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Researchers create single-atom lithography in graphene

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(PhysOrg.com) -- A little zinc can do a lot of damage to graphene. Rice University researchers have taken advantage of that to create single-atomic-layer lithography.

The Rice lab of chemist James Tour reported this week in the journal Science that sputtering zinc onto multilayered graphene enabled the team to remove a single layer at a time without disturbing the layers beneath.

The discovery could be useful as researchers explore graphene's electrical properties for new generations of microcircuitry and other graphene-based devices. Graphene, the one-atom-thick form of carbon, won its discoverers the most recent Nobel Prize in physics.

The researchers created a graphene checkerboard by removing horizontal and vertical layers to create a three-dimensional pattern.

They also printed a micro owl, Rice's mascot, about 15 millionths of a meter wide.

"The removal of a single sheet of graphene or graphene oxide was a surprise," said Tour, Rice's T.T. and W.F. Chao Chair in Chemistry as well as a professor of mechanical engineering and materials science and of computer science. "We thought multiple layers would be removed by this protocol, but to see single layers removed is one of those exciting events in science where nature gives us far more than we expected."

Tour said the ability to remove single layers of graphene in a controlled manner "affords the most precise level of device-patterning ever known, or ever to be known, where we have single-atom resolution in the vertical dimension. This will forever be the limit of vertical patterning -- we have hit the bottom of the scale."

Ayrat Dimiev, a postdoctoral scientist in Tour's lab, discovered the technique and figured out why graphene is so amenable to patterning. He sputtered zinc onto graphene oxide and other variants created through chemical conversion, chemical vapor deposition and micromechanically (the "Scotch-tape" method). Bathing the graphene in dilute hydrochloric acid removed graphene wherever the zinc touched it, leaving the layers underneath intact. The graphene was then rinsed with water and dried in a stream of nitrogen.

For the owl, Dimiev cut a stencil in PMMA with an electron beam and placed it on graphene oxide. He sputter-coated zinc through the stencil and then washed the zinc away with dilute hydrochloric acid, leaving the embedded owl behind.

Sputter-coating graphene with aluminum showed similar effects. But when Dimiev tried applying zinc via thermal evaporation, the graphene stayed intact.

Investigation of the sputtered surface before applying the acid wash revealed that the metals formed defects in the graphene, breaking bonds with the surrounding sheet like a cutter through chicken wire. Sputtering zinc, aluminum, gold and copper all produced similar effects, though zinc was best at delivering the desired patterning.

The researchers were able to create a 100-nanometer line in a sheet of graphene, which suggests the only horizontal limit to the resolution of the process is the resolution of the metal patterning method.

"The next step will be to control the horizontal patterning with similar precision to what we have attained in the vertical dimension," Tour said. "Then there's no more room at the bottom at any dimension, at least if we call single atoms our endpoint -- which it is, for practical purposes."

More information:
www.sciencemag.org/content/331/6021/1146.short

Provided by Rice University