Bond Length of Ge Dimers at Si(001)

In a recent Letter, Fontes, Patel, and Comin [1] reported x-ray standing wave measurements of the displacement and asymmetry of Ge dimers on Si(001). By replacing Si surface layer atoms with Ge atoms they could discriminate the fluorescent Ge dimer signal from the background subsurface Si fluorescence. Determining the amplitude F and the phase P of the charge density Fourier coefficient for the (004) and the (022) lattice reflections they were able to determine the bond length L and the tilt angle Θ of the asymmetric Ge dimers on Si(001). Constraining the center of mass position of the dimer by the phases P_{004} and P_{022}, the vector displacement between the two dimer atoms was calculated from the amplitudes F_{004} and F_{022} using a two-parameter model (L,Θ) for the planar dimer. Fontes, Patel, and Comin arrived at a dimer bond length of $L=2.60\pm0.04$ Å and a tilt angle of $\Theta=12.1^\circ\pm0.2^\circ$. From these values, a dimer height displacement $\Delta z=0.55\pm0.02$ Å results.

This extremely large Ge dimer bond length on Si(001) is amazing in view of the following facts: (a) The Ge bulk bond length is 2.45 Å; (b) twice the covalent radius of Ge is 2.44 Å; (c) the dimer bond length at the clean Ge(001)-(2×1) surface as measured and evaluated by fully self-consistent calculations ranges from 2.41 to 2.46 Å (see Table I); (d) a number of self-consistent *ab initio* calculations for Si(001)-(2×1) yield Si dimer bond lengths ranging from 2.21 to 2.30 Å; (e) from the physical properties and the symmetry of Ge:Si(001)-(2×1) one would expect a Ge dimer bond length in between the values for the two clean Si and Ge surfaces; and (f) this latter expectation is indeed born out by the results of total energy calculations for Ge monolayers on Si(001).

We have very recently carried out local density calculations for Ge:Si(001)-(2×1) using our self-consistent scattering theoretical approach as described in Ref. [2]. Our results clearly favor asymmetric dimers in agreement with Ref. [1]. But, as expected, our calculated dimer bond length of 2.39 Å (see Table I) lies between the respective values at the two clean surfaces and it is smaller by about 8% as compared to the value determined in Ref. [1]. This discrepancy is far beyond the uncertainties of fully converged structure optimizations within LDA which yield excellent agreement with experiment in bond lengths within about 1%. For bulk Ge, e.g., we calculate a bond length of 2.42 Å as compared to the experimental value of 2.45 Å. For the dimer bond length at the clean Ge(001)-(2×1) surface we calculate 2.41 Å which is in very good agreement with the value of 2.44 Å, as determined from recent x-ray diffraction results [3].

TABLE I. Experimental (E) and theoretical (T) Ge dimer bond lengths L (in Å) and tilt angles Θ (in °) for the clean Ge(001)-(2×1) surface and for Ge:Si(001)-(2×1). The values [*] refer to this work.

		L	Θ
Ge	T [*]	2.41	19
	T [5]	2.46	13
	E [3]	2.44	21
Ge:Si	T [*]	2.39	17
	E [1]	2.60	12

Of course, we have no reason to question the experimental data presented in Ref. [1]. But in view of the above-mentioned facts and the outcome of our calculations for Ge:Si(001)-(2×1), we have to question the interpretation of the data in Ref. [1]. First, it is not obvious to us that constraining the center of mass position of the dimers by P_{004} and P_{022} is unique. Much more importantly, it seems that the analysis of the amplitudes and phases has been done approximately in Ref. [1] according to

$$Fe^{i2\pi P}=\frac{1}{N}\sum_{n=1}^{N}e^{i\mathbf{q}\cdot\mathbf{r}_n}e^{-1/2q^2\langle u^2\rangle}, \qquad (1)$$

employing the same isotropic mean-square displacements (MSD) for both dimer atoms.

Now it is well known that the MSD's at semiconductor surfaces are strongly anisotropic. This has quantitatively been shown, e.g., for Si(001)-(2×1) in Ref. [4]. In particular, we found in that case that the MSD's for the two dimer atoms and their anisotropies are distinctly different, a result which should obtain for Ge dimers on Si(001), as well. When the differences in the MSD's for the two dimer atoms are taken into account, the determination of the phases according to the corresponding generalization of Eq. (1) changes the resulting values strongly. In addition, the anisotropy of the MSD's entering in the exponent of Eq. (1) should influence the amplitudes and thus the derived structure parameters drastically.

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Received 16 July 1993
PACS numbers: 68.55.Ce, 68.35.Bs, 81.10.Bk

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0031-9007/94/72(7)/1130(1)$06.00