RICE UNIVERSITY

Meniscus-Mask Lithography

by

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ABSTRACT

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This dissertation describes meniscus-mask lithography (MML): a planar top-down method for the fabrication of precisely positioned narrow graphene nanoribbons (GNRs) and metallic and semiconducting nanowires. The method does not require demanding high resolution lithography tools. The mechanism behind the method involves masking by atmospheric water adsorbed at the edge of the lithography pattern written on top of the target material.

Chapter 1 describes the fabrication of sub-10 nm GNR from graphene sheets using MML technique. The electronic properties of resulting GNRs depend on the graphene etching method with argon reactive ion etching yielding remarkably consistent results. The influence of the most common substrates (Si/SiO$_2$ and BN) on the electronic properties of GNRs is demonstrated. The MML technique is also shown to be applicable for fabrication of narrow metallic wires, underscoring the generality of MML for narrow features on diverse materials.

In chapter 2 the MML method is shown to be effective for fabrication of narrow wires in a variety of materials. Si, SiO$_2$, Au, Cr, W, Ti, TiO$_2$, Al nanowires are fabricated and characterized. A wide range of materials and etching processes are used and the generality of approach suggests possible applicability of MML to a majority of materials used in modern planar technology. High reproducibility of MML method is shown and
some fabrication issues specific to MML are addressed. Crossbar structures produced by MML demonstrate that junctions of nanowires could be fabricated as well, providing all the building blocks required for fabrication of nanowire structures of any complex planar geometry.

Chapter 3 is focused on nanoscale menisci behavior and provides additional insights into the mechanism of MML. The width of structures formed by the MML process in concave corners is found to be much more sensitive to changes in the process than the width of MML nanowires. The possibility of change in lateral dimensions of menisci and therefore the nanowire width through webbing formation and through the changes in surface roughness is demonstrated. The water-based meniscus theory is additionally supported.

In chapter 4, the chemical modifications of MML-fabricated GNRs are targeted at improving of the GNR electronic properties. Oxygen-containing groups on GNRs edges, mostly carbonyls and hydroxyls, are supposedly generating charge traps and therefore they considerably reduce charge carrier mobilities in GNRs. Those groups are demonstrated to be efficiently removed from the edges of GNRs with lithium aluminum hydride (LAH) treatment combined with tosylation, treatment with Na/K alloy and annealing in H₂ atmosphere at 900°C, which is supported by XPS spectroscopy of GNRs. Some alternative methods are shown to be inefficient.

Overall, the work accomplished in this dissertation is a step forward toward integration of nanowires and graphene nanoribbons into modern planar semiconductor technology using the simple method of MML.
Acknowledgments

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# List of Symbols and Abbreviations

- **\( a \)**: unnamed coefficient; distance between hyperbola center and hyperbola vertex
- **A**: ampere(s)
- **\( A \)**: prefactor in Arrhenius law
- **\( a \)**: contact angle of water with substrate
- **AFM**: atomic force microscop(e/y)
- **ALD**: atomic layer deposition
- **ar-GNR**: GNR produced using Ar RIE
- **a.u.**: arbitrary units
- **\( b \)**: hyperbola parameter
- **\( \beta \)**: contact angle of water with sacrificial metal layer
- **BET**: Brunauer, Emmett and Teller model
- **\( C \)**: unnamed coefficient
- **\( ^\circ C \)**: degree Celsius
- **cm**: centimeter(s)
- **\( \text{cm}^{-1} \)**: wavenumbers
- **CVD**: chemical vapor deposition
- **\( d_1, d_2, d_3, d_4 \)**: terrace widths
- **1D**: 1-dimensional
- **2D**: 2-dimensional
DI  
deionized

DME  
dimethyl ether

$d_{SiO_2}$  
SiO$_2$ thickness

$\Delta E$  
additional energy of adsorbed water molecule due to interaction with the solid surface

$\Delta E_s$  
$\Delta E$ at which evaporation rate decreases to a negligible value

Et  
ethyl

$\Delta p$  
pressure drop

e  
electron charge

$\varepsilon_0$  
vacuum permittivity

$\varepsilon_{SiO_2}$  
dielectric constant of SiO$_2$

$\varepsilon_{BN}$  
dielectric constant of BN

e-beam  
electron beam

eq  
equation

$E_g$  
bandgap energy

eV  
electronvolt(s)

FET  
field-effect transistor

FWHM  
full width at half maximum

g  
gram(s)

$\gamma$  
surface tension

GNR  
graphene nanoribbon

h  
hour(s); minimal height of protective meniscus
<table>
<thead>
<tr>
<th>Abbr</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>iLO</td>
<td>in-plane longitudinal optical</td>
</tr>
<tr>
<td>iTO</td>
<td>in-plane transverse optical</td>
</tr>
<tr>
<td>IV</td>
<td>current-voltage</td>
</tr>
<tr>
<td>$I_{sd}$</td>
<td>source-drain current</td>
</tr>
<tr>
<td>J</td>
<td>joule</td>
</tr>
<tr>
<td>K</td>
<td>kelvin(s)</td>
</tr>
<tr>
<td>kV</td>
<td>kilovolt(s)</td>
</tr>
<tr>
<td>LAH</td>
<td>lithium aluminum hydride</td>
</tr>
<tr>
<td>$ln()$</td>
<td>logarithm</td>
</tr>
<tr>
<td>$lim()$</td>
<td>limit operator</td>
</tr>
<tr>
<td>m</td>
<td>meter(s)</td>
</tr>
<tr>
<td>mA</td>
<td>milliampere(s)</td>
</tr>
<tr>
<td>mol</td>
<td>mole(s)</td>
</tr>
<tr>
<td>μC</td>
<td>microcoloumb(s)</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter(s)</td>
</tr>
<tr>
<td>μm</td>
<td>micron(s)</td>
</tr>
<tr>
<td>MML</td>
<td>meniscus-mask lithography</td>
</tr>
<tr>
<td>MOSFET</td>
<td>metal-oxide-semiconductor FET</td>
</tr>
<tr>
<td>mTorr</td>
<td>milliTorr(s)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>mV</td>
<td>millivolt(s)</td>
</tr>
<tr>
<td>mW</td>
<td>milliwatt(s)</td>
</tr>
<tr>
<td>n</td>
<td>linear positive charge carrier concentration; number of meniscus recovery cycle</td>
</tr>
<tr>
<td>N</td>
<td>newton(s)</td>
</tr>
<tr>
<td>ℕ</td>
<td>natural numbers set</td>
</tr>
<tr>
<td>nA</td>
<td>nanoampere(s)</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer(s)</td>
</tr>
<tr>
<td>$\tilde{o}(\cdot)$</td>
<td>little-o notation</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>ohm(s)</td>
</tr>
<tr>
<td>ox-GNR</td>
<td>GNR produced using oxygen RIE</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
</tr>
<tr>
<td>$p_0$</td>
<td>saturated vapor pressure</td>
</tr>
<tr>
<td>$p^{++}$-Si</td>
<td>heavily positively doped Si</td>
</tr>
<tr>
<td>pA</td>
<td>picoampere(s)</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma enhanced CVD</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>$p_{sat}$</td>
<td>saturated vapor pressure for water at room temperature</td>
</tr>
<tr>
<td>%</td>
<td>percent</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of curvature</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
</tr>
<tr>
<td>$\mathbb{R}$</td>
<td>real numbers set</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\rho$, $\rho_x$, $\rho_y$, $\rho_z$</td>
<td>distance between the flat surface and the molecule</td>
</tr>
<tr>
<td>ref.</td>
<td>reference</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive ion etching</td>
</tr>
<tr>
<td>R</td>
<td>planar conductivity</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimeters per minute</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>$sin()$</td>
<td>sine</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$tan()$</td>
<td>tangent</td>
</tr>
<tr>
<td>$trunc()$</td>
<td>truncation function</td>
</tr>
<tr>
<td>Ts</td>
<td>tosyl</td>
</tr>
<tr>
<td>$\theta$</td>
<td>webbing angle</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>V</td>
<td>volt(s)</td>
</tr>
<tr>
<td>$V_g$</td>
<td>gating voltage</td>
</tr>
<tr>
<td>$V_m$</td>
<td>molar volume</td>
</tr>
<tr>
<td>$V_{sd}$</td>
<td>source-drain voltage</td>
</tr>
<tr>
<td>vol. %</td>
<td>Volumetric percent</td>
</tr>
<tr>
<td>w</td>
<td>nanoribbon/nanowire/meniscus width</td>
</tr>
<tr>
<td>W</td>
<td>watt(s)</td>
</tr>
<tr>
<td>wt. %</td>
<td>weight percent</td>
</tr>
</tbody>
</table>
ξ, ξ', ξ, ξ', ξ'  interaction constant
x  distance variable
xs  x coordinate of molecules at the edge of the protective meniscus
XPS  X-ray photoelectron spectroscopy
y  distance variable
z  distance variable
T  room temperature
s  second(s)
S  siemen(s)
σ  planar conductivity
sccm  standard cubic centimeters per minute
SE  secondary electrons
SEM  scanning electron microscopy
sin()  sine
T  temperature
tan()  tangent
trunc()  truncation function
Ts  tosyl
θ  webbing angle
UV  ultraviolet
V  volt(s)
Vg  gating voltage
Vm  molar volume
$V_{sd}$: source-drain voltage

vol. %: Volumetric percent

$w$: nanoribbon/nanowire/meniscus width

W: watt(s)

wt. %: weight percent

$\xi, \xi_x, \xi_y, \xi_z$: interaction constant

$x$: distance variable

$x_s$: x coordinate of molecules at the edge of the protective meniscus

XPS: X-ray photoelectron spectroscopy

$y$: distance variable

$z$: distance variable
Chapter 1

Meniscus-Mask Lithography for Narrow Graphene Nanoribbons

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1.1. Introduction

Fabrication of narrow high aspect ratio objects allows both miniaturization and control of size-dependent properties of materials. The patterning of graphene into sub-10 nm graphene nanoribbons (GNRs) results in objects that are expected to exhibit varied bandgaps depending on the GNR width and edge configurations. There are a number of GNR fabrication methods, including graphene patterning using various lithography methods, shadowing techniques including shadowing by co-polymer masks, processing of carbon nanotubes and graphite, growth on pre-patterned substrates, and direct organic synthesis. However, only a few methods enable both scalable fabrication and controlled narrow GNR positioning on-chip, characteristics that are currently required for industrial use in microelectronics. We disclose here a simple method to prepare sub-10-nm-wide GNRs by a top-down method called meniscus-mask lithography (MML).
1.2. Results and discussion

We demonstrate the MML GNR fabrication sequence in Figure 1.1A. In a typical process (Supporting Information Section S1.1), the lithography pattern is written on the graphene film in such a way that the desired GNR position corresponds to the pattern edge. After the pattern is developed, the exposed graphene is etched via reactive ion etching (RIE). A sacrificial metal layer is deposited and the pattern is lifted-off. Then the structure is once again exposed to RIE, and the sacrificial metal layer is wet-etched. As a result, the graphene near the initial pattern edges remains unaffected, and the process leads to the formation of narrow GNRs (Figure 1.1B-I, Supporting Information Section S1.2).

Two RIE regimes were tested for MML GNR fabrication: oxygen RIE that is conventionally used for graphene etching\textsuperscript{5,21-23} and Ar RIE that is milder since it removes graphene by physical sputtering only. The width was quite uniform over the ribbon length and between similarly fabricated samples (Supporting Information Section S1.3). For GNRs produced using oxygen RIE (ox-GNRs) on Si/SiO\textsubscript{2} and BN substrates, the mean widths were 13.6 ± 1.0 nm and 14.2 ± 1.0 nm, respectively. For GNRs produced using Ar RIE (ar-GNRs) the widths were smaller, 8.7 ± 1.0 nm and 6.4 ± 1.0 nm for Si/SiO\textsubscript{2} and BN substrates, respectively. The resulting GNRs demonstrated remarkably high aspect ratios (> 2000), limited predominantly by the macroscopic defects in the original transferred graphene film.

The method described could also be expanded to other materials. We have substituted graphene with sputtered 15 nm platinum films, and a similar fabrication
sequence resulted in platinum nanowires with mean width $11.7 \pm 1.0$ nm (Figure 1.1J, Supporting Information Sections S1.4-S1.5).

Figure 1.1. MML fabrication. (A) MML GNR fabrication scheme. Formation of GNRs
occurs at the edge of the lithography pattern. Blue arrows point to the meniscus of the adsorbed water which serves as the mask for the ultimate GNRs. (B-I) SEM images of individual GNRs at different magnifications. (B) and (F) ox-GNRs on Si/SiO$_2$; (C) and (G) ox-GNRs on BN; (D) and (H) ar-GNRs on Si/SiO$_2$; (E) and (I) ar-GNRs on BN. The scale bar for images (F-I) is 100 nm. (J) A Pt wire on Si/SiO$_2$. (K) The letter R patterned with ar-GNRs. Inset: magnified image of a part of the ar-GNR comprising the letter R. The mean width is 9.2 ± 1.1 nm.

The GNRs can be fabricated by MML in different shapes (Figure 1.1K, Supporting Information Section S1.6) with the only limitation being that they are located on the edge of the written pattern; the GNR width does not depend on the pattern shape. Note that the fabrication resulted in identical GNRs on all sides of the pattern, thus excluding shadowing due to sample tilt during RIE as a possible formation mechanism.

The GNR widths are robust over a range of the lithography dosages used (Supporting Information Section S1.7). They do not depend on the sacrificial metal used in the fabrication: the GNR widths for Pd, Pt and Al were nearly the same. Thus, the formation of the GNRs does not depend on the ability of the metal to form a native oxide layer, and the mechanism is not related to oxide layer shadowing. Also, GNR widths remained nearly the same for different Al layer thicknesses (Supporting Information Section S1.8).

We propose that MML works for GNR formation by adsorbate protection (shown by blue arrows in Figure 1.1A) of the graphene surface during the second RIE step. The
adsorbate is most likely atmospheric water, confined to the wedge formed by the graphene and sacrificial metal. Such adsorbates could be stabilized by concave surface features (pores, wedges), and could sustain short low pressure procedures such as RIE. The mechanism was experimentally supported by the fact that no GNRs were formed when the sample was heated to 120 °C for 30 min prior to etching nor when the sample was soaked in acetone prior to etching to ensure no contact with atmospheric moisture (Supporting Information Section S1.9). The meniscus in the wedge formed by substrate and sacrificial metal mask is too small to be described with continuum models (Supporting Information Section S1.10.1); however, we show that a few-layer thick adsorbate beading nearby the pattern edge could be explained using a simple first-order approximation molecular model of adsorption (Supporting Information Section S1.10.2). This few-layer meniscus has a size comparable to the width of observed GNRs and likely protects the underlying graphene area from RIE. Note that for MML, the resolution is determined by the shape of the liquid meniscus; this might be controlled with the judicious choice of solvent or substrate treatment, enabling width variations in the final masked object.

Since the GNRs are formed at the edge of the pattern, the procedure does not require lithography setups to have very high resolution. Thus, similar fabrication procedures could be performed even with photolithography (Supporting Information Section S1.11). The GNR mean width of 23 ± 4 nm was slightly higher than for GNRs fabricated using the e-beam lithography procedure. To our knowledge, this is first time that narrow GNRs have been fabricated by photolithography.
Raman spectra of GNRs (Figure 1.2A) revealed characteristic 2D (~ 2700 cm\(^{-1}\)), G (~ 1584 cm\(^{-1}\)) and D (~ 1350 cm\(^{-1}\)) peaks both for ox-GNRs and ar-GNRs on Si/SiO\(_2\) substrates. The G/2D intensity ratio for the GNRs increases as the GNR widths decrease: for undoped graphene the G/2D ratio is ~ 0.3 (ref. 24), whereas it is 1.0 ± 0.2 and 4.3 ± 0.5 for ox-GNRs and ar-GNRs, respectively, which is likely attributed to intrinsic GNR properties.\(^\text{25}\) In all GNR spectra, the G peak is considerably wider compared to that of the starting CVD graphene film, as expected for narrow GNRs;\(^\text{25}\) interestingly, for ar-GNRs the wide G peak could be interpreted as a doublet (Supporting Information Section S1.12).

The ar-GNRs are narrower than ox-GNRs, hence they might have a larger edge-effect. However, the D/G intensity ratio for ar-GNRs is lower (0.6 ± 0.1) than for ox-GNRs (1.1 ± 0.1) indicating that oxygen RIE leaves GNRs more disordered compared to Ar RIE. Assuming the protective adsorbates mechanism, the difference is likely caused by more defects in the narrow region near the edges for ox-GNRs compared to ar-GNRs.
Figure 1.2. Raman spectra and room temperature transport measurements of GNRs. (A) Raman spectra: ar-GNR on Si/SiO$_2$ in blue (top), ox-GNR on Si/SiO$_2$ in red (middle), and the starting CVD graphene in black (bottom). The spectra are normalized so that the G
peak height is approximately the same for all three spectra. (B) Scheme of the device used for transport measurements. (C) SEM image of an ar-GNR device on a BN substrate. The GNR is situated vertically between the horizontal top and bottom electrodes. (D) Room temperature gating curves (for source-drain voltage 0.1 V) for individual ar-GNR FETs on Si/SiO$_2$ (in black) and BN (in red) substrates. $\sigma$ is the planar conductivity and $n$ is the linear charge carrier concentration (positive for electrons).

To investigate the electronic properties of narrow GNRs, field-effect transistor (FET) devices were fabricated (Figure 1.2B,C) with Pd source and drain electrodes placed on the ribbons and a 300 nm thermal oxide coated p$^+$-Si substrate used as a back gate. The channel length was 0.8 to 3.5 $\mu$m. For each type of GNRs at least 12 devices were studied (Supporting Information Section S1.13). The Si/SiO$_2$ substrate is known to cause electron and hole puddles in graphene, resulting in charge trapping effects.$^{26}$ The conventional method to avoid charge trapping in graphene devices is to use a BN flake as the substrate;$^{26,27}$ the charge trapping effects due to Si/SiO$_2$ have been demonstrated in GNRs.$^{28}$ ar-GNR devices both on Si/SiO$_2$ and BN substrates (30 to 70 nm thick) demonstrated remarkably consistent behavior (Figure 1.2D). Room temperature gating curves in Figure 1.2D were averaged over 50 devices for Si/SiO$_2$ and over 12 devices for BN substrates, the conductivity was calculated using the widths of the GNRs as 8.7 nm on Si/SiO$_2$ and 6.4 nm on BN. In contrast to ar-GNRs, wider ox-GNRs on Si/SiO$_2$ substrates had strong variation in both ON/OFF ratios and charge neutrality point positions, while ox-GNRs on BN substrate had consistent charge neutrality point
position, but still large ON/OFF variation (Supporting Information Section S1.13). Interestingly, the room temperature ON/OFF ratio for ar-GNRs is rather modest, ~10. This contrasts with some reports on the electronic behavior of similarly narrow or even larger width GNRs that showed extremely high ON/OFF ratios (up to $10^7$) observed at room temperature.\(^{16}\) We have estimated the holes mobility as $\sim 14 \text{ cm}^2/\text{V} \cdot \text{s}$ for ar-GNRs on Si/SiO$_2$ substrate, which agrees well with published data on charge carrier mobilities in narrow GNRs.\(^{12,18}\) When discussing the electronic properties of GNRs with defective edges, it is important to distinguish the true band gap\(^3,4\) from the so-called transport or mobility gap that originates from Coulomb blockade due to edge defects\(^{21-23,29}\) or substrate-induced alternating electron and hole puddles.\(^{28}\) Both BN and Si/SiO$_2$ substrates result in potential fluctuations over the GNR length; however, the lateral scale and the amplitude of those strongly differ. For Si/SiO$_2$, the characteristic size of the puddle is much smaller and the fluctuations of potential amplitude much higher compared to BN.\(^{26}\)

According to the Raman spectral data, ar-GNRs edges are less defective compared to ox-GNRs. The Si/SiO$_2$ substrate induces potential fluctuations that are comparable with fluctuations caused by edge defects in ox-GNRs (Supporting Information Section S1.13) while they dominate over potential fluctuations caused by edge defects in ar-GNRs; the electronic properties of ar-GNRs on Si/SiO$_2$ are determined predominantly by substrate interactions. In the case of the ar-GNRs on BN substrates, both potential fluctuations due to the edge defects and substrate interaction are rather small. Since the ON/OFF ratio for ar-GNRs on BN is comparable to that observed for ar-
GNRs on Si/SiO\textsubscript{2} substrates, it is likely that the true bandgap is dominating the behavior of ar-GNRs on the BN substrate (Supporting Information Section S1.13). The bandgap for the ar-GNRs could be estimated from theoretical studies.\textsuperscript{3} Accordingly, a 6.4-nm-wide zigzag-edged GNR yields an expected bandgap of \(~0.12\) eV. Bandgap estimation for armchair-edged GNRs is more difficult since the properties of ideal armchair GNRs differ strongly depending on the number of dimer lines in the GNR structure.\textsuperscript{3} Bandgap \(E_g\) dependence on GNR width \(w\) could be summarized\textsuperscript{24} as \(E_g = a/w\), where the coefficient \(a\) takes values between 0.2 and 1.5 eV\cdot nm. This, indeed, could exceed the potential fluctuations due to the BN substrate.\textsuperscript{26}

![Figure 1.3](image)

**Figure 1.3.** Temperature-dependent electronic properties for typical ar-GNR FETs. Gating curves at different temperatures for GNR FETs on (A) Si/SiO\textsubscript{2} substrate or (B) BN substrate. The green line at \(10^{-12}\) A in (B) depicts the approximate instrument noise level. The source-drain voltage was 0.1 V. \(I_{sd}\) is source-drain current, \(V_g\) is gate voltage, \(\sigma\) is planar conductivity and \(n\) is linear charge carrier concentration (positive for electrons). (C) Temperature dependence of minimal conductivity averaged for 6 devices for each substrate type.
Low temperature transport properties of ar-GNRs on Si/SiO$_2$ and BN are shown in Figure 1.3. For ar-GNRs on Si/SiO$_2$ (Figure 1.3A), upon cooling from room temperature to 5 K, the ON/OFF ratio only increased from $\sim 4$ to $\sim 20$, and the gating curves demonstrate, especially at 200 K and below, a clear plateau for low currents which is significantly above the measurement limit of the instrument. The plateau observed could be interpreted in terms of a transport gap.$^{21-23,29}$ Apparently, the source-drain voltage is high enough so that for all gate voltages corresponding to Coulomb blockade, the barrier size is small, which results in measurable tunneling current. The small change in minimal conductivity with temperature agrees with this conclusion and is consistent for all devices measured (Figure 1.3C).

The gating curves for ar-GNRs on BN substrate are quite different. The lowest current (OFF) decreases about three orders of magnitude upon cooling from 300 K to 5 K; near the temperature of liquid helium it reaches the noise level (Figure 1.3B, green line). The ON/OFF ratio for ar-GNRs on BN thus increases from $\sim 10$ to $\sim 10^3$, which together with the current dropping to a minimal measurable value, agrees with the presence of a true bandgap.$^5$

1.3. Conclusions

In conclusion, we have demonstrated a scalable top-down method for fabrication of high aspect ratio narrow objects by means of simple lithography that we termed MML and showed its applicability to prepare very narrow GNRs of arbitrary configuration. The apparent formation mechanism is graphene protection by adsorbates in the wedge formed by the sacrificial metal layer and the graphene on the edge of the lithography pattern. The
Ar RIE process was found to result in fabrication of GNRs with consistent electronic properties. The ar-GNR on Si/SiO₂ behavior could be explained in terms of the transport gap, while the electronic properties of ar-GNRs on BN substrate could be explained by the presence of a true bandgap.

1.4. Methods

Fabrication of GNRs was performed using CVD graphene as the starting films (Supporting Information Section S1). Fabrication of platinum wires was performed starting from a 15 nm thick platinum film sputtered on the substrate using Denton Desk V Sputter system.

Room temperature reactive ion etching (RIE) with oxygen or argon was performed using a Trion RIE instrument and Oxford Plasma Lab 80 Plus RIE instrument. Varying temperature RIE processes with nitrogen were performed using a Trion Orion II Load Lock PECVD instrument. The conditions used are listed in Supporting Information Section.

Sacrificial metal layer was deposited either by sputtering (Al and Pt, Denton Desk V Sputter system) or by e-beam evaporation (Pd). Sacrificial layer thickness was 20 nm unless stated otherwise. For Al wet etching the mixture of H₃PO₄/HNO₃/CH₃COOH/H₂O (80/5/5/10 vol. %) was used. Sacrificial Pt and Pd layers were etched using aqua regia.

GNR FET devices were fabricated via conventional e-beam lithography with 40 nm e-beam evaporated Pd pads. Electrical measurements were performed under vacuum (chamber pressure less than 10⁻⁵ Torr) using a Desert Cryogenic probe 6 system. Prior to measurements the samples were held under vacuum for at least 4 d to ensure the
desorption of atmospheric moisture from GNRs. The IV data were recorded using an Agilent 4155C semiconductor parameter analyzer. Gate voltage was varied in range -40 to +40 V; sweeping was performed from negative to positive voltages. For recording gating curves, the source-drain voltage was set to 0.1 V. Low temperature measurements were performed in the range 5 to 300 K in same system using a LakeShore 331 Temperature Controller with Si diode sensor.

1.5. Acknowledgments

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1.6. References

2008, 92, 113102.
1.7. Supporting Information

S.1.1. Materials and methods

The graphene growth procedure was an adjusted version of conventional CVD graphene synthesis.\(^1\) Prior to graphene growth Cu foils (99.8% pure) were annealed at 1050 °C in an Ar/H\(_2\) atmosphere (overall pressure ~ 8.0 Torr, Ar flow 500 sccm, H\(_2\) flow 50 sccm) for 1 h. The growth process was performed at 1050 °C in a H\(_2\)/CH\(_4\) atmosphere immediately after foil annealing (overall pressure ~ 1.0 Torr, H\(_2\) flow 50 sccm, CH\(_4\) flow 5 sccm). After growth step, the sample was cooled to room temperature in Ar/H\(_2\) atmosphere (overall pressure ~ 8.0 Torr, Ar flow 500 sccm, H\(_2\) flow 50 sccm) with a cooling rate of ~ 100 °C/min. Graphene on Cu foil was covered by spin-coating with PMMA layer, and then the Cu foil was wet etched in CuSO\(_4\)/HCl etchant (20 g CuSO\(_4\)·5H\(_2\)O, 50 mL HCl, 50 mL H\(_2\)O). Graphene with PMMA was washed several times in DI water prior to transfer onto the substrate. After placing on the substrate it was thoroughly dried, and then PMMA was removed in acetone. Annealing of the samples in reducing medium was performed at 350 to 500 °C in Ar/H\(_2\) atmosphere with overall pressure ~ 8.0 Torr and with Ar and H\(_2\) flows of 500 sccm and 50 sccm, respectively. Typical annealing time was 30 min.

Substrates used in this work were heavily p-doped Si wafers with 300 nm thermal oxide layer (Silicon Quest International). Those are denoted as Si/SiO\(_2\) substrates. Prior to use, the substrates were thoroughly washed first with soap and then with piranha solution, rinsed with DI water, dried in nitrogen flow and treated in UV-ozone cleaner (Boekel, model 135500) for 30 min to ensure that the surfaces were clean. BN substrates were
prepared by deposition of mechanically exfoliated (“Scotch tape”) hexagonal BN flakes (Momentive, grade pt110) with a thickness of 30 to 70 nm onto Si/SiO$_2$ chips described above. Chips with BN flakes were annealed prior to graphene transfer at 500 °C in air for 3 h to remove residual glue and make flakes stick better to the substrate.

**Table S1.1. RIE conditions used for graphene and Pt etching.**

<table>
<thead>
<tr>
<th></th>
<th>Graphene etching</th>
<th>Pt etching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxygen RIE</td>
<td>Argon RIE</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>100 mTorr</td>
<td>100 mTorr</td>
</tr>
<tr>
<td>RIE power</td>
<td>23 W</td>
<td>31 W</td>
</tr>
<tr>
<td>Gas flow</td>
<td>15 sccm</td>
<td>20 sccm</td>
</tr>
<tr>
<td>Process time (unless otherwise stated)</td>
<td>20 s</td>
<td>60 s</td>
</tr>
</tbody>
</table>

The conditions used for reactive ion etching are listed in Table S1.1 for graphene etching used in GNRs fabrication and for platinum etching used in platinum nanowires fabrication.

SEM images were acquired with a JEOL 6500 SEM instrument in SE mode with an accelerating voltage of 15 kV. GNR widths were determined by fitting grayscale intensity profiles perpendicular to the GNR axes (acquired using ImageJ software) with Gauss peak. FWHM was used as a width estimate. Averaging was performed for at least 30 profiles in different images. SEM instrumental error was assumed to be ~ 1 nm.

e-Beam lithography was performed with a JEOL 6500 SEM instrument using 950 PMMA A resist at an e-beam current of 300 pA. Photolithography was performed with a SUSS Mask Aligner MJB4 using a S1813 photoresist. Photolithography masks were
fabricated with a DWL66 mask maker. AFM measurements were performed using a Digital Instrument Nanoscope IIIA in tapping mode (with NanoSensors tips, type PPP-NCH-W). Raman spectra were collected using Renishaw inVia Raman microscope with a 514.5 nm laser. The laser polarization was set perpendicular to GNR axes and was kept constant through all experiments. The beam power was ~ 10 mW with laser beam spot ~ 1 to 3 µm in diameter. Data collection was performed with exposure time 60 to 1000 s.

To measure the conductivity of Pt wires, 40 nm thick sputtered Pt leads were placed on Pt wires via conventional e-beam lithography. The equipment that was used for transport measurements is described in Methods Summary section of main text. Both 2-terminal and 4-terminal measurement geometries were tested.

**S.1.2. AFM imaging of GNRs**

Typical AFM image of ox-GNR (Figure S1.1) reveals that the height of elevated region (that supposedly corresponds to the GNR) is ~ 3.5 nm for BN substrate, and considerably exceeds both the expected height for single-layer graphene (0.5-1.0 nm) and layer-to-layer spacing in graphite.²

Both SiO₂ and BN could be partially etched during RIE fabrication steps due to physical sputtering. Indeed, BN flakes patterned and etched on one side with the oxygen RIE protocol resulted in ~ 2 nm steps. This reasonably agrees with the observed ribbons height. For ar-GNRs this step was found to be even larger, ~ 8 nm for BN substrates. The elevation of the GNRs over the BN substrate explains the GNR pronouncement in the SEM images (Figure 1.1 E,G,I).
19

Figure S1.1. AFM image (height mode) of GNR and the height profile perpendicular to GNR axis. Height range in the image is 15 nm.

Thus, in the case of GNRs on BN substrates, it would be more correctly stated that GNRs are located on few-layer BN ribbons (that are formed by RIE and have top layer unaffected by RIE), further atop the BN flake. BN ribbons are not expected to interfere with transport measurements, and the devices without GNR on top were not electrically conductive. The GNR width found from AFM images considerably exceeds that from SEM images, apparently due to tip curvature effects.

S.1.3. GNRs width distribution

Figure S1.2 shows the histograms describing GNR width distributions. The bin size is 1 nm. The number of grayscale intensity profiles analyzed was 218 for ox-GNRs on Si/SiO$_2$, 63 for ox-GNRs on BN, 51 for ar-GNRs on Si/SiO$_2$ and 34 for ar-GNRs on BN. Table S1.2 summarizes mean width and 1$^{st}$ and 3$^{rd}$ quartiles for each GNR type.
Figure S1.2. Width distribution for GNRs fabricated via the MML technique described. (A) ar-GNRs on Si/SiO$_2$ substrate; (B) ar-GNRs on BN substrate; (C) ox-GNRs on Si/SiO$_2$ substrate; (D) ox-GNRs on BN substrate.

Table S1.2. Statistical data summary for GNRs widths.

<table>
<thead>
<tr>
<th></th>
<th>Mean width, nm</th>
<th>Width first quartile, nm</th>
<th>Width third quartile, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ar-GNRs on Si/SiO$_2$ substrate</td>
<td>8.7 ± 1.0</td>
<td>7.9</td>
<td>9.5</td>
</tr>
<tr>
<td>ar-GNRs on BN substrate</td>
<td>6.4 ± 1.0</td>
<td>6.1</td>
<td>6.9</td>
</tr>
<tr>
<td>ox-GNRs on Si/SiO$_2$ substrate</td>
<td>13.6 ± 1.0</td>
<td>12.1</td>
<td>14.9</td>
</tr>
<tr>
<td>ox-GNRs on BN substrate</td>
<td>14.2 ± 1.0</td>
<td>12.9</td>
<td>15.6</td>
</tr>
</tbody>
</table>
S.1.4. Expansion of method to platinum wires fabrication

The fabrication method could be readily expanded to other materials: the changes in the fabrication scheme (Figure 1.1A) needed are the deposition of the desired material as a smooth uniform film and the adjustment of the RIE procedure. We have fabricated platinum wires (Figure S1.3) out of a ~15 nm thick sputtered platinum film using 20-μm-sided squares as a pattern and ~30 nm thick sacrificial Al layer.

According to SEM (Figure S1.3A and B), the wire length is limited mostly by pattern dimensions, and the mean wire width is 11.7 ± 1.0 nm (see Table S1.3). AFM height image (Figure S1.3C) shows that wires are quite uniform in height (~15 nm) which agrees with the starting film thickness.

Figure S1.3. Platinum wires. (A) Low magnification SEM image, inset in (A): width
distribution for Pt wires, bin size 2 nm; (B) high magnification SEM image; (C) AFM height image; scale range is 75 nm; inset: height profile averaged perpendicular to the wire axis.

Table S1.3. Statistical data summary for Pt nanowires widths.

<table>
<thead>
<tr>
<th></th>
<th>Mean width, nm</th>
<th>Width first quartile, nm</th>
<th>Width third quartile, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt wires</td>
<td>11.7 ± 1.0</td>
<td>9.5</td>
<td>13.8</td>
</tr>
</tbody>
</table>

As in GNRs, the apparent wire width from AFM images exceeds that seen from high magnification SEM images, as a result of tip curvature effects.

S.1.5. Transport properties of Pt wires

To study the transport properties of Pt wires, devices with ~2 μm source-drain distance were fabricated (Figure S1.4A and B). Both 2-terminal and 4-terminal measurements were performed and demonstrated converging results (Figure S1.4C).

The mean platinum resistivity derived from the transport measurements (assuming the wire width to be ~ 11.7 nm and the wire height to be ~ 15 nm) was calculated to be \((62 \pm 4) \times 10^{-8} \Omega \text{m}\), which is comparable to \(10.5 \times 10^{-8} \Omega \text{m}\) for bulk Pt.\(^4\) The measured resistivity is actually higher most likely due to wire width non-uniformity and surface scattering effects.
Figure S1.4. Transport properties of Pt wires. (A) SEM image of an individual device with the magnified wire image in the inset. (B) Overall SEM image of device set. (C) Two terminal (black) and four terminal (red) measurements for the same device.

S.1.6. GNRs patterned in different shapes

Following the fabrication method detailed here, narrow GNR could be written in any shape (Figure 1.1, Figure S1.5). For ox-GNRs on Si/SiO$_2$ substrates the effect of pattern shape on GNRs width was tested, and no significant difference was found. For example, for GNRs written individually (Figure 1.1B, the lithography patterns used were rectangles with sides 10-20 µm) the mean width was 13.6 ± 1.0 nm, for multiple closely placed ox-GNRs (Figure S1.5A, the lithography patterns used were 2 µm × 100 µm stripes separated by 2 µm gaps) the mean width was 13.7 ± 1.2 nm.
Figure S1.5. GNRs patterned in different shapes: (A) 2 µm separated lines (inset is a magnified GNR); (B) 90° spiral; (C) 90° angle formed by GNRs.

S.1.7. GNR widths for different lithography doses and different sacrificial layer metals

The optimal dosage for the e-beam lithography setup used was found to be 270 µC/cm², as judged by comparing resulting and expected feature sizes. The study of GNR width dependence on sacrificial metal was performed for ox-GNRs on Si/SiO₂ substrates patterned with 2 µm × 100 µm stripes separated by 2 µm gaps. GNR widths for exposure conditions during lithography steps ranging from slight underexposure to slight overexposure were measured for Al, Pt and Pd sacrificial layers. Pt and Pd metals were
chosen as ones forming minimal if any native oxide layer. Different deposition methods (e-beam evaporation for Pd and sputtering for Pt) were used to exclude the role of specific stresses in the metal film caused by a deposition technique that could potentially result in a shadowing effect. In a wide range of lithography dosages, the GNR widths were found to be approximately constant and the same for Al, Pt and Pd metals (Figure S1.6).

![Figure S1.6](image)

**Figure S1.6.** Mean GNR widths for Al, Pt and Pd sacrificial metal layers in a wide range of lithography dosages.

**S.1.8. GNRs width dependence on sacrificial metal layer thickness and etching time**

The study of GNR width dependence on sacrificial metal thickness was performed for ox-GNRs on Si/SiO$_2$ substrate patterned by 2 $\mu$m $\times$ 100 $\mu$m stripes
separated by 2 µm gaps. Al sacrificial layers of different thicknesses (5 to 60 nm) were deposited. Otherwise standard processing resulted in 15.9 ± 1.2 nm wide GNRs for 60 nm Al, and 13.7 ± 1.2 nm for 20 nm Al (Figure S1.7). Results for a 10 nm Al layer were not distinguishable from the 20 nm Al case, but for the 5 nm Al layer the continuous GNR regions were very small (< 1 µm). The weak dependence of the GNR width on the deposited metal thickness excluded lithography pattern slope as the cause of GNR formations.

![Figure S1.7](image)

**Figure S1.7.** GNRs width dependence on thickness of Al metal layer: (A) 20 nm; (B) 60 nm. Scale bar for both images is 100 nm.

The increase in etching time could be expected to result in a GNR width decrease due to undercut effects;³ 40 s of oxygen RIE process (in contrast to the normal time of 20 s) and 90 s of argon RIE process (in contrast to the normal time of 60 s) resulted in GNRs with continuous regions of < 1 µm.
S.1.9. GNRs formation by adsorbates protection mechanism

The following experiments were performed to support the proposed mechanism.

In the first, two samples were patterned with $2 \mu m \times 100 \mu m$ stripes separated by $2 \mu m$ gaps. The first RIE step for both was performed with argon RIE via the standard procedure following by deposition of a 20 nm sacrificial Al layer. Then one of the samples was, prior to further processing, heated to 120 °C in an RIE chamber under vacuum, held at that elevated temperature for 30 min to ensure the removal of adsorbed water, cooled back to room temperature and etched without exposing to ambient conditions (with N$_2$ RIE procedure). This sample did not have GNRs where they were expected to be found (Figure S1.8A) had the sample been processed under standard conditions (Figure 1.1A). A control sample was processed at room temperature immediately after loading with the same N$_2$ etching procedure, and did have ribbons (Figure S1.8B). Interestingly, the region on the test sample in Figure S1.8A where the GNRs could be expected to form is clearly seen even though there are actually no GNRs; there is observable contrast difference between Si/SiO$_2$ substrate regions exposed to argon RIE and to nitrogen RIE.
Figure S1.8. Samples processed with nitrogen RIE: (A) after being heated and cooled under vacuum; (B) immediately after sample loading. Arrow in (A) shows expected GNR position.

For the second experiment, the sample was patterned with 2 μm × 100 μm stripes separated by 2 μm gaps and had a 20 nm Al sacrificial layer deposited. First etching was performed with Ar RIE at standard conditions. After the lift-off step, the sample was soaked in acetone, and without exposure to ambient moisture (a small droplet of acetone remained on top of the sample), was placed in the RIE chamber, evacuated and processed using argon RIE, resulting in no observable GNRs (Figure S1.9). In Figure S1.9A the traces of the initial pattern of stripes are clearly visible due to image contrast, however, there are no GNRs formed (Figure S1.9B). This can be explained by the higher vapor pressure of acetone when compared to water; the acetone presumably evaporated from the sample, allowing the RIE to etch away all of the unprotected graphene.
Figure S1.9. Sample processed with RIE without exposing to air: (A) low magnification; (B) high magnification. Arrows show expected GNR positions.

S.1.10. GNRs formation mechanism

S.1.10.1. GNRs formation mechanism: continuum models

To support the proposed nanowire/GNR formation mechanism, the shape of the meniscus was estimated using theoretical modeling. The processes to model are the formation of the meniscus, behavior of the meniscus under reduced pressure, and interaction of meniscus liquid and RIE plasma. It should be noted that we do not consider the formation of any meniscus on the first etching step, as the mask layer there is hydrophobic (PMMA). This assumption is supported by the experiments, where after alteration of only the second etching step no formation of GNRs was observed. The meniscus is formed in a process of capillary condensation, described by Kelvin's Law for a cylindrical meniscus in eq 1.1:
\[
\ln \left( \frac{p}{p_0} \right) = \frac{\gamma \cdot V_m}{r \cdot R \cdot T} \quad (1.1)
\]

where \( \frac{p}{p_0} \) is the relative humidity, \( \gamma \) is the surface tension (0.073 N/m for water at room temperature\(^4\)), \( V_m \) is the molar volume of liquid \( (18 \times 10^{-6} \text{ m}^3) \), \( r \) is the radius of curvature for a cylindrical meniscus (negative for concave), \( R \) is the universal gas constant, \( T \) is the temperature. Ambient humidity in this experiment varied at \( \sim 60\% \), so assuming \( \frac{p}{p_0} = 0.6 \), we get \( r \approx -1 \text{ nm} \), which is probably at the limit of applicability of continuum models such as Kelvin’s Law. Moreover, considering the evaporation of water under reduced pressure, the continuum model predicts that the meniscus size may decrease further, producing distances that can only be described by more microscopic approaches. Thus, microscopic molecular models are preferred to explain the observed process.

**Figure S1.10.** Scheme of the continuum model meniscus cross-section orthogonal to GNR/nanowire direction; \( x \) and \( y \) are meniscus linear parameters, \( \alpha \) and \( \beta \) are contact angles.
Even if we assume $r = 1 \text{ nm}$, calculation of the meniscus base ($x$) gives inconsistent results (Figure S1.10). If $\alpha$ and $\beta$ are contact angles with substrate and with sacrificial metal layer correspondingly, then $x = r \left| \cos \beta - \sin \alpha \right|$. The receding contact angles were measured to be $21 \pm 1^\circ$ for graphene on an Si/SiO$_2$ substrate and $10 \pm 1^\circ$ for a sputtered aluminum film. Thus $x \approx 0.6 \text{ nm}$ and not only is it out of the applicability range for continuum models, but it is much smaller than the width of experimentally observed GNRs.

It is also important to note that for any reasonable meniscus geometry, no boiling occurs under reduced pressure. Indeed, the pressure drop on the meniscus surface is governed by Young-Laplace equation for a cylindrical surface in eq 1.2:

$$\Delta p = \frac{2\gamma}{r} \quad (1.2)$$

where $\Delta p = p_2 - p_1$ is the pressure drop, $\gamma$ is surface tension, $r$ is radius of curvature of a cylindrical meniscus (negative for concave). The saturated vapor pressure for water at room temperature is $p_{\text{sat}} = 2.3 \text{ kPa}$ (ref. 4). Assuming the pressure in the RIE chamber to be negligible ($p_2 = 0$), the condition for boiling of water is $p_{\text{sat}} > p_1 = -\Delta p$, which leads to $r > 30 \mu\text{m}$ for boiling to be observed. It is obviously larger than any reasonable value estimated here, and using the wetting parameters and geometry described above, it corresponds to an almost flat meniscus reaching the top of the sacrificial metal layer and extending for $> 50 \text{ nm}$ on the horizontal plane.

S.1.10.2. Microscopic molecular models

As continuum models seem to be less applicable to the case under investigation,
we tried to use the following microscopic molecular models to describe the observed effects.

It is known that there are several layers of water molecules adsorbed on any hydrophilic surface at reasonable atmospheric humidity.\textsuperscript{6} The thickness of this adsorptive film could be estimated by utilizing the BET equation,\textsuperscript{7} but we will not use it since the BET model assumes that binding energies in all water layers except the one closest to the surface are the same, which most probably is not the case for water.\textsuperscript{6}

It is natural to expect some increase of water thickness close to the wedges, where two planes of adsorbed few-layer water meet at a certain angle. One can analyze the possibility of existence of an adsorbed film under reduced pressure, assuming that this film is much more stable and possibly thicker at ambient conditions and thus it will appear before the pumpdown procedure.

It is important to note that any adsorbed water film is actually thermodynamically unstable under vacuum due to the entropic force for molecular evaporation. It suggests that the geometry of the "meniscus" is determined solely by kinetics of evaporation. The evaporation rate could be described using the Arrhenius Law eq 1.3:

\[ \text{rate} = A \cdot e^{\frac{-\Delta E}{RT}} \]  

(1.3)

where \( A \) is a constant, \( R \) is universal gas constant, \( T \) is temperature and \( \Delta E \) is the additional energy of adsorbed water molecules due to interaction with the solid surface (that is, for bulk water \( \Delta E = 0 \)). For bulk water the evaporation rate is sufficiently high to consider this process immediate relative to the characteristic pumpdown time (few min). On the other hand, for an adsorbed water film of certain thickness the evaporation rate
becomes low enough to consider this layer stable over the timescale of fabrication as described. As the method did not demonstrate instability for small pumpdown time variations (within few min), the geometry of the adsorbed film under vacuum is apparently determined by the evaporation rate decrease. The characteristic energy, $\Delta E_s$, is defined to be the energy at which the evaporation rate decreases to a negligible value and the evaporation process effectively stops. This threshold energy $\Delta E_s$ is expected to be higher than the equilibrium energy of surface molecules adsorbed at regular (> 1 %) humidity levels, as the evaporation rate at this equilibrium should be equal to the condensation rate, which is expected to be much higher than the evaporation rate of the kinetically stable adsorbate.

The estimation of $\Delta E$ as a function of distance from the solid surface is a complex problem which is not yet fully understood theoretically for such molecules as water, but one can reasonably use the first order approximation of this unknown potential in eq 1.4,

$$\Delta E = \frac{\xi}{\rho} + \bar{\rho} \left( \frac{1}{\rho^2} \right)$$ (1.4)

where $\xi$ is constant and $\rho$ is distance (x or y) between the flat surface and the molecule. This approximation agrees with experimental data for oxides surfaces\textsuperscript{8} similar to native oxide on an aluminum sacrificial metal layer as described here and has the order corresponding to the interaction between the dipole and polarized surface. Thus, the energy of water molecule adsorbed in the wedge can be written in the following approximate form in eq 1.5:

$$\Delta E \approx \frac{\xi_x}{x} + \frac{\xi_y}{y}$$ (1.5)
where \( x \) and \( y \) are the distances from the molecule to the walls which for estimation purposes are expressed in number of water monolayers, and \( \xi_x \) and \( \xi_y \) are the corresponding potential equation constants. The latter could be estimated from data on adhesion energies and are expected to be on the order of \( 10^4 \) J \( \times \) layer/mol (1.5 \( \times \) 10^4 to 3 \( \times \) 10^4 J \( \times \) layer/mol for alumina by fitting of experimental data from (ref. 8)). These values are expected to be close for different native oxide surfaces, and it was shown earlier that a single layer of graphene negligibly changes the wetting properties of the underlying surface. 9 Thus, for all processes described in this paper, we assume for simplicity \( \xi_x = \xi_y = \xi \), and, limiting \( \Delta E \geq \Delta E_s \), we determine the conditions for non-evaporated water molecules on the surface with eq 1.6:

\[
\frac{1}{x} + \frac{1}{y} = \frac{\Delta E_s}{\xi} \quad (1.6)
\]

\( \Delta E_s \) should be at least higher than the thermal energy, \( \Delta E_s > RT = 2.4 \) kJ/mol, which gives the upper limit of \( \xi/\Delta E_s \approx 10 \) layers. Assuming that there are at least 2 layers of water on flat surfaces under vacuum, 6 far from the wedge in eq 1.6 \( \lim_{x \to \infty} y = 2 \). Thus, we estimate the lower limit as \( \xi/\Delta E_s \approx 2 \) layers.
Figure S1.11. Modeling of adsorbed water profiles obtained from eq 1.6 for different values of $\xi/\Delta E_s$. (A) $\xi/\Delta E_s = 2.25$ layers, (B) $\xi/\Delta E_s = 2.75$ layers, (C) $\xi/\Delta E_s = 3.25$ layers, (D) $\xi/\Delta E_s = 3.75$ layers. Red arrows denote where first additional water layer appears.

The shape of adsorbed layer for different values of $\xi/\Delta E_s$ is shown on Figure S1.11. Depending on parameters used for calculations, there is a point at the distance of few tens layers from the wedge vertex, where the thickness of the water film increases above the thickness of the water film on the flat surface. We speculate that this
position is determined by interaction potentials and defines the nanowire/GNR shape on
the second etching step.

We theorize that this difference in adsorbed water layer thickness may control the
etching process. Unfortunately, the removal of water by sputtering at ambient
temperature by low energy ions is not well studied. In ref. 10, it was shown that for
neutral Ar atoms with 20 eV energy, the sputtering yield of few-layer amorphous solid
water at low temperature is on the order of $10^{-3}$ and decreases as the water layer thickness
increases. The data from ref. 11 could be used to extrapolate the sputtering yield of
amorphous solid water with Ar$^+$ ions: at energies $\sim 20$ eV it is $\sim 0.1$, and the actual yield
may be another order of magnitude smaller if we account for absorption of some kinetic
energy by vibrational states of the molecules (up to 5 eV per degree of freedom$^{11}$). Thus
the sputtering yield will decrease even further for thicker layers of water at room
temperature, as in weakly bound state the molecules could more easily penetrate in the
depth of the medium than ones bound into a crystalline lattice. Thus, even though the
adsorbed water layer in the wedge is thin, it could be sputtered much more slowly than
the underlying solid.

S.1.11. GNR fabrication using photolithography

The GNRs fabrication method demonstrated in this paper also works using
photolithography patterning. A mask patterned with 4 $\mu$m $\times$ 100 $\mu$m stripes separated by
4 $\mu$m gaps was made (the 4 $\mu$m feature size is very close to the mask aligner resolution
limit). Oxygen RIE was used for graphene etching. The resulting GNRs were $23 \pm 4$ nm
wide (Figure S1.12).
Figure S1.12. GNRs fabricated \textit{via} photolithography. The scale bar is (A) 1 µm, (B) 100 nm.

S.1.12. Raman spectra analysis

The CVD graphene films used for GNR fabrication were analyzed with Raman spectroscopy to ensure that high quality monolayer graphene was used to produce the GNRs. Raman spectra were collected from the GNRs confined between the leads that were used for devices testing. Metal leads being exposed to the laser irradiation could partially account for the high background observed for GNRs. The additional peaks observed in GNRs Raman spectra around \( \sim 1300 \text{ cm}^{-1} \) and \( \sim 1450 \text{ cm}^{-1} \) are not related to GNRs, as they are observed from bare substrate as well. For GNRs on BN substrates, the spectral region around the usual position of the D peak was dominated by the strong characteristic BN peak at \( \sim 1366 \text{ cm}^{-1} \) (ref. 12), and although there were pronounced 2D and G peaks, those spectra were not used for further analysis. Repeated Raman
measurements on the same GNRs did not produce any significant changes in the spectra, leading to the conclusion that there was little overheating or decomposition of the sample under the laser irradiation. In addition, a decrease in the collection time and laser power did not significantly change the peak position, resulting only in a decrease in the signal-to-noise ratio. Raman spectra fitting was done with polynomial (up to power 5) background and Lorentz peaks. Fitting parameters were peak intensities, positions, FWHM and background polynomial coefficients. Peak intensity ratios, position and FWHM averaging was performed from analysis of at least 5 fits of Raman spectra collected from different GNRs.

The 2D peak (Figure 1.2A) in GNRs is shifted to higher wavenumbers compared to the starting CVD graphene; for ox-GNRs the average position is 2705.4 ± 0.5 cm⁻¹; for ar-GNRs it is 2702.7 ± 0.4 cm⁻¹; whereas for starting graphene the 2D peak is located at ~ 2685 cm⁻¹ (ref. 13). Though the increase of the G/2D ratio coupled with the 2D peak upshift could indicate some graphene p-doping,13,14 it is more likely to be associated with the intrinsic large edge-effect of narrow GNRs.15 For ar-GNRs the D/G intensity ratio is lower than for ox-GNRs, although the latter are wider. D/G ratio difference between ar-GNRs and ox-GNRs could be attributed to the additional functional groups attached to the near-edge region due to reaction of oxygen with graphene during the oxygen RIE process. Ar plasma species are not thought to react chemically with graphene, and the functional groups on the edges of ar-GNRs are expected to appear only at the edge upon GNRs sample exposure to air after RIE. Note that since GNRs were fabricated from polycrystalline CVD graphene and the RIE process was involved in edge formation,
GNR edges are likely randomized, so the low D/G ratio should not be interpreted as zigzag edge domination.\textsuperscript{16} For ox-GNRs the G-peak was shifted toward higher wavenumbers (1598.7 ± 0.6 cm\(^{-1}\)) compared to the normal G peak position for non-doped CVD graphene (~1584 cm\(^{-1}\) (ref. 13)); this could be attributed either to graphene doping or intrinsic GNR properties. In all GNR spectra, the G peak was considerably wider compared to that of the starting CVD graphene film, as expected for narrow GNRs.\textsuperscript{15} Interestingly, for ar-GNRs the wide G peak could be interpreted as a doublet: a 5-peak deconvolution of the 1100 – 1900 cm\(^{-1}\) region fits the data better than a 4-peak deconvolution (Figure S1.13). Comparison of 4-peak and 5-peak fit was performed by fitting the data in region 1100-1900 cm\(^{-1}\) with polynomial (up to power 2) background and 4 or 5 Lorentz peaks correspondingly. Fitting was performed over background parameters, peak intensities, FWHM and positions (Table S1.4).
Figure S1.13. Raman spectra deconvolution. (A) 4-peak and (B) 5-peak deconvolutions of the spectral region around the G and D peaks for ar-GNRs on Si/SiO$_2$ substrate.


Table S1.4. Summary for 4 peak fit and 5 peak fit for ar-GNRs on Si/SiO$_2$ substrate.

<table>
<thead>
<tr>
<th></th>
<th>4 peak fit</th>
<th></th>
<th>5 peak fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak position</td>
<td>Peak FWHM</td>
<td>Peak position</td>
</tr>
<tr>
<td>4 peak fit</td>
<td>1356.6 ± 0.8 cm$^{-1}$</td>
<td>64 ± 5 cm$^{-1}$</td>
<td>1356.6 ± 0.6 cm$^{-1}$</td>
</tr>
<tr>
<td>5 peak fit</td>
<td>1599.0 ± 0.3 cm$^{-1}$</td>
<td>77 ± 1 cm$^{-1}$</td>
<td>1558 ± 3 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>1604.3 ± 0.6 cm$^{-1}$</td>
<td></td>
<td>67 ± 2 cm$^{-1}$</td>
</tr>
</tbody>
</table>

It is unlikely that the doublet is a combination of the G and D’ peaks since in this case the G peak would be shifted to lower wavenumbers compared to undoped graphene, and doping should only shift it to higher wavenumbers.\textsuperscript{13,14} The shift of the G peak to lower wavenumbers could occur due to sample overheating;\textsuperscript{17} however, this was observed only for laser polarization parallel to the GNR axis. The possible interpretation for the observed doublet is the splitting of the G peak. In graphene, the G peak originates from phonon scattering in the degenerated iLO and iTO bands at the Brillouin zone center.\textsuperscript{18} This degeneracy could be uplifted, for example, by stress,\textsuperscript{19} causing the G peak to split; a similar effect causes G-peak splitting in carbon nanotubes.\textsuperscript{20} The measurable G peak splitting in narrow GNRs was predicted by first principle calculations;\textsuperscript{21} however, the actual value of the split observed here experimentally (\textasciitilde 46 cm$^{-1}$) exceeds the expectations since similar splitting values were predicted for narrower GNRs.\textsuperscript{21} It should be noted that previously experimental observation of G peak splitting has been reported for H-terminated zigzag GNRs and graphene edges;\textsuperscript{22} however, in that case it was interpreted as a superposition of peaks corresponding to zigzag edge regions and internal areas of the GNR.
S.1.13. GNRs FETs fabrication and electronic properties study

Multiple FETs were fabricated and tested for each type of GNR. The yields of device fabrications were \( \sim 50\% \). The leading cause for FETs being non-conductive was missing GNR regions inherited from graphene film defects. For BN substrates, additional cause of device failures were leads broken on the BN flake edges. An important device fabrication step was sample annealing in a reductive Ar/H\(_2\) atmosphere (at 350 °C) prior to patterning of the contacts. Without annealing, the GNRs do not adhere sufficiently well to the substrate and peel away during contacts fabrication. The total number of conductive devices analyzed was 24 for ox-GNRs on Si/SiO\(_2\), 23 for ox-GNRs on BN, 50 for ar-GNRs on Si/SiO\(_2\) and 12 for ar-GNRs on BN. All conductive devices were checked under SEM to ensure that only single GNRs were connecting the leads.

In order to properly compare GNRs on BN flakes of different thicknesses, the gating voltages for all devices were recalculated into linear charge concentration in the classical capacitance approximation\(^{23}\) using the BN flake thickness determined from AFM measurements, and assuming that the SiO\(_2\) layer thickness was 300 nm. Dielectric constants for SiO\(_2\) and BN were assumed to be 3.9 and 4.0, respectively.\(^{24}\) Linear charge concentration was accepted since GNRs are quasi-1D objects. The negative concentration values correspond to holes, positive to electrons.

For GNRs on Si/SiO\(_2\) substrate without BN flakes, linear charge carrier concentration was calculated as in eq 1.7:

\[
n = e \cdot \frac{V_g \cdot 2 \pi \varepsilon_0 \varepsilon_{SiO_2}}{e \cdot \ln \left( \frac{4 \cdot d_{SiO_2}}{w} \right)}^{1.7}
\]
For GNRs on BN substrate linear charge carrier concentration was calculated as in eq 1.8:

\[ n = V_g \frac{2\pi \varepsilon_0}{e} \left( \frac{1}{\varepsilon_{\text{BN}}} \ln \left( \frac{4d_{\text{BN}}(d_{\text{SiO}_2}+d_{\text{BN}})}{w(2d_{\text{SiO}_2}+d_{\text{BN}})} \right) + \frac{1}{\varepsilon_{\text{SiO}_2}} \ln \left( \frac{2d_{\text{SiO}_2}+d_{\text{BN}}}{d_{\text{BN}}} \right) \right) \] (1.8)

Here \( V_g \) is the gate voltage applied, \( \varepsilon_0 \) is vacuum permittivity, \( \varepsilon_{\text{SiO}_2} \) and \( \varepsilon_{\text{BN}} \) are dielectric constants of SiO\(_2\) and BN, respectively, \( d_{\text{SiO}_2} \) and \( d_{\text{BN}} \) are SiO\(_2\) and BN thicknesses, respectively.

The averaging for Figure 1.2D was performed over all conductive ar-GNRs FETs on Si/SiO\(_2\) and BN. The error in mean was estimated using 90 % \( t \)-values. The averaging of low-temperature “OFF” current (Figure 1.3C) was performed over two sets of 6 devices measured in range 77 – 300 K for ar-GNRs on both Si/SiO\(_2\) and BN substrates. The error in mean for the “OFF” current was estimated using 90 % \( t \)-values.

In contrast with ar-GNRs on both Si/SiO\(_2\) and BN substrates, ox-GNRs demonstrate very divergent electronic properties (Figure S1.14). ox-GNRs on Si/SiO\(_2\) substrates (Figure S1.14A) demonstrate a strong variation in both ON/OFF ratios, almost two orders of magnitude, and the position of the charge neutrality point ranging from 0 V to -30 V gate voltage values, which approximately corresponds to 0 to \( 8 \times 10^9 \) m\(^{-1}\) linear hole concentration range. For ox-GNRs on BN substrates (Figure S1.14B) the charge neutrality point positions are much more consistent, with a linear hole concentration range \( 5 \times 10^9 \) to \( 9 \times 10^9 \) m\(^{-1}\), however, ON/OFF variation is still substantial.
Figure S1.14. Electronic properties of individual ox-GNRs on (A) Si/SiO$_2$ and (B) BN substrate. Different colors denote different devices.

The charge neutrality point for devices on BN substrates was consistently shifted to negative gating voltages (high linear hole concentrations) both for ox-GNRs and ar-GNRs. Similar behavior was reported for CVD graphene devices on BN (ref. 24) and was attributed to doping since a shift of the charge neutrality point towards zero was observed for CVD graphene devices after annealing in a reducing medium. For GNRs on BN substrate, however, the charge neutrality point remained unchanged after annealing. Apparently, dopants in this case are thermally fixed up to at least 500 °C.

The results suggest that for ox-GNRs on Si/SiO$_2$ substrates, both the substrate and the edge defects produce potential fluctuations with close amplitudes. Their interaction results in randomization of both energy variation over the GNR length, leading to
ON/OFF ratio variations, and the average potential, leading to charge neutrality point variations. In the case of the ox-GNRs on BN substrates, the potential fluctuations due to edge defects dominate the potential fluctuations due to interactions with the substrate, and as a result, the overall potential profile is determined by edge defects. The average potential in this case is approximately constant over the GNR length; however, the potential variation changes from sample to sample, causing ON/OFF ratio variations. Since Si/SiO$_2$ substrate-induced potential fluctuations are comparable to fluctuations caused by edge defects in ox-GNRs, it is expected that the former will dominate over potential fluctuations caused by edge defects in ar-GNRs. Thus, the electronic properties of ar-GNRs on Si/SiO$_2$ substrates are determined predominantly by substrate interactions. The consistency of ON/OFF ratios and charge neutrality point positions could mean that the potential fluctuations caused by Si/SiO$_2$ substrates are much more uniform compared to those caused by defects introduced during oxygen RIE.

In the case of the ar-GNRs on BN substrates, both the potential fluctuations due to the edge defects and substrate interaction are rather small. The following options are considered: (1) potential fluctuations due to edge defects dominate; (2) potential fluctuations due to substrate dominate; (3) both types have close amplitudes and dominate over the bandgap, if it exists; (4) there is a true bandgap that dominates over both types of potential fluctuations. Option 3 is unlikely since in this case there would be ON/OFF and charge neutrality point variations similar to those observed for ox-GNRs on Si/SiO$_2$ substrates. Both options 1 and 2 would yield the ON/OFF ratios to be lower than those observed for ar-GNRs on Si/SiO$_2$ substrates. The reason for this is that the
fluctuations in potential due to SiO$_2$ puddles are larger than for BN puddles or ar-GNR edge puddles. The ON/OFF ratios at room temperature for ar-GNRs on BN are, however, similar to ar-GNRs on Si/SiO$_2$ substrate. Thus, the option that the ar-GNRs on BN possess a true bandgap is the most probable. It should be noted that in the case of comparable bandgap and potential fluctuations caused by edge defects and/or the BN substrate, transport properties could not be expected to be as consistent.

S.1.14. Supporting references


Chapter 2

Meniscus-Mask Lithography for Fabrication of Narrow Wires

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2.1. Introduction

Narrow metallic and semiconducting wires are important for purposes of miniaturization and harnessing of properties of materials arising from spatial confinement such as band structure distortions and conductivity quantization. Current nanowire fabrication methods can be divided into two major groups: bulk synthesis or lithographic. Bulk methods allow for the synthesis of large quantities of individual nanowires, with control over their crystallinity and sometimes even crystallographic orientation. However, as there is no facile method of positioning of these wires on an integrated circuit plane, bulk synthetic methods are not suitable for integration into the modern planar technology used by the semiconductor industry. In contrast, lithographical methods could be used in an industrial process, but resolution of conventional lithography is limited by the lithographic tool and resists. Even though narrow nanowires could be fabricated by fine-tuned electron beam lithography, their quality remains low.
A separate approach, implemented, for example, in sidewall image transfer technique,\textsuperscript{18-20} uses deposition of the mask on the sidewall of some pattern, as it gives precise control over the resulting nanowire width. Modern film deposition methods such as atomic layer deposition allow for control over the film thickness within a single atomic layer. However, deposition of material onto closely located sidewalls could be difficult due to shadowing and capillary effects.\textsuperscript{21-23} Meniscus-mask lithography (MML), was shown for fabrication of graphene nanoribbons.\textsuperscript{24} This method is based on projection of either electron-beam or photolithography patterned sidewalls using adsorbed water as the mask. In this paper we extend MML to a wide variety of metals, metal oxides and other semiconductors, and further demonstrate that more complex structures, such as junctions and crossbars, can be fabricated.

\subsection*{2.2. Results and discussion}

The general process scheme resembles the one described previously\textsuperscript{24} and is schematically represented in Figure 2.1A. In a typical process a thin film of target material is covered with resist film (1) and patterned so that the edges of the pattern are located at the designated nanowire positions (2). Then, directional dry etching is performed (3) in order to remove material exposed through the lithographic pattern. After that, the sacrificial metal layer is deposited (4) and the resist layer is stripped (5). Finally, a second directional dry etching is performed (6) and the material exposed through the sacrificial metal layer mask is etched, and then the sacrificial metal mask is wet etched (7). During the second dry etching (step 6) the narrow region nearby the sacrificial metal mask is protected by a thin adsorbed water layer which is slightly thicker nearby the
wedge, resulting in consistent formation of long, narrow, precisely positioned nanowires of the target material.

**Figure 2.1.** MML fabrication of wires. (A) MML fabrication scheme. Examples of wires, low and high magnification SEM images: (B, F) Si wires; (C, G) SiO$_2$ wires; (D, H) Au wires; (E, I) Cr wires; (J, N) W wires; (K, O) Ti wires; (L, P) TiO$_2$ wires; (M, Q) Al wires. The scale bars for images (B-E) and (J-M) are 1 μm and for images (F-I) and (N-Q) are 100 nm.
The MML process could be used to fabricate the wires out of a number of materials. We have successfully prepared Si wires (Figures 2.1B, F), SiO₂ wires (Figures 2.1C, G), Au wires (Figures 2.1D, H) with an average width of 7.0 ± 1.0 nm, Cr wires (Figures 2.1E, I) with an average width of 11.4 ± 1.0 nm, W wires (Figures 2.1J, N) with an average width of 15.9 ± 1.0 nm, Ti wires (Figures 2.1K, M) with an average width of 9.8 ± 1.0 nm, TiO₂ wires (Figures 2.1L, O) with an average width of 10.9 ± 1.0 nm, Al wires (Figures 2.1M, P) with an average width of 6.9 ± 1.0 nm. Additionally, we previously reported similar fabrication of Pt wires (average width 11.7 ± 1.0 nm). The etching conditions utilized and other fabrication details are summarized in Tables S2.1-S2.3. The distributions of wire widths are shown in Figure S2.1, and detailed statistical parameters of resulting wires are summarized in Table S2.4.

Typical AFM images of MML fabricated nanowires are shown in Figure S2.2. The nanowires height is uniform over their length, and is equal to or slightly exceeding the thickness of the starting target material film.

In order to demonstrate the versatility of the MML fabrication method, we have thoroughly analyzed the critical process step – the dry etching – demonstrating the water meniscus mask stability against different types of plasma processes.

Reactive ion etching (RIE) is a conventionally accepted term for all plasma etching processes, however, there are several different phenomena occurring in plasma discharges leading to materials etching: (1) physical sputtering when the target material gets removed from the substrate due to bombardment with highly energetic ions, (2) chemical etching when plasma species react with the target material on their own, (3) ion-
enhanced energetic etching when plasma species react with the substrate only if sufficiently accelerated toward it and (4) ion-enhanced inhibitor etching when plasma species cause the formation of a protective inhibitor layer everywhere except the areas exposed to ion flux. All of those mechanisms are directional except chemical etching which works isotropically. Methods relying solely on physical sputtering are easily distinguishable from chemically assisted directional plasma etching. However, ion-enhanced energetic and ion-enhanced inhibitor mechanisms typically coexist in directional dry etching processes.

The typical example of physical sputtering removal of material is etching of noble metals (Au, Pt) with Ar plasma. Sputtering works on diverse materials, however, the typical etch rates are low, and other etching processes are usually preferred for chemically active materials. Redeposition is a common problem for physical sputtering and occurs when sputtered substrate atoms/clusters are not removed from the system, but return to the substrate or stick to the mask walls. Although we successfully fabricated narrow Au and Pt wires in the MML process, their yield was limited by random formation of much thicker irregular objects (Figure S2.3) which we attributed to redeposition effects. The size of those objects suggests they were mostly formed during the first etching step, and indeed we were able to minimize this effect by adjusting the lithography conditions to make the PMMA sidewall slope outward enabling better removal of sputtered material.

Unlike sputtering which is always directional, the chemically assisted dry etching processes are characterized both by the etch rate and the undercut, which is the relative
impact of isotropic etching, i.e. the etching that occurs in a direction parallel to the substrate. For MML fabrication of narrow wires, highly directional processes are desired, as the undercut affects the width of the resulting wires up to their complete disappearance. Unlike the exact process mechanism, undercutting is well-documented in the literature for different plasma etching processes. Preferred compositions of plasma are well known for various materials, for example, fluorine-based plasmas are widely utilized to etch Si (refs. 28, 29), SiO₂ (refs. 30, 31), W (ref. 32), Ti (ref. 33), TiO₂ (ref. 34) and chlorine-based plasmas are used for etching of Si (refs. 28, 29, 35), W (ref. 18), Al (ref. 36), Cr (ref. 37). We have found that wire formation occurs independent of the exact directional etching mechanism for all those systems (Figure 2.1).

In some particularly aggressive plasmas, such as Cl₂/O₂ or Cl₂/O₂/N₂ etching of Cr, and Cl₂/Ar etching of W, an important issue of resist erosion manifested itself in formation of shelf-like structures adjacent to the wire (Figure S2.4). It is observed on the side of the wire exposed in the first etching step, and could not be avoided simply by increasing the first etching time. We were able to remediate this effect by adding a physical sputtering step immediately after the first etching step, as sputtering does not withdraw the resist edge and removes residuals of exposed metal which otherwise would form the shelf.

In order to compare the effect of different etching methods on nanowire formation, we used Si and SiO₂ as model systems. The etching of these materials is well-studied, they are readily available commercially in the form of silicon-on-insulator and thermal SiO₂ coated Si wafers, and they have a smooth uniform surfaces.
Figure 2.2. Si and SiO$_2$ model wires produced with MML. (A-F) Width distribution and typical SEM images of Si wires fabricated with: (A, D) Ar/Cl$_2$ etching; (B, E) HBr/Cl$_2$ etching; (C, F) SF$_6$/O$_2$ etching. (G-L) Width distribution and typical SEM images of SiO$_2$ wires fabricated with: (G, J) CHF$_3$/O$_2$ etching; (H, K) CF$_4$/O$_2$ etching; (I, L) SF$_6$/O$_2$ etching. (M-N) Variation of SiO$_2$ wires width (M) and height (N) with etching time for SF$_6$/O$_2$ etching.

Figures 2.2A-F shows the width distributions and corresponding typical SEM images of Si wires prepared with different etching processes. The average width of Si wires is $15.2 \pm 1.0$ nm for Ar/Cl$_2$ etching, $15.4 \pm 1.1$ nm for HBr/Cl$_2$ etching and $16.4 \pm 1.1$ nm for SF$_6$/O$_2$ etching. In the Ar/Cl$_2$ process an impenetrable non-volatile layer
of SiCl\textsubscript{x} is formed on the Si surface, and the process directionality is achieved due to argon ion bombardment volatilizing SiCl\textsubscript{x} from the bottom.\textsuperscript{25,28} The process of HBr/Cl\textsubscript{2} etching is similar, but the passivating layer contains Br as well.\textsuperscript{28} In the SF\textsubscript{6}/O\textsubscript{2} process, the SiO\textsubscript{2}F\textsubscript{y} film is sputtered from the bottom and redeposited on the sidewalls resulting in etching directionality.\textsuperscript{25,28,29} For the SF\textsubscript{6}/O\textsubscript{2} etching procedure we measured a wider wire width distribution than for other procedures, however, the average wire widths for all three etching methods are very close, indicating that the exact etching mechanism or chemistry involved do not significantly affect the result.

Figures 2.2G-L shows the width distributions and corresponding typical SEM images for SiO\textsubscript{2} wires prepared with different etching processes and in different etching instruments. The average width of SiO\textsubscript{2} wires is 7.9 ± 1.0 nm for CHF\textsubscript{3}/O\textsubscript{2} etching, 8.3 ± 1.0 nm for CF\textsubscript{4}/O\textsubscript{2} etching and 8.0 ± 1.0 nm for SF\textsubscript{6}/O\textsubscript{2} etching. All three processes result in formation of passivating layers on the walls of etched trenches, however, the composition of these passivating layers is different.\textsuperscript{18,29} Also, the CHF\textsubscript{3}/O\textsubscript{2} and CF\textsubscript{4}/O\textsubscript{2} processes work through formation of fluorocarbon film on the etched plane\textsuperscript{18} while the SF\textsubscript{6}/O\textsubscript{2} process depends mostly on fluorine reactivity.\textsuperscript{25,29} The width distributions of wires fabricated using those different processes, however, are similar. Moreover, these results were reproduced in four different RIE instruments showing the method stability.

For the SF\textsubscript{6}/O\textsubscript{2} etching process, we have tested the wire cross-section evolution with etching time. Figure 2.2M shows the average width of the wires which do not change significantly, and Figure 2.2N shows the average height of the wires which increases linearly with etching time. This suggests that the water mask is sufficiently

stable to provide wires of arbitrary height over a wide range. This formation of arbitrary height wires comes with certain requirements: (1) the etching procedure needs to be adjusted so as not to damage the resist or sacrificial metal mask before the desired etch depth is achieved, and (2) the process undercut is minimal.

In order to verify the apparent continuity of the wires and to characterize their electronic transport behavior, we patterned leads onto the wires (Figures S2.5-S2.7). Most types of wires (Au, Ti, Cr, W, Si) were conductive, and Si wires were operating as FET devices when backgated by the handling Si layer (Figure S2.7). However, for native oxide forming metals (Ti, Cr, W), the conductivity was several orders of magnitude lower than expected which could originate from oxidation of the outer wire region. Al wires were found to be non-conductive, most probably, for the same reason.
Figure 2.3. Crossbar structures prepared with MML. (A-B) Schematics of crossbar structure fabrication for (A) homogeneous (both wires are made out of the same material) and (B) heterogeneous (wires are made of different materials) crossbars. (C) SEM image of homogeneous SiO$_2$-SiO$_2$ crossbars. Scale bar is 5 μm. (D) AFM image of homogeneous SiO$_2$ crossbars. Scale bars are (x) 1 μm, (y) 1 μm, (z) 125 nm. (E) SEM image of heterogeneous Si-Pt crossbar structure. Scale bar is 5 μm. Inset: magnified image of individual wire intersection. Note that bright speckles on Pt wire are traces of redeposition, the actual Pt wire is a thin vertical line on the image (see text). Scale bar is 1 μm.
The fabrication method that we demonstrated here permits not only arbitrary shaped individual wires or parallel arrays of those, but also crossbars of wires, both homogeneous with the same material wires intersecting (Figure 2.3A), and heterogeneous with different wire materials wires intersecting (Figure 2.3B). SiO$_2$/SiO$_2$ homogeneous crossbar structures (Figures 2.3C-D, S2.8) were prepared by repeating the same MML fabrication sequence twice, one pattern array perpendicular to another. The magnified image of the intersection site (Figure S2.8A inset) shows that intersecting wires are connected. The AFM image (Figures 2.3D, S2.8B-C) shows that both wires have approximately the same height, and the intersection point is elevated by the height of one wire over another wire, thus twice that elevated over the bottom of the chip. Thus the structure could also be interpreted as a regular array of narrow tips. A Si/Pt heterogeneous crossbar structure (Figure 2.3E) was prepared by depositing Pt onto an array of MML fabricated nanowires and repeating the MML procedure with a pattern perpendicular to the Si wires. Bright speckles on Pt wire are traces of redeposition which was significant here in both etching steps of Pt wire preparation as the Si wires height is $\sim 100$ nm; the actual Pt wire is a thin vertical line on the image.

### 2.3. Conclusions

In conclusion, we demonstrated that the MML approach is suitable for the fabrication of narrow nanowires from Si, SiO$_2$, Au, Cr, W, Ti, TiO$_2$, Al. A wide range of materials and etching processes suggest the applicability of MML to a wide array of materials used in modern planar technology. Also we discussed some fabrication issues specific to materials and processes used and demonstrated that they could be avoided or
remediated. Crossbar structures show that junctions of nanowires could also be fabricated. Thus, MML provides all the building blocks required for fabrication of a host of nanowire structures over various geometries.

2.4. Experimental

Metal wires samples were made using polished, single-sided, heavily p-doped Si wafers with a 300 nm thermal SiO$_2$ layer (Silicon Quest International) as substrates. Starting metal films were deposited onto substrates via sputtering (Denton Desk V Sputter system) or e-beam evaporation. These Si/SiO$_2$ substrates were also used as a starting film in preparation of SiO$_2$ nanowires. Silicon on insulator (SOI) wafers with a 100 nm p-doped <100> oriented device layer (resistivity 8.5-11.5 $\Omega\cdot$cm), a 200 nm oxide layer and a 500 $\mu$m heavily p-doped handling layer were used as a starting material for Si nanowire fabrication. TiO$_2$ films were deposited on Si/SiO$_2$ wafers using an atomic layer deposition system (courtesy of Dr. M. Thomas and Dr. P. J. Joseph, Georgia Tech University). Electron-beam lithography patterning and SEM imaging were performed using a JEOL 6500F scanning electron microscope. Images were acquired at a 15 kV accelerating voltage in SE mode with no additional conductive coating applied. Lithography patterns were written using PMMA 950 A resist at 30 kV accelerating voltage and 300 pA beam current. Reactive ion etching was performed using a Trion RIE instrument, Oxford RIE 80 instrument, Oxford ICP 100 instrument and 790 Plasma Therm RIE instrument. The detailed description of etching conditions is given in the Supporting Information section.
2.5. Acknowledgments

Authors thank the University of Texas Microelectronics Research Center and University of Houston Nanofabrication Facility for access to clean room equipment, and Dr. M. Thomas and Dr. P. J. Joseph, Georgia Tech University for ALD preparation of TiO$_2$ wafers. This work was funded through the Air Force Office of Scientific Research (FA9550-14-1-0111).

2.6. References


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2.6. Supporting Information

S.2.1. Fabrication of nanowires

The thickness of the starting metal films was measured with AFM using a pre-patterned dummy sample on which the metal was deposited alongside with actual samples. The AFM measurements were performed in tapping mode using a Bruker Multimode 8 instrument with TESPA-V2 tips or a Digital Instrument Nanoscope IIIA with NanoSensors tips, type PPP-NCH-W. The thicknesses of the SOI device layer, SiO$_2$ layer and TiO$_2$ layer were provided by suppliers.

The PMMA resist layer was spin-coated onto substrates at 3000 rpm for 40 s or at 1000 rpm for 90 s, the latter being used for cases where longer etching processes were required, and thinner resist degraded too fast to sustain them. Thicker resist was used for all Si wires fabrication, Cr, W, Ti, Al wires fabrication and some SiO$_2$ wires fabrications requiring longer etching.

The sacrificial metal mask material was chosen to be reasonably stable in RIE conditions used to etch the target material and to be wet etched selectively with respect to the target material and the substrate. The mask thickness was chosen in such a way that it
elevates at least 20 nm over the surface of the starting film in order to ensure the meniscus formation. In the case of crossbar structure fabrication, a minimum 20 nm mask elevation over the highest substrate feature was chosen. We used Al masks (both sputtered and e-beam evaporated one worked similarly), and e-beam evaporated Cr masks. Al masks were wet etched using H₃PO₄/HNO₃/CH₃COOH/H₂O (80/5/5/10 vol. %) mixture, Cr masks were wet etched using commercial Cr-etch-200 solution (NB Technologies GmbH).

The etching steps for all Si wire fabrication experiments were performed using Oxford ICP 100 instrument, and the process parameters are given in Table S2.1.

Table S2.1. Etching conditions and mask material for Si wires fabrication. Oxford ICP 100 instrument was used for etching in all cases.

<table>
<thead>
<tr>
<th>Metal mask material</th>
<th>RIE conditions, identical for 1st and 2nd etching</th>
<th>Metal mask material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, from device layer of SOI wafer, named “Ar/Cl₂ etched” in text</td>
<td>pressure = 20 mTorr; RIE power = 150 W; Ar flow = 50 sccm; Cl₂ flow = 5 sccm; process time = 240 s; typical bias = 380 V;</td>
<td>Cr, e-beam evaporated</td>
</tr>
<tr>
<td>Si, from device layer of SOI wafer, named “HBr/Cl₂ etched” in text</td>
<td>pressure = 30 mTorr; RIE power = 100 W; HBr flow = 50 sccm; Cl₂ flow = 10 sccm; process time = 180 s; typical bias = 180 V;</td>
<td>Cr, e-beam evaporated</td>
</tr>
<tr>
<td>Si, from device layer of SOI wafer, named “SF₆/O₂ etched” in text</td>
<td>pressure = 10 mTorr; RIE power = 100 W; SF₆ flow = 81 sccm; O₂ flow = 9 sccm; process time = 60 s; typical bias = 170 V;</td>
<td>Al, sputtered or e-beam evaporated</td>
</tr>
</tbody>
</table>
The process parameters for SiO$_2$ wire fabrication are given in Table S2.2. The metal mask was sputtered or e-beam evaporated Al in all cases. The CHF$_3$/O$_2$ process was tested in a Trion RIE instrument and Oxford RIE 80 instrument, and the CF$_4$/O$_2$ process was tested in a Trion RIE instrument and 790 Plasma Therm instrument. In both cases, the results were statistically indistinguishable.

We also tested SF$_6$/O$_2$ etched SiO$_2$ wire fabrication with Cr masks, and the result was similar to when we used the Al mask, as expected from our previous work.$^1$
**Table S2.2.** Etching conditions used in different RIE instruments for SiO$_2$ wires fabrication. The metal mask was sputtered or e-beam evaporated Al in all cases.

<table>
<thead>
<tr>
<th>RIE conditions, identical for 1$^{st}$ and 2$^{nd}$ etching</th>
<th>RIE instrument used</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$, from oxide layer of Si/SiO$_2$ wafer, named “CHF$_3$/O$_2$ etched” in text</td>
<td>pressure = 150 mTorr; RIE power = 150 W; CHF$_3$ flow = 40 sccm; O$_2$ flow = 10 sccm; process time = 100 s;</td>
</tr>
<tr>
<td>SiO$_2$, from oxide layer of Si/SiO$_2$ wafer</td>
<td>pressure = 150 mTorr; RIE power = 150 W; CHF$_3$ flow = 40 sccm; O$_2$ flow = 10 sccm; process time = 100 s; typical bias = 330 V</td>
</tr>
<tr>
<td>SiO$_2$, from oxide layer of Si/SiO$_2$ wafer</td>
<td>pressure = 100 mTorr; RIE power = 100 W; CHF$_3$ flow = 25 sccm; O$_2$ flow = 15 sccm; process time = 45 s;</td>
</tr>
<tr>
<td>SiO$_2$, from oxide layer of Si/SiO$_2$ wafer, named “CF$_4$/O$_2$ etched” in text</td>
<td>pressure = 100 mTorr; RIE power = 100 W; CF$_4$ flow = 30 sccm; O$_2$ flow = 5 sccm; process time = 40s;</td>
</tr>
<tr>
<td>SiO$_2$, from oxide layer of Si/SiO$_2$ wafer</td>
<td>pressure = 100 mTorr; RIE power = 100 W; CF$_4$ flow = 30 sccm; O$_2$ flow = 5 sccm; process time = 40s; typical bias = 230 V;</td>
</tr>
<tr>
<td>SiO$_2$, from oxide layer of Si/SiO$_2$ wafer, named “SF$_6$/O$_2$ etched” in text</td>
<td>pressure = 20 mTorr; RIE power = 100 W; SF$_6$ flow = 25 sccm; O$_2$ flow = 5 sccm; typical process time = 40s; typical bias = 185 V;</td>
</tr>
</tbody>
</table>

The process parameters for other wire fabrication are given in Table S2.3. For the chemically assisted etching processes in some cases we had to use steps of different duration for the 1$^{st}$ and 2$^{nd}$ etching in order to remove all material from both sides of the pattern. The difference in required etching step duration could be explained by the
loading effect,\(^3\) or etch rate dependence on minor surface contaminants,\(^4\) or etch rate variability due to native oxide layer stoichiometry.\(^5\) The Al wire fabrication was tested both with thin and thick Al starting films, the widths of the resulting wires were statistically indistinguishable.

**Table S2.3.** Etching conditions and mask material for wires fabrication. Oxford ICP 100 instrument was used for etching in all cases.

<table>
<thead>
<tr>
<th>Material</th>
<th>RIE conditions, 1(^{st}) etching step</th>
<th>RIE conditions, 2(^{nd}) etching step</th>
<th>Metal mask material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au, 15 nm, sputtered</td>
<td>pressure = 15 mTorr; RIE power = 150 W; Ar flow = 50 sccm; process time = 120 s; typical bias = 370 V</td>
<td>Al, sputtered or e-beam evaporated</td>
<td></td>
</tr>
<tr>
<td>Pt, 15 nm, sputtered</td>
<td>pressure = 15 mTorr; RIE power = 150 W; Ar flow = 50 sccm; process time = 90 s; typical bias = 400 V</td>
<td>Al, sputtered or e-beam evaporated</td>
<td></td>
</tr>
<tr>
<td>Cr, 30 nm, e-beam evaporated</td>
<td><strong>Stage 1:</strong> pressure = 50 mTorr; RIE power = 100 W; Cl(_2) flow = 50 sccm; O(_2) flow = 50 sccm; N(_2) flow = 50 sccm; process time = 105 s; typical bias = 200 V</td>
<td>pressure = 50 mTorr; RIE power = 100 W; Cl(_2) flow = 50 sccm; O(_2) flow = 50 sccm; N(_2) flow = 50 sccm; process time = 105 s; typical bias = 200 V</td>
<td>Al, sputtered or e-beam evaporated</td>
</tr>
<tr>
<td></td>
<td><strong>Stage 2:</strong> pressure = 15 mTorr; RIE power = 150 W; Ar flow = 50 sccm; process time = 180 s; typical bias = 380 V</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S2.3 (continued).

<table>
<thead>
<tr>
<th>Material</th>
<th>RIE conditions, 1\textsuperscript{st} etching step</th>
<th>RIE conditions, 2\textsuperscript{nd} etching step</th>
<th>Metal mask material</th>
</tr>
</thead>
<tbody>
<tr>
<td>W, 20 nm, sputtered</td>
<td><strong>Stage 1:</strong> pressure = 10 mTorr; RIE power = 150 W; Cl\textsubscript{2} flow = 12 sccm; Ar flow = 48 sccm; process time = 90 s; typical bias = 415 V</td>
<td>pressure = 10 mTorr; RIE power = 150 W; Cl\textsubscript{2} flow = 12 sccm; Ar flow = 48 sccm; process time = 120 s; typical bias = 415 V</td>
<td>Al, sputtered or e-beam evaporated</td>
</tr>
<tr>
<td></td>
<td><strong>Stage 2:</strong> pressure = 15 mTorr; RIE power = 150 W; Ar flow = 50 sccm; process time = 120 s; typical bias = 380 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti, 30 nm, e-beam evaporated</td>
<td>pressure = 20 mTorr; RIE power = 100 W; SF\textsubscript{6} flow = 80 sccm; O\textsubscript{2} flow = 20 sccm; process time = 90 s; typical bias = 180 V</td>
<td>pressure = 20 mTorr; RIE power = 100 W; SF\textsubscript{6} flow = 80 sccm; O\textsubscript{2} flow = 20 sccm; process time = 180 s; typical bias = 180 V</td>
<td>Cr, e-beam evaporated</td>
</tr>
<tr>
<td>TiO\textsubscript{2}, 7 nm, ALD</td>
<td>pressure = 20 mTorr; RIE power = 100 W; Ar flow = 20 sccm; SF\textsubscript{6} flow = 35 sccm; process time = 40 s; typical bias = 200 V</td>
<td>pressure = 20 mTorr; RIE power = 100 W; Ar flow = 20 sccm; SF\textsubscript{6} flow = 35 sccm; process time = 60 s; typical bias = 200 V</td>
<td>Al, sputtered or e-beam evaporated Cr, e-beam evaporated</td>
</tr>
<tr>
<td>Al, 7 nm, sputtered, “thin Al wires”</td>
<td>pressure = 30 mTorr; RIE power = 125 W; Cl\textsubscript{2} flow = 10sccm; BCl\textsubscript{3} flow = 40 sccm; process time = 40 s; typical bias = 270 V</td>
<td>pressure = 30 mTorr; RIE power = 125 W; Cl\textsubscript{2} flow = 10sccm; BCl\textsubscript{3} flow = 40 sccm; process time = 40 s; typical bias = 270 V</td>
<td>Cr, e-beam evaporated</td>
</tr>
<tr>
<td>Al, 50 nm, e-beam evaporated, “thick Al wires”</td>
<td>pressure = 30 mTorr; RIE power = 125 W; Cl\textsubscript{2} flow = 10sccm; BCl\textsubscript{3} flow = 40 sccm; process time = 120 s; typical bias = 270 V</td>
<td>pressure = 30 mTorr; RIE power = 125 W; Cl\textsubscript{2} flow = 10sccm; BCl\textsubscript{3} flow = 40 sccm; process time = 120 s; typical bias = 270 V</td>
<td>Cr, e-beam evaporated</td>
</tr>
</tbody>
</table>
S.2.2. Nanowires width distribution

In order to determine wire widths, we performed a procedure similar to the one described previously. First, the grayscale intensity profiles were acquired from high magnification SEM images perpendicular to the wire direction using ImageJ software. Then the width was determined as FWHM of the Gauss peaks fitting these grayscale profiles. For each type of wire, a minimum of 24 profiles was measured. Figure S2.1 presents the width distribution histograms for various nanowires. The bin size is 1 nm. Table S2.4 summarizes the distributions parameters for the wires in Figure 2.2 and Figure S2.1.

**Figure S2.1.** Width distribution histograms for (A) W wires; (B) Cr wires; (C) Ti wires; (D) TiO$_2$ wires; (E) Au wires; (F) thin Al wires.
Note that this width measurement method allows for the determination of width distribution, but the absolute value of the mean wire width derived is not accurate, since grayscale wire profiles can potentially depend on SEM imaging effects, such as sample and substrate conductivity, electron work function, etc. Therefore, the width of wires made out of the same material could be compared to some extent, but the width of wires made out of different materials should be cautiously compared.

### Table S2.4. Wires width distribution parameters.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean width, nm</th>
<th>Width 1&lt;sup&gt;st&lt;/sup&gt; quartile, nm</th>
<th>Width 3&lt;sup&gt;rd&lt;/sup&gt; quartile, nm</th>
<th>Number of profiles analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si wires, Ar/Cl&lt;sub&gt;2&lt;/sub&gt; etched</td>
<td>15.2 ± 1.0</td>
<td>13.4</td>
<td>16.4</td>
<td>62</td>
</tr>
<tr>
<td>Si wires, HBr/Cl&lt;sub&gt;2&lt;/sub&gt; etched</td>
<td>15.4 ± 1.1</td>
<td>13.7</td>
<td>16.9</td>
<td>59</td>
</tr>
<tr>
<td>Si wires, SF&lt;sub&gt;6&lt;/sub&gt;/O&lt;sub&gt;2&lt;/sub&gt; etched</td>
<td>16.4 ± 1.1</td>
<td>13.9</td>
<td>18.9</td>
<td>53</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; wires, CHF&lt;sub&gt;3&lt;/sub&gt;/O&lt;sub&gt;2&lt;/sub&gt; etched</td>
<td>7.9 ± 1.0</td>
<td>6.7</td>
<td>8.7</td>
<td>24</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; wires, CF&lt;sub&gt;4&lt;/sub&gt;/O&lt;sub&gt;2&lt;/sub&gt; etched</td>
<td>8.3 ± 1.0</td>
<td>7.6</td>
<td>8.8</td>
<td>50</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; wires, SF&lt;sub&gt;6&lt;/sub&gt;/O&lt;sub&gt;2&lt;/sub&gt; etched</td>
<td>8.0 ± 1.0</td>
<td>7.1</td>
<td>8.8</td>
<td>83</td>
</tr>
<tr>
<td>W wires</td>
<td>15.9 ± 1.0</td>
<td>14.7</td>
<td>17.0</td>
<td>44</td>
</tr>
<tr>
<td>Cr wires</td>
<td>11.4 ± 1.0</td>
<td>10.6</td>
<td>12.3</td>
<td>45</td>
</tr>
<tr>
<td>Ti wires</td>
<td>9.8 ± 1.0</td>
<td>8.6</td>
<td>10.7</td>
<td>132</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; wires</td>
<td>10.9 ± 1.0</td>
<td>10.3</td>
<td>11.2</td>
<td>30</td>
</tr>
<tr>
<td>Au wires</td>
<td>7.0 ± 1.0</td>
<td>6.2</td>
<td>7.7</td>
<td>48</td>
</tr>
<tr>
<td>Al wires</td>
<td>6.2 ± 1.0</td>
<td>5.6</td>
<td>6.7</td>
<td>43</td>
</tr>
</tbody>
</table>

#### S.2.3. AFM of nanowires

AFM images of fabricated nanowires and corresponding height profiles are shown in Figure S2.2. The average wire height in all cases is equal to or slightly exceeds the thickness of the starting film. The latter case we attribute to slight overetching, as the
SiO$_2$ layer is susceptible to etching in all plasmas used. In order to ensure that all target material except the wire was removed from the substrate, and that the top of the wire corresponds to the top of the starting film, the AFM images were taken after every fabrication step.

**Figure S2.2.** AFM images and corresponding AFM profiles for wires fabricated via MML method. (A, I) Si wires; (B, J) SiO$_2$ wires; (C, K) Au wires; (D, L) Cr wires; (E, M)
W wires; (F, N) Ti wires; (G, O) TiO$_2$ wires; (H, P) thin Al wires. The lateral scale bar is 1 μm for all images. The height range in the images is (A) 150 nm; (B) 45 nm; (C) 30 nm; (D) 50 nm; (E) 75 nm; (F) 60 nm; (G) 30 nm; (H) 20 nm.

S.2.4. Redeposition

In physical sputtering processes along with the formation of uniform narrow wires, we observed spontaneous formation of much wider and thicker objects that are either planar or vertically standing. We attribute formation of those structures to redeposition effects common in physical sputtering.$^{6,7}$

The schematics of the redeposition process is shown in Figure S2.3A. During the first etching step, etched metal particles are not completely removed from the system, but get partially redeposited on the PMMA mask sidewalls forming irregular fin-like structures with a height up to the PMMA mask thickness. After PMMA removal, these structures may remain vertically standing or fall on the side interfering with wires formation process (Figures S2.3B-D). During the second etching step, these fallen fins are protecting target material adjacent to the mask edge, which results in formation of much wider wires, and during the wet etching step some of those fins may get removed or moved along the substrate (Figure S2.3C). These structures could also be observed in AFM images (Figures S2.3E-G), and the height of the vertically standing fin-like structures (Figure S2.3G, solid line) greatly exceeds the height of a normal wire (Figure S2.3G, dashed line). The resulting structures do not change significantly with increase in etching time for both etching steps. We speculate that redeposition happens in
the first etching step since the width/height of redeposited structures is comparable only to the PMMA layer thickness. The metal mask thickness is much lower, and therefore the redeposition is less likely to happen in the second step, where the resulting fins would be much smaller.

Figure S2.3. Redeposition problem for materials etched via physical sputtering (Pt and Au). (A) Scheme of redeposit formation (first of two etching steps). The metal is removed from exposed area and gets deposited on resist sidewalls, and after resist removal remains on wires as a thick stripe of parasitic material. (B-D) SEM images of Pt
wire regions affected by material redeposition. Scale bar is 200 nm for images (B-C) and 100 nm for image (D). (E-F) AFM images of Pt wires affected by material redeposition. The height range in the images is (E) 200 nm and (F) 150 nm. The lateral scale bars are 500 nm. (G) AFM profiles for image (E), (1) corresponds to a region with redeposit, (2) corresponds to normal wire. (H) Variation in amounts of redeposit with lithography dose for the case of Au wires. Insets show typical resist profiles for underexposure (right) and overexposure (left). The lithography dose corresponding to normal exposure is \(~320\ \mu\text{C/cm}^2\).

To remediate this effect we varied the lithography dose which influences the PMMA sidewall profile enabling easier escape of metal particles (Figure S2.3H). The general dependence of the PMMA sidewall profile on dose for electron-beam lithography is well-studied and modeled.\(^8,9\) In the normal exposure case, the resist walls are expected to be nearly vertical, while underexposure results in the walls being sloped outwards (left inset in Figure S2.3H) and overexposure results in the walls being sloped inwards (right inset in Figure S2.3H). On the same sample chip with Au wires, for various lithography doses, we measured the ratio of the length of wires unaffected by redeposition to the overall length of wires. We observed very few regions affected by redeposition for relatively low lithography doses, and a sharp increase in redeposit amount for higher doses (Figure S2.3H), with a rollover point \(~320\ \mu\text{C/cm}^2\) which corresponds closely to the normal exposure dose for the instrument used. Thus random redeposition effects could be efficiently minimized.
S.2.5. Shelf defect structure formation

For Cr and W wires we observed the formation of what we term the shelf defect structure (Figure S2.4). This is a shallow region adjacent to the normal wire on the side exposed during the first dry etching step (Figures S2.4B, D). We explain the formation of this defect by resist degradation\(^\text{10}\) which is a common problem in chemically assisted etching processes, especially those involving plasmas with high content of oxygen or chlorine. Cr and W are known to be difficult to etch and require harsh plasma conditions.\(^\text{11-13}\)

Figure S2.4. Resist erosion leading to shelf structure formation. (A) Suggested scheme of the shelf formation process. (B) Cr wires with shelf (thick dark shade noted with arrow).
During such processes, resist becomes etched not only vertically, but also parallel to the substrate, and as a result, the resist edge withdraws from its initial position, exposing new regions of target material. Those newly exposed target material regions are not entirely removed during the 1st etching step, forming a shallow underetched region (shelf defect structure) on the side of a normal wire when the wire fabrication process is completed. Schematically this process is shown in Figure S2.4A. We observed that the shelf structure formation could not be avoided by longer chemically assisted etching steps, since the resist degradation continues to withdraw the resist edge through such a process.

In order to remediate this effect, we performed the first etching step in two stages: the first one was chemically assisted etching suitable for a given material which was intended to remove the bulk of the target material and the second one was a physical sputtering step with Ar plasma intended to remove remaining newly exposed target material without further withdrawing the resist edge (process details are given in Table S2.3). Since both W and Cr are remarkably robust, etching with only Ar plasma would be highly inefficient. As the amount of material removed is small, the redeposition in such cases was found to be insignificant.

Figures S2.4B-C compare low magnification SEM images of Cr wires with and
without a shelf defect structure, which manifests itself in Figure S2.4B as a darker region adjacent to the top side of the wire. Similarly, Figures S2.4D-E compare high magnification SEM images of W wires with and without a shelf structure.

S.2.6. Conductivity of nanowires

To study nanowire continuity and transport properties, devices with source-drain distances ranging from 0.5 to 2 μm (Figures S2.5-S2.7) were patterned using conventional electron-beam lithography. The leads were ~ 50 nm thick sputtered Pt.

![Figure S2.5](image)

**Figure S2.5.** Transport properties of Au nanowires. (A) High magnification image of a Au nanowire device. (B) Two terminal conductivity measurement on same device.

For Au nanowires (Figure S2.5) the conductivity is linear, as in the case of Pt wires reported previously.\(^1\) The Au resistivity was calculated to be \(\sim 1.1\cdot10^{-7} \Omega\cdot m\) (assuming the wire width to be \(\sim 7\) nm, the wire height to be \(\sim 15\) nm), which is comparable to \(2.2\cdot10^{-8} \Omega\cdot m\) for bulk Au.\(^1\) As in the case of platinum wires,\(^1\) the measured
resistivity is higher most likely due to surface scattering effects.

Figure S2.6. Transport properties of metallic wires. (A) Low magnification image of Ti wire devices. (B) High magnification of Ti wire device. (C) 2-terminal (black) and 4-terminal (red) measurements for same Ti wire device. Channel length is ~ 1 μm. (D) 2-terminal (black) and 4-terminal (red) measurements for same Cr wire device. Channel length is ~ 1 μm. (E) 2-terminal measurement for typical W wire device. Channel length is ~ 0.5 μm.

For wires made from chemically active metals (Figure S2.6), measured resistance is much higher than estimated using bulk material resistivity. For Ti wires (Figures S2.6A-B) the 2-terminal and 4-terminal measurement curves differ (Figure S2.6C) indicating considerable contact resistance, likely originating from the oxidized outer layer of the wire between the Ti core of the wire and Pt pads. For a pure Ti wire with a width 9.8 nm and a height 30 nm, the resistance of a 1 μm wire is expected to be 1.3⋅10³ Ω (bulk Ti resistivity is 3.9⋅10⁻⁷ Ω·m – ref. 14), whereas mean measured resistance is (4.5 ± 1.0)⋅10⁷ Ω as derived from 4-terminal measurements data. This four orders of magnitude difference could be attributed to decreased channel thickness due to
native metal oxide formation and edge scattering. For Cr wires the difference between 2- and 4-terminal measurements is even more pronounced (Figure S2.6D), and in both cases the conductivity is obviously non-linear. The non-linearity in 4-terminal measurements could not be attributed to contact effects, however, it could be caused by partial oxidation of individual crystallites forming the wire resulting in formation of short non-conductive barriers across the channel. A similar effect was observed for W wires (Figure S2.6E). For a pure Cr wire with a width of 11.4 nm and height of 30 nm, the resistance of a 1 μm wire is expected to be 365 Ω. For a pure W wire with width 15.9 nm and height 20 nm the resistance of a 1 μm wire is expected to be 167 Ω (bulk resistivity is $12.5 \cdot 10^{-8} \Omega \cdot m$ for Cr and $5.3 \cdot 10^{-8} \Omega \cdot m$ for W – ref. 14), which is also much lower than the observed values.

For Al wires (both thin and thick ones) the measured resistance was higher than $10^{14} \ \Omega$ for a 1 μm wire length, probably indicating that the wires were completely oxidized upon exposure to the atmosphere, and should rather be addressed as Al$_2$O$_3$ wires.

**Figure S2.7.** Transport properties of Si wires. (A) SEM image of typical device, (B) SEM image of wire in this device. Scale bar is 100 nm for both images. (C) I-V curves measured at different gate voltages. (D) Gating curve for same device recorded at source-drain voltage $V_{sd} = -1 \ V$. 

Si nanowire FET devices (Figures S2.7A-B) were fabricated using Ar/Cl\textsubscript{2} etched Si wires with Pt source and drain electrodes and a Si handling layer as a backgate. Si nanowires were conductive with clearly nonlinear I-V curves (Figure S2.7C). The measurable conductivity was observed for highly negative gate voltage values and decayed upon gate voltage increase, similar to a p-type MOSFET behavior in the linear region.\textsuperscript{15} We do not have a robust explanation for the I-V curve asymmetry, however, we would expect the wires to be non-uniformly doped over the length, which may cause spontaneous formation of p-n and Schottky junctions. Interestingly, we observed similar behavior from all 6 measured Si nanowire FETs. The typical gating curve (Figure S2.7D) shows a wire threshold voltage of $\sim -20$ V, and a steep increase of conductivity at $<-20$ V.

S.2.7. Crossbar structures

Figure S2.8 shows additional images of homogeneous SiO\textsubscript{2}-SiO\textsubscript{2} crossbar structures. Those could be fabricated over large areas (Figure S2.8A), and the wire intersections are smooth (Figure S2.8A inset).

Figure S2.8. Homogeneous SiO\textsubscript{2}-SiO\textsubscript{2} crossbars. (A) Low magnification SEM image of
crossbars. Scale bar is 10 μm. Inset: magnified image of individual intersection. Scale bar is 100 nm. (B) AFM image of crossbars. Scale bar is 5 μm. The height range in the image is 70 nm. (C) AFM profile through sections (1) and (2).

The double height of the intersection site is clearly seen in the AFM image cross-section profiles (Figures S2.8B-C). The difference in height between adjacent squares arises from deeper etching in one of the etching steps during wire fabrication.

S.2.8. Supporting references


Chapter 3

Meniscus-Mask Lithography Mechanism

Note: A. S. Slesarev contributed equally to the contents of this chapter. This chapter will be used for publication after November 2014.

3.1. Introduction

In previous works we have shown advantages of the meniscus-mask lithography (MML) method for fabrication of high aspect ratio sub-10 nm nanoribbons and nanowires.\(^1\)\(^2\) The mechanism of the process relies on adsorption of water in wedges resulting in material protection from the plasma etching processes. A more descriptive mechanism of the process, the state of those adsorbates, and the parameters governing the menisci shape, however, remain unclear. MML is remarkably consistent and stable. But better understanding of capillary effects and menisci behavior might give a way to MML process tuning. Since the capillary effects should be affecting any nanostructures, the study of the precise MML mechanism could prove important for any nanolithography process. In this work, we propose a model systems that permit study of nanoscale menisci behavior. We demonstrate that changes in the lateral dimensions of the menisci support the MML mechanistic model.
3.2. Results and discussion

As a background, we establish the known experimental facts about the MML fabrication process (Figure 3.1).

Typical MML fabrication sequence consists of following steps (Figure 3.1A): first, the substrate with a layer of target material (Figure 3.1A1) is covered with hydrophobic resist film (Figure 3.1A2), in which a pattern is formed using conventional lithography procedures (Figure 3.1A3). The regions of target material exposed in pattern openings are etched using dry etching process (Figure 3.1A4), and hydrophilic sacrificial mask is deposited (Figure 3.1A5). After lift-off and upon exposure to ambient conditions, atmospheric water gets adsorbed in the wedge between target material and sacrificial mask (Figure 3.1A6). Adsorbed water forms meniscus that protects narrow line of target material nearby the edge during second dry etching step (Figure 3.1A7), and after the sacrificial mask is removed, target material wire formation could be observed (Figure 3.1A8). Typical wires produced with MML method (Figure 3.1B-C) have widths down to sub-10 nm range and virtually no limitations on aspect ration and shape.

Previous studies revealed that the water mask is sufficiently stable under high vacuum to protect the underlying substrate from plasma etching over a wide range of conditions. The width of the protected region, and therefore, the width of resulting wires, has no measurable dependence on material of sacrificial mask, provided that it is hydrophilic. This width also does not depend on sacrificial mask height if the mask is higher than certain critical value below which no protection occurs. Finally, the water has additional evaporation process activation energy compared to bulk phase, which in first
order approximation is inversely proportional to distance between adsorbed species and solid material plane.

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**Figure 3.1.** Scheme and results of the MML process. (A) MML steps sequence. Yellow: target material; green: hydrophobic resist; gray: sacrificial hydrophilic mask; blue: water meniscus. (B) SiO$_2$ nanowires array prepared using MML technique. (C) Magnified image of individual SiO$_2$ nanowire.

In this work, we are studying the general features of the MML process using SiO$_2$ wires as a simple model system. Unless otherwise stated, all experiments were performed
with SiO$_2$ wires.

An important practical question in relation to the MML method is whether we can controllably change the width of the resulting nanowires. A related question is how two menisci will behave when placed close to each other (Figures 3.1A-C). In the MML system the wedge interacts with water molecules at the scale of $< 20$ nm, which means that if another wedge with another meniscus is present in the system at this or smaller distance, the menisci can interact with both wedges. Possible interaction scenarios can be divided into three general categories: the menisci are suppressed in the presence of the additional wedge, making the resulting wires narrower (Figure 3.2A); the menisci do not interact (Figure 3.2B); or are additionally stabilized and probably overlapping, or the resulting wires are wider (Figure 3.2C). For the gaps between the wedges as small as 45 nm and 90 nm for pointed angular masks (Figure 3.2D-E) and for 85 nm gaps between parallel wedges (Figure 3.2F), no observable interaction of menisci was present, supporting the scenario shown in Figure 3.2B. Those gaps were the smallest we were able to reproducibly fabricate using conventional electron-beam lithography, and for even smaller gaps the outcome may change, providing some information on interaction character.
Figure 3.2. Closely placed wires. (A-C) Potential scenarios for menisci behavior between closely placed wedges. (A) Menisci are suppressed by two adjacent wedges. (B) Menisci interact only with the closest wedge and ignore the other one. (C) Larger menisci are stabilized by two adjacent wedges. (D-F) SEM images of SiO$_2$ nanowires formed with closely placed wedges. No menisci interaction is observed. Scale bars are 100 nm.

Although interaction of closely located wedges might alter the width of the resulting wires as depicted in Figure 3.1A, C, we did not observe this in the range of
conditions studied. Another approach to width adjustment is to change the macroscopic wettability of the target material and mask by chemical modification. To study that, we modified the gold surfaces with self-assembled monolayers of thiols. Thiols are known to bind to Au surfaces and could provide macroscopic contact angles ranging from ~ 0° for modification with HS-(CH₂)n-OH and HS-(CH₂)n-COOH (ref. 4) to over 90° for modification with HS-(CH₂)n-CH₃ (ref. 4). We tested the modification of Au surfaces with thiols in two cases: (1) Au as the target material layer in fabrication of Au wires; and (2) Au being the sacrificial mask layer in the fabrication of SiO₂ wires. In both cases we did not observe any measurable difference between samples treated with different thiols and the control samples not treated with thiols. Macroscopic contact angle and microscopic interaction of water with the substrate are governed by different phenomena and should not be directly related to each other.

All process modification we have tested before resulted in one of two outcomes: wires were either formed with the same width or were not formed at all.

**Figure 3.3.** Webbing in triple angle wedge. (A) Schematic representation of a meniscus
in triple edge and the resulting masked shape. The light blue volume corresponds to a thicker water film part that protects the substrate from plasma etching. Note that actual wedges studied could have smaller heights, in which case the thicker film could extend to the top rim of the wedge. (B-D) Modeling of webbing profiles for different angles: (B) $\theta = 90^\circ$; (C) $\theta = 60^\circ$; (D) $\theta = 45^\circ$; (E) $\theta = 30^\circ$. Note that plot (B) exactly coincides with an adsorbed water profile for a regular wedge, up to scaling factor. (F-G) SEM images of actual webbing at different magnifications. Scale bars are (F) 1 μm; (G) 100 nm. (H-I) Schematics of interpretation of images (F-G).

In order to study the detailed behavior of the meniscus mask, we produced a model that will allow us to derive more information on the phenomena involved. Indeed, the width of MML nanowires is pushing the limits of conventional scanning electron microscopy resolution and exceeds atomic force microscopy lateral resolution, while transmission electron microscopy could not be used on planar objects without complex sample preparation. Scanning tunneling microscopes usually require much more flat samples.

A triple angle, where three wedges meet at a single spot, was chosen as the model object (Figure 3.3A). To form this structure, a concave V-shaped pattern would be used as a pattern for MML. In the vertex of the “V”, three planes (substrate and two mask walls) come together forming the desired structure during the second MML process etching step.

According to a first order approximation meniscus model proposed originally, the
meniscus shape is determined by the critical additional activation energy of evaporation process $\Delta E$, for which the characteristic evaporation process time could be considered negligibly large compared to typical vacuum treatment time. The first order approximation for $\Delta E$ could be written as eq 3.1:

$$\Delta E = \frac{\zeta}{\rho} + \rho \left( \frac{1}{\rho^2} \right) \quad (3.1)$$

where $\zeta$ is the interaction constant and $\rho$ is the distance between the flat surface and the molecule. In eq 3.1 nothing is postulated about nature or origin of the $\Delta E$ except that it decreases with distance from the substrate and increases quickly near it. Eq 3.1 does not take into account the possible dependence of $\Delta E$ on the position of the molecules in plane parallel to the surface. However, the surfaces in question are not necessary infinite, and have edges, where the planes meet to form a wedge. But nevertheless we will use this equation as simplest model possible.

For a nanowire forming wedge, eq 3.2 is afforded:

$$\Delta E = \frac{\zeta}{x} + \frac{\zeta}{y} \quad (3.2)$$

where $x$ and $y$ are distances from the molecule to solid planes, and $\zeta_x$ and $\zeta_y$ are corresponding potential equation constants. The nanowire width is determined by the width of the water film layer that is sufficiently thick to resist plasma etching, by position of $x_s = w$ (Figure 3.3B) at which thickness of the layer $y$ (coordinate of the film surface molecules) is larger than some critical value $h$. Hence, if all distances are represented in the number of molecular layers, eq 3.3 is afforded:
\[ \text{trunc} \left( \frac{\xi_y}{\Delta E_s - \xi_x / x} \right) = y > h \]  

(3.3)

where \( \text{trunc}() : \mathbb{R} \mapsto \mathbb{N} \) is some truncation function, as there must be an integer number of molecules in either direction according to the cell model used, and the width of the nanowire is determined by eq 3.4:

\[ w = \max (x) : x \in \mathbb{N} ; \text{trunc} \left( \frac{\xi_y}{\Delta E_s - \xi_x / x} \right) = y > h \]  

(3.4)

But real molecules do not have cubic shapes, and distances cannot be measured in numbers of layers, at least at some distance from the substrate. Transition from this cell theory to actual molecules is not obvious and must be justified separately, which poses as complex a problem as understanding of the MML process in itself. Also, the exact form of truncation operation is not clear, while the result depends on it and on the value of \( h \) in complex and unstable way.¹

For a triple angle wedge, overall \( \Delta E \) will be determined by eq 3.5:

\[ \Delta E \approx \frac{\xi_x}{p_x} + \frac{\xi_y}{p_y} + \frac{\xi_z}{p_z} \]  

(3.5)

where \( \xi_i \) and \( \rho_i \) \((i = \{x, y, z\})\) are interaction constants and distances to each plane, correspondingly (here we generalize distances for it is relatively simple to create triple angle wedges with various angles between planes). Now, assigning plane \( z \) with the substrate plane (horizontal), and introducing the critical film thickness \( h \) again, we get the following condition of meniscus metastability (or the condition for molecules at height of at least \( h \) to stay adsorbed for the process time), eq 3.6:
\[ \frac{\xi_x}{\rho_x} + \frac{\xi_y}{\rho_y} > \Delta E_s - \frac{\xi_z}{h} = \text{const} \quad (3.6) \]

where all distances must correspond to an integer number of molecular layers in our cellular model. Assuming that the $x$ and $y$ planes are made of the same material (which is the case for all experiments described in this work, as these planes are side surfaces of metal sacrificial mask), we can rewrite eq 3.6 as eq 3.7:

\[ \frac{1}{\rho_x} + \frac{1}{\rho_y} = \text{const} \quad (3.7) \]

which, again, should be solved in integer number of molecular layers. However, the metastability condition turns out to be stable against the truncation procedure, as there is another integer eq 3.8:

\[ \rho_x + \rho_y - C \rho_x \rho_y = 0 \quad (3.8) \]

$C$ is a constant, to be solved, and its solutions could be shifted only as much as 1 molecular layer away by truncation procedure, while the macroscopic result will be the same. For simplicity, we will not discuss the quantization error and treat the system as a pseudo-continious phase from now on, remembering though that we are discussing molecular level phenomena.

Interestingly, the form of eq 3.7 closely resembles the form of eq 3.2. The physical meaning of this is that the area protected by the meniscus in the triple angle wedge could be interpreted as a cross-section of meniscus in the wedge in some unknown scale, and the cellular model used originally\(^1\) could be readily applied to the description of objects we called webbings due to their shape (Figures 3.2B-G).

It could be shown from eq 3.8, by substitution of $\rho_x$ and $\rho_y$ with their explicit
cartesian form and some rearrangement, that the webbing edge should have a shape of a
second order curve, more specifically, hyperbolic. Indeed, experimentally we observe the
hyperbolic shape of the webbing. It has a curved tip close to the triple angle tip and then
asymptotically approaches straight lines. Far from the tip, normal straight MML wires are
formed.

The canonical hyperbolic curve equation has only two parameters, and so are the
webbings if their absolute position and rotation are disregarded. The webbings could be
described by the angle $\theta$ between asymptotes (which is equal to the angle between
vertical planes and is defined by lithography with high accuracy) and distance between
hyperbola center (the intersection of the asymptotes, which generally does not coincide
with the triple wedge vertex) and hyperbola vertex – $a$. These parameters can be directly
measured on actual webbing (Figures 3.2B-I) and attributed to the canonical form of
hyperbola (assuming that it is aligned with its transverse axis along axis $x$ on 2D plane,
and its center is located at the origin), as in eq 3.9, 3.10 and 3.11:

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1 \quad (3.9)$$

$$a = d - \frac{w}{\sin(\theta/2)} \quad (3.10)$$

$$\frac{b}{a} = \tan \left( \frac{\theta}{2} \right) \quad (3.11)$$

where $w$ is the MML nanowire width and $d$ is the webbing distance measured from the
wedge vertex to the hyperbola vertex (Figure 3.2B). It is also important to note that
fitting these parameters with real data might provide an indirect measure of the actual
MML nanowire width $w$, if a more accurate form of $\Delta E(x, y, z)$ is derived.

The webbing could be considered just a section of a nanowire with higher width, and so far this is the only method we found that allows significant variation of nanowire width. It could also be possible to create a mask with a jagged edge that would result in formation of wider wires consisting of interlapping webbings. This also suggests that there is the possible influence of mask edge quality on the width of the nanowire, since a rough mask edge is a jagged line with very small features. So far we were unable to observe this.

Webbing has an appearance somewhat resembling the shelf defect structure observed for chemically etched nanowires. To confirm that the webbing is actually a result of capillary effects and not the etching feature, we conducted experiments with the formation of similar structures using physical sputtering to etch the SiO$_2$, and observed similar results.

Since the webbing distance $d$ could be measured with much higher relative accuracy, we attempted to observe the difference in webbing distances for SiO$_2$ wires prepared using Au sacrificial metal masks (Figure 3.4) which were modified in different ways. For unmodified (uncleaned) Au mask, the average webbing distance was $194 \pm 6$ nm; for piranha cleaned Au mask, $173 \pm 5$ nm; for HS-(CH$_2$)$_{15}$-COOH modified Au mask, $167 \pm 4$ nm; and for HS-(CH$_2$)$_{17}$-CH$_3$ modified Au mask, $140 \pm 7$ nm. The sample with the Au mask modified with HS-(CH$_2$)$_{17}$-CH$_3$ had the smallest webbing, which correlated with the highest macroscopic wetting angle for Au films with this modification ($\sim 100^\circ$). The Au films cleaned with piranha and modified with HS-(CH$_2$)$_{15}$-
COOH both had \(~ 0^\circ\) macroscopic contact angle. The similarity in behavior of the corresponding samples was expected. The higher average webbing distance for samples with unmodified Au mask is attributed to the additional surface roughness caused by residual PMMA on the surface, promoting better adhesion of water.

**Figure 3.4.** The webbing distance histograms for Au masks with modified surfaces.

Webbing angle between wedge walls $\theta = 30^\circ$. At least 10 webbing were measured. (A) control with the as-prepared Au mask; (B) Au mask cleaned with piranha; (C) Au mask modified with HS-(CH$_2$)$_{15}$-COOH; (D) Au mask modified with HS-(CH$_2$)$_{17}$-CH$_3$. 
Since the general idea behind the MML mechanism is the formation of a water meniscus in any wedge between two microscopically hydrophilic surfaces, a new meniscus could be formed after etching upon sample exposure to ambient moisture (Figure 3.5A) resulting in protection of material adjacent to the freshly produced sidewall. Cycles of alternating etching and exposure to moisture result in formation of stair-like structures (Figure 3.5A); the number of observed terraces corresponding to the number of etching/recovery cycles.

This meniscus recovery phenomenon was particularly pronounced for triple angle wedges (Figure 3.5B-H). Far from the triple angle wedge vertex, the width of the terrace group made with 4 cycles is 4 times the width of normal MML fabricated wire \( w \) (Figure 3.5I). Interestingly, the shapes of webbing terraces resemble the hyperbolic shape of the first webbing and also could be fitted with hyperbolae. We defined subsequent webbing distances as shown on Figure 3.5J. It is important to note that exposure to ambient atmospheric moisture is essential to meniscus recovery. In control experiments performed without exposure to the atmosphere, a single deep webbing/wire was formed regardless of the number of the etching cycles.
Figure 3.5. Meniscus recovery process. (A) Schematic representation of meniscus recovery. (B-H) 4 cycle meniscus recovery in triple angle wedges with (B) $\theta = 10^\circ$; (C) $\theta = 15^\circ$; (D) $\theta = 20^\circ$; (E) $\theta = 30^\circ$; (F) $\theta = 45^\circ$; (G) $\theta = 60^\circ$; (H) $\theta = 90^\circ$. (I-J) Schematic representation of hyperbolic webbing; $d_i$ are terrace widths; webbing distance for the $n^{th}$ cycle is $\sum_{i=1}^{n} d_i$; mask webbing for the $n^{th}$ cycle is $\sum_{i=1}^{n-1} d_i$.

For smaller $\theta$ values, the first webbing distance $d_1$ was, as with single webbings,
large, but quickly decreased with more cycles, ultimately approaching the width of normal MML fabricated nanowire $w$ (Figures 3.6A-C). For large $\theta$, webbing distances were closer to $w$ from the first cycle and became yet closer to it with more cycles (Figures 3.6D-E). This convergence could be because later webbings have less curvature and locally resemble straight wires. The webbing distance distribution did not depend on the step height in the 7 – 50 nm range, in agreement with threshold wire formation dependence on mask height.\(^1\)

Study of webbing distance distribution should provide valuable information about the MML meniscus nature. The pair of parameters $\theta$ and $d$ allows qualitative comparison of the webbings with higher precision than that for comparison of only the nanowire widths. Ultimately, some relationship between binding $d$ and $\theta$ should exist, and when found would allow one to interpret forces involved in this process. Figure 3.6F provides the raw data for first webbing distance as a function of angle $\theta$. 
Figure 3.6. Distribution of terraces width $d_i$ for different mask shapes. (A-E) Dependence of terrace width $d_i$ from webbing parameter of previous terrace edge for different
webbing angles. (A) $\theta = 10^\circ$; (B) $\theta = 15^\circ$; (C) $\theta = 20^\circ$; (D) $\theta = 30^\circ$; (E) $\theta = 45^\circ$. (F) Dependence of first cycle webbing distance on webbing angle.

The meniscus recovery process is a simple way to narrow gaps. To study the interaction of menisci between closely located wedges, we have repeatedly narrowed the gap between 2 masks by recovering menisci formed near them (Figure 3.7). For pointed angular masks separated initially by ~45 nm, non-interacting menisci are formed in the first cycle, while in the second cycle, when masks are separated by ~25 nm, the menisci join for a wide range of mask geometries (Figures 3.7A-D). For pointed angular masks with an initial separation of ~90 nm (Figure 3.7E), the non-interacting menisci are formed in the first cycle, and subsequent menisci clearly do not overlap up to the fourth etch-recovery cycle. However, it is unclear whether the menisci are suppressed or not due to difficulty with determination of the width of MML nanowires. For the case of parallel wedges initially separated by 25 ± 10 nm gaps (Figure 3.7F), some sections of menisci apparently overlapped in the first cycle of recovery, and all remaining menisci sections overlapped in the second recovery cycle, likely corresponding to regions with narrower and wider parts of initially patterned gap. In the case of parallel wedges initially separated by ~85 nm gaps (Figure 3.7G), non-interacting menisci are formed in the first cycle, some sections of menisci join in the second cycle (corresponding to ~65 nm wedge separation) and the rest join in the third cycle. However, menisci regions near the gap ends did not overlap even after four recovery cycles.
**Figure 3.7.** Meniscus recovery in narrow gaps, 4 recovery cycles. (A-D) Pointed angular masks separated initially by ~45 nm gaps. The angle between opposite mask sides is (A) 30°; (B) 45°; (C) 60°; (D) 90°. (E) Pointed angular mask initially separated by ~90 nm gap. The angle between opposite mask sides is 30°. (F) Parallel wedges separated initially by 25 ± 10 nm gap. Inset: magnified center part. (G) Parallel wedges separated initially by ~85 nm gap. Scale bars are 100 nm.

Numerous experiments previously performed demonstrated, that the formation of nanowires in MML process does not depend on the particular RIE instrument used for fabrication.1,2 Moreover, the webbing distances for single etching in triple angular wedges were identical in different machines. However, we have found that the meniscus recovery process strongly depends on the instrument used. For meniscus recovery experiments we used two instruments: Oxford ICP 100 with exchange lock chamber for experiments
shown in Figures 3.5B-H and a PlasmaTherm 790 RIE with ventable chamber for experiments shown in Figures 3.8A-C. We observed that for the PlasmaTherm instrument, the terraces, starting from the second one, are much wider than those for the Oxford ICP instrument. In the PlasmaTherm, for 4 meniscus recovery cycles we observed only 2-3 microscopic terraces, while the fourth and sometimes even the third extends to at least several microns around the pattern. This indicates that much larger menisci are stable for samples etched with the PlasmaTherm instrument.

It is well known that instruments with ventable chambers are more prone to formation of silicon grass due to higher levels of chamber contamination.\textsuperscript{6,7} Moreover, the base pressure in the Oxford ICP 100 instrument was \(~10^{-6}\) Torr, whereas in the PlasmaTherm 790 RIE instrument is was \(~10^{-3}\) Torr. Our observations on terrace width could be explained by effects similar to those leading to silicon grass formation. The contaminants randomly protect the substrate from etching, thus creating relief over all the exposed areas of the sample and increasing roughness, and hence promoting stronger interaction of water with the substrate. These effects become apparent starting from the second meniscus recovery cycle because the substrate on the first cycle is not yet affected by the instrument.

To investigate this possibility, we performed meniscus recovery experiment alternating RIE machines after 2 recovery cycles. The sample that was treated for the first two recovery cycles in the Oxford ICP and then for third and fourth recovery cycles in PlasmaTherm demonstrated three regular terraces, after which an extended fourth webbing terrace was formed (Figure 3.8D). This shows that the Oxford ICP did not
produce significant roughness of the substrate, but a single etching in the PlasmaTherm produced roughness sufficient to alter the behavior of the meniscus. The sample that was treated for the first two recovery cycles in the PlasmaTherm has extended second and third terraces and a macroscopic fourth terrace. The sample had roughness sufficient to sustain larger meniscus even in the Oxford ICP. Interestingly, etching in the Oxford ICP seemed to further increase roughness created by the PlasmaTherm. Based on these results, it is probable that the roughness produced by 2 recovery cycles in the PlasmaTherm is sufficient to stabilize water on the surface of the sample so that it cannot be removed by Oxford ICP pumping system.

![Figure 3.8](image)

**Figure 3.8.** Meniscus recovery variation with etch apparatus. (A-C) Etching performed with PlasmaTherm 790 RIE. (A) \( \theta = 30^\circ \); (B) \( \theta = 90^\circ \); (C) \( \theta = 150^\circ \); (D) The first two recovery cycles performed in an Oxford ICP 100. This was followed by two more in a PlasmaTherm 790 RIE, \( \theta = 30^\circ \). (E) The first two recovery cycles performed in a
PlasmaTherm 790 RIE. This was followed by two more in an Oxford ICP 100, $\theta = 30^\circ$.

Scale bars are 100 nm

This effect could be used to fabricate rough surfaces demonstrating high stability against plasma due to a thick water film adsorbed onto their structural features. To demonstrate this effect, we patterned an array of 1 μm-sided and 2 μm-separated Al squares, and performed multiple meniscus recovery cycles in the PlasmaTherm instrument (Figure 3.9). After removal of Al, the SEM images of the array side (Figure 3.9A) demonstrate that the fourth menisci of all the squares are overlapping and extending microns away from the starting array. Due to the randomized nature of relief formation, the exact number of cycles needed to form substrates stable in plasma is difficult to determine. However, in typical experiments 3-4 recovery cycles were sufficient to achieve meniscus overlapping across a few microns for this pattern of squares. The AFM image of the resulting surface after mask removal (Figure 3.9B) shows how etching depth increases stepwise away from the center of the array, illustrating the relief development. Squares inside the array have 3 terraces adjacent to them (Figure 3.9C) and the space between is covered with relief of complex geometry (Figure 3.9D).
Figure 3.9. Plasma-resistant surface formation in a PlasmaTherm 790 RIE. (A) SEM of edge of the squares array after 4 recovery cycles. (B) AFM image of the squares array after 6 recovery cycles. Note stepwise decrease in height towards the right corresponding to overlapping macroscopic terraces. (C) SEM of space between the squares inside the array. (D) Magnified SEM image of relief geometry within the overlapped terrace.

Similar meniscus recovery experiments were performed on patterns with holes (Figure 3.10) forming circular wedges. The meniscus recovery procedures were performed on the inner parts of the hole. For 4 cycles of meniscus recovery in an Oxford ICP 100 instrument (Figures 3.10A-E) all 4 expected terraces were observed even for holes as small as ~75 nm (Figures 3.10A, D) in diameter. The overall depth for holes of each diameter was equal to thickness of material removed in all four etchings outside the patterned region. For samples etched in the PlasmaTherm 790 RIE instrument (Figures 3.10F-N), the hole depth was found to strongly depend on the diameter of the hole in the starting mask. We observed the etching to cease after one meniscus recovery cycle for ~75 nm holes (Figures 3.10F, I, K), after 2-3 meniscus recovery cycles for
~ 175 nm holes (Figures 3.10G, J, L) and observed full etching only for ~ 460 nm holes (Figures 3.10H, M).

Interestingly, the results observed for ~ 460 nm holes etched in PlasmaTherm instrument do not exactly coincide with the terrace sizes in terrace overlapping phenomenon (Figures 3.8, 3.9). Although this could be attributed to the instability of rough surface formation process, the difference in terraces sizes is much larger than the usually observed fluctuations for the PlasmaTherm 790 RIE instrument. This could indicate that menisci interaction character in the circular wedge differs from that in parallel wedges or pointed angular wedges.

**Figure 3.10.** Meniscus recovery in holes, 4 recovery cycles. (A-E) Etching performed in
an Oxford ICP 100 instrument. (F-J) Etching performed in a Plasma Therm 790 RIE instrument. (A, D) and (F, I) \( \sim 75 \) nm average hole diameter SEM images; (B, E) and (G, J) \( \sim 175 \) nm average hole diameter SEM images; (C) and (H) \( \sim 460 \) nm average hole diameter, low magnification SEM image. (K-M) AFM images for samples made in a Plasma Therm 790 RIE instrument. The hole depth depends on hole diameter. (K) \( \sim 75 \) nm average hole diameter; (L) \( \sim 175 \) nm average hole diameter; (M) \( \sim 460 \) nm average hole diameter. (N) Typical AFM profiles cut across hole diameter for \( \sim 460 \) nm average hole diameter (in black), \( \sim 175 \) nm average hole diameter (in red) and \( \sim 75 \) nm average hole diameter (in blue). Scale bars are 100 nm for (A-J) and 200 nm for (K-M). Height range in the images (K-M) is 35 nm.

The water in the meniscus, although bound to the substrate, was found to demonstrate the chemical properties of water. For example, the water meniscus could be immobilized (Figure 3.11A) by TiCl\(_4\) hydrolysis and formation of a templated TiO\(_2\) structure in the wedge. For these experiments, we used chemically inert Au metal masks for wedge formation, and the freshly deposited hydrated TiO\(_2\) was annealed to harden the titania, enabling wet etching of the mask layer. The resulting structure manifests itself in both SEM (Figure 3.11B) and AFM (Figure 3.11C) as thick cracked fin-like structure near the former mask edge, partially standing upright and partially fallen to the side.
Figure 3.11. Meniscus immobilization through reaction with TiCl$_4$. (A) Experiment scheme; (B) SEM image of resulting TiO$_2$ structure in the corner. (C) AFM image of TiO$_2$ structures formed on the striped mask sidewalls. Height range is 120 nm.

3.3. Conclusions

To conclude, we have developed several important modifications to the MML process allowing better understanding of the mechanism and enhancing the flexibility of the method. The width of structures formed by the MML process in concave corners is much more sensitive to changes in the process than the width of MML nanowires, while conclusions about meniscus properties derived for triple angle wedges could be extrapolated onto nanowires formation. We have demonstrated the possibility of nanowire width change through webbing formation and through the changes in surface roughness.

Meniscus recovery and immobilization experiments furthermore confirm that the meniscus is indeed present and water-based. Extended menisci could be formed in some RIE machines and they make substrates quite resistant to plasma etching, which could have practical applications.
3.4. Experimental

MML process and general methods

In most experiments we dealt with SiO$_2$ wires and structures. In these experiments we used polished, single-sided, heavily p-doped Si wafers with a 300 nm thermal SiO$_2$ layer (Silicon Quest International) as starting films. SiO$_2$ wires were formed from those substrates using meniscus-mask lithography process sequence as described elsewhere.$^1$ We used Al sacrificial metal mask layers in all experiments unless stated otherwise. Both Al and Au sacrificial metal masks were deposited by sputtering (using Denton Desk V Sputter system). The wet etching of Al masks was performed in a H$_3$PO$_4$/HNO$_3$/CH$_3$COOH/H$_2$O (80/5/5/10 vol%) mixture; for Au masks a mixture of I$_2$/KI/H$_2$O (5/10/85 wt%) was used.$^8$ For experiments with Au wires, we used ~15 nm sputtered Au films on Si/SiO$_2$ substrates as a starting film. In those experiments, sacrificial Al masks were used. The sample patterning was performed using electron-beam lithography with a JEOL 6500F SEM at 30 kV acceleration voltage and 300 pA beam current using PMMA 950 A resist. The SEM imaging of the wires was performed with a JEOL 6500F SEM at 15 kV accelerating voltage without additional applying conductive coating. The AFM measurements were performed in tapping mode using a Bruker Multimode 8 instrument with TESPA-V2 tips. Reactive ion etching of SiO$_2$ was performed in Oxford ICP 100 instrument and in PlasmaTherm 790 RIE instrument. Reactive ion etching of Au was performed in Oxford ICP 100 instrument. The etching conditions are given in Table 3.1.
Table 3.1. Etching conditions.

<table>
<thead>
<tr>
<th>Etching Condition</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ etching in Oxford ICP 100 instrument</td>
<td>pressure = 20 mTorr; RIE power = 100 W; SF₆ flow = 25 sccm; O₂ flow = 5 sccm;</td>
</tr>
<tr>
<td></td>
<td>typical process time = 40s; typical bias = 185 V;</td>
</tr>
<tr>
<td>SiO₂ etching in PlasmaTherm 790 RIE</td>
<td>instrument</td>
</tr>
<tr>
<td></td>
<td>pressure = 100 mTorr; RIE power = 100 W; CF₄ flow = 30 sccm; O₂ flow = 5 sccm;</td>
</tr>
<tr>
<td></td>
<td>process time = 40s; typical bias = 230 V;</td>
</tr>
<tr>
<td>Au etching in Oxford ICP 100 instrument</td>
<td>pressure = 15 mTorr; RIE power = 150 W; Ar flow = 50 sccm; process time = 120 s;</td>
</tr>
<tr>
<td></td>
<td>typical bias = 370 V</td>
</tr>
</tbody>
</table>

**Thiol modification.**

Prior to thiol modification, Au substrates were thoroughly cleaned to remove residual PMMA. Au surface cleaning and modification steps were performed after the sacrificial metal layer mask deposition and lift-off. In Au wires fabrication process, cleaning was performed with UV-ozone cleaner (Boekel, model 135500). In SiO₂ structures fabrication with Au masks, piranha solution (3:1 H₂SO₄:H₂O₂) was used for the cleaning. In a typical modification experiment, ~ 5 mg of solid thiol was dissolved in ~ 5 mL of ethanol, and the sample was placed in the solution for several hours. After that, the sample was rinsed in ethanol, and dried in N₂ flow. The second dry etching step was performed immediately after the thiol modification step.

**Meniscus recovery.**

For meniscus recovery we used a Peltier module to cool the sample below the
dew point to ensure water meniscus recovery during sample exposure to ambient moisture. In experiments with formation of overlapping macroscopic menisci we started from patterning of the metallic mask skipping the first etching step of the standard MML procedure.

**Meniscus immobilization.**

For the meniscus immobilization experiments we used SiO$_2$ substrates patterned with Au masks. For meniscus immobilization process a custom vacuum chamber was made. Small sample chamber (~1 cm$^3$) was connected to a dry nitrogen line, a vacuum pump with a liquid nitrogen trap and a chamber partially filled with TiCl$_4$ liquid so that saturated TiCl$_4$ vapor could be fed into the sample chamber. A trap for acid fumes was installed between the chamber and the pump to prevent damage to equipment and to mitigate hazards. After loading the sample in the vacuum chamber, the system was flushed with dry nitrogen and subsequently evacuated for 1 h. Then the pump was isolated from the chamber and the cold trap was filled with liquid nitrogen. After 10 min of cold trap cooling, saturated TiCl$_4$ vapor was introduced into the system for 10 min. The system was then flushed with dry nitrogen and heated to 80 °C to remove excess TiCl$_4$. Then the sample was removed from the chamber, annealed at 300 °C for 1.5 h in air, and the Au mask was then wet etched.

### 3.5. References


2. Please refer to the Chapter 2 of this thesis.


7. Jansen, H.; Gardeniers, H.; de Boer, M.; Elwenspoek, M.; Fluitman, J.

   761-778.
Chapter 4

Healing edges in MML-produced GNRs

4.1. Introduction

Graphene nanoribbons (GNRs) are highly desirable nanostructures for nanoelectronics and materials science, as discussed in Chapter 1. We demonstrated the method of top-down fabrication of on-chip positioned GNRs using meniscus-mask lithography.\textsuperscript{1} However, the charge carrier mobilities in the resulting GNRs were consistently very low, although comparable to the values reported in the literature for GNRs.\textsuperscript{2,3} In this work we propose chemical methods of edge healing which may be used to improve the charge carrier mobility.

4.2. Results and discussion

For GNRs produced with Ar plasma etching, the estimate for hole mobility was \(~ 14 \text{ cm}^2/\text{V} \cdot \text{s}\) and the electron mobility was \(~ 1 \text{ cm}^2/\text{V} \cdot \text{s}\) in devices on Si/SiO\textsubscript{2} substrate.\textsuperscript{1} It is important to note that although electron mobility is lower, the charge neutrality point corresponds to negative gate voltage values, indicating that some “additional” electrons are present in the system and are not really mobile. These localized electrons might originate from interaction of the charge carriers with oxygen-containing groups at the
edges. The oxygen content can be seen in the XPS spectra for GNR arrays (Figure 4.1). The deconvolution of the C1s peak (Figure 4.1B) reveals the presence of considerable amounts of hydroxyl and carbonyl groups attached to carbon, either of which could be a localized carrier trap site. There could also be other groups present which are not distinguishable by XPS such as carboxyls and peroxides. It is probable those groups are formed on the edges of GNRs after each of the two plasma etching steps used in the fabrication process are completed, and the sample is exposed to ambient atmosphere. The XPS-detectable presence of oxygen-containing groups supports our suggestion, based on transport properties data, that low charge carrier mobilities are caused by the presence of oxygen defects at the edges. In order to improve charge carrier mobility of GNRs we attempt here to substitute the edge functionalities with hydrogen atoms. In this work we demonstrate several chemical approaches to reduce the concentration of oxygen-containing edge groups in GNRs.

Figure 4.1. XPS spectra of dense GNR array on Si/SiO₂ substrate. (A) Survey spectrum.
(B) C1s peak and its possible deconvolution with C=O (in red), C-OH (in blue) and C-\(C/C=C\) (in green) peaks.

While we experimentally observed the consistency of transport properties of individual GNRs produced with Ar plasma,\(^1\) the XPS spectra differ considerably from sample to sample, being very close, however, for different regions of the same sample. Although the number of GNRs excited by the XPS beam is large, the XPS carbon signal does not come solely from GNRs, and could also be partially due to impurities, such as amorphous carbon, that are unavoidable in the synthesis of CVD graphene that we used for fabrication of GNRs. Nevertheless, XPS serves to tentatively determine the reactions suitable for reduction of GNRs, provided the spectra are measured both before and after chemical treatment of the same sample.

The edge chemistry of on-chip GNRs, such as those produced by the MML method, is rather specific, and it raises some challenges as well as simplifies certain procedures. Product isolation is considerably simplified compared to conventional organic synthesis due to heterogeneity as the chip with GNRs can be physically removed from liquid reagents and washed. Similarly, since the amount of GNRs and thus their concentration is very low, the excess of reagents is easily ensured. However, additional care should be taken to avoid GNR peel-off, which limits the choice of solvents and may require additional pre-annealing steps as in the GNR devices fabrication procedure.\(^1\) Also, the GNRs immobilization on substrate makes it difficult to use heterogeneous catalysis, and the presence of the substrate creates additional steric hindrance at the edges, slowing
some reaction types, for example, reactions requiring backside displacement.

The mechanical stresses on GNRs should be minimized to prevent peel-off and structural damage, however, some stirring is necessary to promote the chemical reactions. For all processes we mechanically attached the chip with the GNRs to the stir bar shell by force fit into the slit carved in the stir bar. This way the stir bar does not mechanically damage the chip during the process. After each reaction step, SEM imaging was used to verify that GNRs remained on the chip.

Figure 4.2. Reduction of carbonyls to hydroxyls with LAH, and subsequent removal of hydroxyls through tosylation and reduction. (A) Proposed reaction scheme. (B) XPS spectra of sample as-prepared (in black) and after reaction with LAH (in red). (C) XPS spectra of sample after reaction with LAH (in red) and after tosylation and additional
reduction in LAH (in blue). (B) and (C) show the spectra for two separate samples.

One possible route for removing oxygen-containing groups from GNRs edges is based on (1) reduction of all carbonyl and carboxyl groups to hydroxyls, and then (2) substitution of hydroxyls with hydrogen atoms. For example, lithium aluminum hydride (LAH) reduction and tosylation process scheme is shown in Figure 4.2A. LAH is used to reduce carboxylic acids, aldehydes, ketones (including conjugated ones), and quinones to alcohols/phenols. For reduction of GNRs we tested two solvents commonly used in LAH reactions: diethyl ether and tetrahydrofuran. In both cases, a very small fraction of the LAH dissolved; moreover, during the process aluminum hydroxide was deposited on the surface of the chip, furthermore hindering the reagent access to reaction sites. Nevertheless, GNR reduction with LAH in diethyl ether resulted in substantial decrease of the C=O component (Figure 4.2B, Table 4.1). The reduction with LAH in tetrahydrofuran, however, did not result in any substantial changes, even with repetition (Table 4.1).

For transformation of phenols into arenes, the phenol is typically transformed into tosylate ester or mesylate ester which is subsequently decomposed forming arene. For GNRs we tested the tosylation route with subsequent removal of -OTs groups via reaction with LAH (Figure 4.2A). The C-OH peak indeed has substantially diminished after this process (Figure 4.2C).
Table 4.1. GNRs reduction with LAH. XPS spectra deconvolution.

<table>
<thead>
<tr>
<th></th>
<th>C=O (%)</th>
<th>C-OH (%)</th>
<th>C-C and C=C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAH in diethyl ether,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>room temperature, s#1</td>
<td>before, “as is” 10 ± 2 %</td>
<td>17 ± 2 %</td>
<td>73 ± 5 %</td>
</tr>
<tr>
<td></td>
<td>after reaction 4 ± 1 %</td>
<td>14 ± 2 %</td>
<td>83 ± 5 %</td>
</tr>
<tr>
<td>LAH in diethyl ether,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>room temperature, s#2</td>
<td>before, “as is” 7 ± 2 %</td>
<td>26 ± 4 %</td>
<td>67 ± 5 %</td>
</tr>
<tr>
<td></td>
<td>after reaction 2 ± 1 %</td>
<td>22 ± 3 %</td>
<td>76 ± 2 %</td>
</tr>
<tr>
<td>LAH in tetrahydrofuran,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>elevated temperature</td>
<td>before, “as is” 6 ± 1 %</td>
<td>43 ± 8 %</td>
<td>51 ± 10 %</td>
</tr>
<tr>
<td></td>
<td>after reaction 6 ± 1 %</td>
<td>27 ± 10 %</td>
<td>66 ± 10 %</td>
</tr>
</tbody>
</table>

Another closely related reducing agent is NaBH₄, however, this is a milder reducing agent. We tested the Luche reduction process (Figure 4.3A), reported to reduce aldehydes, ketones and quinones to alcohols/phenols.¹⁰ The on-chip GNRs, however, did not experience any substantial change through this process, based on the XPS data (Figure 4.3B). Similar results were obtained for on-chip GNRs reduction with BH₃·THF; the XPS spectra remained unaffected (Figure 4.4A).

Figure 4.3. Luche reduction process. (A) Reaction scheme. (B) XPS spectra before (in black) and after the process (in red).
Reduction with Na/K alloy revealed substantial decrease in hydroxyl peak (Figure 4.4, Table 4.2). The additional peak in XPS C1s spectra region at ~ 295 eV binding energy corresponds to traces of K. Interestingly, the C=O peak did not appear to be affected by the process. Therefore, it is very likely that eventually certain combinations of reactions should be used for efficient GNRs reduction.
Table 4.2. Reduction of GNRs with Na/K alloy. XPS spectra deconvolution.

<table>
<thead>
<tr>
<th>Na/K process test</th>
<th>C=O</th>
<th>C-OH</th>
<th>C=C and C=C</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduction before, “as is”</td>
<td>6 ± 3 %</td>
<td>38 ± 1 %</td>
<td>56 ± 5 %</td>
</tr>
<tr>
<td>after reaction</td>
<td>7 ± 2 %</td>
<td>14 ± 1 %</td>
<td>79 ± 2 %</td>
</tr>
</tbody>
</table>

Along with chemical reduction methods, we also tested the reduction by annealing in H\(_2\) atmosphere (Figure 4.5). High temperature annealing (600 °C and higher) could not be sustained by Si/SiO\(_2\) substrates, as SiO\(_2\) layer softens and degrades. Therefore, for annealing experiments, GNR arrays were fabricated on Si/Si\(_3\)N\(_4\) substrates that are much more stable at high temperatures.

Annealing at 500 °C (Figure 4.5A) resulted in some decrease of both C-OH and C=O peaks, however, those were not completely removed. This agrees well with past results that ar-GNR devices after annealing at 500 °C did not demonstrate any substantial change in transport behavior.\(^1\)
Figure 4.5. GNRs reduction via annealing in H$_2$ atmosphere. (A) XPS spectra before (in black) and after (in red) annealing at 500 °C. (B) XPS spectra before (in black) and after (in red) annealing at 900 °C.

The annealing at 900 °C (Figure 4.5B) resulted in complete reduction of both hydroxyl and carbonyl groups, their peaks being no longer measurable. The additional small peak at ~281.5 eV observed for annealed samples falls into carbide region, and could be attributed to the formation of C-Si bond, and edge termination onto the substrate.

4.3. Conclusions

To conclude, we tested the reactivity of on-chip GNRs with chemically randomized edges using several common reducing agents to heal GNRs edges. We
observed LAH efficiently reducing carboxyl groups, apparently turning those into hydroxyl groups, and we observed substantial removal of hydroxyl groups in tosylation reaction followed by LAH reduction and in GNRs reaction with Na/K alloy. Also, we demonstrated that annealing in H₂ atmosphere reduces all GNRs oxygen-containing groups, and terminates GNRs edges onto substrate at already 900 °C.

4.4. Experimental

**GNR arrays fabrication.**

GNRs arrays were fabricated using the MML technique with polycrystalline CVD graphene as the starting film. The GNRs were fabricated on edges of 2 μm × 100 μm rectangles with 4 μm pitch, arranged in square arrays separated by 50 μm gaps, 8 × 8 arrays overall. The graphene etching in all cases was performed with Ar plasma, the etching conditions were given elsewhere. The macroscopic alignment marks were mechanically scratched on surface of Si/SiO₂ chip around this set of GNRs. For XPS spectra measurements PHI Quantera XPS instrument with Al cathode was used. The beam diameter was 200 μm, the power was 50 W.

**Reduction with lithium aluminum hydride (LAH).** In a typical experiment, ~ 50 mg of powdered LAH was placed in a round-bottom flask with GNRs on chip attached to stirring bar so that the surface of the chip with GNRs was never touching any solid surfaces while stirring. The scheme of chip mounting on the stir bar is shown in Figure 4.6. The flask then was sealed, and the air atmosphere was exchanged with dry nitrogen. Then, 10 mL of freshly distilled diethyl ether (Et₂O) was slowly added with the flask kept in an ice bath. The mixture was left under N₂ stirring for 24 h at room
temperature. After the reaction, the sample chip was washed in 
H$_3$PO$_4$/HNO$_3$/CH$_3$COOH/H$_2$O (80/5/5/10 vol%) mixture$^{11}$ to remove Al$_2$O$_3$$\cdot$$x$H$_2$O deposited on the surface, then rinsed with DI water, isopropanol and dried in N$_2$ flow. In some experiments, instead of Et$_2$O, tetrahydrofuran (THF) was used as a solvent with the same wt./vol. concentration of LAH, and experiments were performed at elevated temperature under reflux.

**Figure 4.6.** Mounting the on-chip GNRs onto the stirring bar by force fit. This type of mounting was used in all experiments requiring stirring.

**Tosylation.** In a typical experiment, $\sim$ 1.217 g of 4-toluenesulfonyl chloride (TsCl) was placed in a round bottom flask with GNRs on chip attached to stirring bar, and the flask was sealed. Then, $\sim$ 13 mL of pyridine was slowly added, and the system was left under stirring for 24 h at room temperature. After reaction, the sample chip was
washed with ethanol and dried in N$_2$ flow. Then the LAH reduction sequence was repeated to complete the process.

**Luche reduction.** ~ 1.640 g of CeCl$_3$·7H$_2$O was dissolved in ~ 11 mL of methanol in a round bottom flask. After CeCl$_3$ dissolution, the chip with GNRs mounted onto the stirring bar was added, and ~ 0.198 g of NaBH$_4$ was slowly introduced to the mixture. Then the flask was sealed and left under stirring for 24 h. After reaction, the sample was washed with water, isopropanol, and dried in N$_2$ flow.

**Reduction with BH$_3$·THF.** The chip with GNRs mounted onto the stirring bar was placed in a round bottom flask, the flask was sealed, and air atmosphere was exchanged to dry nitrogen. Then 8 mL of freshly distilled THF was introduced into the flask followed by 2 mL of BH$_3$·THF solution, and the system was left under N$_2$ stirring for 2 d, after which the sample chip was washed with water, isopropanol, and dried in N$_2$ flow.

**Reduction with Na/K alloy.** The part of experiment prior to flask sealing was performed in glove box under dry nitrogen oxygen-free atmosphere. The chip with GNRs mounted onto the stirring bar was placed in a round bottom flask with 10 mL of freshly distilled dimethyl ether (DME) and 0.1 mL of Na/K alloy was added. The flask was then sealed, and left under N$_2$ slow stirring for 3 d. After the reaction, the sample chip was washed in methanol, then water, and dried in N$_2$ flow.

**Annealing experiments.** Annealing of the samples was performed at 500 °C or at 900 °C in a H$_2$ atmosphere with overall pressure ~ 1.0 Torr and with H$_2$ flow of 50 sccm. Typical annealing time was 2 h.
4.5. References


