Blue Waters allocation report: Harnessing petascale computing to elucidate fundamental mechanisms driving nanopatterning of multicomponent surfaces by directed irradiation synthesis

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Executive Summary: The use of energetic ion beams to induce quantum dot formation at the surfaces of III-V semiconductors is a promising method for efficient and scalable device fabrication. However, the fundamental physical mechanisms behind the nanopattern formation remain unknown, preventing the development of predictive models to connect surface properties to experimental conditions. Petascale molecular dynamics simulations have been performed to simulate ion irradiation of GaSb(110) from a pristine initial state to an ion fluence of 7.5×10^{15} cm^{-2} or greater for Ne^+, Ar^+, and Kr^+ ions. The purpose of these simulations was to uncover the ion-induced compositional changes leading to compositional depth profile formation and a driving surface instability. Under the ion bombardment, formation of Sb "protoclusters" $\leq$ 1 nm in diameter was observed. Ga atoms did not tend to form protoclusters but instead formed partial shells around the Sb protoclusters. Since the ion-induced mobility of Ga and Sb were identical, prompt ion effects alone cannot explain the compositional depth profile formation, and additional long temporal mechanisms such as asymmetric diffusion of Ga versus Sb are necessary to completely describe the surface evolution.

Key challenges

Directed irradiation synthesis (DIS) and directed plasma nanosynthesis (DPNS) are efficient and scalable techniques for fabrication of complex surfaces and nanomaterials in a single process step. The use of these techniques enables surfaces and interfaces to be driven far from equilibrium, activating a rich variety of physical mechanisms and material responses such as kinetic disordering, compositional phase dynamics, and emergence of metastable material states. Patterns such as ripples, quantum dots, or hole arrays can be acquired on many different materials, and can be controlled by easily-accessible experimental parameters such as the ion beam energy, species, or incidence angle. The versatility and robustness of DIS/DPNS offers a novel pathway towards systematic and rational design of complex next-generation nanomaterials.

Of particular interest is the formation of hexagonally-ordered quantum dots on III-V semiconductor surfaces by low energy ion beams [1]. However, theoretical efforts to understand the pattern formation in this case [2–5] have been fairly unsuccessful in developing a predictive modeling approach, highlighted by the example of two models which predict the same morphology but opposite surface compositional distributions [4,5]. The theoretical work has been hindered by a lack of atomistic computational modeling to understand the fundamental ion-surface interactions and the relevant physical mechanisms that can lead to the emergence of a compositionally-driven, pattern-forming instability at the surface. While some initial computational work has been presented in the literature [6,7], the scale of these efforts has been insufficient to adequately address the complex compositional dynamics that ultimately drive the nanopattern formation.

Recent experimental work has shown [7,8] that the compositional and morphological evolution of ion-irradiated GaSb are closely coupled. **Figure 1** illustrates the nature of this coupling by complementary use of grazing incidence small-angle x-ray scattering (GISAXS) and angle-resolved Auger electron spectroscopy (ARAES). The GISAXS data show several stages of surface evolution, including the formation of periodic nanostructures with ~30 nm spacing, indicated by the “shoulders” in the GISAXS

curves which grow in height with increasing ion fluence. From this data, the threshold fluence for the onset of pattern formation is determined and correlated to the compositional depth profile evolution measured from ARAES spectra at different fluences. Thus, the emergence of the quantum dot morphology at the surface is correlated to a particular compositional profile beneath the same surface.

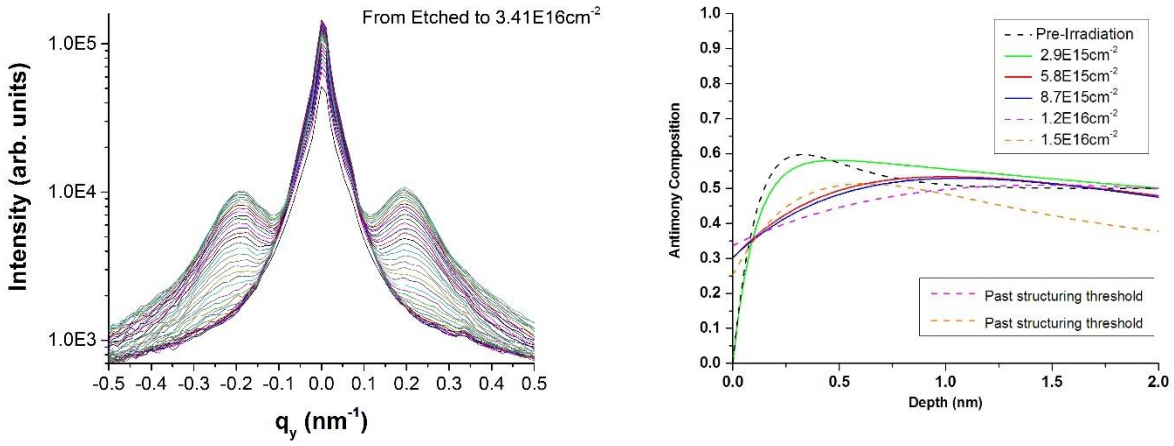

Figure 1: (left) GISAXS data showing the morphological evolution of etched GaSb under 500 eV Kr^+ irradiation, including structure formation with a periodicity of $q_y \approx 0.22$ nm^{-1} (i.e. ~30 nm spacing); **(right)** ARAES data showing the compositional depth profile evolution of cleaved GaSb for the same conditions up to a 2-nm depth [8].

Under a previous allocation on Blue Waters, our group has conducted petascale molecular dynamics (MD) simulations to study the effects of the compositional depth profile. **Figure 2** summarizes the key results from that project, which have been discussed in more detail elsewhere [9]. The initial surface was created prior to bombardment in order to resemble the surface composition at the patterning threshold fluence[1], using a procedure of creating each layer successively with heating and quenching steps to achieve an amorphous state resembling the ion-damaged "real" surface. Even before the ion bombardment, compositional phase separation was observed in the enriched regions into phases of 50/50 GaSb and single-element clusters of the enriched component. Interestingly, as the ion bombardment occurred, the Sb clusters rapidly self-organized into crystalline lattices while the Ga clusters remained amorphous. This behavior

[1] Note that the initial compositional profile in **Figure 2** does not match that in **Figure 1** because the analysis of the ARAES has been through several iterations since the simulations in **Figure 2** were begun, and at the time the compositional depth profile was calculated to look rather different than it currently appears in **Figure 1**.

was replicated in a "control" simulation in which the surface was allowed to evolve without the inclusion of ion irradiation, indicating that the crystallization of the pure Sb clusters was an intrinsic material response to the ion-induced compositional phase separation, but was not directly ion-driven itself. In summary, these simulations showed that the ion-induced compositional depth profile can in fact lead to a lateral compositional gradient, which could then provide the lateral pattern-forming instability leading to nanostructure formation at the surface as the ion irradiation continues.

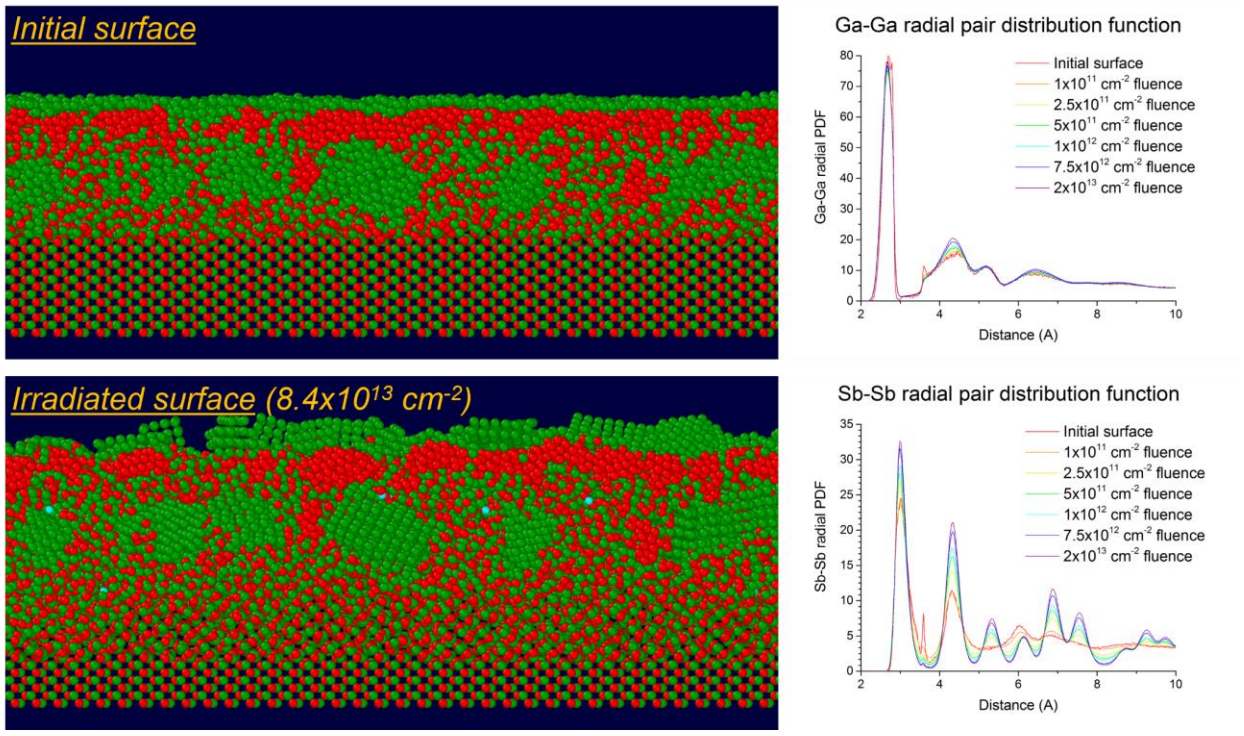

Figure 2: (left) Partial cross-sectional snapshots of the initial and irradiated (500 eV Kr^+ to 8.4 × 10^{13} cm^{-2} fluence) GaSb surface with altered compositional depth profile, showing phase separation of Ga and Sb clusters as well as Sb cluster crystallization; **(right)** fluence evolution of the Ga-Ga and Sb-Sb radial coordination numbers within Ga and Sb clusters, indicating that the Ga clusters remain amorphous while the Sb clusters rapidly crystallize.

A key knowledge gap which remains from the experimental data is to achieve a basic physical understanding of the mechanisms by which the compositional depth profile can form in the first place. Here, atomistic computational modeling is the only tool which is currently able to provide the detailed information necessary to gain this understanding. Experimental techniques are not able to observe the individual single ion impacts, while purely theoretical approaches rely entirely on assumptions about the underlying

processes, rather than providing new knowledge about those processes. To address this knowledge gap, our group has now carried out large-scale MD simulations of ion bombardment of GaSb surfaces from the initial 50/50 crystalline state, observing the structural and compositional changes that result. In addition to the discovery of ion-driven compositional changes in the GaSb surface, ion bombardment was studied for different ion species (Ne^+, Ar^+, and Kr^+) to make inroads in determining how the compositional changes depend on the choice of experimental conditions.

Why it matters

The interactions between energetic ions and the compositionally-complex surface encapsulate a diverse range of scientific fields, from atomic physics and chemical bonding to surface science and statistical mechanics. Fundamentally, the results from these simulations provide the first atomistic picture of not only how the ion and surface interact in a multicomponent environment, but how the environment itself is permanently altered and driven far from chemical or thermodynamic equilibrium, one ion at a time. In these metastable states, the assumptions based on classical, near-equilibrium concepts on which previous models of ion beam nanopatterning are based begin to break down, opening a need for new, disruptive modeling approaches to properly predict the surface evolution.

In practical terms, the ability to fabricate III-V quantum dots and other nanostructures efficiently and consistently is a key goal for the development of semiconductor devices such as quantum dot lasers [10] or solar cells [11]. Thus, the understanding gained from this project will be used to enable the development of predictive modeling capabilities which can in turn direct future experimental investigations. Beyond III-V systems, this knowledge and the models developed from it can be carried forward to studying other technologically-relevant classes of materials, such as metal/semiconductor interfaces which are also known to yield quantum dots under ion irradiation [12].

Why Blue Waters

Conventional MD simulations usually deal with system sizes of 10^3 to 10^4 particles, interacting over time scales on the order of some nanoseconds – or, in the sense of ion impacts, usually hundreds to thousands of impacts, whether sequentially [13,14] or in repeated simulations of the same initial conditions [6,15]. Even for these relatively limited scales, a modest computing cluster is often still necessary to make significant progress, as the simulations described above might still take several months to run on a standard desktop computer. In contrast, the simulations presently being reported on:

- Require a significantly expanded surface size in order to capture lateral features on the scale of several nm, as revealed from the simulations under the previous Blue Waters allocation. Specifically, lateral dimensions for the MD simulation cells were chosen as 25 nm on each side, giving a total surface area of 625 nm^2, while the previously-mentioned studies were limited to surfaces of less than 50 nm^2 area. In total, 150,000 to 200,000 atoms were simulated at any point in time (varying as atoms were added or subtracted from the simulation cell), an order of magnitude or greater beyond previous simulations efforts.
- A fluence scale on the order of 10^{16} cm^{-2} was desired to be reached, which for the given surface area would require > 60,000 cumulative ion impacts, introducing another order of magnitude or greater increase in computational demand over previous works.
- The needed computational resources must finally be multiplied for each of the three ion species studied – Ne^+, Ar^+, and Kr^+.

The cumulative computational demands to run simulations at this scale necessitated the resources and power of a high-performance computing system on the scale of Blue Waters if any significant and timely progress was to be made.

Furthermore, as would be expected from a simulation of this scale, a similarly-large need exists for data output and storage. The volume of data generated from these simulations was nearly 3 TB in total, across

several stages for three ion species. Nearly all of this output data consists of large dump files generated every few thousand time steps (i.e. roughly every 15-20 seconds of wall-clock time). Here, the high-performance file I/O capabilities of Blue Waters were instrumental in the rapid writing of these data files, ensuring that as much simulation time as possible could be dedicated to the simulation itself over the course of the allocation.

Accomplishments

Molecular dynamics (MD) simulations were carried out with LAMMPS [16] to simulate bombardment of GaSb(110) by 500 eV Ne^+, Ar^+, and Kr^+ to a fluence of 7.5×10^{15} cm^{-2} (or greater; only data to this fluence has been analyzed in significant detail thus far). Additionally, much of the post-simulation analysis relies on the OVITO [17] software package. The key results are outlined in **Figure 3** for the specific case of 500 eV Kr^+ bombardment. Three principal observations can be made from these snapshots:

1. No significant compositional depth profile occurs for these simulations. Looking at **Figure 3(b)**, the surface is clearly well-amorphized but shows no global depth dependence of the overall composition. Comparing to the experimental data for the same conditions (**Figure 1**), it can be seen that a compositional change has occurred in experiments even by the relatively low fluence of 2.9×10^{15} cm^{-2}, significantly below the maximum fluence of the simulations. Thus, this leads to the conclusion that *prompt ion effects alone are insufficient to generate a compositional depth profile.*
2. However, ion-induced compositional changes still occur in the simulations. In fact, both Ga and Sb appear to form clusters beneath the surface, with Sb cluster formation being more dominant and at least an order of magnitude more Sb atoms being members of a cluster than Ga atoms for all ion species considered. Due to the small size of these clusters (compared to the ~3 to 5 nm diameter of the clusters in **Figure 2**), and their potential role in generating a surface compositional depth profile if long-timescale mechanisms are accounted for, these clusters have been designated as "protoclusters".

3. Noting that Ga protoclusters are far less numerous than Sb protoclusters, and also noting that little to no preferential sputtering was observed over the course of the simulation, the question can be raised of where the "excess" Ga is located in order to maintain the near-50/50 stoichiometry of the surface. In fact, the excess Ga can be found forming a partial "shell" structure around the Sb protoclusters, as is illustrated in **Figure 4**. The combination with the Sb protoclusters leads to a "core-shell" structure not unlike that observed in experiments of GaSb nanowire formation by ion irradiation [18].

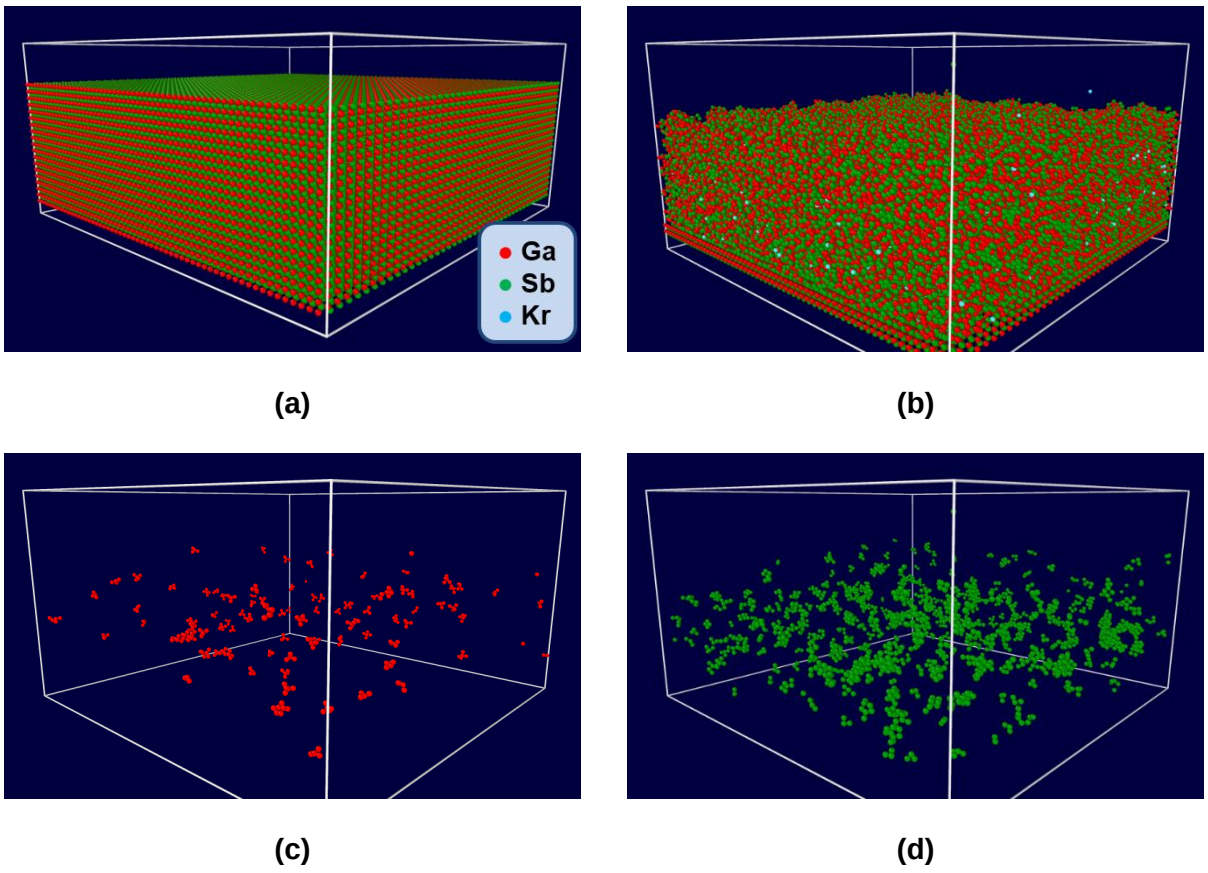

Figure 3: Snapshots of the 500 eV Kr^+ irradiated GaSb surface from MD simulations: **(a)** initial surface; **(b)** surface after bombardment to a fluence of 7.5×10^{15} cm^{-2}; **(c)** same surface as **(b)** showing only the Ga atoms in clusters; **(d)** same surface as **(b)** showing only the Sb atoms in clusters.

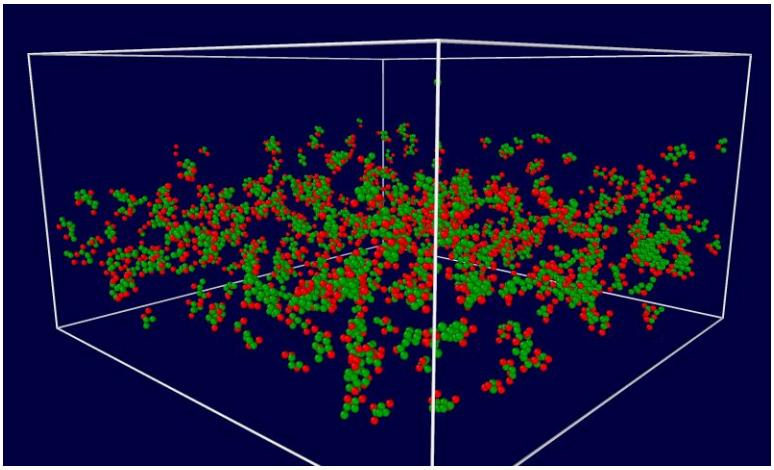

Figure 4: Snapshot of the GaSb surface after 500 eV Kr^+ irradiation (same as in **Figure 3(b)**), filtered to show the Sb protoclusters as well as the next layer of atoms around them (within 0.36 nm of a protocluster). The additional atoms are majority Ga, forming partial shells around the Sb protoclusters.

In general, irradiation by each ion species yields similar phenomena, i.e. formation of Sb protoclusters and partial Ga shells. However, there are quantitative differences between the GaSb surfaces irradiated by different ion species, as shown in **Figure 5**. While the initial evolution up to a fluence of 2.4×10^{15} cm^{-2} is essentially the same for all species, for fluences beyond this point the amount of Sb in clusters drops off for Kr^+ irradiation, while for the lighter Ne^+ or Ar^+ ions clustering continues and eventually the amount of Sb in clusters reaches an asymptote at ~ 5.5% of all Sb atoms being members of a cluster. While the physical implications of this trend are not yet clear, since the role of the protoclusters in depth profile formation and surface morphology evolution are not yet known, an interesting correlation with experiments can still be observed, since Kr^+ irradiation is known to lead to pattern formation at a threshold fluence of only 8.74×10^{15} cm^{-2} [8], which is a factor of four times lower than the threshold fluence for Ar^+ or Ne^+ irradiation. Thus, while its physical implications remain the subject of further analysis, the clear differences in the clustering tendency between Kr^+ irradiation and the rest of the ion species provide some small validation of the simulation results in comparison with experimental work.

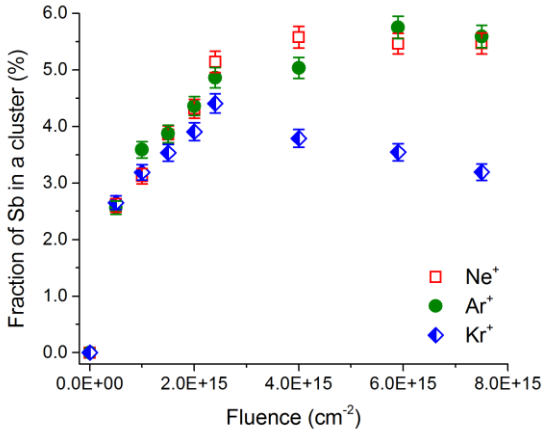

Figure 5: Clustering tendency of Sb protoclusters for each ion species studied, expressed as the percentage of Sb atoms which are members of a cluster at a give fluence.

The mechanism for protocluster formation has yet to be confirmed. One early hypothesis was that Ga receives a higher ion-induced mobility, driving it away from the center of a collision cascade and leaving a Sb-rich region at the center of the cascade. However, results for small-scale single-impact simulations shown in **Figure 6** showed that the ion-induced mobilities of Ga and Sb were virtually identical, so this hypothesis cannot explain the protocluster formation. Furthermore, this indicates that the order-of-magnitude difference in Ga diffusivity compared to Sb observed experimentally [19] cannot be explained by prompt ion effects, and is indeed a long temporal effect.

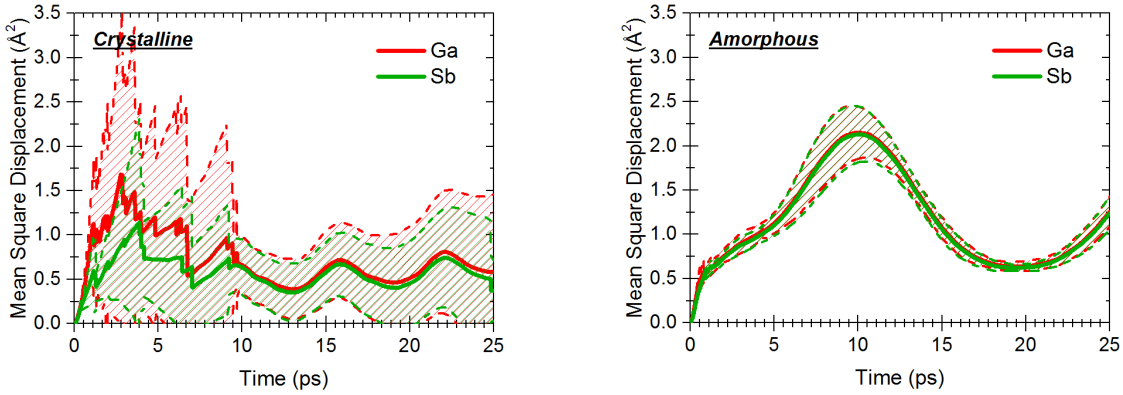

Figure 6: Mean square displacement (MSD) of Ga and Sb near the collision cascade for 500 eV Kr^+ single impacts into crystalline **(left)** and amorphous **(right)** GaSb(110) surfaces. The shading indicates the uncertainty of the MSD data. Aside from some short transients no significant difference in the ion-induced mobility of Ga versus Sb.

Currently, the working hypothesis for protocluster formation is based on Sb precipitation from the ion-induced thermal spike. When an ion impacts the surface, a volume on the order of ~10 nm^3 is effectively heated to temperatures on the order of 10^4 K and melted in the collision cascade. Notably, the melting temperature of Sb is much higher (904 K) than that of Ga (303 K). Thus, as the thermal spike energy dissipates throughout the rest of the GaSb surface, Sb would precipitate out of the GaSb melt well before Ga, allowing the formation of small Sb solid clusters around which Ga would eventually solidify in a shell-like structure. Very small Sb nuclei of even a few atoms formed in this manner would allow for Sb from nearby thermal spikes, caused by succeeding ion impacts, to precipitate out of the thermal spike readily, providing a mechanism for the few-atoms clusters to grow into the protoclusters observed in **Figure 3(d)**. While the complete implications of the protocluster formation still remain uncertain, they may serve as compositional "seeds" for the evolution of a compositional depth profile. Experimentally, it is known that Ga preferentially segregates to the surface in a real system [8], so the asymmetric diffusion of Ga versus Sb [19] may combine with the protoclusters to induce depth profile formation.

Next Generation Work

A critical limitation of MD simulation techniques is the inability to realistically access timescales beyond some μs, which in turn limits the mechanisms which can be considered in most cases to the prompt mechanisms that occur on very short timescales. In particular, long-timescale processes such as the asymmetric Ga-over-Sb diffusion found by Bracht and coworkers [19] is not accessible with existing MD techniques. As has been shown, this limits the ability of the MD simulation to provide information about the overall surface evolution. While though interesting and relevant information can still be obtained, it is limited solely to the prompt effects due to cumulative ion impacts on the surface.

However, it is possible to couple MD and kinetic Monte Carlo (kMC) in a manner which preserves the bond topology of the MD simulations while allowing for the relative time-efficiency of the kMC

approach [20]. However, this approach so far has only been used for relatively small length and time scales, well below those considered in the present (or previous) allocation. Thus, it is likely that the combined approach would require a significant increase in computational power, since kMC diffusion events can easily become dominant over single-ion impacts, especially at higher temperatures.

As a hypothetical model, a hybrid MD/kMC code of the type described in [20] could be implemented by simulating with MD the ion impacts up to a fluence where protocluster formation becomes significant, on the order of 10^{15} cm^{-2}. After this fluence step, the MD particle positions and bond topography can be analyzed to locate point, line, or area defects which enable diffusion, based on DFT or other analysis [21], allowing the construction of a graph of the atoms and defects which can form the basis of a kMC diffusion model. This kMC model would then be run for a time equal to that required to achieve the aforementioned ion fluence (likely on the order of seconds to minutes, depending on the chosen ion beam flux or current), giving an approximation of the diffusive motion of atoms induced due to ion irradiation and the associated compositional changes in the same timeframe. The MD/kMC cycle would then be repeated until the desired total fluence was reached.

This model, first deployed on a high-performance computing platform, could further be used to benchmark the results of more approximate simulations, e.g. those using crater functions of multicomponent materials [6], for accuracy and predictive ability. This would potentially allow the eventual development of high-efficiency simulations, which could be widely deployed and used by material scientists without relying on limited allocations of high-performance hardware, achieving the ultimate goal of enabling disruptive materials design through atomistic computational modeling.

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List of publications associated with this work

Article in press: M. A. Lively, B. Holybee, M. Toriyama, and J. P. Allain, "Massive-scale molecular dynamics of ion-irradiated III-V compound semiconductors at the onset of nanopatterning", *Nucl. Instrum. Meth. Phys. Res. B*, 2017. http://dx.doi.org/10.1016/j.nimb.2017.04.27.

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Thesis, in preparation: M. A. Lively, *Large-scale molecular dynamics investigations of ion-induced compositional dynamics leading to nanopattern formation at semiconductor surfaces*, University of Illinois at Urbana-Champaign 2017.

Article, in preparation: M. A. Lively, B. Holybee, M. Toriyama, J. P. Allain, *Nat. Commun.* (2017).