He, Q. L.; Liu, H.; He, M.; Lai, Y. H.; He, H.; Wang, G.; Law, K. T.; Lortz, R.; Wang, J.; Sou, I. K. Two-Dimensional Superconductivity at the Interface of a B2–x Te2/FeTe Heterostructure. Nat. Commun. 2014, 5, 4247.

57. Xu, C.; Wang, L.; Liu, Z.; Chen, L.; Guo, J.; Kang, N.; Ma, X.-L.; Cheng, H.-M.; Ren, W. Large-Area High-Quality 2D Ultrathin Mo2C Superconducting Crystals. Nat. Mater. 2015, 14, 1135–1141.

58. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Scandolo, S.; Scalmani, G.; Seidl, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Venturelli, G.; Wentzcovitch, R. M. Quantum Espresso: A Modular and Open-Source Software Project for Quantum Simulations of Materials. J. Phys.: Condens. Matter 2009, 21, 395502.

59. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1997, 78, 1396–1396.