Critical development stages for the reactive Cr-GaAs(110) interface

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High-resolution synchrotron radiation photoemission studies provide a detailed microscopic view of reactions at a refractory-metal/GaAs interface. Core-level and valence-band results indicate weak interaction between the Cr adlayer and the substrate at low coverage, i.e., no reaction products are observed although the Fermi level is pinned by ~ 1 Å. Instead, a metastable Cr overlayer forms and, at a critical coverage of ~ 2 Å, it triggers extensive substrate disruption. A model is presented to account for the reaction onset. Between ~ 2 and ~ 8 Å the morphology changes rapidly, corresponding to atomic intermixing and formation of Cr—Ga and Cr—As bonds. Arsenic out-diffuses readily through the intermixed region and is present in chemical states corresponding to a Cr-As phase and surface-segregated As. Gallium out-diffuses very little, but it too forms a Cr-Ga phase. At coverages of ~ 50 Å the valence bands are dominated by Cr *d* states and resemble those of Cr metal, but core studies show that arsenic is still present in substantial quantities ($\sim 20\%$ of original level).

I. INTRODUCTION

The microscopic properties of interfaces between dissimilar materials have come under increasingly critical scrutiny in the last few years. Great strides have been made possible in part by advances in experimental surface-science techniques and in part by rapidly improving schemes for calculating the electronic properties of overlayers on various substrates. In light of the significance of interface phenomena, it is not surprising that many important studies have addressed questions related to the chemical nature of the adatoms, clustering, bonding, intermixing, and the nature of the compounds which form.[1,2]

Much of the research dealing with metal/semiconductor interfaces has emphasized Si with overlayers of noble, near-noble, and simple metals,[1–9] or compound semiconductors with overlayers of the noble and simple metals, with emphasis on GaAs(110).[1,2,10–18] In contrast, much less is known about interfaces involving refractory or rare-earth metals on semiconductors, although recent work with Si (Refs. 19—25) has demonstrated the importance of such systems. Indeed, as noted recently by Oelhafen, Freeouf, and co-workers,[25] one should expect a richness of phenomena for *d*- and *f*-band metal interactions with compound semiconductors.

We have recently undertaken an examination of *d*- and *f*-metal interfaces with GaAs(110). The first results for Cr are presented in this paper. These synchrotron radiation photoemission studies reveal a complex interface with the following properties:

(1) Cr atoms interact weakly with GaAs(110) for low coverages and have little effect on the substrate valence states for overlayers of 0—2 Å. In this range, two-dimensional Cr patches grow laterally, attenuating emission from GaAs states while contributing states within ~ 2 eV of E_F.

(2) Surface- and bulk-sensitive studies show that the Schottky-barrier height is stabilized before the onset of reaction.

(3) Substrate disruption and reactive interdiffusion is triggered at $\Theta=\Theta_c \simeq 2$ Å, where Θ_c denotes critical coverage. Major changes occur for $2 \lesssim \Theta \lesssim 8$ Å. At $\Theta=\Theta_c$, As is released from GaAs-type bonds and its binding energy *increases*, suggesting that it segregates to the surface or near-surface region. At the same time, Cr—Ga and Cr—As bonds form. For both of these, core-level shifts to lower binding energy are observed. No evidence is found for extensive ternary-compound formation.

(4) The reacted layer is relatively stable between ~ 8 and ~ 20 Å, and covering up starts near 25 Å. At heavy coverage, the valence band of the overlayer converges to that of Cr. Nevertheless, core-level studies show the presence of As in two chemical states for $\Theta \sim 50$ Å and much greater out-diffusion of As than Ga.

II. EXPERIMENTAL TECHNIQUES

Photoemission studies were done at the University of Wisconsin Synchrotron Radiation Center Tantalus light source using the 3-m toroidal-grating monochromator. For the high-resolution measurements reported here, the pass energy of the cylindrical mirror electron-energy analyzer (CMA) was set at 15 eV to give a total resolution of 400 meV for the As core levels at $h\nu=85$ and 280 meV, and for the Ga cores at $h\nu=60$ eV (250 and 230 meV, respectively, for bulk-sensitive measurements at 50- and 30-eV photon energies). For the valence-band studies, the resolution was 250 meV. Typical counting rates were 10^4 counts/sec at the Ga or As $3d$ core peaks and 10^3 for the maximum emission of the valence bands. This compromise between resolution and counting rate allowed sensitive measurements of changes in the core and valence-band states as the interface reaction proceeded. Such high-resolution work is absolutely essential if different bonding configurations are to be observed for the

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interface species. The overall precision in determining binding energies is estimated to be 0.05 eV. The photoelectron collection geometry had the sample normal coincident with the acceptance annulus of the analyzer in s polarization, and the angle of incidence of the beam was approximately 45°. Low energy electron diffraction (LEED) studies were conducted to investigate the morphology of the Cr overlayer.

GaAs(110) samples obtained from Crystal Specialties, Inc. were prenotched, etched, and cleaved *in situ* immediately before the measurements began (n-type with Si doping at 4×10^{18} cm^{-3}). Mirrorlike surfaces measuring 4×4 mm^2 were obtained routinely, and their microscopic quality was judged with valence-band and core-level photoemission to ensure homogeneous surfaces with flat-band conditions. Comparisons for Cr overlayers on surfaces where E_F was initially pinned by cleavage defects showed no systematic differences.

All studies were conducted in an ultrahigh-vacuum system which ordinarily operates in the mid 10^{-11} Torr range, as described elsewhere.[26] These low pressures were improved still further by evaporation of Cr. During evaporation, the pressure never rose above 2×10^{-10} Torr, and no evidence of surface contamination was observed. An Inficon thickness monitor was used to determine deposition rates. For low coverages, the thickness was determined by timed evaporations after stabilization of rate at ~1 Å/min. All depositions and studies were conducted at room temperature. In this paper, angstrom units are used with 1 Å=0.9 ML (ML denotes monolayer) corresponding to the surface atomic density of GaAs(110), 8.9×10^{14} atoms/cm^2. We do not use monolayer units because to do so might suggest epitaxy—our results do not show epitaxy.

The spectra shown here represent numerous cleaves and repetitive evaporations. Comparisons of spectra for interfaces produced by a single heavy deposition and those obtained incrementally with the same total coverage showed no substantive differences. Reproducibility of the spectral features was excellent.

III. EXPERIMENTAL RESULTS

In Figs. 1 and 2 we show the effects of Cr deposition onto GaAs(110) for the valence-band region within 10 eV of E_F with corrections made to compensate for band bending. The bottom-most curve represents cleaved GaAs(110). The energy-distribution curves (EDC's) are normalized near 2 eV for coverages of 0–2 Å, and they show little change in the GaAs-derived structures, except for attenuation. However, at these coverages Cr-derived emission grows within 2 eV of E_F. The valence bands vary substantially between ~2 and ~8 Å, but they are relatively insensitive to coverage by the time $\Theta\simeq8$ Å. The valence-band (VB) spectra show gradual convergence to those of bulk Cr above ~20 Å.

In Figs. 3 and 4 we show Ga $3d$ and As $3d$ core EDC's with high surface sensitivity, ~6 Å for both Ga and As.[27] The energy scales have been corrected for changes in the Fermi-level position, with the horizontal lines at the bottom indicating ~700 meV band bending between the un-

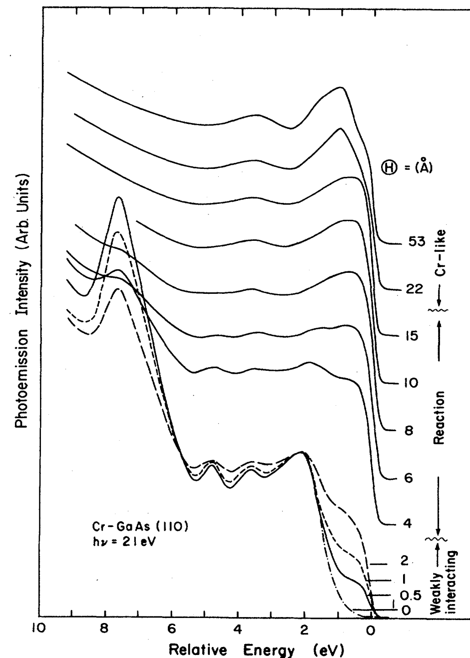

FIG. 1. Photoemission energy-distribution curves (EDC's) for Cr overlayers on cleaved GaAs(110) for $h\nu=21$ eV, showing weak interaction and the evolution of Cr states for coverages $0\leq\Theta\leq2$ Å (Cr induces states near E_F and attenuates those of GaAs). At a critical coverage of ~2 Å, the Cr overlayer triggers reactive mixing with GaAs and compound formation. Above about 20 Å, the Cr overlayer gradually converges to that of Cr metal.

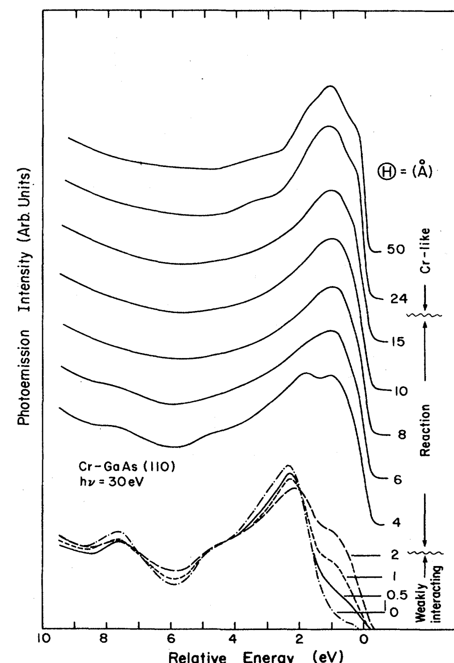

FIG. 2. EDC's for Cr overlayers on GaAs(110) for $h\nu=30$ eV, analogous to those of Fig. 1. Emission from states in the vicinity of 4 eV are better seen at 30 eV than at 21 eV and reflect hybrid As p–Cr d bonding states. With increasing coverage, the valence bands sharpen and these states are replaced by those of Cr metal.

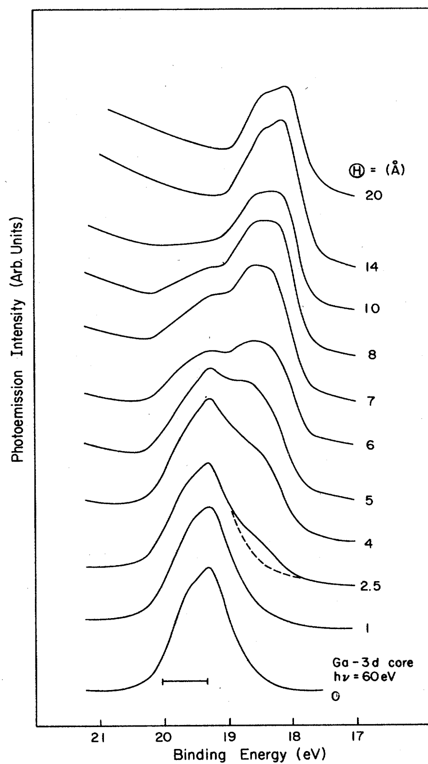

FIG. 3. Core-level results for the Ga 3d level at $h\nu=60$ eV. The magnitude of the shift of E_F upon formation of the Schottky barrier is shown by the horizontal line at the bottom, and corrections for this shift have been made. When reaction is triggered, a second Ga feature appears at lower binding energy and, with increasing coverage, it shifts further and ultimately dominates. Note that the curves are drawn for visual clarity; the magnitude of the total emission falls almost exponentially for $\Theta \leq 10$ Å, as shown in Fig. 5.

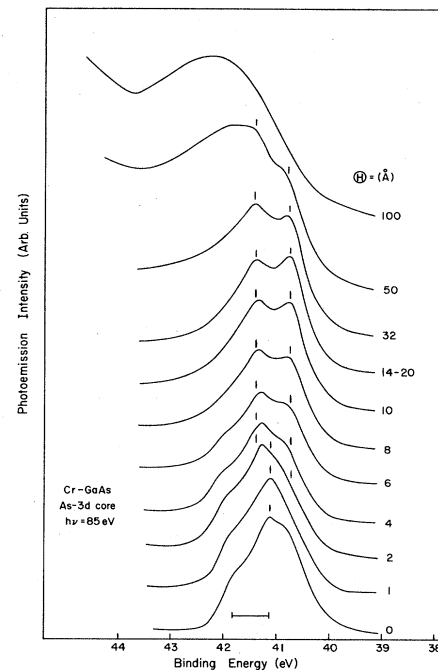

FIG. 4. Core-level results for the As 3d level at $h\nu=85$ eV, with the same escape depth as the Ga core of Fig. 3. Upon reaction, the As core shows the appearance of two new components corresponding to As, which surface-segregates, and to As which reacts to form a Cr-As phase. Cr 3p core emission can be seen to appear at about 32 Å and dominates by the time 52 Å is reached.

pinned and the fully pinned surface. Measurement of Ga 3d and As 3d core lines were also performed at 28 and 50 eV, respectively. The greater bulk sensitivity achieved at these photon energies (escape depth ~ 19 Å, Ref. 27) allows us to isolate the contribution from Ga and As atoms in the GaAs substrate, and to follow that contribution to coverages where the surface-sensitive spectra of Figs. 3 and 4 are dominated by reaction. These bulk components exhibit a rigid shift of 700 meV to lower binding energies from 0 to ~ 1 Å, but no further shift is seen. The rapid attenuation of the substrate contribution did not allow us to monitor reliably the peak position beyond 8 Å coverage. From these results we conclude that the Schottky-barrier height for the room-temperature Cr/GaAs(110) interface is already established at ~ 1 Å and is not modified by the reaction occurring above Θ_c.

The Ga 3d EDC's show little change in shape, a fact which could be related to reactions at the interface for $\Theta \lesssim 2$ Å (see Ref. 27 for detailed surface and bulk deconvolution of the Ga and As cores for cleaved GaAs). Above ~ 2 Å, however, new emission appears shifted to lower binding energy. Between ~ 2 and ~ 8 Å, it grows steadily and becomes dominant. For $\Theta \gtrsim 14$ Å, only the fully shifted Ga core levels are observed, and these attenuate with increasing coverage. Studies of the behavior of the center of mass of the reacted component show that it shifts steadily to lower binding energy with coverage.

EDC's for the As cores have more structure than those of Ga. At 1 Å coverage, the surface-shifted core on the low-binding-energy side of the main line[27] is attenuated but not completely suppressed. New As features appear for $\Theta \gtrsim 2$ Å. Line-shape analyses reveal three As species: As in GaAs, As at lower binding energy, and As at higher binding energy (analysis to be discussed in the next section). The shifted features grow with coverage as the chemical constituency of the probed region changes and the unshifted or bulk contribution is lost. For $8 \lesssim \Theta \lesssim 20$ Å there is little change in the spectra, except for the slight increase of the higher-binding-energy feature relative to the lower. At coverages of 50 Å, the contribution from the Cr 3p core is clearly visible and obscures further As analysis.

In Fig. 5 we show the total integrated core intensities normalized to the clean-surface intensity, $I(\Theta) = \ln[I(\Theta)/I(0)]$, to determine the changing number of Ga and As atoms within the probed region. The results show that the As content is much greater than Ga at high coverages. Indeed, Ga is invisible after ~ 30 Å while the As level at ~ 50 Å is still 20% of its starting value. The

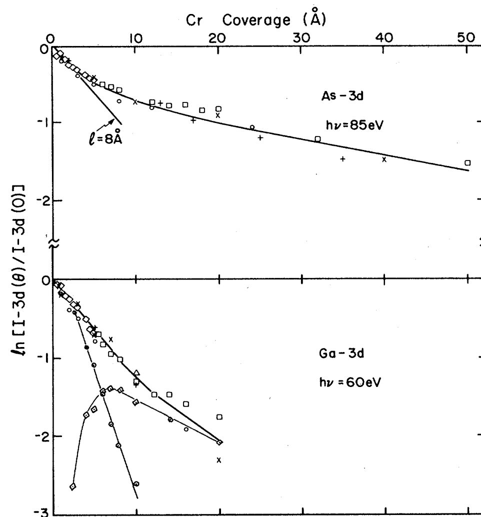

FIG. 5. Integrated emission for the As $3d$ (top) and Ga $3d$ (bottom) cores, normalized to those of the clean surface showing core-level attenuation. For As, a sharp break at 2 Å corresponds to the onset of reaction and release of As from the interface. As persists to the limit of our measurements (see Fig. 4). For Ga, the total attenuation is more nearly exponential, but core-level deconvolution shows the unreacted core to be attenuated very fast and the growth of the reacted phase to reach a maximum at about 7 Å.

different symbols indicate different cleaves and the scatter indicates the reproducibility of the measurements. For Ga, two additional lines are drawn, corresponding to the attenuation of the unshifted $3d$ and reacted components. Whereas the unshifted component vanishes very quickly, the growth and then more gradual attenuation of the shifted component indicates reaction and limited outdiffusion.

IV. DISCUSSION

A. Low-coverage regime

The low-coverage studies, $0 < \Theta \lesssim 2$ Å, make it possible to address questions regarding overlayer ordering, the strength of the Cr—GaAs bond, the onset of chemical reaction, and the mechanism which initiates the surface disruption.

The valence-band emission of Figs. 1 and 2 for $\lesssim 2$ Å of Cr on GaAs can be modeled by attenuated GaAs states plus new Cr-derived states. Analysis indicates a steady increase of emission near and below E_F with a substantial number of metal-induced states at E_F by 2 Å. The core studies demonstrate that the Ga and As $3d$ emission is unshifted and unbroadened—only the surface core-level shift is lost (Figs. 3 and 4). Qualitative information on the morphology of the Cr overlayer is obtained from the evolution with coverage of the LEED pattern. The 1×1 pattern from the substrate was observed to fade progressively into the increasing background and disappear between 2 and 3 Å with no evidence for a metal-induced superstructure. We can therefore exclude the formation of an epitaxial layer of Cr on the GaAs(110) surface. The persistence of the substrate pattern at coverages larger than 1 ML shows that a substantial fraction of the GaAs surface is still uncovered and indicates a nonuniform distribution of the metal atoms as observed, for example, by Skeath *et al.*[13] for Ga on GaAs(110). No evidence for Cr adatom ordering on the substrate was found (epitaxy).

Our core-level, valence-band, and LEED results show that Cr adatoms interact weakly with the substrate during the first stage of interface formation. Changes observed in the valence bands of Figs. 1 and 2 show the Cr contribution to be dominated by states 0.5—1 eV below E_F, i.e., by d states which appear much narrower than for bulk Cr. With increasing coverage, the valence-band emission near E_F grows smoothly and a gradual transition to a system having a large number of states near E_F at 2 Å is observed. This is consistent with what might be expected for a weakly adsorbed layer of Cr patches growing laterally with coverage until reaction starts at ~ 2 Å.

The two-dimensional patchwork of Cr atoms which grows on GaAs should not be construed as a layer of Cr having bulk Cr properties. Instead, the photoemission results show narrower d states than for bulk Cr, with evolution toward metallic character. These patches are best viewed as Cr atoms bonded strongly to other Cr atoms with only weak interaction with the substrate. Their instability is reflected by the transition from weak interaction to strong intermixing at the critical coverage of ~ 2 Å.

This patch model is similar to the cluster model proposed recently by Zunger[10] when he considered the energetics of the Al/GaAs interface at low coverage. His calculations indicated that Al_n molecular bonding in three-dimensional (3D) clusters would be energetically favorable to Al—GaAs bonds. As with Al/GaAs, we propose that the Cr patches provide the energy necessary to create defects to pin the Fermi level. However, it must remain for a total-energy calculation to examine the stability of the cluster and correlate its instability with the triggering of surface disruption. It should be noted, finally, that studies of Ce/Si(111) provided compelling evidence for 3D island growth[23] and disruption at a critical coverage. In that case, the metal-induced d and f states appeared well below E_F—a "fingerprint" of transition-metal clusters observed in all photoemission studies to date[28]—and the attenuation of the unshifted core was less than expected for uniform coverage by a highly efficient scatterer like Ce.[23]

B. Intermediate-coverage or reactive regime

The results for the intermediate phase, $2 \lesssim \Theta \lesssim 20$ Å, shed light on questions related to variations in bonding, changes in morphology, and compound formation.

If the first stage is characterized by the transition from weak interaction to the instability threshold, the second stage is associated with very strong interaction and intermixing. Core-level analysis shows surface disruption triggered at 2 Å, as discussed above. At that point, the As core line shape is complicated, exhibiting components at

higher and lower binding energy relative to the initial As position. Unfortunately, quantitative line-shape deconvolution in this reacted region is complicated by the close proximity of the different features at low coverage (overall separation 0.65, resolution 0.40 eV) and by the Cr $3p$ emission at high coverage. Nevertheless, semiquantitative analysis shows that *three* distinct As species are observed. Each has a well-defined binding energy which does not shift with coverage. Instead, the observed EDC's change in appearance because of changes in relative concentration of the different As species. At low coverage, As bonded in the GaAs configuration is still present within the escape depth of the photoelectron. At the same time, the second species appears at 0.4 eV lower binding energy (shoulder at $\Theta=4$ Å) and the third feature is present at 0.25 eV higher binding energy. From simple electronegativity considerations, the component at lower binding energy should be associated with reacted As in a Cr—As bond (Pauling electronegativity 1.81 for Ga, 2.18 for As, and 1.66 for Cr). The component at higher binding energy appears more like elemental As than As in GaAs and can be associated with surface-segregated covalently bonded As or, at least, As near the surface in a less ionic configuration than GaAs. It is then analogous to the final Si component often observed for metal/silicon systems (see Ref. 23 for a detailed discussion of the Ce/Si interface, for which line-shape analysis showed the onset of reacted and segregated Si species). The three As components exhibit the following hierarchy: reacted As in a CrAs phase, unshifted As in GaAs, shifted As in a surface-segregated state.

For $\Theta=4$ Å, the CrAs component accounts for $\sim$ 40% of the total As emission, and the other two are approximately equal. With increasing coverage it grows relative to the others and the unshifted component is attenuated rapidly. Analysis at high coverage, $\Theta\simeq14$—20 Å, shows As in the outer layers of the interface to be $\sim$ 67% reacted As with the remainder of the EDC accounted for by surface As and the emerging Cr $3p$ core EDC. From analysis of the simpler Ga $3d$ core EDC's, to be discussed shortly, we can conclude that the unshifted As component is negligible at ~10 Å because residual Ga in the GaAs state is fully attenuated (intensity e^{-3} of original intensity). Hence, the core analysis for As shows that the reacted phase first appears at 2 Å, grows quickly to dominance, and persists to very high coverage with a line shape different from the simple As $3d$ doublet by a contribution from surface As (and ultimately Cr).

Support for the identification of the high-binding-energy component with surface As comes from its continued presence at high coverage but also from studies of As on GaAs surfaces by van der Veen *et al.*[29] They showed the binding energy of free As on GaAs(100) to be greater than that of As in a Ga—As bond. Furthermore, Ley *et al.*[30] reported the binding energy of crystalline As to be 41.7 eV, slightly greater than that of our surface As component.

The results for these As species are particularly interesting because they show that when reaction is triggered there is a segregated component as well as a reacted component. This suggests a complex morphology involving covalently bonded As coexistent with the CrAs phase when the total extent of the interface is limited to a few monolayers (2 ML average Cr deposition plus an unknown thickness of disrupted GaAs).

The behavior of Ga is very different from As upon disruption of the GaAs surface. Line-shape analyses for the Ga $3d$ EDC using two sets of spin-orbit-split doublets corresponding to unreacted Ga and fully shifted Ga proved unsuccessful. Even for the fully shifted Ga $3d$ EDC for 20 Å (Fig. 3), the high-binding-energy component of the doublet appears too strong, based on comparison with the branching ratio of Ref. 27 for clean GaAs. We suggest, therefore, that Ga atoms are present in a variety of slightly different environments in the intermixed regime and that a single well-defined phase does not form.

The core-level EDC's show the total shift to be 1.25 eV at 20 Å coverage, a shift which exceeds that for free Ga.[31] An analogous shift was observed in x-ray photoelectron spectroscopy (XPS) studies of thick layers of Ti on GaAs(100) (Ref. 32) and was attributed to formation of a Ti-Ga intermetallic. The formation of a similar Cr-Ga intermixed phase which exists over a range of stoichiometries is consistent with our results. The spatial extent of the Cr-Ga phase can be estimated from the attenuation of the total, the unshifted, and the shifted Ga $3d$ emission. As shown in Fig. 5, the total emission falls rapidly with coverage, appearing exponential with an attenuation coefficient of ~8 Å for $\Theta\leq10$ Å. This is misleading, however, because the EDC's of Fig. 3 show that the unshifted Ga is negligible above ~14 Å. Better insight comes from the attenuation of the unshifted core, which drops to $\sim e^{-3}$ by 10 Å (attenuation length 3 Å). At the same time, the reacted component grows with coverage to a maximum at about 7 Å, and is then slowly attenuated at higher coverage (attenuation length 13 Å). From these facts we conclude that the unreacted surface retreats from the initial surface because of extensive disruption (the apparent attenuation length is too short to be explained by escape-depth-driven attenuation through an overlayer). The reacted-Ga content in the outer layer is greatest at ~7 Å. Hence, we conclude that reactions involving Ga are very limited in scale and that the interface-reaction products act as diffusion barriers (or chemical traps) for Ga but not for As. Our observations that Ga is quickly depleted from the interface while As is not and that reacted As has a constant binding energy throughout the surface, suggestive of unchanging chemical environment, show that the products of the room-temperature (RT) reaction are predominantly binaries rather than ternaries involving Ga, As, and Cr.

Comparison of the valence-band EDC's for the intermixed phase with those for the analogous intermixed phase at the Cr/Si interface shows several similarities. Indeed, one should expect that many of the ideas developed for bonding of metals with silicon should be applicable to bonding with arsenic.[33] In particular, experiment and theory for Cr/Si showed that Si p—Cr d bonding states were formed.[20,22] These bonding states extended to ~6 eV below E_F, were dominated by Cr d states, and contributed relatively unstructured emission to the EDC's

in our photon-energy range because of the larger cross section of the nonbonding d states. Hence, we postulate the existence of such bonds for the Cr-As phase and identify the states close to E_F as being derived primarily from nonbonding Cr d states. In this model the observed sharpening of the valence bands with increasing coverage after $\Theta \simeq 20$ Å reflects the formation of a Cr-rich overlayer. The relatively unchanging appearance of the valence-band spectra between ~ 10 and ~ 20 Å is consistent with out-diffusion of As into the overlayer and continued Cr-As phase formation. The nearly constant As content of the outer layers is shown by the slight attenuation of the total As $3d$ emission between 10 and 20 Å (Fig. 5).

C. High-coverage or covering-up regime

The photoemission results of Figs. 1–5 show that after 20–25 Å the valence band converges to that of bulk Cr. These results are somewhat misleading, however, because photoemission is most sensitive to states having the highest photoionization cross sections. For the transition-metal/semiconductor interfaces this implies dominance by nonbonding d states over nonmetal-derived s and p states. As has been shown for interfaces involving silicon,[8,20,22] d states which hybridize with the p states of Si (bonding or antibonding) are less resolved at low energy than at high.[9] Hence, as we find here, core-level studies of the nonmetal are important to adequately model the interface morphology.

The As $3d$ core results of Figs. 4 and 5 provide clear evidence that As continues to out-diffuse. Both the Cr-As phase and surface-segregated As are present for high coverage, with the relative importance of the surface component growing compared to the reacted component. Overlap of the Cr $3p$ and As $3d$ core emission makes it impossible to follow the As content of the outer layers after $\Theta \geq 50$ Å, but continued out-diffusion seems likely. We would then anticipate that the surface component would continue to grow relative to the reacted As because of gradually reduced out-diffusion of As through successively thicker reacted layers. Significantly, the unvarying core line shapes and binding energies indicate that the local environment of the As atoms does not change—reaction of Cr with As from the bulk then continues, limited only by the availability of As. Indeed, from Fig. 5 we see that the total As content of the outer few monolayers is $\sim 20\%$ of the concentration of the cleaved surface for 50 Å of Cr coverage. Note also that the concentration of Ga at this surface is negligibly small.

V. CONCLUSIONS

One of the most significant results of this study was the demonstration of a critical coverage at which reaction is triggered. Qualitatively, this triggering has been correlated to energy instabilities due to Cr aggregates. It remains, however, to form a quantitative picture of such a surface disruption. Such studies represent the logical extension of the interesting models for electronic interactions at surface and are now possible with superfast supercomputers. Experimentally, it remains to demonstrate whether the triggering phenomenon is common to other metal/semiconductor systems by considering systems likely to share the characteristic and systems likely to react immediately. Such studies are presently underway, as are temperature-dependent investigations of surface ordering.

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