

# Control of melting using nanoscale coatings

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## Abstract

This article summarizes previous work using density-functional simulations to investigate the effects of nanoscale surface coatings on the dynamics of semiconductor surfaces near their melting points. We demonstrate that a coating of GaAs only a single monolayer thick causes a dramatic reduction in the diffusive motion of the surface atoms of a Ge(110) crystal, and causes superheating of the bulk at temperatures well above the Ge melting point, on the 10 ps time scale. In direct contrast, a similar single-monolayer coating of Ge will induce melting of a GaAs(110) surface, even 300 K below the bulk GaAs melting point. Using these atomic-scale simulations, we suggest that the Ge monolayer causes the GaAs(110) surface to melt through transient penetration into the bulk, initiating collective diffusive motion of the Ga and As atoms. This work has important implications for high-temperature materials design, while simultaneously uncovering the fundamental causes of the melting phase transition.

## Introduction

Though the melting phase transition has been the subject of numerous chemical and physical studies, a complete understanding of this complicated phenomenon is still elusive [1, 2, 3, 4, 5, 6]. Nevertheless, all melting behaviors are governed by several unifying principles. In particular, melting is usually initiated by the appearance of defects in an otherwise perfectly periodic crystal [5]. Besides the possibility of bulk defects such as point defects, line defects and grain boundaries [2, 4, 7, 8], every experimental sample has inherent defects at the free surfaces [6], where the crystal abruptly stops. Both experimental [9, 10, 11] and theoretical studies [8, 12, 13, 14] have elucidated the importance of free surfaces in the initiation of melting.

Several experiments have demonstrated that a solid substrate covered by a thin coating of a different material can be heated beyond its melting point, without the solid melting [9, 16, 11, 15]. Daeges *et al.* showed that a silver crystal coated with  $\sim 10 - 20 \mu\text{m}$  of gold can be superheated by 25 K for one minute, in which the core Ag is prevented from melting by replacing the Ag-air interface with a Ag-Au interface [11]. Similar superheating behavior has also been observed in quartz/cristobalite crystals surrounded by fused silica [9] and Ar bubbles in Al [16]. However, in all of these classical superheating experiments,

the dimensions of the materials are macroscopic (at least tens of microns). Qualitatively, these experiments can be explained by the following reasoning. The surface is known to play an important role in initiating melting, so a core material can be maintained in a solid phase above its melting point if the exposed surface is replaced by a coating with a higher melting point. At the molecular level, the coating creates a coherent interface that prevents nucleation of melting. However, the above experiments above seem to require coatings on at least the micron length scale, and to our knowledge, there has been no suggestion in the literature that superheating is possible with nanoscale coatings. Moreover, the argument above relies critically on the coating having a higher melting point than the substrate so that a nucleation barrier to melting exists. The opposite scenario, where the coating has a lower melting point, has not been considered either theoretically or experimentally.

The purpose of this work is to investigate, at the atomic scale, the role of the surface in the melting transition. To do this, we ask whether superheating can be achieved when the coating is only a *minimal* addition to the underlying surface [13, 14]. Moreover, we ask whether such coatings can cause other macroscopic behavior, namely induced melting of an otherwise stable underlying surface. We will study Ge and GaAs at the (110) surface, which is the natural cleavage plane of GaAs. The only significant difference between these semiconductors is their bonding nature (covalent vs. ionic); thus a single monolayer of GaAs on Ge or vice versa can be considered a textbook example of how coatings alter the melting behavior of a substrate. Given that the melting temperature of GaAs is over 300 K higher than the melting temperature of Ge, what happens when Ge and GaAs coexist at a temperature in between their melting points?

The experimental melting point of Ge is  $T_m(\text{Ge}) = 1211$  K, while GaAs does not melt until  $T_m(\text{GaAs}) = 1540$  K [17]. The similarities between Ge and GaAs make this large difference in melting temperatures all the more intriguing. Ga, Ge, and As are three consecutive elements in the periodic table, thus the individual ion masses are very similar, and in fact the average masses of Ge and GaAs are nearly identical. In addition, Ge and GaAs have almost identical lattice constants,  $a = 1.07$  a.u. [17]. Therefore, the significant differences between these two materials must derive from the bonding character; the tetrahedral bonds in Ge are fully covalent, while these bonds in GaAs have some amount of ionic character.

The simulations in this work utilize a molecular dynamics approach based on pseudopotential density functional theory energy minimization. Melting can be studied over much longer length and time scales using empirical potentials [7], due to the lower computational requirements in comparison to corresponding quantum mechanical studies. However, a high quality empirical potential for heteropolar materials like GaAs that works well around the melting point does not yet exist. Aside from accuracy, the density-functional approach also provides the electronic band structure and charge density in addition to ion trajectories. Previous work has shown that this information can be used to identify the timing of the electronic transition from a solid to a liquid phase [12].

In this article, we first demonstrate that a Ge(110) surface can be superheated in the presence of a coating of GaAs that is only a *single monolayer* in thickness (see the Ge(110) surface in Fig. 1(a) and the GaAs-coated surface [Ge(110)+GaAs] in Fig. 1(b)). We identify a melted liquid with the presence of diffusive motion and compare measurements of diffusion constants in melted layers. Second, we show that in the novel heterostructure with a monolayer coating of the low-melting-point material Ge on the high-melting-point substrate GaAs, melting is induced on the GaAs surface at a temperature far below the bulk GaAs melting point (see the GaAs(110) surface in Fig. 3(a) and the Ge-coated surface [GaAs(110)+Ge] in Fig. 3(b)). This finding provides an exception to the classical preconception that coatings

protect against melting by acting as barriers to nucleation; in this case, the Ge coating initiates the formation of defects that ultimately lead to melting. We utilize a simplification of this Ge-coated GaAs(110) surface to suggest that melting is generally induced by the penetration of surface atoms with reduced coordination number.

### Superheating of a Germanium surface

In this section, we study the effects of a single-monolayer coating of GaAs on a Ge[110] surface at temperatures above the bulk Ge melting point. At temperatures between the bulk melting points of Ge and GaAs (1211 K to 1540 K), we expect that the dynamics of Ge surfaces will be qualitatively different from the dynamics of GaAs surfaces; namely, a bare Ge surface will melt quickly with large atomic displacements, while a bare GaAs surface will remain a stable solid, with very small, nondiffusive motions about the equilibrium atomic positions. Given this distinction, it is a natural extension to ask whether the superheating effects seen in the gold-on-silver coating experiments of Deages *et al.* [11] can be produced by a coating of GaAs on Ge. However, rather than the  $\sim 60000$  layers of gold coating which led to superheating 25 K above the silver melting point, we ask whether a *single-monolayer* coating of GaAs on Ge can stabilize the surface enough to produce significant changes in the state of the surface and/or bulk and lead to a higher resistance to melting.

In Fig. 1, we separate the ions into layers and plot the trajectories, projected onto the  $(x, y)$  plane, over a 10ps period at  $T = 1240$  K. The initial positions are given by the equilibrium configuration at  $T = 0$  K. We have initiated each simulation at the final temperature to avoid the prohibitive costs of gradually raising the temperature that would mimic bulk heating, though we note that experiments are more likely to involve ultrafast laser heating, as in recent work that has demonstrated superheating of bulk ice [15]. In comparing the second, third, and fourth layers with and without a GaAs coating, it is clear that the presence of the coating dramatically reduces the magnitude of the atomic displacements. In the second and third layers of the GaAs-coated surface, the motion of some atoms is still large enough that bond-breaking events must occur. However, the ions in the fourth layer are completely localized to their ideal crystal positions, appearing solid. This stability is not an artifact of the frozen layer below, because the fourth layer has an equipartition of kinetic energy, though its motion is nondiffusive [14].

We cannot distinguish a melted liquid from an amorphous solid purely by the maintenance of a lattice structure; rather, the most obvious sign that distinguishes a melted liquid from an amorphous solid is diffusive motion. Diffusive motion is characterized by a linear increase in the mean-squared displacement,  $\langle \Delta R^2 \rangle$ , as a function of time, while pure thermal motion will result in a constant  $\langle \Delta R^2 \rangle$ . Although in principle the atoms are free to move in all three dimensions, the motion is primarily in the atomic planes parallel to the surface, so we consider

$$\Delta R^2 = \Delta x^2 + \Delta y^2 \quad (1)$$

and ignore motion in the  $z$ -direction normal to the surface when estimating diffusion constants. (We note that the GaAs coating and underlying Ge layer do not form a mixture, and the layer identification remains well-defined throughout the 10ps simulation, except for rare events to be discussed later).

The collective behavior of the layers is more clear from the plots of  $\langle \Delta R^2 \rangle_j$ , averaged over the atoms in each layer  $j$  of the bare and GaAs-coated Ge(110) surfaces in Figs. 2(a) and (b), respectively. As indicated by Fig. 1, all four layers of the bare Ge(110) surface appear to melt within the first few picoseconds, displaying diffusive motion with linear  $\langle \Delta R^2 \rangle$ . In

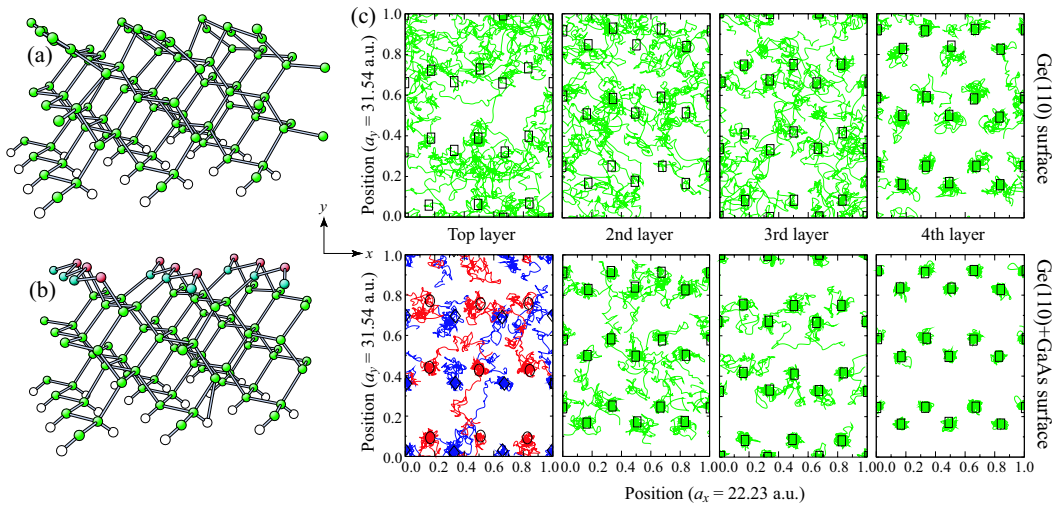


Figure 1: Trajectories of the atoms on a Ge(110) surface at 1240 K for 10 ps, without (see (a) and (c)) and with (see (b) and (c)) a single-monolayer coating of GaAs, as they appear looking down the (110) direction. The ions are broken into groups based on their positions along the  $z$ -axis (perpendicular to the surface) at  $t = 0$ . Trajectories of Ga atoms are shown in blue, As in red, and Ge in green. The black diamonds (Ga), ovals (As), and rectangles (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, especially in the fourth layer where melting is practically quenched.

the GaAs-coated system, the second and third layers also appear to have melted, though the initiation of linear growth in  $\langle \Delta R^2 \rangle$  appears to be delayed and the slope is significantly reduced. However, the most significant change is the roughly constant  $\langle \Delta R^2 \rangle$  in the fourth layer; these atoms are vibrating due to thermal motion about their initial positions, still solid. We conclude that with a single-monolayer coating of GaAs, we can achieve significant superheating of the fourth layer and the remainder of the bulk, though it is possible that over longer time scales the bulk would eventually melt as well. Regardless, this surface melting state represents a significant alteration of the ion dynamics of the homogeneous surface, and is similar to the state observed by Takeuchi *et al.* on the Ge(111) surface [12]. One might ask whether superheating could be observed in a gold-on-silver heterostructure with nanoscale coatings; we expect this not to be the case since the  $\sim 10 - 20 \mu\text{m}$  coating of gold forms a mixture with the silver substrate whose extent is roughly equal to the coating thickness.

To quantify the diffusion constant  $D_j$  for the atoms in a liquid layer  $j$ , we fit to the equation  $\langle \Delta R^2 \rangle_j(t) = 4D_j t$ , where  $\langle \Delta R^2 \rangle_j$  indicates an average of the mean-squared displacement over ions in layer  $j$  (see Table 1). The factor of 4, rather than 6, is due to our previously-stated assumption of predominantly two-dimensional motion. The diffusion constant of the second layer,  $D_2$ , is reduced by a factor of 2.4 in the presence of the GaAs coating, while  $D_3$  is reduced by a factor of four. The diffusion constant for the fourth layer is zero, at least on the 10 ps time scale. As we have shown previously [14], the solid-liquid transition is signified by a metallization of the bandgap, as shown in Fig. 2(c).

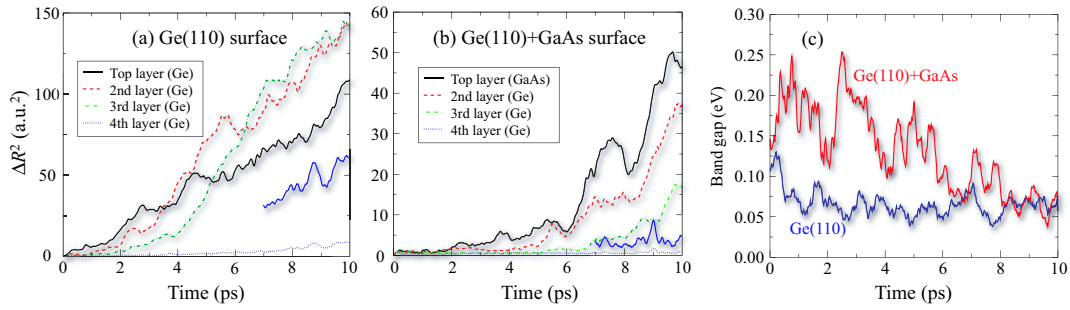


Figure 2: Mean-square displacement  $\langle \Delta R^2(t) \rangle$  averaged over the atoms within each of the top four layers of a Ge(110) surface at 1240 K (a) without and (b) with a monolayer coating of GaAs. The solid blue curves extending from  $t = 7$  ps to  $t = 10$  ps show  $\langle \Delta R^2 \rangle$  for the fourth layer of atoms magnified by a factor of 5 to accentuate the distinction between diffusive motion (linear  $\langle \Delta R^2 \rangle$  in (a)) and constant  $\langle \Delta R^2 \rangle$  in (b)). The metallization of the Ge(110) bandgap and collapse of the bandgap of the Ge(110)+GaAs surface near 6 ps is shown in (c).

Surface $T$ (K)	Ge(110)				Ge(110)+GaAs				GaAs(110)+Ge	
	$D_1^{\text{Ge}}$	$D_2^{\text{Ge}}$	$D_3^{\text{Ge}}$	$D_4^{\text{Ge}}$	$D_1^{\text{GaAs}}$	$D_2^{\text{Ge}}$	$D_3^{\text{Ge}}$	$D_4^{\text{Ge}}$	$D_1^{\text{Ge}}$	$D_2^{\text{GaAs}}$
1240	80	120	120	10	70	50	30	N/A	40	10

Table 1: Diffusion constant averaged over the atoms in each layer. Columns 2-5 correspond to the free layers of a Ge(110) surface, columns 6-9 correspond to the free layers of a Ge(110)+GaAs surface, while columns 10-11 correspond to the top two layers of a GaAs(110)+Ge surface. All quantities are given in units of  $10^{-6}\text{cm}^2/\text{s}$ . There is no detectable diffusive motion in the fourth layer of the Ge(110)+GaAs surface, indicated in the table by the N/A symbol.

### Induced melting of a Gallium Arsenide surface

Though other studies have probed the superheating phenomenon via a coating with a higher melting point, the behavior described above is remarkable due to the nanoscale of the GaAs coating. However, the opposite structure, where the coating has a lower melting point, has been completely unexplored. Given that the dynamics of the Ge surface are affected so strongly by the presence of a GaAs coating, it is natural to ask whether a single-monolayer coating of Ge on a GaAs surface will have similarly dramatic effects. It is clear from Figs. 1 and 2 that a bare Ge(110) surface will melt at all temperatures between 1240 K and the GaAs melting point of 1540 K, while we expect a GaAs(110) surface to remain solid throughout this spectrum. We entertain three possibilities for the effects of a Ge-coating on a GaAs substrate: (i) the GaAs bulk will remain solid and stabilize the Ge monolayer, (ii) only the Ge coating will melt, forming a liquid monolayer diffusing on top of a solid GaAs bulk, or (iii) the Ge monolayer will melt, and the resulting disorder will induce melting in the GaAs surface. Though these possibilities might be equally well considered anywhere in the temperature range between the Ge and GaAs melting points (1211 K to 1540 K), we study the dynamics of a bare and Ge-coated GaAs surface at the same temperature  $T = 1240$  K, for the purpose of comparison with Figs. 1 and 2. This temperature constitutes an extreme test of the induced melting hypothesis described in point (iii) above.

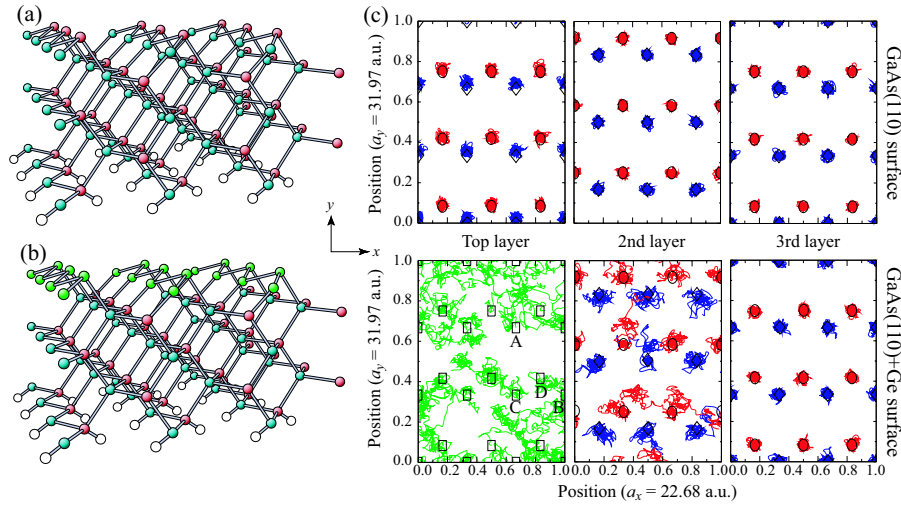


Figure 3: Trajectories of the atoms in the top three layers of a GaAs(110) surface at 1240 K for 10 ps, without (shown in (a) and top row of (c)) and with (shown in (b) and bottom row of (c)) a single-monolayer coating of Ge, as they appear looking down the (110) direction. The color scheme is the same as in Fig. 1. Note how the Ge monolayer induces melting in the underlying layer of the GaAs crystal. The four atoms labeled A, B, C, and D are highlighted because they display significant motion in the  $z$ -direction. The fourth layer of each system remains solid through  $t = 10$  ps.

We analyze these two surfaces in the same manner as before. In Fig. 3, we compare the trajectories of the ions of a bare GaAs(110) surface, and the surface when the top layer has been replaced by Ge atoms. As before, we find that the ion dynamics of the entire heterostructure are dominated by the character of the top layer. In the presence of the Ge coating, we find that the melting of the Ge monolayer determines the liquid phase of the surface, even more than the GaAs coating stabilizes the Ge bulk in the Ge(110)+GaAs heterostructure. As expected, there is virtually no motion in any layer of the GaAs(110) surface, since the temperature is 300 K below the bulk GaAs melting point. In stark contrast, both the Ge atoms and the underlying layer of GaAs atoms in the coated GaAs(110)+Ge surface have large displacements.

To determine layer diffusion constants, we analyze the mean-squared displacement in the top three layers of each system in Fig. 4. As expected,  $\langle \Delta R^2 \rangle$  is constant for every layer of the bare GaAs(110) surface, with low magnitude. This signifies a nondiffusive, solid crystal undergoing thermal motion. However,  $\langle \Delta R^2 \rangle$  increases linearly for the top two layers of the Ge-coated GaAs surface, with diffusion constants comparable in magnitude to the structures in Table 1. The third and fourth layers in each system remain solid for 10 ps, as can be seen from the constant  $\langle \Delta R^2 \rangle$  of these layers in Fig. 4. It is unclear whether this state is purely surface melting, as observed by Takeuchi *et al.* on the Ge(111) surface [12], or whether successive GaAs layers will melt at longer time scales. Regardless, this remarkable behavior represents a state of induced melting, 300 K below the GaAs melting point.

It is clear that for the purposes of studying the process of melting, to a first approximation the Ge monolayer and the underlying GaAs layer can be treated as the only free-moving atoms of any significance. In this simplified two-layer system, we can more easily isolate potential mechanisms of melting nucleation. Since the presence of the Ge monolayer is

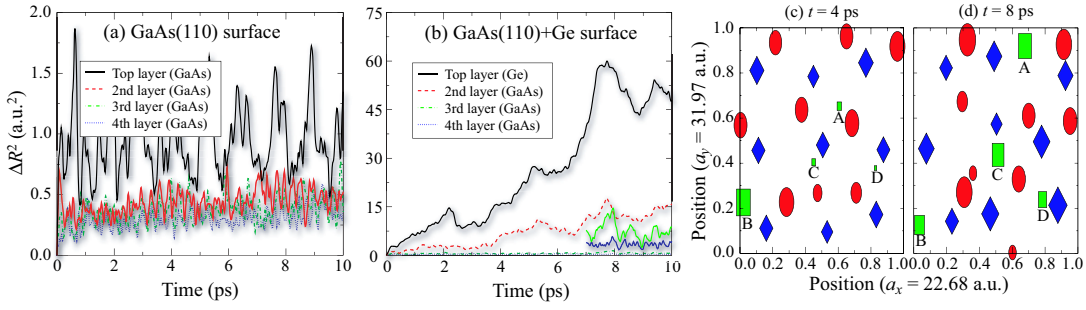


Figure 4: Mean-square displacement  $\langle \Delta R^2(t) \rangle$  averaged over the atoms within each of the top four layers of a GaAs(110) surface at 1240 K (a) without and (b) with a monolayer coating of Ge. Note the large difference in scales between (a) and (b). The solid blue and green lines in (b) extending from  $t = 7$  ps to  $t = 10$  ps show  $\langle \Delta R^2 \rangle$  for the third and fourth layers of atoms, respectively, magnified by a factor of 10 to accentuate the absence of diffusive motion. (c-d) Positions of atoms near the plane of the second layer in the GaAs(110)+Ge surface, including Ge atoms marked A-D in Fig. 3(c). The size of each atom is proportional to its penetration distance into the crystal. The largest object is at  $z \approx 10$  a.u., the smallest is at  $z \approx 16$  a.u. (c) At  $t = 4$  ps, atom A has transiently penetrated the GaAs layer ( $z \approx 11.2$  a.u.) and returned to the surface, while atom B remains in the second layer, disrupting the nearby Ga-As bonds in one row. (d) By  $t = 8$  ps, all four atoms have penetrated into the second layer and the distortion is widespread.

directly responsible for the melting of the GaAs(110)+Ge surface, we investigate whether isolated motions of individual atoms play a significant role in the propagation of the melting interface, through bond-breaking and penetration into the bulk. We find that the onset of diffusive motion of the Ga and As atoms in the underlying layer is precipitated by a few bond-breaking events in the Ge monolayer that subsequently involve a single ion transiently penetrating into the GaAs substrate.

To show that these penetration events are coincident with an increase in disorder in the crystal structure, we plot the positions of these four atoms and the second-layer Ga and As atoms at  $t = 4$  ps and  $t = 8$  ps in Figs. 4(c) and (d), respectively. These planes of atoms are viewed from inside the bulk, thus larger spheres are atoms located farther into the bulk (decreasing  $z$ ). Clearly the penetration of atom B in Fig. 4(c) disrupts the bonding network and nucleates disorder in the surrounding atoms, and the entire GaAs layer become more and more disordered as additional Ge atoms penetrate. The motion of these four atoms perpendicular to the surface is connected to the liquid dynamics of the second layer. Thus, we propose melting nucleation can occur from transient penetration of surface atoms, and does not require permanent mixing of the surface with the underlying substrate.

In addition, we also have additional evidence that the GaAs-monolayer coating prevents melting of the fourth layer of atoms in the Ge(110)+GaAs heterostructure. Since none of the atoms in the upper three layers penetrate within 2 a.u. of the initial plane of the fourth layer, this layer sees little intrusion from foreign ions and consequently can remain solid. It is likely that this penetration mechanism is also the cause of melting in other structures.



## Discussion

Our qualitative conclusions of superheating and induced melting are readily apparent from the sharp changes in melting dynamics in the supercells studied in this work. Since we are concerned only with relative dynamics between system pairs (with and without a coating), we can ignore many of the errors due to supercell size, cutoff energy, time step, and ambiguities in the definition of the melting temperature, which can vary with system size and geometry. (See Ref. [14] for a detailed discussion of the relative importance of error sources). Taken together, we have provided compelling evidence that a simple monolayer coating is sufficient to dramatically alter the melting behavior of semiconductor surfaces. Further studies with similar pairs of lattice-matched materials with large differences in melting temperatures will serve to validate our conclusions. The natural extension of our results would be to heterostructures of InSb and Sn, whose lattice constants and average masses are again equal, but whose melting points differ by almost 300 K ( $T_m(\text{InSb}) = 800$  K,  $T_m(\text{Sn}) = 504$  K) [18]. We note that the appeal of all of these heterostructures is the potential for relatively straightforward fabrication using molecular beam epitaxy [19].

In conclusion, our work has provided nanoscale evidence that the composition of the surface defines the melting behavior of a crystal. Using ion trajectories and electronic structure information, we have described methods to identify the timing of the solid-to-liquid phase transition, and have proposed a novel mechanism in which transient penetration of surface atoms removes the nucleation barrier to melting and initiates layer-by-layer melting of the substrate. Using a GaAs-coated Ge crystal, we have demonstrated that single-monolayer coatings may be sufficient to achieve superheating, a novel concept in semiconductors. Furthermore, we have postulated the novel phenomenon of induced melting in the context of a single-monolayer coating of Ge on an otherwise stable GaAs surface. It is tempting to think that these phenomena can be generally observed at other interfaces between materials with a large difference in melting temperatures. Ultimately, the ability to control semiconductor melting points using nanoscale coatings promises to play an important role in the design of high-temperature materials.

## Computational method

The molecular dynamics simulations in this work are based on pseudopotential density-functional theory (DFT) energy minimization. We separate the ion degrees of freedom from the electron degrees of freedom during the time evolution of each system, in accordance with the Born-Oppenheimer Approximation. During each time step, we minimize the total electronic free energy and calculate the band structure for a given set of ionic coordinates, using DFT in the local-density approximation (LDA). We then calculate the forces on each atom and shift their positions using classical molecular dynamics.

To update the ion positions, we use the Verlet Algorithm [20, 21], with a standard discretization of Newton's equation:

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

We maintain the temperature,  $T$ , using an isokinetic molecular dynamics approach, in which the velocities are renormalized after each time step to maintain a fixed total kinetic energy of  $3k_B T/2$  per atom. Our approach is similar to an earlier study of melting of the Ge(111) surface by Takeuchi *et al.* [12].



Our computational supercells (see Figs. 1-3(a) and (b)) are composed of four freely-moving layers, with 18 atoms per layer, of either Ge or Ga and As atoms. The bottom layer is capped by a frozen layer of the substrate material, terminated with H atoms. The frozen layer is positioned at  $z = 0$ . To eliminate artificial interactions between the top (surface) layer and the bottom (frozen) layer of the cell above, we insert  $\sim 15$  a.u. of vacuum above the surface [12].

The supercells have lattice constants  $a_x$  and  $a_y$  parallel to the plane of the surface that match the bulk values for the substrate material (either Ge or GaAs). To determine the initial ionic coordinates, the positions of the free atoms were relaxed at  $T = 0$  K. Simulations were performed using the freely-available plane-wave density-functional software package DFT++ [22]. Unless otherwise noted, we have used the following standard parameters: the first 200 bands in the electronic iterations, including eleven valence bands, a cutoff energy of 5 hartrees, and a time step of  $dt = 16$  fs for the ionic motion. Due to the large supercell size, accurate dynamics can be obtained using only the  $\Gamma$   $k$ -point. With these parameters, we have studied time scales of up to  $\sim 12$  ps.

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