Fe$_3$O$_4$/ZnO: A high-quality magnetic oxide-semiconductor heterostructure by reactive deposition

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We demonstrate the epitaxial growth of Fe$_3$O$_4$ films on ZnO by a simple reactive deposition procedure using molecular oxygen as an oxidizing agent. X-ray photoelectron spectroscopy results evidence that the iron-oxide surface is nearly stoichiometric magnetite. X-ray diffraction results indicate monocrystalline epitaxy and almost complete structural relaxation. Scanning transmission electron micrographs reveal that the microstructure consists of domains which are separated by antiphase boundaries or twin boundaries. The magnetite films show rather slow magnetization behavior in comparison with bulk crystals probably due to reduced magnetization at antiphase boundaries in small applied fields. © 2011 American Institute of Physics. [doi:10.1063/1.3540653]

Magnetite (Fe$_3$O$_4$) has attracted strong interest for its potential use as a spin aligner in prospective spintronic devices. Its most relevant property in this context is the $-100\%$ spin polarization of the conduction electrons, which was predicted by density-functional theory. The integration of magnetite with other materials, needed in such devices, is therefore required.

Epitaxy of magnetite has been demonstrated on a variety of substrates, e.g., MgO(001), α-Al$_2$O$_3$(001), Pt(111), Si, InAs, or GaAs. MgO, which could be used as a tunnel barrier in such spintronic applications, has an almost perfect lattice match with magnetite and is the most frequently used substrate. If one is interested, however, in a direct current injection from magnetite into a semiconducting channel, the direct growth on a semiconductor substrate is essential. Si, InAs, or GaAs substrates suffer either from a relatively poor lattice match with respect to magnetite or the occurrence of interfacial reactions. For example, it has been shown that arsenic and gallium oxides exist after the deposition of magnetite onto GaAs. In contrast, the oxidation state of the ZnO substrate does not change upon oxide deposition. The heterostructure has, however, a large lattice mismatch of $-8.6\%$ if one assumes that the O sublattices in both materials have to be aligned across the interface. Therefore, it seems to be questionable whether high-quality films of magnetite can be grown on ZnO at all. A well-ordered interface structure is a prerequisite for good spin-transport and magnetic properties, though. For this reason, we have investigated the growth of Fe$_3$O$_4$ onto ZnO by reactive deposition using O$_2$ as an oxidizing agent. The growth of this structure has, however, a large lattice mismatch of $\sim 8.6\%$.

We document the good stoichiometry of our grown films by means of x-ray photoelectron spectroscopy (XPS). Structure and microstructure are investigated by x-ray diffraction (XRD) and scanning transmission electron microscopy (STEM). Moreover, we detail the magnetic properties by magnetometry with a superconducting quantum interference device (SQUID).

Magnetite films were grown by reactive deposition of Fe from an electron-beam evaporator in an oxygen partial pressure of about $p$(O$_2$)$=4 \times 10^{-6}$ mbar at a substrate temperature of approximately 400°C. XPS, which is a valuable tool to discriminate between the various iron oxides, was performed in situ directly after growth to check for the stoichiometry of the grown films.

Spectra were taken at different electron emission angles θ with respect to the surface normal to vary the electron mean escape depth, $\lambda_{eff} = \lambda \cos \theta$, and hence the surface sensitivity. Here, λ was calculated using the expression of Tanuma et al. We have fitted the spectra with a linear combination of spectra of bulk reference compounds (Fe$_3$O$_4$, α-Fe$_2$O$_3$) to extract the stoichiometry. The derived off-stoichiometry parameter δ (in Fe$_{3-\delta}$O$_4$, see Fig. 1) is small and decreases for larger bulk sensitivity. We conclude that only a surface layer with a thickness in the range of λ is

![FIG. 1. (Color online) Background-corrected XPS spectra of a 40.5 nm thick Fe$_3$O$_4$/ZnO film with corresponding electron mean escape depth $\lambda_{eff}$ and off-stoichiometry parameter δ.](image-url)
off-stoichiometric. This small off-stoichiometry is probably connected to the exact experimental conditions while terminating growth. Here, the surfaces were postoxidized in \( p(O_2) = 5 \times 10^{-8} \) mbar for 1 to 2 min after closing the shutter of the Fe beam.

The XRD \( \omega -2\theta \)-scan in Fig. 2(a) demonstrates that only \( \text{Fe}_3\text{O}_4(\ell \ell \ell) \)-planes are present parallel to the hexagonal substrate surface, i.e., \( \text{ZnO}(001) \). The out-of-plane lattice constant was determined from the \( 2\theta \)-position of these peaks and found to be on average only \(-3.2\%\) smaller than the lattice constant of bulk magnetite in this direction. For asymmetric reflections, which include in-plane component, \( \phi \)-scans were performed. It is evident from these scans [see Fig. 2(b)] that the in-plane epitaxial relationship is \( \text{Fe}_3\text{O}_4(112) || \text{ZnO}(100) \). From the \( 2\theta \)-position of these asymmetric reflections, the in-plane lattice constant was found to be \(+0.6\%\) of the bulk value. Therefore, the film structure grows almost completely relaxed onto \( \text{ZnO} \).

A simulation of the x-ray reflectivity (XRR) curve in Fig. 2(c) was used in order to determine the film thickness, the interface roughness, and the surface roughness of \( \text{Fe}_3\text{O}_4 \) films. The simulation yielded a surface roughness of 0.82 and 0.50 nm, and an interface roughness of 0.60 and 0.56 nm for a 62.4 and a 40.5 nm thick film, respectively.

Figures 3(a) and 3(b) show STEM micrographs of \( \text{Fe}_3\text{O}_4/\text{ZnO} \) along the \( \text{Fe}_3\text{O}_4[112] \) and the \( \text{Fe}_3\text{O}_4[110] \) direction, respectively. Both images demonstrate the good atomic order of films with a thickness of 62.4 nm (a) and 14 nm (b) and a sharp interface \( \text{Fe}_3\text{O}_4(111) \) being parallel with the \( \text{ZnO}(001) \) substrate. The images also show the occasional presence of antiphase boundaries (APB) inside the film and preferentially located along (220) planes [see Fig. 3(b)]. APBs are structural defects which are formed when islands with shifted sublattices coalesce. The occurrence of APBs in magnetite thin films is known for deposition onto various substrates. As Hibma et al.\(^6\) have pointed out, neighboring antiphase domains in \( \text{Fe}_3\text{O}_4 \) are related by a phase shift vector of the type \( \frac{1}{2}(100) \) or \( \frac{1}{2}(110) \) or a combination of these for deposition onto \( \text{MgO} \). In the image along the \( \text{Fe}_3\text{O}_4[112] \) direction, the observable sublattice shift is \( \frac{1}{2} \) along the [111] direction, while for the \( \text{Fe}_3\text{O}_4[110] \) image, the shift is \( \frac{1}{2} \) along the [111] direction and \( \frac{1}{2} \) along the [111] direction, consistent with a displacement vector \( R = \frac{1}{2}(110) \). We also observed the presence of twin boundaries in these films. Domains separated by twin boundaries are related by rotation about 180° in the (111) plane (rotational twinning). The twin character is seen by the different orientation of the pseudohexagonal features on both sides of the boundary [see Fig. 3(b)]. Such rotational twinning has also been found for \( \text{Fe}_3\text{O}_4 \) growth on Pt and \( \alpha -\text{Al}_2\text{O}_3 \).

Finally, Fig. 4(a) shows the in-plane magnetization of an \( \text{Fe}_3\text{O}_4/\text{ZnO} \) sample determined by SQUID magnetometry. The curve indicates a slow approach to saturation (with respect to the field) in comparison with single crystals, which saturate at the magnetocrystalline anisotropy field of 31 mT.
From minor magnetization loops measured at different temperatures, it can be concluded that the coercive field is slightly increasing at lower temperature [see inset (b) in Fig. 4], which is the behavior established in the literature. The coercive field is about $\mu_0 H_c = 60$ mT at room temperature. Coercive fields and remanence are comparable to literature results for epitaxy of Fe$_3$O$_4$ on ZnO, MgO, and $\alpha$-Al$_2$O$_3$.\textsuperscript{13-15}

Both, slow saturation behavior and the slightly reduced saturation moment compared to the bulk are in accordance with earlier reports on Fe$_3$O$_4$ thin films (see, e.g., Refs. 3, 6, 9, and 10). In comparison with measurements of bulk crystals,\textsuperscript{11} the approach to saturation is markedly slow due to reduced magnetization at APBs in small applied fields. Margulies \textit{et al.}\textsuperscript{30} have shown that the approach to saturation is similar to the model case of a one-dimensional chain of ferromagnetically coupled spins with an additional antiferromagnetic coupling at the APB. This one-dimensional model describes the competition between the Zeeman energy and the exchange energy at the APB, resulting in an approach to saturation like $M = M_s (1 - b / \sqrt{H})$, where $b$ is connected to the APB density.

The approach to saturation of the $M(H)$-curve in our data is well described by this law with best fit parameters of $M_s = 450 \text{ emu/cm}^3$ and $b = (0.14 \pm 0.002) (T)\textsuperscript{1/2}$. These fit parameters are within the typically observed range of values for films on MgO or $\alpha$-Al$_2$O$_3$.\textsuperscript{9,12} Since the fit parameter $M_s$ is comparable to the bulk saturation ($M_s = 480 \text{ emu/cm}^3$ cf. Ref. 13), the magnetization behavior of the investigated thin film corresponds to a stoichiometric single crystal which exhibits a considerable density of APBs.

The temperature-dependent magnetization measured in an applied field of 0.06 T is shown in Fig. 4(c). The zero-field cooled warming cycle (red curve) exhibits a large increase of the magnetization at a temperature of $T_c = 128$ K from almost zero magnetization in the low-temperature phase to a sizable value in the high-temperature phase. In contrast, the field cooling cycle shows a small peak instead of a magnetization jump at the transition temperature. We interpret this anomaly in the $M(T)$-curve as the sign of the Verwey transition, or more exactly the spin-reorientation transition which occurs at the isotropic point, i.e., the point of vanishing magnetic anisotropy constants, which lies approximately 10 K above the actual Verwey-transition temperature $T_V$.\textsuperscript{14,15}

It is known that transition temperature and width of the transition in bulk single crystals depend strongly on the off-stoichiometry.\textsuperscript{16} For thin films, the transition can be additionally broadened and its temperature lowered because of residual stress inside the sample or higher APB densities.\textsuperscript{17} We thus conclude that the occurrence of this phase transition and the magnitude of the magnetization jump evidence good stoichiometric and structural properties of the shown 40.5 nm thick magnetite film.

In conclusion, high quality Fe$_3$O$_4$ films on ZnO with near-to-bulk properties and sharp interfaces can be grown by comparably simple reactive deposition.

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