Magnetic and electronic properties of the interface between half metallic Fe$_3$O$_4$ and semiconducting ZnO

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We have investigated the magnetic depth profile of an epitaxial Fe$_3$O$_4$ thin film grown directly on a semiconducting ZnO substrate by soft x-ray resonant magnetic reflectometry (XRMR) and electron energy loss spectroscopy (EELS). Consistent chemical profiles at the interface between ZnO and Fe$_3$O$_4$ are found from both methods. Valence selective EELS and XRMR reveal independently that the first monolayer of Fe at the interface between ZnO and Fe$_3$O$_4$ contains only Fe$^{3+}$ ions. Besides this narrow 2.5 Å interface layer, Fe$_3$O$_4$ shows magnetic bulk properties throughout the whole film making highly efficient spin injection in this system feasible.

Half metallic Fe$_3$O$_4$ (magnetite) is a promising candidate for the injection of spin polarized currents into semiconducting material for spintronic applications.1 The good conductivity match between Fe$_3$O$_4$ and most semiconductors together with the very high polarization of its minority band at room temperature1,2 are key requirements for such devices.3 However, whereas epitaxial growth of Fe$_3$O$_4$ is easily achieved on insulating materials such as Al$_2$O$_3$(001) or MgO(001), deposition on Si or GaAs leads to rather poor results.4–6 Absolute values of the absorption (not shown) are in excellent agreement with previous single crystal results17 and the XMCD reveals a clear magnetite signature 18,19 showing three distinct peaks which are associated with octahedral Fe$^{2+}$ and tetragonal Fe$^{4+}$.16,18

Resonant x-ray reflectometry was measured at three different energies across the Fe L$_{2,3}$ edges: at 707.8 eV (max. XMCD effect for octahedral Fe$^{2+}$), at 708.8 eV (max. XMCD of the tetragonal Fe$^{4+}$), and at the Fe L$_2$ edge at 720 eV. These measurements probe the chemical contrast resulting from the largely enhanced resonant absorption cross section shown in Figure 1(a). They were fitted, based on the data from Figure 1(a), using the software remagx (Ref. 20) and Figure 2 shows the measured reflectivities, their respective fits, and the chemical profiles, i.e., roughness and thickness.

Each curve was fitted independently but with the same stoichiometry and mass density for the film. All three fits reproduce the measurements with high quality, yielding with high spatial resolution. X-ray magnetic circular dichroism (XMCD), absorption, and XRMR (Ref. 13) were measured at the PGM3 and UE56/2-PGM1 beamlines at the BESSY II synchrotron of the Helmholtz Center Berlin. To complement the x-ray investigation, scanning transmission electron microscopy (STEM) and EELS were measured at the EMAT laboratory of the University of Antwerp. Room temperature absorption and XMCD spectra of the Fe L edges were measured by total electron yield in a magnetic field of $H_{ext} = 3$ T and at an angle of incidence of 20° with respect to the surface. The data were normalized and scaled to tabulated scattering factors14 to obtain the absolute absorption cross section $\sigma$. This was then used to calculate the real and imaginary part for the optical $(\delta, \beta)$ and magneto-optical $(\delta_{mag}, \beta_{mag})$ contributions to the Fe$_3$O$_4$ $(\rho = 5.17 \text{g/cm}^3)$ complex index of refraction $n = (1 - \delta + i\beta) \pm (\delta_{mag} - i\beta_{mag}) \cos (\delta, \hat{M})$. The result for the optical and magneto-optical contribution is shown in Figure 1. More details on the processing can be found in Ref. 15.

Half metallic Fe$_3$O$_4$ was grown on oxygen terminated ZnO (0001) using oxide MBE (for details see Ref. 6). Its bulk magnetic properties are comparable to those of epitaxial thin films grown on other substrates like MgO.5,12 As mentioned above, the properties of the Fe$_3$O$_4$/ZnO interface are crucial for any application of this system as a spin injector. We use XRMR in combination with scanning EELS to investigate the chemical and magnetic properties of the Fe$_3$O$_4$/ZnO interface.

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consistent depth profiles. The Fe$_3$O$_4$ film has an average overall thickness of $(421 \pm 2)\text{Å}$ and a roughness of $(3.7 \pm 0.3)\text{Å}$ at the substrate/film interface corresponding to approximately 1-2 monolayers of ZnO. The surface roughness of the Fe$_3$O$_4$ film is $8.0\text{ Å}$ for the $707.8\text{ eV}$ and $720\text{ eV}$ profiles whereas the $708.8\text{ eV}$ profile differs slightly in position and width. XPS measurements indicated the presence of a thin layer of off-stoichiometric Fe$_{3-x}$O$_4$ on the sample surface. Since $708.8\text{ eV}$ corresponds to the maximum of the L$_3$ absorption white line (see Figure 1), the reflectivity at this energy is more sensitive to such an off-stoichiometry.

To confirm the chemical properties of the Fe$_3$O$_4$/ZnO interface, a precise STEM/EELS investigation was carried out on a 8 nm Fe$_3$O$_4$ sample grown under similar conditions. Figure 3 shows a high resolution high-angle annular dark field (HAADF)-STEM image on the right and an EELS z-position/energy map recorded along the green line indicated in the STEM image. Details about instrument and acquisition parameters are given in Ref. 21.

The EELS map clearly shows the Fe L$_3$ and L$_2$ edges between 700 and 730 eV and three different oxygen K edge peaks. The double peak feature found at position A is typical for oxygen in Fe$_3$O$_4$ (Ref. 22) whereas the broad single peak at B is oxygen hybridized with Zn. Note, how the pre-peak feature associated with Fe$_3$O$_4$ vanishes below $z = 0$. A line profile of the z dependent intensity of the Fe L$_3$ EELS signal was extracted along the black dashed line indicated by C and

FIG. 1. (Color online) Optical (a) and magneto-optical (b) contributions to the index of refraction of Fe$_3$O$_4$. The gray markers denote the photon energies used in XRMR. The maxima in the magnetic $\beta$ ($\propto$ XMCD signal) are labeled according to Ref. 16. The inset shows the unit cell of bulk Fe$_3$O$_4$ with respect to the $\langle 111 \rangle$ growth direction of the film. The individual Fe layers of bulk Fe$_3$O$_4$ exhibit a mixed distribution of Fe$^{2+}$ and Fe$^{3+}$ valencies.

FIG. 2. (Color online) (a) X-ray reflectivity at three different energies across the Fe L$_{2,3}$ edges. The red curves show the best fit result for each measurement. For $Q_z < 0.05 \text{ Å}^{-1}$ all measurements show a systematic deviation due to an incomplete illumination of the sample. This region was excluded from the fitting process. Subfigure (b) shows the resulting chemical profiles for the Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/vacuum interface derived from x-rays and EELS.

FIG. 3. (Color online) Depth dependent EELS spectra measured along the indicated line in the HAADF-STEM micrograph shown on the right side. The STEM is measured along the Fe$_3$O$_4$ $[\bar{1}2\bar{1}]$ and $[110]$ the axis of ZnO similar as in Ref. 6.
the result is plotted in Figure 2. The relative intensity of the Fe L₃ absorption derived from the EELS map perfectly matches the XRMR profiles thus confirming the reflectometry results.

From magnetometry,⁶ it is found that the films investigated here exhibit a saturation magnetic moment of 450 emu/cm³ and a coercive field of \( H_c = 60 \) mT at room temperature. Room temperature XRMR curves have been measured at photon energies of 707.8 eV and 708.8 eV using circular polarized x-rays. By flipping the external magnetic field of \( \mu_0H_{\text{ext}} = \pm 140 \) mT for every angle value, a set of two reflectivity curves per energy is obtained. The magnetic asymmetry is calculated from the reflectivities according to \( A = (R^+H - R^-H)/(R^+H + R^-H) \). These asymmetry curves, like their XMCD counterpart for absorption, measure the change of the reflectivity due to the x-ray magnetic circular dichroism contrast. The results are plotted in Figure 4(a).

Both magnetic asymmetries show a signal which is in relative strength and sign consistent with the XMCD at the corresponding energy (cf. Fig. 1). The curves were fitted independently by simulations based on a model proposed by Zak et al.²³ using the magneto-optical constants (Fig. 1(b)) scaled by a factor to account for incomplete magnetic saturation at \( \mu_0H_{\text{ext}} = 140 \) mT. Further details on the analysis process can be found in Refs. ¹⁵ and ²⁴. The best fit results are shown as red solid lines in Figure 4(a). Good convergence between measurement and simulation is achieved for both measurements and the corresponding magnetic profiles are shown in Figure 4(b). It is found that the onset of the magnetic signal at the ZnO interface depends on the probing energy. For tetragonal Fe³⁺, the signal rises directly at the chemical interface whereas the octahedral Fe²⁺ signal is offset by 2.5 Å. Such a high sensitivity for position and valence of the Fe stems from the enhanced magnetic contrast of XRMR which in the case of Fe₃O₄ is especially strong between Fe³⁺ and Fe²⁺ (sign change in Fig. 1(b))₁⁸,₁⁹. The resonant x-ray reflectometry (cf. Figure 2) curves on the other hand do not show this effect implying that the chemical contrast for the interface layer is, even in resonance, not sufficient to resolve this small local difference. The observed offset of the Fe²⁺ XRMR signal by 2.5 Å coincides directly with the distance between two Fe planes along the \((11\bar{1})\) growth direction of Fe₃O₄ as illustrated in Figure 1. Hence, the discrepancy between the octahedral and tetragonal Fe XRMR indicates that the first Fe layer at the interface contains mostly Fe³⁺ ions. This is in strong contrast to the distribution of Fe²⁺ and Fe³⁺ ions found in bulk Fe₃O₄ where the individual planes always exhibit a mixed valence (cf. Fig. 1). And it is also despite the presence of antiphase boundaries in Fe₃O₄ on ZnO (Ref. ⁶) which should in principle promote a more heterogeneous interface valence due to the changes in the volume termination.

Further information about the interface valence of Fe is derived from the EELS data from Figure 3. Figure 5 shows individual EELS linescans of the Fe L edge in the vicinity of the Fe₃O₄/ZnO interface. The spectra show a position dependent shift of the Fe L₃ spectral weight from higher to lower energies indicating a change of the Fe valence.

By fitting these Fe L₃ energy spectra²⁵,²⁶ with the software EELSMODEL (Ref. ²⁷) using FeTiO₃ and Fe₂TiO₅
reference spectra for Fe$^{2+}$ and Fe$^{3+}$, respectively, it is possible to extract a depth profile for each Fe valence individually. The resulting profiles for Fe$^{2+}$ and Fe$^{3+}$ are shown in Figure 4(b) along with the XMRM derived magnetic profiles. The EELSMODEL fit shows an offset of 2.4 Å of the Fe$^{2+}$ intensity with respect to the Fe$^{3+}$ at the interface. The magnetic profiles derived by XMRM and the chemical profiles derived from EELS thus independently confirm that the first Fe layer in Fe$_3$O$_4$ contains mostly Fe$^{3+}$ ions whereas the rest of the film has the nominal mixed valence distribution of 2.5+.

Spins polarized transport in Fe$_3$O$_4$ depends on the mixed valence state of Fe. LSDA+U calculations of the partial density of states for Fe in Fe$_3$O$_4$ show that the transport current relies on the highly polarized, occupied Fe$^{2+}$ states at the Fermi level and the unoccupied $t_{2g}$ orbitals of octahedral Fe$^{3+}$ ~0.15 eV above $E_F$. The change from a mixed, Fe$^{2.5+}$, valence to a pure Fe$^{3+}$ in the interface Fe layer as it is observed here introduces a local disturbance of this spin polarized band structure. However, the width of 2.5 Å is three orders of magnitude smaller than the spin diffusion length in Fe$_3$O$_4$ of $\delta_{\text{Diff}} \approx 100$ nm from Ref. 28 and should, therefore, only marginally affect the spin injection from the bulk of the film. It might however have an impact on the resistance matching between ZnO and Fe$_3$O$_4$ which will be subject to further investigations.

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