Two-dimensional electron system at the magnetically tunable EuO/SrTiO$_3$ interface

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We create a two-dimensional electron system (2DES) at the interface between EuO, a ferromagnetic insulator, and SrTiO$_3$, a transparent non-magnetic insulator considered the bedrock of oxide-based electronics. This is achieved by a controlled in situ redox reaction between pure metallic Eu deposited at room temperature on the surface of SrTiO$_3$ – an innovative bottom-up approach that can be easily generalized to other functional oxides and scaled to applications. Additionally, we find that the resulting EuO capping layer can be tuned from paramagnetic to ferromagnetic, depending on the layer thickness. These results demonstrate that the simple, novel technique of creating 2DESs in oxides by deposition of elementary reducing agents [T. C. Rödel et al., Adv. Mater. 28, 1976 (2016)] can be extended to simultaneously produce an active, e.g. magnetic, capping layer enabling the realization and control of additional functionalities in such oxide-based 2DESs.

Introduction.- Two-dimensional electron systems (2DESs) in functional oxides have gained strong interest as a novel state of matter with fascinating and exotic interface physics. For instance, the 2DES in LaAlO$_3$/SrTiO$_3$ (LAO/STO) interfaces can host metal-to-insulator transitions, superconductivity and magnetism – all of them tunable by gate electric fields [1–9]. The prospect of creating and manipulating a macroscopic magnetic ground state in oxide-based 2DESs is of enormous interest, as this would pave the route towards oxide spintronic applications with novel quantum phases beyond today’s semiconductor technology.

Recent studies aimed at supporting the existence of magnetic ordering at the LAO/STO interface, e.g. by the observation of tunnel magnetoresistance (TMR) [10] or the inverse Edelstein effect [11, 12]. The magnetic field dependence of TMR was attributed to a Rashba-type spin-orbit coupling, potentially allowing the manipulation of spin polarization in a 2DES, whereas its spin-momentum locking may enable a high efficiency of the conversion of an injected spin current into a charge current. In fact, in the case of the LAO/STO interface, it was recently demonstrated that additional epitaxial ferroic oxide layers can be used to tune the spin polarization of the 2DES by an electric field [13] or to control its conduction in a non-volatile manner by ferroelectric switching [14].

So far, the design of functional 2DES required a single layer growth control of epitaxial LAO onto SrTiO$_3$. The emergence of interfacial quantum states, such as magnetism, superconductivity or spin-orbit coupling, only sets in at a critical LAO thicknesses of 4 unit cells and in certain regions of the 2DES phase diagram [10]. This conundrum was circumvented by the finding that 2DESs could be fabricated at the bare surface of several oxides, through the creation of oxygen vacancies at their surface [15–22]. These surface 2DESs can also show magnetic domains [23], thus constituting an appealing alternative for the use and control of electric and magnetic properties of confined states in oxides.

Here, we show that insulating and ferromagnetic EuO can be grown on SrTiO$_3$ while simultaneously creating a 2DES at the interface. As schematized in Fig. 1, the fabrication of the 2DES is simply accomplished by the deposition of pure metallic Eu at room temperature in ultrahigh vacuum. We find that the resulting EuO capping layer can be tuned from paramagnetic to ferromagnetic, depending on the Eu metal coverage ($d_{Eu} = 1$ ML and 2 ML, respectively), and show, using angle-resolved photoemission spectroscopy (ARPES), that the integrity of the 2DES is preserved in both cases, thus providing an ideal knob for tuning the spin-transport properties of the 2DES. This bottom-up approach to create a 2DES by an interfacial redox process relies on recent results demonstrating that the evaporation of an amorphous ultra-thin layer of Al metal on top of an oxide surface generates a homogeneous 2DES [24]. As the redox reaction between oxides and elementary metals with a large heat of formation of the corresponding metal oxide is a general phenomenon [25], 2DESs can be created in various oxides, e.g. SrTiO$_3$, TiO$_2$, and BaTiO$_3$ [24]. In the present study, we advance this exciting possibility simultaneously creating a 2DES and forming a functional metal oxide overlayer – i.e. in a macroscopic ferromagnetic ground state – by choosing a suitable elementary metal (Eu). Our experiments demonstrate how to elegantly link the simplicity and universality of an interfa-
hemi-spherical energy analyzer at FZ Jülich. The Eu 3d and Ti 2p core-levels are analyzed to quantify the oxidation state of the deposited Eu-metal and to observe the redox process with the substrate surface. Before the ex situ magnetization measurements, realized with a Quantum Design MPMS SQUID magnetometer, the EuO/SrTiO$_3$ samples are further capped with 15 nm of e-beam evaporated MgO to avoid additional oxidation. A hysteresis loop of $H = \pm 1500$ Oe at $T = 5$ K is performed, while temperature dependence is recorded with an aligning field of $H = 500$ Oe for $T = 5$ to 150 K. All magnetization data was measured in-plane.

The ARPES measurements are conducted at the CAS-SIOPEE beamline of synchrotron SOLEIL. The beamline is equipped with an MBE chamber allowing the in situ preparation of the SrTiO$_3$ surfaces and evaporation of the pure Eu-metal using the same above-specified conditions. We furthermore checked that a surface cleaning using a much faster annealing (about one minute) creates a negligible amount of bulk oxygen vacancies. Eu evaporated hereafter then results in an identical 2DES, as for example shown by the red arrows.

The preparation of ultrathin EuO films by oxide molecular beam epitaxy (MBE) poses several experimental challenges. The oxygen partial pressure, the substrate temperature, and the rate of impinging Eu-metal atoms must be carefully controlled. However, only the stoichiometric compound yields the desired simultaneous occurrence of magnetic and semiconducting behaviors. In this paper a novel method to synthesize ultrathin EuO is demonstrated and put into practice, i.e. a controlled interfacial redox reaction with oxygen provided by the substrate material only.

The undoped TiO$_2$-terminated SrTiO$_3$ samples are prepared using a well established technique. Atomic force microscopy images show a flat surface with steps of unit cell height and a roughness within one terrace of typically 150 pm and a c-direction miscut angle $< 0.1^\circ$. The samples are then annealed in vacuum to 500 °C for 0.5 h in a MBE chamber at a base pressure of $1.3 \times 10^{-10}$ mbar prior to Eu evaporation and photoemission experiments. The cleanliness and crystallinity of the so-obtained surfaces are checked by in situ X-ray photoemission spectroscopy (XPS). Pure Eu metal is then evaporated at 480 °C at a rate of 0.3 Å min$^{-1}$ using a low temperature Knudsen cell, while the SrTiO$_3$ substrate is kept at room temperature. The deposition rate of Eu metal is monitored by a calibrated quartz microbalance.

The redox-created oxidation state of the Eu on the SrTiO$_3$ surface is analyzed using XPS with Al K$_\alpha$ radiation from a SPECS X-Ray anode and a PHOIBOS-100 hemispherical energy analyzer at FZ Jülich. The Eu 3d and Ti 2p core-levels are analyzed to quantify the oxidation state of the deposited Eu-metal and to observe the redox process with the substrate surface. Before the ex situ magnetization measurements, realized with a Quantum Design MPMS SQUID magnetometer, the EuO/SrTiO$_3$ samples are further capped with 15 nm of e-beam evaporated MgO to avoid additional oxidation. A hysteresis loop of $H = \pm 1500$ Oe at $T = 5$ K is performed, while temperature dependence is recorded with an aligning field of $H = 500$ Oe for $T = 5$ to 150 K. All magnetization data was measured in-plane.

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EuO overlayer is ferromagnetic (blue curve) with a saturation magnetization of $M_S = 4\mu_B$ per formula unit (f.u.). The measured saturated magnetic moment for 2 ML of EuO capping is close to the corresponding theoretical values for EuO at $T = 0$ K, represented by horizontal dashed lines. Now the underlying 2DES (see next) is interfaced with a magnetic material, which may ultimately enable a control of the spin degrees of freedom in this system.

The formation of oxygen vacancies near the SrTiO$_3$ surface, induced by the redox reaction with the Eu evaporated on top of it, results in a local electron doping of the substrate and the creation of a 2DES, in analogy with the 2DESs formed by oxygen vacancies at the UV-irradiated surface or Al-capped interface of SrTiO$_3$ or other oxides. This is directly demonstrated by the ARPES data shown in Fig. 4. Figs. 4(a, b) show the circular Fermi surfaces around $\Gamma$ of the two 3d$_{xy}$ subbands at the interfaces between 1 ML and 2 ML EuO films on SrTiO$_3$, respectively. Figs. 4(c, d) present the corresponding energy-momentum ARPES intensity maps along the $k_{\perp}$ direction at $k_{\parallel} = 2\pi/a$ ($a = 3.905$ Å is the lattice parameter of SrTiO$_3$). These correspond to the two Ti 3d$_{xy}$ light subbands previously reported for the 2DES in SrTiO$_3$. For the 2DES at the EuO(1 ML)/SrTiO$_3$ interface, the band bottoms ($E_D \approx -200$ meV and $-90$ meV for the outer and inner subbands, respectively), Fermi momenta ($k_F \approx 0.19$ Å$^{-1}$ and 0.12 Å$^{-1}$), effective masses ($m^*/m_e = 0.7 \pm 0.05$ for both subbands, estimated from a parabolic approximation to the band dispersions, where $m_e$ is the bare electron mass), and the observation of a kink at $E \approx -30$ meV below $E_F$, ascribed to a band renormalization due to electron-phonon interaction, are all in agreement with previous reports. As shown in Fig. 4(c), the ellipsoidal Fermi surfaces, associated with the Ti 3d$_{xz/yz}$ heavy subbands, are also observed using horizontal light polarization. From the total area $A_F$ enclosed by all the Fermi surfaces, the density of carriers of the 2DES at the EuO/SrTiO$_3$ interfaces is $n_{2D} = A_F/(2\pi^2) \approx 2.0 \times 10^{14}$ cm$^{-2}$, which is comparable to the density of states of the 2DES at the bare SrTiO$_3$ surface. The thickness of the 2DES can be directly inferred from the number of subbands, their band bottoms and energy separations. Thus, as the electronic structure of the 2DES at the EuO(1 ML)/SrTiO$_3$ interface is essentially the same as the one observed at the bare surface of SrTiO$_3$, or at the Al-capped surface of SrTiO$_3$, we conclude that its thickness is also the same, namely about 4–5 unit cells.

ARPES measurements are performed under zero external magnetic field, to guarantee conservation of the photo-emitted electron momentum. Thus, while magnetizing the capping EuO film is not feasible for these measurements, it is nevertheless instructive to compare the ARPES data between the 1 ML and 2 ML EuO.
FIG. 4. ARPES data of the EuO/SrTiO$_3$ interface. (a, b) Fermi-surfaces taken around the $\Gamma_{102}$ point of SrTiO$_3$ for nominally 1 ML (raw data) and 2 ML (negative values of second derivatives) EuO coverage, respectively, using $47\,\text{eV}$ photons with linear vertical (LV) light polarization. These photon energy and polarization enhance the photoemission intensity of the $3d_{xy}$ circular Fermi surfaces. (c, d) Corresponding dispersion of the two Ti $3d_{xy}$ light subbands. (e) Fermi-surfaces taken around the $\Gamma_{103}$ point of SrTiO$_3$ for 1 ML EuO coverage using $90\,\text{eV}$ photons with linear horizontal (LH) light polarization. These photon energy and polarization enhance the photoemission intensity of one of the two orthogonal $3d_{xz/yz}$ ellipsoidal Fermi surfaces. As with our previous results on Al-capped SrTiO$_3$ [24], we crosschecked that for both 1 ML and 2 ML EuO the 2DEG forms instantaneously after the Eu deposition, and its carrier density is independent of the dose of UV light used to measure the ARPES data. In other words, the 2DEG is entirely due to the oxidation of the capping layer.

Conclusions. In summary, we demonstrated that the deposition in vacuum, at room temperature, of Eu-metal on SrTiO$_3$ results in the simultaneous creation of a 2DES in the oxide substrate and a capping EuO layer that can be tuned from paramagnetic (1 ML thickness) to ferromagnetic (2 ML). These results open new perspectives for investigating the interaction of the magnetic and electronic properties of the 2DES in SrTiO$_3$. More generally, these results lay a new ground for the simple and versatile design of all-oxide devices in which the functionalities of the constituting elements, and their mutual coupling, can be obtained from controlled physicochemical reactions and vacancy engineering at their interfaces.

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[1] A. Ohtomo and H.Y. Hwang, Nature (London) 427, 423 (2004).
[2] S. Thiel, G. Hammerl, A. Schmehl, C.W. Schneider, and J. Mannhart, Science 313, 1942 (2006).
[3] N. Reyren, S. Thiel, A.D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C.W. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, M. Gabay, D.A. Muller, J.-M.
