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FERROMAGNETISM AND REACTIVITY OF FE DEPOSITED ON GaAs(001) BY MAGNETRON SPUTTERING

V. VASILACHE, G. A. LUNGU[a], C. LOGOFATU[a], R. V. MEDIANU[b],
C. M. TEODORESCU[a*]
"Stefan cel Mare" University of Suceava, University Str. 13, 720229 Suceava, Romania
[a]National Institute of Materials Physics, P.O. Box MG-7, 077125, Magurele-Ilfov, Romania
[b]National Institute for Lasers, Plasma and Radiation Physics, P.O. Box MG-54, 077125 Magurele-Ilfov, Romania

Iron layers are grown on GaAs(001) single crystal wavers by magnetron sputtering and characterized by magneto-optical Kerr effect (MOKE) and X-ray photoelectron spectroscopy (XPS). It is found that all deposited layers, starting with 2 nm thickness, are ferromagnetic at room temperature with a relatively high coercitive field (500 to 750 Oe). The average Fe magnetic moment is larger for the thinnest Fe film deposited, of about 0.52 Bohr magnetons per Fe atom. The average Fe magnetic moment decreases to 0.26 Bohr magnetons, then to 0.17 Bohr magnetons for 4 and 8 nm, resepctively. XPS evidenced that the outermost Fe layers are oxidized; however, the thinnest Fe film presented the lower oxidation state. We may connect this reaction with Fe-As bonds, resulting in a nonferromagnetic interface compound. Indeed, XPS depth profiling of the 8 nm sample evidenced the formation of a very thin (about 1.4 nm) Fe metal layer immediately at the interface with GaAs. In this layer, Fe may reach an atomic magnetic moment as high as 1 Bohr magneton.

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1. Introduction

Spintronics is believed to be a consistent development in microelectronics for the next decades. This technology aims to employ not only the nature of charge carriers, but also their spin orientation [1]. Consequently, synthesis of ferromagnetic contacts on high technological semiconductors, such as GaAs, and also accurate control of the interface reactivity are of crucial importance [2]. The intermixing of Fe with Ga and As results in complicated interface compounds [3], drastic reduction of the Fe magnetic moment [4,5] and of the spin injection efficiency [6]. It was shown that Fe deposition on InAs(001) proceeds with a lower interface reaction [7-10]. These studies were concentrated on the molecular beam epitaxy (MBE) method, with complete structural characterization of the growth mechanism via reflection high energy electron diffraction [7-9] and *in situ* measurements of magnetic properties by X-ray magnetic circular dichroism [8,9]. The main mechanism inducing enhanced magnetic properties of Fe grown on InAs was intimately connected to the lower reactivity of Fe with the substrate [10]. Coming back to Fe/GaAs(001), Ref. [10] has shown that the Fe magnetic moment evolves from 0.04 μ_B (Bohr magnetons) for 1 monolayer (ML) Fe deposited, to about 0.3-0.4 μ_B for 3-5 ML, ending with about 1 μ_B for thicknesses exceeding 10 ML (note that 1 ML ≈ 0.143 nm). Achieving the Fe bulk magnetic moment of 2.2 μ_B

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[*] Corresponding author: teodorescu@infim.ro

was still not demonstrated with nm thick Fe/GaAs, although the results from Ref. [10] are more encouraging than that obtained two decades ago [3,4].

Nevertheless, the MBE method performed in ultrahigh vacuum is expensive, time-consuming and its integration towards routine technology is not straightforward. It is of interest to investigate also other deposition methods than MBE, namely magnetron sputtering, which may easily be performed on larger area semiconductors with considerably increased deposition rates [11]. Even if the Fe magnetic moment obtained is lower than by using MBE, the simplicity and the reduced cost of this other method deserves to be exploited further. Consequently, the aim of this work is to offer a picture on the interplay between magnetic properties and surface reactivity for Fe/GaAs(001) obtained by magnetron sputtering. It will be shown that magnetic layers may be readily obtained, though with reduced average Fe magnetic moments as compared with the MBE method. Surprisingly, fewer amount of Fe induce a weaker reactivity and an increased average magnetic moment; however, applications need higher absolute magnetization and this is achieved by increasinmg the Fe thickness. In the final part of the paper, a model will be proposed which supposes the formation of a burried Fe ferromagnetic layer of about 1.4 nm thickness, below the sample surface.

2. Experimental details

Fe layers are grown on GaAs(001) by magnetron sputtering by using a Varian ER3119 setup, with 3 kW discharge power in Ar (99.99 %) at a partial pressure of 0.2 Pa. The deposition rate was 1 Å/sec., as controlled by a thickness monitor. Targets are metal disks (Fe and Au) of high purity (99.998 %). The GaAs(001) substrates are plasma etched and outgassed to about 500 °C prior to metal deposition. For this study, three Fe thicknesses (2 nm, 4 nm and 8 nm) were deposited onto different substrates. All Fe deposition were capped by 3 nm Au prior to their removal from the sputtering facility.

Magneto-optical Kerr effect (MOKE) measurements were performed by an AMACC Anderberg and Modéer Accelerator AB setup at room temperature in longitudinal geometry. The applied field is parallel to the polarization vector in the sample plane. The light polarization is modulated and the detection is phase-sensitive using a lock-in amplifier. Previous calibration experiments on ferromagnetic Fe thin layers yielded a Kerr rotation signal of 2.5 mdeg per 1 nm Fe thickness [12]. It could be argued that the case of metal/semiconductor surfaces may differ from this calibration owing to the interdifussion of the metal with the semiconducting substrates. However, consistent results using this calibration were obtained for Fe/Si(001) [13,14] and Sm/Si(001) [15].

X-ray photoelectron spectroscopy (XPS) was performed in a VG ESCA Mk II setup, by using Mg K_α excitation (1253.6 eV) and a 100 mm radius hemispherical energy analyzer operating at a pass energy of 50 eV. The estimated minimum linewidth of the spectra is about 1.4 eV in these conditions. All samples were measured at the Fe 2p, Ga 3d and As 3d core levels. The 8 nm thick sample was also investigated by depth profile analysis, by using a Ar^+ sputter gun operating at 5 keV energy and 20 μA ion current. Sputtering cycles of 1 minutes were performed by following the decrease of the Au 4f core level. When the Au $4f_{7/2}$ core level intensity decreased below 10 % of its maximum value, the Fe, Ga and As core levels started to be measured. Previous and actual calibrations (including the follow-up of Au signal) yielded with convenient accuracy that, in these operation conditions, 1 minute of sputtering removes 1 nm from the sample surface.

The Ga 3d and As 3d core levels were simulated by using spin-orbit split doublets described by Voigt profiles together with associated inelastic backgrounds, simulated by Voigt integrals [11,16]. The relevant parameters (spin-orbit splittings, branching ratios, linewidths) were in good agreement with data obtained on similar systems [Fe/GaAs(001) and Fe/InAs(001)] prepared by molecular beam epitaxy [8-10].

3. Results and discussions

Figure 1 presents the MOKE hysteresis loops obtained on the three samples discussed in this work. These cycles were obtained after careful subtraction of a diamagnetic signal given by uncovered GaAs and recorded separately. All samples presented a clear ferromagnetic signal, which was a good result and pushed to investigate further these samples.

According to the previous calibration discussed in Refs. [12-15], the Fe average atomic magnetic moment obtained from the saturated MOKE signal results as 0.52, 0.26 and 0.17 (± 0.02) μ_B/Fe atom for the samples with 2, 4 and 8 nm, respectively. This is a surprising result in itself, since the general belief was that thinner Fe layers will have an elevated relative 'magnetically dead' Fe owing to the reactivity with the substrate [3-5]. MBE grown Fe/GaAs(001) layers behave as follows [10]: 1 ML (0.14 nm) of Fe was barely magnetic (0.04 μ_B/Fe atom), 3 ML (4.3 nm) increased the magnetization to 0.38 μ_B/Fe atom, ending with about 1 μ_B/Fe atom for layers exceeding 10 ML (1.43 nm).

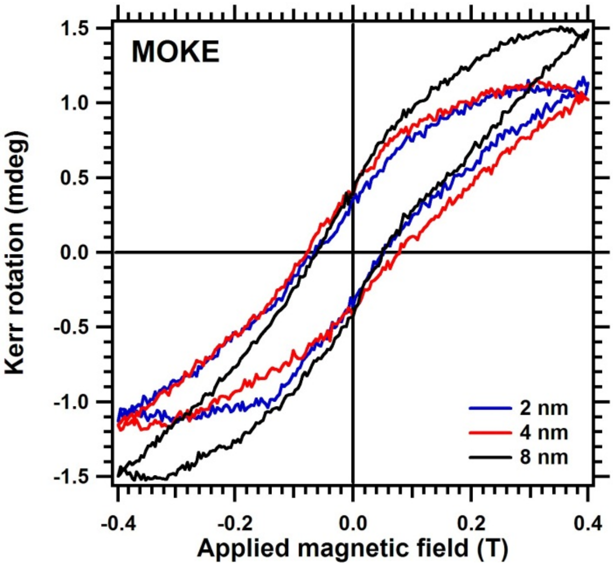

Fig. 1. Magneto-opticall Kerr effect (MOKE) obtained at room temperature on 2, 4 and 8 nm thick Fe deposited on GaAs(001).

In the actual case, the maximum momentum is obtained for the lower Fe thickness investigated. Therefore, the reactivity develops with further Fe deposition. This is visible from the XPS spectra presented in Figure 2. Increasing the Fe thickness promotes layers where Fe is found in a higher ionization state (more oxidized). Especially for Fe $2p_{3/2}$ core level (Fig. 2b), this trend is quite clear. The Fe $2p_{3/2}$ peak is found at a minimum binding energy for the 2 nm film, with progressive increase of the binding energy and hence of the ionization state with increasing Fe thickness. According to the NIST X-ray photoelectron spectroscopy database [17], the binding energy of metal Fe is 707.0 ± 0.5 eV, whereas Fe^{2+} is found at 709.6 ± 0.3 eV and Fe^{3+} is reported at 711.0 ± 0.3 eV. Consequently, the lowest Fe thickness stabilizes Fe^{2+}, whereas for thicknesses exceeding 4 nm the Fe trivalent state is stabilized. Note also that the XPS method has the well known surface sensitivity owing to the photoelectron inelastic mean free path λ, which is of about 1 nm for electrons of about 520 eV kinetic energy [18], such as the electrons originating from Fe $2p_{3/2}$ level excited with the Mg K_α emission line (1253.6 eV). The common assertion is that a layer of 3 λ is visible at most by the XPS method. Therefore, the data from Fig. 2(b) cannot be used to state on the Fe reactivity over the entire layer deposited for thicker layers (4 and 6 nm), but only on the uppermost 2-3 nm of this film.

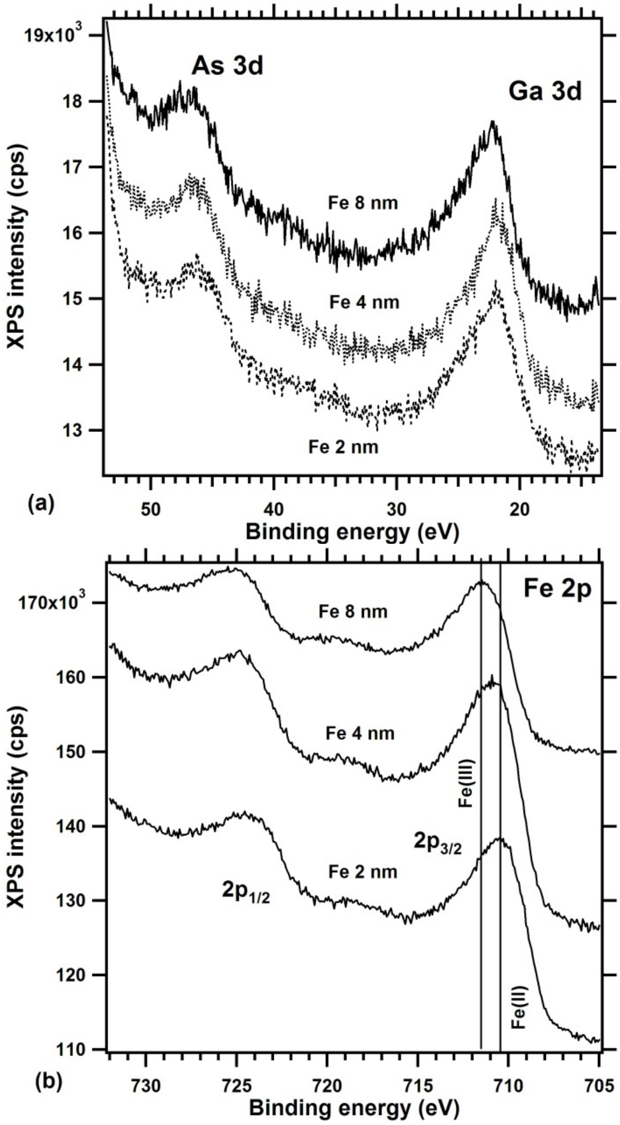

Fig. 2. X-ray photoelectron spectroscopy of Ga 3d and As 3d core levels (a), and of Fe 2p core levels (b), for as-introduced samples of different Fe thicknesses. Note that the samples are covered with a 3 nm layer of gold.

Aditionally, Fig. 2(a) shows that the Ga 3d and As 3d spectra are not sensibly depending on the Fe thickness deposited. These spectra are also quite similar to the reported spectra for clean GaAs [19]. Therefore, it seems that all the Ga 3d and As 3d signal comes from an unreacted semiconductor surface layer.

Consequently, one needs to investigate deeper the thick Fe layers. This was achieved by depth profiling, i.e. sputtering controlled quantities of the 8 nm thick sample and recording Ga 3d, As 3d and Fe 2p spectra. The results are presented in Fig. 3. This time, the Ga 3d and As 3d are sensibly modified as function on the sputtering depth. The as-introduced sample presents only one As line and mainly two Ga lines. According to Ref. [20], the higher BE line of Ga 3d is ascribed to oxidized Ga at the surface (Ga_2O_3). As soon as the layer is deeper investigated, oxide components are revealed for both Ga 3d and As 3d spectra, together with lower binding energy components, ascribed to the formation of Fe-Ga and Fe-As compounds. Interestingly, these additional components have the weaker relative weight for the sample when 6 nm of the outermost layers have been sputtered. This resulted in the closest spectrum to clean GaAs. Looking now to the Fe 2p spectra in Fig. 3(b), we obtain that for 6-7 nm sputtered from the surface, the position of the Fe $2p_{3/2}$ line has definetly the lowest binding energy reported in this study, below 709 eV. Therefore, there exists a layer of about 2 ± 1 nm situated at about 6 ± 1 nm under the surface where Fe is in the most reduced state and the Ga and As spectra are affected by the Fe reactivity at the lowest level.

As poisoning of magnetism in ferromagnetic layers deposited on GaAs was computed two decades ago [21]. More recent studies demonstrated this fact [8-10,19]. It was also demostrated that sulfur pasivation of GaAs reduces the reactivity with Fe and enhances its magnetic properties [22] and, more recently, that Sb passivation of GaAs(011) reduces the reactivity and enhances the magnetic moment of Co/GaAs(011) [23,24]. In this 'surfactant-assisted growth', S or Sb atoms permanently migrate at the surface of the metal layer and their presence inhibits As diffusion into the metal layer. Consequently, there is a clear interplay between reactivity, As mixing with the ferromagnetic metal and the lowering of the ferromagnetic properties.

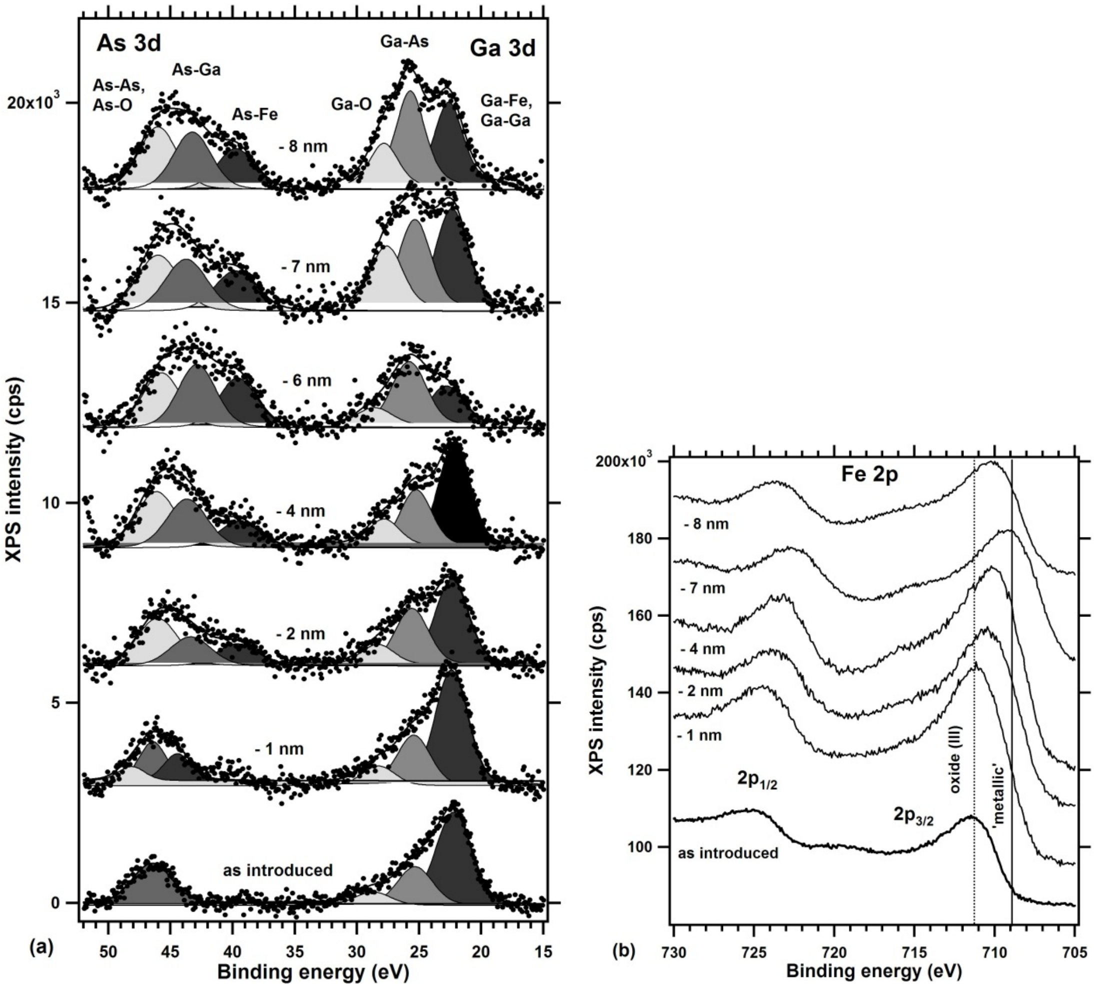

Fig. 3. XPS depth profiling with Ga 3d and As 3d (a), and with Fe.2p (b) core levels. In (a), a curve fitting using Voigt profiles is employed to discriminate between different chemically shifted components of Ga 3d and As 3d.

Note also that even in the case of the formation of a ferromagnetic layer on GaAs, it was never found an Fe magnetic moment close to the bulk Fe, 2.2 μ_B/Fe. The observed value in most previous reports is about half of this value, abou 1.0-1.1 μ_B/Fe. This is not the case of Fe/InAs(001), when one observes the growth of a ferromagnetic Fe layer with almost 2 μ_B/Fe starting from a few single Fe layers deposited [9]. We cannot offer a clear explanation of this fact, but obviously this cannot be disconnected from intermixing phenomena and eventual tensile stresses on the Fe lattice. However, for sake of simplicity, in the following when discussing the properties of the ferromagnetic compound, we will use the abbreviation 'ferromagnetic Fe'.

This study confirms the results obtained on MBE-grown films. Moreover, the reactivity is found to be quite strong. According to Fig. 3(b), about two thirds of the Ga and As atoms are in reacted state when Fe is deposited. The only exception is presented by the very thin layer of 1-2 nm situated at 6-7 nm beneath the surface.

Note also that the magnetic measurements infered about 0.17 μ_B/Fe atom for this layer, when the MOKE calibration is performed by using the entire Fe thickness. If now we rescale this value by considering that only the 1-2 nm thick layer identified by depth profile is ferromagnetic (at least at room temperature), the corresponding Fe magnetic moment yields between 0.7 and 1.4 μ_B/Fe atom, value which exceeds the derived MOKE value for the thinner Fe film. A reasonable value to suppose for the Fe magnetic moment in this layer is of about 1 μ_B/Fe, in agreement with many other studies of ferromagnetic Fe layers grown on GaAs [4,5,10]. In these conditions, the ferromagnetic Fe layer yields of 1.36 nm, representing about 9-10 atomic Fe planes. Conversely, by considering that this would be the thickness of the ferromagnetic Fe film, an observed Fe magnetic moment of 0.68 μ_B should result for the 2 nm film (to be compared with 0.52 μ_B, observed experimentally); in the same way, the observed value for the 4 nm film should have been 0.34 μ_B, to be compared with 0.26 μ_B (experimentally). At least the evolution is in the correct sense and, by taking into account all the possible cummulated errors from multiple calibrations by using different techniques and different reports spanning over almost two decades, the agreement is fair enough.

4. Conclusions

Fe layers were deposited by magnetron sputtering and investigated by MOKE and XPS, including depth profiling using Ar^+ sputtering of the reactivity occuring at the interface. Magnetron sputtering is a cheaper technique as compared with MBE and this work demonstrates that ferromagnetic interfaces may be stabilized also by this technique. The interface reactivity is stronger as compared with that of layers grown by MBE. For the samples analyzed here, it is found that ferromagnetism occurs in a thin layer of 1-2 nm situated beneath the surface. This layer presents also the lowest Fe reactivity with Ga and As, manifested in the lowest relative weight of Ga-Fe, As-Fe and of oxidized components. Also, Fe in this layer is found to be in a (+2) state, whereas at the surface and deeper inside the GaAs it is in a (+3) state. The outermost Ga and As atoms seem to be unaffected by the Fe deposition. It is not the purpose of this work to formulate dynamical hypotheses for the stronger reactivity of Fe with GaAs when deposited by magnetron sputtering as compared with the MBE case. These are complicated phenomena induced by the deposition plasma which for sure enhances the Fe mobility and the disruption of the GaAs surface.

As a general conclusion, in spite of the stronger reactivity and the reduced Fe average magnetic moment, magnetron sputtering remains a cheap option for the synthesis of ferromagnetic layers on GaAs substrates.

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