Magnetic and chemical aspects of Cr-based films grown on GaAs(001)

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Abstract
We have investigated the magnetic and chemical properties of very thin films
of Cr, CrAs, and arsenized Cr, grown by molecular beam epitaxy on GaAs
(001), using x-ray photoemission spectroscopy and SQUID magnetometry. The
substrate was kept at 200 °C in an As-rich environment for incoming Cr atoms at
the GaAs surface. Gallium segregation and the chemical reactivity between Ga
and Cr have negligible contribution to the formation of different thin films. A
clear ferromagnetic response, even at room temperature, suggests the formation
of a very thin buried interfacial layer during the growth process.

1. Introduction

In the last decade the integration of magnetic materials on semiconductors has been intensively
investigated due to the potential applications for spin-based electronics [1, 2]. Mono-arsenides
integrated on GaAs play an important role since they are ferromagnetic with high Curie
temperatures. Recently, *ab initio* theoretical calculations [3] have predicted a ferromagnetic
state at room temperature with half-metallic electronic band structure for CrAs with the zinc
blende structure. These interesting properties motivated us to investigate the CrAs/GaAs
system [4]. Previous results have shown that very thin CrAs epilayers on GaAs(001) have an
orthorhombic structure with a magnetic response at room temperature due to strain constraints
of the epitaxial growth, causing an expansion of the **b** axis. The crystallization and chemical
interaction at the interface between Cr and GaAs has been explored for different substrate
temperatures and film thickness [5]. Even at room temperature, diffusion and chemical
reactions may occur close to the interface for many transition metal/GaAs systems [6]. The
interface characteristics and compound formation have recently been investigated [7–14], but
available results are very limited when arsenization of Cr is considered.

In the present study, we have investigated the magnetic and chemical aspects concerning the interfacial layer properties formed between Cr and GaAs under different growth procedures using x-ray photoemission spectroscopy (XPS) and SQUID magnetometry. In a previous work [8, 9] the reactivity between Cr and GaAs was minimized growing Cr thin films at room temperature on GaAs(001) surfaces. More recently, Qian *et al* [14] have shown that the structure of Cr films on GaAs(001) strongly depends on the growth temperature. Now, our investigation considers samples prepared under different As-rich environments keeping the substrate at 200 °C. The aim of this study is to investigate the growing conditions, focusing on the role of the arsenic chemistry in the beginning of the interface formation that favours the growth of the ferromagnetic compound (strained CrAs epilayers reported in [4]).

2. Experimental details

The samples investigated in this work are thin chromium films, CrAs films and arsenized Cr films (hereafter named Cr–As). All samples were grown using a conventional molecular beam epitaxy system equipped with reflection high-energy electron diffraction (RHEED) and x-ray photoelectron spectroscopy (XPS) facilities. An undoped GaAs buffer layer 1000 Å-thick was initially grown on epiready GaAs(001) substrates, following standard growth conditions. Finally, an As-rich (2×4) GaAs surface was stabilized. All samples described below were grown on GaAs surfaces at 200 °C. The Cr thin films were grown at a growth rate of 4 Å min^{-1}. The RHEED diagrams observed during growth of the Cr thin film (not shown) initially fade away, revealing later a body-centred cubic structure with a three-dimensional growth front, as the thickness increases. Arsenized Cr thin films were obtained from 80 Å-thick Cr thin films annealed under As$_4$ flux for 30 min at 320 °C. CrAs thin films were evaporated using separate Cr and As cells with a growth rate of 8 Å min^{-1} under As-rich conditions.

In situ photoemission measurements were performed at different growth stages using unmonochromated Mg Kα (1253.6 eV) radiation and an energy analyser with an overall resolution of about 0.8 eV. For *ex situ* photoemission depth-profile and magnetic measurements, some samples were protected with an amorphous 100 Å-thick ZnSe capping layer deposited at room temperature. This procedure was checked to protect the sample against air exposure for many weeks and the negligible capping layer contribution to the magnetic measurements was confirmed.

DC magnetic moment measurements were performed with a SQUID (Quantum Design MPMS-5S) magnetometer from 5 to 350 K and applied magnetic fields up to 5 T. Low-field magnetic moment measurements were carried out combining a conventional zero-field cooling (ZFC) warming run, followed by a field cooling (FC) experiment for different values of applied magnetic fields.

3. Results and discussion

3.1. Photoemission experiments

Figure 1 shows core level spectra of Ga 2p$_{1/2}$ for CrAs and Cr ultrathin overlayers grown on GaAs(001). Unreacted Ga lineshape is detected during CrAs/GaAs(001) interface formation. During Cr/GaAs(001) interface formation, only a small secondary component may be identified in the spectrum positioned at 0.8 eV lower binding energy.

The behaviour of the As signal at the evolving Cr/GaAs interface (cf figures 2 and 3) is significantly different from that of Ga, since the As 3d and As 3p core levels do not show detectable chemical changes induced by the initial Cr coverage (for less than 12 Å coverage).
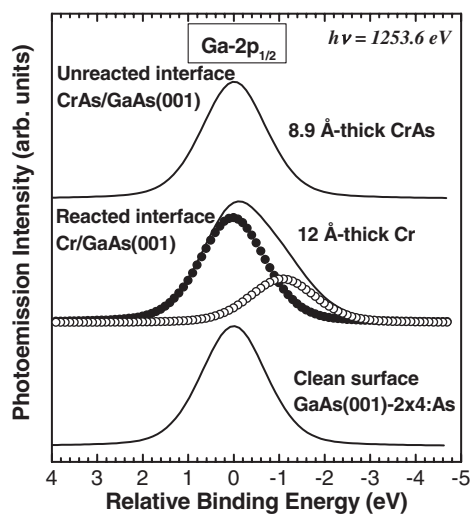
Figure 1. *In situ* Ga 2p core-level spectra measured during growth of Cr and CrAs thin films on GaAs. The Ga 2p core-level spectrum of the clean surface is also shown. Ga 2p reacted (open circles) and unreacted (solid circles) interface components are shown at a coverage of 12 Å Cr.
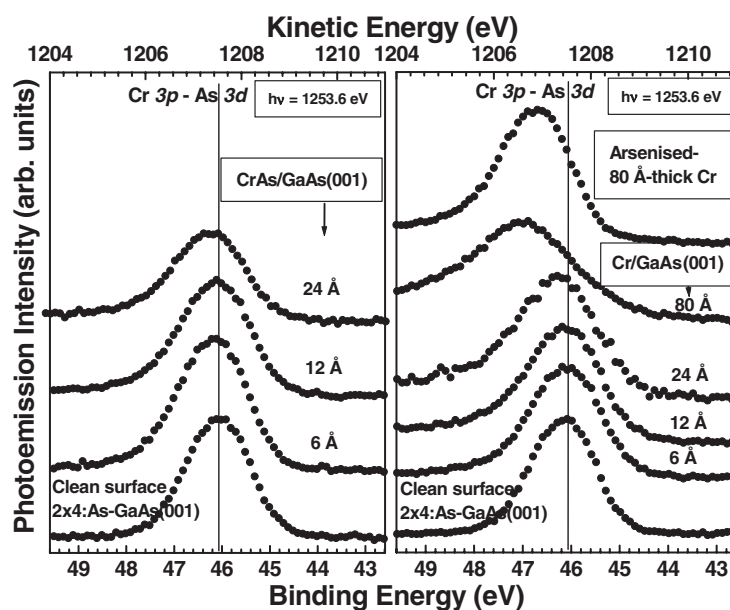
Figure 2. Photoemission spectra of the As 3d core-level for CrAs overlayers on GaAs(001) in the left-hand panel and for Cr overlayers on GaAs(001) in the right-hand panel. The topmost right-hand panel also shows the spectrum of post-growth arsenized 80 Å-thick Cr. Cr 3p core emission becomes clearly visible at about 1.2 nm overlayer thickness and dominates after 80 Å-thick Cr is reached.

The core lineshape is not shifted with increasing Cr coverage; indeed the only feature detected is a broadening of the full width at half maximum from 1.6 to 1.8 eV. The Cr/GaAs interface has been previously analysed in detail by Weaver *et al* [7] with higher resolution and greater surface
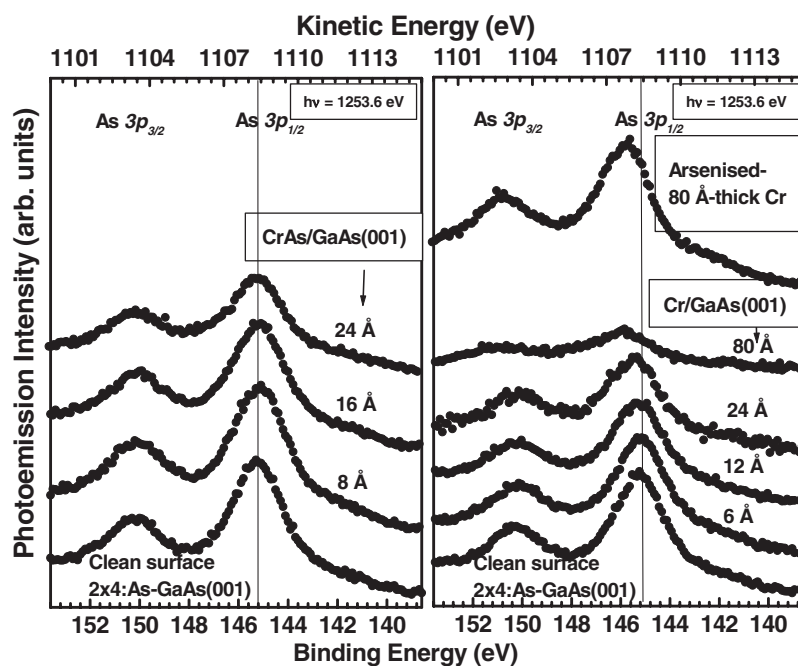
Figure 3. As 3p core spectra corresponding to analogous coverage to those shown in figure 2.

sensitivity in synchrotron-radiation photoemission experiments. Two different As chemical environments have been evidenced, namely As from the GaAs substrate and As from a reacted layer. The As-reacted species were associated with As atoms in a Cr–As bond with 0.25 eV energy shifted toward the lower binding energy, with respect to As emission signal from the GaAs substrate [7]. Unfortunately, the core-level emission studies cannot distinguish the two As chemical environments due to our total energy resolution of 0.8 eV, therefore limiting our conclusion to attribute the broadening of the As lineshape to a Cr–As phase formation. As the Cr coverage increases (above 12 Å), the As core-lines move towards higher binding energy until the contribution from the Cr 3p core becomes clearly visible, growing in relative importance until it obscures the As 3d core lineshape (figure 2). For 80 Å nominal Cr thickness, the As 3p core level is still about 10% lower than its starting value, while the Ga signal is no longer detectable. This attenuated behaviour from substrate emission indicates that the Cr/GaAs interface is buried deeper, i.e., into a depth greater than the photoemission probing depth (of about 60 Å $= 3\lambda$, where λ is the mean free path of 3d and 3p photoelectrons). Further, the shift of the As signal towards higher binding energy is likely due to the presence of As atoms at the surface, even for high coverage (As surface-segregated). Above a thickness of 12 Å, the overlapping of As 3d and Cr 3p spectra and the attenuation of total emission signal from the Ga-substrate core-line are consistent with the formation of a continuous and uniform Cr overlayer. Concomitantly a body-centred cubic-like structure is observed by RHEED after the early stage regime of the Cr growth.

The spectra in the topmost right-hand panels of figures 2 and 3 show the post-grown arsenized 80 Å-thick Cr film. These results reveal that the binding energy position of the As core level does not shift, whereas the intensity ratio between the As and Cr signal changes, indicating an As-enrichment of the film surface. In the case of CrAs/GaAs (left-hand panel of figures 2 and 3) a gradual transition of the As core-level from GaAs to CrAs is found, i.e.,

without evidence of As chemical reaction during interface formation, in accordance with a well-defined interface observed by HRTEM (see figure 1 in [4]),

Our Cr/GaAs samples have interfaces with a distinct chemical nature as compared to those previously reported by Weaver *et al* [7–11]. It is worth noting that the Cr thin films studied by Weaver and co-workers were grown at room temperature on Ga-rich GaAs(001)-c(8×2) surfaces cleaned by Ar$^+$ bombardment. The interface Cr/GaAs of these films exhibits a significant modification under subsequent thermal annealing between 200 and 320 °C [8, 9]. In contrast, in our case Cr thin films were grown on As-rich 2×4 surfaces reconstructed from GaAs(001) [4, 13] at a moderate substrate temperature of 200 °C, without evidence of Cr in-diffusion upon annealing at temperatures of about 220 °C [9]. We think that the main reason for the different interfacial chemistry observed by us comes from the different chemical environment found by incoming Cr atoms reaching the surface. When a Ga-rich environment is available for Cr atoms, segregation of Ga atoms towards the Cr thin film can occur concomitantly with diffusion of Cr atoms into the GaAs substrate. In such a mixed interfacial layer the formation of Cr–Ga, Cr–As or even Cr–Ga–As compounds can easily occur under subsequent thermal activation. In our study, an As-rich environment for incoming Cr atoms is favoured. The moderate substrate temperature of 200 °C promotes an initial chemistry between Cr and As atoms impinging the interface, reducing the Cr–Ga interactions and favouring an interfacial CrAs layer formation.

Based on our results, we suggest that the Cr–As phase formation is not attained by arsenization despite the thermally assisted (at 320 °C) procedure. The evidences are that CrAs compound formation is obtained by direct reaction of Cr atoms impinging on the As-terminated GaAs(001) surface and/or by kinetic Cr-trapping of some As atoms released from the GaAs substrate due to a Cr–Ga chemical reaction observed at the early stage of Cr deposition. The growth of CrAs compound using co-deposition, where Cr atoms and As molecules (As$_4$, As$_2$) impinge on the GaAs substrate, is successful because Cr–Ga interaction is probably suppressed by As overpressure at the substrate surface.

3.2. Magnetic measurements

Magnetization as a function of applied magnetic field, for the three samples, is shown in figure 4 for temperatures of 10 and 300 K. A clear saturation magnetization and characteristic ferromagnetic hysteresis loops are observed even at 300 K, for all samples. The results of figure 4 show evidence of ferromagnetic response with moderate coercive field and low remanent magnetization (see insets along the panel).

According to our previous work [4], the saturation magnetization obtained for the 30 Å CrAs films are approximately 1000 emu cm^{-3}, corresponding to $\sim$3 μ_B/Cr for an orthorhombic CrAs, assuming that only chromium atoms contribute to the magnetic moment. Indeed, our results are similar to those of Akinaga *et al* [12], as far as the saturation magnetization of $\sim$3 μ_B/Cr for CrAs and concerning to coercive field around 200 Oe and remanent magnetization of about 20% of the saturation magnetization for our three samples.

It is worth noting that none of the bulk equilibrium phases of CrAs present ferromagnetic order, and chromium thin films are well known itinerant antiferromagnets. Only metastable interfacial compounds or phases and small Cr clusters can be responsible for the observed ferromagnetic response.

In order to better understand the ferromagnetic behaviour, all samples were measured under field cooling (FC) and zero-field cooling (ZFC) conditions. As shown in figure 5, all three samples present a magnetic irreversibility below 280 K even for cooling fields above 0.1 T, applied parallel to the film plane.
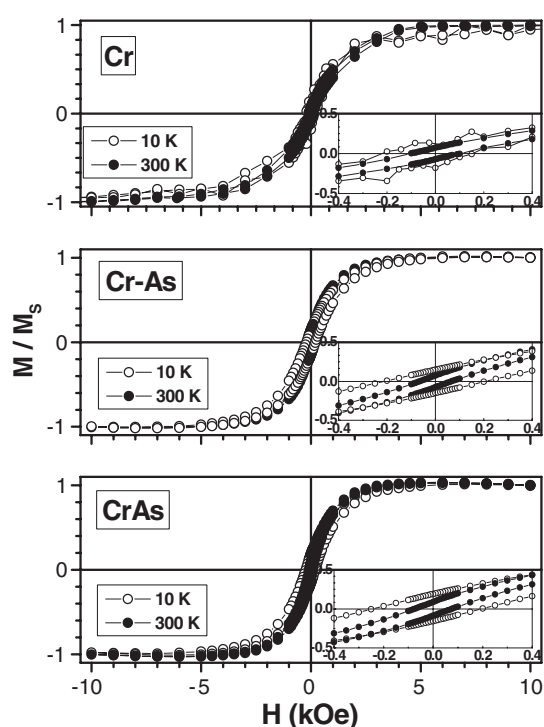
Figure 4. In-plane magnetization normalized to saturation magnetization as a function of the applied field measured for Cr, Cr–As and CrAs thin film samples. The inner parts of the hysteresis loops are shown in the insets along the panel.

The normalized magnetization M/M_s is quite similar for CrAs and for Cr–As films. For Cr film on GaAs, the temperature dependence of the magnetic moment seems to be due to a ferromagnetic-like contribution. This behaviour suggests a magnetic response of the interface layer, resulting from the interaction of the Cr atoms with an As-rich environment stabilized at the GaAs(001) surface. Additionally to the magnetic irreversibility, a clear peak around 40 K is observed for the FC and ZFC magnetization curves, indicating the presence of frustration processes of the magnetic moments at low temperatures and the presence of interacting antiferromagnetic clusters. Metallic Cr segregation and antiferromagnetic Cr-based compound formation could certainly be invoked to explain such a magnetic signal with appreciable magnetic irreversibility. The stronger magnetic irreversibility, indicated by a more pronounced bifurcation between the FC and ZFC curves for Cr–As thin films, supports the assumption of compositional fluctuations.

The strongest magnetic irreversibility for Cr–As films corroborates the photoemission findings, indicating that the arsenization of Cr film leads to an As-enrichment of only a few Cr atomic plans close to the film surface, rather than a bulk Cr–As compound. We believe that compositional fluctuations could occur between CrAs precipitation during formation of the Cr/GaAs buried interface and arsenized Cr-topmost atomic planes formed by the arsenization procedure. However, we would like to point out that only an intrinsic and very thin interfacial layer buried at the interface between Cr and GaAs could explain a similar behaviour for three samples with a rather distinct composition. It seems that a predominant contribution to the magnetism of these thin films comes from a very thin interfacial layer, which could
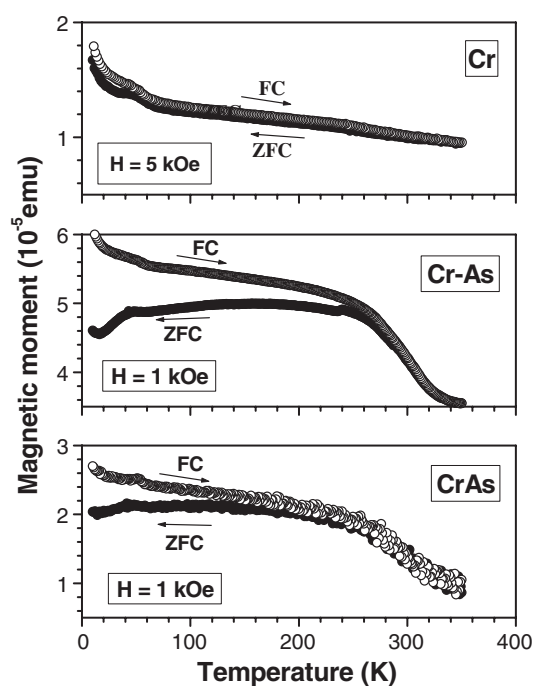
Figure 5. Field cooling (FC) and zero-field cooling (ZFC) magnetic moment curves measured for Cr, Cr–As and CrAs thin films.

intrinsically be formed when Cr atoms interact with the As-rich GaAs surface, forming a new CrAs ferromagnetic phase [4].

The local order and the chemistry of the interface Cr/GaAs deserves a more detailed investigation and modelling considering also the crystalline structure [14].

A more comprehensive interpretation concerning the crystalline structure and the detailed magnetic properties of the interfacial layer between Cr and the GaAs substrate remains open. More sensitive studies of the buried interface would be interesting to complement these investigations to clarify the local order and chemistry at the effective interface Cr/GaAs.

4. Conclusions

Three thin films with distinct elemental profiles consisting of Cr, arsenized Cr (Cr–As) and CrAs have shown similar ferromagnetic magnetic behaviour, as well as magnetic irreversibility features. The origin of the ferromagnetic response of all samples is suggested to be the strained interfacial layer resulting from the interaction of Cr atoms with an As-rich environment stabilized at the GaAs(001) surface. *In situ* photoemission experiments show no evidence of Cr–Ga reaction.

Acknowledgments

References

[1]   Prinz G 1998 *Science* **282** 1660
[2]   Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488
[3]   Shirai M 2001 *Physica* E **10** 143
[4]   Etgens V H, de Camargo P C, Eddrief M, Mattana R, George J M and Garreau Y 2004 *Phys. Rev. Lett.* **92** 167205
[5]   Shirai M 2003 *J. Appl. Phys.* **93** 6844
       Mizuguchi M, Akinaga H, Manago T, Ono K, Oshima M and Shirai M 2002 *J. Magn. Magn. Mater.* **239** 269
       Kubler J 2003 *Phys. Rev.* B **67** 220403
[6]   Waldrop J R and Grant R W 1979 *Appl. Phys. Lett.* **34** 630
[7]   Weaver J H, Grioni M and Joyce J 1985 *Phys. Rev.* B **31** 5348
[8]   Xu F, Lin Z D, Hill D M and Weaver J H 1987 *Phys. Rev.* B **35** 9353
[9]   Xu F, Lin Z D, Hill D M and Weaver J H 1987 *Phys. Rev.* B **36** 6624
[10] Trafas B M, Hill D M, Benning P J, Waddill G D, Yang Y N, Siefert R L and Weaver J H 1991 *Phys. Rev.* B **43** 7174
[11] Seo J M, Chen Y and Weaver J H 1991 *J. Appl. Phys.* **70** 4336
[12] Akinaga H, Manago T and Shirai M 2000 *Japan. J. Appl. Phys.* **39** L1118
[13] Carbonell L, Etgens V H, Koebel A, Eddrief M and Capelle B 1999 *J. Cryst. Growth* **201** 502
[14] Qian D, Loison G L D, Dong G S and Jin X F 2000 *J. Cryst. Growth* **218** 197