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From Electroburning to Sublimation: Substrate and Environmental Effects in the Electrical Breakdown Process of Monolayer Graphene†

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We report on the characterization of the Electrical Breakdown (EB) process for the formation of tunneling nanogaps in single-layer graphene. In particular, we investigated the role of oxygen in the breakdown process by varying the environmental conditions (vacuum and ambient conditions). We show that the density of oxygen molecules in the chamber is a crucial parameter that defines the physical breakdown process: at low density, the graphene lattice is sublimating, whereas at high density the process involved is oxidation, independent on the substrate material. To estimate the activation energies of the two processes, we use a scheme which consists of applying voltage pulses across the junction during the breaking. By systematically varying the voltage pulse length, and estimating the junction temperature from a 1D thermal model, we extract activation energies which are consistent with the sublimation of graphene in high vacuum and the electroburning process in air. Our study demonstrates that, in our system, a better control of the gap formation is achieved in the sublimation regime.

Control of the molecule-electrode interface remains one of the main challenges in the field of molecular electronics. As variations in the molecular-junction geometry have a huge impact on the charge transport properties1–3, establishing a way to reliably form nanometer-sized gaps is a crucial step towards the realization of reproducible molecular devices with well-defined contact geometries. Another key aspect is the electrode material, which critically determines the binding process4 and junction stability5,6. Graphene, by its unique properties, is a good candidate to address this problem as it offers a flat and gateable platform with new binding possibilities. Another key benefit is the high structural stability, even at room temperature7.

The use of graphene as electrode material has been demonstrated experimentally8–10, and relies on the formation of nanogaps using the electroburning process8,9,11. In a previous study, we have reported on the fabrication such nanogaps with sizes down to a few nanometers using an optimized Electrical Breakdown (EB) protocol. Eventough we achieved a junction formation yield of > 95%12, the details of the EB process itself are still not fully understood. Here, in order to identify the key parameters in the EB process, we study the influence of the environmental conditions, and in particular, the role of the oxygen content. We find that at ambient conditions the EB is caused by the conventional electroburning process, while in high vacuum, sublimation takes place. By using a simple heat-transport model, we extract estimates for the relevant activation energies, which are consistent with the proposed electroburning and sublimation processes. To exclude the substrate as a source of oxygen, we also performed a comparative study of the EB process on SiO2 and Si3N4 substrates. In contrast to previous reports13, we find that the presence of oxygen in the substrate does not play a role in the EB process.

Graphene structures are fabricated using chemical vapor deposited (CVD) graphene grown on Cu foil. The selected CVD growth process produces single layer graphene with a typical grain size of 10 μm14. The graphene is transferred using a wet etching method15 to two different substrates: doped silicon substrate coated with either 300 nm of thermal oxide (Si/SiO2), or 80 nm thermal oxide and 140 nm of Si3N4 (Si/SiO2/Si3N4). The graphene is first patterned into narrow bridges (400 nm wide and 800 nm long) using standard e-beam lithography and then contacted with Ti/Au (5/55 nm) deposited by e-beam evaporation.

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The schematic of our samples is shown in the inset of Fig. 1a. Nanogaps were formed using EB of the graphene bridges. The EB process was performed by high voltage pulses with increasing amplitude. The current response was measured for each pulse (Fig. 1b), from which the high bias resistance was calculated ($R_{\text{high}}$). At each EB step the pulse height, $V_{\text{high}}$, was increased by 5 mV, and the process was stopped after the first pulse, when $R_{\text{high}}$ exceeded 500 kΩ. This corresponds often to a jump in the resistance. The influence of the pulse length on the EB process was systematically studied using 5 µs to 5 s pulses. Between subsequent pulses an offset voltage of 100 mV was applied to determine the low bias resistance, $R_{\text{low}}$. The measurements were performed both at ambient conditions (in air) and in high vacuum (down to $p = 10^{-7}$ mbar).

Fig. 1a shows the evolution of $R_{\text{high}}$ and $R_{\text{low}}$ for a typical EB process in vacuum with a pulse length of 10 ms. Due to Joule heating, $R_{\text{high}}$ increases as the pulse height is increased, whereas $R_{\text{low}}$ remains almost constant until the breakdown occurs at $V_{\text{bd}}$. Changes of the low bias resistance can occur because of annealing effects. Different polymer residues from the transfer and lithography resist can lead to a change of the graphene resistance due to increased scattering or doping effects. The high current during EB induces cleaning of the devices and hence changes of the resistance.

Fig. 1c shows the I-V curves of a graphene bridge before and after EB. Before EB, the current-voltage characteristic of the graphene bridge is linear with a resistance of 12.5 kΩ. After EB, the device shows S-shaped I-V curves, characteristic for tunneling. Assuming a rectangular barrier, we can fit the curves to the Simmons model and obtain an estimate of the gap size of about 1.5 nm for this particular device. The details of the fitting process and the distribution of the fitted gap sizes can be found in the supporting information and in Ref. 12. The low bias resistance of the graphene nanogaps after EB provides a first indication about the size and the cleanliness of the gap. It has been suggested that an ideal device should have a resistance of a few GΩ. Very wide gaps will exhibit larger resistance values resulting often in unresolvable tunnel currents. Lower resistances, in the MΩ regime, can be explained by the presence of carbon islands or residues bridging the gap. To test the latter, we have systematically performed gate dependent measurements of the tunneling behavior at room temperature. A few devices were also characterized at low temperature (see supporting information). The majority of the devices, typically more than 70% of the devices, do not show any gate dependence at room temperature. Fig. 1d shows the distribution of the low bias resistances after EB for SiO$_2$ and Si$_3$N$_4$ substrates.
both in vacuum and in air at zero gate voltage.

In our measurements the EB always happens immediately: even if we apply ultrashort pulses (down to 5 µs width), we cannot detect any precursor of the breakdown before the last, breaking pulse. In agreement with our previous report\(^\text{12}\) on SiO\(_2\) substrates, here we observed that for both substrates a measurable tunnel current corresponding to a few nm gap size is achieved with a yield of 95% if the EB is performed in vacuum (see the gap size distribution in the supporting information). In air, however there is a much higher chance to achieve unmeasurably large gap size, and thus a large and uncontrolled gap size. We note, that in Refs.\(^{8,11,19,23}\) gradual breakdown, and smaller gap sizes are achieved in air using real time feedback controlled EB protocol with >200µs response time, and different sample geometries (e.g. multilayer exfoliated graphene\(^\text{8,23}\) and and single-layer CVD graphene with a bow-tie geometry\(^\text{11,19}\)). It is not yet clarified, whether this different behavior can be attributed to fabrication differences or distinct driving protocols.

The EB of graphene is commonly attributed to an electroburing process\(^\text{8,9}\): due to the current induced high local temperature the graphene atoms oxidize at the hottest point of the junction and form a nanogap. Under high vacuum, however, a much smaller number of oxygen molecules are available and other processes may take place, similarly as in the study of carbon nanotubes\(^\text{21}\), where electroburing is replaced by oxide failure/sublimation as the pressure is decreased. To study this effect, we performed EB measurements both in air and in high vacuum. In addition to the pressure, we also varied the length of the voltage pulses.

For all pulse lengths, an average power was calculated from measurements on 2 to 5 devices on Si\(_3\)N\(_4\) and SiO\(_2\) substrates (Fig. 2a, small symbols) under ambient conditions and in vacuum (\(p = 10^{-7}\) mbar). The figures clearly show that for both substrates a higher power is needed for the breakdown in vacuum than in air. We also notice that on average, a higher power is required to break a junction on a SiO\(_2\) substrate than on Si\(_3\)N\(_4\).

A larger number of devices were measured in vacuum with 10ms pulse length for both substrates. The corresponding distribution of breakdown power is shown in Fig. 2b. An average value and a standard deviation are extracted from the data using a Gaussian fit. The values of the fit parameters are plotted in the left panel (bigger symbols with error bar representing the standard deviation). We can notice that the values extracted from measurements of a higher number of devices are in a good agreement with the trend observed during the change of the pulse length.

To study the effect of oxygen from the atmosphere on the EB process, we first estimate the number of oxygen molecules arriving on a single atomic site during the breakdown process. According to the kinetic theory of gases the flux of oxygen molecules from 2\(\pi\) solid angle to the graphene sample is \(J_{\text{ox}} = n_{\text{ox}} \bar{v} / 4\), where \(n_{\text{ox}}\) and \(\bar{v}\) are the density and the average speed of the oxygen molecules. These quantities are defined as \(n_{\text{ox}} = \alpha_{\text{ox}} p / (k_B T)\), where \(\alpha_{\text{ox}} = 0.21\) is the fraction of oxygen molecules in air, \(p\) is the pressure, \(T = 300 K\) is the temperature and \(k_B\) is the Boltzmann constant. The average speed of the oxygen molecules is expressed as \(\bar{v} = \sqrt{8 k_B T / \pi m}\), where \(m = 5.31 \times 10^{-26}\) kg is the mass of an oxygen molecule.

From these the number of oxygen molecules arriving to a half unit cell of graphene (single atomic site) during a single pulse is \(N \approx 1.5 \times 10^7 \cdot T \cdot p / p_{\text{ambient}}\), where \(T\) is the pulse length in seconds, and \(p_{\text{ambient}}\) is the atmospheric pressure. Since the carrier cooling time for graphene is in the order of picoseconds\(^\text{22}\), we consider the heating/cooling time constant much shorter than our pulse length, i.e. we assume that all graphene bridge is hot only during the pulse. Based on all these, with the pressure (10\(^{-7}\) mbar to 1 bar) and with the pulse length (5 µs to 5 s) we can experimentally tune the number of oxygen molecules hitting an atomic site during a single pulse by 16 orders of magnitude.

To interpret the data in terms of electroburing, it is useful to give a common axis to Figs. 2a showing the number of oxygen molecules hitting an atomic site during a single pulse. This rescaled top axis is shown in Fig. 3, such that the vertical axis is scaled to temperature (see later), and the raw power data with
of $\kappa_g = 1000\,\text{WK}^{-1}\text{m}^{-1}$, which is consistent with the data from J. O. Island et al.\textsuperscript{23} For the SiO$_2$ substrate the thermal conductance to the substrate is calculated as:

$$g_{\text{ox}} = \frac{1}{\kappa_{\text{ox}}} + \frac{\rho_{\text{ox}}}{W},$$  \hspace{1cm} (2)

where $t_{\text{ox}}$ corresponds to the 300nm oxide thickness, $\kappa_{\text{ox}}$ is the thermal conductivity of the oxide and $\rho_{\text{ox}}$ is the thermal boundary resistivity between the graphene constriction and the oxide substrate. In the case of Si$_3$N$_4$, we use the following expression:

$$g_{\text{nii}} = \frac{1}{\kappa_{\text{nii}}} + \frac{\rho_{\text{nii}}}{W},$$  \hspace{1cm} (3)

where $t_{\text{nii}}$ corresponds to the 80nm nitride thickness, $\kappa_{\text{nii}}$ to the 140nm nitride thickness, $\rho_{\text{nii}}$ to the thermal conductivity of the nitride and $\rho_{\text{nii}}$ to the thermal boundary resistivity between the graphene constriction and the nitride substrate.

The parameters used for our model are given in the caption of Fig. 3. All the parameters were taken from literature\textsuperscript{23,24}, except the thermal boundary resistivity between Si$_3$N$_4$ and graphene, for which we are not aware of any prior measuremant. Relying on the assumption that the breakdown should happen at the same temperature using SiO$_2$ or Si$_3$N$_4$, we use $\rho_{\text{nii}}$ as a fitting parameter to obtain the least squared deviation between the breakdown temperatures on both substrates at the various pulse lengths and pressures. This fitting yields a value of $\rho_{\text{nii}} = 4.8 \times 10^{-7}\,\text{m}^2/\text{W}$ for the thermal boundary resistivity. Note, that this value is more than an order of magnitude larger than the thermal boundary resistivity for SiO$_2$, which indicates weak van der Waals interactions between graphene and the Si$_3$N$_4$ substrate.

As both the electro-burning and the sublimation are activated processes, the number of reactions per unit area and unit time can be written as:

$$\frac{N}{A \cdot t} = C \cdot e^{-\frac{E_a}{k_B T}},$$  \hspace{1cm} (4)
where $E_a$ is the activation energy, and $C$ is a pre-exponential parameter. We assume that in all the breakdown processes a similar number of carbon atoms are involved in the reaction, and so $N/A$ is assumed to be the same for any pulse length. With this

$$\log_{10}(\tau) = \log_{10}\left(\frac{N}{C\cdot A}\right) + \frac{E_a}{k_B} \cdot \frac{1}{T}$$  \hspace{1cm} (5)$$

follows, where the first term on the right side is constant, thus the slope between $\log_{10}(\tau)$ and $1/T$ yields the activation energy. Fig. 3 presents the Arrhenius plot of the inverse of the calculated temperature at $x = 0$ (left axis) as a function the logarithm of the pulse length for both substrates, together with the common linear fits. On the right axis the corresponding temperature is shown. For the EB in vacuum all the data points are close to the fitting line, whereas at ambient conditions a larger scattering of the data is observed, nevertheless it is clear that the two regions yield significantly different activation energies. From the slopes of the fits the activation energy in vacuum is $10.4 \pm 2.4$ eV, whereas in air it is $1.38 \pm 0.28$ eV, where the uncertainties are related to the statistical error of the linear fit, but do not include the error of the calculated temperature due to the uncertainties in the parameters of the thermal model. As an example, changing the heat conductance $k_2$ to $2000 \, W \, K^{-1} \, m^{-1}$ would result in activation energies of $7.5 \pm 1.7$ eV in high vacuum and $1.15 \pm 0.22$ eV in air. A more detailed analysis on the sensitivity to the parameters of the thermal model are given in the supporting information. As a comparison, prior studies have reported $\sim 7$ eV activation energy for the sublimation of carbon atoms in the graphene lattice in presence of defects$^{25-27}$, and $1-2$ eV activation energy for the burning process$^{28}$. Based on all these we can state that the interpretation of the EB process as graphene sublimation in high vacuum and as electroburning in air is consistent based on the estimated activation energies. In our previous study$^{12}$, we have shown that a better yield of junctions formation is achieved with our technique to make nanogaps in graphene. We think that this might be related to the exothermic nature of the burning process, i.e. once the burning starts, further heat is released, which boosts the burning of further atoms in the vicinity, and so the process is less controlled, and a wider gap is established. This self-sustained nature of the EB process is absent in the case of sublimation.

In summary, we have studied the EB process, used for creating graphene nanogaps, under different conditions. We have shown, that the process of breakdown is different for low and high oxygen concentration. At high oxygen concentration a conventional electroburning process takes place. As pressure is lowered, the system enters a regime where no oxygen molecules can reach the junction during a single voltage pulse. In this regime, the EB process can still take place but at a significantly higher power than in ambient conditions. Based on the systematic study of the breakdown power at various pulse lengths, and the conversion of power to contact temperature based on a thermal model we have estimated the activation energies of the involved processes. According to this analysis the EB process is shown to be consistent with electroburning at ambient conditions and sublimation in high vacuum. By performing a comparative study using SiO$_2$ and Si$_3$N$_4$ substrates we have also shown, that the oxygen originating from SiO$_2$ does not play a substantial role in the breakdown process.

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