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

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We examine the arsenic bonding in the near-surface region of initially arsenic-capped MnAs(1$\underline{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 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 room temperature.

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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 non-magnetic orthorhombic β-MnAs phase abruptly transforms at ~40°C into the ferromagnetic hexagonal α-MnAs phase. However, in MnAs films grown on GaAs(001) and 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($1\underline{1}00$) 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 (MBE). 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 (BEP) 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 room temperature 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 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=13300 eV^2) describing the corresponding inelastic-scattering cross section and providing better-fitting backgrounds were exactly coincident with the cross-section parameters previously reported[11] to be appropriate for transition metals.

Dramatic changes in the As 3*d* photoemission spectral shape are observed upon desorbing the residual top arsenic [see Fig. 2(a)]. To understand the changes, we calculated theoretical As 3*d* envelope curves by adding up spin-orbit split doublets [characterized by $3d_{5/2}$ binding energy (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 3*d* spectrum recorded after the first decapping step (curve "1") is fitted by three components: A (BE=41.31 eV, γ=0.10, FWHM=0.40 eV), α (BE=40.65 eV, γ=0.13, FWHM=0.34 eV), and I (BE=40.93 eV, γ=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, γ=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").

Okabayashi et al. and Ouerghi et al. previously reported photoemission results for bare MnAs films grown on GaAs.[9,10] The As 3*d* spectrum reported[9] by Okabayashi et al. for a thick MnAs film grown on GaAs(001) much resembles the As 3*d* spectrum reported[10] by Ouerghi et al. for a (3x1)-reconstructed MnAs film grown on GaAs(111)B, and it is similar to the As 3*d* 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 binding energy 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 3*d* 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 3*d* components: whereas Ouerghi et al. interpreted the low binding energy 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 towards a bulk (rather than surface) origin of the spectral features. These appear better interpreted as all bulk components. We assign the low

binding energy 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 binding energy 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 room temperature 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 [curve “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), α1 (BE=40.52 eV, γ=0.18, FWHM=0.41 eV), and α2 (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 α1 and α2 doublets. This α component (BE=40.63 eV) is centered at roughly the same binding energy as for spectra “1” and “3”. The spreading in binding energy of the α component for stage “2” may reflect structural distortions in the α-MnAs phase of the film, assumed to be caused by the lateral constrain inhomogeneity.

In summary, we have performed room-temperature photoemission spectroscopic analyses of the arsenic bonding in the near-surface region of initially arsenic-capped MnAs($1\underline{1}00$) 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($1\underline{1}00$) 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 room temperature.

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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.

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 room temperature following two different pathways: (i) cooling down from high (T>60ºC) temperature [solid symbols in Fig. 2(b)] and (ii) heating up from low (T<0ºC) temperature [open symbols in Fig. 2(b)].

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

Figure captions

Figure 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" to "3". Spectra have been normalized to the area of the As 3*p* peak after background subtraction.

Figure 2. (a) High-resolution As 3*d* photoemission spectra recorded with 154 eV photons for the decapping stages "1" to "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 $\alpha 1$ and $\alpha 2$ subcomponents. Theoretical envelope curves are shown superimposed to the experimental data. (b) As 3*d* spectra for stage "3" (bare MnAs), recorded at room temperature following two different pathways: (i) cooling down from high (T>60ºC) temperature (solid symbols) and (ii) heating up from low (T<0ºC) temperature (open symbols).

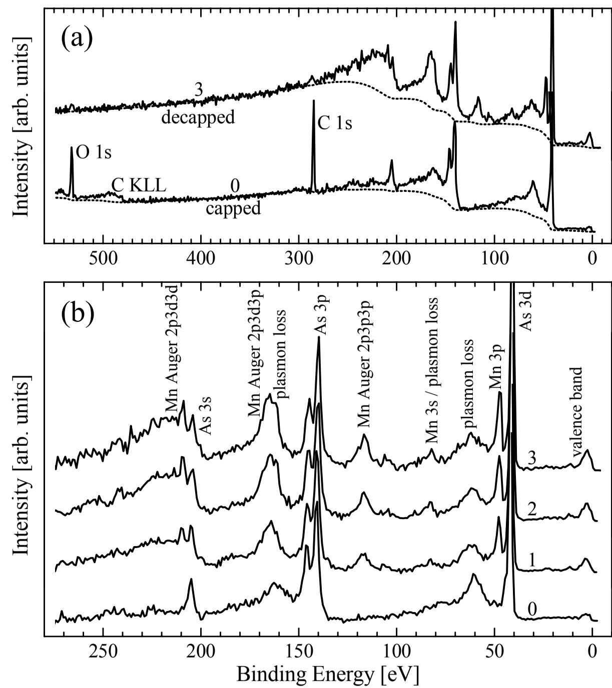

Fig. 1 - Appl. Phys. Lett.
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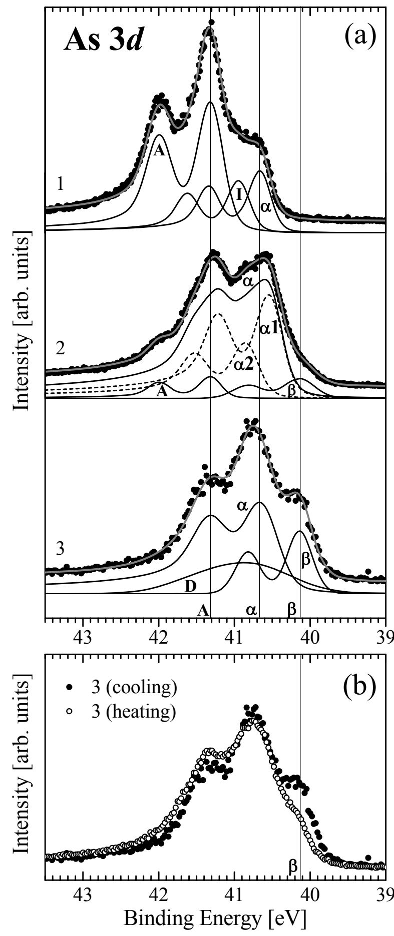

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