

## Interface bonding for Fe thin films on GaAs surfaces of differing morphology

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Formation of a common type of Fe-As local bonding in Fe thin films on GaAs surfaces of differing orientation and preparation is evidenced through a common charge transfer at the interface. X-ray absorption studies of unoccupied  $3d$  states for Fe thin films on sputtered GaAs(100) and cleaved GaAs(110) display a similar amount of  $3d$  charge transfer into the GaAs substrate even though the mode of surface preparation leads to reduced intermixing in the (100) case. Implications of these results for the understanding of the role of the Fe-GaAs interface in both electronic and magnetic properties are discussed.

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Intermixing at metal-semiconductor interfaces is of vital importance in semiconductor device physics. Formation of Schottky barriers,<sup>1</sup> as well as metallic interconnects on semiconductor-based electronics, are strongly influenced by the structure and disorder of the interface.<sup>2</sup> With the recent explosion of magnetic-based electronics,<sup>3</sup> there is a growing need to efficiently integrate magnetic and semiconductor-based electronic structures. In this way one can utilize the spin degree of freedom as an additional handle for the modification of electron transport to produce spin-based electronics.<sup>4–6</sup> However, the integration process has several barriers that must be overcome. First is the reduction of interfacial intermixing commonly found at metal-semiconductor interfaces, which degrades the spin transport performance. Second, to tailor magnetic device properties for specific tasks requires an understanding of the detailed chemistry and physics at the interface.

Iron on GaAs was one of the first ferromagnetic-semiconductor systems studied due to the lattice match for epitaxial growth.<sup>7,8</sup> The GaAs lattice parameter (5.65 Å) is nearly twice that of Fe (2.86 Å) and allows for growth of the bcc phase with only 1.3% mismatch. Early studies showed that high-quality bcc Fe films could be produced that were magnetically inactive for thin layers and showed magnetic anisotropies very different from those expected for bcc Fe. Studies of the occupied electronic states near the Fermi level provided clear evidence for outdiffusion of As and Ga into the Fe overlayer.<sup>9,10</sup> More recent studies have focused on the GaAs surface structure to determine if the unique magnetic properties of the overlayer are related to the wide variety of possible surface reconstructions. However, Fe grown on As-terminated ( $2 \times 4$ ) and  $c$ -( $4 \times 4$ ),<sup>11</sup> Ga-terminated ( $4 \times 6$ ),<sup>12,13</sup> and ( $2 \times 1$ ) S-passivated<sup>14</sup> GaAs(100) all display similar magnetic properties. For thicknesses less than  $\sim 4$ – $6$  monolayers (ML), all systems are found to be magnetically inactive, while thicker films ferromagnetically order and display a strong uniaxial magnetic anisotropy along the (110) direction, in contrast to bulk Fe. While the surface preparation might play a role in the initial growth or reduce interdiffusion, such results suggest that influence on the magnetic properties are due to a common type of interfacial bonding.

In this Brief Report we present evidence for the formation of Fe-As local bonding at the interface between Fe thin films and GaAs surfaces of differing orientation and preparation. Changes in the unoccupied electronic states of Fe thin films on sputtered GaAs(100) and cleaved GaAs(110) display a similar amount of  $3d$  charge transfer into the GaAs substrate even though the mode of surface preparation leads to reduced intermixing in the (100) case.

Experiments were performed at the high-resolution spectroscopy beamline (2-ID-C) at the Advanced Photon Source, which operates in the intermediate x-ray range of 500–3000 eV.<sup>15</sup> At all absorption edges studied, beamline resolution was sufficient that the measured absorption was limited only by the natural linewidth. X-ray photoelectron spectroscopy (XPS) was performed using a hemispherical energy analyzer with 100 meV resolution. Absorption measurements were acquired in total electron yield (TEY) and fluorescence yield (TFY) modes by monitoring the sample current and using a photodiode, respectively. Iron was deposited at room temperature (300 K) at a growth rate of  $\sim 1$  Å/min from a high-purity Fe wire heated resistively. For the (100) orientation, polished GaAs wafers were cleaned with 1 keV Ar<sup>+</sup> ion sputtering until the core level spectra showed no traces of oxygen and carbon. The (110) surfaces were achieved by *in situ* cleaving of notched GaAs blocks. In both cases the GaAs substrates were  $n^+$  doped to promote the necessary conductivity required for spectroscopy measurements. Core level spectra were used to confirm that the surface was free of contamination after each deposition cycle. Fe overlayer thickness was determined from both a quartz crystal oscillator and from a combination of the absorption edge jumps and XPS intensities.

First one needs to understand the GaAs substrate surface before Fe deposition. By probing the As and Ga  $L_3$  edges, the influence of the substrate surface structure on the unoccupied electronic states may be determined (shown in Figs. 1 and 2). To the best of the authors' knowledge, these are the first reported high-resolution  $L$  edge spectra for Ga and As. Since this edge probes the unoccupied  $4sp$  states, it is very sensitive to the nearest neighbor geometry and chemistry. Fluorescence and total electron yield have probing depths of

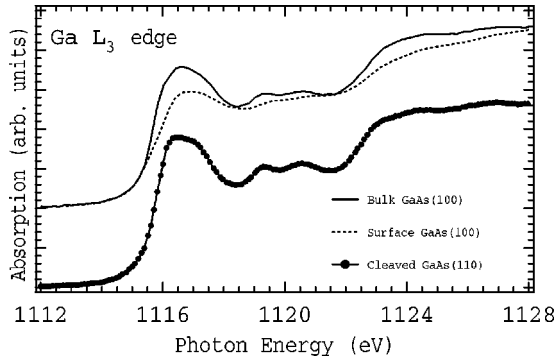


FIG. 1. Ga  $L_3$  edge absorption spectra detailing the changes in substrate electronic structure due to surface preparation and orientation.

1000 Å and 50 Å, respectively, enabling comparisons of the bulk and surface regions of the (100) substrate to understand modification due to sputter damage. For the cleaved (110) orientation the bulk and surface results are identical so only the TEY results are displayed. The general line shape appears to be consistent with features in the band structure leading to high densities of unoccupied states.<sup>16</sup> Our band structure calculation for bulk GaAs shows that the density of states (DOS) within the first 10 eV above the band gap exhibits mainly  $s$  and  $p$  character.<sup>17</sup>

Sputtering the (100) surface causes great changes to the Ga  $L_3$  edge intensity in the surface region, while the As  $L_3$  intensity remains relatively unchanged (solid vs dashed lines in Figs. 1 and 2). Significant modification of the surface spectrum indicates that the damage is present tens of angstroms deep into the substrate and is sufficient to dramatically modify the Ga unoccupied states in the near-surface region. Scanning tunneling microscopy studies have observed a depletion of As in the near-surface region due to sputter damage.<sup>18,19</sup> Since As is more electronegative, Ga must gain charge upon removal of As if the surface region is to maintain charge neutrality. Return of charge to Ga will cause unoccupied orbitals of Ga to be filled, resulting in a drop in the white line intensity. The As absorption remains unaltered, aside from total intensity, since it still involves As in a fully coordinated environment.

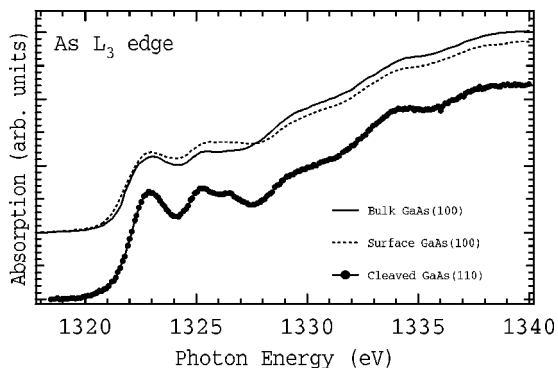


FIG. 2. As  $L_3$  edge absorption spectra detailing the changes in substrate electronic structure due to surface preparation and orientation.

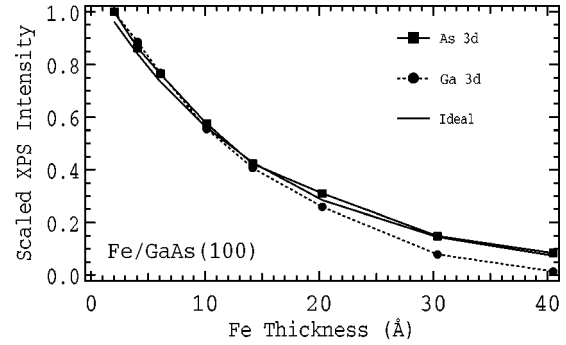


FIG. 3. Ga and As  $3d$  XPS intensities as a function of overlayer coverage for the (100) case. Note close agreement with the ideal case discussed in the text.

Intermixing with the Fe overlayer for the cleaved vs sputtered surface preparations was investigated by taking core level XPS measurements of the occupied Fe  $3p$  and Ga and As  $3d$  electronic states. At a given incident photon energy, the probing depth of electrons,  $\lambda_e$ , from these core levels can be determined<sup>20</sup> and core level intensities can be traced as a function of overlayer coverage (see Figs. 3 and 4). If there is no elemental intermixing, the line intensities of the Ga and As  $3d$  levels will drop off as  $e^{-d_{\text{Fe}}/\lambda_e}$  with increasing thickness of the Fe overlayer,  $d_{\text{Fe}}$ . Comparison of the results to the ideal case for no intermixing, which are not presented here due to space limitations, clearly shows that, for the sputtered (100) system, there is almost no intermixing, while there is significant intermixing for the cleaved (110) system. The main difference between the two substrates is the amount of As on the surface. For cleaved (110) the surface is As terminated,<sup>9</sup> whereas the sputtering leaves the (100) surface Ga terminated.<sup>13</sup>

The difference in the amount of intermixing between the sputtered and cleaved surfaces is consistent with previous results. Calculated bulk heats of formation for Fe-As and Fe-Ga seem to imply that the Fe-As reaction drives the intermixing.<sup>9,10</sup> The heats of formation for the structurally compatible phases are  $\Delta H_{\text{Fe}_2\text{As}} = -38$  kJ/mol and  $\Delta H_{\text{Fe}_2\text{Ga}} = -16$  kJ/mol. Energy minimization would favor direct bonding of Fe and As at the interface over an Fe-Ga bond. When As is depleted from the near-surface region by sput-

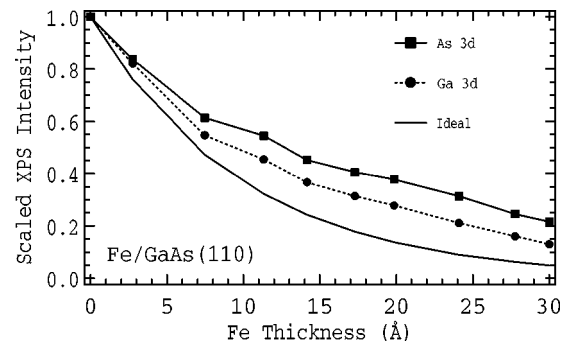


FIG. 4. Ga and As  $3d$  XPS intensities as a function of overlayer coverage for the (110) case. Note the large deviation from the ideal case.

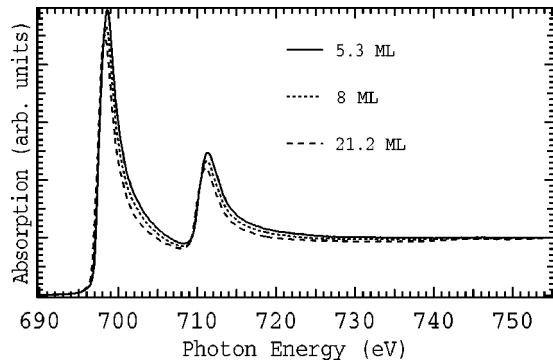


FIG. 5. Fe  $L_{2,3}$  ( $2p \rightarrow 3d$ ) TEY absorption spectra as a function of Fe overlayer coverage. Note the dramatic decrease in the line-width with increasing coverage.

tering, the amount of As able to react with Fe is reduced and intermixing is decreased. Lack of intermixing was previously reported for Ga-terminated surfaces, which is consistent with the above conclusion.<sup>12,13</sup> The amount of intermixing for the cleaved surface has been previously quantified and indicates that the topmost As layer is removed along with 1 ML of Ga.<sup>9,10</sup> Additionally, the lack of intermixing for the sputtered (100) surface is confirmed by the lack of a higher-binding-energy shoulder in the As  $3d$  core level spectra, which has been attributed to interstitial As in the Fe overlayer.<sup>10</sup>

Of most interest in the study of magnetic materials on semiconductors is the change in the Fe overlayer. Since the  $3d$  electrons of Fe carry the magnetic moment, any intermixing or charge transfer at the interface will alter the  $3d$  band occupancy and directly influence the magnetic order. To determine the amount of charge transfer at the interface, Fe  $L_{2,3}$  ( $2p \rightarrow 3d$ ) absorption spectra were measured as a function of overlayer coverage (see Fig. 5). Changes in the white line intensity are directly related to the number of  $3d$  holes,<sup>21</sup> and the spectra shown in Fig. 5, show major changes with increasing coverage. Most important is the dramatic change in the width of the absorption line. Since the corresponding Fe  $2p$  core level spectra, however, are found not to change with coverage, this change must be associated with an increase in the density of  $3d$  unoccupied states, as is consistent with significant transfer of charge from Fe into the GaAs substrate.

After correction of saturation effects,<sup>22</sup> removal of the background from excitation into the continuum, and integration of the white line intensity,<sup>23,24</sup> the transfer of  $3d$  charge from the Fe into the substrate can be constructed as shown in Fig. 6. Most importantly though, as a function of monolayer coverage, the two systems show a similar amount of charge transfer even though preparation occurred on two uniquely different surfaces. While extrapolation of the data to 1 ML coverage cannot be done accurately, it does indicate that the Fe overlayer is in a configuration in the neighborhood of  $3d^5$  for both substrate orientations. The charge transfer is consistent with a local Fe-As bonding configuration at the interface and a resultant balancing of the Fermi levels in the two materials. Due to the large difference in electronegativities, As will tend to draw charge away from Fe. Ga has an electronegativity close to that of Fe, which implies that Ga could not

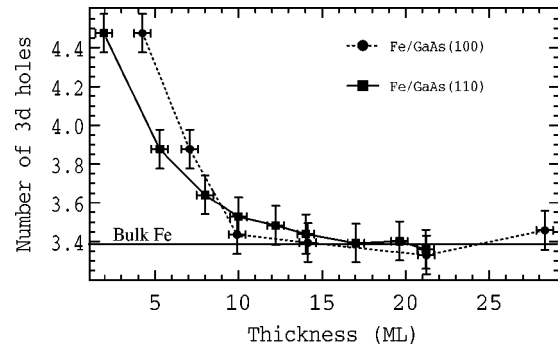


FIG. 6. Extracted  $3d$  charge transfer as a function of overlayer coverage. Observing the same charge transfer in both orientations is a direct indication that the transfer is predominantly due to the interface bonding and not a result of intermixing.

be responsible for such a large transfer. For the (110) system, the Fe-As interface is formed using an intermixing reaction to create the desired interface with the extra surface components migrating into the Fe layer. For (100), even though no diffusion is observed, it is possible that the Ga at the interface is displaced but lacks sufficient energy to move farther than a few monolayers into the overlayer. Another interesting facet of this result is that intermixing and surface roughness do not much affect the  $3d$  charge transfer. Typically intermixing is one of the key factors in modification of material properties.

While these results relate to the interface electronic structure, inferences concerning the magnetic structure can be made. Results for calculated properties of transition metal impurities in Fe indicate that  $3d^5$  occupancy is near the crossover from ferromagnetic to antiferromagnetic order.<sup>25</sup> The charge transfer data aid in explaining why the depletion of charge in low-coverage Fe films could lead to the reported loss of magnetic order.<sup>11-14</sup> Previous studies assigned the loss of order to intermixing,<sup>26</sup> which from the perspective of charge transfer is clearly not the case here. With both sputtered and cleaved samples showing the same amount of charge transfer, intermixing cannot be a major factor for films grown at room temperature. For higher-temperature growth, the intermixing may be much more pronounced and results might be different. Of course there is also evidence for superparamagnetism for thin layers.<sup>13</sup> This together with the charge transfer data might imply a more complicated mixed ferromagnetic-antiferromagnetic phase structure, as has been observed for other magnetic systems.<sup>27</sup>

Lastly, the unique anisotropy in these systems is still an unanswered question. Given the results above, it is quite plausible that the magnetic anisotropy is connected to the strong Fe-As local bonding configuration. This might explain why unique surface preparations lead to similar magnetic anisotropies. Consider Fe on a perfect As-terminated GaAs(100) surface where Fe in the top layer resides in a Ga site, which would correspond to a  $Fe_2As$  environment. This implies a spatial arrangement with fourfold symmetry. The coordination of the bonding however may be quite different. Bonds in bulk GaAs are tetrahedral and should influence the bond directionality at the interface with Fe. With the As

bonded to a (110) oriented line of Ga in the layer below, it should preferentially bond to the Fe above along  $(1\bar{1}0)$  to preserve tetrahedral symmetry. Fourfold symmetry of bonding to Fe is then broken, resulting in a modification of the  $3d$  orbital moment preferential direction and thus the magnetic anisotropy. This model is consistent with the uniaxial anisotropy along  $(1\bar{1}0)$  observed for Fe/GaAs, in contrast to the bulk easy axis of (100).<sup>11-14</sup>

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