Magnetism of the Fe/ZnSe(001) Interface

M. Marangolo,[1] F. Gustavsson,[1,2,*] M. Eddrief,[1] Ph. Sainctavit,[1] V. H. Etgens,[1] V. Cros,[2] F. Petroff,[2] J. M. George,[2] P. Bencok,[3] and N. B. Brookes[3]

[1]*LMCP, Laboratoire de Minéralogie-Cristallographie, Universités Paris 6 et Paris 7, CNRS UMR 7590, 4 Place Jussieu, 75252 Paris Cedex 05, France*

[2]*Unité mixte de Physique CNRS/THALES, Domaine de Corbeville, 91404 Orsay Cedex, France and Université Paris Sud, 91405 Orsay Cedex, France*

[3]*European Synchrotron Radiation Facility (ESRF), BP 220, 38043 Grenoble Cedex, France*

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The magnetism of epitaxial ultrathin films of Fe on ZnSe(001) has been investigated by x-ray magnetic circular dichroism down to the submonolayer regime. In contrast to other metallic ferromagnet/semiconductor interfaces, no reduction of the Fe magnetic moment was found at the Fe/ZnSe(001) interface. Furthermore, a significant enhancement of the Fe magnetic moment compared to the bulk value was observed for coverages up to one monolayer in agreement with theoretical predictions. We also demonstrate that the magnetic properties of the Fe/ZnSe(001) interface remain stable against thermal annealing up to 300 °C, a prerequisite for the future development of efficient spintronics devices.

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The control of the electron's spin degree of freedom in semiconductors could pave the way to a new generation of electronic devices such as spin memories, spin transistors, and spin quantum computers [1]. The challenge is to induce spin-polarized carriers in a semiconductor by sourcing spins from a magnetic reservoir. Recently, efficient spin injection has been reported from diluted magnetic semiconductors but only under high magnetic fields and at low temperatures due to the low Curie temperature of these compounds ($T_C \simeq 60$ K) [2]. This precludes, at the moment, the development of useful devices.

In principle, a convenient way to inject a spin-polarized current into a semiconductor is from ferromagnetic metals like Co and Fe which exhibit a significant spin polarization even at room temperature. However, a fundamental problem must be solved before spins can be injected efficiently: the reactivity of transition metals with semiconductors can lead to magnetically dead layers which suppress the spin polarization across the interface by spin-flip mechanisms. As a classical example, GaAs(001) is not a suitable candidate for the growth of $3d$ ferromagnetic/semiconductor/$3d$ ferromagnetic junctions [3] because of the strong reduction of magnetization that results from the formation of reacted phases at the interface [4].

A more promising system for which these interfacial difficulties could be overcome is Fe epitaxied onto the wide band gap semiconductor ZnSe(001) [3,5,6]. In addition, recent research shows that it is feasible to transfer spins coherently and with high efficiency across the GaAs/ZnSe interface [7]. The Fe/ZnSe(001) heterostructure has a low lattice mismatch (1.1%) between two Fe cells and one of ZnSe and, more importantly, the Fe reactivity is lower than with other semiconductors like GaAs, Si [3], or Ge [8]. Thin epitaxial Fe films have been successfully grown on ZnSe(001) and characterized magnetically [3,9–11], but so far the magnetic properties of the Fe atoms at the interface, a critical issue for spin injection, have not been addressed. Jonker *et al.* [9] showed that the growth of thin Fe films on ZnSe(001) epilayers at around 180 °C *predominantly proceeds in a layer by layer mode* but they also detected a significant reduction of the Fe magnetic moment in comparison to the bulk value [11]. Therefore, in order to avoid this anticipated intermixing at the Fe/ZnSe interface, Reiger *et al.* [3] deposited ultrathin Fe films at room temperature at the expense of an increased surface roughness unfavorable from the device aspect. The authors ruled out any significant reduction of the Fe magnetic moment based on extrapolated results from films down to 5.4 ML in thickness, without probing the actual interface. Consequently, the many theoretical reports describing the magnetism of the Fe/ZnSe(001) interface remain, up to now, without any experimental confirmation [6,12,13]. In this Letter we show, by an investigation down to submonolayer thicknesses, that the magnetic moments of Fe layers deposited at 180 °C on the ZnSe(001) surface is preserved or even enhanced compared to bulk Fe, thus excluding the existence of magnetically dead layers. Furthermore, the stability of the Fe/ZnSe(001) interface with respect to thermal annealing is also demonstrated.

The samples were prepared by molecular beam epitaxy (MBE) in a multichamber system. First, a GaAs buffer layer was deposited on GaAs(001) substrates using standard growth conditions [14], followed by transfer to a II-VI chamber for ZnSe growth using a two step procedure [15]. At the end, a $c(2 \times 2)$ Zn rich surface [16] was stabilized on top of a 100 Å pseudomorphic ZnSe epilayer. The Fe was grown *in situ* at 180 °C with a rate of 1 monolayer (ML) per minute at a base pressure below 3×10^{-10} mbar. During the Fe growth, the reflection high-energy electron diffraction (RHEED) diagram changes from the usual streaky (2D) ZnSe diagram to a diffuse one around 0.5 ML followed by elongated spots

characteristic of Fe above 1 ML. The best growth quality was obtained for Fe deposited on a $c(2 \times 2)$ Zn rich surface. One monolayer of Se is always found floating at the growth front independently of the Fe film thickness leading to a 2×2 reconstruction observed on RHEED diagrams [3,17]. X-ray photoemission spectroscopy (XPS) studies have shown that Fe grows in a *predominantly layer by layer mode* [9]. This information was extracted from the evolution of the Zn 3*d* signal as a function of Fe thickness presented in Fig. 1, by using a standard 2D growth exponential decay. Moreover, some of us have recently performed a detailed study of the core and valence states of the heterostructure as a function of Fe coverage, presented in Ref. [18].

The layer by layer growth mode is confirmed by scanning tunneling microscopy (STM) studies. After the end of the growth, the sample was quickly transferred under UHV to the STM stage directly connected to the growth chamber. The STM images were collected at room temperature in a constant current mode for Fe epilayers grown on a $c(2 \times 2)$ ZnSe(001) Zn rich surface. In Fig. 2, we show a STM image corresponding to an equivalent thickness of 10 Å Fe. We observe a flat and continuous film, with terraces showing sharp edges along the [110] and $[1\bar{1}0]$ directions. The 4 Å surface lattice period is due to Se atoms floating on the surface, leading to the aforementioned 2×2 reconstruction [3,17].

The homogeneity of the Fe film observed at such small scales persists for larger scans. Scanning tunneling spectroscopy (STS) on a monolayer thick sample displays metallic properties all over the film confirming XPS results [18]. By combining STM and XPS studies we were able to attest that the Fe growth is homogeneous and the surface is smooth as already claimed by Jonker *et al.* [9].

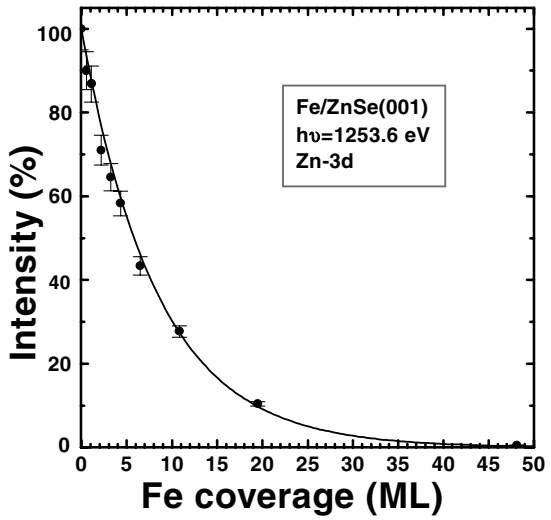

FIG. 1. XPS normalized Zn 3*d* intensity (integrated area) as a function of Fe thickness. A standard exponential decay characteristic of a 2D growth perfectly matches the experimental results (solid line).

We now focus on the magnetic properties of these ultrathin Fe epilayers, using x-ray magnetic circular dichroism (XMCD). Apart from its element specificity, its high sensitivity makes it an ideal technique to study small thicknesses, down to the submonolayer. XMCD measurements were performed on the ID-12B beam line at the ESRF using a 93% circularly polarized light from a helical undulator. Fe deposition and magnetic characterization were performed *in situ* in a UHV system with a base pressure better than 10^{-10} mbar equipped with a 7 T superconducting cryomagnet allowing measurements from 5 to 320 K.

The same samples used in the STM-XPS experiments (with 100 Å thick ZnSe epilayers) were capped with amorphous Se to protect the surface against air [16]. Once introduced in the XMCD experimental setup, the samples were heated slowly up to 320 °C both to desorb the amorphous Se and to stabilize the $c(2 \times 2)$ Zn terminated surface [16]. The sample was then cooled down to 180 °C and Fe was deposited using an *e*-beam evaporator. The thickness control was performed both by quartz microbalance and by using the absorption edge jump [19] with an estimate accuracy of 15%. A new substrate was used for each Fe coverage studied.

XAS (x-ray absorption spectroscopy) and XMCD spectra at the Fe $L_{2,3}$ absorption edges, recorded in total electron yield detection mode, were carried out under a saturating magnetic field of 5 T applied along the normal

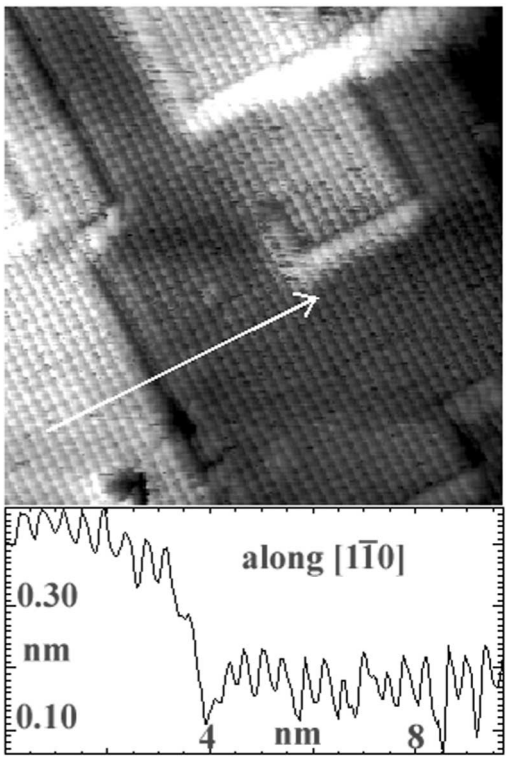

FIG. 2. STM images (1.5 V, 0.2 nA) showing (a) 10 Å of Fe grown on ZnSe(001). We observe flat terraces with sharp edges along $[1\bar{1}0]$ and [110] directions; (b) cross section along the white arrow.

to the film plane (either parallel or antiparallel to the x-ray beam). XMCD measurements were performed for Fe thicknesses from 5 ML down to 0.3 ML and on the reference sample (120 ML film). In the inset of Fig. 3, we show typical XMCD spectra for 0.3 ML coverage. Magneto-optical sum rules were used to extract the orbital and spin magnetic moments from the XMCD spectra [20]. The ratio $N_h/\sigma_{\mathrm{tot}}$ present in both sum rules was directly deduced from the comparison between an Fe reference $L_{2,3}$ absorption spectra and a simple two-step-like function. A linear background was subtracted from the XAS spectra for the three lowest coverages in order to make the pre- and postedge regions coincide with the spectra at higher coverages. For the Fe reference sample, the number of $3d$ holes N_h was set to 3.39 [21]. This evaluated ratio was then incorporated into the sum rules to evaluate the Fe magnetic moments in the other samples. In Fig. 3, we present the thickness variation of the magnetic moment per Fe atom (i.e., the sum of the magnetic spin moment, the magnetic orbital moment, and a magnetic dipolar term which describes the anisotropy of the spin moment: $m_{\mathrm{tot}} = m_{\mathrm{spin}} + m_{\mathrm{orb}} + m_{\mathrm{dip}}$) at $T = 10$ K and at room temperature (RT). The measured values, $m_{\mathrm{tot}} = (2.1 \pm 0.1)\mu_B$ at both 10 K and at RT, for the 120 ML film, are in good agreement with previous experiments on thick Fe films. The most striking result is that in the whole thickness range, the magnetic moment is equal or even larger than the bulk reference. To our knowledge, this is the first *direct* experimental proof of the persistence of a bulk magnetic moment at a transition metal/semiconductor interface. Thus the smooth character of the Fe films as revealed by our aforementioned studies implies a sharp magnetic metal/semiconductor interface for the Fe/ZnSe system.

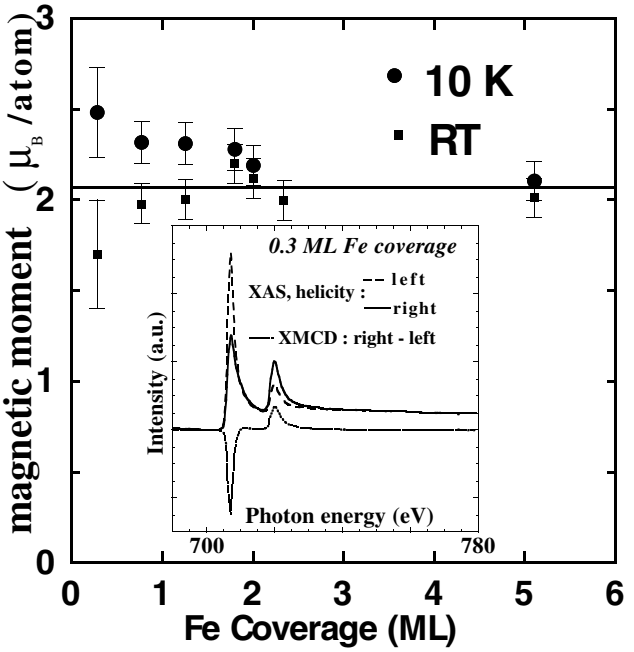

FIG. 3. Thickness dependence of the total Fe magnetic moment at $T = 10$ K and at room temperature (RT) as measured by XMCD. Inset: Typical XMCD spectra for a coverage of 0.3 ML of Fe/ZnSe(001) collected at $T = 10$ K (raw data). The absorption of left and right helicity are shown (taking the direction of the magnetic field as the quantification axis). The horizontal line corresponds to the measured bulk Fe magnetic moment.

Additional comments on Fig. 3 should be made. First, for low coverages at $T = 10$ K, an increase of the magnetic moment m_{tot} up to $(2.5 \pm 0.25)\mu_B$ is found, correlated to an increase of N_h, observable through the intensity changes of the absorption white lines. This trend is in good agreement with band structure calculations of thin Fe layers on ZnSe(001) [12,13] and has also been observed for Fe deposited on metallic substrates [22]. The evaluation of the spin moment in ultrathin ferromagnetic films using the second sum rule always raises the question of the relative importance of the magnetic dipole term. In order to exclude a dominant role of the m_{dip} term in our measured m_{tot}, we have performed XMCD experiments as a function of the angle between the incident light and the surface normal as proposed by Stöhr and König [23] for two samples (0.8 and 2.0 ML). Both samples reveal that the dipole term is small ($m_{\mathrm{dip}}/m_{\mathrm{tot}} \simeq -0.04$) and that m_{tot} underestimates the spin magnetic moment in agreement with electronic band structure calculations for Fe(001) surfaces [24] ($m_{\mathrm{dip}}/m_{\mathrm{tot}} \simeq -0.09$). Accordingly, the orbital magnetic moment is also found to increase from about $(0.065 \pm 0.01)\mu_B$ for the thicker layers to $(0.090 \pm 0.01)\mu_B$ at 0.3 ML. Furthermore, the small decrease of the magnetic moment at RT as the film becomes thinner can be understood in terms of a reduced Curie temperature at the surface due to the weaker coordination between atoms expected for a 2D Fe film [25]. All these features at low Fe coverage are coherent with a low dimensional picture of the system resulting in a modified band structure. It is worthwhile to mention also that, following the model of Bruno [26], we studied the angular dependence of the magnetic orbital moment at 0.8 ML Fe coverage without detecting any anisotropy within the experimental accuracy.

To further investigate the magnetic properties of the Fe/ZnSe interface, we have sequentially annealed a 2 ML thick Fe sample. As the total magnetic moment is constant up to annealing temperatures of 300 °C (see Fig. 4), we thus evidence the high thermal stability of this metal/semiconductor interface. It is only after annealing above 350 °C that a lowering of the total magnetic moment could be detected. This decrease coincides with a reduction of the absorption edge jump which is proportional to the probed quantity of Fe atoms (from 2 to 0.5 ML), and thus suggests the onset of intermixing at these high temperatures, already observed by XPS measurements [27]. We can exclude an eventual oxidation since an Fe-O contribution would be detected in the XAS spectra of Fig. 4 as observed in Ref. [28]. The thermal stability of the Fe/ZnSe(001) interface could thus represent an additional advantage

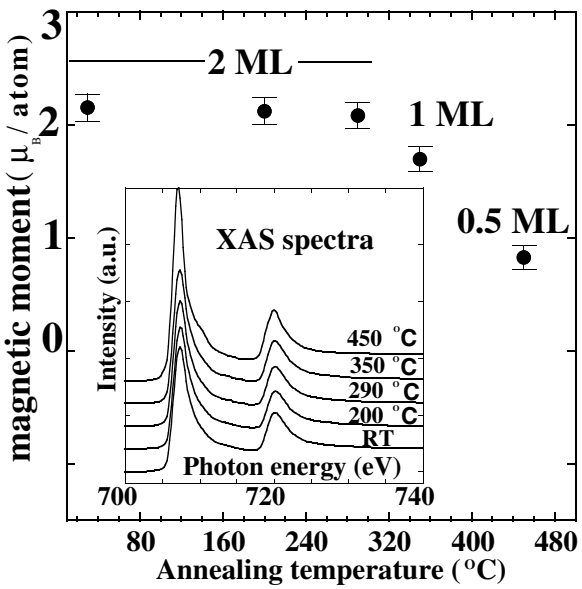

FIG. 4. Magnetic moments as a function of annealing temperature for 2 ML Fe film. The reduction of the probed quantity of Fe atoms on the top of the heterostructure (from 2 to 0.5 ML) suggests the onset of intermixing at such high temperatures. Inset: XAS spectra indicate no evidence of oxidation.

for the development of spintronic devices using this system.

In conclusion, we have studied the growth morphology and the magnetic properties of Fe layers on the ZnSe(001) surface. XPS and STM/STS measurements indicate that, even at submonolayer coverages, Fe growth is homogeneous resulting in a sharp semiconductor/metal interface. The Fe magnetic moment is preserved at the interface compared to bulk Fe and even enhanced below 2 ML. No evidence of dead or magnetically modified interfacial layers has been detected, confirming the ideal character of this interface with respect to intermixing. The chemical stability of the interface has been checked by UHV annealing up to 300 °C without any observable changes. Thus, our work demonstrates that the Fe/ZnSe(001) junction satisfies the conditions of interfacial magnetism and temperature stability required for spintronic devices.

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*On leave from the Materials Physics at Uppsala University, Sweden.

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