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Electronic transport in helium-ion-beam etched encapsulated graphene nanoribbons

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ABSTRACT

We report the etching of and electronic transport in nanoribbons of graphene sandwiched between atomically flat hexagonal boron nitride (h-BN). The etching of ribbons of varying width was achieved with a focused beam of 30 keV He^+ ions. Using in-situ electrical measurements, we established a critical dose of 7000 ions nm^{-2} for creating a 10 nm wide insulating barrier between a nanoribbon and the rest of the encapsulated graphene. Subsequently, we measured the transport properties of the ion-beam etched graphene nanoribbons. Conductance measurements at 4 K show an energy gap, that increases with decreasing ribbon width. The narrowest ribbons show a weak dependence of the conductance on the Fermi energy. Furthermore, we observed power-law scaling in the measured current-voltage (*I-V*) curves, indicating that the conductance in the helium-ion-beam etched encapsulated graphene nanoribbons is governed by Coulomb blockade.

1. Introduction

Graphene-based research has seen significant developments in the past decade, thanks to its unique band structure and extremely high mobilities [1,2]. Despite the high mobilities, graphene is a semi-metal without a bandgap which precludes applications in post-silicon electronics. Nevertheless, one can modify the electronic band structure by trimming graphene into nanoribbons. Under this geometrical constriction, quantum confinement and edge effects lead to a finite source-drain gap or a transport gap [3,4]. In their review paper, Bischoff et al. [4] noted that a stern distinction has to be made between a *source-drain gap —i.e.,* the suppression of conductance in a limited source-drain voltage range— and a *transport gap — i.e.,* the suppression in a limited gate voltage range. Also, it is known that the gap is greatly influenced by the presence of disorder in the graphene nanoribbons (GNRs) themselves [4,5]. Numerous techniques have been developed to create nanoribbons in graphene, such as plasma etching [4,6–9], chemical synthesis [10–13], electron beam etching [14–16], and ion beam etching [17–21]. It is not straightforward, however, to make near-defect-free nanoribbons using the aforementioned techniques and, hence, it remains unclear how much the conductance and the presence of a gap are affected by edge effects, quantum confinement, and disorder [4].

Graphene devices are often fabricated on oxidized silicon substrates (SiO_2), which unfortunately lowers the mobility due to the presence of electron-hole puddles [22], charged impurity scattering [23], and contamination [18]. These adverse issues can be suppressed by encapsulating the graphene in hexagonal boron nitride (h-BN) [24]. As a consequence, the mobility in encapsulated graphene is typically an order of magnitude higher, comparable to that in suspended graphene [2,25,26]. In fact, Wang et al. [2] developed encapsulation with the specific purpose to safeguard graphene from effects caused by surface contaminations, such as PMMA residues introduced during device fabrication.

Because of its short de-Broglie wavelength, its sub-nanometer probe size, and the small beam spreading in materials [18,27,28], the focused ion beam (FIB) of a helium ion microscope (HIM) is an attractive tool for precise etching of encapsulated graphene devices. A recent experiment by Abbas et al. [21] with a He-FIB has

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shown indications of bandgap opening in arrays of 5 nm wide graphene ribbons. Also, Nakaharai et al. [29] have shown, by conductance tuning, bandgap opening in narrow graphene channels, etched with a He^+ beam. However, these measurements show very low conductance (~10,000 times higher resistivity than for pristine graphene), likely caused by the high number of beam defects and their pinning of surface contaminants. Since the paper by Kalhor et al. [30] it is known that exposure of graphene to helium ions leads to collateral damage in the non-exposed adjacent areas and to ion-beam-induced surface contamination [18]. A recent study by Nanda et al. [24] has shown that encapsulation of graphene in h-BN, with a $\leq$ 15 nm top h-BN layer, slows down the build-up of He^+ beam damage in the exposed graphene and precludes detrimental effects due to beam-induced surface contamination. Moreover, this material shows *n*-doping and self-healing. However, fabrication of encapsulated graphene devices via focused He^+ beam etching requires a good understanding of graphene's response to ion-beam bombardment and, thus, proper optimization of ion exposure doses. This understanding and process optimization are still wanting. For sure, a focused beam of 30 keV He^+ ions can easily pass through several tens of nanometers of BN with limited loss of energy and without noticeable beam broadening [24,31]. If encapsulation influences ion-beam etching of graphene, the influence is direct and not via a change of the beam properties.

In this article we present transport properties of He^+ beam etched encapsulated GNRs (graphene nanoribbons). The aim is to investigate the interaction between a focused helium ion beam and encapsulated graphene and the role of beam-induced damage in the conductance of graphene nanoribbons. The sub-nanometer He^+ beam allows us to precisely control the size of the etched areas and in-situ electrical probes in the helium ion microscope enable us to determine quickly the minimal dose needed to isolate different parts of the graphene. The low-temperature measurements show an energy gap opening in narrow GNRs. We conclude that the gap arises due to the beam-induced disorder, leading to Coulomb blockade; the transport is governed by hopping between randomly distributed charged islands and localized states in the GNRs. We fabricated boron nitride/graphene/boron nitride sandwiches by stacking h-BN and graphene flakes via the van-der-Waals pick-up technique [24,32]. Ribbons were cut with a focused helium ion beam and devices were made by e-beam lithography, plasma etching, and Cr/Au deposition. Details of the entire procedure are reported in the supplementary data.

2. Experimental

2.1. Helium beam exposures and in-situ measurements

The fabrication procedure of the encapsulated graphene samples was similar to that of Nanda et al. [24]. We verified optically that the thickness of the top h-BN layer of all samples was 15 nm or less. Ion irradiation has been performed using a Carl Zeiss Orion NanoFab helium/neon ion microscope and the NPVE pattern generator from FIBICS Inc. The NanoFab is equipped with four MM3A-EM Kleindiek micro-manipulators for in-situ electrical probing. We used a 30 keV He^+ beam at normal incidence and an ion current of 0.5 pA. The beam dwell time was 0.2 μs and the beam step size 0.2 nm. The smallest aperture of 5 μm was selected, giving the narrowest ion beam. The number of repeats was varied to achieve the desired dose (in steps of 1000 ions nm^{-2}). Before each exposure, we took a low-resolution and low-dose image ($\leq$ 0.5 ions nm^{-2}) to locate the sample.

In-situ conductivity measurements in the ion microscope have been performed using two micro-manipulators with tungsten probes having tip radii below 100 nm. To minimize damage to the BN/Gr/BN sandwich, the probes have been carefully brought into contact with the patterned gold leads. With a third probe placed onto the gold leads we checked that low resistance between the first two probes and the gold lead had been established. A source meter connected to the probes was used to measure the conductivity during ion irradiation.

2.2. Electrical and Raman spectroscopy measurements

Low-temperature direct current (DC) measurements were performed in a Leiden Cryogenics MCK-50 3He/4He dilution fridge. The DC currents and voltages were applied and probed with a home-built set-up. We carried out our low-temperature measurements at 4 K, although the set-up is able to reach a base temperature of 40 mK. Raman spectroscopy measurements were performed in air at room temperature with a Renishaw inVia Raman microscope. The spectrometer is equipped with a 514 nm laser with $\sim$ 350 nm spot size. Sample heating is avoided by keeping the laser power below 1 mW.

3. Results and discussion

3.1. Device milling and characterization

Fig. 1a shows an optical image of the HIM chamber with microprobes for the in-situ electrical measurements. The inset is a HIM micrograph of a number of devices with two probes in contact with one of them. The in-situ probes allow direct measurement of the relation between the ion dose and the electrical conductivity. Fig. 1b is a HIM micrograph of an array of encapsulated graphene devices, most of them 1 μm $\times$ 1 μm in size. The devices were exposed to line doses ranging from 1000 to 10,000 ions nm^{-2} with simultaneous monitoring of the resistance. All line cuts had a width of 10 nm. One example of a 1.2 μm long and 10 nm wide cut is depicted in Fig. 1b and c as a white dotted line. The pristine devices had resistances between 5 and 10 kΩ, corresponding to resistivities between 5 and 10 kΩ/□. Several independent measurement series were conducted on different samples and we observed good reproducibility in the resistance.

The resistance vs. ion dose is plotted in Fig. 1c. One sees that the resistance increased almost exponentially up to a critical dose of 7000 ions nm^{-2}, where the circuit became open. In this regard, the in-situ measurements provide a unique knob to monitor the endpoint detection and dose determination of the encapsulated graphene devices. Although this critical dose is specific for our experimental conditions, we expect that scaling via the nuclear energy loss, ion-target mass ratios, and binding energies can be used to estimate the critical dose for other ion species and energies and other encapsulated 2D materials. Subsequently, we used this critical dose to etch nanoribbons in encapsulated graphene of 200 nm in length and with widths of 90, 70, 50, 35, 25, and 10 nm. Fig. 2a–c shows helium ion micrographs of various GNRs. Fig. 2d shows a device (Dev1), also shown in Fig. 1b, where a dose of 7000 ions nm^{-2} is applied to make a 35 nm wide ribbon. The two side contacts (SC1 and SC2) are used to check that there is no residual conductivity between the isolated regions. The inset shows that indeed no measurable current flowed between SC1 and SC2; the resistance is $>$ 1 GΩ. Fig. 2e shows an AFM image of three 10 nm line exposures with 7000 ions nm^{-2}. The full-width-at-half-maximum (FWHM) of the etched line is 10 nm, see the AFM profile. Note that the widths of the etch line in the HIM image (Fig. 2b) and in the AFM profile are both equal to the designed line width of 10 nm.

We performed Raman mapping around the etched line to investigate the lateral damage in the exposed graphene. Ion-induced defects in single-layer graphene can be studied via the