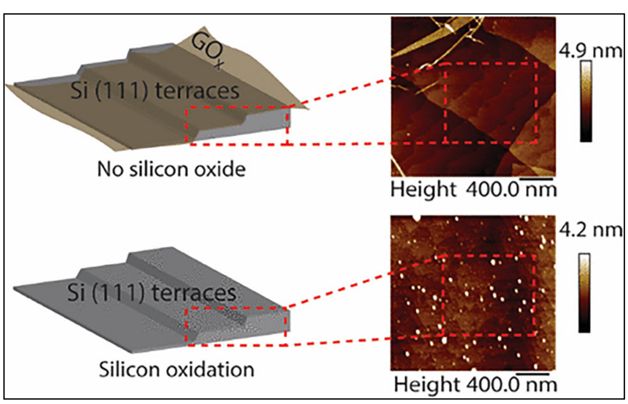
Graphene oxide shields nano-etched silicon from oxidation

Silicon forms the bedrock of modern electronics. Modern microchips contain millions of arrays of nanosized transistors that are carved out of this semiconducting material with atomic-scale precision. An unavoidable step of nanolithography processing, which yields these patterned devices, involves the use of chemicals such as ammonium fluoride to etch silicon. Unfortunately, the resulting exposed surface of silicon is highly reactive: oxygen from ambient air readily binds to the surface to form silicon oxide. This non-conductive film blocks electron transfer through the transistor and significantly impedes performance. Although protective polymers can be grown on these exposed surfaces, their molecular weight and deposition methods must be carefully controlled for the resulting coating to shield silicon from air-induced degradation.

Graphene oxide is a two-dimensional (2D) material cousin of the 2D all-carbon graphene that was discovered in 2004. Binding of carbon atoms in graphene oxide's surface layer to oxygen enables hydrophilicity and allows resulting flakes to remain stable in water. Researchers from Australia's Curtin University, in collaboration with scientists from Flinders University, determined that these layers of graphene oxide readily bond to the exposed silicon surfaces. Once graphene oxide is firmly in place, it shields the semiconductor from further oxidation for more than a month. The researchers published their methods and findings in a recent issue of *ACS Applied Materials and Interfaces* (https://doi.org/10.1021/acsami.1c06495).

Curtin University Professor Nadim Darwish, who is the principal researcher of the work, told *MRS Bulletin,* "While ours is a basic-research study, its potential applications are far reaching. For instance, silicon solar cells often require the application of a layer of alumina, silica, or other materials to increase their efficiency for transforming sunlight to electricity. The process is referred to as surface passivation, in which the protecting passivating layer improves solar-cell efficiency by reducing electron–hole recombination on the surface of silicon. Our study demonstrates that graphene oxide may perform this passivation, which opens exciting new opportunities for solar cells. It also has implications in the emerging field of molecular electronics, which envisions integration of silicon with molecules and two-dimensional materials."



Graphene oxide forms a stable and defect-free coating on nano-etched, high-resolution silicon terraces. Atomic force microscopy confirmed the material's stability, which remained oxidation- and degradation-free for over 30 days. In contrast, uncoated silicon formed numerous oxide pockmarks and defects during the same period. Credit: *ACS Applied Materials and Interfaces.*

The research team analyzed the starting silicon surface, into which the researchers had etched nanosized terraces. Following an initial wet chemical procedure, which had stripped oxygen from the surface with a solution of ammonium fluoride and ammonium sulfite, the silicon surface became covered in hydrogen atoms chemically bonded to silicon. Once this material was submerged in an aqueous dispersion of graphene oxide, this hydrophobic silicon hydride surface repelled water. However, graphene oxide readily adsorbed onto the surface and interacted with it. X-ray photoelectron analysis showed that the oxygen formed a single bond each with the silicon in the substrate and the carbon in the graphene. Extended duration chemical characterization revealed that the oxygen content of the surface, along with the overall bonding behavior, remained remarkably constant for over 30 days. This effective shielding stands in stark contrast to conventional, hydrogen-terminated silicon, which readily reacts with air to form a damaging silicon oxide coating only four hours after initial etching.

This material shield substantially affected the performance of silicon in actual device applications, such as metal–semiconductor junctions that are present in various transistor configurations. Conventional silicon, once covered with an oxide layer, conducts virtually no electrical current to platinum contacts. Conductivity tests by Darwish and colleagues showed no such loss in performance for silicon shielded with graphene oxide. Moreover, the presence of the 2D graphene oxide material allows current to flow in both directions, unlike the more unidirectional flow that a hydrogen-terminated silicon surface favors. Chemical annealing of this material, and removal of many oxygen atoms from graphene, enables even higher electronic conductivity capabilities of resulting metal-silicon junctions.

The researchers showed a scalable and highly effective method to coat finely patterned features with a versatile material that, through self-assembly, enables novel transistor architectures for emerging memory and molecular devices. This material platform still has room for application-specific tuning and optimization. To demonstrate some of these capabilities, Darwish's research team grafted diazonium, which is an organic salt molecule, onto the silicon-shielding graphene oxide layer. In turn, this molecule is electrochemically active and may link with additional materials. This versatile architecture is poised to enable new capabilities for molecular devices, such as sensors and memory systems.

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