Fabrication of hybrid molecular devices using multi-layer graphene break junctions

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Abstract

We report on the fabrication of hybrid molecular devices employing multi-layer graphene (MLG) flakes which are patterned with a constriction using a helium ion microscope or an oxygen plasma etch. The patternning step allows for the localization of a few-nanometer gap, created by electroburning, that can host single molecules or molecular ensembles. By controlling the width of the sculpted constriction, we regulate the critical power at which the electroburning process begins. We estimate the flake temperature given the critical power and find that at low powers it is possible to electroburn MLG with superconducting contacts in close proximity. Finally, we demonstrate the fabrication of hybrid devices with superconducting contacts and anthracene-functionalized copper curcuminoid molecules. This method is extendable to spintronic devices with ferromagnetic contacts and a first step towards molecular integrated circuits.

Keywords: hybrid molecular device, multi-layer graphene, break junction, helium ion microscope, heat equation, Simmons tunneling model, copper curcuminoid molecule

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(Some figures may appear in colour only in the online journal)

In recent years, molecular electronics has greatly benefited from the fabrication of nanometer spaced gold electrodes in the form of electromigrated and mechanical break junctions [1–7]. While these advances have led to a wealth of new physics in molecular devices, there are improvements to be made and a continuing focus in the field is toward making robust and reliable contact to single molecules [8]. One recent direction is the use of graphene or multi-layer graphene (MLG) as an electrode and contacting molecules by covalent bonding or \( \pi - \pi \) stacking of aromatic rings [9–12]. This method resulted in observation of the gating of a single molecule device at room temperature [13]. While gold atoms are mobile at room temperature [14, 15], MLG can be used as a stable intermediary material to contact molecules. In addition, two-dimensional MLG bridges better the size discrepancy between single molecules and bulky 3D electrodes where screening of the gate can reduce coupling to the molecule. Using MLG as an intermediary material also allows the option of contacting superconducting or ferromagnetic metals without changing the anchoring chemistry of the molecules. This opens the door to the fabrication of hybrid devices to study superconductivity and spintronics in single molecules. Up to now, the added complexity in fabricating hybrid superconducting-molecular devices has kept their exploration to a minimum [16].

In this paper, we present further steps in the development of MLG electrodes with gold contacts and improve yield and stability through the localization of a few-nanometer gap, created by electroburning, that can host single molecules or molecular ensembles. By controlling the width of the sculpted constriction, we regulate the critical power at which the electroburning process begins. We estimate the flake temperature given the critical power and find that at low powers it is possible to electroburn MLG with superconducting contacts in close proximity. Finally, we demonstrate the fabrication of hybrid devices with superconducting contacts and anthracene-functionalized copper curcuminoid molecules. This method is extendable to spintronic devices with ferromagnetic contacts and a first step towards molecular integrated circuits.
gap created by a process of electroburning. In comparison with as-exfoliated devices (without a constriction), MLG break junctions (with a constriction) show a 15% increase in yield due to a reduction in abrupt breaks and reconnected junctions after electroburning [17]. The key to using MLG as opposed to graphene or even few-layer graphene is two-fold: the conductance of MLG is independent of back-gate voltage making electron-transport measurements solely a study of the molecular characteristics of the device and not of the MLG electrodes, and we have found, as detailed in [17], that the highest yield for nanogap formation is in devices having a resistance of 500–1 kΩ corresponding to devices with a MLG flake of 10 nm thickness with a variation of approximately 5 nm. Furthermore, we explore the possibility of fabricating hybrid superconducting-molecular devices. The constriction results in a significant reduction in the power required to start the burning process making it possible to fabricate MLG break junctions with superconducting contacts. We use the superconducting alloy, molybdenum-rhenium (MoRe 60/40) which has a higher melting temperature ($T_M = 1150 \, ^\circ\text{C}$) as compared with commonly used superconductors such as aluminum ($T_M = 660 \, ^\circ\text{C}$) [18]. Out of 26 fabricated MLG break junctions with MoRe contacts, 16 junctions resulted in tunnel gaps with an average low bias ($V_b = 10 \, \text{mV}$) resistance of $17 \pm 11 \, \text{G}\Omega$.

A brief summary of the fabrication and electroburning process for MLG electrodes is given here which is detailed in [13, 17]. MLG devices are fabricated starting with heavily-doped Si wafers with a 285 nm-thick SiO$_2$ film. The Si substrate is used as a gate electrode for three-terminal devices. MLG flakes are deposited by mechanical exfoliation onto the SiO$_2$ and flakes with a thickness of approximately 10 nm are chosen by their color contrast under an optical microscope. Typical flakes have a deep purple color under white light illumination and a red channel contrast of about 16% (see supplement information (stacks.iop.org/JPhysCM/26/474205/mmedia)). Gold contacts, or MoRe contacts in the case of hybrid devices, are created by patterning with e-beam lithography and thin-film metal deposition.

Electroburning is performed at room temperature and in air. A bias voltage up to 10 V, corresponding to an electric field of more than $10^8 \, \text{V} \cdot \text{m}^{-1}$ for typical devices, is ramped up across the flake. At large current densities, removal of carbon atoms in the MLG flake occurs due to the interaction with oxygen triggered by the high temperatures of Joule self heating [13, 17]. Feedback controlled software is used to control the voltage across the flake. When the conductance drops by 10% the voltage is swept down at a rate of 0.1 V $\mu$ s$^{-1}$ to arrest the burning process and prevent the formation of a large gap. This cycle continues until the low bias ($V_b = 10 \, \text{mV}$) resistance is greater than 10 GΩ, independent of sample geometry. This resistance ensures the electroburning of any last remaining nanometer-sized graphene islands which have been shown to act as large addition energy quantum dots [19]. By controlling the voltage in this way, a gap is burned across the entire flake with a width of a few nanometers at its closest point [20].

In figure 1 we show the electroburning results of as-exfoliated MLG flakes. Figure 1(a) shows an atomic force microscopy (AFM) image of a few-micron-wide MLG flake before electroburning. Without localization of a constriction, the electroburning process is believed to most frequently start along the edge of the flake at an unsaturated carbon atom site where a lower displacement energy (7 eV) is required to remove an atom from the lattice as compared to removing a saturated atom from the flake center (30 eV) [21, 22]. In figure 1(b) the resulting few-nm gap is shown near the top of the electrode (white arrow). Electroburning of as-exfoliated flakes often results in gaps with unpredictable locations. Here, the close proximity of the gap to the gold electrode could result in screening of an applied gate field. Ideal devices should have gaps located near the center of the flake where the gate coupling to the molecule is unaffected.

In figure 1(c), the critical power required to start the electroburning process for the flake shown in figure 1(a) is plotted along with several other flakes (red circles). Critical powers reach hundreds of mW for the widest flakes and decrease with the flake width. Assuming comparable flake width (W) and length (L), the critical power as a function of width can be estimated by $P_c = I_c^2R = (j_eW)^2R/LW \approx (j_e)^2R/W^2$, where we take $j_e = 5.8 \times 10^7 \, \text{A} \cdot \text{cm}^{-2}$ as the average critical current.
density in these devices [13] and $R_t = 100 \, \Omega \, \text{sq}^{-1}$ as the sheet resistance for MLG [23]. Using these values and an average flake thickness of $t = 10 \, \text{nm}$, we plot this critical power relation as a dashed line in figure 1(c) where the scatter in the data is mostly due to differences in flake geometry and thickness.

The electroburning is triggered by the high temperatures from Joule heating of the MLG flake. It is interesting to estimate the temperatures reached given the critical power of the electroburning process for as-exfoliated MLG devices. An estimate of the temperature distribution along the flake (in the direction of current) can be made using the 1D heat equation [24–26]:

$$\frac{A \delta}{\delta x} \left( k \frac{\delta T}{\delta x} \right) + p' \frac{\delta x}{g} - g(T - T_0) = 0,$$

where $A = Wl$ is the cross-sectional area of the flake, $k$ is the thermal conductivity of the MLG flake, $p' \frac{\delta x}{g}$ is the Joule heating rate in watts per unit length, and $g$ is the thermal conductance to the substrate per unit length and is calculated given the thermal resistance of the SiO$_2$ and Si substrate beneath the MLG flake ($g = 1/[L(R_{ox} + R_S)]$, where $L$ is the length of the flake (in the direction of current), $R_{ox} = t_{ox}/(k_{ox}WL)$, where $k_{ox} = 1.4 \, \text{WK}^{-1} \, \text{m}^{-1}$ and $R_S = 1/(2k_S(WL)^{1/2})$, where $k_S = 50 \, \text{WK}^{-1} \, \text{m}^{-1}$) [25]. Heat convection to air is neglected as the heat convection coefficient for air ($10–100 \, \text{Wm}^{-2} \, \text{K}^{-1}$) is four orders of magnitude smaller than the coefficient for heat conduction to the substrate (calculated below).

An analytic solution to the 1D heat equation is arrived at by assuming that $k$ is constant and that there is a uniform heat generation along the flake given by $p' \frac{\delta x}{g} = P/R/L$. The temperature in the flake at position $x$ is then given by:

$$T(x) = T_0 + \frac{P'}{g} \left( 1 - \frac{\cosh (x/L_H)}{\cosh (L/2L_H)} \right).$$

(2)

Here, $T_0 = 300 \, \text{K}$, is the temperature of the electrodes and $L_H = (kA/g)^{1/2}$ is the characteristic healing length along the flake and is a measure of lateral heat dissipation in the flake. Using equation (2), we estimate the critical temperature distribution for the widest as-exfoliated flake in figure 1(c) ($W = 4.5 \, \mu m$, $L = 2 \, \mu m$) with a critical power of nearly 190 mW. We take the $L = 2 \, \mu m$ on SiO$_2$ 

Figure 2. (a) Helium ion microscopy (HIM) image of a MLG device before milling between two Au electrodes. (b) HIM image of the same device after milling. The resulting constriction is 100 nm wide. (c) $I - V_x$ characteristics for the electroburning of the constriction in (b). (d) AFM image of the same device after electroburning. The inset shows the final gap across the constriction. The scale bar is 100 nm.

Figure 2(a) is a HIM image of a MLG flake before milling. This image is used to pattern rectangles that define the areas where the flake will be milled. After defining the milling area, the beam is focused on the edge of the flake and moved to the...
The fit using the Simmons model is plotted along with the tunnel current (black dashed line). (b) $I - V_g$ characteristics for the devices after electroburning at a bias voltage of 500 mV.

Figure 3. Electrical characterization after electroburning for two typical devices. (a) A characteristic tunneling curve is measured for the device after electroburning (red circles for device 1, blue circles for device 2). The Simmons model fit is plotted along with the tunnel current (black dashed line). (b) $I - V_g$ characteristics for the devices after electroburning at a bias voltage of 500 mV.

Figure 4. (a) AFM image of a device without pre patterning. The high temperature of the electroburning process deforms the lower electrode. The inset shows the location of the nanogap near the deformed electrode (scale bar 500 nm). (b) AFM image of an electroburned MLG break junction pre-patterned using an oxygen plasma etch. The inset shows the resulting constriction from etching (scale bar 100 nm). The width is ~80 nm. (c) $I - V_b$ characteristics of the device in (b) (red circles) as well as a fit of the Simmons model (black dashed line). (d) $I - V_g$ characteristics of the device in (b) at a bias voltage of 500 mV.

A $= 1000 \text{ nm}^2$ given the cross sectional area of the fabricated constriction ($W = 100 \text{ nm}, t = 10 \text{ nm}$). From the fit, we extract a tunnel gap distance of $d = 2.1 \text{ nm}$ and a barrier height of $\phi = 0.52 \text{ eV}$ for device 1 ($d = 2.1 \text{ nm}$ and $\phi = 0.65 \text{ eV}$ for device 2). The low barrier height, as compared with that of graphene (4.5 eV), is common for the Simmons model when applied to small junctions (e.g. Au nanogaps) but could also include a barrier lowering due to water or OH groups absorbed at the gap edge [34–36]. While the barrier height has been found to deviate from the expected value, scanning tunneling microscopy studies of Au nanogaps have shown a consistency between the extracted gap size from the Simmons fit and the actual electrode separation [37]. We expect that this is the case for MLG nanogaps as well but further SEM studies should be carried out to verify this. In figure 3(b) we plot the $I - V_g$ characteristics for the empty tunnel gap at a bias voltage of 500 mV. The current is independent of back-gate voltage.

The high temperatures from electroburning as-exfoliated flakes are detrimental to the fabrication of MLG break junctions with superconducting contacts. Moreover, to achieve proximity effects in MLG for hybrid devices, channel lengths of $<0.5 \mu m$ are needed [38]. The combination of high flake temperature and short channel length result in melting of the MoRe alloy for the wider ($>3 \mu m$) as-exfoliated devices. This can be seen in figure 4(a) which is an AFM image of an as-exfoliated flake device after electroburning. Deformation of the lower contact can be seen which is near the gap shown in the inset of figure 4(a). By pre-patterning the MLG flake, the electroburning process pattern. For ion beam milling an acceleration voltage of 25 kV is used with a beam current of 1 pA. Typical line doses are about 120 nC cm$^{-2}$. Two rectangular patterns, one on each side of the flake, become 10 nm-wide trenches after direct helium ion beam writing forming the final constriction in the center of the flake. In figure 2(b) we show the device after milling with the HIM. The resulting constriction is about 100 nm wide. The trench width and depth (=40 nm from AFM scan) ensure no residual connection between the milled multi-layer graphene edges. While the trench does extend into the oxide, we find no evidence for substrate damage or gate leakage after milling.

After pre-patternning with the HIM, electroburning is performed as before but the constriction results in a significant reduction of the critical power required to start the process. Figure 2(c) shows the $I - V_b$ characteristics of the electroburning process for the patterned device in figure 2(b). The critical power is ~1 mW which is more than an order of magnitude smaller than the narrowest as-exfoliated MLG device in figure 1(c). Critical powers for devices with wider pre-patterned constrictions are also shown in figure 1(c) (blue circles). Critical powers steadily increase to 11 mW for constriction widths up to 500 nm. In figure 2(d) we show an AFM image of the device after electroburning. The inset shows the gap formed across the constriction.

We perform electrical measurements at room temperature and in vacuum to characterize the tunnel gap of the MLG break junctions. In figure 3 we show the $I - V_b$ and $I - V_g$ characteristics for two typical devices after electroburning. A tunneling current is measured through the vacuum barrier and shown in figure 3(a) (red and blue circles for devices 1 and 2, respectively). From the tunneling current, we estimate the gap distance using the Simmons model for tunneling through a thin insulating film [13, 33].

$$I_{s Simmons}(V) = A \frac{e}{2\pi \hbar d^2} \left( (\phi - \mu_L) e^{-\frac{2\sqrt{\phi(\phi-\mu_L)}}{d}} - (\phi - \mu_R) e^{-\frac{2\sqrt{\phi(\phi-\mu_R)}}{d}} \right)$$

(3)

Here, $\phi$ is the potential barrier height, $A$ is the cross sectional tunneling area, $d$ is the gap distance, and $\mu_L = +eV/2$, $\mu_R = -eV/2$ are the chemical potentials in the left (right) lead. The fit using the Simmons model is plotted (black dashed line) along with the data in figure 3(a) where we have set $A = 1000 \text{ nm}^2$ given the cross sectional area of the fabricated constriction ($W = 100 \text{ nm}, t = 10 \text{ nm}$). From the fit, we extract a tunnel gap distance of $d = 2.1 \text{ nm}$ and a barrier height of $\phi = 0.52 \text{ eV}$ for device 1 ($d = 2.1 \text{ nm}$ and $\phi = 0.65 \text{ eV}$ for device 2). The low barrier height, as compared with that of graphene (4.5 eV), is common for the Simmons model when applied to small junctions (e.g. Au nanogaps) but could also include a barrier lowering due to water or OH groups absorbed at the gap edge [34–36]. While the barrier height has been found to deviate from the expected value, scanning tunneling microscopy studies of Au nanogaps have shown a consistency between the extracted gap size from the Simmons fit and the actual electrode separation [37]. We expect that this is the case for MLG nanogaps as well but further SEM studies should be carried out to verify this. In figure 3(b) we plot the $I - V_g$ characteristics for the empty tunnel gap at a bias voltage of 500 mV. The current is independent of back-gate voltage.

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be seen located at the defined constriction in the inset of figure 4(b). In figures 4(c) and (d) we show the $I - V_b$, $I - V_g$ characteristics for the MLG electrodes with MoRe contacts shown in figure 4(b). Again, the Simmons model is fit to the tunnel current setting $A = 800$ nm$^2$ given the cross sectional area of the constriction ($W = 80$ nm, $t = 10$ nm) and extract a gap distance of $d = 1.6$ nm, a barrier height of $\phi = 1.4$ eV. For the 16 devices that resulted in tunnel gaps after electoburning, the average tunnel gap from the Simmons fit is $2.1 \pm 0.3$ nm and the average barrier height is $0.89 \pm 0.3$ eV.

To demonstrate the fabrication of hybrid devices, we have performed deposition of anthracene-functionalized copper curcuminoid molecules ([\(\text{Phen})\text{CuCl}(9\text{Accm})\]) on the MoRe MLG break junctions [39]. Figure 5(a) shows a scheme of the molecule. Contact with the molecule is mediated through the interaction of two $\pi$-systems; the $\pi$-conjugated system of the anthracene groups on the molecule and that of the MLG break junction. For deposition, a powder of synthesized molecules is dissolved in dichloromethane ($\text{CH}_2\text{Cl}_2$) at a concentration of 0.1 mM. The electoburned junctions are kept in the solution for 30 mins which results in a sub-monolayer of molecules on the surface of the Si/SiO$_2$ substrate [13]. Of the remaining sixteen tunnel junctions after electoburning, one junction showed a significant change in the $I - V_b$ and $I - V_g$ characteristics after deposition. The inset of figure 5(b) shows the tunneling characteristics of the junction (low bias resistance of 14 G$\Omega$) and the inset of figure 5(c) shows that the current is virtually independent of gate voltage before deposition. After deposition, the $I - V_b$ characteristics become linear and the low bias resistance is 9 M$\Omega$. In addition, the current shows a strong dependence on gate voltage, changing by two orders of magnitude over 80 V on the back-gate. To ascertain the presence of a single molecule or a few molecules in the junction, further transport measurements can be performed at low temperature.

In conclusion, we have studied the yield and stability of MLG break junctions for use in hybrid molecular devices. Using HIM milling or an oxygen plasma etch to localize a constriction in the MLG flake, we control the position of a few nm gap created by electoburning. The critical power needed to start the electoburning process can be controlled by the width of the constriction. For lower powers ($\approx 1$ mW), we fabricate MLG break junctions with MoRe contacts. Using these hybrid devices, we aim to study superconducting effects in single molecule transport.

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References

[1] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 Conductance of a molecular junction Science 278 252–4

[2] Park H, Lim A K L, Alivisatos A P, Park J and McEuen P L 1999 Fabrication of metallic electrodes with nanometer separation by electromigration Appl. Phys. Lett. 75 301–3

[3] Kergueris C, Bourgoin J-P, Palacin S, Esteve D, Urbina C, Magoga M and Joachim C 1999 Electron transport through a metal–molecule–metal junction Phys. Rev. B 59 12505

[4] Park H, Park J, Lim A K L, Anderson E H, Alivisatos A P and McEuen P L 2000 Nanomechanical oscillations in a single-60 transistor Nature 407 57–60

[5] Smit R H M, Noat Y, Untiedt C, Lang N D, Van Hemert M C and Van Ruitenbeek J M 2002 Measurement of the conductance of a hydrogen molecule Nature 419 906–9

[6] Park J et al 2002 Coulomb blockade and the Kondo effect in single-atom transistors Nature 417 722–5

[7] Tao N J 2006 Electron transport in molecular junctions Nature Nanotechnol. 1 173–81

[8] Lötscher E 2013 Wiring molecules into circuits Nature Nanotechnol. 8 381–4

[9] Bailey S, Visontai D, Lambert C J, Bryce M R, Frampton H Lörtscher E 2013 Wiring molecules into circuits

[10] Garcia-Suárez V M, Ferradás R, Carrascal D and sewer and J 2013 Universality in the low-voltage transport response of molecular wires physisorbed onto graphene electrodes Phys. Rev. B 87 235425

[11] Wang G, Kim Y, Che M, Kim T-W and Lee T 2011 A new approach for molecular electronic junctions with a multilayer graphene electrode Adv. Mater. 23 755–60

[12] Cao Y, Dong S, Liu S, He L, Gan L, Xu X, Steigerwald V, Wang W and Li Z 2011 Potential barrier of graphene edges Nano Lett. 11 4607–11

[13] Prins F, Barreiro A, Ruitenbeek J W, Seldenthuis J S, Aliaga-Alcalde N, Vandersypen L M K and van der Zant H S J 2011 Room-temperature gating of molecular junctions using few-layer graphene nanogap electrodes Nano Lett. 11 12505–9

[14] Prins F, Hayashi T, De vos V, Sikkema J A, Gao B, Osorio E A, Muraki K and van der Zant H S J 2009 Room-temperature stability of pt nanogaps formed by self-breaking Appl. Phys. Lett. 94 123108

[15] Strachan D R, Smith D E, Fischbein M D, Johnston D E, Guiton B S, Drndić M, Bonnell D A and Johnson A T 2006 Clean electromigrated nanogaps imaged by transmission electron microscopy Nano Lett. 6 441–4

[16] Winkelmann C B, Roach N, Wernsdorfer W, Bouhaciat V and Balestro F 2009 Superconductivity in a single-60 transistor Nature Phys. 5 876–9

[17] Burzuri E, Prins F and van der Zant H S J 2012 Characterization of nanometer-spaced few-layer graphene electrodes Graphene 1 26

[18] Witcomb M J and Dew-Hughes D 1973 The σ-phase in molybdenum-ribbon; microstructure and superconducting hysteresis J. Less Common Met. 31 197–9

[19] Barreiro A, van der Zant H S J and Vandersypen L M K 2012 Quantum dots at room temperature carved out from few-layer graphene Nano lett. 12 6906–100

[20] Molina-Mendoza A J, Rodriguez J G, Island J, Burzuri E, Rubio-Bollinger G, van der Zant H S J and Agrait N 2014 Note: long-range scanning tunneling microscopy for the study of nanostructures on insulating substrates Rev. Sci. Instrum. 85 026105

[21] Barreiro A, Börnert F, Rümmeli M H, Büchner B and Vandersypen L M K 2012 Graphene at high bias: cracking, layer by layer sublimation and fusing Nano Lett. 12 1873–8

[22] Warner J H, Rümmeli M H, Ge L, Gemming T, Montanari B, Harrison N M, Büchner B and Briggs G A D 2009 Structural transformations in graphene studied with high spatial and temporal resolution Nature Nanotechnol. 4 500–4

[23] Park J-U, Nam S, Lee M-S and Lieber C M 2012 Synthesis of monolithic graphene–graphite integrated electronics Nature Mater. 11 120–5

[24] Pop E 2010 Energy dissipation and transport in nanoscale devices Nano Res. 3 147–69

[25] Bae M-H, Ong Z-Y, Estrada D and Pop E 2010 Imaging, simulation and electrostatic control of power dissipation in graphene devices Nano lett. 10 4787–93

[26] Yiğen S, Tayari V, Island J O, Porter J M and Champagne A R 2013 Electronic transport measurements in intrinsic graphene Phys. Rev. B 87 241411

[27] Ghosh S, Bao W, Nika D L, Subrina S, Pokatilov E P, Lao C N and Balandin A A 2010 Dimensional crossover of thermal transport in few-layer graphene Nature Mater. 9 555–8

[28] Alkemade P F A, Köster E M, van Veldhoven E and Maas D J 2012 Imaging and nanofabrication with the helium ion microscope of the van Leeuwenhoek laboratory in Delft Scanning 34 90–100

[29] Bell D C, Lemme M C, Stern L A, Williams J R and Marcus C M 2009 Precision cutting and patterning of graphene with helium ions Nanotechnology 20 455301

[30] Bohm S A, Moktadir Z, Bagnall D M, Mizuta H and Ruth H N 2011 Focused helium ion beam milling and deposition Microelectron. Eng. 88 2452–5

[31] Lemme M C, Bell D C, Williams J R, Stern L A, Baughew B H, Jarillo-Herrero P and Marcus C M 2009 Etching of graphene devices with a helium ion beam ACS Nano 3 2674–6

[32] Zhou Y and Loh K P 2010 Making patterns on graphene Adv. Mater. 22 3615–20

[33] Simmons J G 1963 Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film J. Appl. Phys. 34 1793

[34] Mangin A, Anthore A, Della Rocca M L, Boulat E and Lafarge P 2009 Reduced work functions in gold electromigrated nanogaps Phys. Rev. B 80 235432

[35] Curtis K S, Ford J B, Anderson D, Beere H E, Farrer I, Ritchie D A and Jones G A 2012 Reduced tunnel-barrier height in sub-10 nm Au nanoelectrodes 12th IEEE Conf. on Nanotechnology (Birmingham, Aug. 2012) (Piscataway, N J: IEEE) pp 1–9

[36] Wang W and Li Z 2011 Potential barrier of graphene edges J. Appl. Phys. 109 114308

[37] Steinmann P and Weaver J M R 2004 Fabrication of sub-5 nm gaps between metallic electrodes using conventional lithographic techniques J. Vac. Sci. Technol. B 22 3178–81

[38] Kanda A, Saito T, Goto H, Tomori H, Takana S, Ootuka Y and Tsukagoshi K 2010 Dependence of proximity-induced supercurrent on junction length in multilayer-graphene Josephson junctions Phys. C: Supercond. 470 1477–80

[39] Aliaga-Alcalde N, Marqués-Gallego P, Krajnikamp M, Herranz-Lancho C, den Dulk H, Gomer H, Rouboue O, Teat S J, Weyhermüller T and Reedijk J 2010 Copper curcuminoids containing anthracene groups: fluorescent molecules with cytotoxic activity Inorg. Chem. 49 9655–63