Reactions at a rare-earth-GaAs interface: Ce/GaAs(110)

J. H. Weaver, M. Grioni, J. J. Joyce,* and M. del Giudice

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

(Received 30 November 1984)

We present results of a detailed microscopic study of an evolving rare-earth-compoundsemiconductor interface. High-resolution synchrotron-radiation photoemission results for Ce coverages in the range 0.08-30 monolayers (ML) (0.25-90 Å) on cleaved GaAs(110) show that three new and distinct As environments are produced by disruption of the surface. The As 3d core lines in these Ce-As configurations are shifted to lower binding energy relative to GaAs. They reflect surface-bonded As and two different Ce-As bulk configurations. These As configurations have very different growth and attenuation behaviors, as revealed by line-shape decomposition at each coverage and component-specific attenuation studies. The attenuation of substrate As is very rapid because of semiconductor disruption and growth of the reacted phases. The first reacted phase reaches its maximum near 1.3 ML and is replaced by a second, fully reacted phase. Above 3.2 ML, this second reacted phase is also attenuated by a developing Ce overlayer. The final surfacecoordinated As signal appears when the metallic Ce overlayer starts to form. Arsenic is then visible in small quantities to high coverage, representing 0.7% of the initial As concentration at $\Theta = 30$ ML. Ga 3d core studies indicate that Ga forms a Ce-Ga intermetallic of variable composition (total core shift 1.78 eV to lower binding energy). Likewise, Ga is much more mobile than As at the reacted interface (7% of initial signal at 30 ML). Valence-band studies at 30 and 60 eV show dominant Asderived p states for the intermixed region and provide evidence for strong ionic bonds. Comparison to single-crystal CeAs shows that the local environment of the bulk-coordinated As at the reacted interface is CeAs-like, having similar valence-band and 4f emission with differences which can be explained by disorder.

INTRODUCTION

Studies of the electronic and structural character of metal-semiconductor interfaces have shown that interfaces need not be atomically abrupt, as was once envisioned.^{1,2} Instead, interdiffusion is the norm and the resulting intermixed region can have novel interfacestabilized properties where bonding is dominated by local chemistry. Quite recently, experimental investigations have examined the behavior of interfaces at monolayer and submonolayer coverages, and these have shown that intermixing appears to be spontaneous in some instances but is triggered only after well-defined coverages in others.³

At the moment, it is not possible to predict the onset of reaction, the moving species, the spatial scale over which reaction occurs, the reaction product(s), or the likelihood of surface segregation, although phenomenological rules of thumb have been suggested.¹ Studies which reveal the morphology of an evolving interface are then crucial if any predictive capability is to be achieved.

In this paper we present high-resolution synchrotronradiation photoemission studies of Ce overlayers on GaAs(110). These are the first such studies of interactions between a rare-earth metal and a compound semiconductor. While this work should be viewed in the broader context of reactive metal overlayers on GaAs, the rare-earth studies offer a special opportunity to assess ionic bonding at an interface—the extremely large electronegativity difference of Ce and As suggests that Ce-As bonding with substantial charge transfer might modify interface diffusion and segregation.¹

EXPERIMENTAL DETAILS

The photoemission experiments were done at the Synchrotron Radiation Center using the Tantalus ring and a toroidal grating monochromator. To obtain the resolution necessary for identification of the different interface species, the commercial electron-energy analyzer was operated at 10-15-eV pass energy and the monochromator slits were adjusted to provide overall resolution (electrons plus photons) of 250-400 meV. The experimental system was optimized for in situ cleaving and metal deposition at operating pressures in the low- 10^{-11} -Torr range.⁴ GaAs(110) samples were obtained from Crystal Specialties (*n* type with $\hat{S}i$ doping at 4×10^{18} cm⁻³). Mirrorlike cleavage surfaces measuring $4 \times 4 \text{ mm}^2$ were routinely obtained, and their microscopic quality was checked with valence-band and core-level photoemission studies to assure flat-band conditions. Deposition of high-purity Ames Laboratory Ce was done from resistively heated W coils at pressures of less than 2×10^{-10} Torr. An Inficon thickness monitor was used to adjust the deposition rate to $\sim 1 \text{ Å/min}$. Thicknesses are reported here in monolayers where 1 ML = 8.9×10^{14} atoms/cm²=3 Å of Ce.

In the following paragraphs, we first discuss the corelevel results taken at 85 and 60 eV to show the stages of reaction. These energies were chosen to give approximately the same high surface sensitivity for both Ga and As core studies [~ 6 Å (Ref. 5)]. Having shown the uniqueness of the species which form and identified their growth and attenuation behaviors, we use valence-band information derived from interface and bulk CeAs studies at 30 and 60 eV to discuss the character of the reaction products. These photon energies make it possible to distinguish the Ce-derived character of the valence bands and to follow changes in bonding configurations, most notably with the 4f emission feature.

RESULTS AND DISCUSSION

Core-level results

In Fig. 1 we show the behavior of the As 3d core emission as a function of Ce coverage. As demonstrated by Eastman *et al.*,⁵ the total 3d core emission for the clean surface is broadened by a surface component shifted by 0.37 eV to lower binding energy relative to the bulk. With coverage, however, we find increased broadening to low energy as a shoulder grows and becomes clearly visible by 0.6 ML. As the reacted component grows, the unshifted As component diminishes rapidly. Most interesting, however, is that a dramatic line-shape change occurs between 6.4 and 9.6 ML, with a doublet shifted back toward the initial position. This component grows in relative intensity as the fully shifted one disappears. By 19.2 ML it is the only As feature observed. The total shifts are 0.65 eV and 1.00 eV, as noted in Fig. 1.

This intriguing arsenic behavior suggests that the intermediate coverage range might be characterized by the growth of reacted As species and the high coverage range could have an As species of lower (surface) coordination.



FIG. 1. As 3d core emission for the Ce/GaAs interface as a function of Ce coverage, Θ . The spectra have been corrected for changes in band bending totaling 750 meV. The spectra on the right-hand side show the decomposition of the core EDC into substrate, reacted, and surface As contributions, as discussed in the text. Core EDC's at all coverages could be fitted with only three sets of spin-orbit-split doublets with only variations in their relative weights.

Hence, the spectra could be described as superpositions of distinct As species characterized by unique binding energies so that intensity variations would reveal the morphology of the surface region. Line-shape analysis indicates that such an interpretation is indeed correct. On the right-hand side of Fig. 1 we show the deconvolution of representative As 3d energy distribution curves (EDC's) into three sets of spin-orbit-split doublets. As-1 corresponds to As in the original GaAs configuration, As-3 is the species which is shifted the greatest amount, and As-2 is the species which dominates at highest coverage. We will discuss these in terms of fully reacted (As-3) and surface-segregated (As-2) species. At the same time, within our uncertainty in line-shape analysis, we must also introduce an As component at low coverage which has the same binding energy as the As-2 configuration. Its identification is the most difficult, but we will term it a partially reacted specie. The reason for such terminology will be made clear in later paragraphs.

To obtain the fittings shown in Fig. 1, we adopted the following procedure. First, the clean surface spectrum was decomposed into surface-shifted and bulk components. The resulting branching ratios, spin-orbit splittings, and surface shifts were found to be in excellent agreement with the higher-resolution results of Eastman et al.⁵ Subsequent fitting of the reacted line shapes was based on the line shape of the clean surface using doublets which are shifted a fixed energy relative to the unreacted line and with variation in full width at half maximum (FWHM) of less than 0.1 eV. Self-consistency was sought in which the entire coverage range was fitted with the same doublets, allowing only their relative intensities to vary. For the highest coverage, we note that the As 3dline was sharper than for the clean surface. With these approximations, the EDC's could be fit quite well, as shown in Fig. 1.

Guided by these line-shape decompositions we see that the partially reacted As component labeled "2" is already strong by Ce coverage of 0.6 ML and that it is the dominant species by 1.3 ML. This behavior is indicative of a highly reactive interface with no evidence for a reaction threshold or a weakly interacting precursor stage. By 1.6 ML the fully reacted As component labeled "3" must be introduced to fit the experimental line shape. With further coverage, the contribution of the first reaction product is reduced as the second product grows. Another reversal occurs near 3.2 ML as the relative intensity of the fully reacted species diminishes and the final component appears. This final component then dominates the spectra for all further coverages.

The best way to follow the relative growth and attenuation of the different As contributions is to consider their integrated intensities as a function of coverage. In the lower panel of Fig. 2 we show the integrated intensities of the total emission and each of the deconvolved As emission features, $\ln[I(\Theta)/I(0)]$. The different symbols represent different cleaves and coverages and the scatter is indicative of our experimental reproducibility. As shown, the attenuation of the total As content of the probed region is not exponential, as would have been expected if a uniform metal layer were growing on a nonreacting GaAs



FIG. 2. Attenuation curves for the Ga and As 3d core emission $\ln[I(\Theta)/I(0)]$ plotted for the total emission in the uppermost curve in each panel. Deconvolution of the core emission of Fig. 1 allowed component-specific growth and attenuation plots, as shown. For As, the solid line connecting open squares is the attenuation of the substrate component, the short dashed line with open circles is the first reacted component, the solid line with open triangles is the fully reacted component, and the dot-dashed line is the final As component which persists to high coverage. For the Ga core, the total emission was deconvolved into substrate (dashed line with solid circles) and reacted components (solid line with solid triangles). Note that the coverage scales are different for Ga and As.

substrate. Instead, the total attenuation exhibits structure near 4-ML coverage and has a decay rate which is far too slow. In contrast, if only the unreacted or substrate As component is considered, then we see a more nearly exponential decay with characteristic 1/e length of 4 Å. This length is smaller than expected for As 3d electron propagation through GaAs ($\lambda \sim 6$ Å at this kinetic energy⁵) and is consistent with the retreat of the overlayer-GaAs boundary away from the surface as reaction converts As-1 to As-2. By $\Theta = 4$ ML the unreacted component accounts for only $\sim 2\%$ of the initial signal.

The first reacted As component behaves quite differently from As in the substrate. As shown by its growth and attenuation curve in Fig. 2, it increases in relative intensity to a maximum at ~ 1.2 ML (dashed curve through open circles). This rapid growth indicates strong reaction, but subsequent peaking at such a low coverage and the appearance of a more fully reacted As component indicates that the first product is not the stable configuration. Its rapid decrease after the fully reacted component grows $(\Theta \ge 1.3 \text{ ML}, \lambda = 4-5 \text{ Å})$ parallels that of As in GaAs and is consistent with the conversion of partially reacted to fully reacted As in the surface region. The growth of the fully reacted As-3 component can be seen from Fig. 2 to reach a maximum near 3.2 ML (solid line through open triangles). The slower decay of this component at higher coverage shows that As out-diffusion into the surface region continues (characteristic decay length ~ 10 Å). Apparently, the Ce-rich overlayer which forms over the reaction products does not produce an abrupt interface.

The behavior of the last component is also significant for modeling the interface (dot-dashed curve). As noted above, its binding energy is indistinguishable within our modeling approximations from that of the partially reacted As component which appears at lowest coverage. However, analysis of the growth and attenuation curve for this doublet shows a distinct kink near 3.2 ML, i.e., the coverage at which the Ce-rich film starts to form. The very slow decay above 3.2 ML suggests that there are indeed two different Ce-As configurations which have similar binding energies. The first is the partially reacted product and the second is the component which segregates to the near surface region of the Ce overlayer. The persistence to very high coverage (characteristic decay length ~26 Å, total contribution 0.7% at $\Theta = 30$ ML) and intermediate binding energy indicates a lower coordination than the fully reacted, fully shifted As component.

Examination of the magnitude of the binding-energy shifts to lower energy shows that all of the As reaction products are more ionic than GaAs. In contrast, the binding energies reported for covalently bonded As overlayers on GaAs (100) (Ref. 6) or elemental As (Ref. 7) are greater than for As in GaAs. Hence, there is no evidence from our results of arsenic clusters on the surface. Instead, the ionic content of the bond is consistent with the highly electropositive character of Ce, a conclusion supported by comparisons between the valence-band emission for the reacted phases and bulk CeAs, to be discussed shortly.

Core-level studies for Ga show that Ga behaves quite differently from As, as seen in Fig. 3. For Ga, attempts to fit the core EDC's with doublets shifted by fixed



FIG. 3. Ga 3*d* core emission showing the steady progression of the reacted component (tic marks) to lower binding energy as the nominal overlayer thickness increases (total shift 1.78 eV). The spectra were corrected for changes in band bending. It was not possible to fit the Ga line shape with a set of spin-orbit-split doublets. Extra low-energy broadening of the Ga core is observed for $\Theta \ge 10$ ML because of overlap with the Ce 5*p* emission.

amounts relative to the clean surface were unsuccessful. Instead, there is a steady variation in energy for the reacted component, starting at lowest coverage and saturating at about 9.6 ML (total binding-energy shift 1.78 eV). The total chemical shift exceeds that observed for Ga droplets⁸ and, instead, indicates that Ce-Ga bonding is important in the interface region. The steady shift with coverage indicates that Ga senses a continuously changing environment as the relative Ce concentration increases, i.e., Ce-Ga bonding is unable to stabilize a unique local chemical environment or stoichiometry. At high coverage, however, the local bonding of Ga becomes better defined, as indicated by the sharpening spin-orbit doublet. It should be noted that previous studies of interface reactions for Ti/GaAs and Cr/GaAs (Refs. 3 and 9) have suggested the formation of transition-metal intermetallics, based on observations analogous to ours.

The rate at which the total Ga signal is attenuated by Ce deposition is shown in the upper panel of Fig. 2. Although detailed line-shape fitting was not possible, it was straightforward to assess the relative contribution of unshifted and shifted Ga. The behaviors of unshifted Ga and unshifted As were similar, as they must be since they represent the GaAs substrate (note that the coverage scales are different for Ga and As in Fig. 2). On the other hand, from the attenuation of the reacted components we see that Ga diffuses more easily at this interface than As. Indeed, when the As concentration has been reduced to $\sim 0.7\%$ of its starting value at 30 ML or 90 Å, Ga is still present at $\sim 7\%$ of its starting value. Since Ga and As exhibit such different growth and attenuation behavior, we conclude that ternary Ce-Ga-As compound formation is not significant at room temperature.

It is interesting to compare the present results with those for an interface like Cr/GaAs (Ref. 3) where the ionic contribution to the bond in the reacted region is far less important. Both Ce and Cr are highly reactive on GaAs, but the interfaces differ at lowest coverage in that Ce induces reactions immediately while Cr exhibits a delayed reaction ($\Theta \simeq 2$ ML). Quantitative comparisons of the attenuation of the semiconductor atoms shows that Ga has very similar concentration profiles at the two interfaces, with attenuation of the total Ga emission to e^{-2} at coverages corresponding to about 20 ML for both Ce and Cr (coverages normalized to the atom density of GaAs instead of angstroms to make comparisons meaningful). Likewise, the reacted components behave analogously, with similar Ga core line shapes but greater overall shift for Ce-Ga than for Cr-Ga because of the greater ionic content of the bond. The similarities in the Ga behavior are consistent with Brillson's conclusion that Ga diffusion is relatively insensitive to the metal species within the group of reactive metal overlayers.¹ However, examination of the arsenic behavior at the two interfaces shows dramatic differences. For Ce/GaAs, we have shown in Figs. 1 and 2 that As is attenuated rapidly and Ga is more persistent. Hence, the surface is richer in As than Ga below 6.4 ML but a crossover occurs at higher coverage. For Cr/GaAs, we found³ that the surface was always richer in As than Ga and that for coverages of 45 ML the As content was still $\sim 20\%$ of that of the initial

surface. These results clearly suggest that the outdiffusion of As is radically different for the two systems. Furthermore, if we characterize the width of the interface as the coverage at which the combined Ga and As emission falls to 1/e of the starting value, then the Ce/GaAs interface is 8 ML wide while that for Cr/GaAs is 27 ML wide. The difference is almost entirely due to the outdiffusion of As.

Brillson *et al.*^{1,10} recently related the width of an interface to the chemical reactivity of the overlayer, dividing reactive (Ti, Al, Ni) and nonreactive (Au, In, Zn) overlayers and considering heats of formation. The results presented here point to the need to further distinguish the abruptness of the interface according to the details of the chemical bonding. We find that chemical trapping of As will be substantially greater for highly electropositive metals like Ce than for transition metals like Cr. (Studies are presently underway to compare other reactive metals, including Ti, V, and Sm.)

Valence-band results

Insight into the character of the compounds which form can be gained by following the evolution of the valence bands, particularly when results are available for bulk samples of the probable reaction products. For the present studies, we can profit from prior electronic structure studies of Ce metal¹¹ and CeAs.¹² Furthermore, by exploiting the variability of the 4f photoionization cross section, we can obtain the 4f fingerprint for comparison to bulk compounds.^{11–13} In this paper we will then use the 4f fingerprint for that purpose, deferring a discussion of the origin of the double 4f peaks to a paper on finalstate, many-body interactions in Ce photoemission.¹⁴ With guidance from calculations of the electronic structure of CeAs, it is possible to assess the ionic content of the bonds of CeAs.¹⁵

In Figs. 4 and 5 we show valence-band energy distribution curves for $h\nu=30$ eV and 60 eV as a function of overlayer coverage. These results have been corrected for changes in band bending and are drawn in arbitrary units to emphasize variations in spectral features. Photon energies of 30 and 60 eV were chosen because previous work with α - and γ -Ce,¹¹ the cerium pnictides including CeAs,¹² and other Ce compounds¹³ showed that 4*f* contributions to valence-band emission could be distinguished by comparing EDC's at these energies. In particular, the EDC's at 30 eV emphasize Ce *d*-derived states while EDC's at 60 eV include substantial 4*f* character. Difference curves obtained by subtracting the two then highlight the 4*f* character.

Comparison of EDC's for $h\nu=30$ to those at 60 eV shows substantial differences at all coverages as the *d* and *f* character is alternately emphasized. Below about 2.5 ML, the results for $h\nu=30$ eV show gradual growth of emission within ~ 2 eV of E_F and the loss of GaAs substrate emission. The results for $h\nu=60$ eV reveal greater Ce-induced changes in that a double structured emission feature is visible at coverages as low as 0.1-0.2 ML. Indeed, at the bottom of Fig. 5 we show the result of subtracting representative low coverage EDC's. The Ce-



FIG. 4 Valence-band energy distribution curves for Ce/GaAs as measured with a photon energy of 30 eV. As discussed in the text, the prominent features for $\Theta \leq 6.5$ ML is As *p* derived. The emergence of emission at E_F at ~3.2 ML occurs long after reaction has occurred and is associated with the covering up of the reacted region by a Ce-rich film. By ~10 ML, the valence band is dominated by Ce-derived emission near E_F .

induced doublet has a splitting of 2.6 eV and apparent energies of 1.25 and 3.85 eV. This doublet grows with coverage. However, at 3.2 ML a new structure can be seen at -2.5 eV and there is emission at E_F indicative of the



transition to a metallic overlayer. The feature at -2.5 eV (Fig. 5) subsequently grows, sharpens, and shifts to a final position at -2.1 eV. Simultaneously, the emission at E_F (Fig. 4) sharpens and grows to dominance as all other features are lost. By 19 ML, the resulting EDC's resemble Ce metal. Clearly, these valence bands exhibit complex evolution. Without insight gained from the corelevel studies discussed above, they might be impossible to interpret at intermediate coverage. At high and low coverage, the 4f emission reflects its environment in a manner analogous to the *d* cores of Ga or As since it does





FIG. 6. Comparison of selected valence-band EDC's for $h\nu$ =30 and 60 eV from Figs. 4 and 5. Difference curves obtained by subtracting the 30-eV results (long-dashed line) from the 60 eV (solid line) highlight the Ce 4f emission. Normalization of the results followed the procedures discussed in Refs. 11–13. At low coverage these difference curves resemble those for CeAs (bottom curve, see Ref. 12) indicating the Ce-As-like configuration of As at these coverages. At high coverage, the results converge to Ce metal.

not participate in bonding and can be used to identify the Ce atomic configuration.

In Fig. 6 we show representative EDC's from Figs. 4 and 5 drawn normalized near 2.5 eV for the low coverage (reacted) regime and near 1 eV for the high coverage (Celike) regime, following procedures discussed in Refs. 11 and 12. Again, difference curves obtained by subtracting these two EDC's highlight the 4f character of the valence bands. From Fig. 6 we see that these difference curves vary substantially from low to high coverage. At lowest coverage, a doublet structure appears with the leading feature at -1 eV. Between 0.6 and 3.2 ML, the splitting changes from 2.8 to 2.4 eV, but there is no systematic variation in the relative heights of the two features. The existence of two 4f-derived features is extremely unusual, but can be understood by analogy to bulk CeAs.¹² Comparison indicates that the low coverage Ce-As reaction products identified above by core-level shifts are locally coordinated Ce-As systems, both of which possess strong 4f-ligand hybridization. We conclude, therefore, that at low coverage both species have Ce coordinated with nearest neighbors of As. For the partially reacted component, the 4f doublet is split more than that for the fully reacted component. By 3.2 ML, when the fully reacted component is dominant, we see that the atomic configuration is close to that of CeAs, as judged by comparison to the results for bulk CeAs. The differences in the relative peak heights can be attributed to deviations from the NaCl structure of CeAs and the absence of long-range order.

Band-structure calculations¹⁵ for CeAs show substantial charge transfer from Ce to As. The resulting semimetallic compound has nearly empty Ce d states but dominant As-derived states centered 2 eV below E_F , consistent with the results discussed above for the reacted regime. Indeed, the "fingerprinting" of the reaction products explains the relatively unchanging character of the valence bands studied at low photon energy: since the Ce d states are effectively empty, one should not expect the growth of Ce d—derived emission. Instead, Ce-As reaction produces a compound whose arsenic p states are centered where strong GaAs emission occurred. In contrast, the results for $h\nu = 60$ eV do show major Ce-derived emission, but it is 4f related as in CeAs.

The results of Figs. 4–6 show that for coverages above ~ 9.6 ML the probed region increasingly resembles a cerium overlayer. The Ce d states near E_F , the well-defined 4f emission at -2 eV, and even the smaller 4f feature at E_F at high coverage are all consistent with the results from the core studies which showed covering up of the reacted phase and diminishing Ga or As content. The Ga or As atoms present in the surface region at these high coverages emit too weakly to be observed in valence-band studies and are obscured by the stronger metal emission, analogous to what was found for surface segregated Si on silicides.¹⁶

In summary, we have shown that the reactions which occur at the Ce/GaAs interface are triggered by the arrival of the first Ce atoms—that the heats of formation or large electronegativity differences are sufficient to disrupt the surface. The Ce/GaAs system is then quite different from Ce/Si where cluster formation was observed³ at low coverage and reaction was not detected before 0.6 ML. We have then shown that well-defined As species can be identified from core-level and valence-band analysis, and we have modeled the developing complex interface. Gallium was shown to form an intermetallic of variable composition. Ongoing studies will examine the systematics of compound formation and diffusion of the semiconductor atoms as a function of the character of the overlayer.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research under Grant No. N00014-83-K-0579 and by the University of Minnesota Microelectronics and Information Sciences Center. The Synchrotron Radiation Center (SRC) is supported by the National Science Foundation. We gratefully acknowledge the cheerful assistance of the staff of the SRC.

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