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Electronic structures of As/Si(001) 2 × 1 and Sb/Si(001) 2 × 1 surfaces

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The electronic structures of the As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces with symmetric dimers are calculated self-consistently with the use of planar basis functions made of two-dimensional plane waves and one-dimensional Gaussian functions, based on local-density-approximation and norm-conserving pseudopotentials. The calculations show that both the As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces are semiconductors with energy gaps of about 1.0 eV. Both As and Sb surface bands have similar dispersion and are very different from that of the Si(001) 2×1 surface. The calculated dispersion of surface states for As/Si(001) is in good agreement with the angle-resolved photoemission measurements. The calculated work functions are 5.56 eV and 4.03 eV for As/Si(001) and Sb/Si(001) surfaces, respectively. We find substantial charge transfer for the As/Si(001) surface, indicating a strong ionic character in the As-Si bonds and small charge transfer for the Sb/Si(001) surface, indicating covalent character in the Sb-Si bonds. The strong polar covalent bonding between surface As atoms and underlying Si atoms may be responsible for the stability of the As/Si(001) surface.

I. INTRODUCTION

With the development of modern crystal growth techniques, such as molecular-beam epitaxy (MBE), chemical vapor deposition (CVD), and atomic-layer epitaxy (ALE), detailed understanding of the surface atomic structures and electronic states becomes increasingly important. The existence of an unoccupied surface band on the clean Si(001) 2×1 surface within the fundamental gap due to surface dangling bonds leads to strong chemical activity of the Si(001) surface. This has stimulated many studies on the adsorption of atoms on the surface in an attempt to passivate the surface.[1–7] A great deal of research has been devoted to Si(001) 2×1 surfaces terminated by group V elements, such as As and Sb. Growth of GaAs on a Si substrate has important technological implications, and the deposition of As on the Si(001) 2×1 surface, in general, is the starting step for the growth, because it has been shown experimentally that As on Si(001) 2×1 is a very stable surface, even when exposed to air.[1] Furthermore, both As and Sb are important dopants for silicon semiconducting devices, and δ doping and doping engineering also promise potential device applications.

Grazing-incidence x-ray scattering and surface extended x-ray-absorption fine structure (SEXAFS) experiments[2,3] indicate that either monolayer As or Sb coverage on the Si(001) surface has a 2×1 reconstruction with a symmetric dimer. The bond length is found to be 2.55 Å between the As dimer atoms and 2.88 Å between the Sb dimer atoms. The first sublayer of silicon atoms under the surface has a small relaxation with respect to its ideal position when As atoms are on top, but practically no relaxion when Sb atoms are on top. The As/Si(001) 2×1 surface is nearly defect-free, but the Sb/Si(001) 2×1 surface has a high density of defects, either vacancies or antiphase defects.[3] These defects also occur in clean Si(001) 2×1 surfaces.[4]

Angle-resolved photoemission spectroscopy (ARPES) experiments[5–7] have been used to investigate the electronic structure of As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces. Surface bands for both As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces just below the Fermi level were found. In a symmetric-dimer model, these surface states correspond to the bonding and antibonding states of the lone pairs associated with the two dimer atoms. Both surface bands are fully occupied and they lie below the top of the bulk Si valence band. Photoemission experiments performed on the Sb/Si(001) 2 ×1 surface by Rich *et al.*[6] showed that a degenerate doping occurs when a whole layer of Sb atoms is adsorbed on the silicon surface. On the other hand, the angle-resolved photoemission (ARPES) and surface differential reflectivity experiments performed by Cricenti *et al.*[7] indicate that the Sb/Si(001) 2 ×1 surface has a semiconducting behavior with a minimum optical gap of 1.4 eV.

In the present paper, electronic structures of As/Si(001) 2 ×1 and Sb/Si(001) 2 × 1 surfaces are calculated self-consistently. The electronic density distributions of surface states are examined to identify the surface bonding character. The work functions of both surfaces are calculated and results are compared with that of the Si(001) 2×1 surface. We find that the As-Si backbond in the As/Si(001) surface has a strong ionic character which seems to make the bond stronger than the covalent backbond found in either the Sb/Si(001) surface or the clean Si(001) surface. This may provide an explanation for the fact that the As/Si(001) surface is more stable than the Sb/Si(001) and the clean Si(001) surface.

II. COMPUTATION METHOD

The present *ab initio* calculation of the surface electronic structure is based on the local-density approxima-

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tion (LDA).[8] The Ceperley-Alder exchange-correlation potential[9] parametrized by Perdew and Zunger,[10] and norm-conserving pseudopotentials[11] of the Kleinman-Bylander form,[12] in which the d component is local and the s and p components are nonlocal, are used. We use planar basis functions which are products of two-dimensional (2D) plane waves (in the x-y plane) and one-dimensional (1D) Gaussian functions along the growth (z) axis.[13] This type of basis function has some advantage over conventional plane-wave basis functions in terms of describing the electronic structures of surfaces. In particular, since the planar basis functions are localized along the direction normal to the surface, a slab model (instead of a supercell model) can be used to describe the surface, thus allowing the calculation of absolute energies (i.e., with respect to the vacuum level), and hence the work function of the surface.

A slab model with eight layers of Si and two layers of As (Sb) is used for the band structure calculation of the As/Si(001) 2 × 1 surface and the Sb/Si(001) 2×1 surface. Experimental values for the bond length between the surface dimer atoms are used, i.e., 2.55 Å for As/Si and 2.88 Å for Sb/Si. For the As/Si(001) surface, the Si atoms under the As surface layer have a small relaxation with respect to their ideal (bulk) positions with parameters taken from Ref. 3. For the Sb/Si(001) surface, the Si atoms under the Sb surface layer are assumed to be unrelaxed. A schematic diagram for the slab model is shown in Fig. 1. The origin of the coordinate system is marked "×", which is chosen at a 2D inversion center so that the Hamiltonian matrix is real.

Two symmetric Gaussian functions of the form $e^{-\alpha_s z^2}$ and two antisymmetric functions of the form $z e^{-\alpha_p z^2}$ multiplied by 2D plane waves with a 6.0 Ry cutoff are used for each Si atomic layer in the slab and three symmetric and antisymmetric Gaussian functions (multiplied by the same number of 2D plane waves) are used for the surface As (Sb) layers. The local and nonlocal potentials are accurately fitted by ten Gaussian functions and matrix elements of these potentials within our planar basis can be evaluated analytically. The long-range Coulomb tail and self-consistent effective potential are treated by proper numerical methods. Four special **k** points in the irreducible segment of the surface Brillouin zone are used. The total energy of the slab converges better than 0.01 eV.

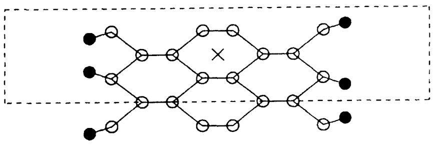

FIG. 1. The slab model used in the calculation of surface electronic states. Open circles indicate Si atoms and full circles indicate As (Sb) atoms. The symbol "×" marks the origin of the coordinate system that defines the planar basis functions.

III. RESULTS AND DISCUSSION

The calculated band structures of As/Si(001) 2 × 1 and Sb/Si(001) 2 × 1 surfaces are shown in Fig. 2. There are 84 electrons in the ten layer [eight Si and two As(Sb)] 2×1 slab model. In the ground state the lowest 42 bands are occupied. It is clearly seen that both As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces are semiconductors with a gap of about 1.0 eV between the occupied and unoccupied bands, in agreement with the experimental findings.[5,7] Since the energies obtained in the present calculation are measured with respect to the vacuum level, the work function can be obtained directly from this figure. Here, we define the work function to be the energy required to remove an electron from the top of the corresponding bulk valence band. Thus we obtain a work function of

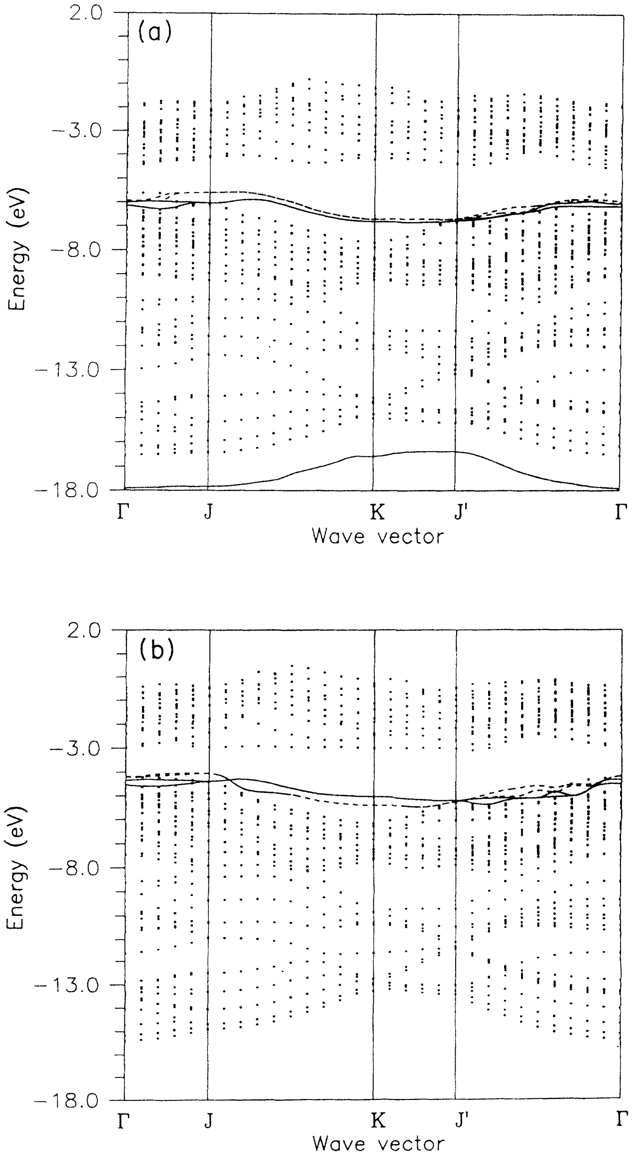

FIG. 2. Band structures of the (a) As/Si(001) 2×1 surface and (b) Sb/Si(001) 2×1 surface. The solid and dashed lines indicate the well resolved surface bands.

5.56 eV for As/Si(001) and 4.03 eV for the Sb/Si(001) surface.

For any V/Si(001) 2×1 surface (V denoting a group V element) in a symmetric-dimer model, each surface group V atom has threefold coordination. Out of the five electrons for each group V atom, two participate in the two V-Si backbonds, one participates in the V-V dimer bond, and the remaining two contribute to a fully occupied lone pair. The bonding and antibonding states of the two lone pairs for each surface dimer contribute to two pairs of surface states with energies near the top of the valence bands, as shown by solid and dashed lines, respectively, in Fig. 2. In a slab model, the interaction of surface states from two ends of the the slab leads to a small splitting (about 0.1 eV) of surface bands for wave vectors (**k**) along Γ-J and J'-Γ. Such a splitting does not exist for (**k**) along J-K-J' due to symmetry. In the limit of a infinitely large slab, each pair of surface bands will become degenerate, which can be approximated by the average of the two surface bands.

Figure 3 shows an enlarged view of the dispersion of the surface bands (averaged over each pair of states) derived from the lone-pair states in comparison with photoemission data. More **k** points have been used and wave functions have been examined in the determination of the surface states for **k** along Γ-J and J'-Γ, since the surface states are buried in the bulk bands in this region. For comparison, the photoemission data of Refs. 5 and 7 are reproduced here, but rigidly shifted upward by a constant energy of 0.8 eV (after matching the Fermi level in Refs. 5 and 7 with the valence band maximum here). The agreement in surface-band dispersion between the theory and experiment for the As/Si(001) 2×1 surface is quite good. Both As/Si(001) 2×1 surface and Sb/Si(001) 2×1 surface band dispersion widths are about 1 eV. The rigid shift used in the comparison is needed, because the local-density approximation used here tends to overestimate the surface-state energies with respect to the bulk bands, due to the difference in charge density between the surface and bulk.[5] The amount of shift here is consist with the value of 0.75 eV reported in Ref. 5 for the As/Si(001) 2×1 surface.

To identify the character of the surface states, the electronic density contours for the two surface states at point K are shown in Fig. 4 for the As/Si(001) 2×1 surface and in Fig. 5 for the Sb/Si(001) 2×1 surface. Both surface states are found to have either the π-bonding or π-antibonding character. The π-bonding character in the lone-pair states was also found in the Si(001) 2×1 surface with a symmetric dimers.[13] In the case of the Si(001) 2×1 surface the energy separation between the π-bonding and π-antibonding bands at the same **k** is about 1 eV, with the π-bonding band located near the top of the valence band and the π-antibonding band near the bottom of the conduction band.[13] However, for the As- or Sb-covered

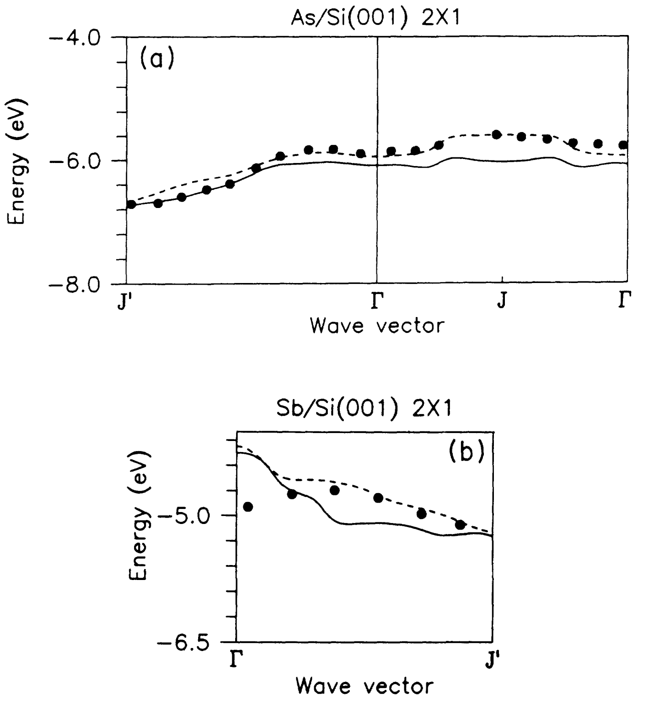

FIG. 3. Enlarged view of the averaged surface bands derived from the lone pairs of the (a) As/Si(001) 2×1 surface and (b) Sb/Si(001) 2×1 surface. The solid and dashed lines are theoretical results and the filled circles are experimental data taken from Refs. 5 and 7.

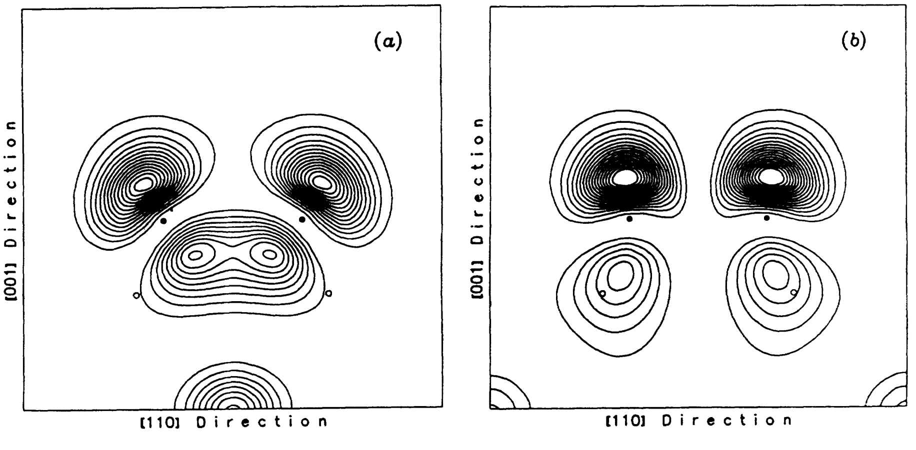

FIG. 4. Electron density contour at point K of the Brillouin zone for the As/Si(001) 2×1 surface for (a) the lower branch of surface bands displaying a π-bonding character and (b) the upper branch of surface bands displaying a π-antibonding character. Scale: both the outermost contour and the increment between two adjacent contours are 0.002 a.u.$^{-3}$.

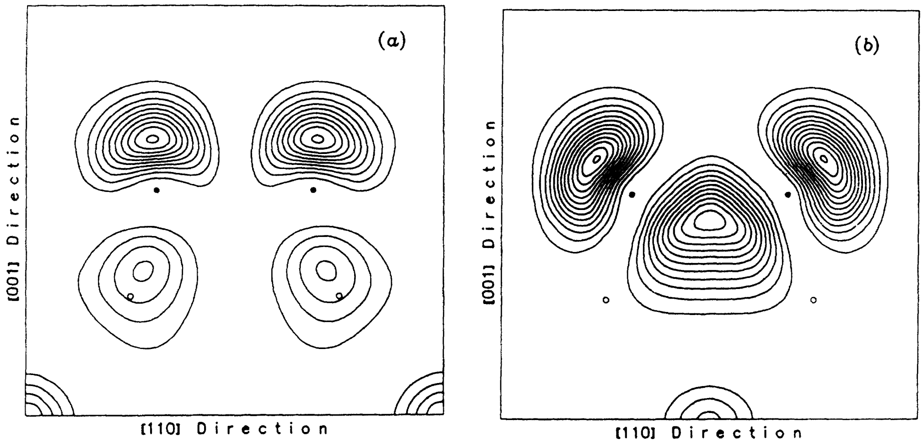

FIG. 5. Electron density contour at point K of the Brillouin zone for the Sb/Si(001) 2×1 surface for (a) the lower branch of surface bands displaying a π-antibonding character and (b) the upper branch of surface bands displaying a π-bonding character. Scale: both the outermost contour and the increment between two adjacent contours are 0.002 a.u.$^{-3}$

Si(001) 2×1 surface, the two surface bands are almost degenerate and lie near the top of the valence bands. For the Sb/Si(001) 2×1 surfaces, we find an interesting anticrossing behavior for the π-bonding and π-antibonding bands for **k** along J-K-J' and near the J point. The energy ordering of the bonding and antibonding states is found to be reversed in this region of the Brillouin zone with the antibonding bands lying below the bonding band at the K point [see Fig. 3(b)]. The above results indicate that, as the dimer bond length increases from 2.23 Å for Si to 2.55 Å for As, then to 2.88 Å for Sb, the interaction between the lone-pair orbitals associated with two dimer atoms gets weaker from Si to As and to Sb. For Si and As dimers, such an interaction is negative (thus favoring bonding states) and it becomes positive for the Sb dimer for **k** in the crossover region [see Fig. 3(b)] (thus favoring the antibonding state).

Figure 6 shows the electron density distribution as a function of z (the coordinate perpendicular to the surface), integrated over the x and y coordinates. It is seen that surface layers have rather a small effect on the electron density distribution in inner Si layers, which is almost the same as that of bulk Si. There is, however, a substantial difference in electron density distribution in the surface layer between the As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces. In particular, the electron density between the surface As layer and the next Si layer is much stronger than that between two inner Si layers, whereas the electron density between the surface Sb layer and the next Si layer is much weaker. In order to investigate the change of work function caused by the surface dipole, we take the slab center as origin and calculate the dipole moment as a function of z for As/Si(001) 2×1, Sb/Si(001) 2×1, and clean Si(001) 2×1 surfaces, all in the symmetric-dimer model. The results are also shown in Fig. 6. The dipole moments for As/Si(001) and Sb/Si(001) surfaces are $-0.393\,e$ a.u. and $0.113\,e$ a.u. with respect to that of the clean Si surface. These charge

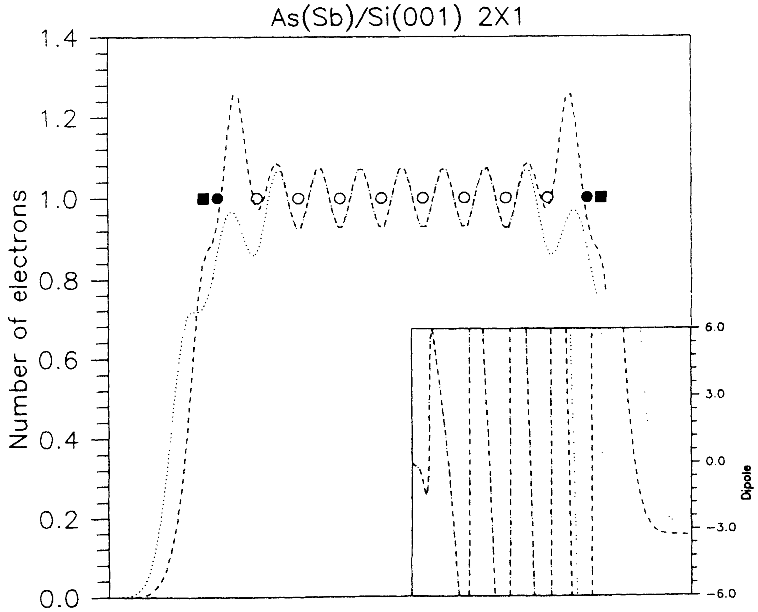

FIG. 6. Electron charge distribution integrated over x and y as a function of z. Dashed line: As/Si(001) surface. Dotted line: Sb/Si(001) surface. The hollow circles indicate atomic positions of Si, the filled circles indicate those of As, and the filled squares indicate those of Sb. The inset shows the dipole moments (in units of e a.u.) for As/Si (dashed curve) and Sb/Si surface (dotted curve) as functions of z.

transfers indicate that if the charge distribution of the Si surface is considered as standard, the electron density shifts toward the surface with respect to the As ion in the As/Si(001) surface and it shifts toward the substrate with respect to the Sb ion in the Sb/Si(001) surface. The energy difference in the work function between the clean Si surface and the As/Si(001) surface is −1.23 eV and the corresponding value for the Sb/Si(001) surface is 0.30 eV. These values are approximately proportional to the surface dipole moments above, indicating an intimate relation between the surface dipole moment and the work function.

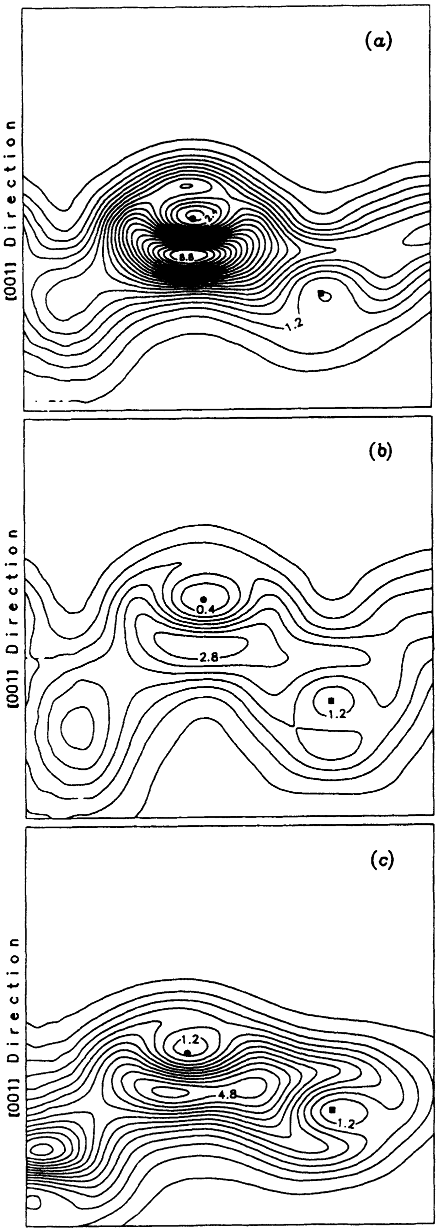

FIG. 7. Electron density contour of the lowest band of the surface at Γ in a plane parallel to [001] including a surface dimer atom and one of its nearest neighbor atoms below the surface. (a) As/Si(001) surface, (b) Sb/Si(001) surface, (c) clean Si(001) surface.

In the band structure of the As/Si(001) 2×1 surface, we also find an interesting feature corresponding to a "hyperdeep" surface state located at energies near −18 eV (with respect to the vacuum level), about 1.5 eV below the bottom of bulk Si valence bands [see Fig. 2(a)]. This hyperdeep surface band is not found in either the Sb/Si(001) 2×1 surface or the clean Si(001) 2×1 surface. Examination of the local density of states reveals that this hyperdeep surface state is related to the backbonds between surface As atoms and Si atoms just below the surface. Figure 7(a) shows the electron density contour for this state at the Γ point in a plane parallel to [001] containing a surface As atom and one of its neighboring Si atoms below the surface. The figure reveals a strong ionic character in the As-Si backbond, indicating substantial charge transfer from the Si atom to the As atom. For comparison, we also plot the electron density contour for the lowest valence band at the Γ point for the Sb/Si(001) 2×1 surface and the clean Si(001) 2×1 surface (in a symmetric-dimer model) in Figs. 7(b) and 7(c), respectively. The plots indicate a clear covalent nature for the Si-Si backbond and a weak ionic character in the Sb-Si backbond. We believe that it is this strong ionic character in the As-Si backbond that increases the bond strength and make the As-passivated Si(001) surface very stable. This implies that the As-passivated Si surface is more stable and less subjective to defect formation than either the clean Si surface or the Sb-passivated Si surface.

IV. CONCLUSION

The electronic states of As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces with the symmetric-dimer structure are calculated based on the local-density approximation and a norm-conserving pseudopotential. The As/Si(001) 2×1 and Sb/Si(001) 2×1 surfaces both show semiconducting behavior with a clear energy gap about 1.0 eV wide between the occupied and unoccupied bands. The dispersion of the surface states is quite different from that of the clean Si(001) surface, where the surface states are present near the middle of the fundamental gap. This difference leads to the desired passivation of the Si(001) surface via monolayer coverage of As atoms or Sb atoms.

The work function for the As/Si(001) surface is found to be about 1.23 eV higher than the clean Si(001) surface, while that of the Sb/Si(001) surface is found to be about 0.30 eV lower. The difference in work function is attributed to the surface dipole moment.

A hyperdeep surface state is found for the As/Si(001) surface and it exhibits a strong ionic character in the As-Si backbond. The existence of such a state is consistent with the large charge transfer found. We believe that the polar covalent character of the As-Si backbond is responsible for the stability of the As-passivated Si(001) surface versus either the clean or the Sb-passivated Si(001) surface, since in general a charge transfer tends to enhance the bond strength due to the Coulomb interaction. The existence of such a hyperdeep state as predicted here awaits confirmation by photoemission measurements.

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