Graphene antidot lattice transport measurements

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Abstract: We investigate graphene devices patterned with a narrow band of holes perpendicular to the current flow, a few-row graphene antidot lattice (FR-GAL). Theoretical reports suggest that a FR-GAL can have a bandgap with a relatively small reduction of the transmission compared to what is typical for antidot arrays devices. Graphene devices were fabricated using 100 keV electron beam lithography (EBL) for nanopatterning as well as for defining electrical contacts. Patterns with hole diameter and neck widths of order 30 nm were produced, which is the highest reported pattern density of antidot lattices in graphene reported defined by EBL. Electrical measurements showed that devices with one and five rows exhibited field effect mobility of ~100 cm²/Vs, while a larger number of rows, around 40, led to a significant reduction of field effect mobility (<5 cm²/Vs). The carrier mobility was measured as a function of temperature, with the low-temperature behaviour being well described by variable range hopping, indicating the transport to be dominated by disorder.

Keywords: graphene; antidot lattice; nanomesh; nanoarray; electron beam lithography; EBL; variable range hopping; nanopatterning.


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1 Introduction

Graphene has been suggested for analogue electronics, including high-speed transistor-based devices owing to the extreme room temperature mobility and the possibility of very high operating frequencies [1]. While the lack of a band gap prevents the current on/off ratios necessary for analogue electronics [1–3], several strategies have proven successful in inducing a gap-like behaviour, such as nanopatterning of graphene. While introduction of a bandgap is generally associated with a decrease in mobility [1] nanopatterning invariably introduces disorder, which further decreases the carrier mobility [4]. Transport gaps in graphene devices have previously been reported [5,6] for nanoribbons and graphene antidot lattices (also termed graphene nanomesh) structures, where a typical gap size is given by $E_g = 1 \text{eVnm}/W$ [3], where $W$ is the width of the constriction (for nanoribbons) or the neck width (for antidot lattices). To achieve lateral pattern dimensions in the 10 nm range required for a 100 meV transport gap, samples are often patterned using an etch-mask fabricated from a block co-polymer (BCP) [7–9] (antidot lattice) or by hydrogen silsesquioxane (HSQ) negative resist [10] (nanoribbons). In comparison with EBL, BCP is a parallel process which can be used to make sub-10nm feature sizes across large areas. Despite the superior resolution, BCP lithography offers little control of pattern geometry, position, and orientation compared to EBL, which by selection of positive (i.e., PMMA) [11] or negative (HSQ) [9] resist, can approach lateral dimensions of tens of nanometres for antidot lattices or nanoribbons, respectively.
While nanopatterning unavoidably introduces edge disorder and often also residue contamination, electron beam lithography (EBL) through a hexagonal boron nitride embedded protective layer, has been shown to improve the transport characteristics considerably [12], at the cost of higher complexity and lack of scalability. In contrast with isolated nanoribbons which have been fabricated with lateral dimensions of order 10 nm, the formation of dense arrays or antidot lattices to increase the source-drain current by EBL is very challenging due to proximity effects [13].

We report here a study of few-row graphene antidot lattices (FR-GAL), with below 30 nm neck widths, and compare these to large GAL arrays. FR-GAL structures have been predicted to exhibit similar band gap as large antidot lattices, however with significantly higher transmission [14]. While high mobility values were found as expected for the FR-GAL compared to GAL, all measured structures showed clear signatures of variable range hopping rather than activated behaviour, indicating that the transport is strongly dominated by disorder.

2 Methods

The fabrication of devices is outlined in Figure 1. Single-layer graphene is produced via mechanical exfoliation [15] on highly-doped silicon wafers with a 300 nm silicon dioxide layer grown on top (Figure 1(a)). Graphene is identified via optical microscopy and Raman spectroscopy. Electrical contacts were patterned (JEOL JBX-9500 EBL system) and 3 nm Cr/30 nm Au was deposited via electron-beam deposition (Wordentec QCL 800) (Figure 1(b)). The wafer was then spin-coated with 40 nm of PMMA (with a molecular weight of 995 k in solution of 2% in anisole) on top of which a 17 nm of aluminium was used as a charge-dissipation layer. EBL was again used to define an etch mask for the antidot lattice as well as the overall Hall bar geometry. After removal of the aluminium, the pattern was developed in IPA : water 7 : 3 for 30 s. The pattern (CAD layout shown in Figure 1 (d + e)) was transferred to the underlying graphene using a SPTS RIE system (10 W, oxygen/argon 40 sccm/5 sccm, 12 s). PMMA was then removed in warm acetone and devices were ready for electrical characterisation.
The devices were electrically characterised in a Linkam LTS600P probe station with possibility of controlling device temperature and chamber gas composition, with electrical measurements performed via LabView controlled Keithley 2400 Source Meter SMUs and Keithley 2000 Digital Multimeters. Tylan flow controllers enabled a 100 sccm flow of nitrogen into the chamber at all times. Before measuring, devices were annealed at 225°C for 30 min in a nitrogen atmosphere to remove surface water and other surface contaminants. The device design allows all sections to be measured simultaneously (Figure 2).

![Circuit diagram with simultaneous four-point measurements of each GAL section](see online version for colours)

### 3 Results and discussion

A completed device is shown in Figure 3(a), with the hole pattern clearly visible in the SEM image. For the five and 42 row devices we find average hole diameters of 27.2 ± 4.4 nm and 28.3 ± 5.4 nm, with neck widths of 27.8 nm and 26.7 nm, respectively. We note that the finite resolution of the SEM images is of the order of 5 nm. This is to our knowledge the highest density antidot or nanoribbon array defined in graphene via EBL. In the shown device, a crack is observed in the array section, see Figure 3(a), which appears to leave an unharmed section available for electrical characterisation.

The electron and hole field-effect carrier mobilities as well as the gate bias required to observe a charge-neutrality point (CNP) were determined as a function of temperature (–195°C to 150°C in steps of 25°C); this data is shown in Figure 3(b)–(d). For each temperature the conductance curve was fitted to a Gaussian function using least-squares method [16] to determine the position of the CNP and to extract the field effect mobility, 

\[ \mu = LW^{-1}C_{ox}^{-1}\left(\frac{dG}{dV}\right) \]

where \( \mu \) is the mobility, \( C_{ox} \) is the capacitance per area for the silicon dioxide, and \( L \) and \( W \) are the nominal length and width of the measurement region. For the region containing a crack, Figure 3(a), our carrier mobility is likely to be underestimated owing to the crack as the actual width of the channel is smaller than the apparent width \( W \). Apart from this, the behaviour of the 42-row device was consistent with measurements of large GAL structures on other samples.
Figure 3  (a) SEM image of device 1 including close-up of (blue) 1 row; (green) 5 row and (red) 42 row GAL. Transconductance gate sweeps shown for (b) 1 row; (c) 5 row and (d) 42 row GAL, with five sweeps for each temperature in the –195°C to 105°C range. (e) Typical Raman spectra from device 1 showing areas with no patterning as well as spectra for each nanopatterned section. (f) SEM image of device 3 after measurement. (g) and (h) Temperature dependent gate characteristics from –195°C to 130°C (device 2) and –195°C to 80°C (device 3) (see online version for colours)
It should be noted that there is a small amount of hysteresis in some of the one- and five-row conductance measurements, which turned out not to affect the Gaussian fit. All sections of the devices show a low-to-moderate level of doping, with residual carrier density of up to $2 \times 10^{12}$ cm$^{-2}$. Since the measurements were performed over a fairly large temperature range, thermal expansion could lead to development of stress in the graphene, which potentially triggers an electrical response [17,18], that was not observed in our measurements. We assume that the effect of nanopatterning by far overshadows stress-induced electrical characteristics in our experiments.

Raman spectra were recorded using a Thermo Fisher DXR spectrometer with 445 nm laser, 100× objective and 5 mW laser power. In Figure 3(e), we present representative spectra from each of the four types of device area: no patterning, one row, five rows and 42 rows (large array). We see that the 2D to G peak intensity ratio, $I(2D)/I(G)$, is greater than 1 for all sections, indicating single-layer graphene [19]. Unsurprisingly, $I(D)/I(G)$ is increasing from 0.17 to 0.93 for an increasing number of rows, reflecting the higher number of holes and thus lattice defects [19] in the roughly 1 µm spot size of the laser. We see no relative shift in the 2D or G peaks as for the nanopatterned compared to unpatterned regions, which indicates low levels of stress, as well as doping [20], the latter being consistent with the low doping levels found from field effect measurements.

While the hole mobilities for the one and five row sections (Figure 4(a) and (b)) are comparable, the electron mobility for the five row section is higher than for the 1 row section, which is unexpected. The large arrays consistently show lower conductance and mobility, see Figure 4. We attribute the differences between the one and five row devices to unavoidable doping and lithographic variations across the sample. While neither the electron or hole mobility values for the one row and five row samples show any clear temperature dependence, the electron and hole mobility for the large GAL are increasing with temperature.

In literature, typical room temperature mobility values for nanoribbon/GAL structures made by BCP are of order 100 cm$^2$/Vs with the neck width in the 10 nm range [21–23]. While the one and five row devices have mobilities of this magnitude, the carrier mobility of the large GAL structures is less than 10 cm$^2$/Vs, despite having neck widths of ~30 nm.

The temperature dependent conduction for one row, five row and large GAL structures shown in Figure 3 (b)–(d) could either be due to the presence of a bandgap, a disorder gap [24], or variable range hopping all of which give rise to an exponential conductance dependence of temperature,

$$G \propto e^{-T/T^\alpha},$$

where $\alpha = 1$ for transport and disorder gap, and $\alpha = 1/3$ for variable range hopping in two dimensions [25]. From Figure 4(c), it is clear that the temperature dependence of the conductance is described well with the VRH [26]. The $R^2$ values corresponding to linear regression in the log($G$)–$T^\alpha$ plots are shown for both VRH and transport gap models (Arrhenius) in Table 1. The one and five row structures show a slight tendency of increasing on-off ratio increasing from 1 : 1.25 to 1 : 1.4, and 1 : 1.5 to 1 : 1.9, respectively, but these on-off ratio values (including the array) are low compared to literature, consistent with the transport being dominated by VRH. It has been predicted that even moderate disorder in graphene antidot lattices can be detrimental for formation of a band gap [27].
In comparison, the gate characteristics for five-row and large array (Figure 3(h)) structures from other devices (2 and 3), show comparable temperature behaviour to device 1. Also in these devices, the \( R^2 \) values from linear fits (\( \alpha = 1/3 \)) are 0.90 and 0.97 for 5 row and large array sections, respectively, consistent with device 1 (Table 1).

Our results for highly dense electron beam lithographic patterning using PMMA shows that although the carrier mobility is comparable to results obtained for block copolymer lithographic patterning [28], the expected transport gap of 30 meV is either closed due to disorder, or masked by the dominating VRH transport. While the regularity and uniformity of the antidots appear to be comparable to those shown in literature, and the Raman spectra do not suggest extensive amorphisation, but rather moderate amount of lattice-defects (\( I(D)/I(G) < 1 \)).

It is possible that the etching process leaves a fraction of the edges with zigzag termination, which are predicted to introduce metallic states that could in turn decrease the observed on-off ratios and decrease the carrier mobilities [27]. The VRH temperature behaviour, however, suggests that edge disorder is playing a major role in limiting the transport characteristics. Edge disorder is an inevitable consequence of etching through a PMMA mask. While it is possible to replace PMMA with other electron beam sensitive resists with higher etch selectivity, and better edge definition, they will typically have poorer resolution. An exception is HSQ, which being a negative resist, is not suitable for patterning of antidots. In fact, the recent demonstration of semiclassical ballistic scattering in EBL defined antidot lattices etched through a protective hexagonal boron nitride layer, suggests that such an approach is more promising than conventional high resolution EBL for bandgap engineering. It remains to be seen if lithography through embedded graphene stacks can be achieved with resolution in the 10 nm range, and if the edge disorder is low enough to form an electronic bandgap as predicted by theory [29].
4 Conclusion

Exfoliated graphene was nanopatterned with very high density antidot lattices using EBL. The electron and hole field-effect carrier mobilities determined as a function of temperature are consistent with the prediction that a few rows of antidots significantly improves the carrier mobility. The temperature dependence of the patterned sections seems to be well described by variable range hopping, questioning the viability of conventional EBL for bandgap engineering, and underlines the importance of controlling or reducing edge disorder for quantum transport devices.

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