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Dimer Reconstruction of Diamond, Si, and Ge (001) Surfaces

Peter Krüger and Johannes Pollmann
Institut für Theoretische Physik II–Festkörperphysik, Universität Münster, Münster, Germany

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Ab initio calculations of structural and electronic properties of the C(001)-(2 × 1) diamond surface are reported and discussed in direct comparison with Si(001) and Ge(001). Our results strongly favor a symmetric dimer reconstruction of C(001)-(2 × 1) as opposed to an asymmetric dimer reconstruction of Si and Ge (001). The physical origin and quantitative nature of the dimer reconstructions are investigated systematically, and it is shown by analyzing chemical trends why Si(001) is the most subtle case for an unequivocal surface structure determination.

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The origin and nature of dimer reconstructions at (001) surfaces of elemental semiconductors is one of the most intensively discussed issues in semiconductor surface physics. Certainly, most of the efforts have been concentrated on the Si(001) surface [1] for obvious reasons and to a lesser extent on Ge(001). For the C(001)-(2 × 1) surface, which is of particular technological importance in the context of diamond thin film growth [2], no fully self-consistent local density approximation (LDA) calculations have been reported in the literature to date. A precise knowledge of the reconstruction of C(001) certainly can shed light on the controversially discussed reconstruction behavior of the (001) surfaces. For Si(001), conflicting evidence from both theory and experiment favored either symmetric or asymmetric dimers as building blocks of the room-temperature (RT) disordered (2 × 1) and the low-temperature ordered $c(4 \times 2)$ reconstructions. The energy difference between asymmetric and symmetric dimer models as calculated by well-converged first-principles investigations turned out to be of the order of 0.1 eV per dimer only. Most of these calculations addressed the (2 × 1) phase while Northrup [3] studied the real $c(4 \times 2)$ phase. On the experimental side, low-temperature scanning tunneling microscopy (STM) investigations have shown that the dimers in the $c(4 \times 2)$ geometry are asymmetric [4] while they appear to be symmetric in STM results at RT [5]. This might be due to thermal flipping motions of the dimers between their left- and right-tilted positions, as has been suggested by Dabrowski and Scheffler [6]. The picture is further complicated by the fact that at RT defects are abundant at the Si(001) surface [4]. In order to resolve this general issue on surface reconstruction and to contribute at the same time to a basic understanding of diamond surfaces which are becoming increasingly important in semiconductor technology in recent years we have studied the (001) surfaces of C, Si, and Ge by a systematic first-principles investigation.

In this Letter, we analyze the reconstruction of C(001)-(2 × 1) in direct comparison with that of Si and Ge (001). There are clear physical and chemical trends to be observed in our results. C(001) is at the one limit showing symmetric dimers and Ge(001) is at the other limit clearly showing asymmetric dimers. Si(001) resides at the borderline between these two extremes. We scrutinize the differences in reconstruction behavior. From our analysis of the chemical nature of the reconstruction-induced dimer bonds a clear physical picture emerges.

We have used the LDA of density functional theory [7] to determine energy-optimized surface structures and to calculate the electronic surface band structures. The (001) surfaces are described by *semi-infinite* systems. We have solved the Kohn-Sham equations [8] using our scattering theoretical method based on localized orbitals and Green's functions as described in detail in Ref. [9]. We use two shells of Gaussian orbitals with s, p, d, s^* symmetry per atom whose decay constants are 0.19 and 0.50 for Si and Ge and 0.35 and 1.70 for C (lengths in atomic units). At the surface atoms we take ten additional Gaussian orbitals into account to enlarge the flexibility of the basis set in the surface region. The corresponding decay constants are 0.8 for Si and Ge and 0.19 for C. We use the norm-conserving separable pseudopotentials of Sabisch [10] for C and of Gonze, Stumpf, and Scheffler [11] for Si and Ge and the exchange-correlation potential in the Ceperley-Alder form [12]. Brillouin zone integrations are carried out using 32 $\mathbf{k}_\parallel$ points in the whole (2 × 1) unit cell. Our calculated bulk lattice constants of 3.52 Å for C, 5.37 Å for Si, and 5.58 Å for Ge agree within 1% with the respective experimental values of 3.57, 5.43, and 5.65 Å. Our band gaps of 4.14 eV for C, 0.54 eV for Si, and 0.42 eV for Ge, calculated at the *theoretical* lattice constants for reasons of consistency with the surface structure optimizations, show deviations from experiment as is typical for the LDA.

The surface structure optimizations are carried out by the elimination of forces [9]. We have relaxed all atoms in the topmost four layers of the semi-infinite (2 × 1) unit cell. For C(001)-(2 × 1) we have considered many different asymmetric configurations as a start. We always end up with the same symmetric dimers and thus find no stable asymmetric dimer configuration for this surface. The calculated dimer bond length turns out to be only 1.37 Å. Previous empirical and semiempirical calculations except for the non-self-consistent LDA calculation by Yang, Drabold, and Adams [13] found symmetric dimers as well, with bond lengths ranging from 1.40 to 1.43 Å. For a detailed account of that work, see Ref. [14]. Experimental information on C(001)-(2 × 1) is currently still scarce. Lurie and Wilson [15] have reported a (2 × 1) reconstruction after annealing at high temperature above 1573 K in ultrahigh vacuum. No evidence for any higher order reconstructions such as the $c(4 \times 2)$ was seen in their work and in other investigations [2]. Thus there is no evidence for a ground state of correlated asymmetric dimers. The results of our structure optimization completely agree with these findings.

Our results for Si and Ge (001) have been presented in comparison with experimental data in Ref. [16]. For Si(001)-(2 × 1) we find asymmetric dimers with a buckling angle of 19° and a bond length of 2.25 Å in excellent agreement with the results of other highly converged *ab initio* pseudopotential calculations [3,17] who obtained 2.29 and 2.27 Å, respectively. Measured bond lengths spread over a wide range from 2.20 to 2.47 Å sensitively depending on the experimental method and on surface preparation (see, e.g., the discussion in Ref. [16]). For the metastable symmetric configuration we find a dimer bond length of 2.25 Å as well. The symmetric dimer model (SDM) is 0.14 eV per dimer higher in energy than the asymmetric dimer model (ADM). This energy gain per dimer confirms previous values of 0.1 and 0.14 eV as obtained in Ref. [6] for the (2 × 1) and in Ref. [3] for the $c(4 \times 2)$ surface. For Ge(001)-(2 × 1) we obtain asymmetric dimers as well, with a bond length of 2.41 Å and a buckling angle of 19°. The corresponding values of a supercell *ab initio* calculation by Needles, Payne, and Joannopoulos [18] are 2.46 Å and 14°, while Spiess, Freeman, and Soukiassian [19] have determined a bond length of 2.48 Å and a buckling angle of 15° within an LDA cluster calculation. Culbertson, Kuk, and Feldman [20] have measured a buckling angle of 20° while Rossmann *et al.* [21] obtained best agreement with their x-ray diffraction data for a fit model with a dimer bond length of 2.44 Å and a buckling angle of 21°. In our results the ADM is 0.3 eV per dimer lower in energy than the SDM.

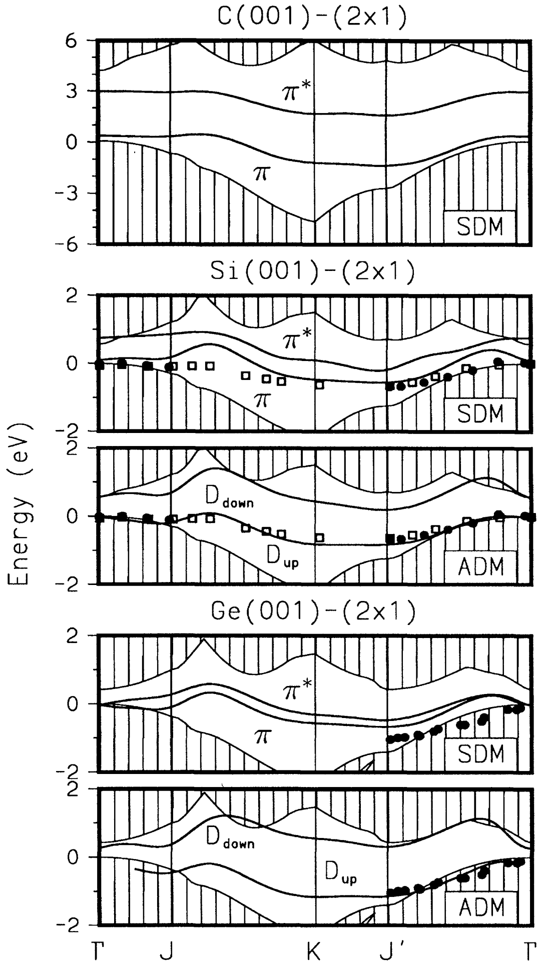

FIG. 1. Section of the surface band structure of C, Si, and Ge (001)-(2 × 1) in comparison with salient experimental ARPES data of Ref. [22] (squares) and of Ref. [23] (circles) for Si(001) and of Refs. [24] and [25] for Ge(001).

To analyze the reconstructions of the three surfaces in more detail we have calculated the electronic surface band structure for the SDM of C(001)-(2 × 1) and for the SDM and ADM of Si and Ge (001)-(2 × 1). Our results are shown in Fig. 1 in comparison with most recent angle-resolved photoemission spectroscopy (ARPES) data. The electronic properties for the SDM of the three surfaces are qualitatively similar but show drastic quantitative differences. In the SDM two equivalent dangling-bond orbitals per dimer occur. They exhibit a π interaction giving rise to a bonding π band and an antibonding π^* band. The interaction between dangling bonds at neighboring dimers leads to a strong dispersion of these bands along the J-K and Γ-J' directions. The filled π band and the empty π^* band of C(001) are separated in energy by 1.2 eV. Thus the C(001) surface is semiconducting in the SDM. For the SDM of the Si and Ge (001) surfaces, on the contrary, the π and π^* bands overlap and the surfaces turn out to be metallic, in marked contrast to experiment. In this case a Jahn-Teller-like distortion occurs leading to asymmetric dimers in both cases. The asymmetry of the dimers in the ADM of Si and Ge (001) leads to a pronounced splitting of the two related bands $D_{\rm up}$ and $D_{\rm down}$, as can be seen in Fig. 1. The $D_{\rm up}$ ($D_{\rm down}$) states are mainly localized at the up (down) atoms of the dimers. There is a gap of 0.10 eV between the two bands at Si(001) and of 0.26 eV at Ge(001). In both cases the surface is semiconducting. The asymmetry yields an energy gain which stabilizes the buckled geometry. In Fig. 1 we have also shown ARPES data from Refs. [22–25]. There is a much better agreement between our calculated electronic structure for the ADM of Si and Ge (001) with the respective ARPES data than for the SDM. The π bands of the SDM are hard to reconcile with the measured dispersions and bandwidths of the most pronounced dangling-bond band in both cases. We mention that there is an additional weak structure in the gap (not shown in Fig. 1) observed experimentally near J' for Si(001) [23] and Ge(001) [24]. This feature can be explained as a second dangling-bond band resulting from local $c(4 \times 2)$ regions existing already at RT on the disordered nominal (2×1) surfaces of both materials [3,24].

The mechanism of reconstruction at Si and Ge (001) resembles that of the Jahn-Teller effect in molecules with a symmetry-degenerated ground state. At the considered surfaces, however, the dangling-bond bands of the SDM are not symmetry degenerate. There is only an accidental degeneracy. Therefore symmetric dimers at (001) surfaces of group IV semiconductors are not necessarily unstable with respect to symmetry breaking by dimer buckling. This is confirmed by our results for the SDM of C(001) for which the surface is already semiconducting. An asymmetry of the dimers does not yield any energy gain. Therefore a Jahn-Teller-like transition does not occur at C(001)-(2×1) in agreement with experiment.

To further highlight salient chemical trends in the reconstruction behavior of the three considered surfaces we have compiled in Table I characteristic energies for these systems. Table I shows that the reconstruction energy per surface unit cell E_{rec} follows exactly the same trend as the cohesive energy per bulk bond E_{coh}. They agree roughly within 0.3 eV. Thus E_{rec} results in each case essentially from the formation of a new bond, namely the dimer bond. E_{rec} is lower than E_{coh}, since the back bond rotations accompanying the dimer formation cost small energies of about 0.3 eV in each case. The energy gain due to asymmetric as compared to symmetric dimer formation E_{asy} increases from 0.14 eV for Si to 0.30 eV for Ge (001) and amounts to 7% and 18% of the total reconstruction energy E_{rec}, respectively. As a consequence, the dimer flipping rate for Ge(001) is about 10^3 times smaller than for the Si(001) surface at RT and thermally induced dimer flipping is strongly suppressed at the Ge(001)-(2×1) surface, therefore. This conclusion is in excellent agreement with the experimental results of Kubby *et al.* [26].

The bond lengths in Table II exhibit very clear chemical trends as well. The bulk bond lengths are basically identical with the single bond lengths in respective molecules, as was to be expected. The dimer bond lengths d_D show a distinctively different behavior. At C(001) d_D is very close to the length of a C=C double bond in the C_2H_4 molecule while at Ge(001) d_D almost agrees with the length of a Ge—Ge single bond in the Ge_2H_6 molecule. The Si dimer bond length resides in the middle between the single or double bond lengths placing Si(001) again at the borderline between the clear-cut cases of C and Ge (001), respectively.

This very different behavior of d_D can be traced back to the electronic properties of the constituting atoms. C-$2p$ valence orbitals are more localized than the C-$2s$ orbitals since there are no p states in the C core. Therefore p-like C orbitals are able to concentrate charge in the bonding region very efficiently leading to a strong tendency of π bond formation. Actually it is the strong π and σ bonding between the occupied dimer states which strengthen the dimer bonds of C(001) so much that they become double bonds. For Si and Ge the tendency of forming π bonds is clearly suppressed, since in these materials the p valence orbitals are more extended than the s valence orbitals. The electrons in the occupied D_{up} states of the ADM of Si and Ge (001) do not give rise to π bonding and thus contribute only little to the dimer bonds. Therefore, double bonds are not established at Si(001) and, in particular, not at Ge(001). These notions are clearly supported by the valence charge density $\rho(\mathbf{r})$ (left panels) and valence charge density *difference* $\Delta\rho(\mathbf{r})$ (right panels) contours in Fig. 2. For C(001) there is a huge charge accumulation in the dimer bond region with maxima of 27 e/Ω which is much larger than the respective bulk bond maximum of 20 e/Ω. This results from the C=C double bond formed by the σ and π orbitals of the C dimer atoms. The $\Delta\rho(\mathbf{r})$ contours for C(001) clearly show that the lobes of the dimer bond charge density are oriented parallel to the bond direction. For Si and

TABLE I. Calculated reconstruction-induced energy gain per dimer (E_{rec}) for the (001) surfaces of C, Si, and Ge in comparison with measured (Ref. [27]) cohesive energies per bulk bond (E_{coh}). Their difference $\Delta = E_{\text{coh}} - E_{\text{rec}}$ is given as well. E_{asy} is the energy gain per dimer due to asymmetric as compared to symmetric dimer formation.

	E_{rec} (eV)	E_{coh} (eV)	Δ (eV)	E_{asy} (eV)
C	3.36	3.68	0.32	⋯
Si	1.94	2.32	0.38	0.14
Ge	1.66	1.93	0.27	0.30

TABLE II. Calculated bond lengths d_B of bulk C, Si, and Ge in comparison with the calculated dimer bond lengths d_D at the respective (001) surfaces. Bond lengths of X = C, Si, Ge for some molecules (see Ref. [28]) are given in columns 4 and 5.

	d_B (Å)	d_D (Å)	$d_{\text{H}_3X\text{—}X\text{H}_3}$ (Å)	$d_{\text{H}_2X\text{=}X\text{H}_2}$ (Å)
C	1.52	1.37	1.55	1.34
Si	2.33	2.25	2.33	2.15
Ge	2.42	2.41	2.40	2.30

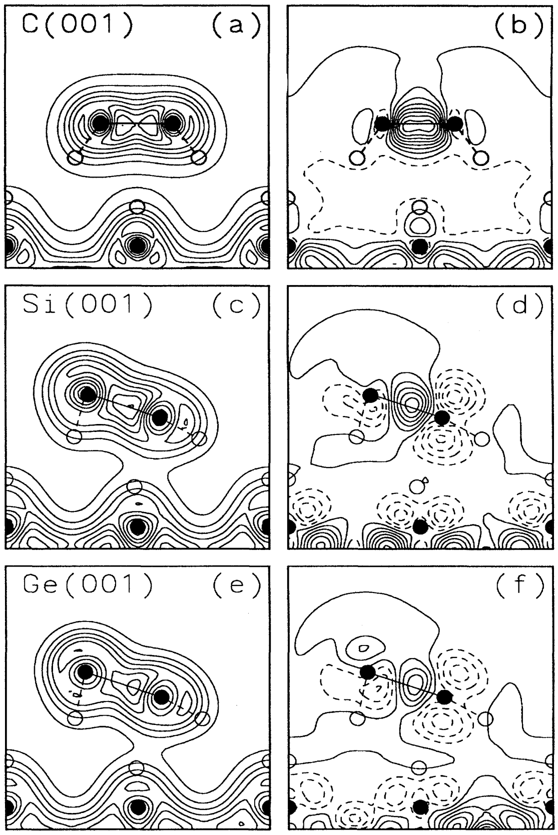

FIG. 2. Contours of total valence charge density $\rho(\mathbf{r})$ [(a), (c), (e)] and differences $\Delta\rho(\mathbf{r})$ between $\rho(\mathbf{r})$ and a superposition of atomic valence charge densities [(b), (d), (e)] for C, Si, and Ge (001). The contour steps are 3 e/Ω (Ω: volume of respective bulk unit cell) in [(a), (c), (e)] and 1 e/Ω in [(b), (d), (f)]. Dashed contours denote negative charge differences.

Ge (001) $\rho(\mathbf{r})$ shows a pronounced maximum in the dimer bond region residing slightly closer to the down atom in both cases. Contrary to the case of C(001), the bond lobes in the $\Delta\rho(\mathbf{r})$ contours for these two surfaces are oriented perpendicular to the bond direction. From Fig. 2 it becomes fully apparent that the reconstruction of C(001) is qualitatively different from the extremely similar reconstructions of Si(001) and Ge(001). This is related to the fact that both Si and Ge have p orbitals in the core while they are missing in the core of C. Between Si and Ge (001) only quantitative differences occur.

In summary, we have presented chemical trends that rationalize the specifically different reconstruction behavior of C(001) as compared to Si and Ge (001). Our first-principles results for semi-infinite systems highlight the physical origins of the reconstruction behavior and show clear evidence for the SDM at C(001) and for the ADM at Si and Ge (001).

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