Superheating and Induced Melting at Semiconductor Interfaces

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We present *ab initio* density-functional simulations of the state of several semiconductor surfaces at temperatures near the bulk melting temperatures. We find that the solid-liquid phase-transition temperature at the surface can be altered via a microscopic (single-monolayer) coating with a different lattice-matched semiconducting material. Our results show that a single-monolayer GaAs coating on a Ge(110) surface above the Ge melting temperature can dramatically reduce the diffusion coefficient of the germanium atoms, going so far as to prevent melting of the bulk layers on the 10 ps time scale. In contrast, a single-monolayer coating of Ge on a GaAs(110) surface introduces defects into the bulk and induces melting of the top layer of GaAs atoms 300 K below the GaAs melting point. To our knowledge, these calculations represent the first *ab initio* investigation of the superheating and induced melting phenomena.

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Melting is the phase transition from a solid phase to a liquid phase. An all too familiar example is the melting of ice to water. However, a complete understanding of this complicated phenomenon has not yet been achieved [1–6]. Nevertheless, among all the complexities, there are several unifying principles governing all melting behaviors. It has long been understood that melting usually initiates from defects within the otherwise perfectly periodic crystal [5]. They can be defects inside the bulk such as point defects, line defects, and grain boundaries [2,4,7,8]. They can also be free surfaces [6], where the crystal abruptly stops. The role of free surfaces in initiating melting has been studied both from an experimental point of view [9–11] and from theoretical investigations [8,12].

It was shown experimentally by Daeges and co-workers that thin (macroscopic) coatings of a different material can change the melting behavior of the substrate. In Ref. [11], they described an experiment where a Ag crystal coated with a ~10–20 μm thick layer of Au achieved superheating of 25 K for 1 min. By replacing the Ag-air interface with a Ag-Au interface, the core Ag material does not melt since its surface is maintained in a solid phase by the coating. Similar superheating behavior has also been observed in quartz/cristobalite crystals surrounded by fused silica [9] and Ar bubbles in Al [13].

To investigate the role played by the interface in the melting transition, we ask whether such superheating phenomena are possible when the coating is a minimal perturbation to the underlying surface. Moreover, we ask whether the opposite phenomenon, in which such a minimal coating actually induces melting of the otherwise stable underlying surface, is possible. We study the (110) surface of GaAs, which is the natural cleavage plane of GaAs, and the corresponding surface of Ge. With the only significant difference being their covalent or ionic bonding nature, a single monolayer of GaAs on Ge or vice versa can be considered a textbook example of how a coating could alter the melting behavior of a substrate. Moreover, fabrication of such systems is possible using molecular beam epitaxy. Although Ge and GaAs have almost identical lattice constants and average masses, the melting temperature of GaAs (1540 K) is higher than that of Ge (1211 K) by over 300 K. So what might happen if Ge and GaAs coexist at a temperature between their melting points? We approach the problem by looking at the microscopic behavior of melting at the surface. In doing so, we hope to shed light on how one may control or alter the behavior of materials near the melting point, which could have implications for high-temperature materials applications. In this Letter, we demonstrate that a coating of GaAs only a single monolayer in thickness can cause superheating in a Ge crystal, while a single-monolayer coating of Ge can induce melting in a GaAs crystal at a temperature between their melting points. While coatings are generally thought of as a protective barrier to defect nucleation, the latter study demonstrates that a surface layer can actually *initiate* defect formation, ultimately causing the solid to melt by weakening surface bonding.

The time evolution of the system is determined according to the Born-Oppenheimer approximation, separating the ion degrees of freedom from the electron degrees of freedom. At each time step, the ion locations are fed into the electronic calculations, where density-functional theory (DFT) is used to minimize the total electronic free energy. The forces on the ions are then calculated and the ions moved using classical molecular dynamics. The positions of the ions are updated using the Verlet algorithm, which uses a standard discretization of Newton's equation:

$$m\frac{\partial^2 \mathbf{x}(t)}{\partial t^2} = \mathbf{F}(t) \Rightarrow \mathbf{x}_{i+1} = 2\mathbf{x}_i - \mathbf{x}_{i-1} + \frac{dt^2}{m}\mathbf{F}_i. \quad (1)$$

In this, our study follows the same spirit as an earlier work done by Tosatti and co-workers [12], which used the same method to study the melting of the Ge(111) surface. We employ *ab initio* norm-conserving pseudopotentials generated using Hamann's scheme [14]. Key to our studies is the fact that we compare the relative differences in dynamics between two systems (with and without a coating),

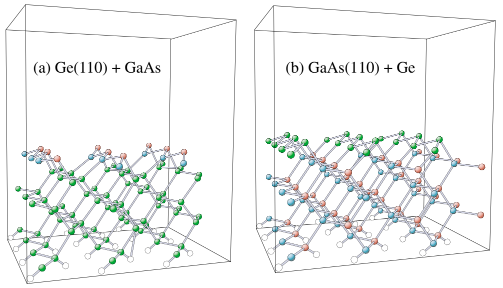

FIG. 1 (color). Computational supercells: (a) The (110) surface of Ge with a single-monolayer coating of GaAs and (b) the (110) surface of GaAs with a single monolayer of Ge. Ge atoms are shown in green, Ga in blue, As in red, and H in white.

which eliminates many of the errors due to supercell size, cutoff energy, time step, and ambiguities in the melting temperature, which can vary with system size and geometry.

There have been studies of melting with empirical potentials [7]. For example, for melting of Si there exist high quality three-body potentials such as those from Stillinger and Weber, which can reproduce a wide variety of physical properties [15]. These studies usually can access a much longer time scale than corresponding quantum mechanical studies, because of the lower computational requirement of empirical potentials. However, for heteropolar materials such as GaAs, high quality empirical potentials which work well around the melting temperature have not yet been produced. The changes in bonding character during melting require an accurate description of the electronic states that is provided by density-functional theory. Furthermore, the quantum mechanical treatment of the electrons has the added benefit that it provides the electronic band structure and the charge density information, in addition to ionic trajectories. Previous DFT calculations involving the Ge(111) surface [12] were successful in identifying a charge density transformation that occurs in the surface atoms near the melting temperature.

The computational supercells (see Fig. 1) that we consider are composed of four free layers (18 atoms/layer) of either Ge or GaAs, capped by a frozen layer terminated with hydrogen atoms. To eliminate interactions between the top (surface) layer and the hydrogen layer in the cell above, the supercells are separated by ~15 a.u. of vacuum [12]. Using a cutoff energy of 5 hartree, 200 bands, and a time step of $dt = 16$ fs, we have studied up to time scales of ~12 ps, more than enough to compare melting behaviors in these surface structures [16].

We first compare the dynamics of a Ge surface at 1240 K to a similar structure where the top layer of Ge has been replaced by a GaAs monolayer. The bare Ge surface simulation is used to make sure that the temperature is above the melting point of our supercell of Ge. Whereas the gold-on-silver experiments use coatings with ~60 000 layers [11], we ask whether a coating of only a *single monolayer* can produce a significant change in the state of the surface and/or bulk. The lattice constants a_x and a_y in the plane of the surface were fixed to be the same as the bulk values for the substrate. Before each simulation, the atomic positions were relaxed. In Fig. 2, we plot the trajectories of the ions in each layer projected onto the (x, y) plane over a 10 ps period, starting with an equilibrium $T = 0$ configuration. It is clear that we are operating at a temperature above the melting point of Ge. In the GaAs-coated system, while there are still bond-breaking events in the GaAs monolayer and the Ge layers below, the motion of the Ge ions in the second, third, and fourth layers is dramatically slowed by the presence of the GaAs coating.

One straightforward way to distinguish between a melted liquid and an amorphous solid is by testing the linearity of the average displacement, $\langle \Delta R^2 \rangle(t)$. In Fig. 3, we plot $\langle \Delta R^2 \rangle(t)$ for the atoms in each layer of the Ge surface with [Ge(110)] and without [Ge(110) + GaAs] the GaAs monolayer. Clearly the top four layers of the Ge(110) crystal are melted, whereas only the GaAs and the first two Ge layers are melted in the GaAs-coated system. The diffusion constant D_i for the atoms in layer i, fitted to the

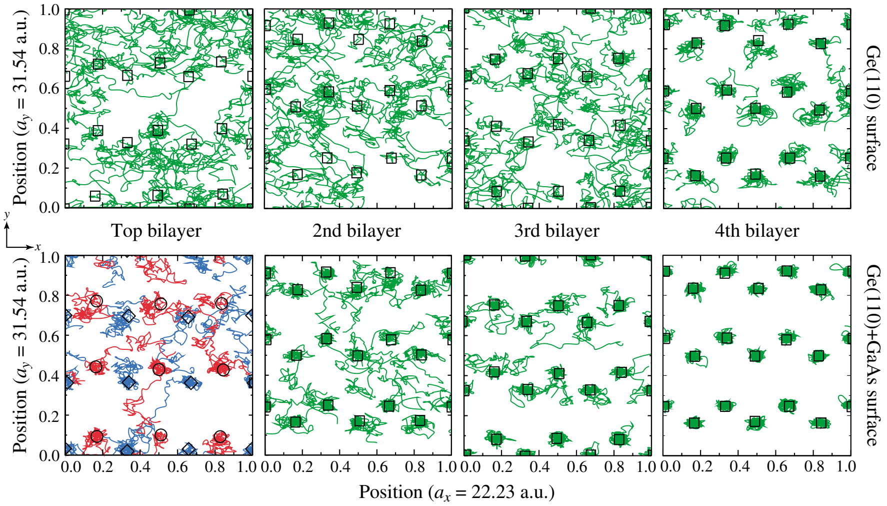

FIG. 2 (color). Ion trajectories of the atoms on a Ge(110) surface at 1240 K, with (bottom) and without (top) a single-monolayer coating of GaAs, as they appear looking down the (110) direction. Ga trajectories are shown in blue, As in red, and Ge in green. The black diamonds (Ga), circles (As), and squares (Ge) mark the initial positions of the atoms at $t = 0$. Note the decrease in diffusive motion of the Ge atoms in the presence of a GaAs monolayer coating.

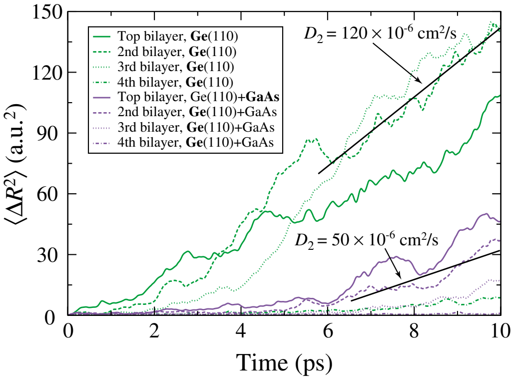

FIG. 3 (color). Mean-square displacement $\langle R^2 \rangle$ averaged over the atoms within each of the top four layers of a Ge(110) surface at 1240 K with (purple) and without (green) a monolayer coating of GaAs. The diffusion constant of the second layer, D_2, is calculated from the equation $\langle R^2 \rangle_j = 4D_j t$ using the slopes of the black lines.

relation [17] $\langle \Delta R^2 \rangle_i(t) = 4D_i t$, is given in Table I. The diffusion constant of the Ge atoms in the second layer is reduced by a factor of 2.4. Note that the fourth layer of atoms in the Ge(110) + GaAs crystal is essentially vibrating about its initial configuration (constant $\langle \Delta R^2 \rangle$). At least on this time scale, it appears that the GaAs-coated system is incompletely melted with a liquid layer of GaAs and two of Ge capping the superheated solid Ge bulk. It is possible that with a larger supercell or longer time scales, the bulk would eventually melt as well. Regardless, this system represents a dramatic change from the rapid melting of the homogeneous Ge surface.

TABLE I. Diffusion constant averaged over layer. The first section is for the top four layers of a Ge surface with and without a single-monolayer coating of GaAs. The last section is for the top two layers of a GaAs surface with and without a monolayer coating of Ge. All values are given in units of 10^{-6} cm^2/s. The third and fourth layers of the Ge(110) + GaAs surface and all layers of the GaAs(110) surface have a constant, rather than linear, $\langle R^2 \rangle$ vs t relationship.

Layer	$D_{\mathrm{Ge(110)}}$	$D_{\mathrm{Ge(110)+GaAs}}$
1 (Ge/GaAs)	110	70
2 (Ge)	120	50
3 (Ge)	120	30
4 (Ge)	10	N/A
Layer	$D_{\mathrm{GaAs(110)}}$	$D_{\mathrm{GaAs(110)+Ge}}$
1 (GaAs/Ge)	N/A	40
2 (GaAs)	N/A	10

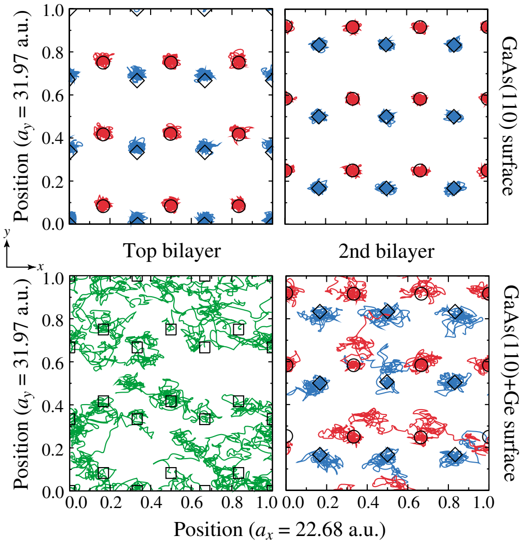

FIG. 4 (color). Ion trajectories of the atoms on the two top layers of a GaAs(110) surface at 1240 K, with (bottom) and without (top) a single-monolayer coating of Ge, as they appear looking down the (110) direction. The color and symbol scheme is the same as in Fig. 2. Note how the monolayer coating of Ge induces melting in the underlying layer of the GaAs crystal.

Given that the behavior of the Ge surface is so strongly regulated by the presence of a GaAs coating, we next ask what effect a Ge monolayer will have on a GaAs surface. In Fig. 4, we compare the trajectories of the ions in the top two layers of a GaAs surface to the system where the top layer has been replaced by Ge atoms. As before, the ion dynamics are dominated by the character of the top layer. Clearly, we are operating well below the melting point of our GaAs supercell. The bare GaAs surface shows very little motion in any layer, in stark contrast to the surface with a Ge coating, where both the Ge atoms and the layer of GaAs below are highly diffusive.

In Fig. 5, we plot the average displacement of the atoms in the top two layers of each system. We see that the motion of the bare GaAs surface is nondiffusive, while the diffusion constant of the GaAs layer covered by Ge is significant (10×10^{-6} cm^2/s; see Table I). Upon closer examination, the diffusive motion of the Ga and As atoms in the second layer is precipitated by bond-breaking events

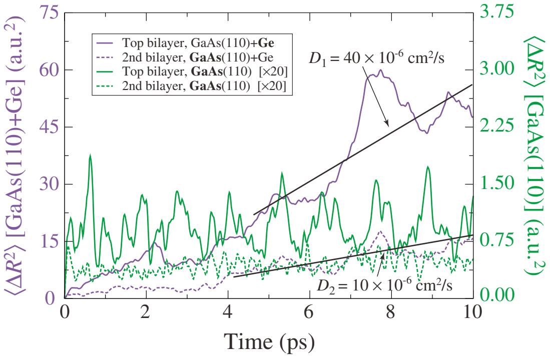

FIG. 5 (color). Mean-square displacement $\langle R^2 \rangle$ averaged over the atoms within each of the top two layers of a GaAs(110) surface at 1240 K with (purple) and without (green) a monolayer coating of Ge. The diffusion constant of the top two layers of the GaAs(110) + Ge surface is calculated using the slopes of the black lines. Note the difference in scales for the two surfaces.

in the top Ge monolayer and the subsequent penetration of a few Ge atoms into the GaAs surface. It appears that Ge atoms that penetrate for as briefly as 1 ps cause the GaAs layer to become disordered, even at a temperature *hundreds* of degrees below the bulk melting point. This coating-induced melting is a physical phenomenon that has not been previously observed, to our knowledge. The third and fourth layers in each system remain solid up to $t = 10$ ps with very little motion ($\langle R^2 \rangle \approx 0.5$ a.u.^{2}).

The dependence of the surface stability on the composition of the top layer is likely due to the highly localized nature of the surface states in a semiconductor. When an individual Ge atom in the coating of a GaAs surface undergoes large dynamical movements, it can break covalent bonds within its own layer and nucleate defects in the GaAs layers below, if it penetrates inside the bulk. The fact that melting is clearly proceeding from the surface inwards indicates that the induced melting is a surface, rather than a mixture, effect. Using the additional electronic state information from our DFT simulations, we observe that a large-scale transition into a liquid state is initiated by penetration of four Ge surface atoms, which is coincident with the metallization of the band gap and a number of bond-breaking events [12]. In contrast, the relatively stable GaAs coating on a Ge surface in Fig. 2 drastically reduces the diffusive motion in the normal direction. We observe little penetration of foreign atoms into the fourth layer, where we find a stable crystal with minimal disturbance to the bonding structure in the charge density.

There are several computational limitations on the simulations presented in this Letter that are possible sources of error. To test this, we examined the system with perhaps the most interesting dynamics, the Ge monolayer on a GaAs surface. We increased the cutoff energy from 5 to 8 hartree, with little qualitative effect on the surface melting observed in Fig. 4. The diffusion constant D_2 remains at 10×10^{-6} cm^2/s. Similarly, reducing the time step to 8 fs had little effect on the surface melting ($D_2 \rightarrow 9 \times 10^{-6}$ cm^2/s).

In addition, doubling the size of the supercell along the direction with the most diffusion (the y axis in Figs. 2 and 4 did not appreciably affect the dynamics ($D_2 \rightarrow 8 \times 10^{-6}$ cm^2/s). Including additional layers (thereby increasing the supercell size in the z direction) will certainly have a quantitative effect on the diffusion due to the unphysical nature of the frozen atoms 4 layers below the surface. However, it is clear from the Ge(110) surface in Fig. 2 that the frozen layer does not prevent melting in the atoms above. We also note that although the fourth layer of Ge atoms has far less mean-square deviation, the kinetic energy of these atoms is roughly equivalent to the upper three layers. We have assumed vacuum conditions in the volume above the surface, since it is likely that foreign atoms and molecules such as H_2O will desorb at high temperatures. Indeed, our simulations predict the rapid desorption of H atoms from the surface at 1240 K. We have initiated each simulation run with a temperature of 1240 K to avoid the prohibitive costs using DFT of gradually increasing the temperature to mimic bulk heating. Because our main results involve *comparisons* of similar systems, any errors associated with this approach are likely to be systematic and therefore would not affect the occurrence of superheating or induced melting. Thus, the results of this work provide compelling evidence that a simple monolayer is sufficient to dramatically alter the melting behavior of a semiconductor surface.

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[17] The factor of 4, rather than 6, is due to the fact that the diffusive motion is primarily two dimensional, in the (x, y) plane of each layer of atoms at $T = 0$.