Metallization and Incomplete Melting of a Semiconductor Surface at High Temperature

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We present a first microscopic study of the state of a semiconductor surface, clean Ge(111), close to the bulk melting temperature. Both electronic states and ionic motion are fully treated via first-principles molecular dynamics. Results indicate a clear dynamical disordering, confined, however, to the first atomic bilayer. This region acquires a liquidlike diffusion, and is metallic. Lack of melting of the second and deeper bilayers, found to be in good quantitative agreement with recent x-ray data, indicates an incomplete wetting of the semiconducting solid by its own metallic melt. Previously conflicting data on Ge(111) are also reconciled within this picture.

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This Letter is aimed at understanding the behavior of Ge(111), chosen as a prototype clean semiconductor surface, when its temperature is raised (in equilibrium) close to the bulk melting point T_M. There are several reasons which make this problem of general interest. (a) The recognized impossibility to use either phenomenological theories or classical simulations for a dependable prediction of semiconductor surface behavior close to melting. Bulk group IV and III-V semiconductors, in particular, turn into good metals upon melting. A convincing theory of the hot semiconductor surface must therefore include the full role of electronic states, which represents a challenging open problem. (b) There is for Ge(111) a multiplicity of recent results bearing on the high-temperature phase transition at $T_c \sim 1050$ K [1], only 160 K below $T_M = 1210$ K. Conflicting pictures have been offered for the state of the surface between T_c and T_M. Low energy electron diffraction (LEED) [1] and ellipsometric data [2] were interpreted to imply static disordering at T_c, involving a few surfaces layers. X-ray data demonstrated lack of roughening well above T_c, and suggested a proliferation of random vacancies in the first bilayer [3]. Conversely, different x-ray [4], ion scattering [5], and photoelectron diffraction (PED) data [6] have been interpreted in favor of a dynamical, liquidlike surface disorder above T_c. Very recently the finding of sharp Bragg spots plus a 180° surface symmetry reversal in He scattering above T_c has led to yet a third suggestion, namely, a kind of order-order transition at T_c [7]. One of our scopes will be to sort out this controversial situation. (c) Our general ignorance of the surface melting habit for *any* semiconductor surface. Among the three different options, complete melting, incomplete melting, and surface nonmelting [8], only the last two are open, since regular surface melting of semiconductors is barred by a negative Hamaker constant [9]. Incomplete melting, that is, incomplete wetting of the solid by its own melt at $T \sim T_M$, is rather rare and of particular interest. It takes place when both the dry and the completely wetted states are unstable, yielding a stable state with a microscopically thin wetting film [10]. There is, however, no additional wisdom we can presently use to decide what habit will prevail in a generic case. Ge(111) offers an ideal case study in this unexplored area.

We study Ge(111) at $T \sim T_M$ by first-principles molecular dynamics (MD) [11]. Calculations are carried out for a 6-layer (3-bilayer) periodically repeated slab, with $M = 16$ Ge atoms/layer and 7 Å of empty space between slabs. The sixth Ge layer is frozen and saturated with 16 H atoms. The first surface layer is decorated with four Ge adatoms, as in the well-tested static description of the low-temperature $c(2 \times 8)$ structure of Ge(111) [12]. For the present and much more demanding MD study, we describe electronic states with the same accuracy, using separable norm-conserving pseudopotentials, 8 Ry cutoff and Γ-point electronic states. Altogether $5 \times 16 + 4 = 84$ Ge atoms are fully mobile. Canonical averages are implemented using two Nose thermostats [13]. Our chosen temperature is $T = 1200 \pm 150 \sim T_M$. We find that no less than 10 ps or $\sim 35\,000$ MD steps (one step $= 2.9 \times 10^{-16}$ s) are needed for a meaningful thermal average at this size and temperature [14].

Starting from the perfect $c(2 \times 8)$ configuration [12], we first observe adatom disordering in a few hundred MD steps. This state, where only the adatoms diffuse, is metastable and survives for ~ 3 ps; then [Fig. 1(a)] the surface begins to transform, with a gradual, but definite rise of total energy [Fig. 1(b)]. After another ~ 5 ps the transformation is complete. Averages are then taken over a long run of ~ 13 ps. Mean square displacements show that the outermost bilayer has become diffusive, with an estimated two-dimensional diffusion coefficient, $D = (3.5 \pm 2) \times 10^{-5}$ cm^2/s, smaller, but comparable with that of l-Ge at T_M, $D_0 = 8 \times 10^{-5}$ cm^2/s. However, the second bilayer shows no diffusion at all, and remains completely solid and stable [Figs. 2 and 3(d)]. To check whether this stability is genuine, and not an ar-

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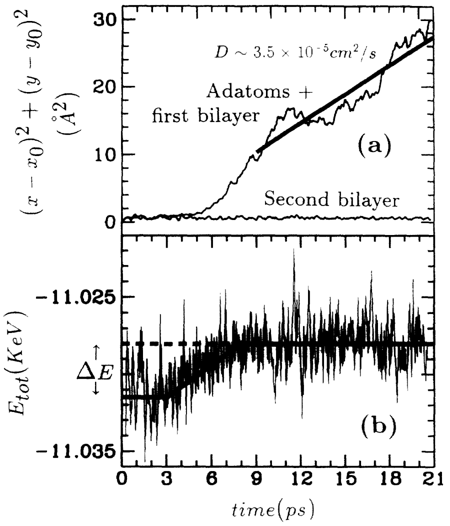

FIG. 1. (a) Mean square displacement of all first bilayer (z < 5.1 Å) and second bilayer atoms. The straight line gives $\langle r^2 \rangle = 4Dt$. (b) Total energy of the whole slab. The initially nondiffusive metastable system (t < 3 ps) transforms (3 < t < 8) and becomes diffusive only in the first bilayer.

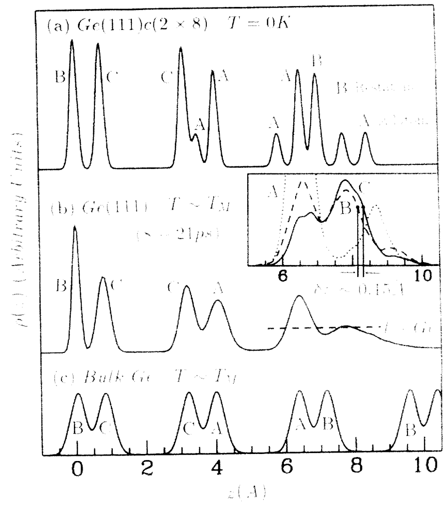

FIG. 2. (x,y) average atom density profile for (a) the Ge(111)c(2 × 8) surface at T = 0 K, (b) the Ge(111) surface at $T \sim T_M$, and (c) crystalline bulk Ge at $T \sim T_M$. Note in (b) the disordering of the first bilayer with atoms distributed between different sublattices (inset).

tifact of the thin slab, we have run an additional 10^4 MD steps with an external force $F = 0.1$ eV/Å applied to all atoms in the slab along the [1$\bar{1}$0] or the [$\bar{1}\bar{1}$2] directions, parallel to the layers. Atoms in the second bilayer are robustly crystalline, and do not flow, while atoms in the first bilayer flow with large drift velocities of $\sim 4\times10^4$ cm/s. Had the second bilayer been on the brink of instability, it would have readily melted under the action of this strong force [15]. There must therefore be a much larger free energy barrier protecting the disordered bilayer state than simply the effect of the sixth layer, estimated to a few meV/atom. This strongly argues in favor of genuine incomplete melting for Ge(111) at our chosen temperature. Returning to the field-free case, we focus on the structure of the outermost bilayer. This is analyzed using the density profiles of Fig. 2(b), as well as the trajectory plots of Fig. 3. Peaks in the density profile identify layers, namely, a "second layer" ($z \sim 6.5$ Å), a "first layer" ($z \sim 7.7$ Å), and an "adatom" layer ($z \sim 8.7$ Å). Trajectories show that atoms in each of these layers, while diffusing, still spend a large fraction of time in the neighborhood of one of three sublattice sites, marked A, B, and C. Conventionally defined sublattice populations n_{is} (i=layer index, s = A, B, C) are extracted, e.g., by integrating the z-dependent populations of Fig. 2 (inset). Starting with the third layer, which is solid and entirely A, $n_{3A} = 16$, we find that the second layer has become mixed, $n_{2A} = 12.7$, $n_{2B} = 4.6, n_{2C} = 3.0$, and also laterally denser, $\sum_s n_{2s} = 20.3$. The 4.3 excess atoms come from relatively frequent exchanges (one every few ps) with the first layer. This is in turn strongly depleted: $n_{1A} \sim 0$, $n_{1B} = 5.2$, $n_{1C} = 5.9$, $\sum_s n_{1s} = 11.1$, with large random local fluctuations of in-plane density [Fig. 3(b)]. Hence in the first layer both the regular diamond (B) and the hexagonal diamond (C) sublattices are occupied *with very similar probabilities.* Were they actually identical, the first layer would display a full 60° rotational symmetry. In reality, there is a small but unmistakable C excess, $n_{1C} - n_{1B} = 0.7$, and also a small outward protrusion of 0.1–0.2 Å of the C relative to the regular B sites, due to a repulsion from the distant C sites in the *fourth layer* [16]. This effect restores a weak asymmetry, now dominated by the C sites, and therefore opposite

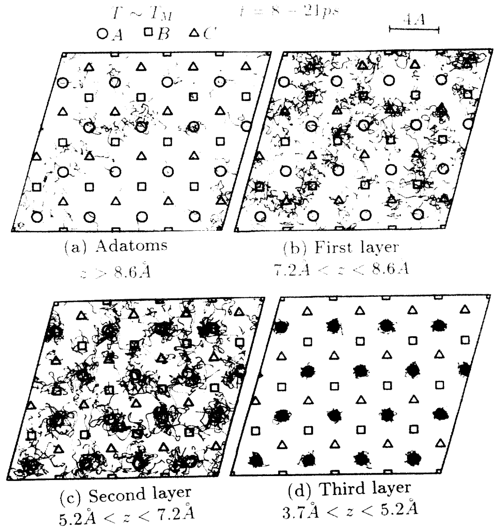

FIG. 3. Trajectory plots showing atomic motions projected onto the (x,y) plane, superposed with ideal sublattice sites. The third layer remains crystalline, while in the outer layers there is diffusion, largely between sites.

to that present below T_c, where only B sites are occupied. Moving further out, we still find 80% of A adatoms, $n_{0A} = 3.2$, as well as a smaller population in a successive layer of "ad-adatoms," centered around $z \sim 9.2$ Å, $n_{-1B} = 0.9$, $n_{-1C} = 0.5$. The adatom pair correlation function (not shown) has now lost the strong peak at $r \sim 7.5$ Å, typical of the 2×2 local ordering present for $t < 3$ ps. Moreover, the complex deep-reaching relaxation pattern due to adatom-restatom pairs [Fig. 2(a)] is washed out. We also note the large mixing of sublattices in all the outer layers. Recent work on lattice models [17] has identified sublattice disordering as the main and earliest feature associated with loss of surface order without loss of facet flatness, typical of so-called preroughening [18]. Our calculation thus suggests that preroughening of Ge(111) might take place at T_c, with no proper roughening until T_M [1,3].

We have also obtained relevant thermodynamical information. The total energy increase of Fig. 1(b), $\Delta E = 3.5 \pm 0.3$ eV (for the whole slab), can be interpreted as a latent heat of melting for surface atoms in a constrained geometry. If $\Delta E = N k_B T_M \Delta S$, where N is the number of atoms involved, we obtain $\Delta S \simeq 1$, if we attribute ΔE to the surface bilayer ($N = 32$). Comparison with the bulk entropy jump at melting $\Delta S_{\text{bulk}} = 3.2$ confirms that only a fraction of the full liquid entropy is liberated in the surface bilayer, consistent with the presence of strong crystal order in the deeper layers, and with hopping diffusion. We have therefore arrived at a well defined picture of incomplete melting for the Ge(111) surface. Although we have studied only one temperature $T \sim T_M$, we believe that this picture actually provides a good description for the whole temperature range $T_c \leq T \leq T_M$, insofar as most experiments indicate very little evolution between T_c and T_M. Also, classical simulations for metals [19] confirm that the incompletely melted state remains basically unchanged for increasing T, even above T_M, where it is only metastable.

The transition from the crystalline to the disordered surface is accompanied by important changes in the surface electronic structure, an element which could not be included in previous classical simulation work [20]. We have used 15 configurations, separated by 2000 MD steps, for a calculation of the thermally averaged density of electron states. We distinguish between surface and bulk states through the wave function weight which is required to be > 50% in the first bilayer ($z \geq 5.2$ Å) for the former, and vice versa for the latter. As Fig. 4 reveals, there is a clear surface metallization, while the deeper layers remain semiconducting. Metallization appears to be related mainly to the loss of a covalent bond by most atoms in the first bilayer.

We now turn to a discussion of experimental data on Ge(111). First of all, incomplete melting explains very well the coexistence of lateral disordering with vertical layering originally found by LEED [1]. The random vacancy islands we find in the first layer correlate well with x-ray diffraction [3]. Incomplete melting also agrees with the qualitative picture suggested by different x-ray [4], ion scattering [5], and PED [6] work. Based on our equilibrium atomic trajectories, we have calculated approximate x-ray scattering intensities and find (Fig. 5) a very good quantitative fit with the data of Silfhout [4]. By comparison, alternative proposals, e.g., of a crystalline surface with the first-second layer spacing shrunken by 10% or of a crystalline surface with a hexagonal stacking fault [7] can be ruled out, at least in their literal form. The observed changes of optical response seen in ellipsometry [2] may be related to the disappearance of adatom-restatom-induced deep strains involving a depth of 10–15 Å, which are *inside* the semiconducting region. Coming finally to He scattering [7], we note that the sharp observed Bragg spots are perfectly compatible with incomplete melting, since Ge(111) does not roughen. In addition, our predicted loss of 2×2 correlations among adatoms provides a natural explanation for the experimental disappearance of 1/2 order spots. Last, and most convincingly, the subtle B/C sublattice mixing in the first layer predicts precisely the peculiar weak reversal of

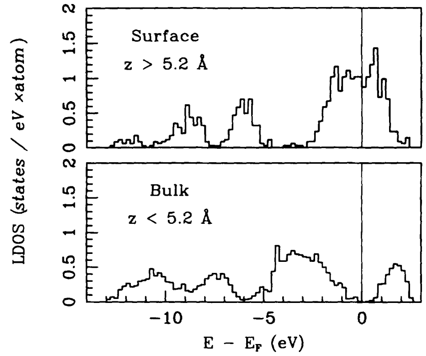

FIG. 4. Surface and bulk electronic density of states for Ge(111) at $T \sim T_M$. Note the strongly metallic surface character.

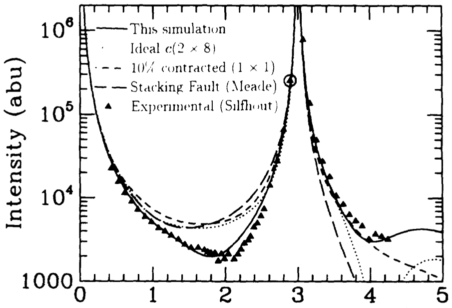

FIG. 5. Kinematical intensities (structure factor) along the (00) rod. Full line: present calculation. Dashed line: ideal c(2 × 8) structure. Dotted line: no adatoms, and first bilayer contracted by 10% [7]. Long-dashed line: hexagonal surface (stacking fault) as in Ref. [16]. Normalization constant chosen to fit experiment at the point encircled.

asymmetry, from B-like to C-like, which is seen to take place across T_c [7].

We close with a discussion of the physical reasons why a semiconductor surface such as Ge(111) should incompletely melt. In metals, incomplete melting or nonmelting is normally attributed to strong layering forces [19,21]. This mechanism has been invoked also for Ge(111) by Van der Gon *et al.* [5]. However, there is a large mismatch between the Ge bilayer spacing $d = 3.2$ Å and the known period of the pair function oscillations in metallic l-Ge of $\lambda = 2.7$ Å. It is intuitively clear, and confirmed by classical simulations [22], that in these circumstances, i.e., when d and λ are very different, layering no longer opposes, and may even favor, surface melting. Hence, there must be a different reason, which we now address, why melting of Ge(111) is incomplete.

The free energy change upon melting n surface crystalline bilayers at temperature $T < T_M$ is $\Delta F = 2nk_B\Delta S(T_M - T) + [\sigma_{\rm LV} + \sigma_{\rm SL} + V(n)] - \sigma_{\rm SV}$, where $\sigma_{\rm SV}$($\approx$ 720 meV/atom), $\sigma_{\rm LV}$($\approx$ 530 meV/atom), and $\sigma_{\rm SL}$ ($\approx$ 220 meV/atom) are solid-vapor (SV), liquid-vapor (LV), and solid-liquid (SL) interface free energies [23], and $V(n)$ is an effective interaction between the SL and LV interfaces. Free electrons in the metallized film come into play in at least two separate ways. First, there is a flow of electrons from the surface to the bulk, caused by an estimated work function difference $\Delta\Phi \sim 0.25$ eV [24]. This, however, lowers $\sigma_{\rm SL}$ by only a small amount. A more decisive effect arises from the exchange-correlation contribution to the interface interaction. The effect is similar to that taking place between a closed-shell polarizable atom and a metal surface. As shown by Lang [25], there is in this case an attraction, which arises between the electron in the atom and its exchange-correlation hole in the metal. The long-range tail is van der Waals, but the short-range part is stronger, and is well described within local density. The semi-infinite semiconductor and the thin metal film on top of it experience precisely the same kind of attraction, giving rise to a large negative contribution to $V(n)$ for small n. A crude but conservative estimate is obtained by simple extrapolation of the long-range tail. This is H/l^2 where $H \sim -4.6 \times 10^{-21}$ J is the Hamaker constant of Ge [9], and l is the metal (liquid) film thickness. This gives, for example, ~ -100 meV/atom for $l = 2$ Å, which is of the right magnitude needed to overcome all other repulsive terms and make ΔF negative, stabilizing the liquid film even for a T_c well below T_M. Conversely, growth of l with increasing temperature is prevented by the strongly confining form of the attraction. In summary, we have found that surface metallization provides both the reason why melting of Ge(111) begins early, and why it stops at the first bilayer. Because the mechanism of attraction is in no way specific to this surface, or even to Ge, we finally surmise that incomplete melting due to a similar metallization-related attractive $V(n)$ is not unlikely to occur (modulo different layering forces) on other semiconductor surfaces, including those of Si and GaAs.

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