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Charge-state-dependent atomic geometries for isolated metal adatoms on GaAs(110)

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Self-consistent tight-binding calculations confirm recent scanning-tunneling-microscope studies of low coverages ($\Theta \sim 0.1$ monolayer) of Cs and Au on GaAs(110) which found that the Ga site is favored over the As site for isolated neutral adatoms. The calculations extend this result to other metals. However, the As site is predicted to be lower in energy if the adatoms are positively charged as they will be at still lower coverages ($\Theta \sim 0.01$ monolayer).

The study of metal-semiconductor interfaces has a long history.[1] Recently, both experimental[2,3] and theoretical[4,5] attention has been focused on very low metal coverages where the Schottky barrier is still being formed. In the hope of creating a simpler experimental system, Kahn and co-workers[2] and Spicer and co-workers[3] have performed photoemission studies on samples held at liquid-nitrogen temperatures. At these temperatures the metal adatoms tend to remain isolated at submonolayer coverages rather than clustering as they do for room-temperature deposition. These isolated metal adatoms will be the focus of the study here. In particular, we will calculate the minimum-energy geometry for a number of different metals on GaAs(110).

There is a growing opinion that these metals exhibit a donor level in the energy gap at low temperatures and low coverages.[4-9] The presence of this donor level has immediate consequences for the band-bending behavior as a function of coverage and doping.[4] For p-type GaAs, electrons are donated from this gap level to the semiconductor bulk, producing a positive surface charge and a negative space charge which leads to quadratic band bending as a function of coverage. This band bending saturates when the Fermi level at the surface coincides with the donor level in the gap. For coverages below this saturation point the isolated metal adatoms are all positively charged. The saturation point occurs at a coverage of approximately 0.01 monolayer (ML) for a doping of 10^{19} cm^{-3}. At higher coverages (greater than 0.1 ML) these isolated charged adatoms are very small in number compared to the total number of adatoms that are nearly all neutral. Although the majority of adatoms are neutral, they do form polar bonds with the substrate and the resulting bond dipoles shift the donor level lower in the gap.[4] At coverages near 1 ML these dipole shifts saturate. The behavior for n-type doping is much different. Since there is only a donor level in the gap, but not an acceptor level, there is no band bending for n-type doping at low coverages and the adatoms are all neutral. At coverages near 1 ML, when the overlayer is becoming metallic, the Fermi level for n-type doping rapidly moves into coincidence with that for p-type doping.[4] The behavior for both n and p-type doping is illustrated in Fig. 1.

The general behavior in Fig. 1 can be understood simply in terms of a donor level in the energy gap. However, in order to perform quantitative calculations that can be compared with experiment we need to know the specific geometry of the adatoms at the semiconductor surface. For the GaAs(110) surface there are two logical possibilities. This surface consists of zig-zag chains of Ga and As atoms as shown in Fig. 2(a). Each atom in these chains is bonded to two other atoms in the chain and one atom in the layer below. The physics of tetrahedral semiconductors is well described by forming sp^3 hybrids on each atom.[10] These hybrids are oriented at tetrahedral angles and, thus, one hybrid points toward each nearest neighbor in the bulk. At the (110) surface each atom has only three nearest neighbors, and thus we have one dangling hybrid per surface atom which is oriented toward the vacuum, but at an angle of 54°44′ with respect to the plane of the surface [see Fig. 2(b)]. The two most likely

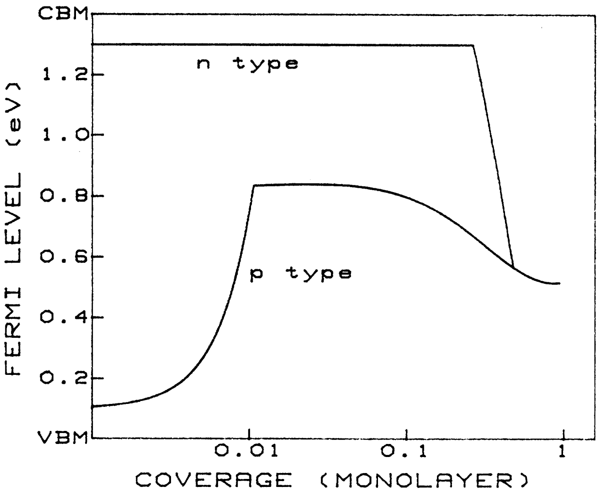

FIG. 1. Illustration of the coverage dependence of the Fermi level relative to the semiconductor bands at the surface for a case in which there is a donor level in the energy gap and the adatoms are uniformly distributed. The curves are based on a tight-binding calculation discussed in Ref. 4 with a p-type doping of 10^{19} cm^{-3}.

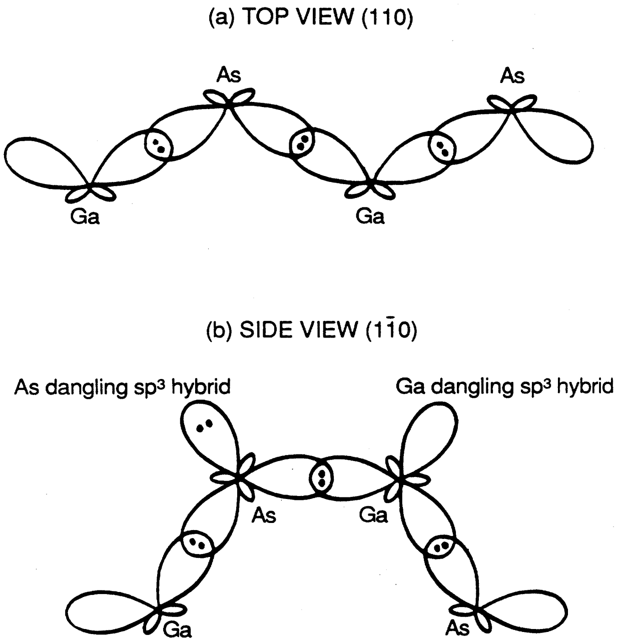

FIG. 2. Orientation of the sp^3 hybrids at the ideal GaAs(110) surface. The (110) projection in (a) shows the zig-zag chains, and the $(1\bar{1}0)$ projection in (b) shows the As and Ga dangling sp^3 hybrids. The As dangling hybrid is doubly occupied, while the Ga dangling hybrid is empty.

adsorption sites are for the adatom to be bonded to either the Ga or the As dangling hybrid. We will refer to these sites as the Ga site and the As site, respectively.

Two recent experiments have been performed which address the question of adsorption geometry. Using scanning tunneling microscopy (STM), First *et al.*[11] have observed Cs on GaAs(110) and Feenstra[12] has observed Au on GaAs(110). In both cases the metal adatoms were found to be beside a surface Ga atom (Ga site). The coverages in these two experiments were such that the adatoms were expected to be nearly all neutral.

In order to compare the total energy of different geometries theoretically, we use Harrison's tight-binding formulation[10] with Coulomb effects included as described previously.[13,14] In this formulation the total energy can be written as

$$E_{\text{tot}} = \sum_i [Z_i \varepsilon_i + \tfrac{1}{2}(Z_i - Z_i^{(0)})^2 U_i] + \tfrac{1}{2} \sum_{i,j} (Z_i - Z_i^{(0)})(Z_j - Z_j^{(0)}) \frac{e^2}{d_{ij}} + E_{\text{bond}} + E_{\text{rep}} , \qquad (1)$$

where E_{bond} and E_{rep} are the bond energy and repulsive overlap energy described by Harrison.[10] The $(Z_i - Z_i^{(0)})$ are the effective charges defined in Ref. 10, and $Z_i^{(0)}$ is the valence of the ith atom. The ε_i and U_i are the term values and intra-atomic Coulomb repulsion energies tabulated in Ref. 13. The first term is a sum of self-energies, which we call the occupation energy, while the double sum is just the Madelung energy. We write the wave function as a product of bonding combinations of atomic orbitals. We then perform a variational calculation by minimizing Eq. (1) with respect to the coefficients of the atomic orbitals in the wave function. We will not present the details of this calculation, but merely summarize the results in terms of simple bonding arguments.

We first examine the two geometries which are illustrated in Fig. 3. As a first approximation, we assume an ideal GaAs(110) surface. This assumption is not completely unrealistic since there is both experimental[2] and theoretical[15] evidence that the underlying reconstruction is removed upon adsorption of the metal atom. At an ideal surface two electrons occupy each of the bonds between nearest neighbors (in the bulk these form the filled valence bands). This configuration leaves one electron per surface atom. Since the As hybrids have lower energy, the As dangling hybrid is doubly occupied, leaving the Ga dangling hybrid empty (this configuration already captures the essence of the actual reconstruction). We consider a simple metal bonded to either a Ga atom [Fig. 3(a)] or an As atom [Fig. 3(b)]. We form two sp hybrids

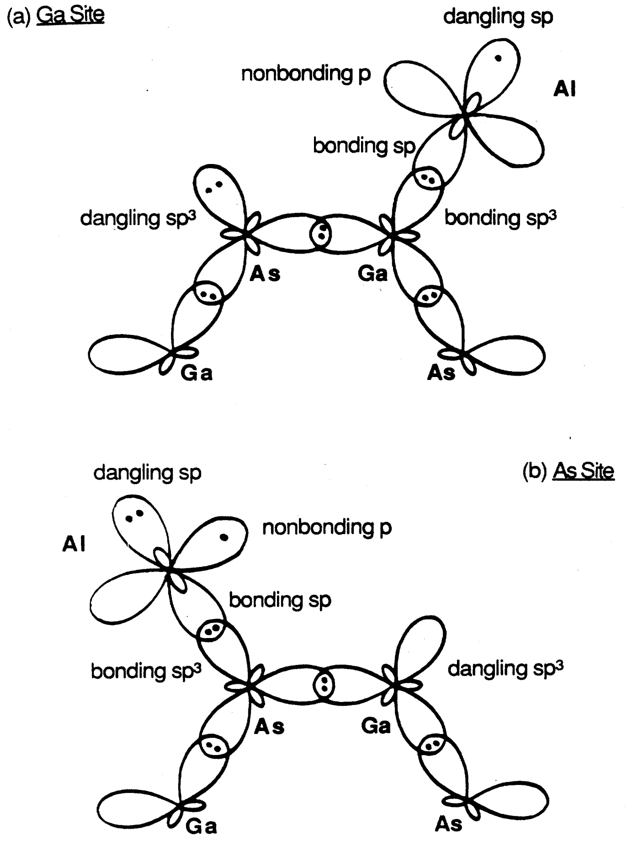

FIG. 3. The two bonding geometries considered in this paper. For both the Ga site in (a) and the As site in (b) we form two sp hybrids on the Al adatom, leaving two nonbonding Al p states, one of which is shown. The occupation of the orbitals is shown for the neutral case, while for the positively charged case the Al dangling sp hybrid in (a) and the nonbonding Al p state in (b) are both empty.

(one-half s and one-half p in character) on the metal atom; one is oriented toward the surface dangling hybrid and the other is oriented away from it. There are also two nonbonding p states oriented perpendicularly to the surface dangling hybrid. This geometry is the same for both the Ga and the As site (see Fig. 3).

The difference between the two sites starts with the occupation of the orbitals, which is also shown in Fig. 3. We consider a neutral Al atom which has three valence electrons. For Al bonded to Ga, two of these electrons occupy the bonding state made up of the Ga dangling hybrid and the Al sp hybrid oriented toward it. The third electron occupies the Al dangling sp hybrid, which has lower energy than the nonbonding p states. For a neutral Al atom bonded to As we have five electrons, three from the Al and two from the As dangling hybrid. We occupy the same orbitals for the Ga site, but, in addition, the Al dangling sp hybrid is doubly occupied and there is one electron in a nonbonding Al p state. In the more complete calculation the distinct orbitals described here become mixed, but the dominant character of the orbitals remains as we have described.

We find that a neutral Al atom has lower energy bonded to Ga than to As. We can understand this result as follows. Since the Al atom is neutral, the Madelung energy is nearly the same for the two geometries. In addition, there are two electrons occupying a bonding level in each case, and so the bonding energies are also similar. In our formulation the repulsive overlap energy is approximately one-half the magnitude of the bonding energy.[10] We are left with the occupation energy [first term in Eq. (1)]. This term favors the Ga site for the following reasons. In each case we have two electrons in a bond, one lone pair of electrons in a dangling hybrid, and a single electron in a nonbonding level. In both cases the single electron sits on the Al. The primary difference between the two geometries is that for the Ga site the lone pair is on the As, while for the As site the lone pair is on the Al. Since the As dangling hybrid has lower energy, the Ga site is preferred.

We have performed the same calculation for the trivalent metals Al, Ga, and In, and also for the monovalent metals Na, K, Rb, Cs, Cu, Ag, and Au. In each case except for Cu it was found that the Ga site was preferred for isolated neutral adatoms. However, for Ag and Au it was found that the difference in energy between the two sites was less than 0.1 eV, which is of the order of the errors introduced by the approximations made in the calculation. On the other hand, our result is in agreement with the Au STM experiment.[12]

For a positively charged Al atom we have one less electron than in the configurations shown in Fig. 3. For the Ga site this means the Al dangling sp hybrid is empty and for the As site the nonbonding Al p states are empty. As in the neutral case, the bonding energies are similar and the occupation energy favors the Ga site. However, since the Al atom is charged, the Madelung energy is quite different for the two geometries and this term in the total energy dominates over the occupation energy. The Madelung energy for a positively charged Al atom is much lower near an As atom than it is near a Ga atom, and thus we find that the As site is preferred for this case. We carried out this calculation for the same monovalent and trivalent metals as in the neutral case. For each metal atom the As site was preferred over the Ga site by approximately 1 eV. We should note that, due to the net positive charge in the system for this case, we included the effect of the polarizable substrate approximately through the static dielectric constant (see Ref. 14).

We point out that positively charged adatoms should be observable for p-type doping at very low coverages (see Fig. 1). For the doping of 10^{20} cm^{-3} used in the Au STM experiment,[12] all of the adatoms should be charged below a coverage of approximately 0.04 ML (the p-type doping in Fig. 1 is only 10^{19} cm^{-3}). Although this coverage is quite small, it should be accessible experimentally and, therefore, our prediction can be checked.

Now that we have determined the adatom geometry, we can calculate the energies of the donor levels and compare them with experiment. From Fig. 3(a) we see that for the trivalent metals the donor level arises from the metal dangling sp hybrid. Since this orbital is only half-occupied, it also gives rise to the acceptor level, which is higher in energy as a result of Coulomb repulsion.[4] For the monovalent metals the relevant orbital is the bonding combination of the Ga sp^3 hybrid and the inward oriented metal sp hybrid. We have, in fact, performed these calculations, generally finding the donor level to be in the upper part of the energy gap, as expected. These results will be presented elsewhere.

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