PHYSICAL REVIEW B VOLUME 27, NUMBER 8 15 APRIL 1983

Study of the reconstructed GaAs(100) surface

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(Received 20 April 1982)

The reconstruction of an As-terminated GaAs(100) surface has been studied using the self-consistent pseudopotential method. Total energies for the (1×1) ideal surface and the $c(2\times2)$ and $p(2\times2)$ reconstructed surfaces within the dimer model are compared. Unlike the Si(100) surface, at least two inequivalent dimers are required to produce the semiconducting surface and stabilize the system. Important features in the density of states and the valence-charge distribution are presented.

I. INTRODUCTION

The GaAs surface has been one of the most studied compound semiconductor surfaces because of its technological importance. As a result of the enormous efforts devoted to the study of the system, the microscopic structure of the clean GaAs(110) surface is now very well understood. On the other hand, an understanding of the (100) surface of the same material is still absent because of the experimental and theoretical difficulties involved in dealing with a polar surface. The (100) surface exhibits a variety of reconstruction patterns[1–11] depending on the As coverage and other preparation conditions, and the experimental control over the behavior of the reconstruction has been possible only recently.[1] The theoretical work[12–15] has been mostly limited to the ideal unreconstructed surface. The lack of information on the positions of the surface atoms has been the major obstacle to the quantitative study of the system.

Recently, the tight-binding energy minimization method has been applied to study this system and yielded approximate atomic coordinates for the stable surface.[16] By using these structural models, *ab initio* pseudopotential calculations have been performed in the present study. In the reconstruction which doubles the size of the surface unit cell [$c(2\times2)$ structure], formation of the asymmetric dimer is found to lower the energy. However, this reconstructed surface is metallic like the ideal surface. This structure is unstable with respect to a larger reconstruction, that is, the $p(2\times2)$ structure. In this geometry, two inequivalent dimers, one asymmetric and the other nearly symmetric, exist, and the surface is semiconducting. It was argued in the literature that the semiconducting GaAs(100) surface requires reconstruction at least four times as large as the unreconstructed unit cell.[2,15] The argument goes as follows. Suppose opposite sides of the GaAs sample are both As-terminated (100) surfaces. Then we have an odd number of electrons in the reconstructed unit cell perpendicular to these two surfaces. Half-integer electrons are associated with each surface and the unit cell should be quadrupled to fill a band completely (including the spin degeneracy). Of course, this argument does not tell how surface atoms are rearranged (relaxation, rebonding, buckling, etc.) in the reconstructed geometry.

We have studied (1×1), $c(2\times2)$, and $p(2\times2)$ surfaces and have indeed observed the metal-semiconductor transition between the $c(2\times2)$ structure which has an odd number of electrons and the $p(2\times2)$ structure which has an even number of electrons. We have obtained the total energy and the self-consistent charge distribution for each system using the coordinates from a tight-binding energy minimization procedure.[16] In principle, we could have determined the exact atomic coordinates corresponding to the stable geometry by the pseudopotential energy minimization method.[17] However, the method is impractical for very large unit cells [e.g., the $p(2\times2)$ structure]. Consequently, we have determined the coordinates approximately using the empirical tight-binding method and use those coordinates as inputs to the self-consistent pseudopotential calculations. Comparisons are made among the (1×1) ideal surface, the $c(2\times2)$ reconstructed surface with an asymmetric dimer, and the $p(2\times2)$ reconstructed surface with two inequivalent dimers. Experimentally, the As-covered (100) surface exhibits $c(4\times4)$ reconstruction. The pesudopotential calculation for the $c(4\times4)$ structure is far beyond our present computing capabilities. Nevertheless, we believe that the $p(2\times2)$ structure retains the essential features of the exact reconstruction; namely, the reconstruction leading to a semiconducting surface. In fact, the tight-binding calculations[16] show that the atomic and the electronic structures of the $c(4\times4)$ and the $p(2\times2)$ surfaces are quite similar. The pseudopotential by Hamann-Schluter-Chiang[18] is used with the density-functional exchange-correlation potential from the Wigner interpolation formula.[19] For the $p(2\times2)$ structure, the unit cell consists of eight layers of GaAs plus a vacuum region equivalent to five layers in thickness. About 450 plane waves are included in the basis set and another 1800 plane waves are included through the second-order perturbation. For the structures with smaller unit cell [(1×1) and $c(2\times2)$], a thicker slab is also tested. The results are summarized in Sec. II.

II. RESULTS

Figure 1 shows the atomic coordinates of the $c(2\times2)$ and the $p(2\times2)$ surfaces we studied. Surface As atoms form asymmetric dimers on the $c(2\times2)$ surface as shown in Fig. 1(a). Among the two kinds of dimers possible in a $p(2\times2)$ geometry, one of them is asymmetric and the other is almost symmetric in Fig. 1(b). Inequivalence between two dimers helps open up the gap in the band structure. The As-As bond length of the asymmetric dimer is 2.4 Å for both $c(2\times2)$ and $p(2\times2)$ structures. It indicates a strong bonding between surface As atoms (the bulk As bond length is 2.5 Å). A similar result was obtained in the pseudopotential calculation of the asymmetric dimer of the Si(100) surface.[20] The total energy of the system is lowered by 0.8 eV per dimer for the $c(2\times2)$ geometry and by almost 2.0 eV per dimer for the $p(2\times2)$ geometry. It is rather surprising that two reconstructed surfaces, both of which are basically dimerized surfaces, show significant difference in energy. This behavior may be explained by the metal-semiconductor transition occurring between the two. The tight-binding calculations[16] give metal-semiconductor transitions between the $c(2\times2)$ and the $p(2\times2)$ geometries. For comparison, the energy of the Si(100) surface[20] is reduced by 1.7 eV per dimer by forming a (2×1) asymmetric dimer and no additional reduction by a larger reconstruction has been observed. (The reduction should be within order of 0.1 eV even if a larger reconstruction happens at all.) Note that the Si(100) surface is already semiconducting with a (2×1) reconstruction.

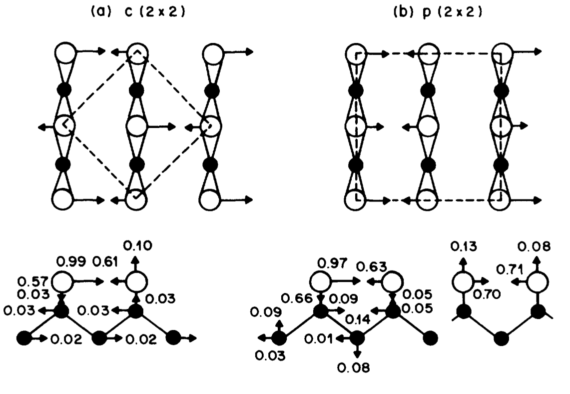

FIG. 1. Atomic coordinates of the (a) $c(2\times2)$ and the (b) $p(2\times2)$ reconstructed GaAs(100) surface. Open circles represent the surface As atoms and the heavy dots represent subsurface atoms. The dashed square denotes the surface unit cell for each case. The top figure is the top view and the bottom figure is the side view of the surface. The arrows and the numbers (in Å) indicate displacements of the atoms with respect to the ideal geometry. Two types of dimerization are shown for (b).

The density of states for the ideal and the $c(2\times2)$ surface is shown in Fig. 2. We include contribution of six layers counting from the surface in this density-of-states curve. Prominent peaks related to surface states are labeled in the figure. Peaks A and A′ in the heteropolar gap are anion s surface states split from the bulk continuum states. Peaks B and B′ are dangling-bond states. They are partially filled, giving rise to a metallic surface. The surface state band for the ideal surface induces a sharply peaked density of states (DOS), while that of the reconstructed surface gives rise to a broader but smaller peak because of stronger interactions between surface atoms. Still, the $c(2\times2)$ structure has partially filled dangling-bond states.

The peaks due to unoccupied surface states are labeled as C and C′. They are so-called bridge-bond states.[12] For the ideal surface the peak (C) is located below the conduction-band minimum. On the other hand, this band moves up above the bottom of the conduction band and gives a less pronounced peak (C′) for the $c(2\times2)$ reconstructed surface. There are some additional structures in the range of −6 to −4 eV, but these states are less localized and do not modify the DOS significantly.

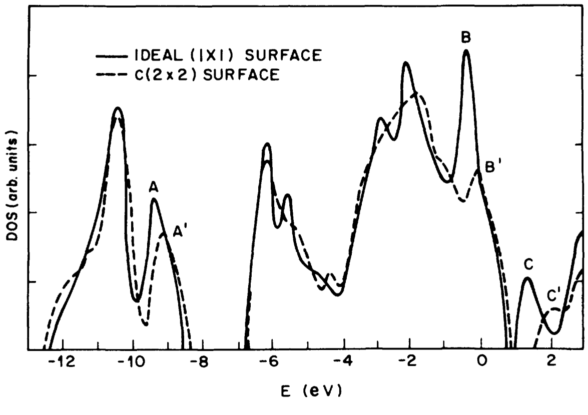

FIG. 2. Plots of the density of states for the ideal and the $c(2\times2)$ reconstructed As-terminated GaAs(100) surface. Prominent peaks originated from surface states are labeled.

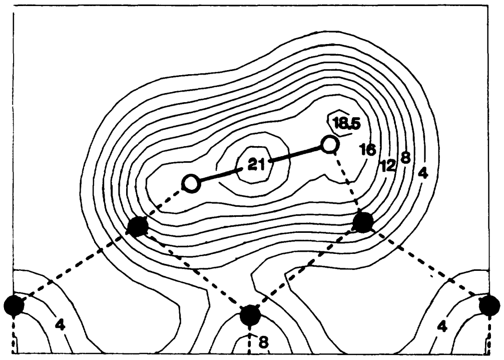

FIG. 3. Total valence-charge density of the $p(2\times2)$ GaAs(100) asymmetric dimer. The contour plot shows the cross section of (011) plane cutting the (100) surface at right angles. The open circles represent the surface As atoms on the plane and the solid circles indicate the Ga and As atoms not on the plane. The solid line is the As—As dimer bond on the plane and the dashed lines denote the Ga—As bonds not on the plane. The charge density is in terms of electrons per bulk GaAs unit cell (298 a.u.).

Unfortunately, it is not possible with the present computing facilities to calculate the density of states for the $p(2\times2)$ structure with desired accuracy. It suffices here to say that, even with a very small number of $\vec{k}$-point sampling, we clearly see the gap opening up. The calculation of the valence-charge density is much simpler and the result is presented in Fig. 3. This contour plot shows the valence-(pseudo)charge density in the (011) plane perpendicular to the (100) surface. The plane contains the asymmetric dimer bond as indicated in the heavy solid line. The maximum charge density for the bulk GaAs bond is 20 in the same calculation. Therefore, the charge density at the asymmetric dimer is 5% larger than the bulk counterpart. The maximum charge density at the other dimer which is nearly symmetric (not shown here) is also 20. The overall charge distribution around the asymmetric dimer is similar to that of the Si(100) asymmetric dimer in Ref. 21. The difference is that the asymmetric dimer between As atoms has an extra charge accumulation at a back-bonding site (the 18.5 peak in the figure) because the As atom has a residual charge compared with the Si atom.

ACKNOWLEDGMENTS

The work at Xerox was supported by the U.S. Office for Naval Research under Grant No. N00014-79-C-0704 and the work at Massachusetts Institute of Technology was supported by the Joint Services Electronics Program (U.S.) under Contract No. DAAG-29-80-C-0104. One of us (J.D.J.) would like to thank the J. S. Guggenheim Foundation for a fellowship.

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