Rev.Adv.Mater.Sci. 8 (2004) 92-96

INFLUENCE OF HYDROGEN ON MAGNETIC PROPERTIES OF Fe FILMS AND MULTILAYERS

K. Fronc[1], W. Szuszkiewicz[1], F. Ott[2], B. Hennion[2], M. Aleszkiewicz[1], M. Chernyshova[1], L. Kowalczyk[1], R. Minikayev[1] and W. Paszkowicz[1]

[1] Institute of Physics, Polish Academy of Sciences, Al. Lotnikyw 32/46, 02-668 Warsaw, Poland
[2] Laboratoire Léon Brillouin, CEA-CNRS UMR 12, CEN Saclay, 91191 Gif-sur-Yvette, Cedex, France

Received: October 26, 2004

Abstract. There is a great interest in the properties of thin magnetic layers and quantum structures containing classical ferromagnets deposited on semiconductor substrates. In particular, structural and magnetic properties of BCC-Fe films on GaAs have been extensively investigated in the past. However, up to now, little is known about the influence of hydrogen atmosphere during deposition on the magnetic properties of systems involving such films.

The goal of the present studies was to look for the modification of the magnetic properties of Fe layers deposited in the hydrogen atmosphere and for the relation between the change in the magnetic properties and the changes in the layer structure. Both 100 nm thick Fe layers (with and without hydrogen) and Fe/Fe:H multilayers, were deposited in UHV sputtering system and characterized by X-ray diffraction. Lattice parameter value *a* of pure Fe film in the growth direction is higher than that corresponding to the bulk BCC-Fe. This parameter value decreases to its bulk value after an addition of H_2 to sputter atmosphere. The change of the lattice parameter value is accompanied by a decrease of the coercivity of such film. Neither the spin-polarized neutron reflectometry nor small-angle elastic neutron scattering are able to show a direct evidence of possible presence of hydrogen in the investigated layers.

1. INTRODUCTION

There exists a wide interest in the physical properties of ferromagnetic-metal layers deposited onto the semiconductor substrates. This is due to the potential application of such heterostructures as injectors of the spin-polarised carriers to semiconductor devices. Thin ferromagnetic layers can also be constituents of more complicated systems like, magnetic multilayers. The discovery of the giant magnetoresistance (GMR) effect in magnetic multilayers at the end of 80s has stimulated a progress in technology and understanding of physical phenomena occurring in magnetic metallic films.

It is well known that one can inject polarised spins from iron contact to GaAs (due to a tunnelling through a Schottky barrier) [1-3] or to InAs (by an ohmic contact) [4]. This is the reason for the extensive studies of thin iron layers deposition processes on these well known semiconductor materials as well as of influence of the technological parameters on the structural and magnetic properties of these layers. BCC-Fe (lattice parameter value *a* = 0.2866 nm) can be epitaxially grown on FCC-GaAs (for which the lattice parameter value is equal to *a* = 0.5653 nm) with a 1.38% lattice mismatch [5]. Because of almost perfect lattice matching, high-quality, single-crystal Fe films on GaAs substrate can be grown by the variety of deposition techniques (metalorganic chemical vapor deposition (MOCVD) with hydrogen as carrier gas [5], molecular beam epitaxy (MBE) [6-8], or magnetron sputtering [9,10]).

It was demonstrated that an addition of small amount of molecular hydrogen (H_2) into the atmo-

---

Corresponding author: K. Fronc, e-mail: fronc@ifpan.edu.pl

sphere over Fe layer on Cu (100) substrate (both during the deposition or after it) results in the iron phase transition and modifies the Fe magnetic properties [11]. Only very thin Fe films (up to 12 monolayers) were investigated in the cited paper. Much thicker Fe layer (300 nm) on MgO substrate was studied in Ref. [12], but the analysis in this paper was limited to the structural properties. Magnetic and structural properties of thick Fe layers epitaxially grown on GaAs substrate by MOCVD method with hydrogen as carrier gas were investigated in Ref. [5]. Unfortunately, in the cited study the properties of samples grown with and without hydrogen in the atmosphere were not compared. The hydrogen incorporation and its influence on magnetic properties of the nanocrystalline iron particles were investigated in Ref. [13], in this case the change in magnetic properties is attributed to hydrogen accumulation at grain boundaries of nanocrystals. A modification of the magnetic properties of the epitaxial BCC-Fe layers by an addition of hydrogen during the layer deposition is still poorly understood. This gave a motivation for the present investigations.

This paper is devoted to the structural and magnetic properties of the Fe layers deposited by the magnetron sputtering on (100) GaAs.

2. EXPERIMENTAL

The epitaxial Fe layers were deposited at room temperature on (100) oriented GaAs substrates in ultra-high vacuum (UHV) sputtering system at the Institute of Physics PAS. The sputtering system was equipped with four planar magnetrons with targets of 50 mm diameter in co-sputtering geometry. During the deposition process, the substrate rotated in order to improve the sample uniformity. DC magnetron sputtering mode was applied. The basic vacuum was $5 \cdot 10^{-7}$ Pa.

The growth of thick Fe layers (nominal thickness 100 nm) took place at two different atmospheres: at pure argon or at Ar (67%) + H_2 (33%) mixed atmosphere, in both cases under pressure of 0.3 Pa with very low deposition rate equal to 0.7 nm/min. In addition, one sample was grown with hydrogen supply periodically changing from 0 to 33% in time during the deposition. Nominal thickness of Fe and Fe:H layer in Fe/Fe:H multilayer obtained in such a manner was equal to 4 nm and 2 nm, respectively, with a number of repetitions equal to 22. In order to avoid the oxidation of iron, all samples were covered by amorphous Ge cap layers (16.5 nm thick in the case of the multilayer and 10 nm thick for other samples).

The structural and magnetic properties of samples were investigated at room temperature. For the structure characterization of samples, X-ray diffraction, X-ray reflectometry, neutron diffraction, and neutron reflectivity have been measured. First, X-ray reflectometry and the small-angle diffraction measurements were performed at the Institute of Physics using a reflectometric attachment at an X'Pert MPD (Philips) diffractometer. The Cu $K\alpha$ radiation (wavelength $\lambda = 0.15418$ nm) was used for this purpose. The wide-angle X-ray diffraction was studied with the use of the same diffractometer. The neutron scattering studies were performed at Laboratoire Lйon Brillouin (Saclay, France). Both, the small-angle neutron diffraction and the spin-polarized neutron reflectometry with the use of cold neutron beams (wavelength $\lambda = 0.43$ nm) were applied. Additionally, the surface morphology for all samples was checked with the use of atomic force microscopy (AFM).

The magnetic properties of investigated samples were studied at the Institute of Physics of the Polish Academy PAS by the Kerr rotation and magnetic force microscopy (MFM). The first method made it possible to observe a difference in the hysteresis loops determined for samples deposited in the presence of hydrogen (or without it) in the sputter atmosphere. The experimental set-up for Kerr effect in longitudinal geometry consists of HeNe CW laser (wavelength 632.8 nm, output power 0.1 mW), photoelastic modulator (the modulation frequency f = 50 kHz), linear light polarisers and Si photodiode as a detector. The magnetic field up to 2000 Gs was applied for the Kerr rotation effect. MFM measurements permit to observe magnetic domain structure on the surface of investigated sample. For this method the MultiMode DI microscope was used.

3. RESULTS

3a. X-ray diffraction.

The X-ray diffraction data for three investigated samples are shown in Fig.1. Only the 200 Bragg peak is observed for thick Fe layers and for Fe/Fe:H multilayer a small 110 peak is also detected. This finding means that both thick Fe layers are grown epitaxially with a single, (100) crystal orientation, but Fe/Fe:H multilayer has a small contribution of (110) orientation.

From Fig.2 it is clearly seen that lattice parameter value a of Fe film in the direction perpendicular to the surface decreases to its bulk value after an addition of H_2 to sputter atmosphere. It means that

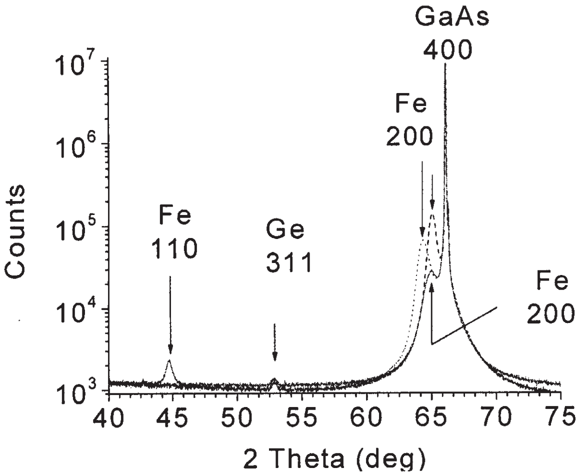

Fig. 1. X-ray diffraction pattern for Fe films deposited on GaAs (100) substrate in Ar sputter atmosphere (dotted line), in Ar+H_2 sputter atmosphere (dashed line) and for Fe/Fe:H multilayers (solid line).

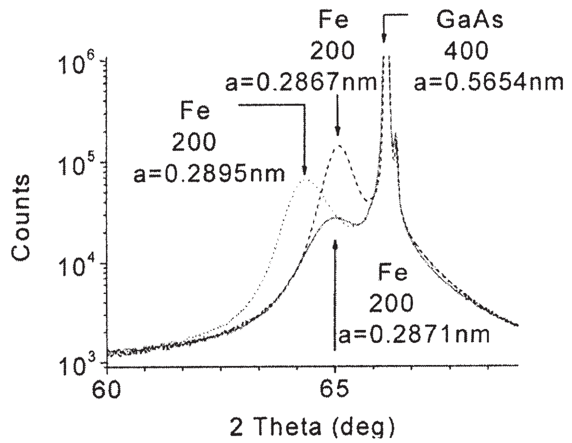

Fig. 2. X-ray diffraction data near 200 Fe Bragg peak. Fe film deposited in Ar sputter atmosphere (dotted line), in Ar+H_2 sputter atmosphere (dashed line). Solid line corresponds to the Fe/Fe:H multilayers.

Fe film relaxes because of the presence of hydrogen. However, it is not clear does the hydrogen simply modify the layer growth conditions or is it also introduced into the sample volume.

3b. Neutron scattering

In order to check possible presence of hydrogen in Fe, neutron scattering studies on multilayer structure were performed. Due to periodically distributed small amount of hydrogen the multilayer Bragg peaks due to periodic distribution of hydrogen should be observed in this case. The small-angle neutron diffraction performed on the multilayer did not show any Bragg peaks resulting neither from a chemical nor from a magnetic scattering in the sample. There is no Bragg peak for the *q* value predicted for the nominal thickness of Fe/Fe:H bilayer (see Fig.3). It suggests that hydrogen concentration is below the detection limit of this technique.

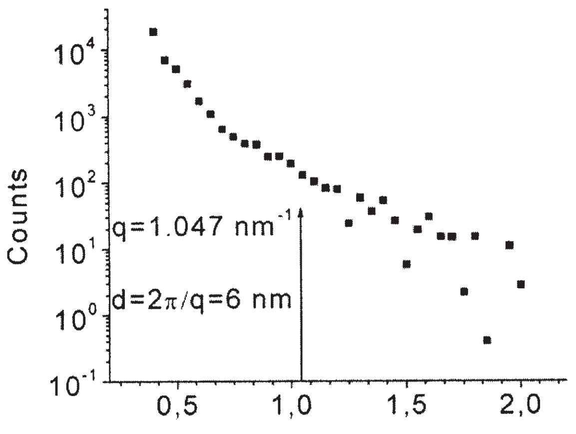

Fig. 3. Small-angle neutron diffraction on Fe/Fe:H multilayer. Arrow indicates an expected magnetic Bragg peak position (numerical values of the wave vector *q* corresponding to the period of the multilayer *d* are given).

The X-ray reflectometry dates fit for thick Fe layers, gives 89.7±0.3 nm thickness value for Fe layer and 10.9±0.3 nm one for Ge cap layer for sample grown in Ar+ H_2 atmosphere and 90±0.3 nm and 10.9±0.3 nm respectively, for sample grown in pure Ar. Because of longer wavelength the neutron Kiessig oscillations due to the thick iron layer are better pronounced. From the fit of the theoretical curve to the experimental neutron reflectivity data, thickness of Fe and Ge cap layers equal to 88.0±2.5 nm and to 12.0±0.4 nm respectively, were obtained for sample grown in Ar+H_2 atmosphere. The X-ray and neutron results agree within the experimental errors of the methods.

Fig.4 shows details of the neutron reflectivity curves for two thick layers in the vicinity of the critical angle θ_c with the use of the spin-polarised neutrons. As can be seen, the critical angle for both samples is close to the value $\theta_c = 0.8°$. The difference between two samples under consideration is equal to 0.02°. The hydrogen concentration as high as 6% could explain this small shift. However, the same effect can be explained by the change of the magnetization value by 4% only.

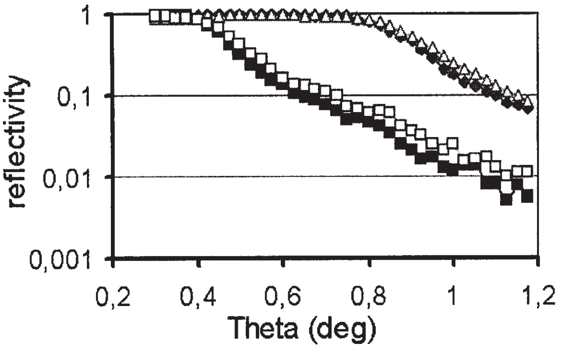

Fig.4. Neutron reflectivity pattern for two thick Fe layers. All points represent the experimental data, diamonds (pure Fe) and triangles (Fe:H) correspond to the 'spin up – spin up' neutron polarisation during the scattering process, grey squares (pure Fe) and black squares (Fe:H) – to the 'spin-down – spin down' neutron polarisation.

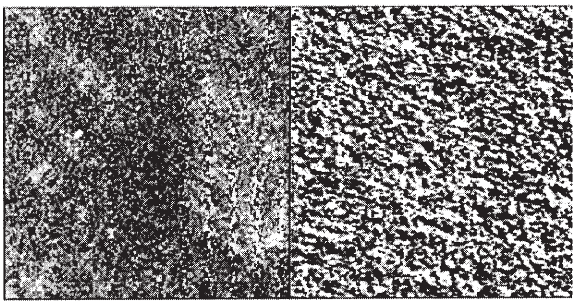

Fig. 5. Surface (10 x 10 μm) of Fe/Fe:H multilayer observed by AFM (left panel) and the same area observed by MFM (right panel). The distribution of magnetic domains is not related to the shape of the multilayer surface.

3c. Magnetic properties

Magnetic properties of both thick layers and the multilayer were investigated by means of the MFM and the Kerr rotation. MFM measurements show that there is no magnetic domain structure for single thick Fe and Fe:H layers. Irregular magnetic domain structure was found in the case of Fe/Fe:H multilayer (see Fig. 5). The typical linear size of a single domain is of the order of 150 nm. One can suppose that such magnetic structure could be due to the strain in the system caused (there is some lattice mismatch at the Fe/Fe:H interfaces).

Normalized hysteresis loops of Kerr rotation measurements are shown in Fig. 6. As it is well seen, the width of the loop being close to 30 Gs for pure Fe layer, is strongly reduced for iron layer deposited in the presence of hydrogen and reaches about 15 Gs. The width of the hysteresis loop observed for Fe/Fe:H multilayer is in between the two above mentioned values. It is a clear evidence of the influence of the sputter atmosphere during the deposition on the magnetic properties of samples. It should be mentioned that the results of Kerr rotation measurements repeated on the same samples a few months after their deposition were exactly the same. It means that the observed phenomena are time–independent and are not related to unbounded ('free') hydrogen, which can be present in the iron lattice just after the deposition process and slowly disappears with time due to the diffusion to the surface.

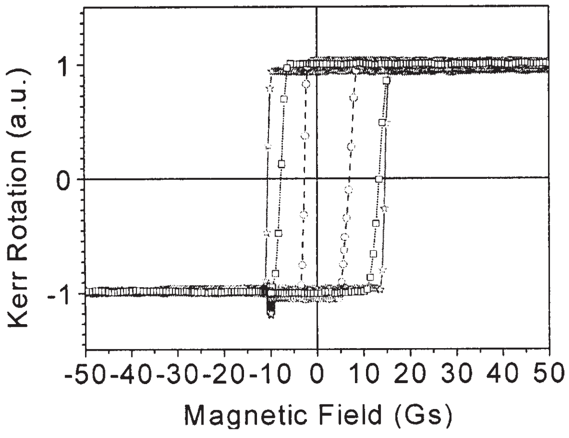

Fig.6. Influence of hydrogen in the sputter atmosphere on the hysteresis loop observed by Kerr rotation at room temperature. Asterisks: – pure Fe layer, circles – Fe:H layer, squares – Fe/Fe:H multilayer.

4. DISCUSSION

The obtained results demonstrate an important difference between the properties of ~90 nm thick Fe layers deposited on (100) GaAs substrates in pure Ar and in Ar + H_2 atmosphere. The lattice parameter value corresponding to the Fe layer deposited in the presence of H_2 (a = 0.2867 nm) is slightly higher than that corresponding to pure BCC-Fe. This finding is in contradiction to the result found in the literature [12]. Kerr effect measurements indicate that the presence of H_2 in the sputter atmosphere results in reduction of the coercivity.

The most probable explanation of all observed differences is a presence of hydrogen in samples deposited in the Ar + H_2 atmosphere. The neutron scattering methods are not sensitive enough to confirm possible presence of small amount of hydrogen in investigated samples. There is no other direct evidence that samples under consideration contain hydrogen. However, several indirect results suggest such possibility. In particular, the observed relaxation of the lattice parameter of Fe epilayer due to a presence of H_2 in sputter atmosphere probably occurs because of a weakening of Fe-Fe bonds due to hydrogen presence. According to the literature, such weakening of bonds may be reduced down to about 30% of the bond strength observed without hydrogen [11,14]. Further experimental studies are required in order to confirm that the hydrogen presence in the lattice causes the observed effects.

ACKNOWLEDGEMENTS

This work was supported in part by the European Community programs G1MA-CT-2002-4017 (Centre of Excellence CEPHEUS) and SPINOSA IST-2001-33334, by the grant PBZ/KBN/044/P03/2001 from the Committee for Scientific Research (Poland), and by ACI NR0095 'NANODYNE' from the French Ministry of National Education and Research. The experiments at LLB were supported by the European Commission through the Access Activities of the Integrated Infrastructure Initiative for Neutron Scattering and Muon Spectroscopy (NMI3), supported by the European Commission under the 6th Framework Programme through the Key Action: Strengthening the European Research Area, Research Infrastructures, Contract N°: RII3-CT-2003-505925.

REFERENCES

[1] H.J. Zhu, M. Ramsteiner, H. Kostial, M. Wassermeier, H.P. Schőnherr and K.H. Ploog // *Phys. Rev. Lett.* **87** (2001) 016601.

[2] A.T. Hanbicki and B.T. Jonker // *Appl. Phys. Lett.* **80** (2002) 1240.

[3] M. Zenger, J. Moser, W. Wegscheider, D.Weiss and T. Dietl // *J. Appl. Phys.* **96** (2004) 2400.

[4] K. Yoh, H. Ohno, Y. Katano, K. Sueoka, K. Mukasa and M.E. Ramsteiner // *Semicond. Sci. Technol.* **19** (2004) S386.

[5] H.J. Haugan, B.D. McCombe and P.G. Mattocks // *J. Magn. Magn. Mater.* **246** (2002) 296.

[6] G.A. Prinz, G.T. Rado and J.J. Krebs // *J. Appl. Phys.* **53** (1982) 2087.

[7] M. Brockmann, M. Zőlfl, S. Miethaner and G. Bayreuther // *J. Magn. Magn. Mater.* **198-199** (1999) 384.

[8] B.Lépine, C. Lallaizon, S. Ababou, A. Guivarc'h, S. Deputier, A. Filipe, F. Nguyen Van Dau, A. Schuhl, F. Abel and C. Cohen // *J. Crystal Growth* **201/202** (1999) 702.

[9] S.D. Bernstain, T.Y. Wong and R.W. Tustison // *J. Appl. Phys.* **72** (1992) 4358.

[10] M. Zőlfl, M. Brockmann, M. Kőhler, S. Kreuzer, T.Schweinbőck, S. Miethaner, F. Bensh and G. Bayreuther // *J. Magn. Magn. Mater.* **175** (1997) 16.

[11] R. Vollmer and J. Kirshner // *Phys. Rev. B* **61** (2000) 4146.

[12] M. Takahashi, H. Takahashi, H. Nashi, H. Shoji and T. Wakiyama // *J. Appl. Phys.* **79** (1996) 5564.

[13] A.A. Novakova, T.Yu. Kiseleva, O.V. Agladze, N.S. Perov and B.P. Tarasov // *Int. J. Hydrogen Energy* **26** (2001) 503.

[14] A. Juan and R. Hoffman // *Surf. Sci.* **421** (1999) 1.