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Two-Dimensional Wedge-Shaped Magnetic EuS: Insight into the Substrate Step-Guided Epitaxial Synthesis on Sapphire

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ABSTRACT: Rare earth chalcogenides (RECs) with novel luminescence and magnetic properties offer fascinating opportunities for fundamental research and applications. However, controllable synthesis of RECs down to the two-dimensional (2D) limit still has a great challenge. Herein, 2D wedge-shaped ferromagnetic EuS single crystals are successfully synthesized via a facile molten-salt-assisted chemical vapor deposition method on sapphire. Based on the theoretical simulations and experimental measurements, the mechanisms of aligned growth and wedge-shaped growth are systematically proposed. The wedge-shaped growth is driven by a dual-interaction mechanism, where the coupling between EuS and the substrate steps impedes the lateral



growth, and the strong bonding of nonlayered EuS itself facilitates the vertical growth. Through temperature-dependent Raman and photoluminescence characterization, the nanoflakes show a large Raman temperature coefficient of $-0.030 \text{ cm}^{-1} \text{ K}^{-1}$ and uncommon increasing band gap with temperature. More importantly, by low-temperature magnetic force microscopy characterization, thickness variation of the magnetic signal is revealed within one sample, indicating the great potential of the wedge-shaped nanoflake to serve as a platform for highly efficient investigation of thickness-dependent magnetic properties. This work sheds new light on 2D RECs and will offer a deep understanding of 2D wedge-shaped materials.

1. INTRODUCTION

Two-dimensional (2D) materials have attracted much attention in recent years because of their appealing unique properties and potential applications in next-generation electronic and spintronic devices.^{1,2} Nowadays, the exploration of 2D materials primarily focuses on graphene,^{3,4} hBN,⁵ transition metal chalcogenides (TMCs),6 elemental 2D materials,⁷ and ternary materials (such as transition metal oxyhalides,⁸ MnBi₂Te₄,⁹ Fe₃GeTe₂,¹⁰ etc.) owing to their rich electrical, optical, and magnetic properties.¹¹ However, even with promising properties such as magnetism, luminescence, and charge density wave due to the unique 4f electron configurations and 4f-4f transitions,¹²⁻¹⁵ 2D rare earth (RE) materials, especially 2D RE chalcogenides (RECs), have been scarcely studied. Therefore, it is highly desired to synthesize new kinds of 2D RECs and investigate the intrinsic properties. Among the RECs, EuS presents unique magnetic and optical properties, exhibiting great potential in spintronic and luminescent devices.¹⁶⁻¹⁸ EuS is described by Heisenberg exchange interaction with Curie temperature $T_{\rm C} \sim 16$ K, and the magnetization primarily originates from the strongly localized 4f electrons of Eu²⁺ with spin S = 7/2.¹⁹ Because of the wide bandgap (\sim 1.65 eV) and large exchange coupling J (~10 meV), EuS was intensively applied as the adjacent

magnet, which induces proximity effects with graphene,²⁰ TMCs,²¹ and some superconductors such as Al.¹⁸ However, experimental investigations of monocrystalline 2D EuS nano-flakes are limited because of the challenge in their controllable synthesis.

Over the past few decades, EuS films have been usually obtained using various physical vapor deposition (PVD) methods, including molecular beam epitaxy^{22,23} and evaporation.^{24,25} However, PVD techniques have high demands for ultralow pressure, and the domain size of the as-grown films is comparatively smaller, which impedes the full insight into the 2D limit. Notably, chemical vapor deposition (CVD) has been known as a much more facile and inexpensive method for growing 2D nanomaterials (especially for chalcogenides),²⁶ which is highly promising for the synthesis of EuS nanoflakes. Moreover, the substrates play a key role in the 2D materials' nucleation and growth processes, including the lattice constant

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Figure 1. Growth and characterizations of 2D EuS nanoflakes. (a) Schematic diagram of the CVD setup for the synthesis of EuS nanoflakes on sapphire with mixed EuBr₂ and NaCl. (b) Schematic view of the probable occupation of EuS (111) domains on sapphire (0001) with matching lattice constants. (c) Optical image of typical 2D EuS nanoflakes. The scale bar is 20 μ m. (d) Histogram of the orientation distribution of EuS nanoflakes on sapphire. (e) AFM image and the height profile of an EuS nanoflake with a thickness gradient. The scale bar is 4 μ m. (f) XRD pattern of the as-synthesized EuS nanoflakes. (g,h) XPS spectra of S 2p (g) and Eu 4d (h) orbitals.

matching, surface catalytic activity, and smoothness.²⁷ As a commercial substrate, sapphire shows perfect potential in epitaxial growth of III-V semiconductors.²⁸ The steps on the sapphire's surface have a critical influence on the growth of materials.^{29,30} For example, the modified sapphire with steps along the $(10\overline{10})$ axis has been designed to synthesize waferscale MoS₂ because the step edges break the degeneracy of nucleation energy, which is essential for the unidirectional alignment.³¹ Centimeter-scale bilayer MoS₂ films were obtained on *c*-plane sapphire with an engineered terrace height,³² and the mechanism for the growth of multilayer MoS₂ induced by steps of sapphire was theoretically proposed.³³ However, the step-guided gradient growth during the CVD process is rarely reported. It is worth noting that the unique wedge-shaped structure can open up new possibilities for investigating novel physical phenomena or thickness-dependent properties.^{34,35} For instance, direct evidence for a three-dimensional (3D) quantum Hall effect formed by Weyl orbitals was observed in wedge-shaped Cd₃As₂ nanosheets.³⁶ However, the further experimental explorations regarding thickness-dependent magnetism in a wedge-shaped nanoflake are still limited.

Here, we design and synthesize 2D EuS nanoflakes on a sapphire substrate by the molten-salt-assisted CVD method. Almost all the EuS nanoflakes grow oriented in the same direction with the thickness gradient (wedge-shaped) because of the coupling between sapphire and EuS. The crystalline structure and elemental compositions were verified by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM). In particular, the aligned growth and wedgeshaped growth mechanism are investigated via first-principles calculations and in-depth atomic force microscope (AFM) measurements. It is worth noting that the steps of sapphire are prerequisite to the thickness gradient of nonlayered EuS. Raman and photoluminescence (PL) measurements demonstrate the large Raman temperature coefficient and a blue shift of band gap with increasing temperature. Moreover, the thickness variation of the magnetic signal is revealed by magnetic force microscopy (MFM) within an individual nanoflake. This work provides new insights into the controllable synthesis of wedge-shaped 2D materials and other 2D RECs.

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Figure 2. TEM characterization of the as-grown EuS nanoflakes on Cu grids. (a) Low-magnification TEM images of a typical EuS nanoflake. The scale bar is 1 μ m. (b) HRTEM image and (c) corresponding SAED pattern. The scale bar is 2 nm in (b) and 5 nm⁻¹ in (c). (d) Elemental analysis of the sample by EDS. (e,f) EDS elemental mapping images of the flake shown in (a). The scale bar is 1 μ m.

2. RESULTS AND DISCUSSION

2D nonlayered EuS was obtained by applying the NaClassisted CVD method. As shown in Figure 1a, the process was carried out at ambient pressure with sulfur powder and EuBr₂ grains as the precursors. NaCl powder and EuBr₂ were mixed to decrease the melting point, increase the vapor pressure, and to promote the lateral growth, which has been discussed in previous studies.^{37,38} The anisotropic growth of 2D EuS flakes can be carried out on a sapphire substrate at a temperature of 1000 °C with Ar flows of 50 sccm and H₂ flows of 5 sccm. It is important to emphasize that H₂ and S powder can be introduced only after reaching the set reaction temperature to make EuBr₂ melt and have a certain vapor pressure above the sapphire substrate to avoid the direct conversion to bulk EuS. Notably, EuSe nanoflakes can also be synthesized by the same procedure with Se powder as the precursor (Figure S1). The EuS crystals belong to the space group Fm3m and possess a cubic structure with 0.487 nm lattice constant for the (111) plane, presenting only -2.3% mismatch with the (0001) plane of sapphire (crystalline α -Al₂O₃, a = b = 0.476 nm) (Figure 1b). This match promotes the heteroepitaxial growth of EuS on sapphire. Figure 1c illustrates an optical microscopy image of EuS nanoflakes. The shapes vary from a triangle to truncated triangle, and the well-defined shapes indicate good crystallinity. Moreover, the edges of the nanoflakes arrange in the same orientation (Figure 1d). The aligned domains are speculated to attribute to the coupling between EuS and the substrate, and the mechanism will be discussed in the latter section.



Figure 3. Exploration of the growth mechanism of wedge-shaped EuS. (a) AFM image of a regular triangle EuS with a thickness gradient. The scale bar is 3 μ m. (b) Magnified AFM image of a region of interest in (marked by the square in (a)). The scale bar is 0.4 μ m. (c) Height profiles along the arrows in (a). 1, 2, and 3 correspond to the arrows parallel to SE and 1', 2', and 3' correspond to the arrows parallel to FE. (d) Height profiles along the arrows 2, 4, and 5 in (a). The angle between arrow 4/5 and 3 is 30°. (e) Cross-section height profile of the steps along the blue line in (b). (f) AFM image and height profiles of EuS nanoflakes with the same thickness gradient direction. The light blue parallel dotted lines are the guidelines. The scale bar is 7 μ m. (g) Schematic diagrams highlighting the growth mechanism model. (h) Theoretical calculations of the binding energy of three possible configurations: (i) 'downhill', (ii) on the top of the preexisting EuS, and (iii) on the surface of sapphire.

Remarkably, there is a uniform thickness gradient in the nanoflakes down to 7.9 nm, as confirmed by the representative AFM image shown in Figure 1e. The thicker edge may originate from the accumulation of source species at the edges during or after the heating process of CVD and has been reported in many CVD-synthesized 2D materials.^{39–41} There is no sodium element detected at the edges by energy-dispersive spectroscopy (EDS) (Figure S2), indicating that the edges are not caused by the accumulation of salt. For comparison, we synthesized EuS without NaCl, and only thick EuS flakes over 600 nm were obtained (Figure S3). It is also worth mentioning that the thickness gradient and the thick edges still exist, indicating they are not determined by the effect of NaCl.

To examine the crystal phase of the as-synthesized EuS nanoflakes, XRD characterization was performed. There are several peaks observed which correspond well to the face-centered cubic (*fcc*) EuS phase (PDF # 26-1419) (Figure 1f). In addition, the strong peaks of (111) and (222) also reveal that the preferred growth plane is (111). XPS was used to elucidate the chemical composition and valence state of the

samples. For Eu ions, the redox potential of the Eu²⁺/Eu³⁺ couple is very high.⁴² Consequently, if the sample is characterized directly without any processing, Eu³⁺ is observed (Figure S4) originating from the oxidized layer because an electron transfer from Eu²⁺ to any oxidizing neighbor is more accessible.⁴³ To detect the internal valence state, the 10 nm top layer was removed by Ar ion etching before the measurement. The S 2p and Eu 4d spectra after etching have been presented. The S $2p_{3/2}$ (~161.1 eV) and $2p_{1/2}$ (~162.3 eV) peaks can be assigned to S²⁻ as shown in Figure 1g. In Figure 1h, the peaks at 134.1 and 129.0 eV indicate the existence of Eu²⁺ 4d_{3/2} and Eu²⁺ 4d_{5/2}, respectively. However, the Eu³⁺ peaks still exist, but the intensity is significantly reduced, which may be attributed to the residual oxygen in the XPS chamber.^{44,45}

The detailed structural information of the EuS nanoflakes was revealed by transmission electron microscopy (TEM) as displayed in Figure 2. Figure 2a,b shows the low-magnification TEM and HRTEM images of EuS nanoflakes. In Figure 2b, the lattice plane spacing_is measured to be ~0.21 nm which corresponds to the (220) plane of the *fcc* EuS crystal. Figure 2c

shows the selected area electron diffraction (SAED) pattern, and only one set of diffraction spots with 6-fold symmetry is observed, indicating the formation of a single-crystalline structure and preferential growth of (111) planes. Meanwhile, the chemical composition is characterized by EDS, and the atomic ratio is estimated to be 30.3:25.1 for the Eu and S, roughly consistent with the stoichiometric ratio of EuS (Figure 2d). Moreover, the uniform dispersion of Eu and S within the nanoflake presented by the EDS mapping confirms the singlecrystal nature of the flake (Figure 2e,f). Based on the above characterization, the CVD-synthesized single-crystalline 2D EuS nanoflakes are single crystals with a (111) preferred growth plane.

The wedge-shaped nanoflakes are attractive, which prompts us to investigate further the growth mechanism. For van der Waals (vdW) materials, because of the weak interaction between the layers, the growth usually follows a layer-by-layer mode (Frank-van der Merwe growth) that the lateral growth rate is much faster than the vertical one.^{46,47} Nonlayered materials usually grow as three-dimensional particles or bulk. By choosing the appropriate substrate and growth parameters, the shape of materials can be limited to two dimensions.⁷ On a sapphire substrate, the sharp steps formed when the temperature is above 950 °C due to the surface reconstruction.^{29,30} As the growth temperature of EuS is 1000 °C, the steps are likely to contribute to the gradient growth, and they are observed on sapphire after the reaction (Figure S5a,b). A typical equilateral triangle nanoflake was used for the AFM measurements. As shown in Figure 3a, it is found that the thickness of the material has a gradient in a certain direction. We performed a magnification measurement on the edge, and obvious steps on the sapphire substrate exist. It is speculated that the steps have a critical effect on the gradient growth, and a more detailed study was performed. As displayed in Figure 3b, the direction of the step edge (SE) is not the same as the edge of the flake (FE), and the angle between them is $\sim 5^{\circ}$, making us wonder whether the direction of the thickness gradient is perpendicular to the SE or the FE. Three locations were selected to measure the height profiles along the same direction. Lines marked 1, 2, and 3 are along the SE and 1', 2', 3' are along the FE. As displayed in Figure 3c, the lines along the substrate are almost horizontal, indicating that the substrate is not tilted. The heights of the nanoflake are uniform along the SE but inclined along the FE, manifesting that there is still a gradient in the thickness along the FE. This proves that the thickness gradient is perpendicular to the SE. To further prove our findings, we measured lines 4 and 5 (rotating 30° clockwise and counterclockwise of line 2) and found that the two curves are symmetrical with respect to line 2 (Figure 3d). Here comes another question: is the gradient going 'uphill' or 'downhill'? Extracted from the height profile (Figure 3e), the gradient direction is 'downhill'; that is, the nanoflakes become thinner in the upward of the steps. Moreover, Figure 3f shows the nanoflakes with a shape angle of 180°, and the gradient can be observed from the contrast and corresponding height profiles. It can be found that regardless of the direction of the shape, they have the same thickness gradient direction and the gradient is nearly equal, which further proves that the thickness gradient is step-dependent rather than shape-dependent. For comparison, EuS nanoflakes without a thickness gradient were synthesized in a similar way on mica whose surface is flat with no dangling bonds and steps (Figure S6a). A typical flake was characterized via AFM and PL, indicating the uniform

thickness (Figure S6b-d). Thus, it is expected that the mechanism of the step-governed thickness gradient must differ from that of other vdW materials.^{31,48,49}

To deeply understand the phenomenon, combined with the characterization results and density functional theory (DFT) calculations, it is found that the wedge-shaped growth of EuS on the sapphire surface is guided by a dual-interaction mechanism. The first one is the interaction between EuS and the step edge of α -Al₂O₃, where the crossing of 'downhill' growth is strongly suppressed, and the 'uphill' edge impedes the expansion of EuS domains. The second one is the coupling of non-vdW EuS itself: different from the weak interlayer coupling of vdW materials, the interaction of the chemical bond is strong in the z direction so that the surface of EuS also serves as active sites. As exhibited in Figure 3g, it is assumed that each nanoflake originates from one nucleus; that is, the new clusters should nucleate on the pregrown EuS. In the measurement of the step height in Figures 3e and S5, the average step height is about 0.2 nm (c/6, where c = 12.3 Å is the lattice constant of α -Al₂O₃) and the terrace width is about 70 nm, which is quite large for molecular clusters (less than 1 nm). In addition, the more dangling bonds and defects at the SE are higher energy sites than the surface. Therefore, (i) the initial nuclei can be formed on the terrace with high probability or along the edge with high reactivity. Because of the existence of high-energy dangling bonds of EuS, new reactants should choose the site beside the nuclei. (ii) When the growing EuS domain meets the SE, hanging growth across the 'downhill' edge or climbing growth across the 'uphill' edge is unfavorable. At the same time, growing vertically on the surface of EuS is also attractive to the new clusters because of the nonlayered structure. (iii) When the 'second layer' meets the 'uphill' edge, the domain could expand without climbing. (iv) As a result, the lateral growth rate v_1 is severely reduced and the vertical growth rate v_2 is relatively increased. In addition, the growth promoter salt enhances the lateral growth rate v_1 , resulting in a thinner flake compared to without NaCl. Because the 'downhill' growth is entirely suppressed, the flakes are wedge-shaped rather than pyramidal.

Considering that the thickness gradient still exists without salt (Figure S3), for simplicity, NaCl was not included in the simulation. Quantitatively, the calculations (Figure 3h) estimate that the binding energy when the clusters are bound 'downhill' (-98.4 meV/atom) or at the top of the preexisting EuS (-105.8 meV/atom) is much larger than that on the surface of sapphire (-157.6 meV/atom), indicating that growing on α -Al₂O₃ is the most favorable way and hanging growth is the worst way, consistent with our analysis about steps (i) and (ii). The absorption energy between Eu_4S_8 and sapphire (0001) $E_{EuS-Sap}$ is -4.57 eV, which is smaller than the energy between Eu₄S₈ and EuS (111) ($E_{EuS-EuS} = -6.94$ eV) (Figure S7). The extra four sulfur atoms are used to stabilize the clusters. The energy difference $\Delta E = (E_{EuS-EuS} - E_{EuS-Sap})/$ *n*, where n = 12 is the atom number of the Eu₄S₈ cluster. The thermodynamic probability of growing on the EuS surface is 1/ $(1 + \exp(\Delta E/k_{\rm B}T)) \approx 85.8\%$, where T = 1273 K is the reaction temperature and $k_{\rm B}$ is the Boltzmann constant. The stronger coupling of EuS (111) itself indicates the (ii) step that the sites on the EuS surface are more favorable when the terrace is covered by EuS. From the above results and analysis, the growth mechanism of wedge-shaped EuS nanoflakes on sapphire can be well explained.



Figure 4. Theoretical simulations to explain the aligned growth of EuS on sapphire. (a–d) Top (up) and side (down) view of the structure of the Eu_4S_8 cluster on sapphire with 0°, 10°, 20°, and 30° orientation and the corresponding calculated formation energy of the four configurations. (e) Formation energy as a function of the orientation angle between the Eu_4S_8 cluster and sapphire substrate. (f) Schematic illustration of the growth of EuS nanoflakes on a sapphire (0001) substrate.

The aligned growth of some vdW materials, such as graphene and MoS_{2} , is reported to originate from the atomic steps on the surface of c-plane sapphire substrates.^{31,50,51} However, as shown in Figure 3b, the in-depth AFM image reveals that the angle between SE and FE is $\sim 5^{\circ}$, indicating that the atomic steps of sapphire may not be the dominant factor for the aligned growth. In contrast to the vdW heteroepitaxial one, the epitaxial growth of EuS is much closer to a conventional mode because of the non-vdW structure of EuS and sapphire. As a result, the lattice mismatch-the differences of lattice constant or angle of the lattice vectors—is probably the key factor. To further understand the mechanism of the aligned growth of EuS flakes, the DFT simulations were performed. In the simulations, an Eu₄S₈ cluster with a rotation of 0° , $\pm 10^{\circ}$, $\pm 20^{\circ}$, and $\pm 30^{\circ}$ was placed on the (0001) plane of sapphire. Because the surface of the sapphire substrate is passivated by oxygen, and the bonds between the metal atom and oxygen are stronger, Eu atoms were chosen to contact the substrate, which is also in line with epitaxial growth. The 4×4 sapphire (0001) slab with three-layer-Al-atoms is used with the bottom atoms fixed. As shown in Figure 4a-d, the absorption energies (E_a) of the EuS cluster and sapphire at a rotation angle of 0°, 10°, 20°, and 30° are -4.57, -4.15, -2.99, and -3.10 eV, respectively. The E_a as a function of orientation angle was collected in Figure 4e. It is noted that the deviation from the minimum point will increase the energy drastically. Consequently, rotated domains are energetically unfavorable, resulting in the epitaxial growth in the same direction as illustrated in Figure 4f.

In addition, there are some wedge-shaped truncated triangles grown on the substrate, and it is also significant to investigate the growth mechanism. It is speculated that the growth process is similar to that of triangular nanoflakes, except that the short edge is truncated by steps during the growth. We performed AFM measurements of a truncated triangle on another substrate (Figure S8). The direction of the SE is the same as the short edge of the flake (SFE), and the angle between the long edge (LFE) and the SE is $\sim 12^{\circ}$ (Figure S8a,b). The different angle from that in Figure 3b is attributed to the different step orientation within or across the sapphire wafers because of the uncontrolled mis-cut angle during manufacturing.⁵² The variable angle further indicates that the aligned growth is not determined by the steps. Height profiles along the four arrows indicated in Figure S8a were analyzed (Figure S8c). Dotted lines 1 and 2 are parallel to the SE/SFE, and lines 3 and 4 are parallel to the LFE. The heights are uniform along SE/SFE while decreasing along the LFE. These findings prove that the growth follows the dual-interaction mechanism as we discussed before and the short edge results from that the steps truncated the 'uphill' growth. The slight difference of the terrace width and step height, as shown in Figures 3b and S5a, may determine whether EuS can climb over the steps, resulting in the shape discrepancy.

To identify the phonon modes of EuS, Raman spectroscopy has been performed for the nanoflakes grown on sapphire. The EuS crystallizes in the NaCl structure, and the first-order Raman effect is forbidden. However, some anomalous features are presented in the paramagnetic-phase EuS. The Raman spectrum at 300 K is shown in Figure 5a. A fundamental ω_0 at

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Figure 5. Temperature-dependent Raman and PL investigation of EuS nanoflakes. (a,d) Raman (a) and PL (d) spectrum of EuS nanoflakes at room temperature. (b,e) Temperature-dependent Raman (b) and PL (e) spectra. (c,f) Corresponding Raman peak position (c) and optical band gap (f) evolution at different temperatures. (g) Normalized transient dynamics of the EuS nanoflakes. (h,i) Calculated DOS (h) and electronic band structure (i) of EuS.

 ${\sim}240~{\rm cm}^{-1}$ and an overtone sequence at ${\sim}480~{\rm and}~{\sim}720~{\rm cm}^{-1}$ are observed, which only contains longitudinal optical (LO) phonon modes. Four scattering components were contained in the broad Raman peak, including a transversal optical phonon and LO phonons at the Γ -point and X-point, and in particular the strong antisymmetric component at the L-point of the Brillouin zone. 53-55 In the Raman scattering process, the photon-electron, electron-phonon, and spin-orbit interactions are considered. First, the photon incidents to the EuS and excites a d electron and an f hole. Then the phonon and spin excitations are created by the interaction between spin and the f hole via spin-orbit coupling. Finally, the electron-hole pair recombines and yields a Stokes-scattered photon.⁵³ We carried out the temperature-dependent Raman measurements to elucidate the temperature coefficient of 2D paramagneticphase EuS. Figure 5b displays the Raman spectra of the triangular EuS nanoflake with the temperature ranging from 85 to 300 K. The detailed variations of the Raman peak position are plotted in Figure 5c. By lowering the temperature, the peak of fundamental ω_0 at ~240 cm⁻¹ displays an expected red-shift from \sim 241 cm⁻¹ at 300 K to about \sim 249 cm⁻¹ at 85 K. The variation of the peak frequency as a function of temperature

presents a linear relationship which can be described by $\Delta \omega$ = $\omega(T_2) - \omega(T_1) = \chi_T(T_2 - T_1) = \chi_T \Delta T$, where $\Delta \omega$ is the frequency variation of ω_0 and $\chi_{\rm T}$ is the temperature coefficient.⁵⁶ The $\chi_{\rm T}$ was determined using a linear fit as $-0.030 \text{ cm}^{-1} \text{ K}^{-1} \pm 0.002 \text{ cm}^{-1} \text{ K}^{-1}$, which is larger than those of many layered materials and nonlayered materials but smaller than that of SnSe (-0.03773 cm⁻¹ K⁻¹).⁵⁷ The χ_T values of other 2D materials are displayed in Table S1. Moreover, the Raman scattering from room temperature to the ferromagnetic phase at 4 K is obtained (Figure S9). The Raman shift of ω_0 at \sim 251 cm⁻¹ with a narrowed line may be caused by the longrange magnetic ordering.⁵⁵ However, there is no obvious shift near the T_C. The temperature-dependent PL of the EuS nanoflake was also investigated. The PL spectra at room temperature are presented in Figure 5d. A high-intensity peak centered at 774.5 nm is observed, corresponding to a band gap of ~1.60 eV. The sharp peak at 693 nm belongs to α -Al₂O₃. Figure 5e shows a sequence of PL spectra as the temperature changes from 85 to 300 K. With the increase of the temperature, the emission peak wavelength blueshifts from 850.0 to 774.5 nm, corresponding to a band gap from 1.46 to 1.60 eV. In stark contrast, the PL peak position of sapphire has

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Figure 6. Magnetic characteristics of EuS flakes. (a) Temperature dependence of the magnetization with in-plane $(H_{//})$ and out-of-plane (H_{\perp}) magnetic field. (b,c) Magnetic hysteresis loops of EuS at different temperatures with $H_{//}$ (b) and H_{\perp} (c). (d) Schematic diagram of the MFM measurement. (e–h) MFM images at different magnetic field acquired at 1.7 K. (i) AFM image of the nanoflake at room temperature. (j–m) MFM images at different temperatures without magnetic field. (n) MFM contrast extracted from the marked circles in (e) as a function of the applied field. (o) MFM contrast along the profiles indicated in (h) as a function of thickness. (p) Correlation between temperature and the respective MFM signal.

no significant changes. The values of band gaps are read out and plotted in Figure 5f. The band gap almost linearly increases with temperature, in contrast to the normally observed decrease in semiconductors.⁵⁸ We fitted the relationship by $\alpha = \partial E/\partial T$ and obtained the temperature coefficient to be (0.67 ± 0.01) meV K⁻¹. For many semiconductors, (i) the shifts partly originate from the change of the band structure caused by the thermal expansion, resulting in the increasing bandgap with temperature. (ii) The major contribution comes from the electron-phonon interaction, resulting in the decreasing bandgap with temperature.⁵⁸⁻⁶⁰ However, for EuS nanoflakes, the lattice dilatation probably dominates the effect. Such an increasing linear band gap change was also observed in organometal halide perovskites.^{60,61} The thickness-dependent Raman and PL spectra were obtained from 10.1 to 57.4 nm, and no obvious shift was observed within this range (Figure S10). Figure 5g shows the time-resolved PL spectrum. The data were analyzed with biexponential decay fit, and the decay time constants consist of two components: a faster decay time constant $\tau_1 \sim 0.67$ ns and a slower $\tau_2 \sim 2.13$ ns. Moreover, the electronic structure of bulk EuS was investigated by the GGA + U method (Figure 5h,i). The inclusion of the correlation effect of f states gives rise to an indirect energy gap between the top of the valence band at the Γ point and the bottom of the conduction band at the X-point. With the increasing U value for the Eu element from 7 to 12 eV, the band gap increases from 0.69 to 1.47 eV (Figure S11). The gap obtained for U = 11 of 1.37 eV reaches close to the experimental results extended to 0 K (1.40 eV). The value of $U \sim 11$ eV is obtained from experiments,⁶² which is in good agreement with our calculations.

To investigate the magnetic property of the EuS nanoflakes, magnetic measurements were performed using Physical Property Measurement System (PPMS). The EuS system is expected to have a quite weak magnetic anisotropy and has been investigated as a standard model of isotropic Heisenberg ferromagnet.^{19,63,64}Figure 6a displays the temperature-dependent magnetic properties. Zero-field-cooled magnetization and field-cooled magnetization were characterized with both inplane $(H_{1/})$ and out-of-plane (H_1) magnetic field. The magnetic moment as a function of temperature shows an obvious ferromagnetic behavior, with a ferromagnetic-toparamagnetic transition occurring at ~ 16.3 K, which is comparable to the previous studies (Table S2).^{20,65,66} In addition, the magnetization curves separate for $H_{1/}$ and $H_{1/}$ and the magnetization for $H_{I/I}$ is much larger than that for H_{\perp} when the applied magnetic field is 100 Oe, indicating that the EuS nanoflakes on a sapphire substrate are more susceptible to be magnetized at in-plane field. The anisotropic magnetization behavior originates from the shape anisotropy⁶⁷ and is consistent with the in-plane easy axis of the EuS films.^{22,68} The magnetization curves from 5 to 30 K with $H_{//}$ and H_{\perp} magnetic field are shown in Figure 6b,c, respectively. For $H_{1/2}$ a typical hysteresis is observed below 18 K. At 5 K, the coercivity is only about 20 Oe, and the saturation field is \sim 5 kOe (Figure 6b), indicating the soft ferromagnetic property of the EuS flakes. For H_{\perp} , the magnetization saturates at a higher field ~15 kOe at 5 K, and the coercivity reduces to 14 Oe (Figure 6c). The difference is consistent with the temperaturedependent magnetic results in Figure 6a. Moreover, the 's'shaped curves without hysteresis at 18 and 20 K are typical of paramagnetism and demonstrate the saturation trend with the increasing magnetic field, agreeing with the single-crystal EuS.⁶³

The current approach to investigate the thickness-dependent properties is mainly achieved by varying the nanoflakes with different thickness. In contrast, wedge-shaped materials have great potential to explore the thickness-dependent behavior within a nanoflake. To gain a deeper insight into local magnetic properties, we turn to image the magnetic behavior for individual nanoflakes using microscopic ways. As one of the magnetic characterization techniques to probe the local magnetization of materials, MFM is capable of detecting the nanoscale spatially resolved magnetic signal, offering exciting opportunities to study the thickness dependence of magnetism with samples grown in the form of a wedge. The schematic of the MFM measurements was illustrated in Figure 6d, and the tip was perpendicularly magnetized up to the sample surface prior to imaging. As shown in Figure 6e-h, an out-of-plane magnetic field from 600 to 0 Oe at 1.7 K was applied, and the corresponding MFM images were acquired. The interaction between the tip and the substrate is set to zero, and the negative shifts represent the attractive force. The clear magnetic contrast between EuS and sapphire reveals the attractive magnetic interaction between the tip and the nanoflake. These results are consistent with the fact that the EuS nanoflake was magnetized by the magnetic field, and an outside re-entrant stray field was created to interreact with the magnetic tip. As expected, the signal weakens, and the signal contrast inside the nanoflake progressively fades with decreasing magnetic field strengths, indicating the fielddependent and thickness-dependent perpendicular magnetic moments. The residual signal detected at zero magnetic field (Figure 6h) is caused by the small remanence at low

temperature, in agreement with the hysteresis loops (Figure 6c).

To quantitatively analyze the magnetic signal as a function of the applied field, we estimated the MFM contrast from the four regions marked by the white circles in Figure 6e. The corresponding thicknesses are roughly extracted from the AFM result at room temperature in Figure 6i. Figure 6n displays the summarized field-dependent MFM signals. We observed similar trends in the four considered regions that the signal diminishes as the magnetic field decreases. Moreover, the signal shows more rapid decreases for the thicker region. The MFM contrast is directly related to the local magnetization of the nanoflake and a geometric factor which depends on the magnetization state of the tip and its position relative to the nanoflake.⁶⁹ Because of the hard-magnetic Co-Cr tip and enough lift height, the phase angle (θ) should be positively related to the magnetic moment (m) strayed out from the outof-plane direction of the sample. The dependence can be expressed by the following relations:

 $\theta \propto m = \chi \cdot H \cdot t \cdot A \tag{1}$

where χ is the magnetic susceptibility, *H* is the applied magnetic field, *t* is the thickness of the EuS, and *A* is the area. At a fixed thickness, θ is positively related to χ and *H*. The sublinear demagnetization process reveals that χ increases with decreasing magnetic field, in good agreement with the hysteresis loops shown in Figure 6c.

To investigate the thickness-dependent magnetism, a path of different height was selected (Figure 6h), and the MFM phase angle signals as a function of thickness at different magnetic fields were extracted as shown in Figure 6o. The simple linear dependence reveals that the magnetic moment is positively related to thickness within this range, making the wedge-shaped nanoflake an efficient model to explore the thickness-dependent properties.

To characterize the temperature-dependent magnetic behavior, we performed a warming up process and obtained MFM images at different temperatures (Figure 6j-m). The shape difference at 10 K may be caused by the different experimental drift of the x, y piezo of the instrument at different temperatures. The signal of the nanoflake diminishes and finally vanishes at 20 K, which is above $T_{\rm C}$. The corresponding signals at the white circle marked in Figure 6j are summarized in Figure 6p, indicating the weakening of ferromagnetism and transition to paramagnetism. From the above results and discussion, it is concluded that the microscopic magnetic behavior of the wedge-shaped EuS has an obvious thickness dependence. Meanwhile, the magnetic field and temperature dependence is consistent with the dynamic magnetic behavior, confirming the magnetic evolution of the sample. The experimental investigation provides an exciting opportunity to advance our knowledge of the wedgeshaped materials by MFM characterization. As compared to growing a series of samples with different thicknesses, this study approach is much more time-efficient and can avoid the variation of growth conditions between different batches.

3. CONCLUSIONS

In summary, we have successfully prepared 2D ferromagnetic wedge-shaped EuS on the sapphire substrate. Combining indepth characterization and theoretical calculations, the models of coupling-induced aligned growth and step-induced thickness gradient growth were demonstrated. The mechanism should also be applicable for other nonlayered materials epitaxially grown on the substrate with steps, providing an excellent opportunity to synthesize wedge-shaped 2D crystals. The temperature-dependent Raman and PL properties of as-grown EuS nanoflakes are investigated. In particular, the magnetic properties within an individual nanoflake were investigated by low-temperature MFM, providing an efficient way to explore the thickness-dependent magnetism. This study extends the understanding of interactions between 2D materials and substrate in CVD process and promotes the research progress in 2D RECs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c06023.

Experimental details, supporting figures, and tables (PDF)

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Notes

The authors declare no competing financial interest.

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