RAPID COMMUNICATIONS

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Early-stage formation of metal-semiconductor interfaces

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We have analyzed the early-stage formation of a GaAs(110)-Ag interface by using a consistent tight-binding method. Our results are in agreement with experimental evidence showing that the Schottky barrier is practically formed with the deposition of a metal monolayer. We conclude that it is not necessary to claim defects in order to explain the barrier formation at low metal coverages.

I. INTRODUCTION

Schottky-barrier formation is a long-standing problem. Different models have been proposed to explain metal-semiconductor interface behavior.[1–4] The two most widespread models are the defect model[5,6] (DM) and the induced density-of-interface-states model[7,8] (IDISM): the first one resorts to defects created by the metal deposition to explain the barrier formation, while the second one uses the metal-induced gap states.

One of the most striking properties of the early stage formation of semiconductor Schottky barriers has been obtained by depositing a complete or fractional metallic monolayer onto the semiconductor (typically GaAs and InP).[9–12] The evidence obtained in this case shows that a small fraction of a monolayer can affect substantially the interface Fermi level, forming the barrier completely. This result has been presented as a disproof of the IDISM since, it has been argued, a monolayer (or a fraction) cannot be operative enough to create the metal-induced gap states pinning the Fermi level.

The purpose of this Rapid Communication is to present calculations of the Schottky-barrier formation, within the IDISM, for the deposition of 1, 2, 3, 4, and 5 monolayers of Ag on GaAs(110). In our approach we use a self-consistent tight-binding model (SCTBM)[13] which is an extension of the IDISM; this approach has been applied to the problem of semiconductor-semiconductor formation[14] and band-offset calculations for heterojunctions,[15] giving good results compared either with experiments or with more sophisticated calculations using a local-density approach.[16] Although we do not analyze a fraction of a monolayer, it can be argued that this case is similar to the monolayer case if the metal adatoms have enough mobility: then, the atoms woud aggregate in islands behaving locally as a monolayer.

II. MODEL AND METHOD OF CALCULATION

In the SCTBM we introduce sp^3s^* orbitals in the semiconductor to describe the band structure and use Vogl's parameters.[17] For Ag we use a simplified approach with two s orbitals, simulating the s and the d bands (the Fermi level is inside the s band and d-band effects are not important[18]). The surface geometry used in the calculation is shown in Fig. 1: the first layer of Ag atoms is determined by the cation-continued position of the ideal semiconductor crystal, with a density similar to the one of Ag metal. The distance between nearest As and Ag atoms is 2.45 Å, while the distance between nearest Ga and Ag atoms is 2.83 Å. Let us remark that we assume that the surface reconstruction is removed when the metal atoms are deposited. This fact is in agreement with the experiments of Belmont, Chen, Proix, and Sebenne[11] and also with a recent total energy calculation done by Zhang, Cohen, and Louie.[19] Next layers are determined by the ideal lattice constants of the Ag crystal: notice that the ideal positions taken in this paper for the first Ag layer are plausible but hypothetical: from the point of view of our discussion that is not crucial since we are mainly interested in discussing how the barrier height changes with the further deposition of layers. Moreover, as discussed elsewhere,[7] the metal-

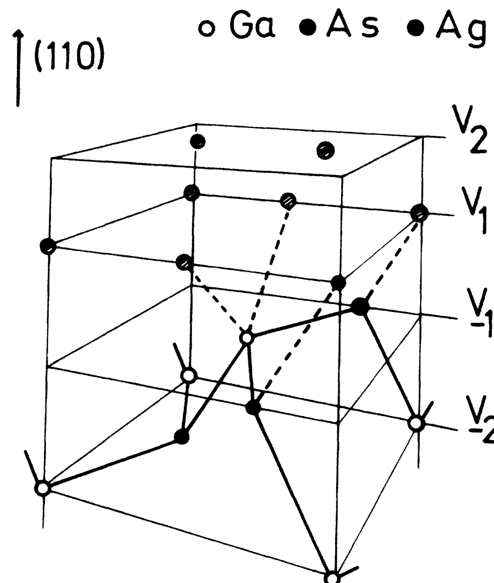

FIG. 1. Geometry of the GaAs(110)/Ag metal-semiconductor junction for the deposition of two metal layers. The diagonal perturbations V_i for each layer are plotted. The distance between the last semiconductor layer and the first metal layer is taken equal to $a/2\sqrt{2}$ while the distance between neighboring metal layers is $a/4$; $a = 5.66$ Å.

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TABLE I. Interactions between the orbitals of GaAs and the nearest metal-atom orbitals (in eV). The first index refers to the metal orbital (s or d) and the second one refers to the semiconductor orbital (s or p). The interactions with the s^* orbitals are taken equal to zero.

	As	Ga
V_{ss}	−1.10	−1.19
V_{sp}	1.63	1.60
V_{ds}	−0.73	−0.41
V_{dp}	1.07	0.59

atom position at the interface induces some changes of the Fermi energy around the semiconductor charge-neutrality level; these energy shifts are not, however, too large, and the effect of further deposition of layers can be expected to be independent of the initial geometry of the first layer.

Interactions between Ag and the cation and anion orbitals of GaAs are given in Table I. Calculations have also been performed by either increasing or reducing the interaction parameters between the Ag d orbitals and the semiconductor by a factor of 2, and no substantial change in the conclusions of this paper we found. This is in qualitative agreement with the recent results of Yeh *et al.*[19] who have found that the d electrons play a minor role in the chemical bonding of the Ag/Si interface. Finally, we mention that in our method of calculation[13] we introduce diagonal perturbations in the Ag layers and the two first layers of GaAs, related to the transfer of charge between Ag and GaAs. This allows us to introduce a kind of Hartree consistency, related to the charge neutrality conditions and the charge neutrality level of the IDISM (tight-binding approaches without the consistency discussed in this paper have often been used in the literature; see, for example, the review of Pollman and Mazur[20] and references therein).

III. RESULTS

In Fig. 2 we show the local density of states in the first GaAs layer for a clean surface and the interfaces having 1, 2, 3, 4, and 5 monolayers of Ag. In this figure, the main result of our work is apparent: For a monolayer of Ag, an important density of states appears in the semiconductor energy gap, these states pinning the Fermi energy at a level close to its final value. For 2 layers, these metal-induced gap states increase, and for 4 and 5 layers they are stabilized in their final value although a small decrease seems to appear for 3 layers.

Similar results can be found in Table II, where the self-consistent potentials introduced in the two last layers of GaAs and the different layers of Ag are given for the free surface and the different interfaces. Notice that the Fermi level for the free surface $E_F \cong 0.70$ eV is shifted to 0.90 eV for one and two monolayers of Ag, this value practically coinciding with the ones calculated for 4 and 5 layers; only for 3 layers the Fermi level is somewhat larger due to the decrease in the density of states seen in Fig.

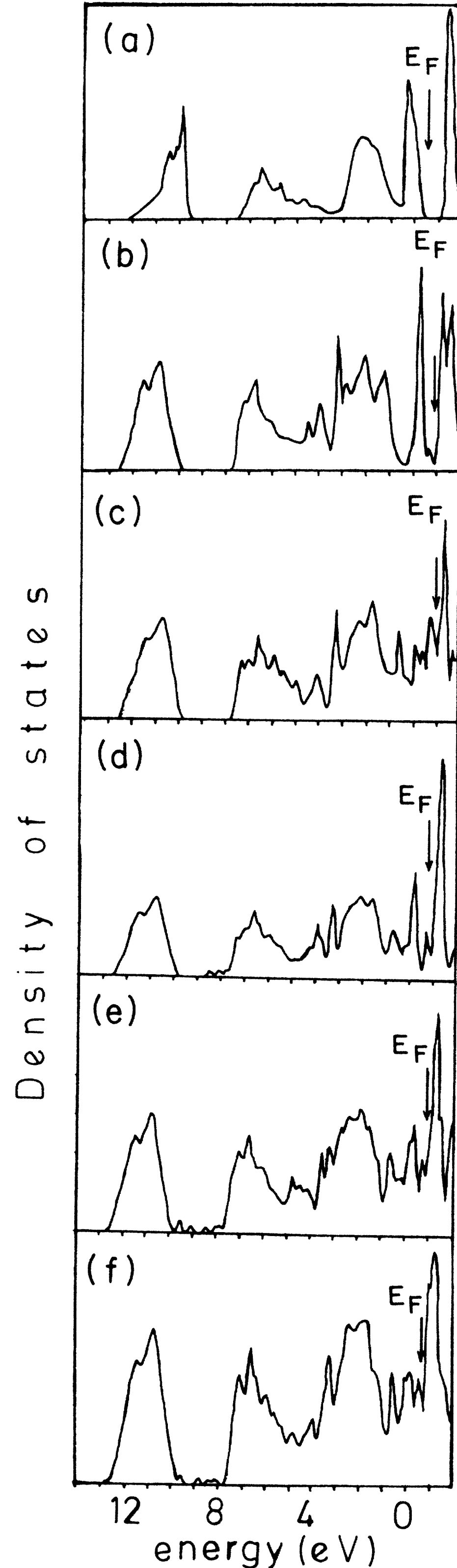

FIG. 2. Local density of states in the interface GaAs layer for different number of monolayers of Ag deposited: (a) clean surface (ideal); (b) 1 monolayer of Ag; (c) 2 monolayers; (d) 3 monolayers; (e) 4 monolayers; (f) 5 monolayers. The zero of energy coincides with the top of the valence band.

TABLE II. Values of the diagonal perturbations and the Fermi energy (in eV) as a function of the number of Ag layers deposited on GaAs(110).

	AsGa V_{-2}	AsGa V_{-1}	Ag V_1	Ag V_2	Ag V_3	Ag V_4	Ag V_5	E_F
Clean surface	0.05	0.00						0.72
1 monolayer	0.06	−0.34	−0.87					0.85
2 layers	0.06	−0.14	−1.02	−0.92				0.89
3 layers	0.05	−0.21	−0.87	−1.01	−0.79			1.02
4 layers	0.05	−0.23	−0.96	−1.02	−1.14	−0.89		0.89
5 layers	0.06	−0.19	−0.91	−0.94	−0.89	−1.02	−0.78	0.93

1(d) near the Fermi level. On the other hand, the results for the diagonal perturbations given in Table II for the cases of 4 or 5 layers show that the metal-semiconductor interface extends practically to one monolayer in the semiconductor and one monolayer in the metal; once the first monolayer of Ag is crossed the different diagonal potentials in different Ag layers are practically constant except for the values near the surface where again we find that perturbations are localized near the last atomic layer. All these results show that a monolayer of Ag is enough to pin the interface Fermi level forming the barrier at a low level of metal deposition onto the semiconductor.

We finally comment that the final barrier height given by our calculation is rather small when compared with the experimental evidence. For $E_F = 0.9$ eV, $\phi_{bn} = 0.52$ eV, while the experimental evidence yields $\phi_{bn}(\mathrm{expt}) \approx 0.78 \pm 0.1$ eV (Ref. 21). We think that this result is related to the approximation we are using for the semiconductor band structure; in other words, we cannot expect to have a very accurate charge neutrality level having used parameters that only include first neighbors interactions. Our calculations yield, however, with a higher accuracy[1] the difference between the final and the initial Fermi energy. If we take for the initial value the charge neutrality level given by Tersoff,[8] $E_F = 0.50$ eV, we find for the final Fermi energy $E_F = 0.70$ eV and a barrier of 0.72 eV much closer to the experimental evidence.

Notice that our results for the Schottky-barrier formation of the GaAs(110)/Ag interface are in agreement with the empirical data, supporting the induced density-of-interface-states model (IDISM) and allowing us to conclude that it is not necessary to claim defects in order to explain the pinning of the Fermi level at low-metal coverages.

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