

Surface treatments and magnetic properties of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ thin films

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Available online 18 April 2007

Abstract

As a diluted magnetic semiconductor (DMS), (Ga,Mn)As is a possible candidate for the realization of spintronics devices, due to its intrinsic compatibility with GaAs based electronics. The low Curie temperature still limits its use for practical devices. Despite the huge knowledge on GaAs surface, the (Ga,Mn)As surface is still not well understood and difficult to handle. Standard surface cleaning techniques have many drawbacks, mainly because thermal treatments changes crystal structure. We will compare the magnetic and spectroscopic properties of differently processed (Ga,Mn)As surfaces with X-ray photoemission (XPS), X-ray absorption (XAS) and X-ray magnetic circular dichroism (XMCD). Samples as-grown, chemically etched, Ar^+ sputtered and annealed in oxygen will be compared. © 2007 Elsevier B.V. All rights reserved.

Keywords: X-ray photoelectron spectroscopy; X-ray absorption spectroscopy; Magnetic interfaces; (Ga,Mn)As

1. Introduction

In the growing field of diluted magnetic semiconductors (DMS), (Ga,Mn)As plays a big role due to the predicted possibility of room temperature ferromagnetism [1] and its intrinsic compatibility with GaAs based electronic devices. In recent times a Curie temperature as high as 250 K [2] was obtained with delta-doped samples and moreover it was predicted [3] that carefully designed layered structure could have T_c up to 350 K. Efficient spin injection was proved to be effective in a (Ga,Mn)As based heterostructure [4] and current driven magnetization reversal was also realized [5]. These advances are not supported by a similar knowledge on (Ga,Mn)As surface, which still lacks reliable cleaning and preparation protocols to obtain pure and ordered surfaces.

At the relatively low growing temperature, necessary to avoid Mn segregation in the hexagonal MnAs phase, a significant fraction of Mn atoms are not embedded in the crystal in the Ga sites, but occupy interstitial sites (Mn_I) [6]. In these configurations Mn is highly mobile [7] and tends to accumulate on the surface during crystal growth, resulting in non uniform doping profiles and Mn enriched surfaces. Thermal treatments on thin films in gaseous environment, or on As-capped samples [8], are used to remove Mn_I thus improving the ferromagnetic properties of the material. These procedures causes Mn_I to accumulate on the surface, in the form of a thick, non-magnetic layer. Both in the case of as-grown and post-growth annealed samples there is the problem of the removal of the topmost layers, that does not reflects the bulk ferromagnetic properties of the sample.

The electronic structure of the Mn has been widely studied with surface sensitive techniques like photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS). Many experiments were performed in the past years, such as X-ray photoemission (XPS) [9], resonant

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photoemission (RPES) [10], angular resolved ultraviolet photoemission (ARUPS) [11]. The sample surfaces are routinely prepared by mean of repeated cycles of Ar^+ ion sputtering and thermal annealing, keeping the temperature lower than 250 °C. The surface structure is usually monitored by low energy electron diffraction (LEED), and shows a 1×1 pattern. It is never specified if the samples keep their ferromagnetic properties after the treatments. We are aware of only one experiment made in situ [12]: the results were not compatible with previous photoemission studies. XAS and X-ray magnetic circular dichroism (XMCD), carried out before 2004, showed non-magnetic Mn accumulated at the surface. They were made on unprocessed surfaces in order to keep surface magnetic properties unaffected. This led to the attribution of a wrong valence to Mn atoms, because the measurements did not reflected bulk properties. To our knowledge the only examples of XAS measurements which reflected lineshape of the Mn embedded in GaAs matrix before 2004, were made by Rader et al. [10], on a sputtered and annealed surface, and by Soo et al. [13] on a GaAs capped sample. In 2004 the group of Edmonds [14] showed that HCl etching, followed by rinsing in de-ionized water, can efficiently remove the Mn oxidized layer, allowing the measurement of the Mn embedded in GaAs bulk, leaving the magnetic properties of the surface unaffected.

A better control on (Ga,Mn)As surface quality is desirable for the realization of metal/(Ga,Mn)As junctions. It is well known that the Fe/GaAs(100) interface has a great relevance due to the lack of any magnetically dead layer at the interface [15], and the possibility of realizing efficient spin injection in GaAs [16]. It would be interesting to study the analogous Fe/(Ga,Mn)As, because the behaviour of this hole-doped DMS upon electron spin injection is absolutely unknown. To this end a deeper insight into (Ga,Mn)As surface magnetization and composition is of primary importance, as a function of different surface treatments.

2. Sample preparation and characterization

The (Ga,Mn)As samples were grown on GaAs(100) substrates. The alloy parameter x ranges between 0.02 and 0.06. One representative sample with $x = 0.024$, left without any capping layer after MBE growth, was fractured in three pieces (S1, S2, S3) which were treated differently. S1 was left “as received” i.e. without post-growth treatments, but aged in atmospheric pressure; S2 was etched; S3 was etched and then Ar^+ ion sputtered and annealed in situ, in oxygen atmosphere. Another sample, with $x = 0.06$, capped with arsenide after MBE growth, was fractured in two pieces: Sb3 was chemically etched, while Sb2 was sputtered with Ar^+ ion.

Ferromagnetic samples have been produced at low-temperature growth conditions as described below: prior to (Ga,Mn)As growth, a 300 nm GaAs buffer was grown at standard conditions (substrate temperature $T_s = 600$ °C; arsenic flux $\approx 1 \times 10^{-5}$ Torr beam equivalent pressure

(BEP), GaAs growth rate ≈ 0.28 nm/s). Subsequently, the sample temperature was reduced to 260 °C. Meanwhile the temperature of the gallium effusion cell was reduced, resulting in a GaAs growth rate of ≈ 0.07 nm/s. The arsenic flux was maintained constant. After the substrate temperature had stabilize, 20–50 nm (Ga,Mn)As was grown. The crystal quality of the epilayer was monitored in situ via reflection high-energy electron diffraction (RHEED). The manganese concentration was measured ex situ by XPS and magnetic properties were measured by SQUID.

Chemical etching is a very efficient way to remove the surface Mn oxide layer [14]. Samples S2, S3 and Sb3 were treated by etching the epitaxial film in pure HCl for one minute, then rinsed in de-ionised water up to the insertion in UHV environment (base pressure $P = 4 \times 10^{-10}$ mbar).

In the case of sample S3 the etching was followed, in situ, by Ar^+ ion sputtering ($E = 750$ eV) and by annealing at 200 °C in an oxygen pressure of 7×10^{-7} mbar for 3 h. Sample Sb2 was only subjected to repeated Ar^+ ion sputtering cycles. Its surface was monitored by XPS and XAS at each step.

The samples were transferred in UHV to the main chamber for XPS, XAS and XMCD measurements, where the sample holder is fitted on a liquid helium flow cryostat, capable of refrigerating the sample down to 30 K.

The experiments were performed at the advanced photoemission experiment (APE) INFM undulator beamline at the Elettra Synchrotron radiation facility in Trieste, delivering both linearly and circularly polarized light [17]. Mn $L_{2,3}$ XAS and XMCD measurements were obtained by measuring the sample drain current with an energy resolution of 150 meV and a circular polarization rate of 70%. The photon incidence angle was kept fixed at 45° from the sample surface normal, as indicated in Fig. 1. Both XPS and XAS/XMCD measurements were possible at identical sample positions. XPS data have been acquired by a 7-channel Omicron EA-125 analyzer at normal emission using energies of 880 eV (sample S1, S2, S3) and 1100 eV (sample Sb2, Sb3). The overall energy resolution (photons + analyzer) was about 1.5 eV. In both photoemission and photoabsorption measurements the X-ray beam size on the sample surface was on the order of $100 \times 200 \mu\text{m}^2$. The samples were magnetized by applying a mag-

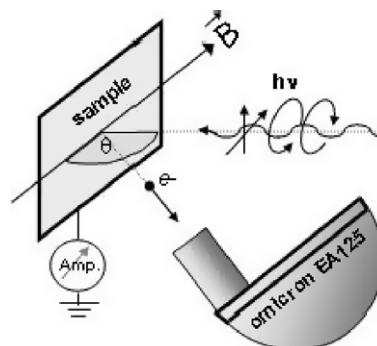


Fig. 1. Experimental geometry.

netic field using a horseshoe magnet able to deliver up to 2000 Oe in pulsed mode and 200 Oe in continuous mode along the sample surface plane. The magnetic field is applied along the (100) easy magnetization axis of the sample.

3. Results

The XAS spectrum of the sample S1, in Fig. 2, has two strong features at 1.4 and 3.6 eV above the L_3 edge (638 eV). These structures can be well simulated starting from an atomic d5 electronic configuration [14], typical of Mn oxides. The XMCD main peak centre is 0.4 eV below the L_3 XAS edge. The XAS spectrum of sample S2, chemically etched, has the L_3 threshold at 637.6 eV, namely 0.4 eV below the L_3 of S1. Its lineshape does not have clear structures, and can be simulated with a mixed state of d4–d5–d6 atomic configurations [14], due to the hybridization of the Mn 3d electrons with As valence band. The shape of the XMCD difference spectrum of S2, and its energy position, correspond the one of the S1 sample. We can thus interpret the lineshape of the S1 as composed two components, corresponding to two distinct Mn populations: the pure d5, with L_3 peaked at 638 eV, and the mixed d4–d5–d6, with L_3 peaked at 637.6 eV. The latter is ferromagnetic and corresponds to the Mn embedded in the GaAs matrix.

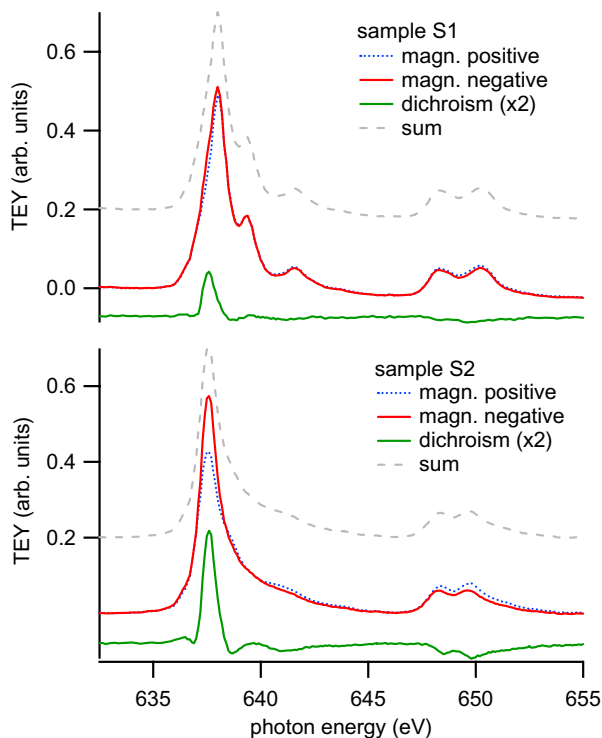


Fig. 2. XAS spectra with opposite sample magnetization (red line and blue dotted line); XMCD spectra (green continuous line); XAS summed spectra (grey dotted lines). The top panel refers to the uncapped sample aged in air (S1), the bottom panel to the sample etched in HCl (S2). Dichroic spectra are multiplied by two for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

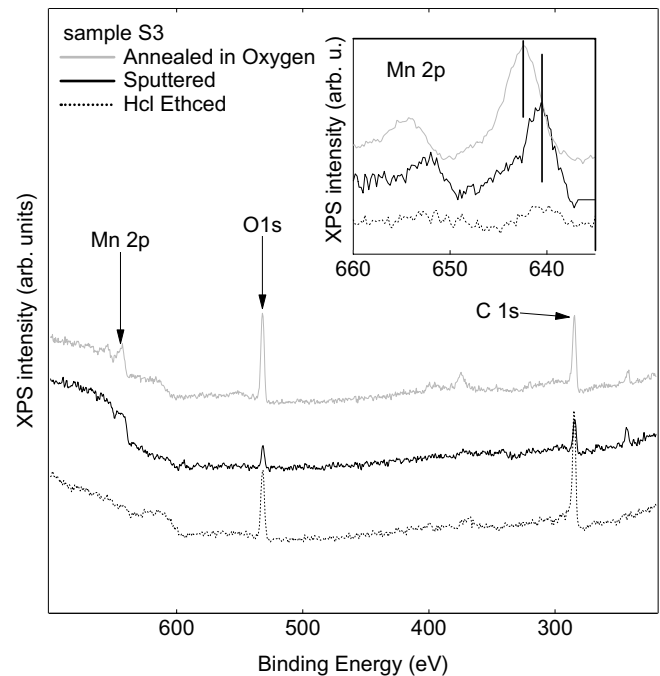


Fig. 3. XPS spectra of sample S3 during the steps of the surface treatment. In the inset the energy region of Mn 2p peaks is magnified. Eph = 880 eV.

It is the only one which is observed on S2 because the surface oxides were removed by chemical etching. The former (d5 configuration) is not ferromagnetic, because we do not observe an XMCD difference signal peaked at 638 eV, and correspond to the surface Mn oxides.

The XPS data in Fig. 3 show that the surface of the S3, after chemical etching, is strongly contaminated by carbon and oxygen, and there is no manganese. The sputtering, whose duration and intensity was calibrated in order to remove a few monolayer of material, reduces the concentration of oxygen and carbon, and uncover some of the buried

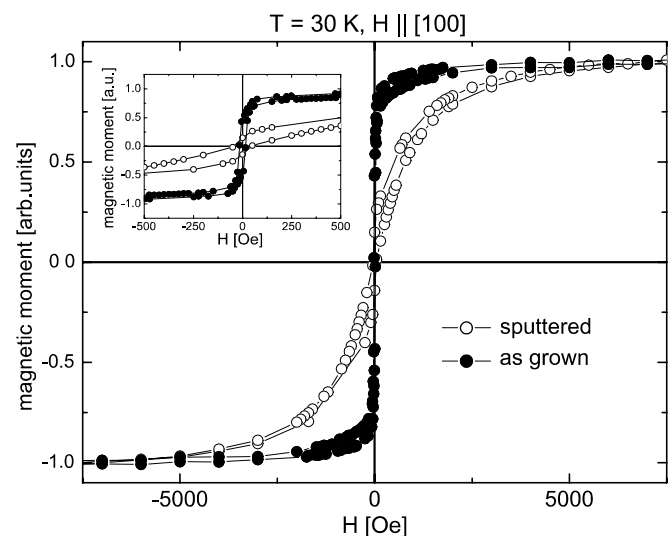


Fig. 4. SQUID measurements of sample S3 before (black circles) and after (empty circles) the surface preparation.

Mn which was visible only with XAS, whose probing depth is much higher. The annealing in oxygen atmosphere causes oxidation of the Mn, as evident from the shift of the Mn2p peaks towards higher binding energies.

After the thermal treatment, the XAS spectral shape did not show remarkable changes, therefore we can state that the thermal treatment did not cause significant segregation of Mn in the MnAs hexagonal phase, whose spectral shape

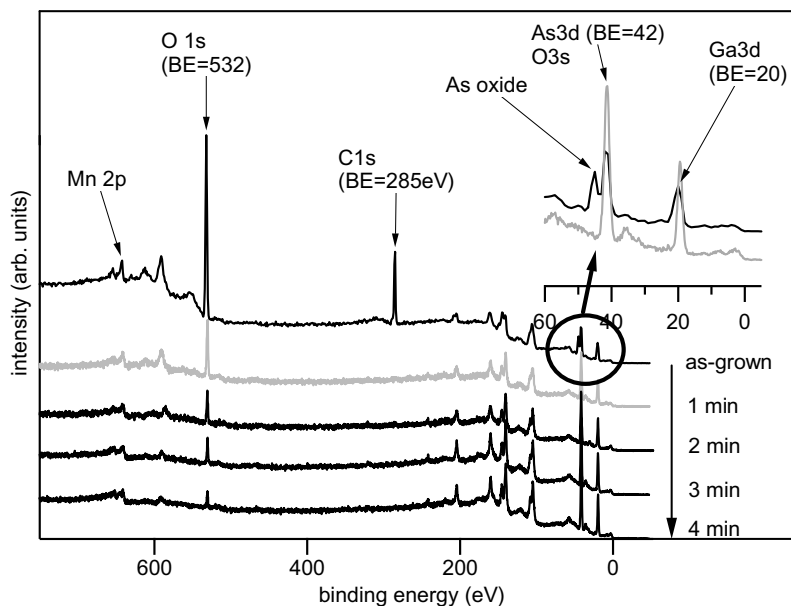


Fig. 5. Sample Sb2 evolution of XPS spectra during Ar^+ ion sputtering. In the inset are represented the As3d and Ga3d peaks of the first two spectra. It is clear the disappearance of the As oxide peak at higher binding energies. Eph = 1100 eV.

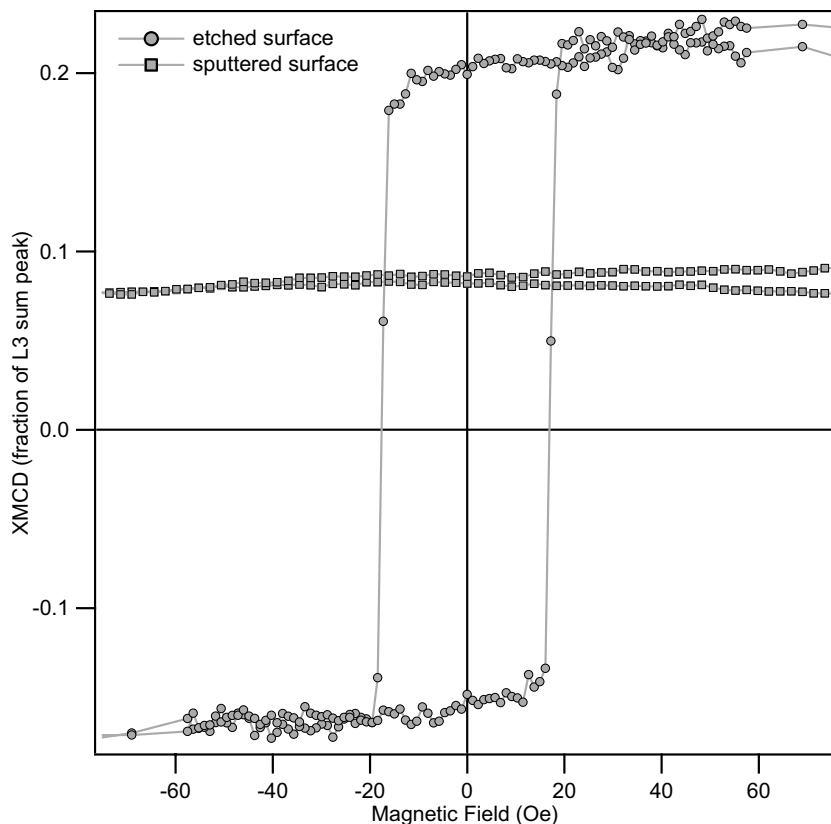


Fig. 6. Hysteresis cycles of sample Sb2 after the HCl etching, and after the Ar^+ sputtering. It was used the XMCD signal both at the Mn L3 edge and in the pre-edge region, for the two light polarization, in order to compensate the effect of experimental artifacts.

is different [18]. Conversely, the XMCD signal was completely absent. The sample S3 was then measured with SQUID magnetometry. In Fig. 4 the hysteresis cycles of the sample before and after the surface treatment are compared. The remnant magnetization is strongly reduced. The ferromagnetic properties of the sample are strongly affected by the Ar^+ ion sputtering, followed by thermal treatment in oxygen atmosphere.

In Fig. 5 it is reported the evolution of the surface of the sample Sb2 during Ar^+ ion sputtering. The carbon and the As oxide (visible in the inset) completely disappear after the first minute of sputtering. The oxygen concentration is progressively reduced at each step of the process and is still present at the end of the treatment. The XAS lineshape (not shown) evolves from the one typical of the oxidized Mn towards the one of the hybridized Mn. Magnetic hysteresis of an etched piece of sample Sb2 and of the sputtered Sb2 were recorded acquiring the XMCD signal at the L3 peak and the results are reported in Fig. 6. After the sputtering the sample does not show hysteresis in the range of explored magnetic field (± 200 Oe).

4. Conclusions

We made a total of three different surface treatments on (Ga,Mn)As samples: chemical etching with HCl, Ar^+ ion sputtering followed by thermal annealing in presence of oxygen, and simple Ar^+ sputtering. The etching efficiently removes all the Mn oxides which affect the XAS and XMCD measurements, leaving a surface still contaminated by carbon and oxygen. The use of sputtering followed by thermal treatment in presence of oxygen reduce strongly the magnetic properties of the film, as obtained using only the sputtering.

References

- [1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* 287 (2000) 1019.
- [2] A.M. Nazmul, T. Ameiya, Y. Shuto, S. Sugahara, M. Tanaka, *Phys. Rev. Lett.* 95 (2005) 017201.
- [3] A. Franceschetti, S.V. Dudy, S.V. Barabash, A. Zunger, *Phys. Rev. Lett.* 97 (2006) 047202.
- [4] E. Johnston-Halperin, D. Lofgreen, R.K. Kawakami, D.K. Young, L. Coldren, A.C. Gossard, D.D. Awschalom, *Phys. Rev. B* 65 (2002) 041306.
- [5] D. Chiba, Y. Sato, T. Kita, F. Matsukura, H. Ohno, *Phys. Rev. Lett.* 93 (2004) 216602.
- [6] K.M. Yu, W. Walukiewicz, T. Wojtowicz, J. Denlinger, M.A. Scarpulla, X. Liu, J.K. Furdyna, *Appl. Phys. Lett.* 86 (2005) 042102.
- [7] K.W. Edmonds, P. Boguslawsky, K.Y. Wang, R.P. Campion, S.N. Novikov, N.R.S. Farley, B.L. Gallagher, C.T. Foxon, M. Sawicki, T. Dietl, M. Buongiorno Nardelli, J. Bernholc, *Phys. Rev. Lett.* 92 (2004) 037201.
- [8] V. Stanciu, O. Wilhelmsson, O. Bexell, M. Adell, J. Sadowki, J. Kanski, P. Warnicke, P. Svedlindh, *Phys. Rev. B* 72 (2005) 125324.
- [9] J. Okabayashi, A. Kimura, O. Rader, T. Mizokawa, A. Fujimori, T. Hayashi, M. Tanaka, *Phys. Rev. B* 58 (1998) R4211.
- [10] O. Rader et al., *Phys. Rev. B* 69 (2004) 075202.
- [11] J. Okabayashi, A. Kimura, O. Rader, T. Mizokawa, A. Fujimori, T. Hayashi, M. Tanaka, *Phys. Rev. B* 64 (2001) 125304.
- [12] H. Åsklund, L. Ilver, J. Kanski, J. Sadowski, R. Mathieu, *Phys. Rev. B* 66 (2002) 115319.
- [13] Y.L. Soo et al., *Phys. Rev. B* 67 (2003) 0214401.
- [14] K.W. Edmonds, N.R.S. Farley, R.P. Campion, C.T. Foxon, B.L. Gallagher, T.K. Johal, G. van der Laan, M. MacKenzie, J.N. Chapman, E. Arenholz, *Appl. Phys. Lett.* 84 (2004) 4065.
- [15] L. Giovanelli, G. Panaccione, G. Rossi, M. Fabrizioli, C.S. Tian, P.L. Gastelouis, J. Fujii, C.H. Back, *Phys. Rev. B* 72 (2005) 045221.
- [16] A.T. Hanbicki, B.T. Jonker, G. Itskos, G. Kioseoglou, A. Petrou, *Appl. Phys. Lett.* 80 (2002) 1240.
- [17] See <<http://www.elettra.trieste.it/experiments/beamlines/ape>>.
- [18] J. Okabayashi, M. Mizuguchi, M. Oshima, H. Shimizu, M. Tanaka, M. Yuri, C.T. Chen, *Appl. Phys. Lett.* 83 (2003) 5485.