

Metal/GaAs interface chemical and electronic properties: GaAs orientation dependence

S. Chang and L. J. Brillson

Xerox Webster Research Center, Webster, New York 14580

D. F. Rioux

Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

Y. J. Kime

Department of Physics, Syracuse University, Syracuse, New York, 13210

P. D. Kirchner, G. D. Pettit, and J. M. Woodall

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 30 January 1990; accepted 2 April 1990)

Synchrotron radiation photoemission results for metals on intentionally misoriented molecular-beam epitaxy GaAs(100) surfaces reveal an orientation-dependent interfacial chemistry and Schottky barrier heights at low temperature (90 K). Previous measurements for different metals on aligned GaAs(100) surfaces show a Fermi stabilization energy range of 0.95 eV. However, for Au and Al on 2° misoriented specimens, narrower ranges are observed: 0.65 eV for GaAs surfaces cut towards [110] and 0.45 eV for surfaces cut towards [111] with either Ga or As dangling bonds perpendicular to the step edges. The decrease in the range of the Fermi level stabilization energies is mainly due to the increase in Schottky barrier heights for Al contacts on misoriented specimens, where a more pronounced interface reaction is observed. Our results indicate that the observed degree of chemical reaction and diffusion increases in the order of GaAs(100) surfaces tilted toward [110], [111]A, and [111]B. Our bonding results emphasize the importance of interfacial chemistry and the perfection of the substrate GaAs in the metal/GaAs junction electronic properties.

I. INTRODUCTION

Metal/semiconductor contact electronic properties have been a subject of intensive study due to both technological and fundamental interests.^{1,2} Past work on the subject has indicated that junction electronic barrier heights are insensitive to the condition of the interface. For example, metals on melt-grown GaAs [such as liquid-encapsulated Czochralski (LEC)] consistently produce Fermi level pinning near the midgap. Only in the last few years, dependence of the junction electronic barrier height on the metal work function has been observed, accompanied by the increase of chemical and structural perfection of semiconductors.³ Recent work has shown that chemically suppressed, abrupt junctions (formed at reduced temperature, less than 100 K) incorporating high-quality GaAs [molecular-beam epitaxy (MBE)] in a ultrahigh vacuum (UHV) environment can exhibit a near-ideal Schottky behavior.⁴⁻⁶ Deviation from the ideal behavior can occur at room temperature where interface chemical interactions are pronounced; this degradation produces extrinsic states. Comparison of low temperature versus room temperature interfaces serve to indicate a role of the interface chemical conditions in the electronic barrier behavior.

In this paper, we present a soft x-ray photoemission spectroscopy (SXPS) study of metals on intentionally misoriented-GaAs(100) interfaces. We examine specifically the effect of steps on the interfacial chemistry and the electronic barrier height. Our results show that the chemically active sites created by the misorientation of the surface can modify elec-

tronic properties from a near-ideal case obtained for oriented MBE-GaAs specimens.

II. EXPERIMENTAL PROCEDURE

All MBE-GaAs(100) specimens used in this experiment were *n*-type ($5 \times 10^{15}/\text{cm}^3$, Si), 7500 Å thick, grown on GaAs substrates (Sumitomo Electric). The misoriented specimens were grown on staircase-like GaAs(100) surfaces, which have been cut 2° off axis toward three different crystal directions: [110] {the (100)2°-[110] surface}; [111] with steps consisting of Ga dangling bonds {the (100)2°-[111]A surface}; and [111] with steps consisting of As dangling bonds {the (100)2°-[111]B surface}. The uncertainty in orientation of the substrate was $\pm 0.1^\circ$. All specimens were capped with $> 1000\text{-}\text{\AA}$ As prior to the removal from the MBE system and then stored in a N₂ environment. Thermal cleaning of the surface in UHV involved a number of ramped anneals up to 570 °C and produced a clean, ordered surface. Pressures during metal deposition were 2×10^{-10} Torr for Al and 6×10^{-10} Torr for Au. A quartz crystal oscillator measured the thickness of the overlayer. A closed-cycle He refrigerator provided the cooling for the specimen (~ 90 K as measured by a thermocouple).

We performed SXPS experiments using synchrotron radiation generated by the 1-GeV storage ring at the University of Wisconsin, Madison, Wisconsin. We examined bulk (surface) sensitive energy distribution curves (EDCs) for As 3*d* and Ga 3*d* core levels using photon energies of 60 eV (100 eV) and 40 eV (80 eV), respectively. Comparison of bulk

versus surface sensitivity spectra enabled separation of the band bending from the chemical shifts of each core level. We employed valence band (VB) spectral features and the Ga 3*d* to As 3*d* core level intensity ratio to determine the quality and the stoichiometry of the thermally-cleaned surface.^{6,7} No evidence of free Ga was observed for these surfaces. The rigid core level shifts and the initial Fermi level (E_f) position above the valence band maximum (VBM) determined the E_f position in the band gap. The intensity of core levels provided a measure of the interface morphology. Overall resolution of the monochromator and electron spectrometer was 0.25–0.35 eV, which was determined by the width of the E_f edge from a 300 Å Au film evaporated onto a thermally cleaned GaAs(100) surface.

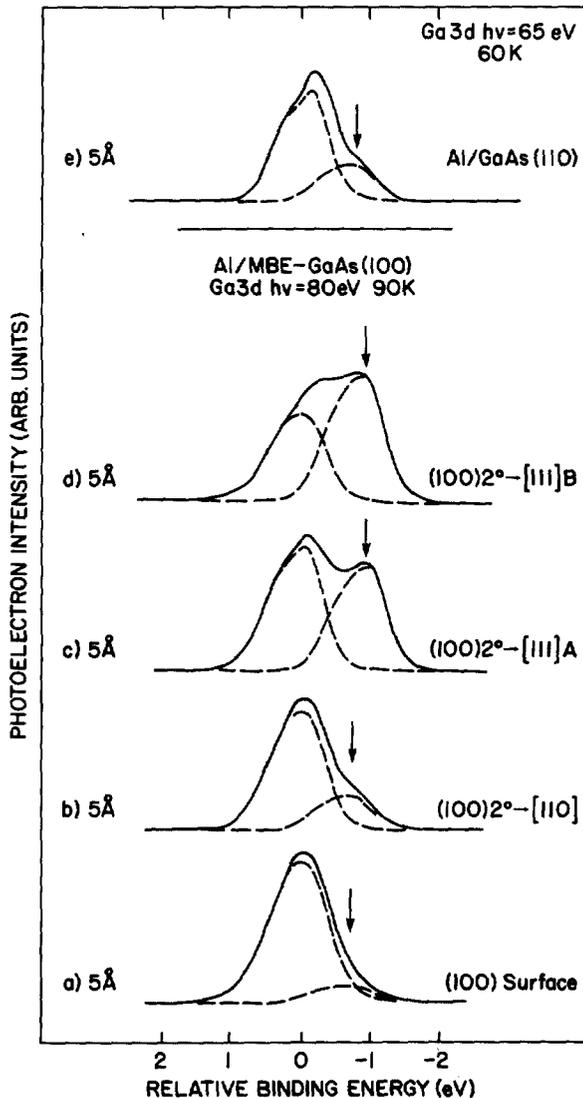


FIG. 1. Ga 3*d* core level spectra at 5-Å Al deposited on clean GaAs surfaces for the (100) and its vicinal surfaces. 5-Å Al on UHV-cleaved GaAs (110) (Ref. 8) shown for comparison. Dissociated Ga peaks (indicated by arrows) reflect extent of reaction, which increases with increasing density of active sites.

III. RESULTS

A. Orientation-dependent interfacial chemistry

Figure 1 depicts surface-sensitive Ga 3*d* core spectra from interfaces formed by deposition of 5-Å Al onto various substrates to demonstrate the effect of substrate orientation. Spectrum 1(a) represents the result from the oriented (100), 1(b) the (100) 2°-[110], 1(c) the (100)2°-[111]A, and 1(d) the (100)2°-[111]B surface. Fig. 1(e) shows an EDC for the Ga 3*d* from the 5-Å Al/GaAs(110) interface taken at a different photon energy with similar probing depth.⁸ All EDCs are normalized to the same peak heights to emphasize line-shape changes. Zero on the binding energy scale is the Ga 3*d* position from the initial clean surface. These spectra have been compensated for band bending shifts. Results of the deconvolution of the Ga 3*d* spectra are presented by the dashed lines, which reveal the familiar components of the substrate Ga plus an additional component at lower binding energy due to dissociated Ga embedded in Al overlayer. A 5-Å Al deposition has a marginal effect on the Ga 3*d* core for the oriented substrate. For the (100)2°-[110] surface, the Ga 3*d* dissociated component is clearly visible, whose relative magnitude with respect to the substrate is comparable to what is observed for the Al/GaAs(110) interface [Fig. 1(c)]. The relative intensity of the Ga 3*d* dissociated component versus the substrate component further increases for the Al/GaAs(100)2°-[111]A interface as compared to the (100)2°-[110] interface. The maximum effect of Al on the GaAs substrate occurs for the (100)2°-[111]B surface.

Ga 3*d* core intensities attenuate rapidly for the (100) surface as a function of Al coverage. This attenuation rate decreases from the (100) surface, to the (100)2°-[110], to the (100)2°-[111]A, and then to the (100)2°-[111]B. The As 3*d* core level intensity attenuates rapidly as a function of Al coverages for all systems. EDCs of the As 3*d* core exhibit minimal line-shape changes upon Al deposition for all MBE specimens. EDCs of the Al 2*p* core reflect interface bonding in the submonolayer regime.

We also do not observe major line-shape changes upon Au deposition on the various MBE specimens mentioned. An increase in out-diffusion in the order of (100), (100)2°-[110], (100)2°-[111]A, and (100)2°-[111]B is evident in the attenuation of both Ga and As 3*d* core intensities.

B. Orientation-dependent Fermi level stabilization energy range

Figure 2 depicts the E_f movement referenced to the VBM as a function of metal coverages observed for Al and Au interfacial with MBE GaAs(100) and its vicinal surfaces. The table inset defines the symbols for each metal/MBE-GaAs system. The starting positions of E_f are at 1.2–1.3 eV above VBM, independent of the orientation of the initial surface. For all systems, no additional band bending is observed up to 1 Å of metal coverage, consistent with previous studies on metal/MBE-GaAs(100) junctions at low temperature.^{4,5} At the final coverage (10–12 Å) for all systems studied, the leading edge of the VB of the interface coincides (<0.1 eV) with the E_f position of the spectrometer. For the

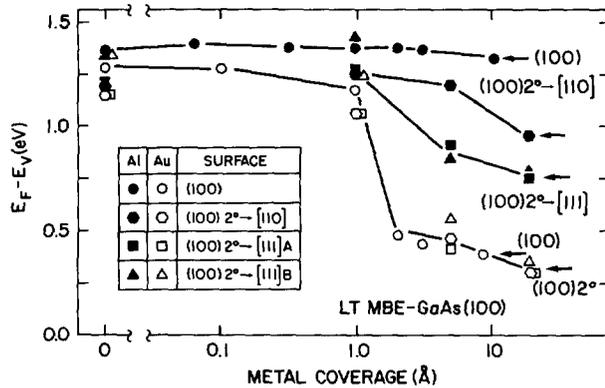


FIG. 2. Fermi level movements within the GaAs band gap as a function of Au or Al deposition for the same (100) oriented and misoriented surfaces as Fig. 1. Al band bending varies by > 0.5 eV for different orientations whereas Au band bending is relatively unaffected.

(100) systems, $E_f - E_{VMB} = 0.35$ eV and 1.25–1.3 eV resulted from 10-Å Au or 10-Å Al deposition, respectively. The range of E_f positions determined by the two metals is 0.9–0.95 eV. E_f movements due to Au deposition on vicinal surfaces differ slightly from the on-axis system. For all three misoriented GaAs(100) junctions, the $E_f - E_{VMB} = 0.3$ –0.325 eV for Au. In contrast, Al on misoriented GaAs(100) surfaces produces significant changes in band bending with respect to the oriented specimens. We observe $E_f - E_{VMB} = 0.95$ eV for the (100)2°-[110] surface and 0.75–0.77 eV for the (100)2°-[111] surfaces at a 12-Å Al coverage. The resultant range of E_f positions in the band gap thus decreases from 0.9–0.95 eV for the (100) surface to 0.65 eV for the (100)2°-[110] and to 0.45 eV for the (100)2°-[111] surfaces.

IV. DISCUSSION

A. Interfacial chemistry

The increasing intensity of the dissociated Ga 3d core in Fig. 1 indicates increased interfacial reaction in the order of [100], (100)2°-[110], (100)2°-[111]A, and (100)2°-[111]B. The rapid and similar attenuation of the As 3d core intensity for all systems rules out significant effects due to island formation. For the Al/GaAs interface, a replacement reaction with AlAs and dissociated Ga as reaction products is thermodynamically favorable and widely observed.^{7,9} For surfaces in the above sequence, we obtain ratios of the dissociated Ga 3d peak to the substrate Ga 3d peak of 0.15, 0.30, 0.85, and 1.44 respectively.

The reconstruction of GaAs(100) vicinal surfaces are not known. However, our photoemission data show that the normalized Ga 3d to As 3d intensity ratio for the misoriented surfaces is within 10% of that obtained for the (100) surface, which represents a Ga-rich surface.^{4–7} Scanning tunneling microscopy studies of the MBE-GaAs(100) surface shows a Ga-rich reconstruction when the specimen is heated to about 550 °C.¹⁰ Assuming our starting surfaces are Ga-terminated, we illustrate in Fig. 3(a)–3(c) the unreconstructed, staircase-like GaAs(100) surfaces 2° misoriented

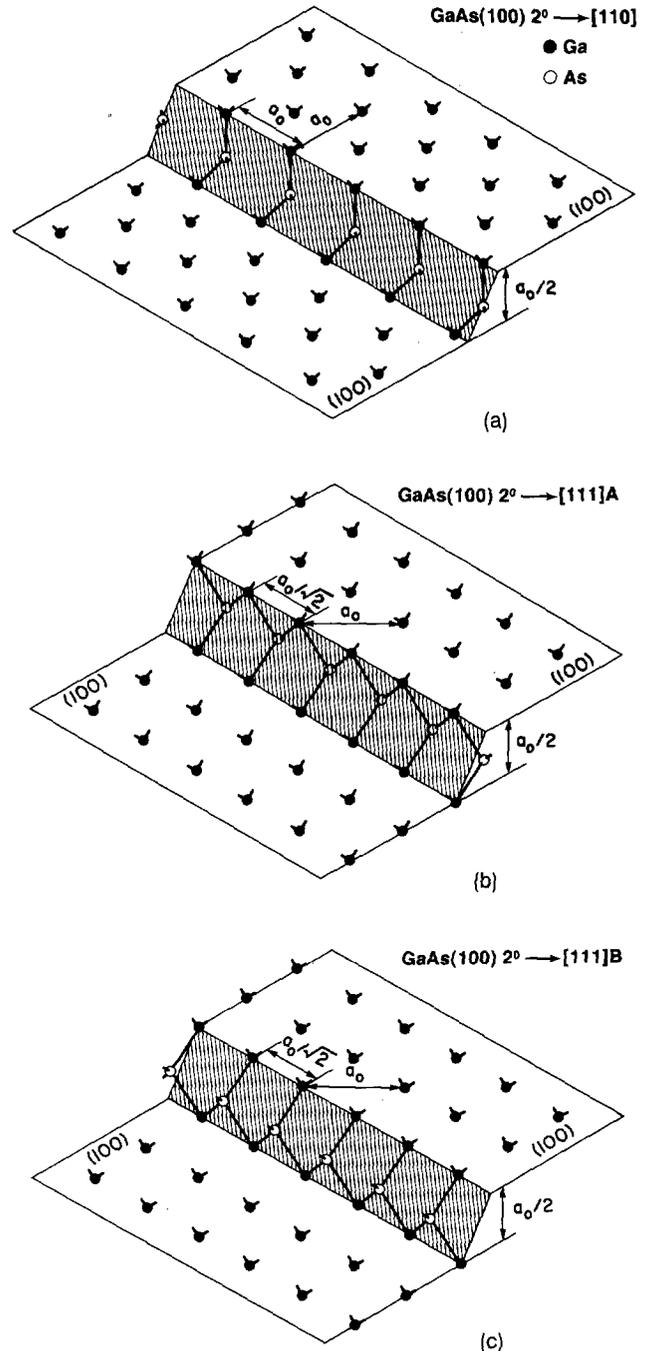


FIG. 3. (a) Unreconstructed, staircase-like GaAs(100) surfaces 2° misoriented in directions of [110], (b) [111] with Ga dangling bonds perpendicular to the steps, and (c) [111] with As dangling bonds perpendicular to the steps.

in directions of [110], [111] with Ga dangling bonds perpendicular to the steps, and [111] with As dangling bonds perpendicular to the steps, respectively. Such a 2° tilting results in a step height of $a_0/2$ (a_0 : lattice parameter) = 2.828 Å and produces an average of 81 Å separations between steps, or a density of 1.234×10^6 steps/cm. The steps on the (100)2°-[110] surface are parallel to the [100] direction with nearest neighbor spacing of a_0 , while the steps on the (100)2°-[111] surface are parallel to the [110] direction

with nearest neighbor spacing of $a_0/\sqrt{2}$. The calculated surface densities of active sites for the vicinal surfaces are $2.18 \times 10^{13}/\text{cm}^2$ for the $(100)2^\circ$ -[110] and $3.09 \times 10^{13}/\text{cm}^2$ for the $(100)2^\circ$ -[111]. The steps on $(100)2^\circ$ -[110] surface consist of As atoms with dangling bond 45° with respect to the step. On the $(100)2^\circ$ -[111] surface, the dangling bond is perpendicular to the step and consists of either Ga (type A) or As (type B) atoms. Thus, the degree of the interfacial reaction increases relative to the density of these structural defects, which in principle are also chemically active sites. For Au, we observed an increasing in As and Ga out diffusion in the same order. Although the reconstruction of the vicinal surfaces are not yet established, the unreconstructed pictures presented in Fig. 3 highlight the differences in atomic density and nature of the associated dangling bonds.

For the $(100)2^\circ$ -[111] surfaces with the same density of chemically active sites, the observed higher degree of the interfacial reaction of the 2° -[111]B face (As dangling bonds) than the 2° -[111]A face (Ga dangling bonds) underlines the importance of the local atomic bonding on the steps in the interfacial reaction. The higher reactivity of the As terminated surface than the Ga terminated surface has been discussed in the literature.^{11,12} Gatot and Lavine¹¹ have proposed that the unshared pair of group V electrons accounts for the pronounced chemical difference between the group V and group III-terminated semiconductor surfaces. They have reported preferential chemical etching as well as oxidation depending on the crystallographic orientation of the III-V semiconductor in the order of $[111]B > [111]A \approx [100] > [110]$. Thus, simple chemical arguments appear to explain the difference observed between $(100)2^\circ$ -[111]A and $(100)2^\circ$ -[111]B.

Following the same argument, the $(100)2^\circ$ -[110] surface should have been more reactive with Al than the $(100)2^\circ$ -[111]A surface since it contains more As dangling bonds. This is at odds with both our SXPS and the chemical etching¹⁰ studies. However, an examination of the exposed step atoms for both suggests that [111]A As atoms in the selvage also may play an active chemical role. Different reconstructions of the vicinal surface may also play a role.

Compared to the LEC-(110) surface, our results show that the oriented MBE-(100) surface appears more stable than the cleaved LEC-(110) surface against reaction with Al. The ratio of the dissociated Ga $3d$ peak to the substrate Ga $3d$ peak shown in Fig. 1 for the (110) surface is 0.36, a value comparable to that from the MBE- $(100)2^\circ$ -[110] surface (0.3) but significantly higher than that from the MBE-(100) surface (0.15). Anderson *et al.*¹³ have shown that the Al growth on the (110) surface at 60 K appears uniform. Thus the Al/MBE-(100) and the Al/LEC-(110) interfaces are different mainly in the extent of the interfacial reaction. For the thermally treated (100) surfaces used in our studies, it is reasonable to expect an As-deficient surface. Larsen and Chadi¹⁴ have proposed that stable GaAs(100) surfaces consist of a larger ordered surface fraction of As vacancies, with dimer ordering of the remaining surface atoms, and a much larger energy gap. In contrast, the reconstructed GaAs(110) surface is less likely to persist under a metallic layer.¹⁵

B. Band banding

Slight misorientations of the GaAs substrate produce large changes in the range of E_f stabilization energies at metal/GaAs junctions, as demonstrated by Fig. 2. The decrease in the E_f stabilization energy range appears to correlate with the increase in the atomic density of active sites on the vicinal surfaces. These sites influence the extent of the interfacial reaction, which is capable of creating electrically active sites at the interface, moving E_f further toward the midgap for Al interfaces. Metal-induced extrinsic interface states have been observed previously.^{6,16,17}

The invariance of the E_f position with respect to the substrate orientation at the initial clean surface and in the low-coverage regime can be explained by photovoltaic charging due to the photoemission process. M. H. Hecht has recently suggested¹⁸ and we have subsequently confirmed¹⁹ that such effects can be considerable at low temperatures. At high coverages, however, such charging can be shorted out by the metallization of the surface. In this study, the matching of the E_f of the interface with that of the spectrometer and the uniform growth of the metal overlayer rule out the possibility of significant photovoltaic charging at high metal coverages.

Using Duke and Mailhot's²⁰ self-consistent electrostatic calculation, one can establish a relationship between the junction electronic barrier height and the density of electrically active sites at the interface. In Fig. 4, we show the result of the calculation to account for barrier heights at Au and Al on misoriented surfaces versus the metal work function. The

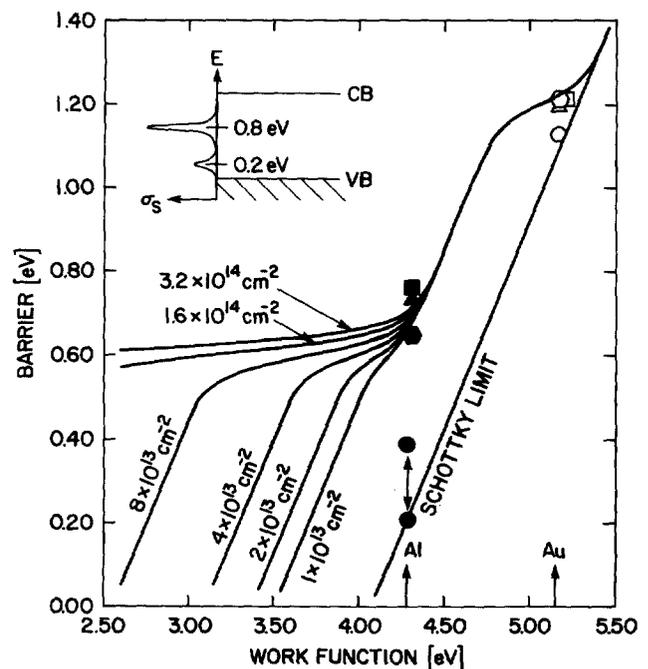


FIG. 4. Self-consistent electrostatic analysis of the metal/GaAs (100) data points. The family of curves represent acceptor densities of $3 \times 10^{13} \text{ cm}^{-2}$ acceptors at $E_{\text{VBM}} + 0.2 \text{ eV}$ and the indicated densities at $E_{\text{VBM}} + 0.8 \text{ eV}$ (see inset energy diagram). Deviations from the Schottky line correspond to midgap densities, which scale with active site densities for the various orientations.

interface charge states are acceptors at 0.2 and 0.8 eV above the VBM. The density of the 0.2 eV acceptor state is $3 \times 10^{13}/\text{cm}^2$ and the density of the 0.8 eV acceptor state is allowed to vary in order to produce the series of plots shown. States at these energies have been observed previously by using cathodoluminescence spectroscopy (CLS).^{6,16} Although there are numerous speculations about the physical origin of deep levels in GaAs,²¹ both SXPS⁵ and CLS^{6,16} suggest that excess As at the interface is associated with the 0.8 eV level. The family of curves depicted in Fig. 4 also describes the barrier height–work function relationship for previous SXPS results of metals on room temperature MBE-GaAs(100) surfaces.^{5,22} The Schottky barrier heights follow from Fig. 2. Symbols for Au or Al on the (100), the (100)2°-[110], the (100)2°-[111]A, and the (100)2°-[111]B surface correspond to those in Fig. 2. The results of Au and Al on oriented (100) surfaces demonstrate a near-ideal Schottky behavior. The double-headed arrow indicates the spread in Al/GaAs(100) barrier heights observed in several different SXPS as well as internal photoemission measurements.^{4,22,23} Comparison of theoretical and experimental data indicates low acceptor state densities ($< 10^{13}/\text{cm}^2$) at metal/oriented GaAs(100) interfaces. For misoriented specimens, the Au barrier heights increase slightly from that obtained for the oriented specimen, which is consistent with the formation of the 0.2 eV acceptor state.

Accounting for the increase in Al barrier heights requires the formation of different densities of the 0.8 eV acceptor state. Figure 4 indicates that at least $1 \times 10^{13}/\text{cm}^2$ states are required to produce the 0.6 eV barrier height observed at the Al/GaAs(100)2°-[110] interface. The density of the step-induced chemically active sites on the (100)2°-[110] surface ($2.18 \times 10^{13}/\text{cm}^2$) can well account for this value. In such a case, the number of chemically active sites are comparable to that of electrically active sites. A density of greater than $5 \times 10^{13}/\text{cm}^2$ is required to produce the 0.75–0.77 eV barrier height obtained at Al/GaAs(100)2°-[111] interfaces. However, the density of the step-induced chemically active sites on the (100)2°-[111] surface ($3.09 \times 10^{13}/\text{cm}^2$) is lower than what is needed. Thus, proportionally more states appear to result in this case. In other words, extended chemical reactions can induce additional states in the gap at the interface. We have shown and discussed the sensitivity of the 0.8 eV state to the interfacial chemical activity previously.¹⁶ Our results indicate that the interplay of the surface imperfections and the extent of the interfacial reaction maximize the effect on the interface electronic behavior.

The dependence of the Schottky barrier height on the interfacial chemistry and the perfection of the substrate surface shed some light on several controversies. (1) The sensitivity of the Al/GaAs(100) interface to the surface perfection observed in this study suggests that different Al/MBE-GaAs(100) barrier heights in the literature²⁴ appear to depend on the nature of the initial surface. (2) The chemical stability of our (100) surface is consistent with a metal–insulator–semiconductor (MIS) model of the metal–GaAs(100) Schottky barrier formation proposed recently by Freeouf *et al.*,²⁵ where the insulating layer is a stable, reconstructed surface layer. Such an insulating layer can at-

tenuate away effects of metal-induced charge states on the E_f stabilization. (3) The major electronic effects of slight surface misorientation suggest that considerable care must be exercised in comparing metal/semiconductor interfaces where step densities and the extent of misorientation are not well established.

V. CONCLUSIONS

We have demonstrated that a slight misorientation of the GaAs(100) surface changes significantly the extent of the interfacial chemistry and the Schottky barrier height. The orientation-induced electrical and chemical modifications of the interface follow the trend of increasing densities of chemically active sites at the step edge. The nature of the chemically active site on the step edge also affects the degree of chemical reaction/diffusion at the interface. The self-consistent electrostatic model describes well the relationship between the barrier height–work function dependence and the density of the charged states at the interface. Our results highlight the key role of the chemistry and the perfection of the substrate surface in obtaining ideal metal/GaAs junction electronic barrier properties.

ACKNOWLEDGMENTS

We are thankful to S. A. Chalmers for his assistance in providing MBE-GaAs materials. We are grateful for assistance of the Synchrotron Radiation Center, which is supported by the National Science Foundation. We acknowledge valuable conversations with D. J. Chadi and R. E. Viturro. This work is partially supported by the Office of Naval Research under Grant No. N00014-80-C-0778.

¹L. J. Brillson, *Surf. Sci. Rep.* **2**, 123 (1982).

²E. H. Roderick and R. H. Williams, *Metal–Semiconductor Contacts*, 2nd ed. (Clarendon, Oxford, 1988).

³L. J. Brillson, *Comments Cond. Mat. Phys.* **14**, 311 (1989).

⁴R. E. Viturro, S. Chang, J. L. Shaw, C. Mailhot, L. J. Brillson, A. Terrasi, Y. Hwo, G. Margaritondo, P. D. Kirchner, and J. M. Woodall, *J. Vac. Sci. Technol. B* **7**, 1007 (1989).

⁵L. J. Brillson, R. E. Viturro, J. L. Shaw, C. Mailhot, N. Tache, J. McKinley, G. Margaritondo, J. M. Woodall, P. D. Kirchner, G. D. Pettit, and S. L. Wright, *J. Vac. Sci. Technol. B* **6**, 1263 (1988).

⁶R. E. Viturro, J. L. Shaw, C. Mailhot, L. J. Brillson, N. Tache, J. McKinley, G. Margaritondo, J. M. Woodall, P. D. Kirchner, G. D. Pettit, and S. L. Wright, *Appl. Phys. Lett.* **52**, 2052 (1988).

⁷R. Z. Bachrach, R. S. Bauer, P. Chiaradia, and G. V. Hansson, *J. Vac. Sci. Technol.* **19**, 335 (1981).

⁸C. M. Aldao (private communication).

⁹A. Kahn, D. Kanani, J. Carelli, J. L. Yeh, C. B. Duke, R. J. Meyer, A. Paton, and L. J. Brillson, *J. Vac. Sci. Technol.* **18**, 792 (1981).

¹⁰M. D. Pashley, K. W. Haberern, W. Friday, J. M. Woodall, and P. D. Kirchner, *Phys. Rev. Lett.* **60**, 2176 (1988).

¹¹H. C. Gatos, P. L. Moody, and M. C. Lavine, *J. Appl. Phys.* **31**, 212 (1960).

¹²*Properties of Gallium Arsenide* (INSPEC, The Institute of Electrical Engineering, New York, 1986).

¹³S. G. Anderson, C. M. Aldao, G. D. Waddill, I. M. Vitomirov, S. J. Severtson, and J. H. Waver, *Phys. Rev. B* **40**, 8305 (1989).

¹⁴P. K. Larsen and D. J. Chadi, *Phys. Rev. B* **37**, 8282 (1988); (private communication).

- ¹⁵ J. Ihm and J. D. Joannopoulos, *Phys. Rev. Lett.* **47**, 679 (1981).
- ¹⁶ R. E. Viturro, J. L. Shaw, and L. J. Brillson, *J. Vac. Sci. Technol. B* **6**, 1397 (1988).
- ¹⁷ R. E. Viturro, M. L. Slade, and L. J. Brillson, *J. Vac. Sci. Technol. A* **5**, 1516 (1987).
- ¹⁸ M. H. Hecht, *J. Vac. Sci. Technol. B* **8**, 1018 (1990).
- ¹⁹ S. Chang, I. M. Vitomirov, L. J. Brillson, D. F. Rioux, P. D. Kirchner, G. D. Pettit, J. M. Woodall, and M. H. Hecht (to be published).
- ²⁰ C. B. Duke and C. Mailhot, *J. Vac. Sci. Technol. B* **3**, 1170 (1985).
- ²¹ A. G. Milnes, *Deep Impurities in Semiconductors*, (Wiley-Interscience, New York, 1973).
- ²² S. Chang, J. L. Shaw, R. E. Viturro, L. J. Brillson, P. D. Kirchner, and J. M. Woodall, *J. Vac. Sci. Technol.* (to be published).
- ²³ S. Chang and R. E. Viturro (unpublished).
- ²⁴ S. A. Chambers, *Phys. Rev. B* **39**, 12664 (1989) and references therein.
- ²⁵ J. L. Freeouf, J. M. Woodall, L. J. Brillson, and R. E. Viturro, *Appl. Phys. Lett.* **56**, 69 (1990).