Structural and Optical Properties of the Ge(111)-(2 × 1) Surface

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We study the two lowest-energy isomers of the Ge(111)-(2 × 1) surface, by a state-of-the-art first-principles calculation of their optical spectra, including the electron-hole interaction effects. A comparison of our results with the available experimental data suggests that, at difference with the silicon case, the stablest isomer *differs* from the standard "buckled Pandey chains" reconstruction. This conclusion is supported by accurate total-energy results.

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The (111) surfaces of Si and Ge are among the most widely and deeply studied surfaces, being the natural cleavage surfaces of the most important elemental semiconductors. Since the work of Takeuchi *et al.* [1] in 1991, the existence of qualitative differences between the Si and Ge (111)(2 × 1) surfaces has been pointed out. From the experimental point of view, Ge(111) surfaces with a good (2 × 1) LEED pattern are more difficult to obtain than in the silicon case, and are more influenced by the cleavage temperature [2]. In particular, the authors of Ref. [1] suggested the existence of two different isomers of Ge(111)(2 × 1), almost degenerate in energy, which could also result in the creation of a multidomain surface. The two isomers, which have also been predicted in the case of Si(111)(2 × 1) [3,4], differ only with respect to the *sign* of the buckling. In the original Pandey geometry [5], there is no buckling at all, i.e., the two uppermost surface atoms in the seven-membered rings are at the same height. Starting from this, one generates the two isomers by tilting these two atoms in the clockwise or anticlockwise direction. As visible in Fig. 1, the two choices are not equivalent with respect to the third atomic layer. The "standard" choice is that illustrated in Fig. 1a, which we call the structure with (conventionally) positive buckling. The other choice, which we call the structure with a negative buckling, was previously also named the "chain left" or "chain high" isomer (Refs. [1] and [3], respectively), and corresponds to the stablest geometry in the present calculation (Fig. 1b).

Surface optical spectra (differential reflectivity) for Ge(111)(2 × 1) at low temperature are available in the literature [6], but the problem of the existence or coexistence of different isomers is an open one, since no conclusion can be drawn from a comparison of the existing theoretical results and the experimental data. This is due to several reasons: first, the electronic structures computed for the two isomers are extremely similar, hence no final conclusion may be drawn from comparing photoemission results with the calculated band structures. Concerning the optical spectra, the occurrence of surface excitons having a much larger binding energy than that of the bulk exciton can be expected, in analogy with the Si case [7–11]. Hence, optical properties deduced from electronic structure results obtained at the one-particle level, i.e., neglecting the electron-hole interaction effects, are not expected to be very helpful. Moreover, despite the fact that in the total energy calculations of Ref. [1] the lowest energy isomer was indeed the structure with negative buckling, the computational accuracy that could be achieved at that time (1991) was not sufficient to determine the tiny energy difference between that structure and the positive buckled one. It was hence concluded that the two isomers should be considered as isoenergetic "within the accuracy of the calculation." In subsequent works, the structure called "Pandey with buckling" was assumed to be the one with positive buckling, despite the absence of experimental evidence in favor of this choice. Finally, since the two isomers yield a surface geometry which differs only starting from the third atomic layer below the uppermost one, experimental probes like scanning tunneling microscopy (STM) can hardly be employed to resolve the issue.

On the other hand, theoretical tools to compute the optical spectra from first principles including the electron-hole interaction effects have been recently developed [12]. The

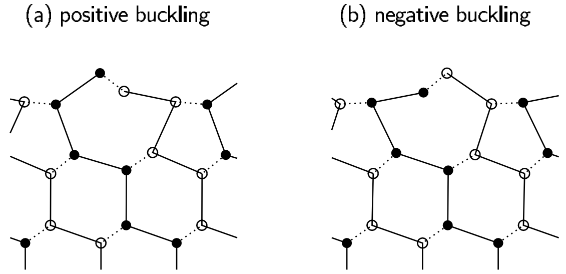

FIG. 1. Side view of the two almost isoenergetic structures of Ge(111)-(2 × 1), displaying "positive" (left) and "negative" (right) buckling of the Pandey chains.

Ge(111)(2×1) problem seems to be an ideal "test case" for these methods: a comparison of the measured optical spectra with accurate enough theoretical results can give the key to clarify the situation. The aim of the present work is hence to shed light on this problem, by computing the equilibrium geometries and the corresponding optical properties of the two Ge(111)(2×1) isomers with the maximum accuracy available to date. This work has also been triggered by recent surface differential reflectance measurements [13], where "anomalous" samples were found, yielding optical spectra which could be explained admitting the presence of multidomain surfaces where the two isomers coexist.

As the first step, we have determined the surface equilibrium geometry, trying to minimize all possible sources of error: in particular we refer to (i) inclusion of d nonlocality and nonlinear core corrections in the pseudopotential scheme (both neglected in Ref. [1]), (ii) use of a large number of k points (up to 32 in the irreducible wedge of the Brillouin zone) in the self-consistent calculations, and (iii) use of a slab thick enough (twelve layers) to make negligible the interaction between the two surfaces, and a large separation (8.9 Å) between the adjacent slabs. Four Ge layers are allowed to relax in the geometry optimization process. An energy cutoff of 15 Ry was employed.

The norm-conserving pseudopotential for Ge has been generated using the Hamann scheme [14], choosing as cutoff radii $R_c = 1.19$, 1.37, and 1.98 bohrs, respectively, for the s, p, and d components. The s component is taken as reference potential, and a Kleinman-Bylander scheme [15] is adopted. The inclusion of nonlinear core corrections (NLCC) [16] turns out to improve substantially the pseudopotential transferability properties, which we have tested not only against logarithmic derivatives, but also by performing explicit atomic calculations in several excited configurations. The resulting equilibrium lattice constant obtained for bulk Ge is 5.62 Å, to be compared with the 5.57 Å obtained using standard Bachelet-Hamann-Schlüter (BHS) pseudopotentials without NLCC [17], and with the experimental value 5.657 Å. The two structures shown in Fig. 1 are both stable minima, with the "negatively buckled" one favored by about 13 meV/surface(1×1) cell. The convergence of this value has been checked against the kinetic energy cutoff and the Brillouin zone (BZ) sampling, which turns out to have the larger effect: calculations using 1, 4, 16, and 32 Monkhorst-Pack special k points in the irreducible wedge of the BZ yield, respectively, a ΔE of 44.8, 19.4, 13.5, and 12.8 meV, respectively, where ΔE is the total energy difference between the positive and negative buckling configurations [18,19]. However, such a small energy difference within the LDA would not allow us to make a definite prediction of the stablest structure based on the total energy results alone.

We now focus on the electronic and optical properties of the two possible structures of the Ge(111)-(2×1) surface. Figure 2 shows the quasiparticle (QP) surface band structure for the positively buckled chain (upper panel) and for the negatively buckled chain (lower panel), as evaluated within the GW approximation for the electron self-energy operator (for details, see Ref. [11]). For both geometries, the band structure exhibits two surface bands, i.e., one occupied dangling-bond state (D_{up}) and one empty dangling-bond state (D_{down}). In between a surface gap is found close to the J and K points of the surface Brillouin zone. For the positively buckled (i.e., the traditional) Pandey-chain structure, the minimum direct surface gap amounts to 0.88 eV (0.60 eV in the LDA band structure); it is located between J and K. This QP gap is significantly larger than the gap of the corresponding Si(111)-(2×1) surface, which amounts to 0.69 eV. The main reason is the stronger buckling at the Ge surface (0.84 Å, compared to 0.51 Å at the Si surface [11]), which widens the gap.

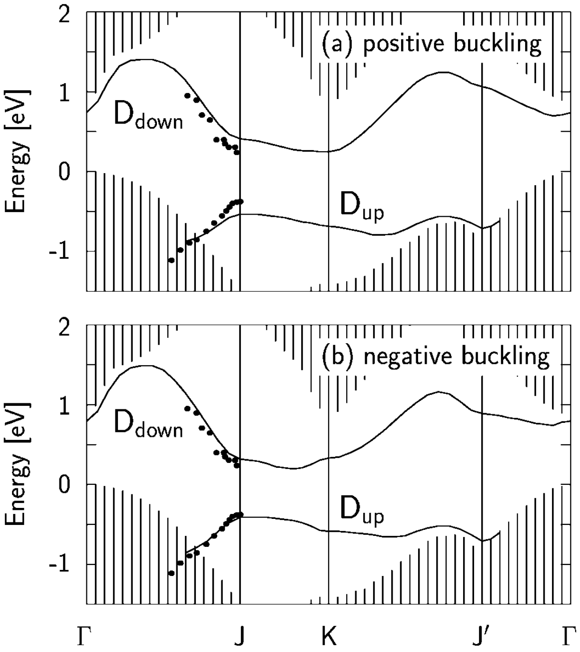

FIG. 2. GW quasiparticle band structure of the Ge(111)-(2×1) surface. The shaded areas denote Ge bulk states. The upper (lower) panel is for the positively (negatively) buckled chain (see text). The experimental data are from Refs. [20,22].

The band structure of the negatively buckled chain (lower panel) is qualitatively very similar to that of the positively buckled chain but shows some quantitative differences. The dispersion of the empty D_{down} band between J and K is different from the positively buckled chain. More importantly, the minimum direct surface gap is significantly smaller, amounting to 0.66 eV (0.38 eV in the underlying LDA calculation). The smaller surface gap results from the opposite chain buckling and the corresponding differences in the underlying bulk crystal, as observed by the dangling-bond surface states. It should be noted that also for the corresponding Si(111)-(2×1) surface the surface gap of the negatively buckled chain is smaller than that of the positively buckled chain [4].

The Ge(111)-(2 × 1) surface band structure has been measured by direct and inverse angle-resolved photoemission spectroscopy (ARPES and ARIPES) [20–22]. The data by Nicholls *et al.* are included in Fig. 2. Both calculated band structures are in qualitative agreement with the measured data; however, the band structure of the *negatively* buckled chain is in even closer agreement with experiment than that of the positively buckled one. In particular, the experimental surface band gap of 0.61 eV seems to support the negatively buckled chain, for which our calculated gap is 0.66 eV. However, this agreement should not be overemphasized since the ARPES and ARIPES measurements were obtained from different samples, which could in principle affect the gap energy evaluated from the two sets of data. It should also be noted that Zhu and Louie [23] observed a much smaller buckling (0.30 Å instead of 0.84 Å in our calculation) and a concomitantly smaller *GW* QP band gap of 0.67 eV for the *positively* buckled chain, in close agreement with experiment, which seems to support the positively buckled chain. The weak buckling, however, disagrees with Ref. [1], and may be an artifact due to the lower accuracy that was reachable at that time (1991), namely to the reduced cutoff (8 Ry versus 15) and *k* points sampling (12 vs 32 special points).

The electronic structure of the Ge(111)-(2 × 1) surface has been addressed in differential reflectivity spectroscopy (DRS) measurements by Nannarone *et al.* [6]. A direct comparison of our calculated band structure with the experimental data is, however, not easily possible. The optical spectrum does not refer to the band structure itself, but it includes excitonic effects due to the electron-hole interaction. These excitonic effects can be very strong, in particular at lower-dimensional systems like the present semiconductor surface. At the corresponding Si(111)-(2 × 1) surface, excitonic binding energies of more than 0.2 eV have been observed, which drastically modifies the DRS spectrum (see the discussion in Refs. [9–11]).

To allow for a quantitative comparison between theory and experiment, we have calculated the DRS spectrum of both possible chain structures, including the electron-hole interaction and excitonic effects (for details, see Ref. [11]). The results are shown in Fig. 3. The upper panel is for the positively buckled (i.e., the traditional) Pandey chain while the lower panel is for the negatively buckled chain. In both panels, the full (dashed) curves include (neglect) excitonic effects. The dots denote the measured data by Nannarone *et al.* [6]. The electron-hole interaction leads to a shift of the DRS peak of 0.25 eV to lower energies. The transition energy of the lowest exciton amounts to 0.70 eV for the positively buckled and to 0.51 eV for the negatively buckled surface, respectively. The excitonic binding energy (taken with respect to the minimum direct surface gap) amounts to 0.18 and 0.15 eV, respectively, for the two geometries, which is a little smaller than the one found for the Si(111)-(2 × 1) surface (0.26 eV) [11]. The difference may be related to the stronger screening in Ge as compared to Si. While the independent-particle spectra (given by the dashed curves) are continuous spectra, the final exciton spectra (solid curves) are dominated by the lowest-energy exciton.

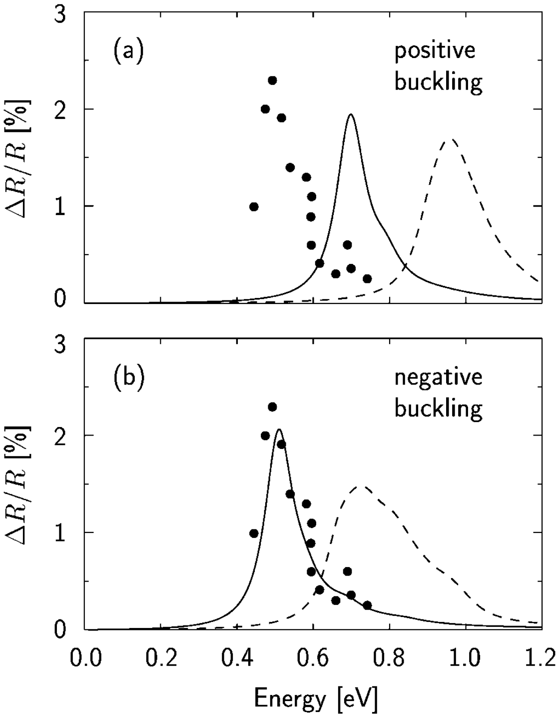

FIG. 3. Differential reflectivity spectrum of the Ge(111)-(2 × 1) surface, calculated for normal incidence. The solid (dashed) curves include (neglect) electron-hole interaction. The upper (lower) panel is for the positively (negatively) buckled chain (see text). An artificial broadening of 0.05 eV is included. The dots denote experimental data by Nannarone *et al.* [6].

The most important observation in Fig. 3 is that the calculated DRS spectrum of the positively buckled chain is in disagreement with the measured data. The difference between the calculated and the measured exciton energy is 0.21 eV, which we believe is too much to be attributed to computational or conceptual uncertainties. The calculated DRS spectrum of the negatively buckled chain, on the other hand, agrees with experiment. This seems to indicate that the positive buckling is not realistic, i.e., that the surface chain is in fact negatively buckled, different from the picture of positively buckled Pandey chains, which is, at least in the case of the Si(111)-(2 × 1) surface, widely accepted.

For the sake of clarity, the transition energies of the Si and Ge surface excitons are compiled in Table I. For the Si(111)-(2 × 1) surface, the positively buckled chain is supported by the good agreement of the calculated DRS spectrum with the measured one (see Refs. [9–11]). The negatively buckled chain would lead to a significantly lower surface gap of the Si(111)-(2 × 1) surface [4] and to a lower exciton energy. Based on the above discussion for Ge(111), we can estimate this exciton energy. For Ge(111), the difference between the two exciton energies

TABLE I. Calculated and measured surface exciton transition energies at the Ge(111)-(2 × 1) and Si(111)-(2 × 1) surface. The calculated data are for the positively and the negatively buckled chain, respectively (see text).

[eV]	"+"	"−"	Exp.
Ge(111)-(2 × 1)	0.70[a]	0.51[a]	0.49[b]
Si(111)-(2 × 1)	0.43[c]	~0.25[d]	0.45[e]

[a] This work.
[b] Ref. [6].
[c] Ref. [11].
[d] Estimated (see text).
[e] Refs. [7,8].

(0.19 eV) is about the same as the difference between the LDA gaps of the two structures (0.22 eV). At the Si(111)-(2 × 1) surface, a similar LDA gap difference (0.18 eV) is found between the positively and negatively buckled chains [4]. Based on the surface exciton energy of 0.43 eV for the positively buckled chain, a surface exciton energy of about 0.25 eV (i.e., 0.18 eV lower than at the positively buckled surface) can thus be expected for the negatively buckled chain. This would be much smaller than the observed exciton energy of 0.45 eV [7]. This seems to indicate that the Si(111)-(2 × 1) surface obtained by cleaving is indeed terminated by *positively* buckled Pandey chains while the Ge(111)-(2 × 1) surface obtained by the same preparation technique is mostly terminated by *negatively* buckled chains.

In conclusion, we have studied the two lowest-energy isomers of Ge(111)(2 × 1) calculating both the total-energy difference at the LDA level, and the optical differential reflectivity spectra including self-energy and excitonic effects. On the basis of both these quantities, the ground-state geometry of Ge(111)(2 × 1) is found to correspond to "Pandey-like" chains with a buckling of −0.8 Å, i.e., with a tilt angle in the opposite direction with respect to that of the geometry commonly assumed for the Pandey model with buckling. Because of the small energy difference between the two isomers, the possibility of a coexistence of both reconstructions, resulting in multidomain surfaces, should be considered. New, accurate experimental data are needed in order to check this possibility. After submission of the present work, STM data on Ge(111)(2 × 1) by Hirayama *et al.* [24] appeared, giving the first experimental evidence of the existence of domains with buckling of different sign. The relative abundance of the two isomers is likely to be sample dependent, as a consequence of the details of the cleavage process. Actually, STM reveals only the *change* of the buckling sign at domain boundaries. Hence, some additional experimental input (e.g., a measure of the optical spectrum, as we suggest here) is needed to know which of the two possible orientations is the dominant one.

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