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Correlation of deep-level and chemically-active-site densities at vicinal GaAs(100)-Al interfaces

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The steps associated with intentionally misoriented GaAs(100) surfaces produce interface charge states that can substantially alter the Schottky barrier height. These interface states are located near midgap in energy with density increasing in nearly one-to-one proportion to the density of step-related bonding sites. This detailed correlation between vicinal step features and deep-level densities demonstrates and gauges the systematic interface electronic perturbation associated with off-axis growth.

Vicinal surfaces are commonly used to facilitate epitaxial growth by molecular-beam techniques.[1] However, little has been known about the electrical properties associated with step-induced nucleation sites. We have recently discovered that, for 2°-off-axis GaAs(100) surfaces, variation in misorientation directions gives rise to substantial changes in chemistry and Schottky barrier heights at Al/GaAs interfaces.[2,3] Those initial results highlighted the effect of surface orientation on the chemical and electronic properties of the metal/GaAs interfaces. They suggested a correlation between the interface gap states and the step-induced, electrically active sites. By extending such studies to encompass both varying step density and misorientation direction, we can now demonstrate a linear dependence between interface charge states and step-induced, electrically active sites. Indeed, we observe a nearly one-to-one proportional increase in electronic state density versus chemically-active-site density. This detailed, self-consistent relationship between geometric and chemical structure, band bending, and deep levels observed spectroscopically provides direct evidence for the role of atomic-scale structure in Schottky barrier formation. Furthermore, this relationship highlights the trade off between step-induced growth efficacy and electronic perturbation caused by substrate misorientation.

Our n-type (5×10^{16} cm^{-3}) GaAs specimens were 7500 Å thick grown by molecular-beam epitaxy (MBE) on GaAs(100) oriented and misoriented substrates. The vicinal substrates were 1°, 2°, 4° (angular uncertainty ±0.1°) tilted toward the [111] crystal direction with As dangling bonds on the steps ([111]B), 2° tilted toward [111] with Ga dangling bonds on the steps ([111]A), and 2°, 4° in the [110] direction. To prevent contamination, the specimens were capped with 0.1–0.2-μm-thick As layers prior to removal from the growth chamber, then stored in N_2 atmosphere until transfer to the analysis chamber. Repeated cycles of rapid annealing up to 570 °C desorbed the As layer and produced a Ga-rich surface. The standard for the initial clean surfaces was set by the surface stoichiometry evaluated from the surface-sensitive intensity ratio of the Ga 3d to As 3d core-level peak (0.95 ±0.1), by the characteristic valence-band features, and by the initial Fermi-level (E_F) positions relative to the valence-band maximum (E_V). We deposited Al from resistively heated tungsten coils at pressures between 2×10^{-10} Torr and 8×10^{-10} Torr. A CTI-cryogenics closed cycle refrigerator maintained the specimen at a constant 90 K (LT in the following text), as measured by a 7%-Fe-Au/Chromel thermocouple. Low substrate temperatures afforded more uniform metal deposition and reduced overall chemical interaction to better identify chemical effects of the vicinal steps. We carried out soft x-ray photoemission spectroscopy (SXPS) using the synchrotron radiation facility at the University of Wisconsin, Madison. Energy distribution curves collected at 100 eV (As 3d) and 80 eV (Ga 3d) photon energies were predominantly surface sensitive and reflected changes in chemistry and morphology of the interface. Similar spectra collected at 60 eV (As 3d) and 40 eV (Ga 3d) photon energies were more bulk sensitive and were used to measure the rigid energy shifts due to band bending. The overall monochromator and electron spectrometer energy resolution was 0.25–0.35 eV. We also performed low-energy (1.5 kV) cathodoluminescence spectroscopy (CLS) on these vicinal surfaces as a function of metallization. Discussion of the CLS experiment and analysis techniques appear elsewhere.[4]

In Fig. 1 we demonstrate the dependence of Al/GaAs Schottky barrier heights on the density of step-related active sites, inclusive of the misorientation direction (which determines the bonding nature of the active sites). Plotted here are values of E_F-E_V versus active site densities of vicinal GaAs(100) surfaces estimated by assuming Ga-terminated, unrelaxed, staircaselike surfaces (since reconstructions of vicinal GaAs surfaces are not yet known).[2,3] As an example, the Fig. 1 inset shows the orientation-dependent E_F movement within the band gap as a function of Al coverage for GaAs(100) vicinal surfaces misoriented by 1°, 2°, and 4° in the [111]B direction. (The initial E_F position at the clean surfaces cannot provide reliable information on the charging of bonding sites due to photovoltage effect on the unmetallized surface at low

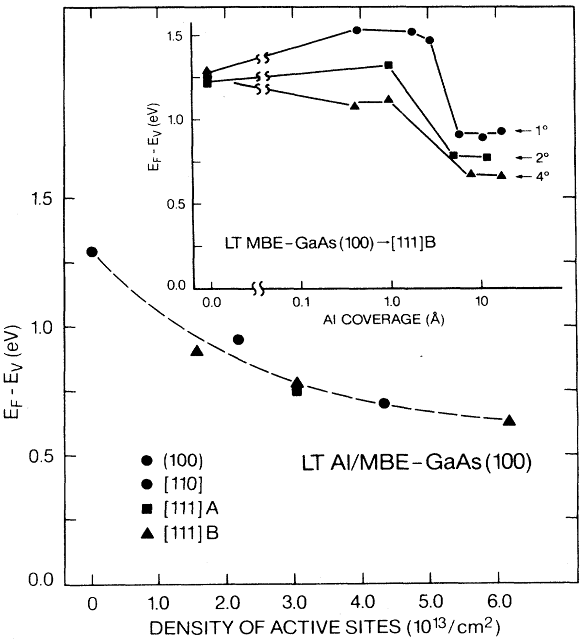

FIG. 1. Dependence of the Al/GaAs E_F-E_V position on the density of misorientation-induced bonding sites. The E_F-E_V difference between Al on GaAs(100) vs GaAs(100)4° → [111]*B* extends over a range of 0.65 eV. Inset shows E_F movements within the GaAs band gap as a function of Al coverage for (100) vicinal surfaces which are 1°, 2°, and 4° misoriented in the [111]*B* direction. The increasing misorientation of the substrate surface promotes an increase in band bending.

temperatures.) Figure 1 illustrates the decrease in E_F-E_V with respect to an increasing density of step-induced atomic sites. A range of 0.65 eV in E_F stabilization positions exists between Al on a "perfect" (100) surface and Al on the most "imperfect" surface used in this study [(100)4° → [111]*B* with active site density of 6.18×10^{13} cm^{-2}]. The decrease in E_F-E_V reflects an increase in negatively charged interface state density with increasing density of chemically active step sites.

In addition to the angle- and orientation-dependent Schottky barrier behavior, Al/vicinal GaAs(100) interfaces exhibit a *surface angle-dependent* interface reaction. We observe that the concentration of the dissociated Ga species within the probing depth of the interface increases in the order of 1°, 2°, and 4° tilting angles for the Al/GaAs(100) → [111]*B* and in the order of 2° and 4° tilting angles for the Al/GaAs(100) → [110].[5] We attribute such an effect to the increase in surface density of As dangling bonds. Earlier, we showed that reactions depended on *surface orientation* and were enhanced in the order [110], [111]*A*, and [111]*B* misorientation direction for the same angle (2°) of misalignment,[2,3] consistent with preferential etching and oxidation observations.[6] Furthermore, SXPS core-level features show such reactions to be localized to within only a few angstroms of the semiconductor surface. (A comprehensive description of the vicinal GaAs-metal interface chemistry appears elsewhere.[5]) The orientation-dependent Schottky barrier formation and interface chemistry indicate that the structural sites resulting from surface misorientation are not only chemically active (a fact well known in MBE growth), but also promote electrical activity. While the localized interface chemistry modifies the regular step structure, the detailed step density and orientation dependence illustrated in Fig. 1 underscores the direct relationship between these initial structural sites and the resultant interface states.

In Fig. 2, we present evidence for the formation of interface states specifically associated with Al deposition on vicinal GaAs(100) surfaces. The bottom CLS spectrum for the Al/GaAs(100)2° → [110] interface illustrates low optical emission from the below-band-gap region, typical for metal/MBE-GaAs interfaces. Curve *a* was obtained by contrasting the metallized surface to the clean surface and illustrates CLS emission from Al-induced states in the band gap for the GaAs(100)2° → [110] surface. Curve *b* illustrates an analogous emission for the aligned GaAs(100) surface. While Al induces deep-level emission from both GaAs surfaces, the difference spectrum *a*-*b* emphasizes the predominant optical transition centered at ~0.9 eV (i.e., $E_g-0.6$ eV) for Al on the stepped surface.

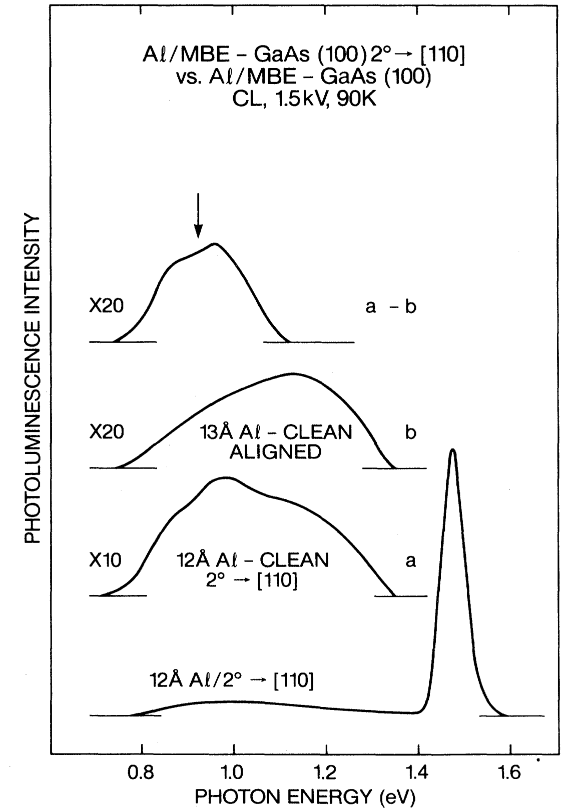

FIG. 2. Comparison between Al-induced interface states at (curve *a*) the Al/GaAs(100)2° → [110] interface and at (curve *b*) the Al/GaAs(100) interface shows an enhanced optical transition at (*a*-*b*) 0.9 eV for the misaligned system. Such an observation underlines an interface bonding-related nature of metal-induced interface states. The CLS spectrum for the Al/GaAs(100)2° → [110] interface (bottom) shows low optical emission from the below-band-gap region, which is typical for metal/MBE-GaAs interface.

Deep-level transitions either to or from the band edges can produce this emission. The complementary 0.6-eV transition lies below the Ge detector's 0.7-eV cutoff. Similar CLS measurements for Au on GaAs(100) and GaAs(100)2° → [110] surfaces exhibit metal-induced features at 1.2–1.3 eV (i.e., $E_g - 0.2$–0.3 eV), similar to the higher-lying emissions in Fig. 2, but Au deposition on the misoriented faces does not appear to introduce the predominant deep-level emission at 0.9 eV shown here.[5] Such observations emphasize the interface bonding-related nature of these metal-induced interface states.

We can describe the electronic perturbation due to surface misorientation in terms of a relationship between interface electronic states and step-induced structural sites. Duke and Mailhiot's self-consistent electrostatic analysis of barrier heights versus metal work function for a given semiconductor provides a method for gauging interface dipole effects and extracting densities and energies for equivalent charge sites located at a given distance below the semiconductor surface.[7] We obtain densities of charge centers from (i) the barrier heights' deviations from ideal Schottky behavior measured via SXPS and (ii) the energy position of these charge centers from our direct observation of discrete interface states via CLS. Aside from the assumption of charge states situated at a constant 10 Å below the semiconductor surface, there are no adjustable parameters in the analysis. Previously, we highlighted the effect of atomic sites associated with misorientation by comparing these Schottky barrier heights with the family of density curves for numerous metals on oriented MBE-grown GaAs(100) surfaces. For oriented surfaces, a constant acceptor density of 2×10^{13} cm^{-2} at $E_V + 0.2$ eV plus a varying acceptor density at $E_V + 0.8$ eV account for deviations from ideal Schottky barrier behavior and correspond well with observed CLS features.[8] While Fig. 2 curve *b* provides indications for such midgap states as well, Fig. 2 curve *a* shows that the step-induced reaction promotes additional state emission with an energy reflecting the different surface interaction. Only the 0.6-eV energy is fully consistent with Fig. 1; it lies just below the 0.65 eV minimum E_F-E_V energy, as expected for the observed energy convergence at high active site densities. Hence, a varying density of acceptors at $E_V + 0.6$ eV is more appropriate for detailed analysis. In addition, a constant acceptor density of 5×10^{12} cm^{-2} at $E_V + 0.2$ eV produces the best agreement with the Au data, although changes in this density produce only minor, systematic changes in the density of its 0.6-eV counterpart without altering its correlation with the active site density. The correspondence between the measured barrier heights and the family of curves calculated for vicinal interfaces provides the density of interface charge states. Following this procedure, one can establish the derived densities of interface states with respect to the densities of step-related bonding sites calculated for the unrelaxed, staircaselike surfaces.

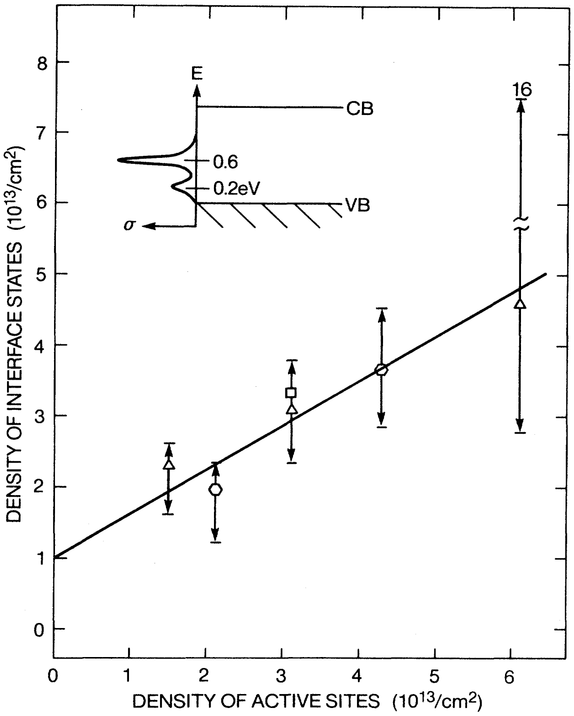

FIG. 3. Density of 0.6-eV acceptor states calculated from measured Schottky barrier heights using a self-consistent electrostatic model (Ref. 7) vs estimated density of misorientation-induced active sites. The linear relationship of interface charge states vs active sites emphasizes the role of step-related sites in interface state formation. The calculation also includes a fixed 5×10^{12} cm^{-2} density of a 0.2-eV acceptor state.

Figure 3 illustrates a linear relationship between the density of 0.6-eV acceptor states and the density of step-related active sites. The straight line in Fig. 3 was determined by linear regression. The error bars follow from a rigorous convolution of the uncertainty in density due to the 0.05-eV CLS precision in measuring the acceptor state energy with the uncertainty in density due to a 0.05-eV precision in the core level shifts measurements defining the barrier heights. The large upper error bar associated with the highest data point is due to the fact that the energies nearest the midgap level correspond to the highest state densities. However, this does not alter the pronounced, systematic dependence of electrical state and structural site densities for all vicinal misorientations. The dependence of the calculated density of interface states on the density of active sites on GaAs(100) vicinal surfaces illustrates a nearly one-to-one relationship between GaAs electronic state and structural site features. The line extrapolates to a 0.6-eV state density of 1.0×10^{13} cm^{-2} for aligned GaAs(100) surfaces, confirming that the aligned GaAs(100) surface has a very low density of interface electronic states.[8] The linear dependence confirms the role of misorientation-induced bonding sites in the formation of interface states. Indeed, the line slope in Fig. 3 suggests that metallization of each chemically active bonding site at a step produces the equivalent of $\sim \frac{2}{3}$ acceptor charge extending 10 Å into the semiconductor. Note that a proportionality of interface states higher than one charge per site would imply that the misorientation-induced defects at the intimate interface alone could not produce the measured Schottky barrier heights. Since both interface state density and chemical disruption increase with misorientation angles,[2] it is not unreasonable to expect that the more pronounced interface reactions might extend beyond the initial 10 Å, leading to a proportionally larger electrostatic effect. The lower proportionality derived from electrostatic analysis plus the observed line shape and attenuation of SXPS core-level features[5] confirm the localized nature of the interface chemical reaction on this scale. In addition to the linear, nearly one-to-one relationship between structural and interface state features, the dependence exhibited in Fig. 3 provides a guideline for the trade off between the efficacy of the epitaxial crystal growth and the minimization of the electronic perturbation.

The vicinal surface studies discussed here shed new light on mechanisms of Schottky barrier formation. Since surface misorientation is the only variable causing the variation in band bending for Al/GaAs(100) interfaces studied here, our results highlight the key role of interface atomic structure in the Schottky barrier formation. They contrast with the predictions of metal-induced gap states that E_F stabilize at a nearly constant energy within the semiconductor band gap, irrespective of surface orientation or step density.[9,10] Likewise, our observations challenge models based on adsorption-induced defects which also predict a constant "pinning" position for all such surfaces.[11] Conversely, these results are consistent with Ref. 8, where deviations from ideal Schottky-like behavior occur when chemical reactions are evident at the metal-semiconductor interface—precisely the case here. Confirming our observations of orientation influence on electronic properties, Palmstrøm *et al.* have recently demonstrated similar orientation-dependent barrier effects for epitaxial metal/GaAs junctions,[12] albeit without relation to specific structural features.

In conclusion, we have identified the density of chemically active sites—inclusive of both misorientation angle and direction—as the dominant parameter in E_F stabilization changes at vicinal GaAs(100)-metal interfaces. We have confirmed the presence of additional midgap states due to these metallized step sites and have found a striking correlation between chemically active structural sites and deep-level interface states.

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