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Electronic states in arsenic-decapped MnAs $(1\bar{1}00)$ films grown on GaAs(001): A photoemission spectroscopy study

M. Moreno,[1,a)] A. Kumar,[2,b)] M. Tallarida,[2,c)] K. Horn,[2] A. Ney,[3,d)] and K. H. Ploog[3]
[1]*Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, 28049 Madrid, Spain*
[2]*Fritz-Haber-Institut der Max-Planck-Gesellshaft, Faradayweg 4-6, 14195 Berlin, Germany*
[3]*Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany*

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We examine the arsenic bonding in the near-surface region of initially arsenic-capped MnAs$(1\bar{1}00)$ films grown on GaAs(001), as it evolves upon arsenic decapping. Line-shape analyses of high-resolution As 3*d* photoelectron emission spectra recorded at room temperature (RT) allow us to identify electronically distinct As-bonding states associated to bulk MnAs phases, bulk arsenic, and interfacial environments. Stable MnAs phases appear to be affected by the presence of a thin arsenic coating, an effect that could be advantageously used to enhance the ferromagnetic properties of MnAs films around RT. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2888953]

As one of the few ferromagnetic metals compatible with III-V semiconductors, MnAs is a candidate to be part of semiconductor-based spintronic and magnetologic devices.[1–3] Despite the large lattice mismatch, high-quality epitaxial MnAs films can be grown on several GaAs substrates.[1,4] MnAs experiences a magnetostructural phase transition close to room temperature (RT). In bulk MnAs, the nonmagnetic orthorhombic β-MnAs phase abruptly transforms at ~40 °C into the ferromagnetic hexagonal α-MnAs phase. However, in MnAs films grown on GaAs(001) or GaAs(111)B substrates, the α and β phases coexist within a relatively wide temperature range (~10–50 °C), in an attempt to minimize the epitaxial strain of the films.[4,5] Thorough structural and magnetic studies[1,4] have shown that the phase coexistence mechanism has a major impact on the properties of MnAs films, limiting their performance as a ferromagnetic material. There is, however, little experimental information available on the electronic properties of MnAs films[6–8] and surface-science studies of this relevant material[9,10] remain to be completed. Here, we report on a photoemission spectroscopic study of arsenic-decapped MnAs$(1\bar{1}00)$ films grown on GaAs(001), providing insight into the electronic configurations in such processed films.

A 120-nm-thick MnAs film was grown on a heavily *n*-type doped GaAs (001)±0.5° epiready substrate by molecular-beam epitaxy. Prior to MnAs growth, a GaAs buffer layer was grown at high temperature (550–600 °C) following standard procedures. MnAs growth was initiated on a carefully prepared As-rich $d(4\times4)$ or $c(4\times4)$ GaAs template and proceeded at a substrate temperature of 230 °C, with a growth rate of 19 nm/h, and an As_4-to-Mn beam-equivalent-pressure ratio of 49. Under these growth conditions, MnAs films are known to have the so-called *A* epitaxial orientation,[4] with MnAs$(1\bar{1}00)$ parallel to GaAs(001). After MnAs growth, the sample was annealed at 286 °C for 12 min. Then, the sample was cooled down and was exposed to As_4 flux in order to deposit a protective arsenic coating. Before the photoemission analysis, the sample was stored under vacuum and only shortly exposed to air during the time necessary to cut it into pieces and to transfer it from the growth to the analysis chamber. Photoemission analyses were carried out in an experimental station connected to the UE56/2-PGM-2 beamline of the BESSY II synchrotron-radiation facility. The arsenic-coated sample was mounted on a variable-temperature holder, using Ga–In eutectic alloy as glue on the back side of the sample. The arsenic coating of the sample was desorbed in three progressive steps by heating with increasing power (pure arsenic and its oxides sublime at roughly 300 °C). Photoemission spectra were recorded at RT after each decapping step. Photoemitted electrons were collected in the direction normal to the sample surface in an angle-integrated mode using an ESCALAB MkII electron energy analyzer. The binding energy (BE) scale of the spectra shown below refers to the Fermi energy. Line-shape analyses were performed with the aid of the CASAXPS software.

Figure 1 shows overview photoemission spectra. Before heating (curves denoted 0), the most prominent features are arsenic core-level signals as well as associated plasmon losses. No Mn-related features are seen, indicating that the MnAs layer is well covered by the arsenic coating. O 1*s* and C 1*s* core-level signals show up, indicating the presence of oxides and hydrocarbons (the most likely compounds) on top of the sample. After the first decapping step, Mn-related features show up [see Fig. 1(b)]. Most of the initial arsenic coating has been desorbed, although a thin layer of pure arsenic appears to remain on top of the MnAs layer. The decapping steps 2 and 3 progressively remove the residual top arsenic. Spectrum 3 [Fig. 1(a)], recorded on the nominally "fully decapped" bare MnAs film, exhibits prominent Mn 3*p* and Mn Auger signals; the sample appears clean. We have used physically meaningful Tougaard-type backgrounds [see Fig. 1(a)].[11] We found that the values of the three parameters ($B=4210$ eV^2, $C=1000$ eV^2, and $D=13\,300$ eV^2) describing the corresponding inelastic-scattering cross section and providing better-fitting backgrounds were exactly coincident with the cross-sectional parameters previously

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[a)] Electronic mail: mmoreno@icmm.csic.es.

[b)] Present address: Department of Physics, Institute of Science and Laboratory Education, IPS Academy, Indore 452012, India.

[c)] Present address: BTU Cottbus, Angewandte Physik und Sensorik, Konrad-Wachsmann-Allee 17, 03046 Cottbus, Germany.

[d)] Present address: Experimentalphysik, Universität Duisburg-Essen, Lotharstrasse 1, D-47057 Duisburg, Germany.

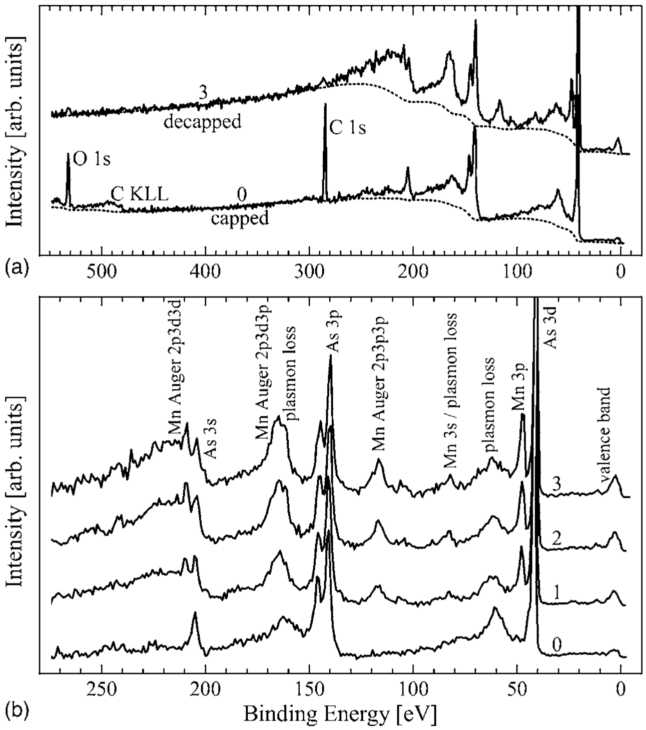

FIG. 1. Photoemission spectra recorded with 750 eV photons on an initially arsenic-capped MnAs thick film grown on GaAs(001), at progressive decapping stages: (a) as-measured spectra (continuous lines) and corresponding Tougaard backgrounds (dotted lines), (b) background-subtracted spectra for the arsenic-coated (unheated) sample (curve 0) and for the decapping stages 1–3. Spectra have been normalized to the area of the As $3p$ peak after background subtraction.

reported[11] to be appropriate for transition metals.

Dramatic changes in the As $3d$ photoemission spectral shape are observed upon desorbing the residual top arsenic [see Fig. 2(a)]. To understand the changes, we calculated theoretical As $3d$ envelope curves by adding up spin-orbit split doublets [characterized by $3d_{5/2}$ BE, asymmetry (γ), and full width at half-maximum (FWHM) values], corresponding to specific As-bonding configurations.[12] For all of the doublets considered, the spin-orbit splitting was fixed to 0.68 eV and the branching ratio (area ratio) was fixed to the theoretical 2:3 value. The As $3d$ spectrum recorded after the first decapping step (curve 1) is fitted by three components: A (BE$=$41.31 eV, $\gamma=0.10$, FWHM$=$0.40 eV), α (BE $=$40.65 eV, $\gamma=0.13$, FWHM$=$0.34 eV), and I (BE $=$40.93 eV, $\gamma=0.13$, FWHM$=$0.35 eV). On the other hand, the spectrum recorded after the third decapping step (curve 3) is fitted by two narrow-width components, α (BE $=$40.63 eV, $\gamma=0.18$, FWHM$=$0.54 eV) and β (BE $=$40.14 eV, FWHM$=$0.39 eV), and an additional broad component, D (BE$=$40.67 eV, FWHM$=$1.15 eV). There is no contribution of type-A component for stage 3. The A component is obviously associated to the arsenic coating (arsenic in a bulk As environment), which desorbs upon heating. We assign the α component to arsenic in a bulk MnAs environment and the I component (spectrum 1) to arsenic at the As/MnAs interface. The D component (spectrum 3) accounts for electronically disordered environments, present in bare MnAs. We next discuss the origin of the β component in the context of previous reports and considering additional data for bare MnAs (stage 3).

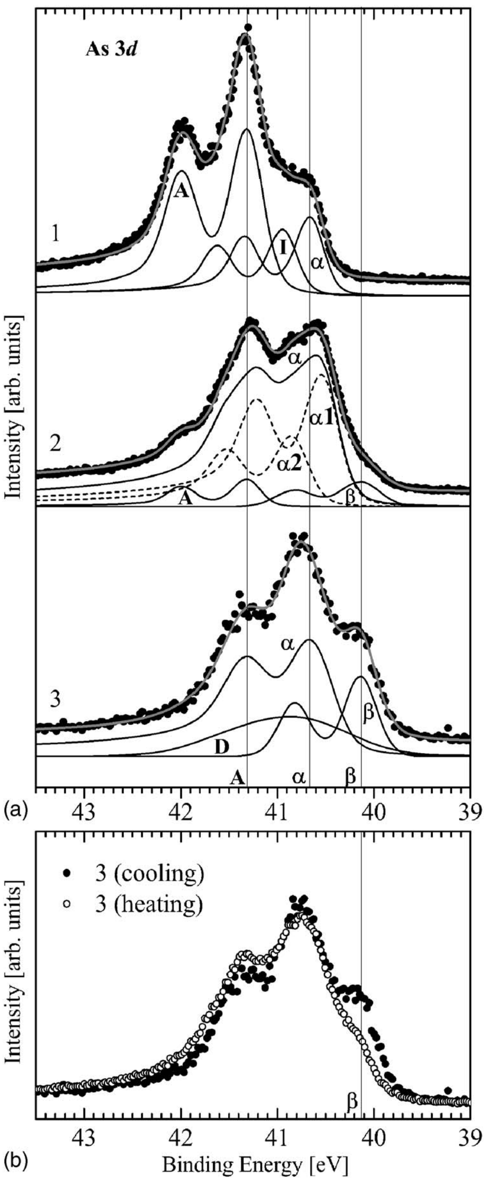

FIG. 2. (a) High-resolution As $3d$ photoemission spectra recorded with 154 eV photons for the decapping stages 1–3 (solid symbols), after background subtraction and normalization to the peak area, and corresponding line-shape analyses. For stage 2, the α component has been constructed by adding up the $\alpha1$ and $\alpha2$ subcomponents. Theoretical envelope curves are shown superimposed to the experimental data. (b) As $3d$ spectra for stage 3 (bare MnAs), recorded at RT following two different pathways: (i) cooling down from high ($T > 60$ °C) temperature (solid symbols) and (ii) heating up from low ($T < 0$ °C) temperature (open symbols).

Okabayashi *et al.* and Ouerghi *et al.* previously reported photoemission results for bare MnAs films grown on GaAs.[9,10] The As $3d$ spectrum reported[9] by Okabayashi *et al.* for a thick MnAs film grown on GaAs(001) much resembles the As $3d$ spectrum reported[10] by Ouerghi *et al.* for a (3×1)-reconstructed MnAs film grown on GaAs(111)B and it is similar to the As $3d$ spectrum reported here for arsenic-decapped bare MnAs grown on GaAs(001) [curve 3 in Fig. 2(a)]. The common feature of these spectra is the pronounced shoulder/peak on the low BE side, which indicates that the line shape is contributed by at least two intense doublets. Both Okabayashi's and Ouerghi's groups interpreted the As $3d$ line shape in terms of a single bulk component and additional surface components. However, despite the line-shape similarity, they invoked different assignments for the As $3d$

TABLE I. Relative intensity of the different components (α, β, D) contributing to the As 3*d* photoemission spectra from the bare MnAs film (decapping stage 3) recorded at RT following two different pathways: (i) cooling down from high ($T > 60$ °C) temperature [solid symbols in Fig. 2(b)] and (ii) heating up from low ($T < 0$ °C) temperature [open symbols in Fig. 2(b)].

	α	β	D
Cooling	57%	20%	23%
Heating	68%	9%	23%

components: whereas Ouerghi *et al.* interpreted the low BE component as a "bulk" component, Okabayashi *et al.* interpreted it as a "surface" component. The observed similarity of the As 3*d* spectral features for bare MnAs films with different epitaxial orientations [grown on GaAs(001) and GaAs(111)B substrates] and subjected to different surface treatments (as-grown versus arsenic-decapped films) points toward a bulk (rather than surface) origin of the spectral features. These appear better interpreted as all bulk components. We assign the low BE β component, centered at 40.14 eV, to the β-MnAs phase and the α component, centered at ~40.64 eV, to the α-MnAs phase. That is, we correlate the peculiar As 3*d* line shape here observed for bare MnAs films at RT [curve 3 in Fig. 2(a)] with the α-β phase coexistence. This correlation might also be valid for other MnAs films on which similar RT line-shape features have been reported.

The As 3*d* spectra shown in Fig. 2(b) provide further support to the interpretation in terms of separated α-MnAs and β-MnAs contributions. These spectra have been recorded at RT on the bare MnAs film (stage 3) following two different temperature pathways. The photoemission signal in the low BE side of the spectra is seen to be weaker for the spectrum recorded following a low-temperature pathway (heating up to RT) than for the spectrum recorded following a high-temperature pathway (cooling down to RT). The relative intensities/amounts of the α and β components/phases, as well as of disorder (D component), derived from the As 3*d* line-shape analysis for the two pathways, are listed in Table I. The thermal hysteresis observed in the As 3*d* line shape finds natural explanation within an interpretation in terms of α-MnAs and β-MnAs related components: it agrees with the well-known hysteresis in the α-β phase coexistence,[4] according to which the β/α phase ratio is higher when RT is approached from high temperature than when it is approached from low temperature.

The α-MnAs phase appears thus stable in arsenic-covered MnAs, constrained by bottom GaAs and top As [spectrum 1 in Fig. 2(a)]. On the other hand, the α-MnAs and β-MnAs phases coexist in bare MnAs, with no top constrain [spectrum 3 in Fig. 2(a)]. The As 3*d* spectrum recorded after the second decapping step [spectrum 2 in Fig. 2(a)] requires at least four components to reach a good fit: *A* (γ=0.12, FWHM=0.34 eV), β (FWHM=0.47 eV), $\alpha 1$ (BE =40.52 eV, γ=0.18, FWHM=0.41 eV), and $\alpha 2$ (BE =40.83 eV, γ=0.18, FWHM=0.41 eV). At stage 2, the sample seems to be covered by arsenic in some regions (there is a small A contribution) and to expose bare MnAs in other regions (there is a small β contribution). Such a situation implies laterally inhomogeneous mechanical constrains on the MnAs film. We constructed the α component drawn for spectrum 2 in Fig. 2(a) by adding up the $\alpha 1$ and $\alpha 2$ doublets. This α component (BE=40.63 eV) is centered at roughly the same BE as for spectra 1 and 3. The spreading in BE of the α component for stage 2 may be related to structural distortions in the α-MnAs phase of the film, assumed to be caused by the lateral constrain inhomogeneity.

In summary, we have performed RT photoemission spectroscopic analyses of the arsenic bonding in the near-surface region of initially arsenic-capped MnAs($1\bar{1}00$) films grown on GaAs(001), as it evolves upon decapping. Arsenic capping has been demonstrated to be an efficient method to protect MnAs films from contamination during short air exposure. In As 3*d* spectra recorded on bare MnAs($1\bar{1}00$) films, we have identified two electronically distinct components, α and β, that we assign to arsenic in α-MnAs and β-MnAs environments, respectively. The β component has been found to be absent for MnAs films covered by a thin As layer. We conclude that different strain-minimization mechanisms are operative in bare and arsenic-coated MnAs films. We propose to use arsenic coating to stabilize the α-MnAs phase against transformation into β-MnAs and, thus, to enhance the ferromagnetic properties of MnAs films around RT.

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[12] To simulate asymmetric photoemission peaks, related to metallic electronic configurations, we used DS(γ,499) line shapes (CASAXPS notation), which stand for Doniach–Sunjic profiles with asymmetry parameter γ, numerically convoluted with a Gaussian described by 499 digital nodes. To simulate symmetric photoemission peaks, we used GL(30) line shapes, which stand for Gaussian/Lorentzian product formulas with 30% of Lorentzian weight, which approximate Voigt-type profiles.