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Selective growth of graphene films on Gallium-Focused Ion Beam irradiated domains

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Graphene a single layer of carbon atoms tightly bound in a hexagonal honeycomb lattice to form a two-dimensional lattice, is a very interesting material with promising electronic, optical, chemical and mechanical applicative potential¹. The properties of graphene make it suitable for a wide range of applications, however, its applicative future still depends on large scale technologies capable to robustly and reproducibly transfer its outstanding intrinsic properties into devices or complex structures. It must be recognized that a crucial technological problem, that still inhibits the applicability of high quality graphene material properties, is related to the patterning of this material using traditional top down instruments and lithographical methods. In this work we will detail our investigations on applying a precise 30 keV Ga⁺ ion irradiation to selectively shape and modify a copper precursor surface for promoting the local growth of graphene surface domains. The morphology of these domains are investigated using Scanning Tunneling Microscopy and Spectroscopy (STM/STS) to probe simultaneously the structural and the electronic properties at the atomic scale of the graphene films.

I. INTRODUCTION

The patterning of samples using the Focused Ion Beam (FIB) techniques is a workhorse in micro / nano-electronic engineering with a main application related to the field

of inspection of Integrated Circuits and electronic devices. This is often denoted as “failure analysis” and is widely used by the semi-conductor industry. Apart of this mainstream the direct write capabilities allowed by FIB instruments have also attracted the attention of many research laboratories². FIB direct write processing allows precisely sculpting, reconnecting devices or extracting and manipulating thinned membranes for subsequent elemental analysis. FIB since its introduction in the 80’s has proven to be an essential complement of main stream lithographic techniques³ and despite some limitations in throughput and gallium ions “left behind” is now accepted as a key enabling technology.

FIB material processing relies on the use of a fine pencil of high velocity projectiles transferring their kinetic energy onto a sample surface and thus creating a variety of processes ranging from secondary electron emission (Scanning Ion Microscopy), 3D material removal using local sputtering or ion implantation, ion mixing and damage injection². Lateral structure definition is achieved by precisely deflecting the focused pencil of ions along X and Y directions while the depth Z is controlled directly by the local ion dose D injected into the sample $D = I/S$ where I is the injected ion current and S the patterned surface. One important advantage for nanoscience and nanotechnology applications relies in the fact that FIB is by essence a surface processing technique with a very limited penetration range of the gallium ions in materials like silicon, typically around 1 nm /keV of incident ion energy. In a previous work using the top down approach we have already demonstrated that graphene structures could be FIB patterned using a precisely shaped gallium ion beam generating local surface defects^{4,5}. In this work our aim will be to evidence the effect of surface bombardment to induce and control target surface atoms displacement thus creating an amorphized region onto a high crystallinity copper substrate. We aim at compare the surface properties of pristine copper surfaces with progressively irradiated areas to evidence if FIB damaged or textured regions can allow selective CVD Graphene growth.

It is widely accepted that graphene produced with chemical vapor deposition (CVD) will form the cornerstone of future graphene-based chemical, biological, and other types of sensors⁶. This production method combined with FIB texturing capabilities could indeed produce high quality tailored graphene structures, potentially on a large scale that is a prerequisite for exploiting graphene excellent mechanical strength, thermal and electrical conductivity, compactness, and potentially low cost.

Scanning Tunneling Microscopy and Spectroscopy (STM/STS) have proven to be unique techniques to probe simultaneously the structural and the electronic properties at the atomic scale of conductive materials. Graphite and later on graphene, directly grown or deposited on various substrates, became archetypical samples for STM/STS studies performed either in atmospheric conditions or under ultrahigh vacuum and low temperature environments. The Scanning Tunneling Spectroscopy (STS) measure the $I(V)$ characteristic. The $dI(V)/dV$ reveals the local electronic density of states, LDOS(x, y, E), of the sample under the STM tip; the energetical resolution is ruled by the Fermi function thermal broadening of the injected tunneling electron which is roughly 25meV at room temperature, 10meV at 77K and 1meV at 4K.

II. MATERIALS AND METHODS

The experiments described here were achieved using a high resolution Focused Ion Beam nanowriter that we have started to develop some years ago with the aim to explore disruptive nanofabrication routes using ultimately focused and precisely scanned gallium ion pencils. The current generation of our instrument exploits the advantages of a very high stability Liquid Metal ion Source. The gallium Electro-Hydrodynamic ion source we have developed demonstrates a brightness improved of more than a factor 2 compared to conventional gallium LIMS with variation of the emitted ion flux below 0.5% per hour. This LMIS is coupled with a FIB column we have designed and realized in our laboratory using a

specific very low acceptance angle design ($< 0.2\text{mrad}$) and an optical architecture collimating the ion beam via a micrometre-sized entrance aperture followed two asymmetric Einzel lenses². In this optics design, the maximum beam current is limited to a few tens of pico Amps but the selectivity and fall distances of the probe current have proven to be of only a few nanometers². The injected ions control is achieved with a specific electrode inside the column with the capability to achieve pixel doses down to 50 ions/pixel. Extended capabilities are achieved using a high precision laser interferometer stage (2nm steps) working in combination with a high speed (10MHz) digital pattern generator. The chamber of the FIB machine is capable of maintaining a vacuum level in the 10^{-8} mbar range avoiding surface contamination.

In the experiment described hereafter the gallium beam energy was 35 kV and we selected a probe current 9pA in a non-crossover ion-optics operation, a mode that allows our FIB technology to be considered as the reference in terms of FIB lateral probe extension²: the so called “tails”. The ion probe was digitally scanned over $50\mu\text{m} \times 50\mu\text{m}$ square patterns having specific designs: (a) straight parallel lines irradiated by digitally scanning each line in a meander mode, (b) Tilted parallel lines to evidence possible ion channeling effects within the copper crystal orientations and (c) zig-zag lines for further assessment of these effects. For each pattern several ion fluences were then tested by varying the pixel residence time and the pixel-to-pixel distance set to allow 5 different ion doses respectively: 10^3 , $5 \cdot 10^3$, 10^4 , 10^5 , 10^6 ions/pixel.

Finally for defining the line spacing within each pattern we used the Stopping Range of Ions In Matter (SRIM) code⁷ developed by Ziegler (). This ion-matter interaction modeling allowed us to predict both: the in depth and lateral projection ranges with an estimate of the sputtering yield induced by 35keV gallium ions colliding onto a copper sample. The results were as follows: The penetration range was found to be about 11.5nm, the lateral range 4 nm

and the sputtering yield about 10 copper atoms per incident gallium ion. Based on these calculations it was assumed that all our ion induced modifications would remain around or below the 10 nm scale.

Since our objective was to evidence the possible growth of graphene lines and the transition from potential graphene isolated lines to bi-dimensional graphene layers, separation distances between parallel adjacent irradiated lines were set respectively at spacing: 50, 100, 300 nm. For the zigzag line pattern a single spacing of 300 nm was selected.

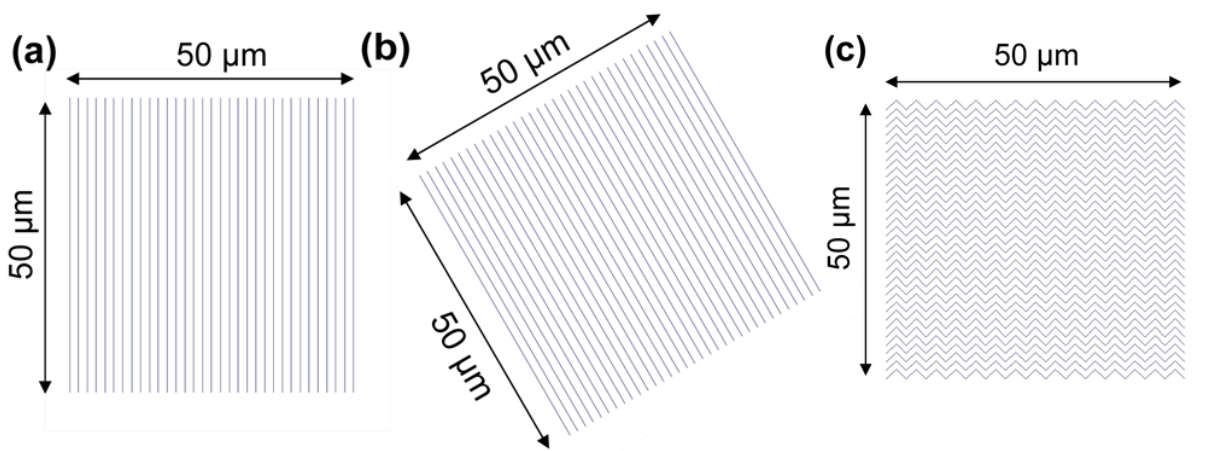


FIG. 1. Schematic of the 3 different FIB irradiation patterns extracted from the machine GDSII layouts. The patterns are consisting of separated lines digitally and sequentially scanned using the meander mode. (a) Straight lines gratings, (b) Tilted lines gratings (30°), (c) Zigzag lines with 300 nm line spacing.

III. RESULTS AND DISCUSSION

A. Graphene Synthesis

After FIB irradiation of the (100) single crystal copper from MTI Corp. Graphene layers were synthesized by Chemical Vapor Deposition (CVD) technique using a commercial system from Aixtron Ltd⁸. Graphene was synthesized using methane and hydrogen gas mixture at 1060°C . Copper crystal is used as the catalytic substrate for graphene growth. The

main advantage of using CVD graphene films is that several square centimeter-sized films having only a few atomic layers can be obtained easily. Once the graphene/copper foil was cooled and removed out of the reactor and were first inspected using interference contrast microscopy (Figure 2a). As a complement, Raman spectroscopy at 532nm is also used to check the quality of the graphene film growth as shown in figure 2b.

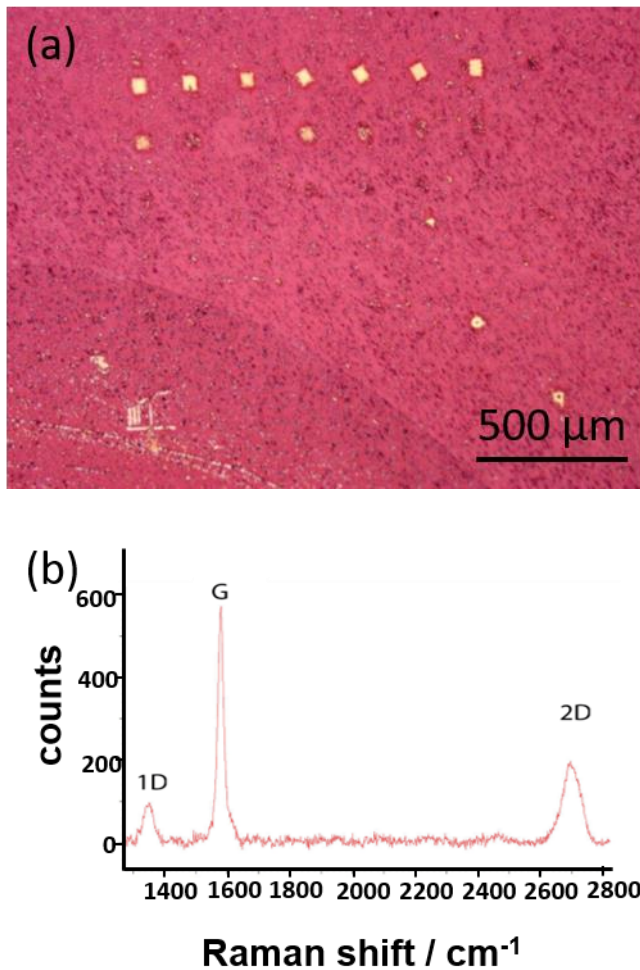


FIG. 2. (a) Optical microcopy image of the patterned structures after CVD growth of graphene. (b): Typical Raman spectrum acquired after graphene growth onto the FIB irradiated patterns. This Raman spectrum reveals the presence of a few layers 2D graphene structures.

On the figure 2a it appears clearly that only the patterns irradiated with the highest ion doses (10^6 ions/pixel) have allowed the growth of graphene localized flakes, having sizes in

coherence with the FIB irradiation patterns dimensions. From left to right it is possible to identify: Straight lines gratings with line spacing: 50,100, 300 nm, Tilted lines gratings (30°) with line spacing: 50,100, 300 nm and finally Zigzag lines with line spacing: 300nm.

B. STM analysis

Within few days after the Chemical Vapor Deposition (CVD) deposition of the graphene 2D structures and subsequent inspection, the FIB irradiated copper monocrystal Cu(100) surfaces, were analyzed using STM techniques. The sample was first degassed in our preparation chamber at 450°C for several hours to desorb the atmospheric contamination layers and then inserted in our low temperature STM ($P < 10^{-10}$ mbar). Thanks to the high resolution optical imaging of our instrument and the exponential shape of our electrochemically-etched tungsten STM tips, we were capable to localize and identify the 50 μm x 50 μm squares irradiated patterns starting with the highest dose, the STM tip could be positioned directly onto the selected area with referenced irradiation conditions (Figure 3).

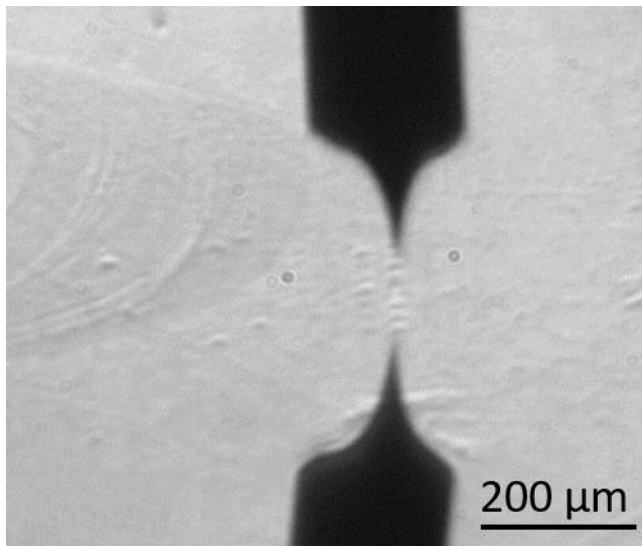


FIG. 3. Optical microscopy image of the STM tip (at the bottom) and the reflected image (on top) by the high quality Cu(100) sample.

On the figure 3 the apex of the STM tip is located directly on top of a column of $50\mu\text{m} \times 50\mu\text{m}$ patterns, which were patterned with the highest FIB irradiation dose (10^6 ions/pixel). The tip could even be moved, by a calibrated step motion displacement, onto adjacent pattern and even onto lower dose patterns that were less or non-visible using the in-situ optical microscope.

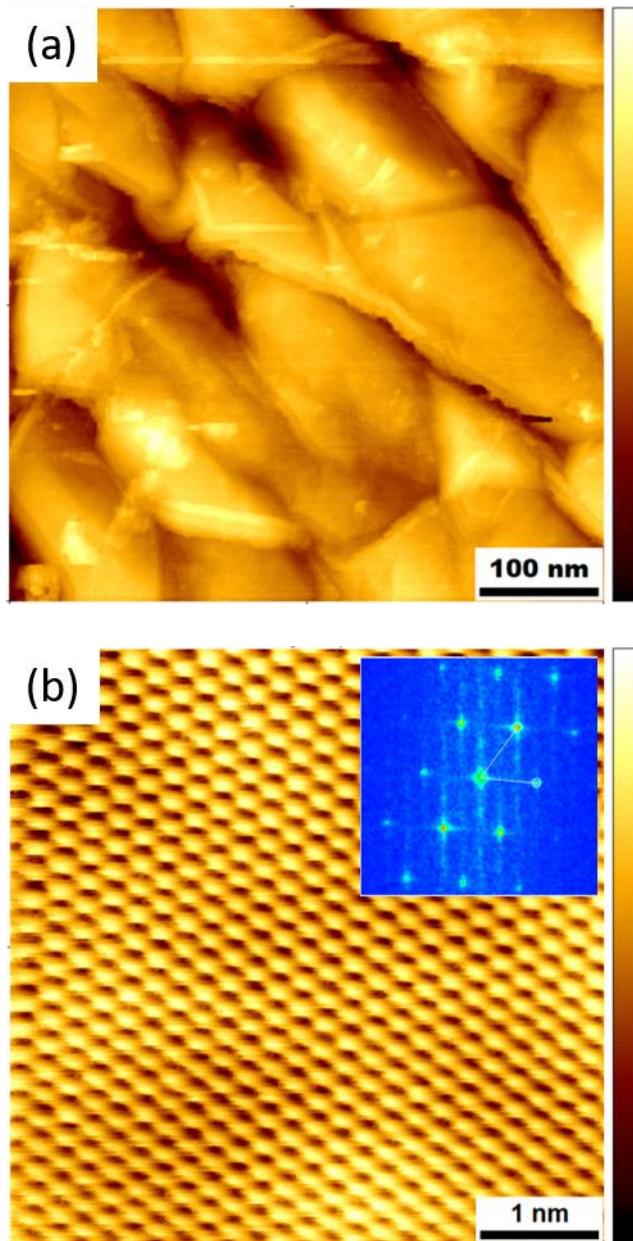


FIG. 4. (a) Constant current STM topographic image ($500\text{nm} \times 500\text{nm}$) obtained on a high dose FIB irradiation (10^6 ions/pixel) of the Cu(100). The Z colored scale varying from 0 to 20 nm is found to be identical to initial bare copper surface. (b) Higher resolution STM image

(5nm x 5nm) performed on the same zone showing atomically resolved STM image of the surface graphene layer and its Fourier pattern in the inset. On this image the Z colored scale is varying from 0 to 130pm. The recorded shape of the individual carbon atoms is attributed to the anisotropic electronic structure of the tip apex atoms.

Figure 4a shows a STM image (500nm x 500nm) acquired in the constant current mode ($I= 500 \text{ pA}$, $V = 2.5\text{V}$, $T=77\text{K}$) revealing a topography consisting large scale flat terraces and steps. The observed topography is identical to the initial bare copper sample demonstrating that according to our SRIM modeling very modest ion sputtering is taking place even at the highest investigated dose (10^6 ions/pixel). Higher resolution scans on the terraces produce typical atomically resolved STM images, see Figure 4b ($I= 500 \text{ pA}$, $V= 50 \text{ mV}$, $T=77\text{K}$) exhibiting the well-known 3-fold symmetry of the one over two atoms multilayer graphene lattice. From Fourier analysis, see the FFT pattern inset of Figure 4b, the lattice parameters are $a=0.22\text{nm}$, $b=0.24\text{nm}$ and an angle $(a, b) = 59^\circ$ (expected values are $a=b=0.242\text{nm}$ with a 60° respective angle); These results show a minor distortion due to the non-perfect calibration of the X, Y piezo tube controlling the scanning of our STM tip. However, the reproducibility of these atomic resolution STM images acquired on several high dose (10^6 ions/pixel) irradiated sample locations confirms the uniformity of the presence of graphene on these areas. Further investigations on the lower dose irradiated areas would help to define the minimum threshold ion dose required to initiate the growth of graphene, thus reducing the FIB writing time and enhancing the productivity of the technique.

The electronic properties of the graphene layer were also studied via acquiring STS spectra on different locations of a FIB-grown graphene structure as marked by the colored stars on the figure 5a and their respective spectra on fig. 5b. From one terrace to the others the $dI(V)/dV$ spectra exhibits a vast diversity of characteristics. We have mostly observed the usual V-shape DOS characteristic of the multilayer graphene⁹ but others spectra were also

observed showing either a sharp resonance or a band gap at the zero energy ($V=0V$ is the Fermi level energy). This peculiar resonance could either be attributed to the presence of atomic scale defect or to the development of a flat band arising from an alternative rhombohedral ABC stacking of multilayer graphene competing with the more common ABA Bernal stacking¹⁰. On the other hand, the $\pm 60\text{meV}$ band gap has been attributed to the phonon assisted tunneling process needed to inject electrons at the K points of the Brillouin zone for isolated graphene monolayer¹¹. Our preliminary results demonstrate the high sensitivity of STS to the local electronic inhomogeneities. It paves the way to further studies that correlate the topographic and electronic properties of the graphene to the underlying production of defects controlled by the spatial, duration and energetics of the FIB irradiations parameters.

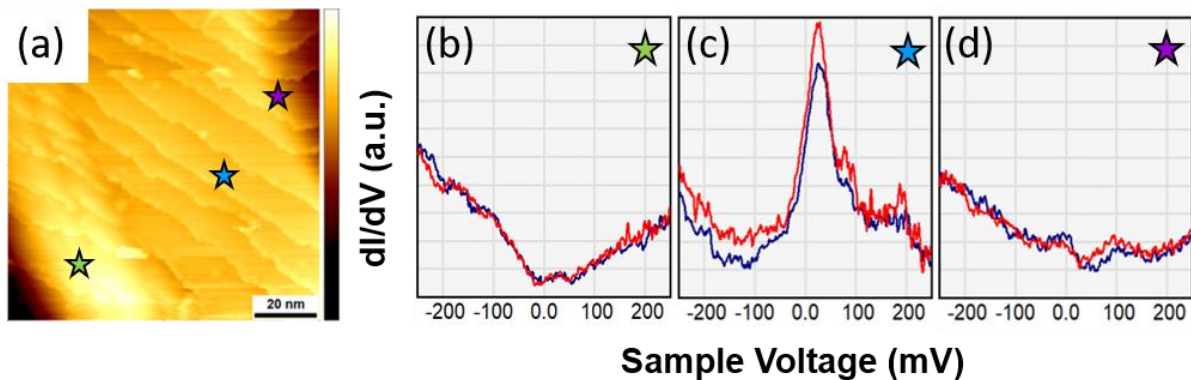


FIG. 5. (a) $100\text{nm} \times 100\text{nm}$ topographic STM image of the Cu(100) substrate with a local graphene growth on a high dose FIB irradiated pattern (10^6 ions/pixel). The Z colored scale varying from 0 to 6nm reveals a surface topography made of terraces separated by monoatomic steps. (b, c, d) $dI(V)/dV$ spectra acquired onto marked areas. The red and blue curves are the raw data acquired when respectively increasing and decreasing voltage ramp. The dI/dV values, acquired using a lock-in technique, are all in arbitrary units.

IV. SUMMARY AND CONCLUSIONS

In this work we have demonstrated that single graphene domains can be fabricated, localized and organized directly via a specific Ga^+ FIB patterning process. We have demonstrated that high FIB irradiation doses (10^6 ions/pixel) can resist the rearrangement process that occurs during the high temperature CVD preparation process, a temperature required in our experimental growth chamber to achieve high quality graphene films. The copper substrate annealing and copper native oxide removal performed around 1060°C induce a significant rearrangement of the copper precursor surface. Below the 10^5 ions/pixel threshold, the thin (around ten nm thick) FIB modified surface are erased by the annealing process. The line spacing, orientation or zigzag irradiation were found to provide identical results in the form of high quality localized 2D graphene films having sizes in coherence with the FIB irradiation pattern dimensions. The procedure we have presented relying on specific FIB irradiation can be carried as a batch process and hundreds of devices could be fabricated within a single patterning run.

Finally the investigated separation distances between two adjacent scanned lines ranging from 50 to 300nm representing a factor around 10 to 75 with respect to the calculated lateral projected ranges of 35 keV gallium ions (40nm), suggest that the sputtered and redeposited copper atoms (sputtering yield around 10) during the FIB irradiation process plays a central role in our approach.

This FIB assisted bottom-up growth technique we have presented would represent a major step towards a better control in the fabrication of structurally well-defined and well positioned 2D graphene flakes. Further work aiming at investigating the lower threshold ion dose required to initiate the growth of graphene is currently under investigation.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CONFLICT OF INTEREST

The authors have no conflicts to disclose.

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