Atomic engineering with electric irradiation

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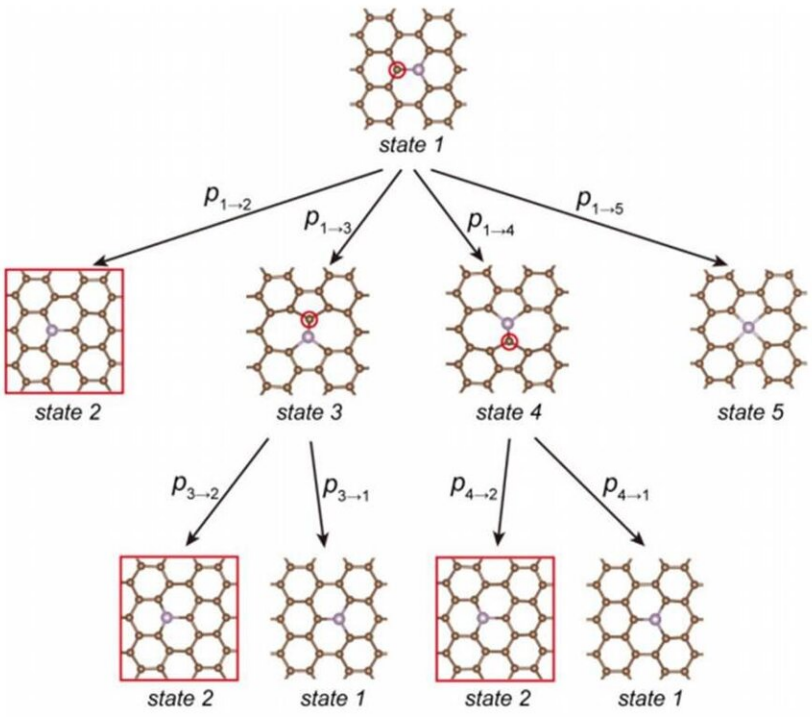


Decision tree for atomic engineering. pi→k stands for the probability of a dynamic process from an initial configuration i to final configuration k. The physicists assumed that the electron incident angles θe and φe are fixed throughout the whole operation. The state outlined in red indicates the final desired state. Red circles indicate the target atoms of for the electron irradiation. Credit: Science Advances, doi: 10.1126/sciadv.aav2252

Atomic engineering can selectively induce specific dynamics on single atoms followed by combined steps to form large-scale assemblies

thereafter. In a new study now published in *Science Advances*, Cong Su and an international, interdisciplinary team of scientists in the departments of Materials Science, Electronics, Physics, Nanoscience and Optoelectronic technology; first surveyed the single-step dynamics of graphene dopants. They then developed a theory to describe the probabilities of configurational outcomes based on the momentum of a primary knock-on atom post-collision in an experimental setup. Su et al. showed that the predicted branching ratio of configurational transformation agreed well with the single-atom experiments. The results suggest a way to bias single-atom dynamics to an outcome of interest and will pave the road to design and scale-up atomic engineering using electron irradiation.

Controlling the exact atomic structure of materials is an ultimate form of atomic engineering. Atomic manipulation and atom-by-atom assembly can create functional structures that are synthetically difficult to realize by exactly positioning the atomic dopants to modify the properties of carbon nanotubes and graphene. For example, in quantum informatics, nitrogen (N) or phosphorous (P) dopants can be incorporated due to their nonzero nuclear spin. To successfully conduct experimental atomic engineering, scientists must (1) understand how desirable local configurational change can be induced to increase the speed and the success rate of control, and (2) scale up the basic unit processes into feasible structural assemblies containing 1 to 1000 atoms to produce the desired functionality.

Researchers had previously used scanning tunneling microscopy to demonstrate good, stepwise control of single atoms to obtain physicochemical insights and technical advances. However, the scalability and throughput of the technique was severely limited by mechanical probe movements and therefore researchers introduced aberration-corrected scanning transmission electron microscopy (STEM) as a versatile tool to characterize the precise atomic structure of

materials. Although still at early stages of development, the technique shows greater promise to control materials at the level of atoms. In two-dimensional (2-D) graphene, for instance, silicon dopants could be controlled stepwise to iterate basic steps that allowed the long-range movement with high throughput. Similar outcomes were also observed in a 3-D silicon crystal.

With STEM-based atomic engineering the scientists aim to use the beam of electrons and achieve a desired configurational change. Drawbacks of the method include imprecise understanding of relativistic electron-nucleus collisions, electronic excitation and relaxation, dynamic ion trajectories and added uncertainties.

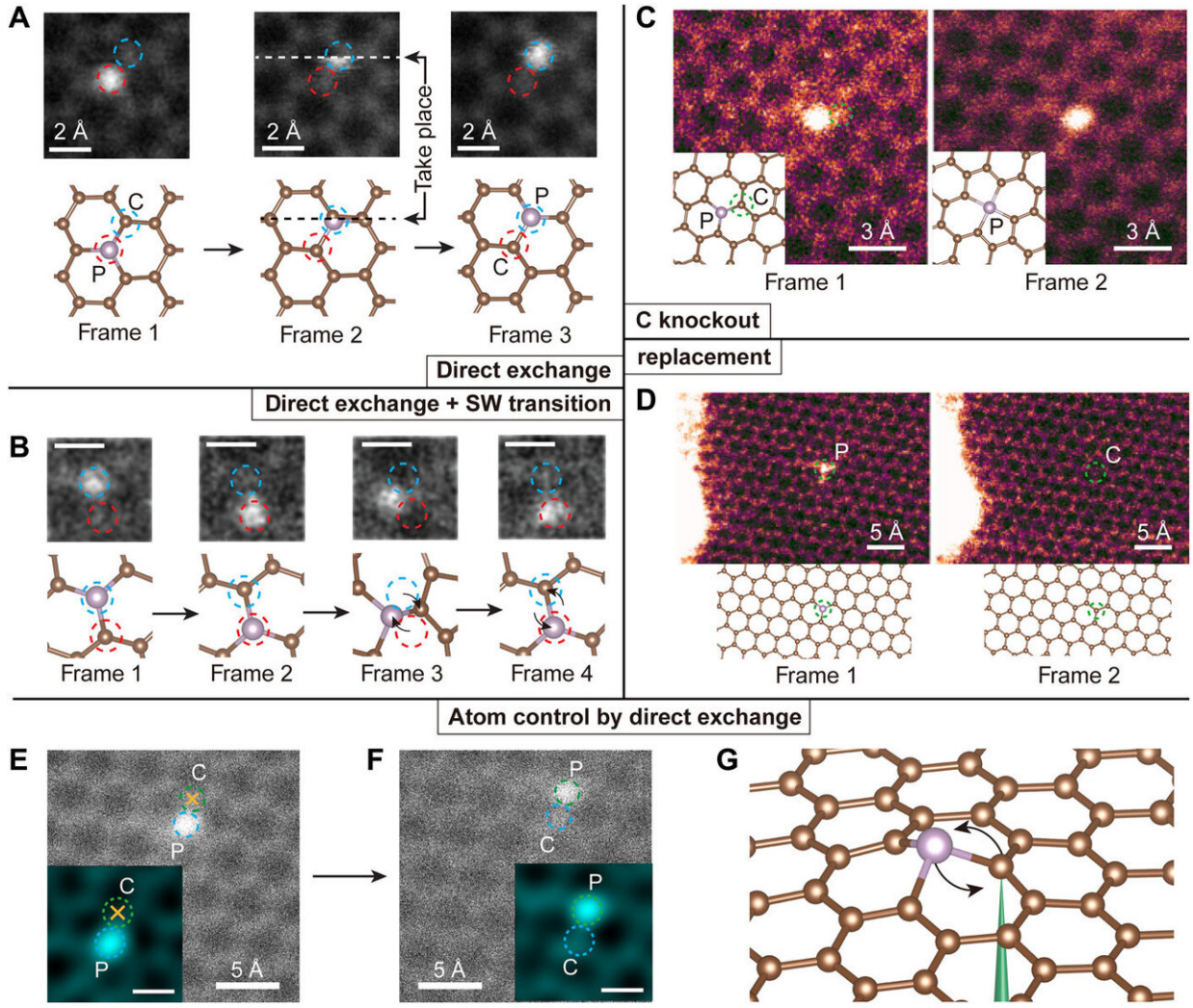
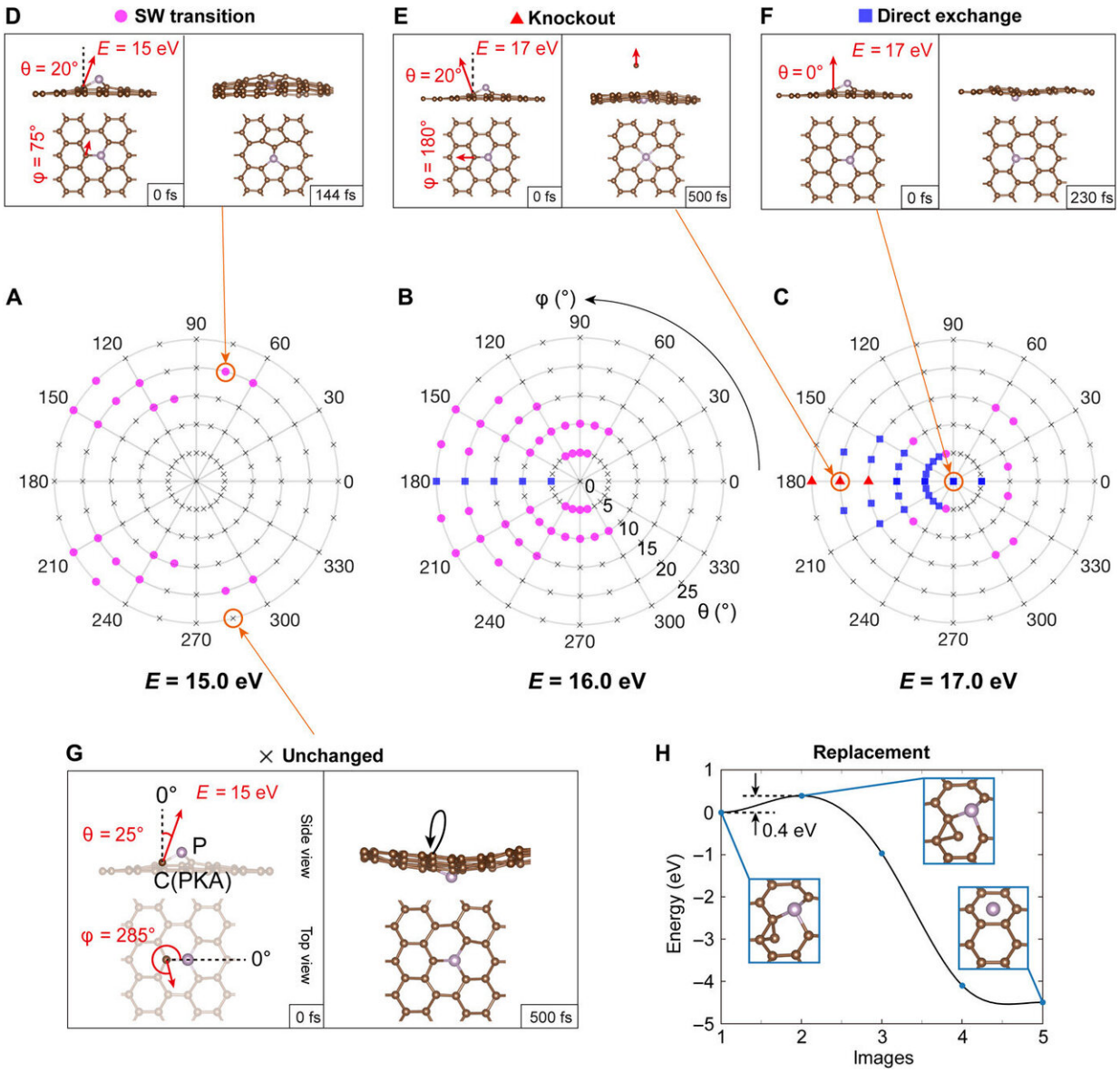


Illustration of competing experimental P dopant dynamics in graphene and its control. The frames are medium-angle annular dark-field images, and the chemical identity of each dopant was confirmed by electron energy-loss spectroscopy (EELS). (A) Three frames showing a direct exchange between the brighter (due to its greater scattering contrast) P atom and a C neighbor, with the initial (frame 1), transition (frame 2), and final configurations (frame 3). White and black dashed lines indicate the row of the scanning beam when the exchange happens. Scan speed, 8.4 s per frame. No post processing was done. (B) Four frames showing both direct exchange (frames 1 and 2) and SW transition (frames 2 to 4). Scale bars, 2 Å. Scan speed, 0.07 s per frame. A median filter with a 2 pixel × 2 pixel kernel was applied for clarity. The SW transition was captured during EELS acquisition in small subscan windows to enhance the signal-to-noise ratio of the spectra used to identify the dopants and to achieve

faster scanning rate frames that can better capture atomic dynamics. (C) Neighboring C atom knocked out by the electron beam, turning a threefold-coordinated P into fourfold-coordinated P. Scan speed, 8 s per frame. No postprocessing was done. (D) P dopant being replaced by a C atom. Scan speed, 4 s per frame. The different image color codings represent different categories: gray represents atom-conserving process and magenta represents atom-nonconserving process. Blue and red dashed circles in (A) and (B) represent the inequivalent lattice sites of graphene, and the green dashed circles in (C) and (D) indicate the location of the atom that has not been conserved. (E and F) intentional control on the direct exchange of P atom. The yellow crosses indicate the location where the electron beam was parked for 10 s to purposefully move the P atom by one lattice site. Green and blue dashed circles indicate the two nonequivalent lattices sites of graphene. Insets: The region of interest after applying a Gaussian filter, (G) a schematic plot of the control process, where the electron beam is represented by a green cone focused on the neighbor C atom. Credit: Science Advances, doi: 10.1126/sciadv.aav2252

In the present work, Su et al. used STEM to drive and identify the motion of atoms in individual phosphorous (P) dopants within graphene. Followed by constructing a theoretical scheme to test relative probabilities of the dopants, compared to electron energy and momentum detection. They categorized the dynamics into four groups:

A. Direct atomic exchange
B. Stone-Wales transition which conserved the atoms (causing important chemical, electrical and mechanical property alterations due to atomic rearrangement.)
C. Knockout of a carbon C neighbor, and
D. Replacement of the dopant atom by carbon C, which did not conserve the local composition of the material.

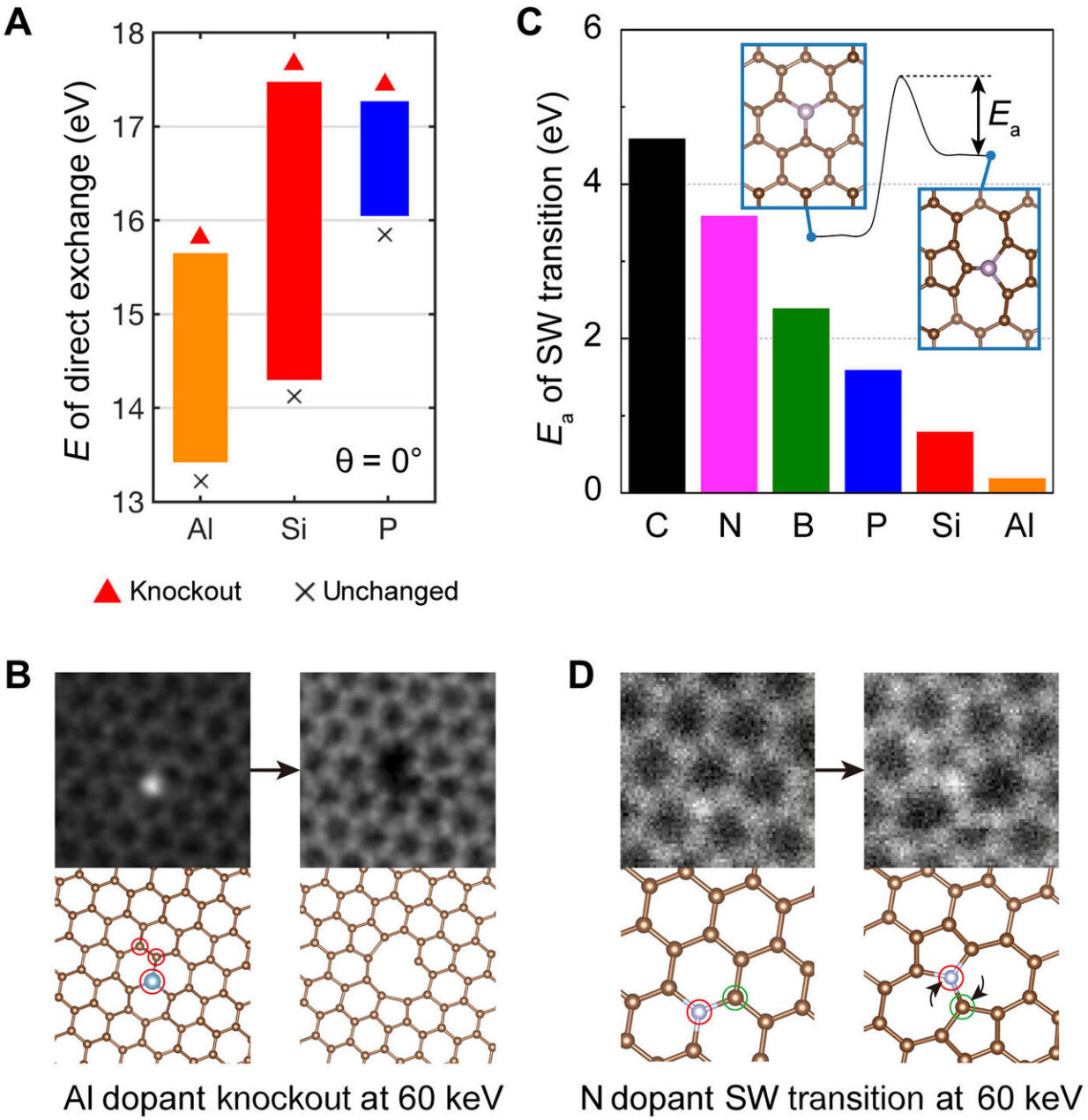


Mechanisms of P dopant dynamics in graphene calculated with abMD. (A to C) Angular distribution maps of different possible lattice transformations obtained when a C neighbor of the P impurity is given an initial out-of-plane momentum. The corresponding initial kinetic energies on the carbon, E, are (A) 15.0, (B) 16.0, and (C) 17.0 eV. The marks in these polar plots indicate the dynamical outcome: C knockout as red triangles, direct exchange as blue squares, SW transitions as magenta circles, and unchanged lattice as black crosses. As examples, snapshots of (D) SW transition (θ = 20°, φ = 75°, E = 15.0 eV), (E) C knockout (θ = 20°, φ = 180°, E = 17.0 eV), (F) direct exchange (θ = 0°, E = 17.0 eV), and (G) unchanged structure (θ = 25°, φ = 285°, E = 15.0 eV) are

shown. The red arrows indicate the direction of the C momentum along the in-plane and normal-to-plane directions (lengths not to scale), with the definition of the spherical coordinate angles θ and φ shown in (G). (H) cNEB barrier for a proposed mechanism of P dopant replacement by C. Insets: The initial, saddle-point, and final configurations. Credit: Science Advances, doi: 10.1126/sciadv.aav2252

The scientists used a 60 eV electron energy beam and maximized the rates of direct exchange and SW transition during electron-atom collision. Su et al. used carbon as the primary knock-on atom (PKA) in the experiments and maintained a post-electron collisional energy of the PKA on the order of 10 eV. In the experiments, they did not aim the electron beam directly at the dopant itself, instead aiming at the carbon neighbor of the dopant.

Su et al. then developed a theoretical scheme in the study known as a "primary knock-on-space" (PKS) to estimate the relative scattering cross sections of diverse electron induced dynamics. The results could be varied due to sample or electron beam tilt to selectively activate the desired outcome. The scientists provided additional experimental verification of the calculations, opening new avenues for atomic engineering with focused electron irradiation.



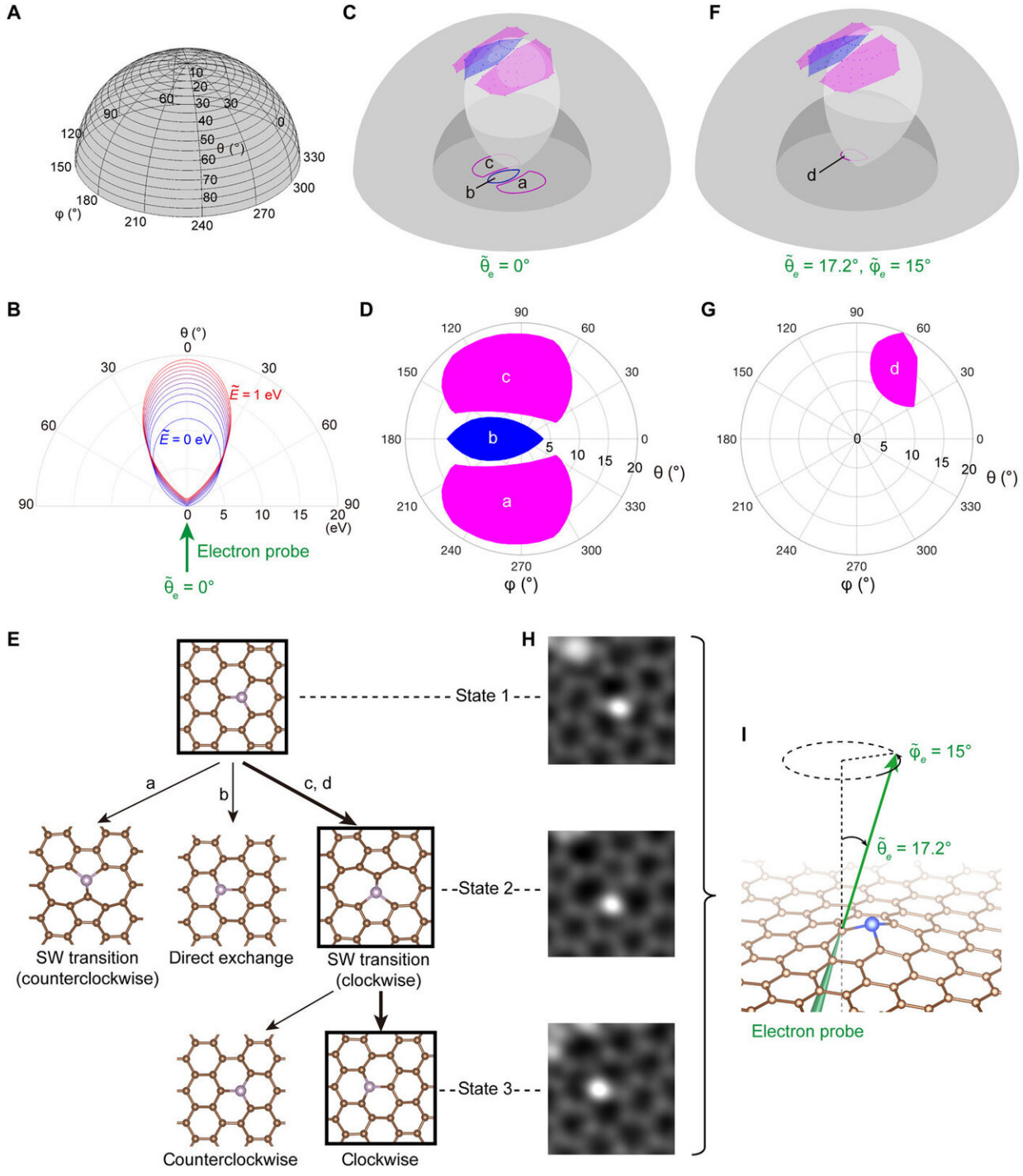
Comparison of dynamics of different impurity elements. (A) Comparison of the direct exchange energy ranges between Al, Si, and P for head-on collision (θ = 0°). (B) Experimentally, the knockout of an Al dopant and two carbon atoms nearby was observed after 7 min of continuous radiation at 60 keV, corresponding to the low displacement threshold predicted in (A). Red circles mark atoms displaced in the second frame. (C) The energy barriers (Ea) of configurational change from 55-77 structures back to the pristine lattice are illustrated for various elements (C, 4.6 eV; N, 3.6 eV; B, 2.4 eV; P, 1.6 eV; Si,

0.8 eV; Al, 0.2 eV). Inset: The definition of Ea in the energy profile of the SW transition, where the original curves can be found in fig. S4. (D) An experimentally observed SW transition of an N dopant at 60 keV. Credit: Science Advances, doi: 10.1126/sciadv.aav2252

In practice, scientists aim to precisely control atoms and their electronic or nuclear states for applications in atomic clocks and atomic memory devices. The long-term vision of atomic engineering is to precisely position individual atoms in desired internal states to include nuclear spin, then image and control the atomic assemblies from 1 to 1000 atoms.

Su et al. realized several atomic dynamics in the present work, which they categorized as atom conserving dynamics (desired) or atom non-conserving dynamics (not desired). For atom conserving dynamics, they included (A) the direct exchange between phosphorous (dopant) and carbon. (B) SW transition with 90 degree rotation of a P-C bond, where the atom-conserving dynamics included a carbon knockout. Then for atom non-conserving dynamics, the scientists included (C) knockout of PKA using an electron beam and (D) replacement of the dopant atom.

To explain the atomic processes, the scientists performed extensive ab-initio molecular dynamics (abMD) simulations and climbing-image nudged elastic band (cNEB) calculations. They visualized the distribution of a variety of P dopant dynamics in correspondence to the initial post-collision kinetic energies of the PKA in graphene. The scientists induced a series of collisions with focused electrons via simulation, expecting to arrive experimentally at a predesigned configuration by controlling the electron beams for atomic configurational evolution, with relative ease.



PKS: A scheme for evaluating cross sections of different dynamic processes. (A) The spherical coordinate system used for describing the PKS (with θ and φ defining the direction of momentum, and the radius defining the postcollisional kinetic energy, E, of the C neighbor). (B) A vertical cross section of the PKS

showing the distribution of function f (dubbed “ovoid” hereafter) for the upward 60-keV electron beam (θ˜e=0°) interacting with a moving PKA (E˜=0 to 1 eV). (C) The ovoid of a vibrational PKA (we use E˜=0.5 eV here for the amplified illustration) intersects with different outcome areas, where in (D), the intersections are projected to a polar plot. The magenta areas marked with a and c represent SW transitions (clockwise and counterclockwise, respectively), and the blue area marked with b represents direct exchange. (E) A decision tree showing possible outcomes of the atom-electron interaction, where the probability of going through each path is proportional to the cross sections. (F) The PKS and the ovoid of a tilted electron beam (θ˜e=17.2°,φ˜e=15°) acting on a vibrational PKA (E˜=0.5 eV), with (G) showing a different intersection projected to the polar plot. Here, only clockwise SW transitions are activated, marked with d in the magenta area. (H) An experimentally observed clockwise SW transition of a Si dopant activated in a tilted sample as in (F) and (G). Three corresponding stages are placed alongside the decision tree in (E), where the experimental states are marked by black squares, and the observed path is indicated by the thicker branches. Field of view: 1 nm × 1 nm. (I) A side perspective view of the electron beam tilted with respect to the graphene plane. The sample was kept tilted like this throughout all the frames in (H). Credit: Science Advances, doi: 10.1126/sciadv.aav2252

In the study, the scientists started with an initial configurational state $I_{iniital}$ that was precisely imaged in its desired trajectory of intermediate configurations to finally arrive at I_{final}; much like a Rubik's cube but with probabilities. Su et al. balanced the "risk" and "speed" when playing the game, as the atomic system could contain trap states (I_{trap}) to severely delay the arrival of atomic configuration to I_{final} or make its achievement improbable. The scientists also compared the probabilistic nature of the process to a game of soccer; where they used the computational prediction and the absolute transition rate to optimally engineer the total risk/speed-off in the experiment.

Since the process of predicting and comparing the scattering cross

sections of dynamic processes is essential for atomic engineering, Su et al. developed a PKS (primary knock-on-space) formalism. Based on this, the scientists showed the momentum distribution of PKA had an ovoid profile after an electron collision, where the shape changed relative to the energy and direction of an incoming electron and due to pre-collisional momentum of the atom. The scientists propose the use of machine learning and artificial intelligence, to understand the unit and assembly processes in the future. In the present work, the scientists used a decision tree to predict the possible paths of evolution during atomic engineering, where the root node indicated the initial structure and child nodes inferred the next possible outcomes.

In this way, Su et al. revealed the physics of atomic engineering and used a computational/analytical framework as a foundation to develop further techniques to control single-atom dynamics in 3-D materials. The scientists aim to ultimately scale up multiple atoms starting from the single atom to assemble 1-1000 atoms in a desired configuration at high speed and efficacy.

More information: Cong Su, et al. Engineering single-atom dynamics with electron irradiation, *Science Advances* (2019). DOI: 10.1126/sciadv.aav2252

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