

## Dimer bond geometry in D/Ge(100)-(2×1): A low-energy electron-diffraction structure analysis

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The asymmetry of the Ge dimer in the (2×1) reconstruction of Ge(100) is removed upon adsorption of deuterium D. The *R*-factor analysis indicates a slight remaining asymmetry which is attributed to the coexistence of bare and D-covered dimers. The Ge-Ge bond length of 2.4(2) Å in the dimer does not change within the error limits when compared to the clean surface. The D atoms bond on top of the Ge atoms, exhibiting a Ge-D bond length of 1.6(2) Å. [S0163-1829(96)51336-6]

Adsorption of hydrogen on the (100) surfaces of Si and Ge is still one of the intriguing topics in surface physics,<sup>1</sup> mainly propelled by its potential to passivate the heavily reactive (100) surfaces. In the past years, for instance, much attention has been drawn to hydrogen passivation during chemical-vapor deposition and hydrogen-plasma etching, which play a key role in the microdevice technology.<sup>2</sup> Since a basic understanding of these technological processes is deeply related to the structural changes induced by hydrogen, not only the chemisorption process itself but also its impact on the geometric structure of the surface has become a matter of growing interest.

The unreconstructed (100) surface of Ge (and also Si) has two dangling orbitals per surface atoms, each of them being filled with one electron. It is generally accepted that the (2×1) reconstruction of the clean (100) surfaces is formed by Si and Ge dimers, respectively, which reduces the number of dangling bonds (per surface atom) from two to one.<sup>3,4</sup> This would explain the presence of symmetric dimers. From recent surface x-ray diffraction (SXRD) analyses,<sup>5</sup> however, it has been shown that the clean Ge(100)-(2×1) surface is characterized by asymmetric dimers with a buckling height of about 0.7 Å. The half-filled orbitals of dangling bonds of a symmetric dimer rearrange themselves into one (more) filled orbital (this Ge atom moves outwards) and one (more) empty orbital (the corresponding Ge atom moves inwards),<sup>3,6</sup> thereby further lowering the surface energy. This kind of symmetry lowering is frequently observed in solid-state physics, and it is referred to as Peierls distortions or Jahn-Teller effect; the crucial point is the existence of half-filled bands in the symmetric configuration. In addition, the dangling bonds within a dimer are not independent but interact and combine to form a weak  $\pi$  bond which is of paramount importance for process of hydrogen adsorption (see the discussion below).

Adsorption of hydrogen on the (100) surface of Si(Ge) is to change this situation and it is believed to lift the Jahn-Teller distortion, resulting in a symmetric dimer configuration with presumably two H atoms per dimer (“monohydride”:  $\theta=1.0$ ).<sup>7</sup> Further uptake of hydrogen is achieved by breaking the dimers and transforming the (2×1) eventually

into a defective (1×1) “dihydride” surface ( $\theta=2.0$ ).<sup>8</sup> The present low-energy electron diffraction (LEED) structure analysis for the deuterized Ge(100) surface is to supplement this general view by crystallographic data. In this study we have used D=<sup>2</sup>H since LEED is more sensitive to the position of D than to that of H because of the smaller thermal movements owing to its larger mass, while H and D have identical chemical properties.

A commercially available Ge wafer (impurity concentration <12 ppm) was etched in fluoride acid (48% HF) and mounted onto the sample holder. The annealing was performed by radiation and resistive heating. Under ultrahigh-vacuum conditions (<10<sup>-8</sup> Pa) the crystal was prepared by repeated cycles of Ar<sup>+</sup> sputtering at 500 eV. A final flash to 700 K served to reduce residual contaminations (mainly H and OH from H<sub>2</sub>O adsorption at the surface) until Auger measurements indicated a clean surface. To form the Ge(100)-(2×1)-D phase the clean (2×1) surface was exposed to about 450 L D<sub>2</sub> (1 L=1.33 10<sup>-6</sup> mbar s) at room temperature. Since dissociative adsorption of D<sub>2</sub> on Ge(100) is negligible, a hot ( $\approx$ 2000 K) tungsten filament was placed about 10 cm in front of the sample to produce *atomic* deuterium. The doses of atomic D can therefore not be specified but the exposure was chosen such that the half-order spots in LEED exhibit maximum intensity. Annealing to 500 K led to a well-ordered (2×1)-D structure. In a previous study<sup>9</sup> the optimum Ge(100)-(2×1)-H structure was prepared by exposing 500 L H<sub>2</sub>. Accordingly, a similar value was chosen here and controlled in a way that the quality of the (2×1) LEED pattern of the clean Ge(100) surface was preserved. Higher doses diminished the (2×1) intensities, most probably due to the evolution of (1×3) and (1×1) elements which occur at much higher exposures.

The LEED *I/V* measurements were carried out at 110 K sample temperature using a mechanically movable Faraday cup. Five integral-order and four fractional-order (symmetry-inequivalent) beams were recorded at energies between 30 and 220 eV (giving a cumulative energy range of 1300 eV). These LEED data were analyzed by using a full-dynamical LEED program<sup>10</sup> in combination with an automated optimization scheme<sup>11</sup> in order to determine the best-fit configuration.

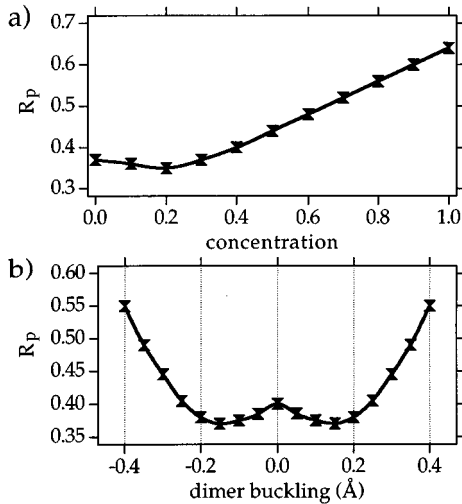


FIG. 1. (a) The reliability factor  $R_p$  vs the magnitude of the dimer buckling assuming a defect-free surface (single domain). (b)  $R_p$ -factor plot as function of the concentration of uncovered (buckled) dimers assuming the coexistence of domains with symmetric dimers (both dimer atoms are capped by D) and buckled dimers (not tied up by D atoms). For the buckled-dimer geometry, the structural parameters were taken from a recent SXRD study (Ref. 5).

The agreement between experimental and calculated data was quantified by the reliability factors  $R_p$  (Ref. 12) and  $R_{DE}$  (Ref. 13) which were also the functionals to be minimized in the optimization scheme. In the analysis we consider first ideal  $(2 \times 1)$  structure models neglecting the presence of defects. When starting with the structural parameters of the clean  $\text{Ge}(100)$ - $(2 \times 1)$  surface<sup>5(a)</sup> and ignoring the D atoms at first, the optimization procedure arrived at a quite poor theory-experiment agreement for the D- $(2 \times 1)$  phase as indicated by  $R$  factors of about 0.6. The fit does not localize the global minimum because of the inappropriate magnitude of the dimer buckling: When reducing the dimer asymmetry in the start model, however, the theory-experiment fit could be markedly improved and leads to a dimer asymmetry of 0.15 Å which was also found in the refinement step including the D atoms. This behavior is demonstrated in Fig. 1(a) which shows the  $R$  factor  $R_p$  as a function of the magnitude of the dimer buckling. In these calculations all parameters but the dimer buckling were refined; a variation of the buckling height is therefore related to a rotation of the dimer. In the final refinement the D atoms were included as well as the first four layer spacings, the vertical positions of the Ge atoms up to the fifth layer, and lateral displacements in the first two Ge layers that are consistent with the  $pm$  symmetry (mirror plane along the Ge dimers) of the structure. Besides the dimer geometry, the third- and fourth-layer buckling turned out to be the most relevant structural parameters.

In the refinement, the D adsorption site was determined to sit above the dimer atoms; however, the present analysis cannot discriminate whether the upper, the lower, or even both dimer atoms are capped. More sensitive was the analysis to the actual Ge-D bond length which in all cases turned out to be 1.56(20) Å. Unconventional adsites for D, such as dimer bridge, cave, and pedestal sites, have been tested as well, leading, however, to a significant deterioration of the  $R$  factors and can therefore safely be ruled out.

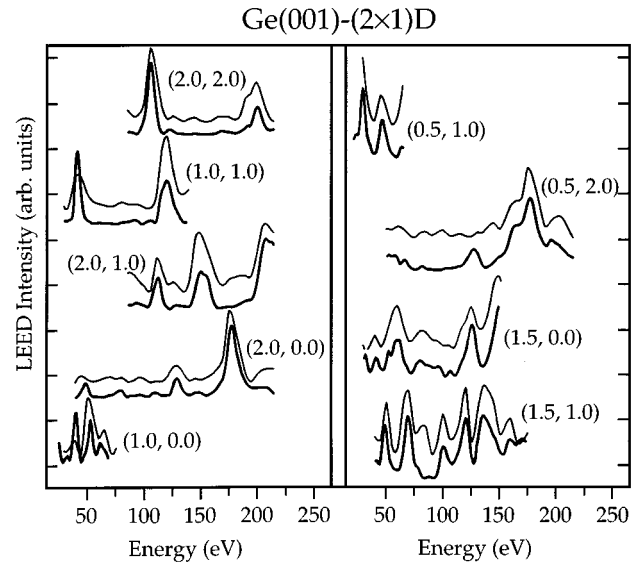


FIG. 2. Experimental (thick lines) and calculated (thin lines) LEED  $I/V$  curves for the best-fit model of Fig. 3.

The analysis indicates a residual buckling of 0.15 Å although the error bars are large (+0.15 Å/−0.45 Å). Because an asymmetry of the dimers is not expected (see the discussion below) we investigated also the role of possible D vacancies. D vacancies may exist either due to incomplete adsorption or insufficient annealing. Hence there remains the possibility that the determined asymmetry of the dimers is the result of a coexistence of asymmetric and symmetric dimers, where the asymmetric dimers are considered to be free of D. There may exist larger domains with the uncovered  $\text{Ge}(100)$ - $(2 \times 1)$  structure or a statistical distribution of uncovered dimers. The former possibility is simulated by an incoherent averaging of the intensities of both structures, the latter corresponds to a coherent average. We investigated both possibilities. The  $R$ -factor plot for the coherent averaging is shown in Fig. 1(b). Here we have assumed for the asymmetric dimer configuration the geometry of clean surface. The results show that a fraction of 20% of uncovered Ge dimers (statistically distributed across the surface) leads to an  $R$  factor of 0.35 comparable to the minimum reached with slightly asymmetric dimers and a fully covered surface. An incoherent averaging of intensities does not improve the experiment/theory agreement so that the presence of larger domains of Ge dimers not being capped by D atoms is unlikely. The comparison of LEED  $I/V$  curves between experiment and theory for the optimal structure is depicted in Fig. 2.

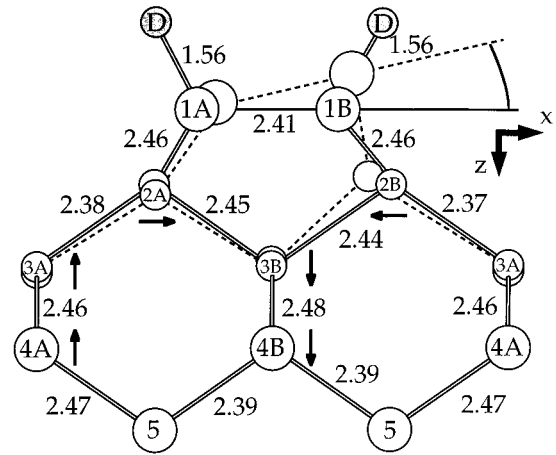
The structural parameters are compiled in Table I and defined in Fig. 3. We discuss at first structural parameters which are common to both the asymmetric and the symmetric dimer model. The dimer bond length 2.41(20) Å is in good agreement with that of the clean surface as obtained from the SXRD study (2.46 Å [Ref. 5a]) and from calculations: 2.41 Å (Ref. 14), 2.43–2.44 Å (Ref. 15). Our result, however, clearly conflicts with recent ion-scattering measurements<sup>6</sup> which seemed to find an increase of the dimer width from 2.26 Å in clean  $\text{Si}(100)$ - $(2 \times 1)$  to 2.97 Å in  $\text{Si}(100)$ - $(2 \times 1)$ -H. Such an increase is abnormally large, hardly conceivable for a covalent bond and can clearly be discarded by the present LEED structure analysis. Within the

TABLE I. Comparison of structural parameters as defined in Fig. 3 of the clean Ge(100)-(2×1) surface (x-ray analysis) and the deuterized surface assuming symmetric dimers (LEED analysis).

No.	Ge(100)-(2×1) (clean) [Ref. 5(a)]		Ge(100)-(2×1)-D (this work)	
	$\Delta x$ (Å)	$\Delta z$ (Å)	$\Delta x$ (Å)	$\Delta z$ (Å)
1A	+1.03(3)	+0.40(10)	+0.80(8)	+0.24(5)
1B	-0.62(7)	-0.30(10)	-0.80(8)	+0.24(5)
2A	-0.06(5)	+0.20(50)	-0.05(10)	+0.12(5)
2B	+0.34(7)	+0.20(10)	+0.05(10)	+0.12(5)
3A		-0.30(10)		-0.01(5)
3B		-0.10(10)		+0.11(5)
4A		-0.20(10)		-0.03(5)
4B		-0.10(10)		+0.11(5)
5	-0.07(1)	-0.10(20)		-0.03(5)

error bars the dimer bond is identical to the bulk bond length (2.46 Å). This result is consistent with *ab initio* calculations<sup>16</sup> of the H/Si system which revealed only a slight elongation of the dimer bond length of about 0.1 Å upon hydrogen adsorption. The dimer-induced distortions in deeper substrate layers turn out to be quite similar in both the clean and the D-covered (2×1) structures in line with the view that the lateral shifting of the topmost Ge atoms forming the dimers is chiefly responsible for these distortions; compare Table I. For the length of the Ge-D bond we obtained 1.56(20) Å which is in reasonable agreement with the corresponding values in Ge-H molecules (about 1.5 Å).

Next, we focus on the discussion of the asymmetry of the Ge dimers and how to resolve the ambiguity of the LEED results. Adsorption of a single D on the Ge dimer will certainly depolarize the dimer and reduce the dimer buckling so that a slightly asymmetric dimer would be consistent with the assumption of a single D atom per dimer. A symmetric dimer necessitates, however, that both Ge atoms constituting the dimer are capped by hydrogen. There is strong evidence from experiment and theory that hydrogen adsorption takes place in a way that both dimer atoms are capped by D. This has been shown directly by scanning-tunneling microscopy (STM),<sup>17</sup> and more indirectly by the desorption taking place with first-order kinetic.<sup>18</sup> We therefore prefer the model of symmetric dimers coexistent with statistically distributed bare and asymmetric dimers. We note, however, that the evidence for the existence of uncovered Ge dimers solely based on the LEED analysis is weak. The minimum of the *R* factor at nonvanishing buckling could well be caused by approximations in the LEED calculations which have not been considered so far or also by experimental errors. From the electronic properties of the Ge(110)-(2×1) surface, this pairing of D atoms is due to an attractive interaction between unpaired dangling bonds ( $\pi$  bonding) rather than by an attraction between the D atoms.<sup>17(a)</sup> Since the adsorption of a single D on a dimer will destroy the attractive  $\pi$  interaction between dangling bonds within a Ge dimer, adsorption for a second D atom on the same dimer is energetically more favorable than occupying another dimer, even though the di-



$$\begin{aligned} \Delta x(1A) &= +0.80(8) & d_1(\text{D-Ge}) &= 1.35(20) \\ \Delta x(1B) &= -0.80(8) & \langle d_{12} \rangle &= 1.18(5) \\ \Delta x(2A) &= -0.05(10) & \langle d_{23} \rangle &= 1.34(5) \\ \Delta x(2B) &= +0.05(10) & \langle d_{34} \rangle &= 1.45(5) \\ \Delta z(3) &= 0.12(5) & \langle d_{45} \rangle &= 1.38(8) \\ \Delta z(4) &= 0.14(5) & d_{56} &= 1.44(8) \end{aligned}$$

FIG. 3. Structure model and fit parameters for Ge(100)-(2×1)-D as obtained from the LEED *I/V* analysis. The dashed lines are the data of Ref. 5 (clean Ge surface). The values indicated are the bond lengths in Å between touching Ge atoms.

rect interaction between neighboring D atoms might be repulsive. It is believed that the presence of this dimer  $\pi$  interaction controls the adsorption of D on the Ge(100) surface. The assumption that the investigated surface exhibits dimers with a single D atom therefore would hardly be reconciled with the above-mentioned hydrogen-pairing model. The coexistence of bare and D-covered Ge dimers receives also some support from recent STM investigations.<sup>17</sup> It has been shown that adsorption of D at room temperature and at low coverages results in a defective (2×1)-D structure with mainly single-occupied Ge dimers. Only after annealing this surface to about 630 K, islands of (2×1)-2D with two D atoms per Ge dimer are formed along with patches of bare (2×1). Since we annealed only to 500 K, it could be possible that the surface is left with some statistical distribution of D-free Ge dimers.

In summary, we presented here a LEED structure analysis of Ge(100)-(2×1)-D which indicates that upon D adsorption the dimer bond length of 2.41(20) Å remains unchanged compared to the clean surface. The still nonvanishing dimer buckling can be attributed to the coexistence of bare (2×1) and (2×1)-2D patches on Ge(100). The D-covered Ge dimers are symmetric so that the main effect of D adsorption on the Ge(100)-(2×1) surface consists in a *back bending* of the Ge dimers from 17° tilting to 0°. The D atoms bond on top of the Ge atoms [Ge-D bond length: 1.56(20) Å], thus saturating the remaining dangling bonds.

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