

## Interdiffusion and reaction at the Fe/GaAs(110) interface

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(Received 22 November 1985)

We report synchrotron radiation photoemission studies of room-temperature deposition of iron on cleaved GaAs(110). Core-level and valence-band spectra indicate substrate disruption with Fe, Ga, and As atomic intermixing. Detailed analysis shows that reacted regions develop which contain significant amounts of both Ga and As for nominal Fe coverages below  $\sim 3 \text{ \AA}$ . Coverage-dependent studies reveal that two different Fe—As bonding configurations form with the first phase being very thin and the second (dilute) Fe—As component persisting to high coverage. In contrast, Fe—Ga bonding does not produce a well-defined chemical environment. Valence-band results indicate that Fe metal starts to form by approximately  $5 \text{ \AA}$ , although the core-level results show that significant amounts of As are always present in the surface region. In contrast, Ga appears to be trapped near the original interface. Recent reports of magnetic properties and epitaxial growth of Fe on GaAs are evaluated in the context of the present results.

## INTRODUCTION

The growth of epitaxial overlayers on semiconductor substrates is of current interest because the anisotropy and periodicity of the resulting crystalline structures can be exploited to produce selected physical phenomena (e.g., create periodic quantum structures<sup>1</sup>) or permit control over surface and materials-related properties (e.g., variations in the growth rate of GaAs with crystal orientation).<sup>2</sup> Epitaxial growth on surfaces occurs most readily when the degree of lattice mismatch is small, the underlying substrate is relatively smooth (close-packed faces have smoother near-surface charge distributions than open faces), and the energetics of overlayer formation favor adhesion of the overlayer to the substrate rather than clustering.<sup>3</sup> Epitaxial growth on semiconductor interfaces has been shown to occur for metals and semimetals which have similar electronic structures and small lattice mismatch [e.g., As or Sb on GaAs (Ref. 4)] or has been induced by surface treatments which produced ordered compounds [e.g., Ni, Pd, and Co on Si(111) (Refs. 5–7)]. Recent studies of transition- and noble-metal adsorption on atomically clean semiconductor surfaces have shown that disordered overlayers usually form at room temperature.<sup>5–10</sup> Interdiffusion produces a wide variety of overlayer structures and reaction products [e.g., V or Cr on GaAs (110) (Ref. 9), V on Ge(111) (Ref. 10)]. Exceptions to the rule of intermixing are Ag on Si, Ge, and GaAs (Ref. 11).

The recent reports that Fe forms epitaxially on GaAs(110) (Ref. 12) and GaAs(100) (Ref. 13) and that Co forms epitaxially on GaAs(110) (Ref. 14) are extremely interesting because other transition metals induce disruption and disordered overlayers. Waldrop and Grant<sup>13</sup> reported the first observation of Fe epitaxy on sputter-annealed MBE-grown GaAs(100) (MBE denotes molecular-beam epitaxy). Low-energy electron diffraction (LEED) revealed that Fe produced integral-order ( $1 \times 1$ ) spots with parallel registry of the overlayer and substrate coordi-

nates. Epitaxy in this system was attributed to the fact that the lattice constant of GaAs was almost double that of bcc Fe ( $a = 5.653$  for GaAs and  $a = 2.866$  for Fe). Recent work by Prinz (Refs. 12 and 14) has shown that stabilized bcc layers of both Fe and Co can be grown on GaAs(110), permitting unique magnetic studies of the metastable bcc phase of Co.

Investigations of the magnetization of Fe on GaAs(110) (Ref. 15) showed that these films exhibit an anomalous decrease in magnetization with decreasing thin-film thickness. This behavior was attributed to lattice strain induced by compressive stresses due to the 1.35% mismatch in lattice constants for Fe at the interface. The range of decrease in the magnetization measured in MBE-grown iron films of  $\sim 50 \text{ \AA}$  thickness was found to be in reasonable agreement with stress-release mechanisms encountered at thin-film interfaces.

Spin-resolved photoemission measurements were undertaken by Schröder *et al.*<sup>16</sup> for Fe/GaAs(110) and Prinz *et al.*<sup>17</sup> for Co/GaAs(110) to determine if the compressive distortion attributed to lattice mismatch could produce measurable changes in the valence-band electronic structure of Fe and Co. Fe films ranging from 40 to 1500  $\text{ \AA}$  were examined and, at the lowest coverages, an increase in the population of the minority-spin electrons was detected along with a shift of the  $\Gamma_{25\downarrow}$  band. These results indicated a reduction in the exchange splitting. Similar results were obtained for Co, which had a structure similar to  $\alpha$ -Fe, and were consistent with the observed demagnetization of the iron films.

Interface-induced effects have been observed for a variety of magnetic thin films.<sup>18</sup> Spin-wave resonance data show that spin-wave excitation can be localized at the interface due to gradients in the magnetization. Vittoria and Schelleng<sup>19</sup> showed that surface states at the yttrium-iron-garnet/gadolinium-gallium-garnet (YIG/GGG) interface resulted from interfacial diffusion of GGG constituents into the YIG overlayer. Since the Fe films discussed above also show gradients in both the magnetization and magnetic properties near the

metal/semiconductor interfaces, it is possible that impurity outdiffusion into the Fe or Co overlayer could influence their magnetic properties.

In this paper we present high-resolution synchrotron radiation photoemission results for overlayers of Fe on GaAs(110). This study was undertaken to determine the chemical composition and structure of the interfacial zone. Atomically clean, relaxed GaAs(110) surfaces were prepared by cleaving at pressures of  $\sim 5 \times 10^{-11}$  Torr. Iron overlayers of nominal thicknesses 0.2 to 70 Å were deposited *in situ* and examined using photoemission techniques. We found that the Fe/GaAs(110) interface exhibited substrate disruption with Ga and As release into the overlayer. Chemical differences indicated by the existence of shifted Ga and As core-level components were found between the thinnest and thickest iron overlayers. Our results suggest that the Fe/GaAs(110) interface can be modeled as thin reacted regions several angstroms thick, a transition layer containing Ga and As in solution, and ultimately Fe metal which has As in the near-surface region.

### EXPERIMENTAL PROCEDURE

Synchrotron radiation photoemission experiments were done at the Tantalus electron storage ring using the Mark II "Grasshopper" beamline. Monochromator bandwidths and cylindrical mirror electron energy analyzer pass energies were selected to give overall resolutions of  $\sim 300$  meV for the surface-sensitive As and Ga 3*d* core levels at  $h\nu = 85$  and 60 eV (photoelectron mean free path about 5 Å), 250 meV for the more bulk-sensitive measurements at  $h\nu = 40$  and 55 eV (mean free path about 20 Å), and 400 meV for the valence-band studies. Instrumentation used to prepare the Fe film and GaAs(110) substrates has been described elsewhere.<sup>9,20</sup> The spectrometer permits the acquisition of angle-integrated photoelectron spectra using monochromatic *s*-polarized synchrotron radiation at  $\sim 45^\circ$  angle of incidence.<sup>20</sup>

GaAs(110) substrates were prepared by cleaving etched and prenotched [110]-oriented GaAs bars obtained from Crystal Specialties (*n*-type, Si doped at  $4 \times 10^{18}$  cm<sup>-3</sup>). Mirrorlike cleaved surfaces measuring  $\sim 3 \times 4$  mm<sup>2</sup> were utilized for this study. Comparison of the core and valence-band spectra with results obtained during earlier studies by ourselves and others indicated flat-band conditions and an absence of inhomogeneous Fermi level pinning.

Room-temperature Fe depositions were done *in situ* using a resistively-heated W boat and electron-beam-purified Fe metal. After extensive degassing, Fe could be evaporated at  $\leq 1 \times 10^{-10}$  Torr. An Inficon thickness monitor was used to measure and stabilize deposition rates at  $\sim 1$  Å/min. This rate was used for all Fe depositions regardless of the incremental change in film thickness. For low coverages, the thickness was computed from timed evaporations. In this paper, Fe film coverages are expressed in angstroms where 1.04 Å = 1 monolayer (ML) relative to the GaAs(110) surface atomic density of  $8.9 \times 10^{14}$  atoms cm<sup>-2</sup>.

Analysis of our As and Ga 3*d* core-level spectra was

done by decomposition into sets of empirically deduced spin-orbit-split doublets which represented substrate and the chemically shifted reacted components. This enabled us to account for changes in line shape and semiconductor core-level branching ratios to investigate increased sample disorder and reaction products. (References 10, 21, and 22 contain descriptions of our fitting procedure and its application for Si-, Ge-, and GaAs-based metal/semiconductor interfaces.)

### RESULTS AND DISCUSSION

Gallium and arsenic 3*d* photoemission spectra taken for ultralow iron coverages are shown in Fig. 1. Figures 2 and 3 show the evolution of those core levels as a function of Fe coverage at higher coverage. These background-subtracted spectra have been scaled to constant intensity and reflect both surface-sensitive (As 3*d* at 85 eV, Ga 3*d* at 60 eV) and bulk-sensitive (As 3*d* at 55 eV, Ga 3*d* at 40 eV) measurements. Representative semiempirical fits of both the As and Ga 3*d* cores are displayed in Fig. 4. Valence-band results for Fe/GaAs(110) are shown in Fig. 5, and changes in the Fe/GaAs surface chemistry are highlighted by difference curves at the right of Fig. 5. Intensity variations of the As and Ga 3*d* core levels during the deposition of Fe are shown in Fig. 6. Figure 6 also summarizes the results obtained from semiempirical decomposition of the Ga and As 3*d* core levels into substrate and reacted components.

The core-level positions for the Fe-covered surface were shifted  $\sim 0.6$  eV to compensate for band bending. The magnitude of the band bending was determined from the rigid shift of the bulk-derived Ga and As 3*d* core components to higher kinetic energy (lower binding energy) for *n*-type GaAs. Shifts of similar magnitudes and direction have been attributed by several authors<sup>23-25</sup> to the movement of  $E_F$  during Schottky barrier formation. The equilibrium Fermi level position was established at Fe coverages below 1 Å.

Modification of the GaAs substrate due to reaction at ultralow coverages is readily apparent from changes observed in both the Ga and As 3*d* core levels. As shown in Fig. 1, they broaden and develop a shoulder at lower binding energy at nominal coverages of 0.5 Å. (We use the word nominal here to denote the number of Fe atoms deposited, not the actual thickness of the reacted layer, since we cannot measure that thickness.) At the lowest coverage examined, 0.2 Å, sharpening of the Ga 3*d* line due to the removal of the surface component was observed, but no change in the overall shape of the As 3*d* cores could be detected at the same coverage (the surface-shifted and reacted-shifted As components fall at about the same binding energy, as shown in Fig. 4). Subsequent growth of the shoulder in the Ga 3*d* core level after 0.5 Å indicates that a substrate-disrupting chemical reaction is taking place.

Further evolution of the Fe/GaAs(110) interface is illustrated by the modification of the Ga and As 3*d* cores shown in Figs. 2 and 3. Disruptive interdiffusion and reaction produces Ga and As core-level chemical shifts which are shown in the fits presented in Fig. 4. The Fe-

As reaction products can be represented by two reacted components (labeled 1 and 2 in the order of appearance), located 0.4 and 0.7 eV to lower binding energy relative to the substrate. The Fe-Ga reaction product can be represented by a single shifted core level which disperses

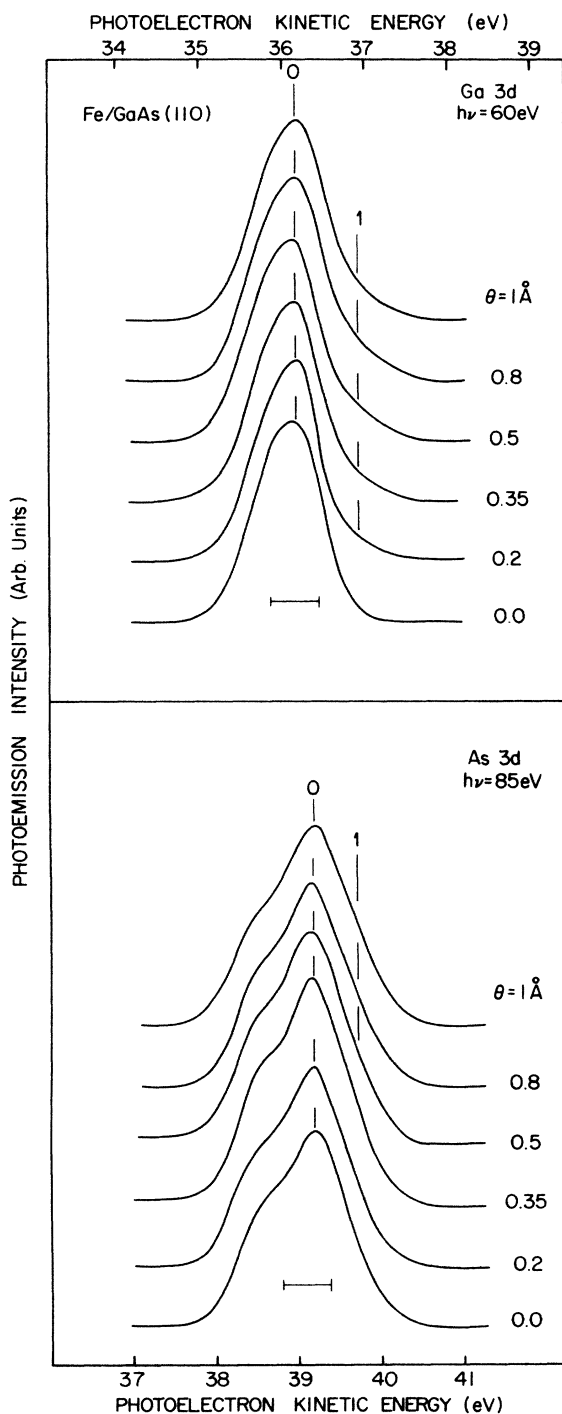


FIG. 1. Photoemission energy distribution curves (EDC's) showing the Ga and As 3d core emission at low Fe coverage for Fe/GaAs(110). The spectra have been shifted to correct for changes in band bending by an amount indicated by the horizontal bar below the first EDC. Tic marks indicate the positions of the substrate and first reacted components.

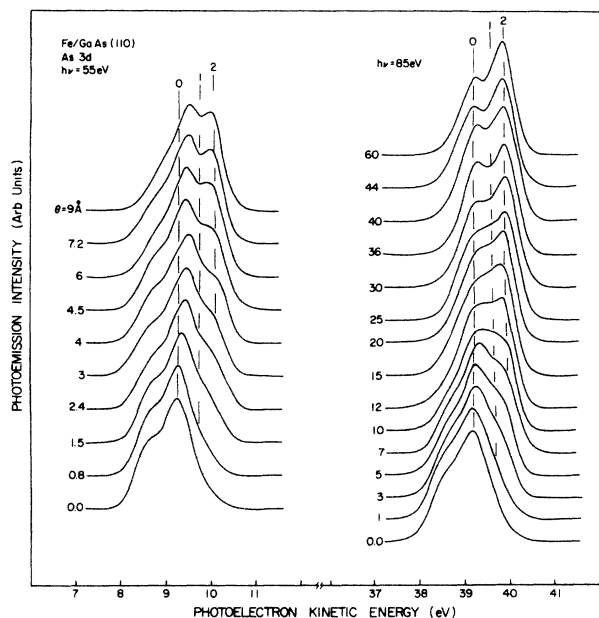


FIG. 2. As 3d EDC's showing changes in the chemical environment of As atoms involved in the reaction at the Fe/GaAs interface. The spectra have been background-subtracted and re-normalized to constant height. Low-coverage spectra have been shifted to correct for band bending. The positions of the bulk-derived substrate component and Fe-induced components inferred from semiempirical curve fitting are indicated by vertical tic marks (chemical shifts of 0.4 and 0.7 eV relative to the substrate).

to 1 eV lower binding energy with increasing Fe coverage (Figs. 3 and 4). The shifting of the Ga 3d reacted component ceases when the nominal Fe coverage exceeds  $\sim 12$  Å, as measured with high surface sensitivity at  $h\nu=60$  eV.

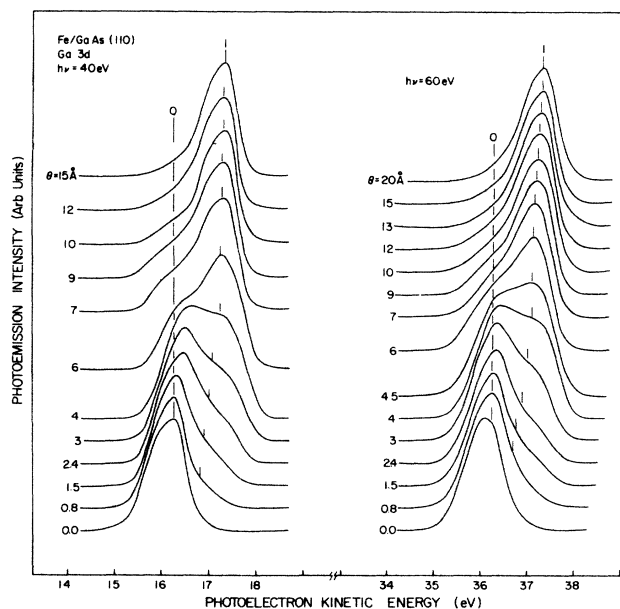


FIG. 3. Ga 3d EDC's analogous to those for As in Fig. 2. The total Ga 3d shift is 1 eV.

The growth and attenuation of the Fe-induced As 3*d* features suggest a two-stage reaction similar to those reported for Ti/GaAs(110),<sup>26</sup> V/GaAs(110),<sup>9</sup> Cr/GaAs(110),<sup>9</sup> Ce/GaAs(110),<sup>27</sup> and Sm/GaAs(110).<sup>27</sup> The first is characterized by bonding environments which produce the smaller core-level shifts, and the second by environments suggestive of greater semiconductor dilution in the Fe matrix at higher coverage. (Interestingly, the ordering is different for the rare-earth metals and the transition metals). Inspection of the surface sensitive Ga and As 3*d* spectra indicates that As intermixes more readily with Fe than with Ga, because the As 3*d* emission persists to much higher Fe coverages.

Examination of the Pauling electronegativities<sup>28</sup> of As, Ga, and Fe (As, 2.18; Ga, 1.81; and Fe, 1.83), the heats of solution<sup>29</sup> of As in Fe (-68 kJ mol<sup>-1</sup>) and Ga in Fe (-8 kJ mol<sup>-1</sup>), and the relative heats of formation<sup>30</sup> of GaAs (-154 kJ mol<sup>-1</sup>), Fe-As, and Fe-Ga compounds (listed in

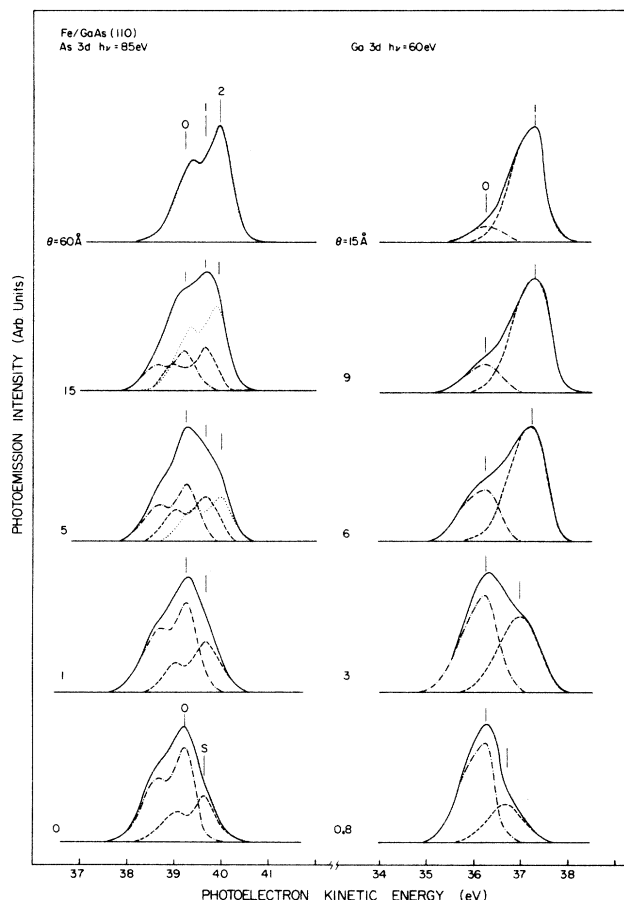


FIG. 4. Representative line-shape decompositions for the As and Ga 3*d* EDC's at  $h\nu=85$  and 60 eV. The As 3*d* emission can be fitted with three doublets corresponding to substrate arsenic, an arsenic-rich Fe-As, and arsenic in solution in Fe. For  $\Theta \geq 40 \text{ \AA}$ , the As core was assumed to be derived from a single component (labeled 2). The Ga 3*d* emission was fitted with two components representing the unreacted substrate and reacted Fe-Ga. The symbol *s* denotes contribution from the surface-shifted core emission for the clean surface.

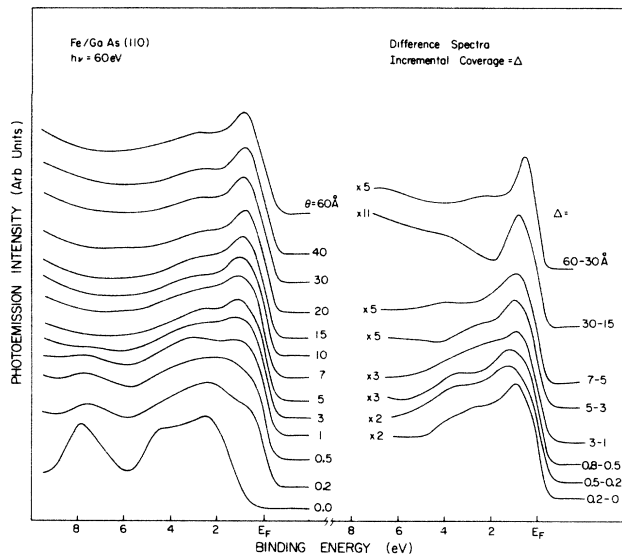


FIG. 5. Valence-band EDC's taken at  $h\nu=60$  eV for selected Fe coverages on GaAs. The incremental difference curves shown on the right illustrate the changing nature of the Fe-Ga and Fe-As interactions as a function of Fe coverage.

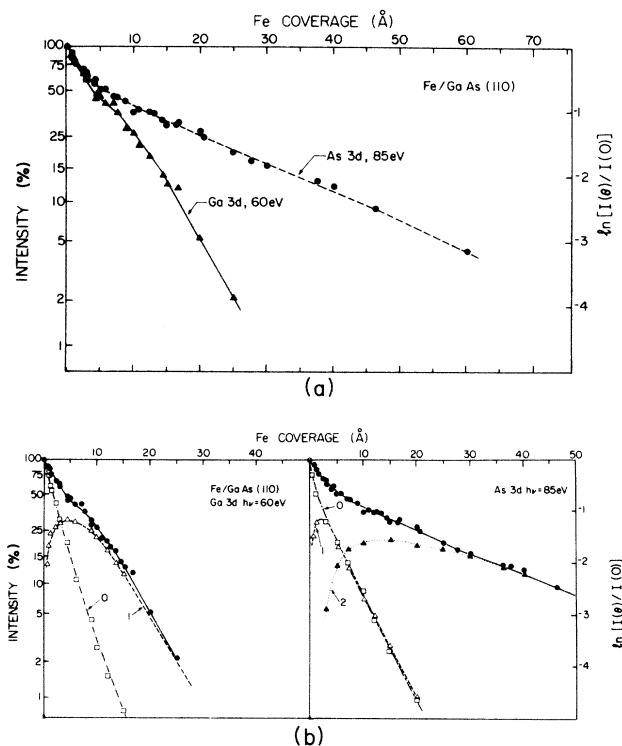


FIG. 6. (a) Attenuation curves for the Ga and As 3*d* emission showing the total attenuation with high surface sensitivity. For coverages below about 5  $\text{\AA}$ , the Ga to As ratio is approximately unity, but it decreases monotonically and approaches zero at high coverage because of the persistence of As in the near-surface region. (b) Attenuation curves for Ga and As 3*d* emission showing the intensity variations of the substrate and the Fe-induced components as a function of Fe coverage and photon energy. The substrate and reacted components are labeled according to the nomenclature of Figs. 1-3.

TABLE I. Calculated heats of formation  $\Delta H_{298\text{K}}^0$  ( $\text{kJ mol}^{-1}$ ) taken from Niessen *et al.* (Ref. 30) and for various Fe-Ga and Fe-As compounds. Values computed for Cr-Ga, Cr-As, Ti-Ga, and Ti-As, using the program discussed in Ref. 29, are included for comparison. Heats of solution of Ti, Cr, and Fe taken from Miedema *et al.* (Ref. 29) are also presented.

<i>M</i>	$\text{FeM}_5$	$\text{FeM}_3$	$\text{FeM}_2$	$\text{FeM}$	$\text{MFe}_2$	$\text{MFe}_3$	$\text{MFe}_5$
Ga	-7	-10	-14	-18	-16	-13	-9
As	-15	-23	-30	-40	-38	-31	-21
<i>M</i>	$\text{CrM}_5$	$\text{CrM}_3$	$\text{CrM}_2$	$\text{CrM}$	$\text{Cr}_2\text{M}$	$\text{Cr}_3\text{M}$	$\text{Cr}_5\text{M}$
Ga	-6	-9	-12	-16	-15	-12	-8
As	-18	-27	-35	-48	-45	-36	-25
<i>M</i>	$\text{TiM}_5$	$\text{TiM}_3$	$\text{TiM}_2$	$\text{TiM}$	$\text{Ti}_2\text{M}$	$\text{Ti}_3\text{M}$	$\text{Ti}_5\text{M}$
Ga	-21	-31	-41	-51	-44	-35	-23
As	-44	-66	-86	-110	-97	-76	-51

<i>M</i>	Heats of solution $\Delta H_{298\text{K}}^0$ ( $\text{kJ mol}^{-1}$ )			
	<i>M</i> /Ga	<i>M</i> /As	Ga/ <i>M</i>	As/ <i>M</i>
Fe	-6	-49	-8	-68
Cr	-2	-66	-3	-92
Ti	-88	-221	-98	-258

Table I) shows that there are no bulk Fe-As or Fe-Ga compounds which are more stable than GaAs. Nevertheless, our results and those of Ref. 13 show that reaction does occur at the interface, starting at the lowest coverage. These bulk thermodynamic predictions suggest that reaction would be driven by Fe-As reactions rather than by Fe-Ga products.

Our experimental results show that there is significant intermixing by nominal Fe coverages of 1 Å. At Fe coverages exceeding 5 Å, there is evidence for the formation of the second reacted As component (Fig. 4) and the continuing shift of the Ga 3*d*. The larger core-level shift of the second As component relative to the first (0.7 versus 0.4 eV) indicates a greater Fe coordination for the second component. Examination of related metal-GaAs (Refs. 9, 26, and 27) and metal-germanium systems (Ref. 10) suggests that these terminal phases are dilute solid solutions of semiconductor atoms in the metal, together with semiconductor atoms segregated at grain boundaries or near the surface.<sup>21,31</sup> Two physical mechanisms could account for the continuous shift to lower binding energy of the Ga 3*d* core in Fe or other transition metals. First, the increased Fe coordination would lead to greater charge redistribution. Second, the increasingly metallic character of the matrix could lead to better core-hole screening in the photoemission final state.

Further information about the chemical environment of the overlayers can be inferred from the valence-band evolution summarized in Fig. 5, together with incremental difference curves obtained by subtracting representative pairs of (energy distribution curves) EDC's. At the lowest coverage examined ( $\Theta=0.2$  Å), the Fe adatoms have attenuated the GaAs-derived states 6–8 eV below  $E_F$ . The

rapid loss of the GaAs-derived features is due to the greater overall photoyield of the Fe valence states relative to those of GaAs. Further Fe deposition produces an overall increase in the valence-band emission and generates a number of poorly resolved features within 6 eV of  $E_F$ . Difference curves show changes in bonding at the lowest coverages due to chemical interaction between Fe and GaAs. Reactive intermixing is illustrated by a shift and a systematic broadening of the most intense Fe-derived feature and the growth of structure 3.7 eV below  $E_F$ . By a nominal coverage of about 5 Å, the valence bands begin to resemble those of Fe. This should, however, be interpreted cautiously because of the difficulty of associating a particular valence-band structure with a particular phase when the system is multiphase and each involves metal-derived *d* states.<sup>27</sup> Indeed, the appearance of the new core-level component characteristic of the second and final stage of interface development is also observed at about 5 Å, indicating that the layers that form are increasingly Fe-rich but with appreciable (but diminishing) amounts of Ga and As. By analogy with the bonding predicted and observed for transition-metal silicides, we believe the feature near  $E_F$  is composed of nonbonding Fe *d* states and that the one at -3.7 eV corresponds to Fe-As and/or Fe-Ga bonding states.<sup>32</sup>

As the nominal coverage increases, the valence-band emission from the probed region converges to that of Fe metal. Between 20 and 60 Å coverage, the main Fe-derived feature broadens and shifts a few tenths of an eV away from  $E_F$ , as new Fe valence-band states appear at -0.5 eV (see difference curve between 30 and 60 Å Fe coverage). These new Fe features may be magnetic in origin and may represent the point at which significant mag-

netic ordering of the Fe overlayer takes place.<sup>16</sup> This conclusion is supported in part by spin-resolved normal-emission valence-band studies of Fe and by Fe band-structure calculations which show that the exchange interaction splits the Fe *d* states into majority- and minority-spin bands (see Fig. 1 in Ref. 16). In this range, our core-level results show that the Ga content of the surface region is negligible, and we speculate that the persistence of As acts to vary the magnetic properties of the region. This would be consistent with the observation of suppressed magnetism for thin Fe layers on GaAs.<sup>15</sup> Unfortunately, we cannot determine the Fe atomic profile from the present results, but studies to do so are planned using angle-resolved Auger spectroscopy.

Detailed examination of the intensity variations for the Ga and As core-level emission makes it possible to extract information about the structure of the Fe/GaAs interface. In Fig. 6(a) we show the total integrated core-level intensities for the Ga and As 3*d* core levels normalized to the emission from the clean surface. Intensity profiles for As at  $h\nu=85$  eV and Ga at  $h\nu=60$  eV have the same escape depth (approximately 5 Å). These show that the Fe-Ga and Fe-As phases have different spatial extents, as demonstrated by the faster extinction of the total Ga emission relative to that of As. At low coverage ( $\Theta \leq 3$  Å) the Ga and As 3*d* core levels show similar attenuation. For  $\Theta \geq 5$  Å, the rate of As attenuation is much slower than for Ga. Both Ga and As intensities show an inflection point at 8–10 Å.

In Fig. 6(b) we plot the results of our semiempirical analysis of the Ga 3*d* and As 3*d* core levels to show the component-specific emission intensities  $I_i$  normalized to the clean substrate. Emission from the undisrupted substrate is rapidly attenuated and is characterized by an escape depth of about 3 Å. This reflects the loss of emission from Ga and As in GaAs due to the overlayer growth and the chemical conversion of GaAs to Fe-Ga and Fe-As. Above  $\Theta \sim 3$  Å, the rate of substrate attenuation diminishes, consistent with the formation of Fe-rich reacted regions and reduced GaAs disruption. The intensity profiles for reacted Ga and As at low coverage grow rapidly with Fe coverage but never exceed  $\sim 30\%$  of the original core-level intensity. The results show that the As(1) contribution to the observed emission peaks at 2–3 Å nominal coverage and is buried by succeeding Fe-Ga and Fe-As species while the reacted Ga component reaches its maximum value at 4–5 Å Fe coverage. The As(2) phase exhibits a slower rise and a very slow decay. By  $\sim 30$  Å nominal coverage, there is only the single As component observed within the probed region (outermost 15–20 Å) and we interpret it as As atoms fully coordinated with Fe.

Comparison of the present results for Fe/GaAs(110) with those for other transition-metal/GaAs(110) systems<sup>9,26,33</sup> shows both similarities and differences. Each transition-metal/GaAs interface is characterized by the formation of overlayers composed of multiple phases or distinct local chemical environments. We see that for Fe/GaAs, the scale over which As out-diffusion persists exceeds that of Ga and the coverage range over which the reacted regions form is smaller than for Ti/GaAs,

Cr/GaAs, or V/GaAs. This is in accord with the decreasing ionic character of the metal-As and metal-Ga bonds (Pauling electronegativity differences relative to As and Ga are 0.64 and 0.27 for Ti, 0.52 and 0.15 for Cr, and 0.35 and  $-0.02$  for Fe). Only the rare-earth/GaAs interfaces are sharper than those observed here.<sup>27,33</sup>

The present results show that Fe induces GaAs(110) substrate disruption, in agreement with the XPS results of Waldrop and Grant.<sup>13</sup> The reaction products that form are limited in thickness, although we find evidence for significant amounts of As in the near-surface region even for thick Fe layers. The spatial extent of this intermixed region is in reasonable agreement with the decreased magnetization for thin films reported by Hathaway and Prinz<sup>34</sup> and the spin-resolved photoemission studies of Schröder *et al.*<sup>16</sup> At the same time, our evidence of disruption and intermixing is difficult to reconcile with epitaxial growth of Fe and Co on GaAs(110) and GaAs(100). Indeed, the photoemission data suggest that bcc Fe or Co epitaxial growth in registry with the substrate would be unlikely on atomically clean GaAs surfaces unless the reacted Fe-Ga and Fe-As components themselves grow epitaxially (epitaxial silicide growth on Si has been observed for a large number of transition-metal silicides). This places constraints on the nature of the initial Fe adatom/substrate interaction and the distribution of atoms in the thin intermixed layer.

Unfortunately, the mechanism for substrate distribution of the sort we observe here is poorly understood. Studies of Al/GaAs have suggested an exchange reaction under suitable conditions of temperature and Al coverage, while studies of other systems have pointed to the importance of cluster-induced disruption.<sup>35</sup> We find here that at ultralow Fe coverage, the valence bands and their difference curves indicate immediate reaction, because the spectra resemble those observed for the reacted overlayer. Hence, there is no evidence for cluster formation or a threshold coverage for reaction. We also observe that the reaction products grow over a very limited range and that by  $\sim 3$  Å nominal Fe coverage, the surface is apparently passivated. We can speculate that the surface reaction products block further direct reaction between the impinging Fe atoms and the substrate. As a result, deposition of additional Fe would produce an Fe film which tolerates the substitutional dissolving of As (predominantly) and Ga since the covalent radii of both atoms are nearly equivalent to the metallic radius of Fe (1.24 Å for Fe, 1.26 Å for Ga, and 1.18 Å for As).<sup>36</sup> Although nucleation should be expected to occur heterogeneously on the surface, the grain boundaries in the growing epitaxial film presumably would be small angle boundaries which would minimize Fe diffusion to the buried GaAs surface, where reaction could continue. Ultimately, the overlayer could develop long-range epitaxy upon suitable thermal processing. This model of epitaxial reaction products allows for heterogeneous reaction on the surface, as it must since there is no reason to assume that room-temperature reaction would be homogeneous.

In summary, we have shown that Fe disrupts the GaAs(110) substrate and that an extended, multiphase interfacial region forms. The observed mixing of As in the

overlayer is greater than that of Ga, consistent with electronegativity and thermochemical data, which show that Fe—As bonds are more ionic and energetic than Fe—Ga bonds. The rate of Ga and As intermixing decreases at  $\sim 3$  Å Fe coverage and this leads to the production of more Fe-rich Fe—As and Fe—Ga bonding environments. Since this coverage is close to the coverage in which the surface is completely covered or capped, our data suggests that free iron atoms are needed at the GaAs surface to promote substrate disruption. Studies of the structure of the Fe/GaAs interface are planned to further reconcile the disruption with Fe epitaxy on GaAs(110), to examine

the issue of heterogeneity, and to determine the distribution of As in the Fe overlayer.

#### ACKNOWLEDGMENTS

The authors wish to thank G. A. Prinz and R. W. Grant for helpful discussions and the staff of the Synchrotron Radiation Center (SRC), University of Wisconsin—Madison, Stoughton, WI, for technical assistance. The SRC is supported by the National Science Foundation. This work was supported by the U.S. Office of Naval Research under Contract No. ONR-N00014-83-K-0579.

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