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ELECTRON DYNAMICS OF ION-IRRADIATED TWO-DIMENSIONAL MATERIALS

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EXECUTIVE SUMMARY

Exploiting the unique properties of two-dimensional materials for next-generation electronic devices and other novel technologies depends on high-resolution techniques for nanoscale imaging and structure manipulation, which often employ focused ion beams. Along with radiation-induced degradation of thin materials and materials' surfaces in space and nuclear applications, solving this technological challenge demands a detailed understanding of the response of thin materials to ion irradiation. In order to accurately study the subfemtosecond electron–ion dynamics in thin materials under ion irradiation, the research team performed first-principles simulations of few-layer graphene irradiated by charged particles ranging from protons to xenon ions. This research lays the groundwork for a predictive computational framework capable of determining optimal ion beam parameters for a desired imaging or patterning application and of indicating a material's susceptibility to radiation-induced defects.

RESEARCH CHALLENGE

Two-dimensional materials have a variety of remarkable properties, making them promising candidates for a wide range of potential applications including flexible electronics, solar cells, nanoscale sensors, and other electronic devices [1]. However, the properties of atomically thin materials are often sensitive to defects, nanopores, functionalization, and other types of nanostructure, which can either degrade performance when undesirable or enable an application when intentional [2,3]. Thus, precise techniques for imaging and patterning 2D materials, likely reliant on focused beams of energetic ions, are necessary for scalable and reliable manufacturing of devices based on 2D materials.

In addition, materials for space and nuclear applications must withstand constant bombardment by energetic ions, and mitigating erosion of nuclear cladding or radiation shielding materials fundamentally involves controlling surface behavior. Overcoming these engineering challenges requires a thorough understanding of the response of 2D materials and materials' surfaces to ion radiation.

However, the vast majority of current knowledge about ion-irradiated materials pertains to bulk materials, leaving surface effects largely unknown. The research team's first-principles approach provides unprecedented insight into electron dynamics in ion-irradiated materials, which is critical for developing both novel devices based on 2D materials and radiation-resistant materials for space and nuclear applications (see Fig. 1).

METHODS & CODES

The research team used Qbox/Qb@ll [4], their highly parallel implementation of real-time time-dependent density functional theory [5], to perform accurate first-principles simulations of excited-electron dynamics. This approach treats nuclei as classical point charges interacting electrostatically with electrons. Electrons are treated quantum-mechanically; their quantum orbitals, represented in a plane-wave basis, are governed by the time-dependent Kohn–Sham (TDKS) equations, a system of coupled partial differential equations. The team used the common adiabatic (without transfer of heat or mass) local-density approximation for the exchange-correlation potential describing the quantum correction to the electron–electron interaction.

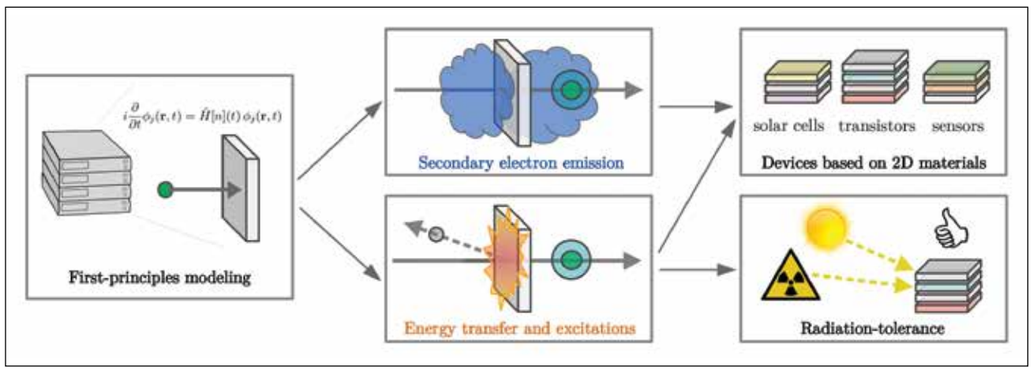

Figure 1: The first-principles simulations of ion-irradiated few-layer materials provide information about secondary electron emission, energy transfer, and excited electron dynamics. Understanding these processes will advance radiation tolerance and improve ion beam imaging and patterning techniques needed to create novel electronic devices based on 2D materials.

Starting with the lowest energy configuration of the material as the initial condition, the electronic orbitals were propagated in time by numerically integrating the TDKS equations. The simulations generated a time-dependent electron density that was further analyzed to extract the secondary electron yield and the charge captured by the projectile, among other quantities.

RESULTS & IMPACT

First, the team explored new numerical methods that could accelerate first-principles simulations of excited-electron dynamics, enabling study of longer timescales and larger systems. Specifically, the researchers interfaced Qb@ll with the PETSc library [6,7], allowing rapid testing of different numerical integration algorithms for propagating the electronic states over time. Thus far, the team has concluded that enforced time-reversal symmetry outperforms all available Runge–Kutta schemes in terms of stability and time-to-solution. Identifying an integrator that reduces computational cost without sacrificing accuracy would help make feasible extremely accurate simulations of defect formation in materials. This capability would deepen the understanding of defect formation mechanisms, provide transformative insight for nanostructure engineering techniques, and expedite the development of novel electronic devices for the benefit of society.

The team also implemented and applied new analysis techniques to extract the projectile charge state and the kinetic energy spectrum of emitted electrons. These methods provide additional information about the charge dynamics and energy dissipation mechanisms occurring as the ion interacts with the material, allowing more detailed insight into surface effects and predictions of projectile parameters most likely to induce defects. While models for bulk materials typically assume an equilibrated projectile charge and do not consider energy lost to electron emission, the team found that a highly charged projectile's effective charge varies dynamically as it traverses graphene and does not reach an equilibrium value within a few-layer sample (see Fig. 2). Furthermore, the initial charge of a heavy projectile strongly influences both energy transfer and electron emission, and accounting for electron emission can change the projectile parameters that maximize energy deposited in the material. These findings not only demonstrate the disparity in behavior between few-layer material and bulk materials but also establish the need for further study of ion-irradiated 2D materials and special tuning of ion beam parameters for imaging and processing 2D materials.

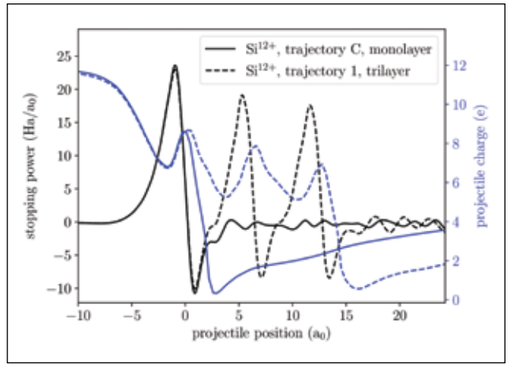

Figure 2: Instantaneous stopping power (black) and effective projectile charge (blue) as a Si^{12+} ion traverses monolayer (solid line) and trilayer (dashed line) graphene. Both the stopping power and projectile charge evolve dynamically, without reaching an equilibrium value characteristic of bulk materials. (Units: a_0 is the Bohr radius of an electron; Ha is an energy unit equal to 27.2 eV.)

WHY BLUE WATERS

Blue Waters enabled the research team to conduct the long simulations of large systems involved in this project. In order to accurately model a few-layer material or a material surface under irradiation, scientists must evolve hundreds or thousands of electrons over thousands of timesteps in an elongated simulation cell containing a large vacuum outside the material. These aspects make the simulations computationally expensive and are only possible with a massively parallel implementation of the first-principles approach and a high-performance supercomputer.

PUBLICATIONS & DATA SETS

K. Kang *et al.*, "Pushing the frontiers of modeling excited electronic states and dynamics to accelerate materials engineering and design," *Comp. Mater. Sci.*, vol. 160, pp. 207–216, Apr. 2019, doi: 10.1016/j.commatsci.2019.01.004.