Maskless Lithography of Nanometer-Scale Circuit Structures in Supported, Single-Layer Graphene Using Helium Ion Microscopy

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ABSTRACT

Here we will discuss the utility of scanning helium ion lithography for fabricating conducting graphene structures that are supported directly by silicon oxide. The lithography is performed in a single step, dry, using high-resolution He- and Ne-ion milling directly on the supported graphene. These structures can have feature sizes ranging from multiple micrometers to less than 20 nanometers, and the graphene structures retain the ability to conduct electrons efficiently. Further we demonstrate that ion beams, due to their positive charging nature, may be used in conjunction with the graphene work function and secondary electron yield to observe the conductivity of graphene-based nanoelectronic devices in situ.

Keywords: graphene, maskless, lithography, circuit, pattern

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1 INTRODUCTION

Graphene is a well-known candidate for advanced electronics and devices but significant challenges remain in the application of graphene. Traditional nanofabrication techniques such as optical and e-beam lithography (EBL) can be used on graphene with great success, but the multi-step processes they require can result in contamination of the graphene with resists and solvents. The electronic transport properties of graphene are subject to modification by surface contamination.

Focused ion beams (FIBs) of many types are well known for their use in patterning films or milling structures without the need for masks and resists. The high-energy ions produced in a FIB are capable of sputtering off atoms from the target material with high spatial fidelity. A wide range of FIBs are commercially available, with beams of very large multi-atom ionic clusters (Ar+) down to Helium (He+) with corresponding sputtering yield and resolution. In the past decade, helium-ion FIBs, or microscopes, have become commercially available and now represent the highest resolution ion milling instruments available. The sputtering yield of the He+ is less than that of other common ions such as Ga+, however the point resolution may be sub-nanometer. Further, while the He+ can implant in the target material, it cannot dope the electronic structure making He+ FIB one of the most promising ways to directly pattern thin films of electronic interest.

The Center for Nanophase Materials Sciences (CNMS) at the Department of Energy's Oak Ridge National Laboratory recently acquired a 3rd-generation Zeiss NanoFab helium-ion microscope (HIM). This tool is located in the CNMS cleanroom, a 10,000 ft^2 class-100 facility with full lithographic capability including electron beam, ion beam, and deposition instruments. This cleanroom complements the world-class synthesis, characterization and modeling capabilities that also reside at the CNMS. These facilities are available to the public at no cost through a competitive user program the details of which are available at CNMS.ornl.gov.

The CNMS HIM is capable of milling and patterning 2D materials such as graphene with outstanding lateral precision, while preserving electronic properties. This 3rd generation tool is capable of both He+ and Ne+ milling. He+ provides very high resolution (sub-nm) with a low sputter yield – approximately 1/30 of comparable Ga+ FIB. Ne+ has a larger point resolution of about 1.5 nm, but a much greater sputter yield of ¼ a comparable Ga+ FIB. The two ions beams Ne+ and He+ then present the capability to mill both large and small, delicate structures in the same film using the same tool, both without the doping problems associated with Ga+. General information regarding helium-ion microscopy is available elsewhere [1].

In this paper, we describe the milling of single-layer graphene on a supporting SiO_2 layer. We report the conditions under which graphene can be milled successfully, the minimum feature achievable and discuss the contributions to that minimum feature size.

2 METHOD

2.1 Graphene CVD graphene on SiO2

Single layer graphene was synthesized using a method by Vlassiouk et al.[2, 3] Briefly, electropolished 125 µm thick copper foils were loaded into atmospheric pressure CVD reactor and annealed at 1065 °C under the flow of 2.5% H2 in Ar for 30 mins. Graphene growth was performed by addition of methane with a gradual increase in concentration from 10 to 20, to 40 ppm for 30 mins in each step. After growth, Microchem PMMA 495A4 solution was spin-coated at 2000 rpm on top of graphene on copper foil. Graphene from the back side of copper was etched away by oxygen plasma and copper was dissolved by 1M FeCl3 in 3% HCl. Graphene/PMMA sandwich floating on water surface was washed by DI water and transferred onto the SiO2 substrate. PMMA was dissolved in acetone with subsequent annealing at 550 °C to remove the PMMA residue.

2.2 Scanning Helium ion microscopy and lithography

Scanning helium ion microscopy and lithography on single layer graphene was performed using a Zeiss ORION NanoFab He/Ne ion microscope, operating at an accelerating voltage of 25-30 kV and a beam current ranging from 1-4 pA. All the graphene devices were fabricated using the ion microscope's built-in patterning software and imported bitmaps. Each milled area was exposed to the He+/Ne+ beam at a field of view and pixel spacing that yielded a fluence of ~ 1×10^{19} ions/cm^2 for He+ beam and ~ 5×10^{17} ions/cm2 for the Ne+ beam. Subsequent high-resolution images were acquired at the same field of view using a 50 µs dwell time.

3 RESULTS

Highly arbitrary structures may be created in the single-layer graphene film without the need for resists, developers, or etchants. Figure 1 shows two similar squares, each with a single strip of unmilled graphene that connects the center of the square. The width of this strip is 14nm for 1a, and 10nm for 1b. Of particular importance is the observable feature size, which is comparable to the best optical lithographic strategies. Additionally, a structure like this can be fabricated in less than 5 minutes, in a single step. These structures were fabricated using He+, and the contrast within the images are indicative of the graphene's electronic transport properties. The change in contrast between panels 1a and 1b is a result of the narrower width of the connecting strip (10 nm for 1b) that results in a more poorly conducting strip. This important phenomenon is discussed below.

Figure 2 shows the opposite – a large structure milled using Ne+. This arbitrary structure illustrates what can reasonably be achieved in about 5 minutes using Ne+. The lack of a change in contrast along the length of the structure illustrates that the graphene is capable of conducting current at least equal to the beam current of 4 pA.

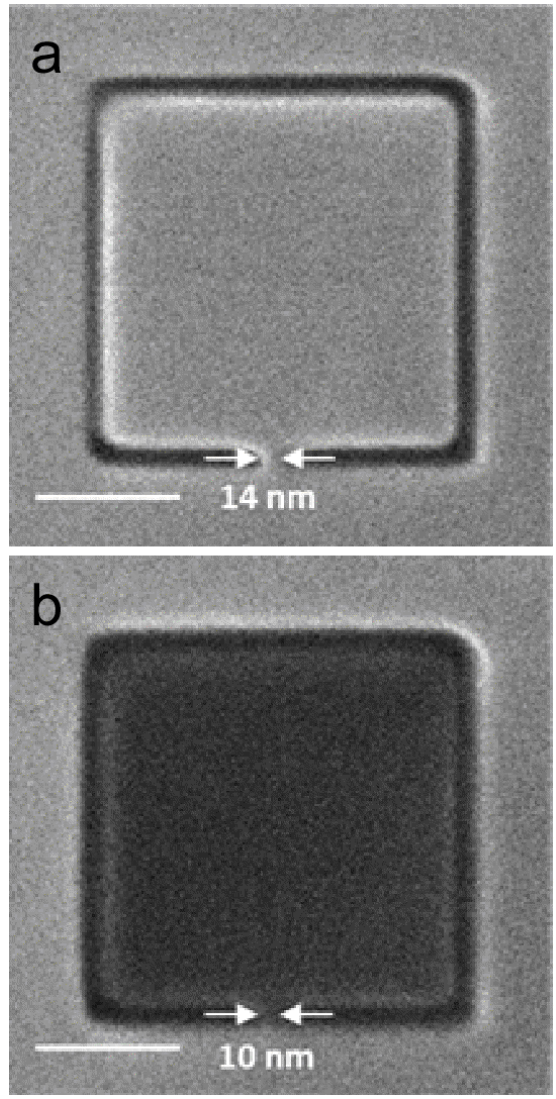

Figure 1: Box structures in single-layer graphene, milled by He+. Box 1B has a narrow strip of graphene which is approaching the lower width limit of graphene conductors as fabricated by this approach. Scale bar = 50nm.

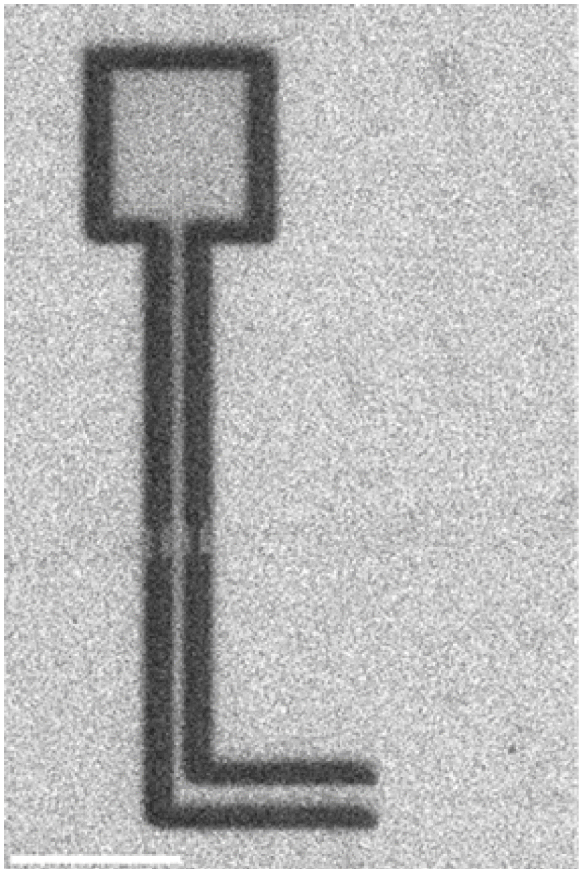

Figure 2: Large arbitrary graphene structure with multi-micrometer length. The lack of any contrast changes within this structure illustrates that Ne+ milling is appropriate for creating large conducting pathways that retain graphene's electronic transport properties. Scale bar = 1 micrometer.

4 DISCUSSION

Ion-beam imaging techniques generally utilize secondary electrons for imaging, similar to scanning electron microscopes. The emission probability of the secondary electron is dependent on the instantaneous electronic state of the sample as described by the work function. Because the ion beam is positive, and the interactions between the ion beam and sample produce secondary electrons, the sample tends to accumulate significant positive charge during milling and imaging experiments. This positive charge must be compensated or the work function becomes depressed, resulting in fewer secondary electrons emitted during imaging.

Charge compensation is achieved in a few different ways including direct electrical grounding of the sample. In the case of Figure 1, the entire graphene layer is grounded although it lies on an insulating SiO_2 layer. The thin strip left between the center of the box and the outer region acts as a ground. When that strip is too damaged or narrow to function as a conductor, positive charge accumulates inside the box and and the image turns dark. This provides a convenient method to observe conductance. In order to charge compensate effectively, the grounding strip must be able to conduct approximately the beam current plus the secondary electron current.

Figure 1b shows that at 10nm strip width, the strip no longer conducts the 4pA beam current. We interpret this to represent a measurement of the smallest achievable feature size for a graphene conductor using this particular technique. The contributions to this lower limit are not fully understood but we hypothesize that backscattered ions impose some damage to the edge of the milled graphene. This damage appears to extend to about 4-5 nanometers past the cut edge, however the defect structure is unknown and also under investigation. The beam point resolution under these conditions is less than 1 nm.

Figure 2 shows a large structure with a very high aspect ratio conducting strip. The conducting strip is no more than 100 nm in width but 5 micrometers in length. The lack of a change in contrast in the context of Figure 1, meaning full charge compensation, indicates that the conductor is intact over the entire length.

In conclusion, helium- and neon-ion milling techniques are effective means to create large arbitrary circuit structures in single-layer, supported graphene films.

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