AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **113**, 17C505 (2013); doi: 10.1063/1.4795010
View online: http://dx.doi.org/10.1063/1.4795010
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/113/17?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **113**, 17C505 (2013)

Ultrathin magnetic oxide EuO films on Si(001) using SiO_x passivation—Controlled by hard x-ray photoemission spectroscopy

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(Presented 18 January 2013; received 31 October 2012; accepted 12 December 2012; published online 13 March 2013)

We present the chemical and structural optimization of ultrathin magnetic oxide EuO films on silicon. By applying a controlled *in situ* passivation of the Si(001) surface with SiO_x in the monolayer regime, metallic silicide contaminations at the interface can be effectively reduced down to a sub-monolayer coverage, as was carefully quantified by interface-sensitive hard x-ray photoemission spectroscopy. Heteroepitaxial growth of EuO on Si(001) is sustained for this ultrathin SiO_x-passivation, and bulk-near magnetic properties are observed for the 4 nm-thin EuO films. Our successful combination of chemically and structurally optimized EuO/Si(001) heterostructures by ultrathin *in situ* SiO_x passivation makes this system promising for an application as alternative spin functional tunnel contacts in spin-FETs. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4795010]

Magnetic insulators are perfect candidates for integrating spin-selective tunnel functionality with semiconductors in spin-FET devices.[1–3] In particular, europium oxide (EuO)[4] is the only binary magnetic oxide which is predicted to be thermodynamically stable in direct contact with silicon, the technologically most relevant semiconductor.[5] However, spin injection and detection functionality are strongly influenced by the chemical and structural quality of the functional interface of the EuO tunnel barrier in contact with the Si electrode—whereas bulk and interface properties of the EuO ultrathin film are notoriously difficult to control during synthesis, e.g., by reactive MBE.[6,7]

In a previous study, we reported the successful stabilization of high qualtity and stoichiometric EuO ultrathin films directly on silicon.[8] Nonetheless, realizing both a chemically well-defined and crystalline sharp interface remains challenging for the system EuO/Si, since high-quality EuO synthesis requires to apply the Eu-distillation condition, in terms of high temperature and Eu-rich growth.[9,10] This approach, however, may readily lead to chemical interdiffusion and interfacial reactions between the magnetic oxide and the Si substrate. Inserting an oxide buffer layer of several nm thickness may improve the structural and chemical quality of the EuO/Si interface;[11,12] however, these buffer layers significantly increase the tunnel path for electrons passing through the oxide barriers.

Here, we present the approach of passivating the Si(001) surface using a fine-adjusted *in situ* SiO_2 formation in the monolayer regime, in order to control the Si surface reactivity and prepare a well-defined EuO/Si interface. To investigate a direct correlation of the EuO thin film crystal structure and the chemical quality of the functional EuO/Si interface with the respective *in situ* Si(001) surface passivation, EuO/Si(001) heterostructures are investigated by reflection high-energy electron diffraction (RHEED) and hard x-ray photoemission spectroscopy (HAXPES). The direct impact of the interface optimization on the EuO magnetic properties is investigated by SQUID magnetometry. By successively improving crystal structure, interface chemistry, and magnetic properties via an ultrathin *in situ* SiO_x passivation, we succeeded in stabilizing chemically and structurally well-defined EuO/Si(001) interfaces.

EuO/Si(001) heterostructures are prepared in an oxide MBE system under ultrahigh vacuum with a residual gas pressure $p < 10^{-10}$ mbar. First, Si(001) wafer pieces are cleaned by thermal flashing ($T_{\mathrm{Si}} \geq 1100\,^{\circ}\mathrm{C}$), followed by surface passivation with either molecular oxygen ($p \sim 10^{-7}$ mbar, $T_{\mathrm{Si}} = 700\,^{\circ}\mathrm{C}$) or atomic hydrogen ($p \sim 10^{-2}$ mbar, $T_{\mathrm{Si}} = \mathrm{RT}$). Any contamination of the Si surface is below the detection limit of Auger electron spectroscopy. The crystalline structure of the passivated Si surface is checked by low energy electron diffraction and a clear (1×1) Si(001) bulk diamond structure is observable, in contrast to a (2×1) surface reconstruction in case of flashed Si(001). Second, 4 nm EuO thin films are grown directly on the Si(001) substrates. In order to stabilize stoichiometric EuO, a low oxygen partial pressure ($p_{\mathrm{O}_2} \sim 1$–2×10^{-9} mbar) and the europium distillation condition[9,10] are applied. During EuO synthesis, the surface crystal structure is monitored with RHEED. Finally, the EuO/Si heterostructures are capped with 5 nm air-protective Al.

The electronic structure studies (HAXPES) of the EuO/Si heterostructures were conducted at the undulator beamline P09 at PETRA III (DESY, Hamburg),[13] and at the KMC-1 dipole beamline at BESSY II (Berlin) with the HIKE endstation.[14] The total energy resolution is $\sim$250 meV for $h\nu = 2.7$ keV (500 meV for $h\nu = 4$ keV) using a Si (111) double-crystal

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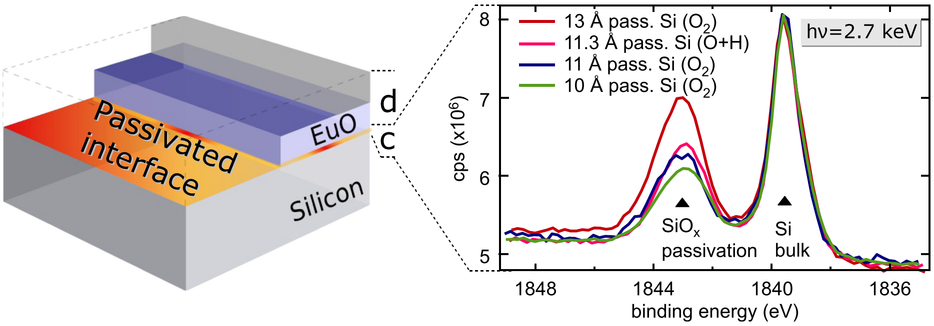

FIG. 1. EuO/Si(001) heterostructure with SiO_x passivation. Right*:* Interface-sensitive Si 1*s* core-level spectra for different SiO_x passivations of the Si(001) surface.

monochromator, and all spectra were recorded at room temperature. The Fermi edge of Au foil on the sample serves as calibration for the binding energy. Tougaard-type backgrounds are used to account for inelastic photoelectron scattering. HAXPES allows to quantify the thickness c of a possible reaction layer (rl) at the EuO/Si interface (see Fig. 1). For this, the spectral weights of the different chemical components in the Si spectra (Figs. 2(a) and 2(b)) are integrated by taking into account an exponential damping by the overlayer of thickness d

$$I_{\mathrm{rl}}(c,d,\lambda) = e^{-\frac{d}{\lambda_{\mathrm{cap}}\cos\alpha}} \int_{d}^{d+c} e^{-\frac{x}{\lambda_{\mathrm{rl}}\cos\alpha}}\,\mathrm{d}x, \tag{1a}$$

$$I_{\mathrm{Si}}(c,d,\lambda) = e^{-\frac{c+d}{\lambda_{\mathrm{cap}}\cos\alpha}} \int_{d+c}^{\infty} e^{-\frac{x}{\lambda_{\mathrm{Si}}\cos\alpha}}\,\mathrm{d}x, \tag{1b}$$

where α denotes the off-normal exit angle and λ the effective attenuation length (EAL) of the photoelectrons,[15] respectively. The fraction f_{rl} of spectral contribution from the interfacial reaction layer with respect to the bulk Si spectral intensity, in which the measured intensities I have to be normalized by λ and the density n of Si atoms,

$$\frac{I_{\mathrm{rl}}(c,d,\lambda)}{I_{\mathrm{Si}}(c,d,\lambda)} \overset{\mathrm{calc}}{=} f_{\mathrm{rl}} \overset{\mathrm{meas}}{=} \frac{I_{\mathrm{rl}}}{I_{\mathrm{Si}}} \cdot \frac{\lambda_{\mathrm{Si}} n_{\mathrm{Si}}}{\lambda_{\mathrm{rl}} n_{\mathrm{rl}}} \tag{2}$$

yields the thickness c of the reaction layer or of the SiO_x passivation. By adjusting the integration limits and λ, Eqs. (1) and (2) also provide the thickness of the $EuSi_y$ reaction layer from Eu spectral intensities (Figs. 2(c)–2(e)).

Interface-sensitive HAXPES spectra of the EuO/Si heterostructures are depicted in Figs. 2(a) and 2(b). Stable silicon oxide is observed at chemical shifts of 3.2 and 4.1 eV in the Si 1*s* spectrum, which identify Si^{3+} (Si_2O_3) and Si^{4+} (SiO_2), in good agreement with the recent PES studies of ultrathin SiO_2/Si(001).[16,17] Another component at the EuO/Si interface with a chemical shift to lower BE is observed in the Si spectra as well as in the Eu 3*d*, 4*d*, and 4*f* spectra, which is identified as a metallic Eu silicide ($EuSi_y$). Due to the small chemical shift of $EuSi_y$ (−0.65 eV for Si2*p*), only the Si spectra and the narrow Eu4*f* multiplet allow for a deconvolution of all silicide components.

A quantitative thickness determination of the SiO_x passivation at the Si(001) interface and of the resulting silicide reaction layer is accomplished by consistent least squares peak fitting of the HAXPES spectra and applying Eqs. (1) and (2), the results are compiled in Fig. 3. Regarding the chemical reactivity of the EuO/Si interface, we found interfacial silicides to exceed 10 Å thickness for flashed Si(001); however, by applying an ultrathin SiO_x interface passivation ($d_{SiO_x} = 10$–13 Å) silicide formation is suppressed to $d_{EuSi_2} \leq 7.5$ Å. The effect of additional hydrogen passivation

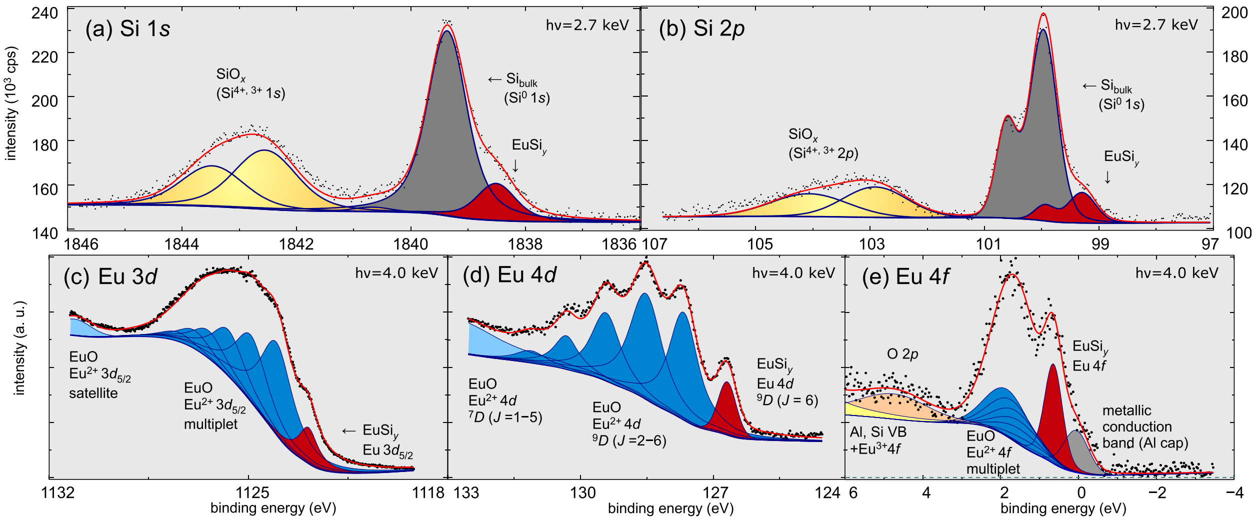

FIG. 2. HAXPES analysis of the EuO/Si interface. (a) and (b) Si 1*s* and 2*p* core-levels recorded at low excitation energy ($h\nu = 2.7$ keV) to probe selectively the Si surface. (c)–(e) Eu 3*d*, 4*d* core, and 4*f* valence-levels (in agreement with Refs. 20–22) recorded at high excitation energy ($h\nu = 4.0$ keV) to fully probe the buried reaction layer at the bottom of the EuO thin film.

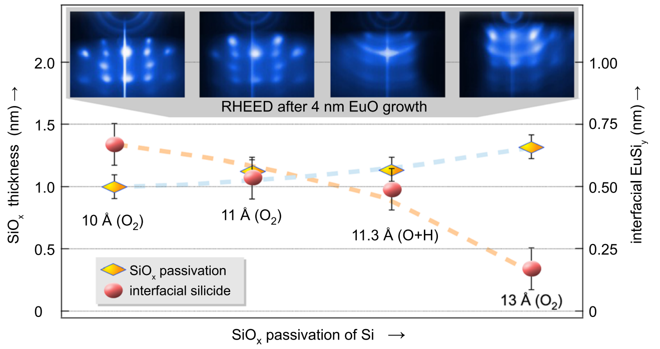

FIG. 3. Chemical properties and crystalline structure of EuO on passivated Si. Thicknesses of SiO$_x$ passivation and the resulting EuSi$_y$ are determined from Si 1*s* and 2*p* spectra. Inset: RHEED after 4 nm EuO growth.

shows a small reduction of EuSi$_y$ of about 9%, whereas the SiO$_x$ passivation (increased from 11 Å to 13 Å) reduces the silicide formation by ∼68%. The optimum value for the quasi-contamination free EuO/Si interface is achieved with 13 Å passivation with SiO$_x$: the silicide is diminished down to 1.8 Å, well below one monolayer of interface coverage.

Next, we use RHEED to investigate the crystalline structure of the EuO thin films grown on passivated Si(001) (Fig. 3 inset), which shows a clear dependence on d_{SiO_x}: for a thin SiO$_x$ passivation ($d_{\mathrm{SiO}_x} = 10$ Å), a sharp EuO(001) *fcc* pattern is observable, with separations of the reciprocal rods indicating an island-like growth mode. For thicker SiO$_x$ passivation ($d_{\mathrm{SiO}_x} = 13$ Å), a RHEED pattern of the EuO(001) *fcc* lattice is still observable; however, circular intensities indicate a polycrystalline fraction of EuO. In the case of an additional hydrogen passivation of the Si, an increased disorder of the H-passivated Si(001) surface[18] leads to the growth of mainly polycrystalline EuO. Finally, we investigate how the magnetic properties of the EuO/Si heterostructures depend on the SiO$_x$ interface passivation. Figure 4 summarizes the in-plane magnetic properties $M(T)$ and $M(H)$ of 4 nm EuO/Si(001) samples with varying SiO$_x$ passivation thicknesses. Not surprisingly, EuO thin films grown on flashed Si(001) without any SiO$_x$ passivation show a strongly reduced magnetic moment and Curie temperature of 10 K (bulk EuO: $T_C \sim 70$ K). As we deduce from the HAXPES results, the formation of a EuSi$_y$ reaction layer largely destroys the EuO ferromagnetic behavior.[19] We note that such a contamination would significantly reduce the spin filter functionality of magnetic oxide EuO/Si tunnel junctions.[1] Applying an SiO$_x$ interface passivation clearly improves the magnetic properties of the EuO thin film. The most effective interface passivation of 13 Å SiO$_x$ yields an M_s of $\sim 5\,\mu_B$/EuO and a T_C of 68 K, close to the EuO bulk values $7\,\mu_B$/EuO and $T_C = 69.3$ K. With increasing SiO$_x$ passivation thickness, however, structural defects and surface roughening cause an increase of the EuO coercive field up to 180 Oe.

Concluding, the chemical and structural optimization of the functional EuO/Si(001) interface was successfully realized by applying the robust *in situ* passivation with monolayer-thin SiO$_x$ on clean Si(001) surfaces. We quantified the thickness of the SiO$_x$ passivation layer by interface-sensitive HAXPES, which revealed SiO$_x$ thicknesses in the lattice constant regime. In particular, an only 13 Å-thick SiO$_x$ passivation layer reduces interfacial silicide contamination down to 1.8 Å, and a heteroepitaxial growth of EuO(001) is observed, with bulk-near EuO magnetic saturation M_S and T_C. Such chemically and structurally optimized EuO/Si(001) heterostructures may be effectively utilized as spin functional tunnel contacts in spin-FET devices in the near future.

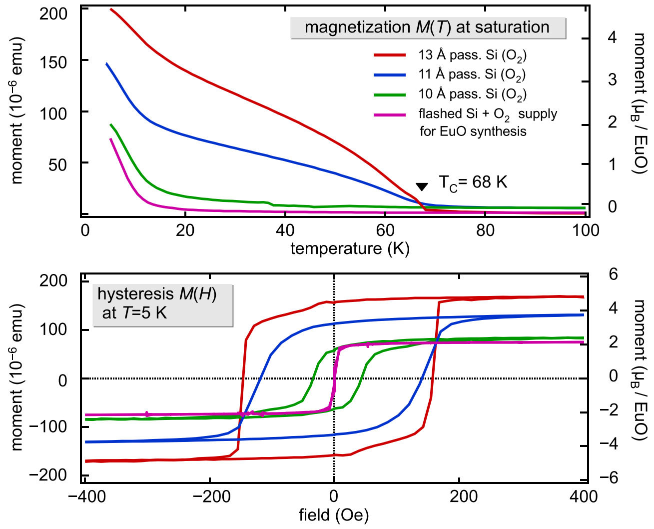

FIG. 4. Magnetic properties of the 4 nm EuO/Si(001) heterostructures dependent on the thickness of the Si(001) surface passivation.

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