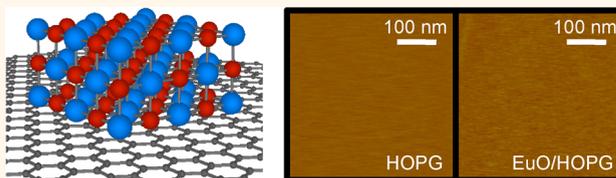


Integration of the Ferromagnetic Insulator EuO onto Graphene

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ABSTRACT We have demonstrated the deposition of EuO films on graphene by reactive molecular beam epitaxy in a special adsorption-controlled and oxygen-limited regime, which is a critical advance toward the realization of the exchange proximity interaction (EPI). It has been predicted that when the ferromagnetic insulator (FMI) EuO is brought into contact with graphene, an overlap of electronic wave functions at the FMI/graphene interface can induce a large spin splitting inside the graphene. Experimental realization of this effect could lead to new routes for spin manipulation, which is a necessary requirement for a functional spin transistor. Furthermore, EPI could lead to novel spintronic behavior such as controllable magnetoresistance, gate tunable exchange bias, and quantized anomalous Hall effect. However, experimentally, EuO has not yet been integrated onto graphene. Here we report the successful growth of high-quality crystalline EuO on highly oriented pyrolytic graphite and single-layer graphene. The epitaxial EuO layers have (001) orientation and do not induce an observable D peak (defect) in the Raman spectra. Magneto-optic measurements indicate ferromagnetism with a Curie temperature of 69 K, which is the value for bulk EuO. Transport measurements on exfoliated graphene before and after EuO deposition indicate only a slight decrease in mobility.



KEYWORDS: EuO · graphene · spintronics · exchange proximity interaction

The exchange proximity interaction (EPI) has been predicted to exist at the interface between a ferromagnetic insulator (FMI) and graphene, originating from an overlap of electronic wave functions.^{1,2} In particular, the ferromagnetic insulator EuO has been estimated theoretically to induce a spin splitting in graphene on the order of 5 meV.¹ EPI has been suggested for novel spintronic device functionality in a wide variety of applications such as induced magnetism in graphene,^{1,3–5} controllable magnetoresistance,^{1,6–8} gate tunable manipulation of spin transport,^{2,9} gate tunable exchange bias,¹⁰ and spin transfer torque,^{11,12} as well as being a necessary requirement for the observation of the quantized anomalous Hall effect in graphene.^{13,14} While theoretical predictions have been numerous, EPI at the FMI/graphene interface has yet to be experimentally observed.

EuO is a model FMI, as it exemplifies an isotropic Heisenberg ferromagnet.¹⁵ EuO has a half-filled 4f shell, which determines the magnetic properties leading to a magnetization of 7 Bohr magnetons per Eu

atom. Further, because the 4f shell is electrically inert due to its localized orbitals, the unoccupied exchange split 5d band governs the charge transport characteristics and exchange overlap in stoichiometric EuO. However, part of the reason that EPI has yet to be observed in the EuO/graphene system is due to the difficulty in materials synthesis of high-quality stoichiometric EuO thin films. EuO is not thermodynamically stable and readily converts to nonmagnetic Eu₂O₃.¹⁶ Furthermore, oxygen-deficient EuO_{1–x} exhibits a metal to insulator transition¹⁷ with a conductive ferromagnetic phase.^{18,19} In typical materials synthesis techniques such as reactive molecular beam epitaxy (MBE), maintaining stoichiometry by flux matching generally leads to the formation of either Eu₂O₃ or EuO_{1–x}. In order to possibly realize EPI in graphene, a critical first step is the integration of high-quality stoichiometric EuO thin films with graphene.

Only recently, through the development of a special growth regime, have reliable stoichiometric films been readily produced.^{19–23} The regime can be understood as follows: a high-purity elemental Eu

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flux is incident upon a heated substrate maintained at a temperature for which the incident Eu atoms re-evaporate off the substrate surface (*i.e.*, distillation). Notably, distillation is highly substrate dependent and works well on certain oxides,^{21,23} but fails in the case of direct growth on GaAs.²² Once distillation is achieved, the introduction of a small oxygen partial pressure allows for the formation of EuO while excess Eu atoms are re-evaporated. This ensures proper stoichiometry of the EuO film.^{19–23} If the oxygen partial pressure is increased, the EuO growth rate increases until a critical O₂ pressure is reached and Eu₂O₃ forms. In this way, the growth rate is determined by the oxygen pressure and is termed adsorption-controlled (distillation) and oxygen-limited. To date, there is no evidence that stoichiometric EuO can be integrated with sp²-bonded carbon-based materials.

In this study, we employ reactive MBE to investigate the deposition of EuO thin films onto graphene. First, we examine the viability of Eu distillation for sp²-bonded carbon materials by examining highly oriented pyrolytic graphite (HOPG) substrate, which allows for standard thin film characterization techniques such as Auger spectroscopy, reflection high-energy electron diffraction (RHEED), and X-ray diffraction (XRD). Within the distillation- and oxygen-limited regime, stoichiometric EuO(001) is shown to grow epitaxially on HOPG(0001) substrate. Such films are shown to be uniform and flat by *ex situ* atomic force microscopy (AFM). Further, EuO is integrated onto mechanically exfoliated graphene flakes as well as large-area graphene grown by chemical vapor deposition (CVD). Raman spectroscopy after EuO deposition on exfoliated graphene exhibits the absence of a D peak, indicating that, despite the high temperatures of deposition, EuO thin films do not induce significant defects to the underlying graphene. This is supported by four-point resistivity measurements that indicate only a slight reduction of mobility. Also, we investigate the magnetic properties of EuO on HOPG and CVD graphene and find a Curie temperature (T_C) of 69 K, the bulk EuO value. This advance in materials synthesis allows for future studies of EPI at FMI/graphene interfaces.

RESULTS AND DISCUSSION

First, we establish the growth parameters by investigating EuO growth on HOPG using Auger spectroscopy, RHEED, and XRD. Fresh surfaces of HOPG (SPI, grade ZYA) are obtained by peeling with 3M Scotch tape and subsequently loaded into the UHV growth chamber and annealed at 600 °C for 30 min. Auger spectroscopy for a pristine HOPG surface is shown in Figure 1 (top curve). The spectrum is characterized by a peak at 272 eV, identifying carbon. Since the temperature required for efficient Eu distillation is highly substrate dependent, we cannot rely on previous results

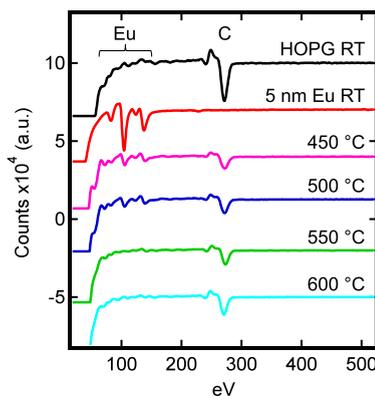


Figure 1. Auger spectroscopy of Eu deposited on HOPG at several different substrate temperatures. Pristine HOPG (black) shows a carbon peak at 272 eV. A 5 nm Eu layer deposited at room temperature (red) shows Eu peaks only. At higher growth temperatures a combination of Eu and C peaks are present. Above 550 °C there is no evidence of Eu in the spectrum.

for distillation temperatures based on oxide substrates.^{19–21,23} Therefore, we first investigated the optimal re-evaporation temperature on HOPG. Without introducing a partial pressure of molecular oxygen, an incident Eu flux (8–9 Å/min) is introduced to the substrate, which is maintained at a fixed temperature. Figure 1 shows Auger spectra for Eu metal deposited at room temperature (RT), 450 °C, 500 °C, 550 °C, and 600 °C. For each substrate temperature, Eu is deposited for the time equivalent to produce a 5 nm Eu film at RT. Eu Auger peaks at 83, 104, 124, and 138 eV can be seen in the RT spectrum of Figure 1. As the substrate temperature is increased, the relative peak height of Eu to C decreases, indicating a smaller amount of Eu material on HOPG. This indicates the onset of re-evaporation of the Eu atoms. For the case of 550 and 600 °C, the Auger spectra show only the carbon peak at 272 eV and no evidence of Eu material. Therefore, full distillation of Eu on HOPG is achieved above 550 °C.

Once in the distillation regime, the introduction of an oxygen flux smaller than the elemental Eu flux should produce stoichiometric EuO films. We investigate the formation of EuO on HOPG substrate by maintaining the substrate at 550 °C for distillation and then introduce a molecular oxygen partial pressure ($P_{O_2} = 1.0 \times 10^{-8}$ Torr) into the UHV system. *In situ* RHEED images probe the sample surface crystalline structure. Figure 2a and b show the RHEED patterns for HOPG and the EuO layer after 5 nm of growth, respectively. The RHEED pattern for the HOPG substrate is unaltered upon in-plane rotation. This is expected since HOPG has out-of-plane (0001) orientation but has in-plane rotational disorder. The RHEED pattern of the EuO layer shows double streak features, and in-plane rotation has no effect on the RHEED pattern, similar to the HOPG substrate. Examination of the EuO RHEED diffraction rods indicates EuO(001) with a

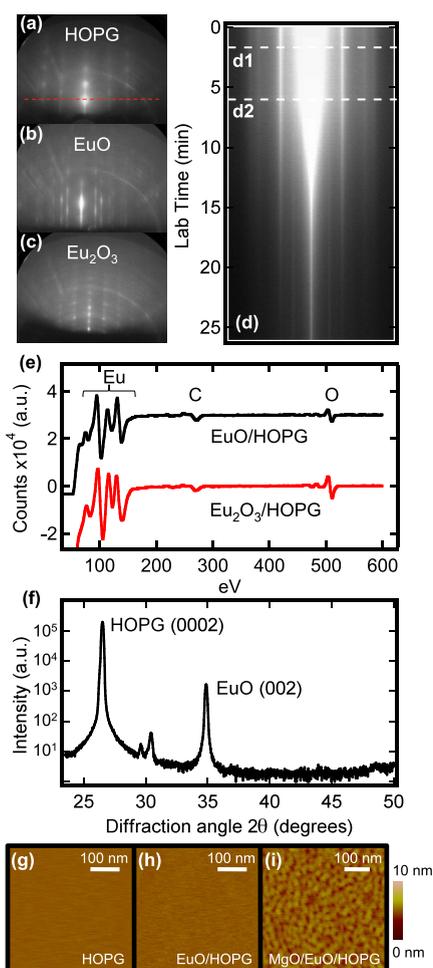


Figure 2. Characterization of EuO thin films on HOPG. (a–c) RHEED patterns for pristine HOPG, 5 nm EuO deposited on HOPG, and Eu_2O_3 on HOPG. (d) Time evolution of dashed red curve in (a). Dashed line d1 indicates the opening of the Eu shutter and incidence of Eu flux to the substrate. Dashed line d2 signifies the introduction of molecular oxygen into the chamber. (e) Auger spectroscopy of EuO/HOPG and Eu_2O_3 /HOPG. (f) XRD θ – 2θ scan showing the HOPG (0002) peak and EuO (002) peak. (g–i) *Ex situ* AFM scans for freshly cleaved HOPG, EuO(5 nm)/HOPG(0001), and MgO(2 nm)/EuO(5 nm)/HOPG(0001) in order from left to right.

superposition of both [100] and [110] in-plane orientations.²³ We can better understand the growth evolution of the EuO film by examining the time lapse of a line cut of the RHEED pattern. A typical line cut, as depicted in Figure 2a (red dashed line), samples the intensity of several diffraction rods across the RHEED pattern. Figure 2d displays the time evolution of a line cut for EuO growth on HOPG in the distillation- and oxygen-limited regime. Between 0 min and dashed line d1, the high-intensity streaks correspond to the diffraction rods as seen in Figure 2a of the pristine HOPG pattern. Dashed line d1 indicates the introduction of Eu flux, during which time the HOPG diffraction rods remain unchanged as Eu re-evaporates from the HOPG surface. A partial pressure of oxygen ($P_{\text{O}_2} = 1.0 \times 10^{-8}$ Torr) is leaked into the chamber at dashed line d2.

The subsequent time evolution shows a smooth transition from HOPG streaks to EuO, indicating epitaxial growth.

Eu_2O_3 can be grown by increasing the O_2 partial pressure to 3×10^{-7} Torr. The Eu_2O_3 RHEED pattern is displayed in Figure 2c and shows a clear distinction from the oxygen-limited growth that produces EuO. We further investigate the difference between the two oxygen regimes by looking at their respective Auger data, as shown in Figure 2e. An oxygen peak at 510 eV is present for both samples. To our knowledge this is the first report on Auger spectroscopy for EuO. Taking the Eu 104 eV peak, EuO has a Eu:O peak ratio of 6.63, while Eu_2O_3 has a Eu:O ratio of 4.34, indicating increased oxygen content in Eu_2O_3 . Comparison of the ratios $6.63/4.34 = 1.53$ to the expected $\text{Eu:O}/\text{Eu}_2\text{O}_3 = 1.5$ shows close agreement. However, it should be noted that while this analysis is useful in verifying oxygen content between the two growths (*i.e.*, EuO vs Eu_2O_3), it is not sufficient for determining precise stoichiometry of the EuO oxidation state.

Ex situ XRD θ – 2θ scans, Figure 2f, serve to elucidate the structure of EuO deposited on HOPG. For XRD measurements, approximately 50 nm EuO was grown on HOPG and capped with 3 nm of polycrystalline Al. A clear EuO (002) peak is seen in the θ – 2θ scan, and there are no other peaks associated with another EuO orientation, indicating that the entire EuO film is oriented (001), in agreement with the RHEED analysis. There are no detectable peaks associated with Eu_2O_3 . There are two small peaks at 29.63° and 30.43° associated with Eu_3O_4 (040) and (320), possibly due to oxidation through the thin capping layer.

It is generally expected that fcc materials (EuO, Ni, *etc.*) would favor (111) orientations with hexagonal materials due to the surface symmetry. However, the RHEED and XRD data clearly indicate the orientation EuO(001)/HOPG(0001) is preferred. In the absence of other factors, the orientation preference may be partly explained by the lattice mismatch between EuO and graphene. EuO has a bulk lattice constant of 0.514 and 0.246 nm for graphite, leading to a lattice mismatch of 4.3% for EuO(001)/HOPG(0001) growth orientations. The mismatch for EuO(111)/HOPG(0001) is either 10% or 17% depending on the ratio of relative lattice spacings (*i.e.*, 1:4 or 1:3 for EuO:graphene). However, while mismatch considerations might suggest a favorable orientation, it cannot explain the lack of symmetry between the rock salt surface and graphene. Previous work²³ has shown lattice mismatch to be less of a key factor for EuO epitaxy than other growth concerns. Surface energies, which are lowest for (100) rock salt surfaces,²⁴ are likely relevant and may provide a possible explanation for the observed growth orientation.

To investigate the surface morphology of the EuO films, we have performed *ex situ* AFM on freshly

cleaved HOPG(0001) substrate, a EuO(5 nm)/HOPG(0001) film, and a MgO(2 nm)/EuO(5 nm)/HOPG(0001) bilayer. The resulting AFM scans are displayed in Figure 2g, h, and i, with rms roughness values of 0.1, 0.2, and 0.5 nm, respectively. It must be noted that the EuO surface is likely oxidized to Eu_2O_3 during the *ex situ* measurement. In any case, the scans clearly show that the films are uniform, relatively flat, and pinhole free. This is crucial for possible use as a gate dielectric.

Due to EuO's large magneto-optic response,²⁵ the magneto-optic Kerr effect (MOKE) serves as a sensitive probe of the magnetic behavior of the sample. Linearly polarized light is reflected off the sample surface, and the resulting polarization rotates an amount, θ_K , that is proportional to the magnetization of the film. The sample structure is Al(2 nm)/EuO(5 nm)/HOPG(0001) and is measured in an optical flow cryostat separate from the UHV growth chamber. Figure 2 inset shows magnetic hysteresis loops measured at 5, 60, and 71 K. At 5 K, the remanence (M_R/M_S) is 0.37, the coercive field (H_C) is 87 Oe, and the saturation Kerr rotation is 0.93°. Figure 3 shows a temperature dependence of the saturation magnetization at $T_C = 69$ K, the bulk value for EuO.

While EuO/HOPG serves as a useful system for examining the epitaxy of EuO on sp^2 -bonded carbon and allows for the use of standard thin film characterization techniques, realization of EPI at EuO/graphene interfaces requires direct integration of EuO on either exfoliated or CVD graphene. Graphene flakes are mechanically exfoliated onto 300 nm SiO_2/Si substrate using standard techniques.²⁶ Single layer (SLG), bilayer (BLG), and trilayer (TLG) flakes are identified under an optical microscope and confirmed by Raman spectroscopy.²⁷ A 5 nm EuO film is deposited on top of exfoliated graphene flakes on SiO_2 and capped with 2 nm MgO. Figure 4a shows an optical microscope image of pristine graphene flakes, while Figure 4b shows the same flakes after EuO deposition with noticeable darkening of the graphene flakes. Raman spectroscopy (535 nm laser) of EuO/graphene for several flake thicknesses is shown in Figure 4c. Several key features are immediately apparent for EuO deposited onto graphene flakes. First, we do not observe a D peak above the noise level of the measurement. The D peak is typically associated with induced disorder,^{28–30} suggesting that the deposition process does not induce significant defects when compared with reports for oxide growth by pulsed laser deposition, e-beam, and sputter deposition.³¹ Second, the G peak shrinks in relative size compared with features above 2200 cm^{-1} due to decreased signal from the impeding EuO overlayer. Lastly, the spectra exhibit a significant modification around the graphene 2D peak. To better understand this behavior, we compare with single-crystal EuO on lattice-matched YSZ(001).^{21,22}

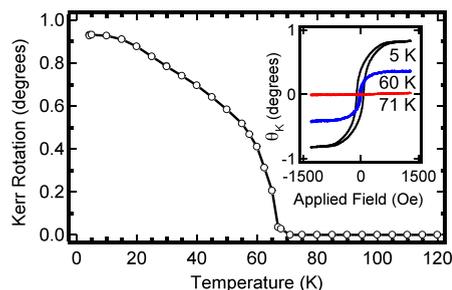


Figure 3. Temperature dependence of the magnetization of EuO/HOPG measured by the magneto-optic Kerr effect. Inset shows several characteristic hysteresis loops at different temperatures.

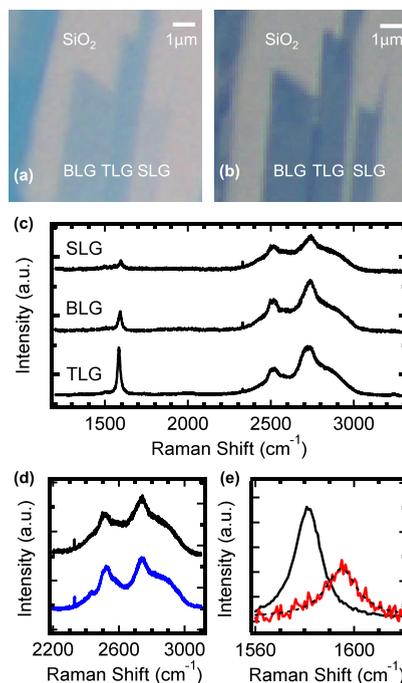


Figure 4. EuO thin films deposited on exfoliated graphene flakes. (a) Optical microscope image of SLG, BLG, and TLG on SiO_2/Si substrate before EuO deposition. The scale bar indicates $1 \mu\text{m}$. (b) Optical microscope image of the same sample after EuO deposition. (c) Raman spectroscopy of EuO deposited on single layer, bilayer, and trilayer graphene. (d) Raman spectroscopy of EuO/SLG (black) compared to EuO/YSZ(001) (blue) in the region around the 2D peak. (e) Raman spectroscopy of the G band for pristine SLG (black) compared to EuO/SLG (red) with the intensities scaled for ease of viewing. Dashed black line is a Lorentzian fit to the G peak for EuO deposited on SLG.

Figure 4d shows the Raman spectra for EuO/SLG and EuO/YSZ around the graphene 2D peak. The features are nearly identical, indicating they are not related to graphene phonon modes.

Raman spectroscopy is a useful technique for investigating external effects on graphene such as doping, strain, and defects.^{29–37} A closer examination of the graphene G peak for 5 nm EuO deposited on SLG (Figure 4e) shows blue shifting of the G peak by 14 cm^{-1} , from 1581 cm^{-1} to 1595 cm^{-1} . We also note blue shifts for EuO/BLG and EuO/TLG of 10 and 6 cm^{-1} ,

respectively. Both charge doping and induced strain could possibly explain the blue-shifted G peak after EuO deposition.^{32–37} For SLG, while a shift of 14 cm^{-1} would suggest an induced charge doping greater than $6 \times 10^{12}\text{ cm}^{-2}$, an increase in the carrier concentration of that magnitude is expected to decrease the fwhm by approximately 8 cm^{-1} .³² Interestingly, for EuO deposited on graphene flakes, the fwhm of the G peak is 13 cm^{-1} for pristine graphene and 15 cm^{-1} with EuO, making charge doping unlikely as the sole cause of the G peak shift. Alternatively, the shift could be caused by strain and is comparable to that reported for annealed $\text{SiO}_2/\text{graphene}/\text{SiO}_2$.³⁴ The 2D peak would shed light on this issue, but is not accessible due to the EuO overlayer.

Next, we discuss the effect of an EuO overlayer on charge transport. Graphene devices are fabricated using standard e-beam lithography techniques with Pd electrodes.³⁸ The resistivity is measured using $1\text{ }\mu\text{A}$ excitation at 11 Hz ac for lock-in detection in a four-point geometry. Figure 5 shows the resistivity for pristine SLG (black curve) with charge neutrality point at $V_{\text{CNP}} = 8\text{ V}$. The device is then loaded into the MBE chamber for growth of 2 nm EuO followed by a 2 nm MgO capping layer. The charge neutrality point after growth (red curve) is $V_{\text{CNP}} = -2\text{ V}$. The electron mobility can be determined from the slope of the conductivity ($\mu = \Delta\sigma/e\Delta n$). The carrier concentration, n , is

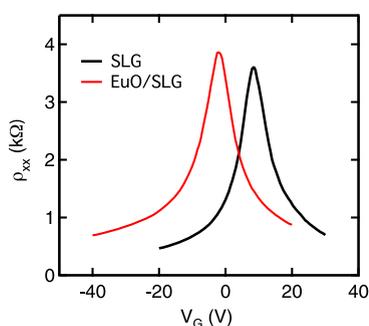


Figure 5. Gate-dependent resistivity for pristine graphene and for the same device with a MgO(2 nm)/EuO(2 nm) overlayer.

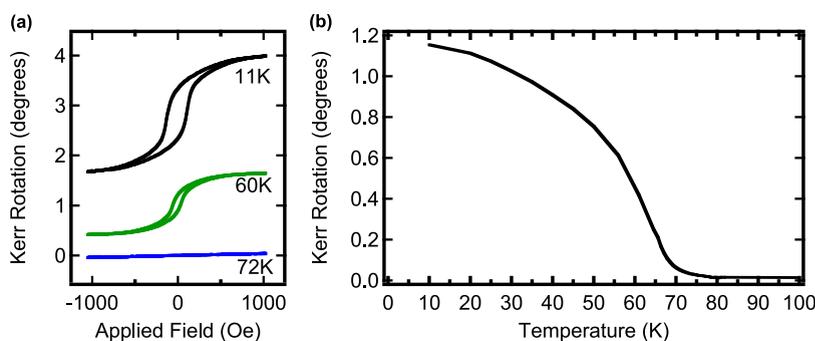


Figure 6. (a) Several characteristic hysteresis loops at different temperatures for 5 nm EuO deposited onto CVD graphene on SiO_2/Si . (b) Temperature dependence of the magnetization measured in degrees.

determined from the relation $n = -\alpha(V_G - V_{\text{CNP}})$, where $\alpha = 7.2 \times 10^{10}\text{ V}^{-1}\text{ cm}^{-2}$ for 300 nm SiO_2 gate dielectric. The resulting electron mobility for pristine SLG and EuO/SLG are $\mu_e = 4600\text{ cm}^2/(\text{V s})$ and $\mu_e = 4080\text{ cm}^2/(\text{V s})$, respectively. Thus, the deposition of EuO on the graphene surface does not significantly decrease the mobility.

Lastly, we investigate the magnetic properties of EuO/graphene. For this, we employ large-area graphene, which has been demonstrated to produce high-quality films with large grains³⁹ and is therefore desirable for MOKE characterization, which has a spot size with a $\sim 40\text{ }\mu\text{m}$ diameter. Large-area graphene is grown by chemical vapor deposition on copper foil and subsequently transferred to SiO_2/Si .³⁹ Next, a 5 nm EuO thin film with a 2 nm MgO capping layer is deposited on the CVD graphene in the distillation- and oxygen-limited regime. Figure 6a shows several MOKE hysteresis loops taken at 11 , 60 , and 72 K . As typical with EuO thin films, we observe a large Kerr rotation above 1° , which subsequently decreases in magnitude as the temperature is increased toward the Curie temperature of 69 K , as shown in Figure 6b.

CONCLUSION

We have investigated the integration of the ferromagnetic insulator EuO with graphene. Using Auger spectroscopy, we find that distillation (re-evaporation) of Eu from the graphene surface occurs for temperatures above $550\text{ }^\circ\text{C}$. Employing the distillation- and oxygen-limited regime, EuO was deposited on HOPG and graphene. The structural, chemical, and magnetic properties of these heterostructures were investigated by RHEED, XRD, AFM, Raman, Auger, and MOKE. EuO films grow epitaxially on honeycomb carbon with (001) orientation, and the EuO does not induce significant defects in the exfoliated graphene. The growth technique presented here demonstrates a significant materials advance in the field of oxide growth on graphene, which is notoriously difficult due to the chemically inert nature of the sp^2 surface. EuO films exhibit ferromagnetism with a Curie

temperature of 69 K, equal to the bulk value. The excellent structural and magnetic properties combined with the direct integration without the aid of

a buffer layer are a key advance toward experimental observation of the exchange proximity effect at the EuO/graphene interface.

EXPERIMENTAL METHODS

Elemental europium metal (99.99%) is evaporated from a low-temperature thermal cell. After proper degassing, a Eu background pressure below 4×10^{-9} Torr is maintained for rates between 8 and 9 Å/min. Molecular oxygen (99.999%) is leaked into the chamber, and the partial pressure is determined by leaking in an amount P_{O_2} above the background pressure as measured by an ion gauge. Typically, a partial oxygen pressure of 1×10^{-8} Torr is used, for which 30 min growth time produces films approximately 5 nm thick.²² The substrate temperature is monitored by a thermocouple located on the platen face. The UHV MBE chamber has a base pressure of $\sim 1 \times 10^{-10}$ Torr and is equipped with *in situ* RHEED. Samples are transferred to an adjacent chamber for 3 keV Auger spectroscopy with a base pressure less than 5×10^{-9} Torr. XRD measurements were performed at UCSB MRL Central Facilities. Longitudinal MOKE is performed in an optical flow cryostat with a p-polarized laser beam (635 nm) and an incidence angle of 45° with respect to the in-plane magnetization direction. The laser intensity is 100 μW focused to a spot size of ~ 40 μm in diameter. Large-area graphene is produced by low pressure CVD as reported by Li *et al.*³⁹ A 25 μm thick Cu foil (Alfa Aesar, item no. 13382) is loaded into a tube furnace and heated to 1035 °C. After a 10 min anneal in H₂ with a flow rate of 2 sccm and pressure $P_{\text{furnace}} = 2.5 \times 10^{-2}$ mbar, 7 sccm of CH₄ is introduced for a total pressure of 1.4×10^{-1} mbar. After cooling and removal from the furnace, the Cu is etched away with iron nitrate and transferred onto SiO₂/Si substrate with the aid of poly(methyl methacrylate) (PMMA) as mechanical support. The PMMA is removed with acetone at room temperature followed by IPA cleaning. Before EuO growth, the large-area graphene sample is annealed at 600 °C under UHV conditions.

Conflict of Interest: The authors declare no competing financial interest.

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