Lutetium-doped EuO films grown by molecular-beam epitaxy

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(Received 24 January 2012; accepted 10 May 2012; published online 29 May 2012)

The effect of lutetium doping on the structural, electronic, and magnetic properties of epitaxial EuO thin films grown by reactive molecular-beam epitaxy is experimentally investigated. The behavior of Lu-doped EuO is contrasted with doping by lanthanum and gadolinium. All three dopants are found to behave similarly despite differences in electronic configuration and ionic size. Andreev reflection measurements on Lu-doped EuO reveal a spin-polarization of 96% in the conduction band, despite non-magnetic carriers introduced by 5% lutetium doping.

The ferromagnetic half-metal europium oxide (EuO) has potential for spin-based devices like spin-injectors based on its >90% spin-polarization or optical devices based on its giant magneto-optic Kerr effect and a Faraday rotation of 8.5 × 10⁴ deg/cm in a field of 2 T. Its low Curie temperature (T_C = 69 K), however, impedes the incorporation of EuO into devices. The T_C of EuO can be increased by doping it with electrons. The interaction between the Eu f-electrons and the dopant electrons enhances the ferromagnetic exchange energy and results in an increased T_C. To date, this has been accomplished through the use of trivalent cations including iron, lanthanum, gadolinium, andholmium. Alternatively, the T_C can be increased by deliberately making oxygen-deficient EuO such that the resulting oxygen vacancies donate an electron.

Each film was nominally 35 nm thick, but the uncertainty in the exact oxygen flux during each growth corresponds to roughly 10% variability in the EuO growth rate and therefore the thickness. Europium and the dopant were co-deposited from separate effusion cells. Prior to growth, the europium flux was calibrated using a quartz crystal microbalance (QCM) to a flux of 1.1 × 10¹⁴ atoms/(cm² s). This flux was 100% higher than the rate at which europium was incorporated into the EuO film. The lanthanum, gadolinium, and lutetium fluxes were calibrated by a QCM to correspond to 4% doping of the EuO for the films characterized by in situ x-ray photoelectron spectroscopy (XPS) measurements and 5% for the films characterized ex situ.

Several films were transferred under ultra-high vacuum immediately after growth into an analysis chamber for XPS characterization using Mg Kα radiation (1253.6 eV). The remaining films were capped with 20 nm of amorphous silicon to protect the films from further oxidation during their ex situ characterization. Structural characterization was performed using four-circle X-ray diffraction (XRD) utilizing Cu Kα radiation. The T_C was determined using superconducting quantum-interference-device (SQUID) magnetometry. The films were measured in zero field after applying a demagnetization routine at 300 K to minimize the spurious magnetic fields originating from parts of the SQUID.

At
this temperature the EuO is in the paramagnetic state without oriented ferromagnetic domains. Bridges were patterned into the doped EuO films using photolithography in combination with in situ ion etching and sputter deposition.\textsuperscript{16} Bridges 1 mm $\times$ 0.1 mm in size were used for four-point resistivity measurements from 4 K to 300 K and Hall measurements at 4 K, and bridges 50 $\mu$m $\times$ 250 $\mu$m in size were used across a ramp-type junction between superconducting niobium and metallic Lu-doped EuO for differential four-point conductivity measurements for Andreev reflection from 1.8 K to 12 K.

The effect of the three dopants on the crystallinity of the epitaxial doped EuO films was assessed by XRD. Figure 1 shows the $\theta$-$2\theta$ XRD patterns of typical EuO films doped with 5% lanthanum, gadolinium, or lutetium. All samples exhibit only 00$\ell$ EuO peaks in addition to the substrate peaks. XRD rocking curves show the full width at half maximum (FWHM) of the EuO 002 peaks to be 0.16 $\pm$ 0.01$^\circ$ for all samples. These data indicate that the doped EuO samples are structurally indistinguishable by XRD.

SQUID magnetometry reveals the $T_C$ of the 5% doped films to be similar. La-doped EuO has $T_C = 116$ K; Gd-doped EuO has $T_C = 122$ K; and Lu-doped EuO has $T_C = 119$ K as seen in Fig. 2(a). The observed kink in the Lu-doped EuO (and to a lesser extent, the La-doped EuO) could be consistent with clustering of dopants in the film.\textsuperscript{10} The temperature dependence of the resistivity for the same samples is shown in Fig. 2(b). Hall measurements for these samples reveal that Gd-doped EuO has the highest carrier concentration with $n = 5 \times 10^{20}$ cm$^{-3}$ followed by both the La- and the Lu-doped EuO with carrier concentrations of $n = 2.1 \times 10^{20}$ cm$^{-3}$ and $n = 1.8 \times 10^{20}$ cm$^{-3}$, respectively. The difference in $T_C$ and carrier concentration is within the accuracy of our doping level control, the accuracy of the film thickness, and the strong dependence of dopant activation on substrate temperature.\textsuperscript{5}

XAS was used to verify the $3^+$ oxidation state of the gadolinium in the Gd-doped EuO films\textsuperscript{17} and XPS was used to verify the $3^+$ oxidation state of the lanthanum and lutetium in the La- and Lu-doped EuO films, respectively. XAS and XPS were also used to confirm that the oxidation state of Eu is nearly completely Eu$^{2+}$, with a small amount of Eu$^{3+}$ attributed to surface oxidation in uncapped samples as documented in the supplementary information of Ref. 16. Figure 3 shows the XPS intensity of the lutetium 4d core-level multiplets for the lutetium in Lu-doped EuO, lutetium metal, and Lu$_2$O$_3$. Lutetium metal was deposited at room temperature in vacuum by MBE, and Lu$_2$O$_3$ was formed by keeping the lutetium metal in vacuum with a background pressure of 2 $\times$ 10$^{-9}$ Torr for at least 1 h. Comparing the peak positions to the literature\textsuperscript{16} confirmed

![FIG. 1. $\theta$-$2\theta$ scans comparing epitaxial EuO films with 5% lanthanum-doping (blue), 5% gadolinium-doping (green), and 5% lutetium-doping (red). All three films are phase-pure with no indication of dopant insolubility. The curves are offset for clarity and the substrate peaks are marked with asterisks.](image1)

![FIG. 3. Comparison of X-ray photoemission intensity of the lutetium 4d core-level multiplets between 4% Lu-doped EuO (blue), lutetium metal (green), and oxidized lutetium (red). The dashed lines are guides for the eye to highlight the similarity in peak position between the 4% Lu-doped EuO and the oxidized lutetium.](image2)
that the lutetium in the Lu-doped EuO film was indeed $3^+$ as expected. A similar process was followed for identifying the oxidation state of lanthanum in the La-doped EuO. From the free carrier concentration, oxidation state, and the doping concentration, it is evident rare-earth dopant ions inject far less than one mobile electron into the EuO conduction band. The dopant activation is less than 40%, in agreement with results for Gd-doped EuO, pointing to the possible ubiquity of the challenge of achieving high dopant activation in EuO. All samples have comparable resistivity curves, reduced dopant activation, and fairly similar carrier concentrations.

Differential conductance measurements were performed on 5% Lu-doped EuO and are shown in Fig. 4. Since Andreev reflection is suppressed at the interface between a material with high spin-polarization and a superconducting material, a drop in conductivity across the Lu-doped EuO/Nb interface for energies less than the superconducting gap of the niobium film at temperatures below the superconducting critical temperature is expected. By fitting the drop in conductance to the Blonder-Tinkham-Klapwijk model$^{25}$ that has been modified specifically for non-negligible series resistance in spin-polarized ferromagnetic semiconductor devices,$^{26–28}$ one can extract the spin-polarization value. The best fit is in accordance with a spin-polarization of 96%, which is in agreement with previous reports of the near-complete spin-polarization of EuO.$^{1}$ The high spin-polarization despite 5% doping of nonmagnetic atoms is critically important, as it shows that EuO retains its high spin-polarization in the presence of a dopant which significantly boosts its $T_C$. This is not so surprising given that doped EuO is a half-metal due to the spin-splitting of the conduction band,$^{29–31}$ so the carriers are spin-polarized anyway despite the nature of the dopant.

In summary, we have explored the properties of Lu-doped EuO. Lutetium donates electrons to EuO in the same fashion as lanthanum and gadolinium dopants. Furthermore, EuO retains near-complete spin-polarization ($P = 96\%$) despite being heavily doped with the non-magnetic ion Lu.$^{3}$

The work at Cornell was supported by the AFOSR (Grant No. FA9550-10-1-0123), the NSF MRSEC program by cooperative agreement 1120296, and NSF DMR-0847385, and a Cottrell Scholars Award (20025). The work in Augsburg was supported by the DFG (Grant No. TRR 80) and the EC (oxIDES). AM gratefully acknowledges support from the NSF IGERT program (NSF Award DGE-0654193) and by the IMI Program of the National Science Foundation under Award No. DMR 0843934. EJM acknowledges NSERC for PGS support.