Pressure Dependence of III-V Schottky Barriers: A Critical Test of Theories for Fermi Level Pinning

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The pressure-induced changes in the Schottky barrier height of Pt/GaAs and Au/GaAs are studied with *ab initio* electronic structure calculations. We show that the pressure dependence of the Schottky barrier offers a critical test of competing models of Schottky barrier pinning. We find that the pressure dependence of Pt/GaAs Schottky barriers with As antisite defects near the interface agrees well with experiment, and that the agreement closely tracks both the measured and calculated pressure dependence of the bulk As antisite. In contrast, poor agreement is found for ideal interfaces in which defects are not included.

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Despite extensive experimental and theoretical work spanning over 100 years, the basic mechanism which determines the Schottky barrier height of metal/semiconductor junctions is still controversial. An especially contentious issue concerns the observed insensitivity of the Schottky barrier height on group III-V semiconductors to metal overlayer, surface preparation, and growth conditions. Several competing theories purport to explain the observed range of pinning positions within the band gap for a given semiconductor. Because the materials conditions, method of deposition, degree of intermixing, and chemical bonding of different metal overlayers differ greatly, the existing data are open to varied and often conflicting interpretations.

From the experimental side, the detailed atomic structure at the interface has not yet been adequately resolved, particularly with respect to the presence and nature of defects at the interface. Cross-sectional transmission electron micrograph reveals a deviation from the lattice stoichiometry near the interface [1] and cathodoluminescence studies find midgap states near the interface [2]. A number of groups [3] have correlated the experimentally observed Fermi-level pinning position with the energy level of point defects as indirect evidence that defects dominate Fermi-level pinning. In particular, the common pinning position for a wide range of metals on group III-V compounds has been attributed to the anion antisite. Using the same data, another group has correlated the observed pinning positions with the work function difference between the anion and the host semiconductor to conclude that anion-rich metallic clusters dominate Fermi-level pinning [4]. However, both the point defects and the anion clusters hypothesized to be at the interface have as yet escaped direct experimental observation.

On the other side, theoretical work has shown that intrinsic interface states can dominate Fermi-level pinning. These states have been described as metal wave functions tunneling into the semiconductor [5,6]. The metal-semiconductor interface is strongly screened, and dipoles arise to shift the Schottky barrier to the "neutral point" of the semiconductor. A theoretical model [7,8] explains the universal pinning position by hypothesizing that the neutral point is an intrinsic property of the semiconductor, which because of the strong screening leads to a narrow range of pinning. One serious difficulty with this model is that there is no adequate justification for this hypothesis; indeed, detailed electronic structure calculations [9] do not support it.

As can be seen, the proposed models give generally similar predictions. The usual approach of comparing barrier heights for a wide range of metal/semiconductor junctions to isolate the mechanism for Fermi-level pinning is of limited value, since the concentration and nature of defects for each system, as well as the relevant electronic and structural properties of the interface vary. We will show that the *pressure-induced* change of the Schottky barrier height Φ_B offers a critical test to distinguish between the different models. This obviates the need for comparison between dissimilar systems produced under different conditions. Study of the temperature dependence of Φ_B may offer a similar advantage [10], but as we show here the pressure dependence $\partial\Phi_B/\partial P$ calculated within the context of local density functional theory allows for a direct comparison between theory and experiment, and therefore provides a more definitive test of the models. As a concrete illustration we will show that Φ_B of ideal Pt/GaAs and Au/GaAs [110] interfaces exhibit a pressure dependence very different from one with a significant concentration of As antisites near the interface.

Here we examine the pressure-induced change in the Schottky barrier height and the As antisite defect levels both experimentally and theoretically, in the context of the *ab initio* local-density approximation (LDA). Com-

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putations of the barrier height are made for both an ideal Schottky barrier, and one with antisite defects present near the interface. We begin with a comparison of the pressure dependence of the energy gap and the As antisite, to demonstrate that the LDA can accurately model these quantities. Next we turn to the Pt/GaAs Schottky barrier and compare the pressure dependence of the barrier height (both theoretical and experimental) to the pressure dependence of the As antisite. We focus on the pressure derivative of the relevant quantities.

Self-consistent calculations of Schottky barriers and defects were carried out within the local-density and atomic spheres approximation (ASA), following Ref. [9]. The method of linear muffin-tin orbitals (LMTO) with the local-density functional of von Barth and Hedin was used. As is customary in the ASA, we fill the interstices in GaAs with empty spheres of equal size to render the sphere packing bcc. For the ideal Au and Pt/GaAs, the Schottky barrier was calculated in a supercell geometry of 9 planes of metal followed by 9 planes of GaAs, repeating along the (110) direction. The [001] direction in the semiconductor was made parallel to $[1\bar{1}0]$ in the metal. The translation state was established by placing a metal atom in the next Ga site beyond the semiconductor surface. (This site was chosen because it results in a lower energy configuration than placing it in the next As site.) The lattice constants for Pt, Au, and GaAs were set to that of bulk GaAs, $10.69a_0$. To incorporate As antisite defects into the Schottky barrier, we substitute As for Ga sites in the third monolayer from the interface. This required a doubling of the cell in the plane of the interface, and also required 13 monolayers of GaAs to ensure that potential was essentially bulklike in the GaAs monolayer farthest removed from the interface.

Before presenting our results for the Schottky barrier, we first consider the pressure dependence of the band gap and the neutral As antisite level, to demonstrate that the LDA accurately models the pressure dependence of the energy levels of interest. Our calculated value of $\partial E_g/\partial P = 98$ meV/GPa compares favorably with the available experimental data measured on lightly doped GaAs, 107 meV/GPa [11]. Thus, the LDA accurately predicts the pressure dependence of the gap, although the magnitude is underestimated (0.4 eV for E_g at a lattice constant of 10.69 Å, as opposed to the observed 1.5 eV). Harrison has shown that the error in E_g arises mainly from an additional Coulomb repulsion U^* an electron experiences when promoted to a conduction band state from the valence band [12]. In Harrison's model, the effective repulsion U^* for this excitation is the bare Coulomb repulsion of the semiconductor (about 10 eV), screened by the dielectric constant, or about 0.8 eV. This simple model gives approximately the right correction to the gap, and moreover tells us also that the correction will be only weakly dependent on pressure. Thus, the local density approximation should describe rather well the pressure dependence of energy levels of interest; we see here that it does so for the band gap, and we will see similar agreement for the As antisite.

The pressure dependence of the As antisite defect level was calculated from the pressure dependence of the Fermi level of a 54-atom supercell of GaAs containing a single As antisite [13]. The density of antisites in this cell is sufficiently dilute to approximate rather well the position of an isolated neutral antisite defect. The neutral As defect, calculated as $E_F - E_V$ [14], was found to have a pressure dependence $\partial(E_F - E_V)/\partial P = 25$ meV/GPa, in agreement with earlier calculations [15]. This is also in good agreement with the measured pressure dependence of the EL_2, 20 ± 2 meV/GPa [16]; see Fig. 1. (It is generally accepted that EL_2 is comprised of an As antisite defect.) A measured pressure dependence of EL_2 very different from this value was reported by Dobaczewski and Sienkiewicz, using deep level transient spectroscopy to determine the energy of the midgap level of EL_2 as a function of pressure [17], because they did not correct for the large pressure dependence of the electron capture barrier.

Thus we see that the local density approximation agrees quite well with the measured pressure dependence of the band gap and As antisite, once properly interpreted. Next we turn to the pressure dependence of Schottky barriers. Φ_B was calculated for Pt/GaAs, in both an ideal geometry and one with antisite defects incorporated, as a function of pressure. We also find that the pressure dependence of Φ_B does not significantly change when atoms near

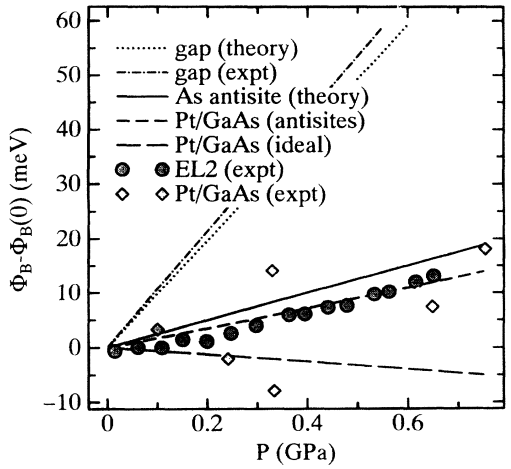

FIG. 1. Theoretical and experimental pressure-induced changes in the Schottky barrier height, the energy gap, and the As antisite. Dotted line: calculated pressure dependence of the band gap; solid line: calculated pressure dependence of the As antisite in GaAs; circles: measured pressure dependence of the same as that discussed in the text; long dashed line: calculated pressure dependence of the ideal Pt/GaAs Schottky barrier; short dashed line: calculated pressure dependence of the Pt/GaAs Schottky barrier with antisites; squares: measured pressure dependence of the Pt/GaAs Schottky barrier.

the interfacial layer are relaxed; we will address this in more detail later. The p type barrier height, $\Phi_B^{(p)} = E_F - E_v$, was calculated as the sum of the self-consistent interfacial dipole and the difference between the bulk metal Fermi level and bulk semiconductor valence band edge, as described in Refs. [9] and [18]. Apart from small discrepancies due to finite size effects, this is equivalent to the position of $E_F - E_V$ in the local gap of the GaAs layer farthest from the interface.

We demonstrate in Ref. [18] that $\Phi_B^{(p)}$ of Au/GaAs shifted dramatically for an ideal interface, from a position low in the gap (0.35 eV) to midgap (0.78 eV) when the antisites were present in the third monolayer from the interface. Also Φ_B changed dramatically from when the antisites were moved from the monolayer nearest the interface to the second monolayer, but only by 0.03 eV when shifted from the second to the third monolayer, suggesting that already by the third monolayer the energy level of the antisite is mostly uncoupled from the interface. If the antisite governs the position of Φ_B, Φ_B for Pt/GaAs should shift in a similar way; moreover, the *pressure dependence* of Pt/GaAs should track the position of the As antisite level in bulk GaAs. Indeed we find that self-consistent local-density calculations support this picture. $\Phi_B^{(p)}$ of the ideal Pt/GaAs was calculated to be 0.32 eV at $10.69a_0$; in the Schottky barrier containing As antisites Φ_B was shifted to 0.83 eV, mirroring that of Au/GaAs. Moreover, the pressure dependence was dramatically different in the two cases. We found $\partial\Phi_B^{(p)}/\partial P = +17$ meV/GPa for the Schottky barrier containing antisites, close to both the calculated value of the bulk As antisite (25 meV/GPa) and the measured value (20 meV/GPa). On the other hand, for the ideal Schottky barrier, which contained no antisites, $\partial\Phi_B^{(p)}/\partial P$ was found to be of the opposite sign, -6 meV/GPa. Also, a least-squares fit to the *measured* pressure dependence of the Pt/GaAs[001] Schottky barrier (Fig. 1) was found to be 20 ± 3 meV/GPa. As with the antisite defect, the measured Schottky barrier data shown in Fig. 1 were taken for an n type sample, and rendered with respect to the valence band by subtracting the data from the observed $\partial E_g/\partial P = 107$ meV/GPa. Earlier Shan *et al.* erroneously concluded that the measured pressure dependence of Φ_B was inconsistent with that of EL_2 [19]. When the pressure dependence of the capture barrier is included, good agreement is found.

Figure 1 shows clearly that the pressure dependence of four quantities, the measured Pt/GaAs Schottky barrier, the calculated antisite-laced Schottky barrier (17 meV/GPa), and the bulk antisite defect level (25 meV/GPa theoretically and 20 meV/GPa experimentally) are all in remarkably consistent agreement. Also, the experimental pressure coefficient $\partial\Phi_B^{(p)}/\partial P = 20$ meV/GPa does not agree with calculated value for the Schottky barrier in which no antisites were included (-6 meV/GPa). Although this extraordinary agreement between the four experimentally determined and theoretically calculated pressure coefficients is not unique to the As antisite, it can be regarded as a very strong argument in favor of a defect model. A similar conclusion has been reached based on the comparison of the temperature dependence of the Schottky barrier height and the energy gap [10].

Similar calculations performed for Au/GaAs yielded results very much like those for Pt/GaAs. For the Schottky barrier containing antisites, $\partial\Phi_B^{(p)}/\partial P$ was calculated to be $+15$ meV/GPa; -9 meV/GPa was calculated for the ideal Schottky barrier without antisites. Patak [20] has recently measured the pressure dependence of the Schottky barrier height in Au/GaAs. He finds that it closely tracks the pressure dependence of the As antisite defect, as does Pt/GaAs, thus suggesting that it too is mediated by the As antisite.

Several workers have shown that interfacial reconstructions can alter the barrier height [21], and thus its pressure dependence. To address this point, we have relaxed the Pt/GaAs and Au/GaAs interfaces. We will show that, while the absolute magnitude of the barrier height depends strongly on interfacial relaxations, the pressure dependence does not for the interfaces considered. Lattice relaxations were accomplished with a full-potential version of the LMTO method [22]. Interatomic atomic forces were calculated following conceptually the prescription described in Ref. [23], although here the forces were obtained by numerical differentiation. The total energy of the supercell was minimized with respect to the translation state of the metallic overlayer and also the atomic positions of the four inequivalent interfacial atoms [24]. Interfacial reconstruction was modest in comparison to that found at a free GaAs(110) surface. This is to be expected, since in the presence of a metallic overlayer the driving force causing the buckling of the free surface is absent, namely a lowering in the energy of the occupied surface band [25]. Reconstruction in the Pt and Au cases were similar, except relaxations were smaller for Pt. The largest displacement was associated with the interfacial Ga, which moved towards the interface by 0.25 Å, roughly opposite to its displacement at a free surface. The metallic interfacial atoms reconstructed only slightly, as they do at a free surface. For the Au/GaAs, the normal component of the translation state was found to be essentially identical to that assumed for the ideal Schottky barrier; for the Pt Schottky barrier, it was found to compress by about 4%. Because real Schottky barriers consist of thin metal overlayers on bulk GaAs, we assume that the metal overlayer compresses congruently with the GaAs in the two directions parallel to the interface only, allowing the metallic layers to compress differently from the GaAs in the [110] direction. A straightforward application of linear elastic theory, in which the Pt is put under uniform pressure but whose dimensions normal to [110] are constrained to follow the dimensions of GaAs, leads to Pt

interplanar spacing compressing at the rate of the GaAs spacing, times

$$1 + 6(B_{\mathrm{GaAs}} - B)/(c_{11} + c_{12} + 2c_{44}),$$

which is equal to -1.6 in Pt, and -1.3 in Au.

Using the relaxed atomic positions, and varying the metallic interplanar spacings as described above, Φ_B was recalculated within the ASA. We find that the reconstruction altered the pressure dependence of Φ_B only slightly. For Pt/GaAs, $\partial\Phi_B^{(p)}/\partial P$ changed from -6 meV/GPa for the unreconstructed case to -5 meV/GPa, even though the barrier height changed from 0.32 to 0.18 eV. For Au, $\partial\Phi_B^{(p)}/\partial P$ changed from -9 to -12 meV/GPa.

As one additional check to ensure that the antisite defects in the Schottky barrier were not so closely spaced that their mutual interaction affected Φ_B, we recalculated the pressure dependence of antisite defect levels located in a (110) plane, with the same geometry and density as used in the Schottky barrier calculations. For a 15 monolayer cell, we find $\partial(E_F - E_v)/\partial P = 24$ meV/GPa, essentially identical to the 25 meV/GPa of the isolated defect. This shows that the interaction between the As antisites is relatively small even at this close spacing, at least with respect to the pressure dependence of the defect level.

In summary, both theoretical calculations and experimental determinations of the pressure dependencies of Pt/GaAs Schottky barrier height and the AsGa 0/+ single donor level show a surprising coincidence, while the calculated value of the ideal Schottky barrier height is in poor agreement. This strongly supports the view that the Schottky barrier height of normally prepared contacts is indeed determined by near-interfacial defects.

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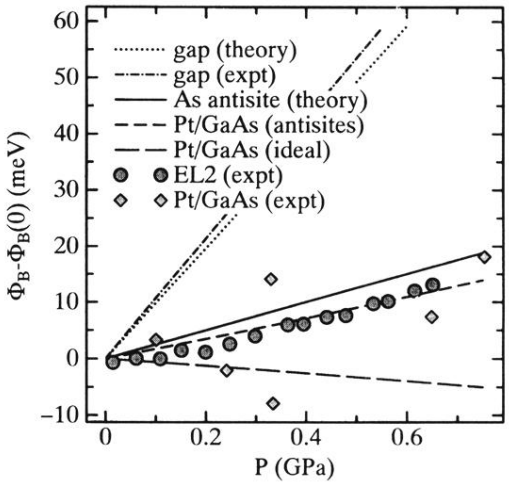

FIG. 1. Theoretical and experimental pressure-induced changes in the Schottky barrier height, the energy gap, and the As antisite. Dotted line: calculated pressure dependence of the band gap; solid line: calculated pressure dependence of the As antisite in GaAs; circles: measured pressure dependence of the same as that discussed in the text; long dashed line: calculated pressure dependence of the ideal Pt/GaAs Schottky barrier; short dashed line: calculated pressure dependence of the Pt/GaAs Schottky barrier with antisites; squares: measured pressure dependence of the Pt/GaAs Schottky barrier.