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Stability of suspended monolayer graphene membranes in alkaline environment

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ABSTRACT

We report on the structural, chemical and electrical compatibility of graphene in an alkaline environment, namely diluted KOH solutions as those used in standard nanofabrication methods. Electron microscopy and Raman spectroscopy indicate that graphene preserves its structural properties during the process. The electrical transport properties such as conductance and shape of the Dirac point, appear degraded after KOH treatment, but can be fully recovered by current annealing. Electron beam-induced etching can provide further nanofabrication subsequent to KOH processing. These results demonstrate that, with the due precautions, graphene-based structures can be integrated in standard fabrication processes involving KOH.

IMPACT STATEMENT

To be implemented in novel (nano) devices, graphene must be compatible with standard fabrication techniques. We show how graphene’s intrinsic properties can be restored after exposure to an alkaline environment.

Since the isolation of monolayer graphene \cite{Novoselov2004} there has been a great research interest in uncovering the physical properties of this two-dimensional system. In particular its remarkable electronic properties \cite{Geim2007,Novoselov2007,Hart2010} make it a candidate for the next generation electronic nanotechnology. Suspended graphene has peculiar properties compared to supported graphene, such as a higher electrical \cite{Ferrari2006} and thermal conductivity \cite{Creppe2008,Restaurant2010,Singleton2010}, mechanical elasticity \cite{Ferrari2009,Chen2012} and sensitivity to gases \cite{Peressi2011}. Therefore it has found specific applications, e.g. in resonators \cite{Kavokin2011,Kavokin2012,Valdes2011}, gas sensors \cite{Garcia2013}, M/NEMS \cite{Cote2014,Schaub2016}, pressure drums \cite{Durin2012} or ballistic nanodevices \cite{Kouwenhoven2001,Li2001} to name a few.

A relevant aspect for the application of both supported and suspended graphene as a component in modern electronic devices or M/NEMS is the possibility to integrate it with both well-established technologies, namely Si-technology, and more recently developed ones such as flexible electronics \cite{Geim2009,Choi2010}. As such it is important to assess the chemical and physical compatibility of graphene to the fabrication steps involved in these technologies. Concerning chemical processes, for instance, graphene has shown very high stability after immersion in both pure and buffered HF (BOE),\textsuperscript{1} while, as a pure layer of carbon, it is damaged by immersion in sulfuric acid, or so-called piranha etchants.

Potassium hydroxide (KOH) is commonly used as an agent to etch silicon \cite{Masir2009,Garnier2010,Schaff2010}, and was recently applied as an etchant for flexible substrates such as PDMS \cite{Gibert2015,Chen2016,Guo2016}. It is thus of interest to study the interaction of KOH with graphene in order to assess the compatibility of KOH-based processes with graphene-based devices. Previous studies on KOH interaction with graphene were limited to its role as an electrolyte \cite{Izquierdo2008,Schön2009,Stocker2010} as well as an agent for chemical modification of graphene \cite{Nagase2009} for supercapacitive applications, or as a processing step to remove graphene from SiO\textsubscript{2} \cite{Xia2009,Gao2010}. However a.

\textsuperscript{1}The chemical composition of the etching solutions of the BOE used here is different to that used by the authors in Ref. \cite{Masir2009}.
comprehensive study on the interaction of KOH processing on the structural and electrical properties of micron-sized single layer flakes is missing. In this paper we present an investigation of the modification of the structural and electrical properties of suspended graphene microribbons after immersion in a KOH solution and successive rinsing in water.

Commercially purchased chemical vapor deposition (CVD) graphene deposited on a 300 nm Si/SiO$_2$ substrate was patterned into microribbons (2.5 $\mu$m $\times$ 20 $\mu$m) using optical lithography, followed by O$_2$ plasma ashing. The microribbons were contacted using standard electron beam lithography and metal deposition (Ti/Au 5/120 nm) followed by lift-off in acetone [36]. A second electron beam lithography step was used to create a rectangular opening in PMMA around the patterned graphene. This opening serves as a mask for under-etching the SiO$_2$ and thus create an electrically contacted, suspended strip of graphene [37,38].

The under-etching was achieved by immersing the sample in buffered HF, followed by rinsing in water at room temperature (RT). The samples were then immersed in a 5–20% water-diluted KOH solution at RT to 60°C, for 1–3 minutes. In order to remove the PMMA mask, the samples were transferred in semiconductor grade acetone for 5–10 minutes, and isopropyl alcohol (IPA) for 5 minutes at the same temperature of the KOH solution. After a final rinsing for 5 to 10 minutes in deionized water at the same temperature as previous solvents, the samples were finally transferred to hot IPA (60°C). This solution is allowed to evaporate, and the low-surface tension of warm isopropanol ensures that capillary forces do not crack the suspended graphene devices during evaporation.

SEM pictures of graphene microribbons, suspended over Si (Figure 1(a)) and SiO$_2$ (Figure 1(b)) substrates after immersion in KOH, showing its structural stability. In (a), the arrow indicate a probable pyramidal shape of KOH-etched silicon visible through the graphene layer, the folded edges are due to the suspension process, and not related to the KOH treatment. (c) top and (d) cross-sectional schematic view of a generic suspended graphene device. W, L, d are the width, length and thickness of the suspended graphene between the two contacts, and h is the thickness of removed SiO$_2$ after etching in BOE.

Figure 1. Graphene microribbons suspended on Si (a) and SiO$_2$ (b) substrates after immersion in KOH, showing its structural stability. In (a), the arrow indicate a probable pyramidal shape of KOH-etched silicon visible through the graphene layer, the folded edges are due to the suspension process, and not related to the KOH treatment. (c) top and (d) cross-sectional schematic view of a generic suspended graphene device. W, L, d are the width, length and thickness of the suspended graphene between the two contacts, and h is the thickness of removed SiO$_2$ after etching in BOE.

Figure 2. Raman spectra of a suspended graphene nanoribbon device, before (black) and after (red) immersion in KOH. Numbers correspond to the positions of the centers of the peaks.

To investigate further the structural modification of samples during KOH treatment, Raman spectroscopy was performed on the sample using a commercial set-up at the intermediate stage of the process, i.e. immediately after suspension, before immersion in KOH, and at the final stage, after exposure to KOH. The Raman spectra of suspended microribbons with and without KOH treatment are shown in Figure 2. The spectra were taken at the same nominal conditions and on the same position of a suspended graphene microribbon using a laser at a wavelength of 532 nm as a source and a spectrometer with 2400 l/mm. The characteristic Raman peaks [39] D, G and 2D (also called $G'$) of graphene are clearly visible in both the spectra. For a better evaluation of the figure, the intensity of the spectra has been normalized so that the intensity of the G peak is equal to $I(G) = 1000$ in both spectra.
Table 1. Evaluation of positions, FWHM, and intensities of the $D$, $G$ and $2D$ peaks before and after immersion in KOH.

<table>
<thead>
<tr>
<th></th>
<th>Pos($D$) [cm$^{-1}$]</th>
<th>FWHM($D$) [cm$^{-1}$]</th>
<th>$I(D)$ [a.u.]</th>
<th>Pos($G$) [cm$^{-1}$]</th>
<th>FWHM($G$) [cm$^{-1}$]</th>
<th>$I(G)$ [a.u.]</th>
<th>Pos($2D$) [cm$^{-1}$]</th>
<th>FWHM($2D$) [cm$^{-1}$]</th>
<th>$I(2D)$ [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before KOH</td>
<td>1347.2</td>
<td>23.4</td>
<td>182</td>
<td>1584</td>
<td>20.8</td>
<td>1000</td>
<td>2689.2</td>
<td>40.3</td>
<td>1828</td>
</tr>
<tr>
<td>After KOH</td>
<td>1348.1</td>
<td>33.2</td>
<td>163</td>
<td>1585.2</td>
<td>15.7</td>
<td>1000</td>
<td>2690.3</td>
<td>34.6</td>
<td>1781</td>
</tr>
</tbody>
</table>

Table 1 shows the numerical values of the principal peaks of the spectra shown in Figure 2. The position, full width half maximum (FWHM) and intensity of the peaks were calculated by fitting the experimental data with single Lorentzian curves. The ratio between the intensity of the $2D$ and $G$ peak $I(2D)/I(G)$ is about $1.81 \pm 0.02$, indicating that graphene conserves its structural properties [39] after immersion in KOH. Both the position of the $G$ and $2D$ peaks show a modest blueshift of 1.1 cm$^{-1}$ after KOH treatment, which suggests a slight residual $p$-doping [40] as also confirmed by the reduction of the FWHM of the $G$ peak after immersion.

The ratio between the intensities $G$ and $D$ peak is around $I(G)/I(D) = 5.5$ before and $I(G)/I(D) = 6.1$ after KOH, while the FWHM of the $D$ peak increases by 42% after KOH treatment. By applying a recent version of the Tuinstra and Koenig model [41], we can estimate the crystallite graphene size as $L_{\text{nm}} = (2.4 \times 10^{-10}) \lambda_{\text{laser}}^4 (I_G/I_D)$ to be 107 and 118 nm, respectively. We explain the increase in crystallite size by the fact that the $D$ peak is highly edge sensitive [42], and residual KOH might fill vacancies or gaps in the defective structure of suspended graphene, but further studies would be necessary for a better understanding of the phenomenon.

In order to establish the effect of immersion of KOH on the electrical properties of suspended graphene, we bonded a suspended sample after full treatment in KOH solution to a chip carrier and inserted it in an SEM with external electrical connections. This system has the advantage that SEM pictures can be taken in situ at any time before, during or after measurement while keeping the sample at the measurement conditions. The electrical measurements took place at RT and at a pressure of $P = 5 \times 10^{-7}$ mBar. A constant potential difference (source drain voltage) of $V_{SD} = 100$ mV was applied between the two contacts holding the suspended graphene device, while a backgate voltage applied to the conductive Si substrate was swept in the range $-15V \leq V_{BG} \leq +15V$. The black curve in Figure 3(a) shows the resistance as a function of the backgate voltage of the KOH-treated sample. The sheet resistance is high, and the Dirac neutrality point is not visible in the explored backgate voltage range. This is due to the presence of residuals and impurities on the surface of graphene, which act as scatterers and degrade the conductance [43,44]. In order to improve the electrical properties of graphene, we performed current annealing [45], that is the application of a controlled large current to recover its electrical properties. In our case, we applied an increasing source drain voltage in steps of $\Delta V_{SD} = 100$ mV monitored the evolution of the device resistance; after each step we waited for the resistance to stabilize and then increased the applied voltage; the annealing process was completed, when successive steps did not show a significant change in resistance. For this device, we increased the voltage up to $V_{SD} = 3.2$ V, after which we noticed that the resistance did not increase any further, a hint that current annealing was complete. This voltage corresponds to a current of $I = 590$ µA and a power $P = 1.9$ mW.

The electrical measurements of the resistance of the same sample after current annealing are shown as the red curve in Figure 3(a). Now a well-centered Dirac point with a sheet resistance of the same order of magnitude
as in pristine graphene [3] is observable. This is due to
the fact that current annealing removes effectively
the KOH residues and other impurities from the surface
of suspended graphene, as shown by the SEM images
of the measured flake before (Figure 3(b)) and after (Figure
3(c)) current annealing. In Figure 3(c) it can be observed
that current annealing was pushed a bit too much and the
graphene layer started to crack at the edges [46].

Characteristic electronic parameters of the cleaned
graphene device, such as contact resistance $R_{\text{cont}}$, mobility $\mu$, and residual carrier concentration $n_0$ can be extrapolated by fitting [47] the gate-dependent resistance data
with the formula:

$$R_{\text{tot}} = R_{\text{cont}} + R_{\text{chan}} = R_{\text{cont}} + (N_{\text{sq}}/e\mu n_{\text{tot}}),$$

where $R_{\text{chan}}$ is the resistance of the graphene channel
region, $N_{\text{sq}}$ the length-to-width ratio (number
of squares) of the graphene device, $e$ the charge of
electron, and $n_{\text{tot}}$ the carrier density in the graphene
channel region. The latter can be expressed as $n_{\text{tot}} = \sqrt{n_0^2 + n_{BG}^2}$ that is the combination of $n_0$, which is the
residual carrier densities generated by defects and charge
impurities, which are present in non-ideal graphene,
and the voltage dependent carrier density given by
$n_{BG} = (C_{\text{eq}}/e)(V_{BG} - V_{\text{Dirac}})$. The equivalent capaci-
tance $C_{\text{eq}}$ is calculated as the series of the two capacitors$C_{\text{eq}} = (h/e_0 + (d_{\text{SiO}_2} - h)/e_0\epsilon_{\text{SiO}_2})^{-1}$, representing the
etched layer (thickness $h$) and the remaining SiO$_2$ layer
(thickness $d_{\text{SiO}_2}$) between graphene and the Si backgate.
Applying the fitting to the electrical measurements
of the cleaned graphene device, for which $h = 115$ nm, and
$N_{\text{sq}} = 0.73$, we extrapolate $\mu = 3800$ cm$^2$/Vs, $R_{\text{cont}} = 4600\Omega$, and $n_0 = 4.1 \times 10^{11}$ cm$^{-2}$.

These values are comparable with those of reference
samples, which were fabricated from the same CVD
graphene and with the same fabrication and annealing
conditions, but without the immersion in KOH. Thus,
the low value of mobility and the high value of impu-

rity carriers compared to the best suspended graphene

samples [5], should be attributed to the overall quality
of processed CVD graphene, and not to the immersion in
KOH.

Finally, we show that suspended graphene, after being
treated after KOH processing, can still be directly pat-
tened using resist free nanofabrication techniques such
as water assisted electron beam-induced etching (EBIE)
[37]. EBIE is a technique based on the selective etching
of graphene by selectively irradiating parts of the sam-
ple with a focused electron beam in the presence of a
water vapor environment. The combined effect of the
electron beam and vapor adsorbate on graphene induces
a chemical reaction which etches the irradiated parts of
suspended graphene with a resolution of 7 nm [37]. To
pattern the samples using this technique, we used an
acceleration voltage $V = 30$ kV, a current $I = 0.69$ nA
and a dose $D = 10\mu C/\mu m^2$. This dose is higher than the
one needed for pristine suspended graphene, (4 $\mu C/\mu m^2$),
because KOH residue forms a protective layer on the sur-
face of graphene. Figure 4 shows the successful patterning
of nanoscopic structures such as nanoribbons (a), asym-
metric constrictions (b), and quantum dots (c). Inter-
estingly, after immersion in KOH, graphene acquires a
remarkable stiffness, and after the cut, graphene remains
suspended, even when attached to only one contact (see
Figure 4(a)).

In summary, we have shown that suspended graphene
is structurally stable after immersion in a KOH solu-
tion and subsequent rinsing in water. The Raman spec-
tra before and after immersion show that the struc-
tural properties of graphene are preserved, apart from
a limited residual doping. Residual contamination of
KOH degrades the electrical properties of graphene with
respect to pristine conditions, causing a high-sheet resis-
tance, and disappearance of the Dirac point, however,
intrinsic conditions can be fully recovered by current
annealing. Furthermore, suspended graphene covered
with a residual layer of KOH can be efficiently patterned
by EBIE with nanometric precision, providing an addi-
tional possibility to subsequent nanofabrication.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{Patterned suspended graphene after KOH process using water assisted EBIE: suspended nanoribbons (a), asymmetric constrictions (b), and quantum dots (c).}
\end{figure}
Notes
1. BOE 7:1 (34.8% NH₄F, 6.5% HF, 58.7% H₂O).
2. Graphene Supermarket.
3. Details of the specific fabrication process for the devices shown in each figure can be found in the supplementary information.

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Disclosure statement
No potential conflict of interest was reported by the authors.

References
[34] Nair RR, Blake P, Blake JR, et al. Graphene as a transparent conductive support for studying biological molecules


