Controlled growth of ultrathin ferromagnetic $\beta$-MnSe semiconductor

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Abstract
Two-dimensional (2D) magnetic crystals with intrinsic ferromagnetism are highly desirable for novel spin-electronic devices. However, the controllable synthesis of 2D magnets, especially the direct growth of 2D magnets on substrate surfaces, is still a challenge. Here, we demonstrate the synthesis of ultrathin zinc-blende phase manganese selenide ($\beta$-MnSe) nanosheets using the chemical vapor deposition (CVD) technique. The 2D $\beta$-MnSe crystals exhibit distinct ferromagnetic properties with a Curie temperature of 42.3 K. Density functional theory (DFT) calculations suggest that the ferromagnetic order in $\beta$-MnSe originates from the exchange coupling between the unsaturated Se and Mn atoms. This study presents significant progress in the CVD growth of ultrathin 2D magnetic materials by thinning bulk magnets, and it will pave the way for the building of energy-efficient spintronic devices in the future.

KEYWORDS
2D ferromagnetism, controllable growth, manganese selenide, morphological engineering, nonlayered crystals

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1 | INTRODUCTION

Two-dimensional (2D) materials have drawn substantial attention because of their outstanding physical properties, including superconductivity,\(^1\) valley polarization,\(^2\) quantum spin Hall effect,\(^3\) and so on.\(^4,5\) Magnetism was initially absent from specifications until the latest discovery of long-range magnetic order in 2D Van der Waals (VdW) crystals.\(^6,7\) These 2D magnetic crystals possess different bandgaps, vary from insulator to conductor, and can be applied in diverse devices.\(^8\) 2D ferromagnetic order was first discovered in 2D insulators Cr\(_2\)Ge\(_2\)Te\(_6\) and Cr\(_i\) at low temperatures.\(^9,10\) And a high tunneling magnetoresistance ratio of 19000\% was realized in Cr\(_i\) nanosheets.\(^11\) Then, 2D magnetic conductor Fe\(_2\)GeTe\(_2\) was successfully synthesized and its Curie temperature was raised to room temperature through ionic gating.\(^12\) 2D magnetic semiconductors are more valuable and become a good platform for spintronics and magnonics.\(^13,14\) For example, the 2D magnetic semiconductor CrBr\(_3\) shows an out-of-plane magnetic anisotropy, which has potential applications in novel optoelectronic and spintronic devices.\(^15\) At present, only a few 2D magnetic semiconductors have been successfully synthesized. To enrich this material system, many efforts have been put in searching for novel 2D magnetic material or attenuating traditional bulk magnetic semiconductors to form their 2D congeners.

Mn-based chalcogenides are excellent magnetic semiconductors in terms of their intrinsic magnetism and optical functions.\(^16,17\) They are not only wide optical-bandgap semiconductors but also possess diverse magnetism, for example, antiferromagnetism,\(^18\) ferromagnetism,\(^19\) and paramagnetism.\(^20\) In particular, manganese selenide (MnSe) exhibits distinct magnetic behaviors with different crystal structures: antiferromagnetism in stable rock-salt MnSe,\(^21\) ferromagnetism in tetrahedrally coordinate metastable zinc-blend and wurtzite MnSe.\(^22\) Such a magnetic system has attracted much attention, and many synthesis techniques, for example, hydrothermal, solvothermal, thermolysis, and spray-produced processes have been used to engineer the magnetic order by controlling the crystal configuration.\(^23\) However, there are few reports on the synthesis of high-quality 2D MnSe nanosheets because its nonlayered crystal structure. So far, 2D nonlayered magnetic Cr\(_2\)S\(_3\) and CrSe nanoflakes with thickness down to 4.8 and 2.5 nm have been epitaxially grown on mica substrates in an ambient pressure chemical vapor deposition (CVD) system,\(^24,25\) showing the remarkable potential of CVD to reduce the thickness of nonlayered materials and thus to grow their 2D congeners. However, the growth mechanism of these nonlayered 2D magnetic materials and the feasibility of the CVD method have yet to be well explored and examined.

In this study, we demonstrate the epitaxial growth of ultrathin nonlayered ferromagnetic zinc-blend MnSe (β-MnSe) semiconductors through the CVD method. Structural and componental analyses were carried out to characterize the quality of β-MnSe flakes. The growth mechanism was analyzed based on the orientation and morphological evolution of β-MnSe flakes. Magnetic properties of the β-MnSe were characterized to reveal its ferromagnetism. Our work provides a feasible way to synthesize various 2D magnetic materials by VdW epitaxy, which could be a significant leap toward the development of future spin-electronic devices.
2 | EXPERIMENTAL SECTION

2.1 | Growth of atomically thin \( \beta - \text{MnSe} \) crystals

A three-zone furnace (Thermcraft XST-3-0-18-2V2) equipped with a 2-inch quartz tube was used to grow the 2D \( \beta - \text{MnSe} \) crystals through an ambient pressure CVD method. Se powder (200 mg, 99.997%, Sigma Aldrich) loaded in an alumina boat was put in the third heating zone. The mica substrate was placed downstream (about 5 cm away from MnCl\(_2\)) and faced down. Before the growth process, the tube was purged with high-purity Ar at a rate of 300 sccm for 5 min. During the growth process, 100 sccm Ar and 10–40 sccm H\(_2\) were introduced into the CVD system. Se powder and MnCl\(_2\) were heated up to 300 °C and 680 °C in 20 min and kept for 10 min to finish the growth of \( \beta - \text{MnSe} \) flakes. After that, the furnace was rapidly cooled down to room temperature with the assistance of electric fans.

2.2 | Characterization

The as-obtained \( \beta - \text{MnSe} \) crystals were characterized by optical microscopy (Olympus BX53M), Raman spectra (WITEC alpha 300 R Confocal Raman system with a 532 nm laser excitation), atomic force microscope (AFM) (Asylum Research Cypher Scanning Probe Microscope system), X-ray photoelectron spectroscopy (XPS) (Kratos AXIS Supra spectrometer with a monochromatic Al K-alpha source). The cathodoluminescence (CL) measurements were performed in a scanning electron microscope equipped with a CL detection system (Attolight Allalin 4027 Chronos) using the following parameters: electron energy \( = 5 \) keV, beam current \( \approx 36 \) nA, and dwell time \( = 10 – 50 \) ms. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was conducted on an aberration-corrected TEM (JEOL ARM-200F) equipped with a cold field emission gun operated at 80 kV and a probe corrector (Advanced STEM Corrector, ASCOR). Magnetic properties were characterized by a superconducting quantum interference device (SQUID, Quantum Design). The MnSe crystals were transferred from mica onto a sapphire substrate because mica has a relatively high diamagnetic background signal.

2.3 | Computational details

Density functional theory (DFT) computations were carried out with the Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) method was used for wave functions. The Mn-3d, Mn-4s, Se-4s, and Se-4p electrons were treated as the valence electrons, and the local spin density approximation (LSDA) + U method was employed through the computations. The spin-orbit coupling (SOC) correction was also involved. The energy cutoff for the plane-wave basis set was chosen as 550 eV, and the systemic energy tolerance and the remaining total force were set as \( 1 \times 10^{-5} \) eV and 0.02 eV/Å, respectively. The Brillouin zone was sampled with a \( 9 \times 9 \times 9 \) \( (9 \times 9 \times 1) \) \( k \)-mesh grid via Monkhorst-Pack method for geometry optimization of bulk (slab), and a denser \( k \)-mesh of \( 15 \times 15 \times 15 \) \( (15 \times 15 \times 1) \) for computations of magnetic properties. The LSDA + U method yielded \( \beta - \text{MnSe} \) bulk with a space group of \( \text{F} \ 4 \ 3 \ m \) and a lattice parameter of 5.84 Å, agreeing well with the experimental measurements and previous theoretical results. Considering the symmetry in the configuration of the \( \beta - \text{MnSe} \) bulk, the corresponding (100), (110), and (111) slabs were examined. To simplify the slab structures and save the computational consumption of resources, each slab consisting of three MnSe sublayers, and only the top sublayer was relaxed during structural optimization, the lower two sublayers were fixed with the bottom saturated hydrogen as the bulk structure (Figure S1). Compared with the Se-terminated (110) and (111) slabs, the Mn-terminated ones were more stable \((\sim 1 \text{ eV per surface MnSe unit lower in energy})\). The Mn-terminated (110) slab [(110)-Mn] had the lowest formation energy, followed by the Mn-terminated (111) slab [(111)-Mn] among the five examined surfaces (Table S1).

3 | RESULTS AND DISCUSSION

Figure 1A demonstrates our simple strategy to grow two-dimensional \( \beta - \text{MnSe} \) crystals. Manganese chloride (\( \text{MnCl}_2 \)) and selenium (Se) powders were used as the precursors to provide manganese and selenium vapors, respectively. A mixture gas of Ar and \( \text{H}_2 \) was employed to transport precursor vapors and control the morphology and size of the as-grown MnSe flakes. More growth details are provided in the Section 2. Figure 1B shows the crystal structure of the nonlayered \( \beta - \text{MnSe} \), which shows a threefold rotational symmetry in the (100) and (111) planes. As shown in Figure 1C, triangle MnSe crystals with lateral sizes up to 20 \( \mu \text{m} \) were grown on the mica substrate with an optimal Ar/\( \text{H}_2 \) ratio of 10:1 (100 sccm Ar and 10 sccm \( \text{H}_2 \)). Meanwhile, the AFM height topography in Figure 1D shows that the thickness of the as-grown MnSe crystals is down to 3.5 nm, corresponding to a thickness of four unit cells of \( \beta - \text{MnSe} \). In Figure 1E, the distinct resonant Raman peak at 250 cm\(^{-1}\) is assigned to the \( A_{1g} \) Mn-Se stretching.
mode. The uniform intensity profile observed in the Raman mapping image collected at \( \approx 250 \text{ cm}^{-1} \) (Figure 1E, inset) verifies the formation of high-purity single-crystalline \( \beta \)-MnSe.

XPS characterization was employed to analyze the bonding states and stoichiometric ratio of Mn and Se atoms in the \( \beta \)-MnSe flakes. As shown in Figure 1F,G, both the Mn 2p and Se 3d spectra consist of doublet peaks, that is, Mn 2p\(_{3/2}\) at 640.9 eV, Mn 2p\(_{1/2}\) at 653.0 eV, Se 3d\(_{5/2}\) at 54.9 eV, and Se 3d\(_{3/2}\) at 55.8 eV. These binding energies are in agreement with the values reported for MnSe crystal in the literature. Moreover, the Mn:Se atomic ratio calculated from the XPS data is close to 1:1, confirming the formation of stoichiometric MnSe. Figure 1H shows the CL spectrum of the \( \beta \)-MnSe flakes. The broad peak centered around 2.28 eV corresponds to the recombination of the neutral excitons in \( \beta \)-MnSe flakes while the sharp peak at 1.77 eV comes from the defect-related emission. Such strong CL peaks confirm the semiconductor characteristic of \( \beta \)-MnSe.

We then use the aberration-corrected HAADF-STEM to determine the atomic structure of the \( \beta \)-MnSe crystals. In Figure 2A, spots with the same contrast represent the overlapped Mn and Se atoms. They are arranged in a hexagonal structure, which is identical to the (111) lattice.
plane of β-MnSe. The six equivalent points in the fast Fourier transform (FFT) image further confirms the hexagonal lattice and monocrystalline structure of the as-grown β-MnSe (Figure 2A, inset). As verified from the magnified STEM image, the interplanar spacing of the β-MnSe (220) plane is ~2.0 Å (Figure 2B), slightly larger than that of α-MnSe (1.93 Å). Then, we employed energy-dispersive X-ray spectroscopy (EDS) to analyze

**FIGURE 2** Atomic structures of the as-grown β-MnSe crystals. (A) Atomic-resolution HAADF-STEM image of β-MnSe (111) lattice plane. The inset shows the corresponding fast Fourier transform (FFT) diffractogram, and the lattice indices are identified. (B) The magnified HAADF-STEM image. (C–E) Low-magnification image of a β-MnSe crystal and the corresponding EDS mappings of Mn and Se elements. EDS, energy-dispersive X-ray spectroscopy; HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy

**FIGURE 3** Morphological engineering of 2D β-MnSe crystals. MnSe crystals grown with H₂ flow rates of (A) 15 sccm, (B) 20 sccm, (C) 25 sccm, (D) 30 sccm, and (E) 35 sccm. (F) Evolution of the fractal dimension versus H₂ flow rates
the macroscopic component of the as-grown $\beta$-MnSe (Figure 2C–E). The calculated stoichiometry of Mn and Se is about 1:1, and the Mn and Se atoms are uniformly distributed throughout the whole flake, revealing the macroscopically componential and structural homogeneity of the as-grown $\beta$-MnSe.

Next, we analyze the growth mechanism of the nonlayered 2D $\beta$-MnSe crystals. All the as-grown $\beta$-MnSe flakes are aligned in the same orientation or rotated by 180° (Figure 3A–E), showing that the $\beta$-MnSe flakes were epitaxially grown on the mica substrate as there is a strong VdW interaction between MnSe and mica. Besides, with the increasing flow rate of H$_2$ (from 10 to 35 sccm), the flake shapes evolved gradually from triangle to windmill, dendrite, and eventually snowflakes. The geometry of the as-grown MnSe flakes becomes more complex. The fractal dimension was calculated using the standard box-counting evaluation, and it increases from 1.02 to 1.4 with the increasing flow rate of H$_2$ (Figure 3F), which quantified the increasing morphological complexity. Considering such radical evolution of the morphology and their thermodynamic stability, the growth of these $\beta$-MnSe flakes is dominated by the kinetic effect. When the low flow rate of H$_2$ is low, Mn and Se atoms together with MnSe molecules have adequate time to diffuse on the substrate surface to form regular triangular flakes, just like the growth of WS$_2$ on sapphire. With a high flow rate, the diffusion rate of Mn and Se is much quicker to provide sufficient precursors for the growth. Meanwhile, the Mn-terminated edges are much energetically favorable as indicated by the lower formation energies calculated by DFT (Table S1) and the Mn-terminated edges grow much faster in an H$_2$-rich environment compared with Se-terminated edges. In this circumstance, branches formed along the trunk with an angle of 120° and eventually grew into MnSe dendrites as illustrated in Figure 3B–E, similar to the formation process of MoS$_2$ dendrites. As a whole, the $\beta$-MnSe crystals were epitaxially grown on the mica substrate by a diffusion-limited kinetic reaction.

Magnetic properties of the as-grown $\beta$-MnSe were investigated using a SQUID magnetometer. Figure 4A,B depicts the magnetic moment against the magnetic field ($M-H$) curves measured at different temperatures with the field parallel and perpendicular to the flake,
respectively. The $M - H$ hysteresis loops observed at 30 K and below well demonstrate the ferromagnetism of the as-grown $\beta$-MnSe. The size of hysteresis loops decreases with the rising temperature, which is indicative of the temperature sensitivity of the ferromagnetism of $\beta$-MnSe. At temperatures $\geq 50$ K, the hysteresis disappears and only the paramagnetic signal leaves (also seen in Figure S2A), demonstrating that the magnetic transformation in $\beta$-MnSe completes at around 50 K. Figure 4C shows the zero-field cooling (ZFC) and field cooling (FC) curves with in-plane and out-of-plane fields. The magnetic moment decreases with the increasing temperature and vanishes at about 50 K. This behavior again verifies the existence of ferromagnetic order in the $\beta$-MnSe flakes. The FC-ZFC bifurcation is directly indicative of magnetic metastability. So, the dramatic change in the inset of Figure 4C again supports the magnetic transformation at about 50 K. Figure 4D shows the corresponding temperature-dependent inverse susceptibility of $\beta$-MnSe under field cooling. Obviously, the ferromagnetic-paramagnetic (FM – PM) transition occurs at a critical temperature ($T_c$) of about 42.3 K, which is determined by the derivative of the susceptibility. We fitted this temperature-dependent data using Curie–Weiss’s law: $\chi(T) = \frac{M}{H} = \frac{C}{T - \theta}$, where $\theta$ and $C$ are the Weiss and the Curie constants, respectively. The fitting yields a $\theta$ of 94.8 K for $H_\parallel$ and 30.4 K for $H_\perp$, respectively. Such a large difference in $\theta$ reveals the anisotropic paramagnetic behavior of the $\beta$-MnSe while the different shapes of the $M - H$ curves, square with the in-plane field and slanted with the out-of-plane field (Figure S2B), suggests the existence of ferromagnetic anisotropy in $\beta$-MnSe flakes. Besides, the $H_\parallel$ curve fits well with the Curie–Weiss law, indicating long-range magnetic order in $\beta$-MnSe. However, the $H_\perp$ curve deviates from the straight line at a temperature ($\approx 220$ K) much higher than $T_c$ (42.3 K), indicating that there are also strong short-range FM spin interactions in $\beta$-MnSe.

To gain an in-depth understanding, we performed DFT computations to reveal the origin of the ferromagnetic orders in $\beta$-MnSe. Considering the symmetry of the configuration of $\beta$-MnSe, the (100), (110), and (111) slabs with either Mn or Se terminations were examined (Figure S1). Only the (110)-Mn, (100), and (111)-Mn slabs are energetically stable (Table S1), whereas the (110) slab is not consistent with the three times meristic of the as-grown flakes. The surface of the (111)-Mn slab was reconstructed after optimization as the surface Mn atoms were dragged down to form Mn–Mn bonds near the surface, making Se atoms become the surface termination. Figure 4E shows the distributions of magnetism in the (111)-Mn slab with three sublayers computed through control of spin-orbital coupling. It is revealed that all the Mn sublayers in this slab possess a ferromagnetic configuration, whereas the adjacent two sublayers have the opposite magnetic orientation, reflected by the alternet red “+” and “−”. The surface Se atoms (Se termination) exhibit ferromagnetism while the interior Se atoms are nonmagnetic. Meanwhile, the (111)-Mn slab exhibited the same easy axis (EA) with the $\beta$-MnSe bulk (001), and the magnetic anisotropy energy (MAE) was in the range of 0.309–0.889 meV per Mn and surface Se atom (Table S2). The (111)-Mn slab with four sublayers shows the same magnetic behavior (Figure 4F) with a reduced MAE of 0.242–0.548 meV per magnetic atom (Table S2). By contrast, (110)-Mn and (100) slabs are both antiferromagnetic (Figure S3 and Table S1). So, it can be concluded that the ferromagnetism of the $\beta$-MnSe flakes derives from the exchange coupling between the unsaturated Se and Mn atoms, and the magnetic anisotropy decreases with the increasing thickness of MnSe flakes.

4 | CONCLUSION

In summary, ultrathin nonlayered $\beta$-MnSe was successfully synthesized via the CVD method. The thickness of as-grown $\beta$-MnSe flakes can be tailored down to 3.5 nm while their lateral size can reach up to dozens of micrometers. A diffusion-limited epitaxial growth mechanism is proposed based on the identical orientation and morphology evolution of the as-grown flakes. Derived from the exchange coupling between the unsaturated Se and Mn atoms, $\beta$-MnSe exhibit excellent ferromagnetism with a magnetic transition temperature of around 42.3 K. Our work provides an innovative approach to grow 2D magnetic semiconductors by thinning traditional bulk magnets, which will facilitate the exploration of the fundamental physics and the applications of 2D magnets in ultra-compact spintronic devices.

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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher’s website.

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