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Ab initio calculations of the geometry and electronic structure of hydrogenated As/Ge(100)

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Arsenic deposited on Ge(100) has been investigated by means of *ab initio* local-density approximation calculations. The results support a previous interpretation of photoemission data in terms of symmetric As dimers. Additional surface states have been found in an energy range not investigated experimentally. Upon adsorption of hydrogen the dimerization is broken and each As atom binds two H atoms instead. The remaining single dangling p_z orbital is shifted into the projected bulk density of states. The modified surface-state band structure is predicted to contain some features that should be clearly visible in photoemission spectra. [S0163-1829(99)05327-8]

I. INTRODUCTION

The structural and electronic characteristics of the outermost atomic layers are of fundamental importance for the understanding of semiconductor properties. In particular, the performance of solid-state devices based upon heterojunctions depends strongly on the character of the interface. Therefore this has been a traditional area for theoretical and experimental studies, and during the last two decades *ab initio* methods have become widely used to study these problems. In the present work we have investigated the As/Ge(100) system and its hydrogenation. While Ge(100) as well as Si(100) surfaces with different adsorbates have been subject to previous studies,[1–3] this particular system has not been investigated theoretically. Indeed, to our knowledge, there are no theoretical studies reported previously on hydrogenation of any group-V/Ge(100) or Si(100) system.

The purpose of our work is to provide a theoretical basis for interpretation of previous experimental data and for devising further experimental tests. Specifically we address the question of the surface geometry in the hydrogenated case. We find that the As dimers should be broken, in accordance with low-energy electron diffraction (LEED) observations.[3] We also present band calculations outside the energy range of existing experimental spectra.

II. THEORY

All wave functions and energy eigenvalues were calculated *ab initio* within density-functional theory[4,5] (DFT) using the local-density approximation (LDA) implemented as in Refs. 6 and 7. For the electron-ion interaction of Ge and As, fully separable, nonlocal pseudopotentials were used,[8,9] based on self-consistent solutions of the relativistic Dirac equation for free atoms.[10–12] The hydrogen pseudopotential by Nardelli, employed in the present calculations, has been tested successfully in several other calculations.[13–15] The calculations were performed using the plane-wave code FHI94MD.CTH,[16] which is an extensively modified version of FHI93CP (Ref. 17) that concerns the computational methods. The geometries were described by the slab supercell method, using the theoretical lattice constants for Ge (5.58 Å) in all calculations.

To establish the minimum energy geometry in the 1×1 structure of 1 ML adsorbed As and 1 and 2 ML H on As/Ge(100) we investigated several different possible structures. We used the same number of **k** points and atomic layers as in the final calculations (see below), but only an 8 Ry cutoff, since this has been found to be sufficient for comparing total energies.[18] For the As/Ge(100) 1×1 surface we considered explicitly As on top of the Ge atoms, in bridge position perpendicular to the continued crystal structure, in the fourfold-coordinated position, and in an epitaxially continued-layer structure (ECLS). The ECLS was found to be clearly the most stable configuration. In the case of adsorbed H on As/Ge(100) we assumed that As kept its ECLS position because of the very strong bonding found for the clean As/Ge(100) surface. The H was then tested in bridge, on top, fourfold-coordinated, and ECLS positions. Again, the ECLS was found to be the minimum energy geometry. In particular it should be mentioned that the on-top arrangement, in which the local As geometry resembles that of AsH_3, is found to be 0.75 eV higher in energy then the ECLS.

Treating the 2 ML coverage of H (i.e., two H atoms per As atom), we placed the H pair both in bridge, ECLS, and diagonally fourfold-coordinated positions. The ECLS was found to give the lowest energy as expected. The diagonally fourfold-coordinated geometry in fact automatically changed into the ECLS upon relaxation. We also calculated hydrogen covered Ge(100) 1×1 with 2 ML H for reference. The details were identical to those of the hydrogenated As/Ge(100) systems.

The 2×1 As/Ge(100) surface was *a priori* assumed to contain symmetric dimers since there is strong experimental support for this kind of geometry for Ge(100)[3] as well as Si(100).[2] In the case of the hydrogen passivated (1 ML H) As/Ge(100) 2×1 geometry we considered both H on top of the As atoms, and a slightly disturbed geometry, i.e., H slightly off the ideal on top position. Through relaxation the H atoms aligned themselves in between the As dimers, establishing a ‘‘double dimerized’’ geometry.

The Ge(100) substrate was described by a 12-layer slab suspended in ten layers of vacuum, including the As and H atoms. The system (supercell) was then repeated periodically. Twenty-seven special Monkhorst-Pack **k** points in the irreducible Brillouin zone (IBZ) were used to sample the

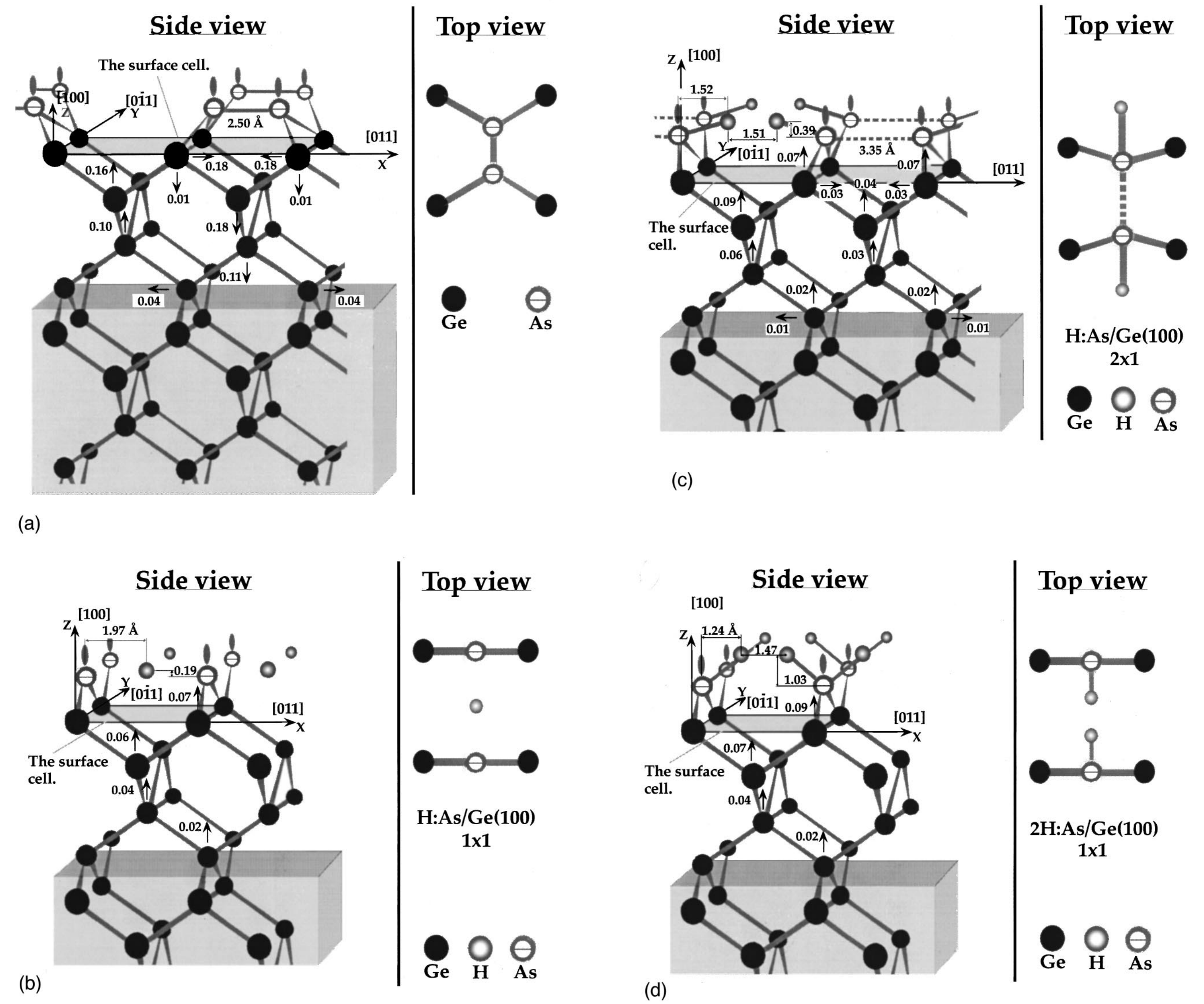

FIG. 1. (a) Atomic positions of the As atoms and the relaxed Ge substrate. The arrows indicate the displacement from the ideal lattice coordinates. All numbers in Å. The Ge atoms submerged into the gray area represent the locked ideal positions in the center of the slab. (b) The geometry of the H:As/Ge(100) 1×1 structure. All details are the same as in (a). (c) Atomic positions of the dimerized hydrogenated As/Ge(100) 2×1 geometry. (d) The atomic structure of 2 ML H on As/Ge(100) 1×1.

wave functions for the 1×1 structure and 36 special **k** points for the 2×1 structure. In both cases this corresponds to 216 points in the full zone. In each case all atomic positions except the four central Ge layers were fully relaxed. The equilibrium geometries were considered as established when all forces were smaller then 0.005 eV/Å, corresponding to an estimated numerical uncertainty of maximum 0.05 Å. When the minimum energy geometries had been established, the stable geometries were recalculated using a 12 Ry cutoff energy. All subsequent results are obtained using this higher cutoff.

The thickness of the vacuum region has been tested by investigating the effective potential and the total charge density in this area. Both go to zero rapidly and are negligible over a distance corresponding to several atomic layers, thus ensuring proper decoupling of the surfaces. The quality of the Ge slab calculation was tested by comparing the partial densities of states (PDOS) in the central layers with those calculated for bulk Ge. Very good agreement was found for the current cutoffs and geometries. The energies of the H_2 and As_4 molecules used in the total-energy calculations [see Eq. (1)] were obtained using an empty cube with a side measuring 25 bohrs. A 12-Ry cutoff and 64 special **k** points in the full Brillouin zone were used, corresponding to 10 and 16 **k** points in the IBZ, respectively.

III. RESULTS

A. As/Ge(100)

We find that the As dimers are stable with 2.12 eV per pair (calculated at 12-Ry cutoff) as compared to the ECLS 1×1 geometry. All the underlying Ge atoms are fourfold coordinated in a relaxed diamond lattice, while the adsorbed As atoms are only threefold coordinated, see Fig. 1(a). The two backbonds to the Ge atoms beneath are completely sym-

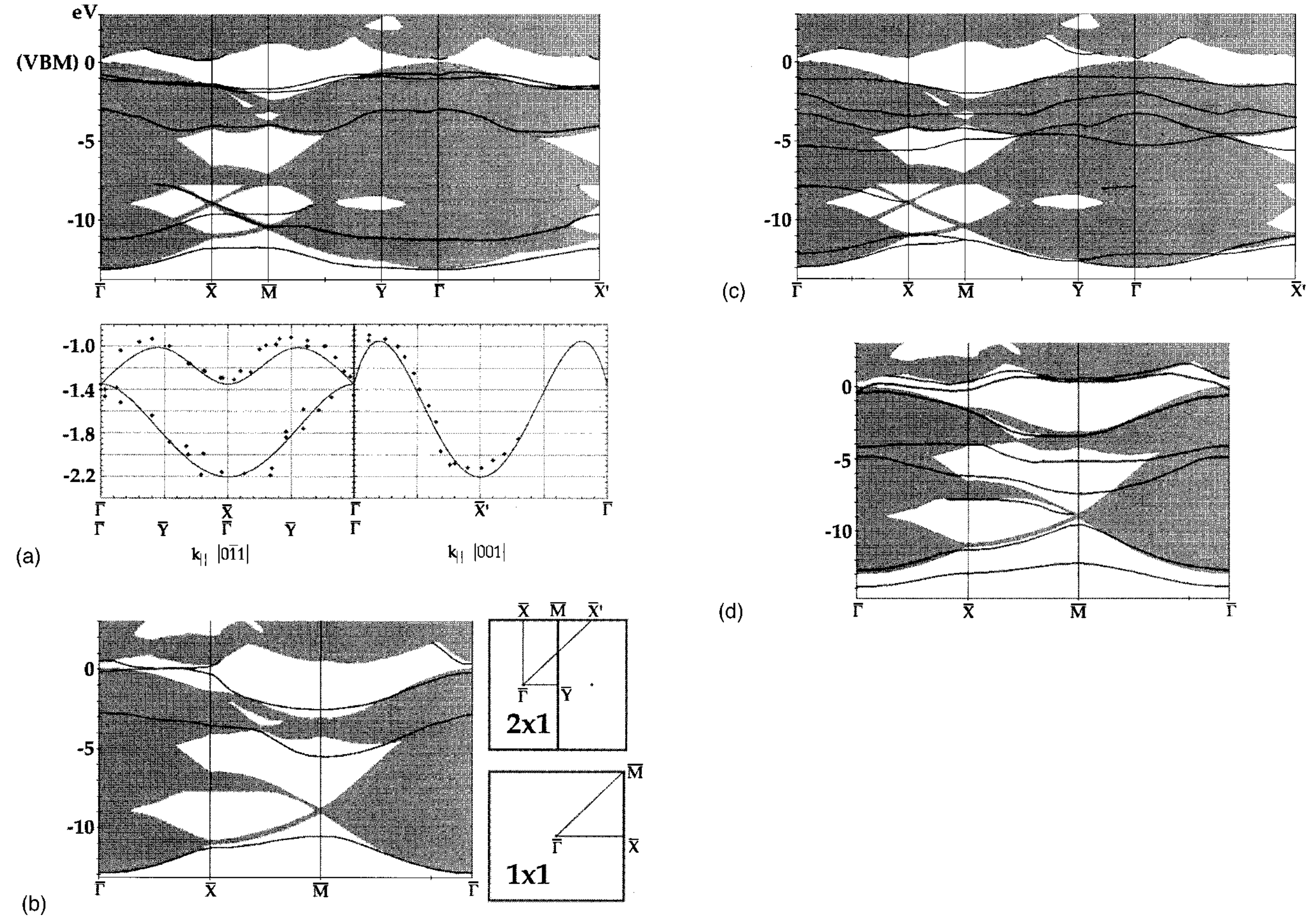

FIG. 2. (a) Plot of the surface states and resonances for the dimerized As/Ge(100) surface; notation as in Fig. 1(a). No surface states originating from the conduction bands are drawn, except when visible in the band gap. The gray area represents the projected bulk bands. Comparison between theory (solid line) and experiment (diamonds) for the π and π^* states is included below the theoretical band plot. The average position of the two theoretical bands is shown. Note that the experimental values refer to the Fermi level, while the theory in (a) refers to the VBM. The theory has therefore been shifted 0.35 eV downwards (half the band gap of Ge.) (b)–(d) The theoretical surface states and resonances for the geometries in Figs. 1(b)–1(d).

metric, 2.50 Å in length, which equals the dimer As-As bond. These values were found after complete relaxation, where the initial dimer bond length was set to 3.0 Å, thus ensuring a proper minimum energy geometry. The Ge substrate relaxes significantly in a zigzag like pattern along the dimerization direction, with the Ge atoms beneath the As dimers displaced inwards, and atoms in the second and third layers located between the dimers displaced outwards [see Fig. 1(a)]. All these displacements can be intuitively expected due to the in-plane contraction of Ge atoms coordinated to the As dimers. All displacements are in the same directions as for symmetric As dimers on Si but somewhat different in lengths.[2]

The surface states were calculated along the $\overline{\Gamma}$-$\overline{X}$-$\overline{M}$-$\overline{Y}$-$\overline{\Gamma}$-$\overline{X}'$ lines, with notations as in Fig. 2. To identify the surface states and/or resonances we classified each band separately in each **k** point from the slab calculation after PDOS distribution and relative weight of the wave function in **r** space on the outer layers. Applying this scheme we found the band structure in Fig. 2(a).

Unlike tight-binding schemes, the present calculations do not provide a simple method for identifying the different bands in terms of atomic orbitals. By investigating the spatial charge distributions at different **k** points, and by comparing our results with those obtained by tight-binding calculations on similar systems [e.g., As-dimer terminated GaAs(100)],[19] we have been able to assign the bands as follows. The two uppermost bands near the valence-band maximum (VBM) originate from the lone pair p_z states on the As atoms. In the dimerized configuration the symmetrical and antisymmetrical combinations of these states result in two nearly degenerate molecular π and π^* orbitals. The maximum theoretical splitting is 0.35 eV. An excellent topological agreement with calculations[2] on symmetric As dimers on Si is noted in the dispersion along $\overline{\Gamma}$-$\overline{X}$, $\overline{\Gamma}$-$\overline{Y}$, and $\overline{\Gamma}$-$\overline{X}'$ (no other **k** points were shown in Ref. 2).

Below the molecular surface states, in the energy range 3.0–4.5 eV below VBM, we find another surface band just above the upper stomach gap in the projected bulk bands. Detailed examination shows that this actually turns out to be a nearly degenerate pair of bands. One of them is due to As-Ge backbonds, the other due to As p_x-p_y mixed bridge bonds. Considering the different spatial distribution of the two states, the similarity between the two bands is surprising. It will be shown below that upon surface hydrogenation the degeneration is actually lifted.

In the energy range 6–11 eV below the VBM two surface related bands are found that should be associated with the As-Ge backbonds. Their similarity with surface bands on the GaAs(100) surface[19] suggests that they can be described as *s*-like backbond states, the upper one primarily cation and the lower one anion derived. While the former is quite weak and can only be traced in the gap region, the latter can be identified throughout the surface Brillouin zone. Finally, again in analogy with the GaAs(100) surface, we find in the range 12–13 eV below VBM a band that should be As *s* derived.

The experimental data available for the As/Ge(100) system[3] are strongly focused on the dispersive properties of the topmost π/π^* bands, primarily aiming at determination of the As dimer structure (symmetric versus asymmetric). In Fig. 2(a) we have replotted this part of the calculated band structure on an expanded energy scale, along with the surface bands as determined by angle resolved photoemission. The agreement between experiment and theory provides support for a symmetric dimer structure, just as concluded previously.[3]

B. H:As/Ge(100)

We first consider the 1 ML 1×1 ECLS structure with both H and As in initially perfect lattice positions. Besides being the apparently simplest case a (1×1) surface geometry for a hydrogen treated As/Ge(100) surface has been indicated by experiments.[3] Complete relaxation did not lead to any atomic displacement parallel to the surface, but some movement of the Ge atoms outward along the surface normal, see Fig. 1(b). One interesting result is that the As-H distance is 1.98 Å, i.e., significantly larger than the sum of the covalent radii (1.19 and 0.37 Å for As and H, respectively). From this we conclude that the As-H bond is not covalent in this case. We also find that the As backbonds are practically the same as for the hydrogen-free dimerized 2×1 surface discussed above. The largest displacement relative to the ECLS geometry occurs for the H atoms, which lie inside the As atomic layer within a few tenths of an Å. Having excluded covalent bonds, we believe that the H atoms donate their electrons into unoccupied surface states of the substrate. In this situation, the almost bare proton should be attracted towards the negative charge of the underlying As/Ge substrate. We believe this to be the driving force behind the ‘‘in plane’’ position of the H atom.

In the electronic structure of the hydrogenated 1×1 system [Fig. 2(b)] we note first that the band gap is bridged by a surface state. The surface is thus metallic. Below the VBM three distinct bands are found, see Fig. 2(b). None of these states is directly hydrogen related—the uppermost one derives from the As lone pair orbitals, the second one is due to As-Ge backbonds, and the lowest state is also As derived. This lack of H-derived bands is consistent with the lack of covalent bonds suggested above.

Allowing the system to reconstruct, we find that the symmetric dimerized hydrogenated structure [see Fig. 1(c)] is energetically favored as compared to the 1 ML (1×1) ECLS geometry, with an energy gain of 0.38 eV for each H-As dimer. The number of atoms per surface area being the same as in the 1 ML (1×1) case, the numerical error is estimated to less then 0.03 eV.

The H atoms are located only 0.39 Å above the As plane, and the As-H distance is 1.56 Å, i.e., in excellent agreement with the expected As-H covalent bond length. All Ge atoms are displaced outwards compared to the ideal lattice positions, even though some of the zigzag pattern remains from the As/Ge(100) 2×1 system. In comparison with the As/Ge surface prior to hydrogenation, the As-As distance is significantly increased, from 2.50 to 3.35 Å. This is an effect of the partial transfer of the bonding charge between the As atoms into the As-H covalent bond. There are no indications of any H-H bonding—the region between the two protons is relatively empty of charge. The length of the backbonds is practically unchanged though (2.49 Å).

The electronic structure of this system [Fig. 2(c)] is more complex than that of the (1×1) surface, but when compared with the band structure of the prehydrogenated surface, several similarities are noted. In contrast to the 1×1 ECLS geometry, this system [like the As/Ge(100)2×1], is clearly nonmetallic. The uppermost dangling-bond-induced π/π^* bands are replaced by a single dangling p_z-bond state. Its dispersion is nearly identical to that of the π and π^* bands. We also recognize the band just above the upper stomach gap. In the present case this is a single band (not degenerated), and the charge distribution reveals that it is derived from As-Ge backbonds. Between the p_z state and the backbond band, in the range 2–3 eV below VBM, a new feature is seen. The charge distribution of these states is strongly concentrated between the As and H atoms. Consequently, we associated this band with the As-H covalent bonds. Within the stomach gap we find another apparently new surface state. By inspecting the charge distribution, however, we find that this state is very similar to the one associated with the p_x-p_y mixed bridge bonds in the case of As/Ge, i.e., one of the apparently accidentally degenerate bands mentioned above. Finally, the three lowest bands are analogous to the lowest bands in the case of As/Ge.

As will be shown below, the little experimental information that is available on the electronic states of the hydrogenated As/Ge(100) system does not support this band structure. We have therefore also considered the surface with two hydrogen atoms per unit cell. In the following we refer to this as a 2 ML H system. With a different number of H atoms, no simple comparison can be made of the total energies. Under the assumption, however, that the extra H atoms are being taken from noninteracting H_2 molecules surrounding the sample, possibly physisorbed on the surface of any of the two geometries discussed above, the energies can be readily compared.[18] Thus the energy gained by the adsorption of an additional layer of H is given by

$$\begin{aligned}\Delta E = & (\text{energy per 1 ML } 1\times1 \text{ surface cell})\\ & +\tfrac{1}{2}(\text{energy of a } \mathrm{H}_2 \text{ molecule})\\ & -(\text{energy per 2 ML } 1\times1 \text{ surface cell}). \qquad (1)\end{aligned}$$

Using this scheme to calculate the energy gain, we observe that the 2 ML (1×1) geometry should be stable by 0.42 eV as compared to the dimerized hydrogenated surface. Unfortunately, the hydrogen pseudopotential gives rise to a relatively large uncertainty. Although very good in describing total energies of similar systems (e.g., the two 1 ML geometries above), the hydrogen pseudopotential is less reliable in regions relatively empty of charge. The reason is that there is no proper core in the H atom which implies that for single atoms as well as for the H_2 molecule, the screening of the proton is not complete. In the vicinity of other atoms, this problem is eliminated. Taking this into account, we estimate the possible numerical uncertainty to approximately 0.6 eV, which should be compared to less then 0.2 eV for comparisons of ''ordinary systems''; see Ref. 18.

Hence the 2 ML (1×1) geometry is numerically degenerate with the dimerized 2×1 structure, although in absolute numbers it is clearly the most stable one. If the hydrogen molecules in the gas are assumed to be in some excited state (in the experiment the gas is activated by a hot filament), then the 2 ML arrangement is clearly favored. This is also consistent with the experimentally observed 1×1 LEED pattern.

Similar to the ECLS 1×1 case above, the Ge substrate relaxes slightly outwards, but keeps its ideal position parallel to the surface; see Fig. 1(d). The As backbonds are slightly shorter (2.47 Å) than in the As-dimer case without hydrogen (2.50 Å), while the As-H distance has increased somewhat (from 1.56 to 1.61 Å) as compared to the 2×1 hydrogenated dimer structure. All changes are within the numerical uncertainty, though. The volume between the As and the H atoms is very dense with charge, while between the two H atoms it is relatively empty. We also note that the angle between the As-H bond and the surface is 56°, i.e., only 2.5° off the ideal direction of the zinc-blende covalent bond. Thus clear covalent bonds between the H and the As atoms are formed in the same way as in the 2×1 case discussed above.

The surface states of this system can be recognized relatively easily when compared to the two hydrogenation cases treated above. Since As is a five valent atom, there still remains one dangling p_z bond, resulting in a surface state just below the edge of the valence band; see Fig. 2(d). The dispersion and character of this band are very similar to that of the p_z state in the 1 ML (1×1) geometry, but lower in energy. The surface is still metallic though, the gap being bridged by surface states. Also the upper As-Ge backbond state is found to have the same qualitative dispersion but is now located at -4 to -5 eV. In the lower part of the upper gap a new H-As bond-related state appears in the region of -5 to -7 eV. Not too surprisingly the dispersions along the $\overline{\Gamma}$-$\overline{X}$ and $\overline{\Gamma}$-$\overline{M}$ lines agree qualitatively well with those of the H-As related band along $\overline{\Gamma}$-$\overline{X}$ and $\overline{\Gamma}$-$\overline{X}'$ in the 2×1 case [Fig. 2(c)], though the state at hand is located several eV lower in energy. The hydrogenation also appears to push down the backbond feature found in the dimer geometries into the lower stomach gap along the edge between $\overline{X}$ and $\overline{M}$. This feature becomes extremely weak, once inside the projected bulk bands. This explains why it is not found in the simpler 1 ML (1×1) case, Fig. 2(b). The second lowest-lying state in the region of -10 to -13 eV, tracing the band edge, is an As-derived state in the same way as for the other geometries. Well below the projected bulk density of states, however, a new H-As bond-related surface state appears. The wave functions of this band have the same character as those of the upper H-As band (-5 to -7 eV). This new band should be expected, since each As atom now binds to two H atoms instead of one as in Fig. 1(c) geometry. The deep location also agrees well with the typical hydrogen binding-energy level of ∼-14 eV.

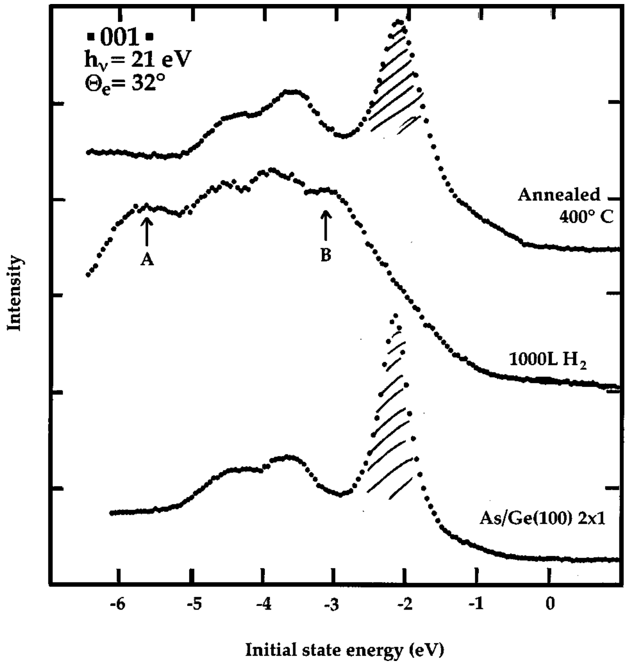

FIG. 3. Photoemission spectra obtained with 21 eV linearly polarized synchrotron radiation. The emission angle is 32° and $\mathbf{k}_{\parallel}$ lies in the [001] azimuth.

C. Comparison with experiment

While the As passivation of Ge and Si surfaces has been studied experimentally quite extensively, relatively little experimental information is available on the hydrogenation of these surfaces. According to Ref. 3, the passivated surface is stable in some form, as no significant loss of As is observed after exposure of the As/Ge(100) surface to activated hydrogen. The (1×1) LEED pattern supports our findings of the ''2 ML'' (1×1) structure as the most stable one, although it could be expected that the observed (1×1) LEED pattern might be a result of a poorly ordered surface with small, random-phase dimerized domains. No photoemission data on the H:As/Ge(100) have been published to our knowledge, but some earlier unpublished data have been found;[20] Fig. 3. At the emission angle chosen here the spectra probe the region around the $\overline{X}'$ point in the 2×1 surface Brillouin zone (SBZ). The shaded peak is interpreted as due to the As-derived π and π^* states. The As/Ge(100) surface was thereafter exposed to 1000 L of activated H_2. As a result of this treatment the dangling-bond state disappeared as did the fractionally ordered LEED spots. By subsequent annealing at 400 °C the initial 2×1 As/Ge(100) surface was restored.

In the hydrogenated case we see that two new structures are developed, labeled *A* and *B*. For the 2 ML (1×1) geometry the spectrum probes the region around the $\overline{M}$ point in the SBZ; see Fig. 2. By comparison with the calculated band structure [Fig. 2(d)], peak *A* can be identified as the p_z band, being pushed down by the hydrogenation, while peak *B* can be associated with the backbond state. The downward shift of the dangling-bond state relative to the prehydrogenated system is fairly well reproduced in the calculation, but the distance between the two peaks, 2.5 eV experimentally, is clearly larger than in the calculation, 1.75 eV. This may be explained by the fact that the LDA is known to result in too small interband values. Assuming instead the 2×1 dimerized structure with adsorbed hydrogen, the H-As band and the bridge-bond state would fit peaks *A* and *B* quite well, with a separation of 2.25 eV. In that case, however, one would have to explain why the upper p_z band would no longer be visible in the spectrum. Considering the photoemission data and the agreement between the LEED pattern and the total-energy calculations, we believe the hydrogenated 2 ML H:As/Ge(100) (1×1) geometry to be the true equilibrium crystal structure (ECS) of this system.

IV. CONCLUSIONS

Our calculations confirm that the stable configuration of 1 ML adsorbed As on Ge(100) is the form of symmetric dimers.[3] The surface-state bands near VBM are in good agreement with experimental data and with earlier calculations on As/Si(100). Similarities are noted with the As-dimer terminated GaAs(100) surface.

Regarding the hydrogenated As/Ge(100) system we find a 1×1 arrangement with two H atoms per As atom to be the most stable one. The H atoms are covalently bonded to As, allowing the As to form fourfold-coordinated bonds in a similar way to an embedded As layer. A single dangling-bond band remains, but is being shifted down into the projected bulk bands. Two new bands related to the H-As bonds emerge at around −6 and −13 eV, respectively. Details in the calculated band structure should be useful for assessing the real surface structure in this case by further experimental work.

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[1] G. Li and Y. C. Chang, Phys. Rev. B **48**, 12 032 (1993).

[2] R. I. G. Urhberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986).

[3] F. Morar, U. O. Karlsson, R. I. G. Uhrberg, J. Kanski, P. O. Nilsson, and H. Qu, Appl. Surf. Sci. **41/42**, 312 (1989).

[4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[5] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[6] D. M. Ceperley and B. I. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[7] P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[8] B. Hamann, Phys. Rev. B **40**, 2980 (1989).

[9] X. Gonze, P. Käckell, and M. Scheffler, Phys. Rev. B **41**, 12 264 (1990).

[10] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[11] G. B. Bachlet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[12] L. Kleinmann and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[13] C. M. Bertoni, M. B. Nardelli, and E. Molinari, Vacuum **41**, 663 (1990).

[14] C. M. Bertoni, M. B. Nardelli, and E. Molinari, Europhys. Lett. **13**, 653 (1990).

[15] M. B. Nardelli, F. Finocchi, M. Palummo, R. D. Felice, C. M. Bertoni, F. Bernadini, and S. Osscicini, Surf. Sci. **269/270**, 879 (1992).

[16] FHI94MD.CTH is based on FHI93CP, purchased from the Computational Physics Communications library in 1995. While the basic computational physics is the same, the changes of computational nature are extensive.

[17] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).

[18] S. Mankefors, P. O. Nilsson, J. Kanski, and K. Karlsson, Phys. Rev. B **56**, 15 847 (1997).

[19] P. K. Larsen, J. F. van der Veen, A. Mazur, J. Pollmann, J. H. Neave, and B. A. Joyce, Phys. Rev. B **26**, 3222 (1982).

[20] F. Morar, U. O. Karlsson, R. I. G. Uhrberg, J. Kanski, P. O. Nilsson, and H. Qu (unpublished).