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AFM and Raman study of graphene deposited on silicon surfaces nanostructured by ion beam irradiation

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ABSTRACT

Nanoscale structures were produced on silicon surfaces by low-energy O ion irradiation: periodic rippled or terraced patterns formed spontaneously, depending on the chosen combination of beam incidence angle and ion fluence. Atomic force microscopy image processing and analysis accurately described the obtained nano-topographies. Graphene monolayers grown by chemical vapour deposition were transferred onto the nanostructured silicon surfaces. The interfacial interaction between the textured surface and the deposited graphene governs the conformation of the thin carbon layer; the resulting different degree of regularity and conformality of the substrate-induced graphene corrugations was studied and it was related to the distinctive topographical features of the silicon nanostructures. Raman spectroscopy revealed specific features of the strain caused by the alternating suspension and

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contact with the underlying nanostructures and the consequent modulation of the silicon-graphene interaction.

KEYWORDS

Atomic force microscopy, graphene, ion beam irradiation, nanostructured surfaces, Raman spectroscopy, strain

INTRODUCTION

Among the 2D materials currently studied, graphene has the highest electronic mobility but is a zero bandgap semiconductor¹. Nevertheless, graphene exhibits remarkable properties, such as chemical durability, weak optical absorptivity, high thermal conductivity, thermal stability, high mechanical strength, flexibility². Together with the high surface area and conductivity, these properties make graphene an ideal material for sensing³, and some applications have been already discussed, for example cancer cell biosensors⁴, or ultrasensitive gas detectors⁵. The spatially non-uniform mechanical strain of graphene has a crucial role⁶, since it can be tailored to open a sizeable bandgap⁷ and engineer graphene-based electronic devices. Besides, unusual physical behaviours with possible applications have been pointed out: as an example, a suitable distortion of the graphene lattice can induce a large pseudo magnetic field⁸ and a zero-field quantum Hall effect⁹. Band structure engineering in graphene requires spatially non-uniform strain, which can be achieved through the interaction with suitable surface patterns on the substrate¹⁰. The substrate-induced graphene corrugations and the consequent modifications of its carrier transport properties can be in turn engineered to modify mechanical, optical, chemical graphene properties and its surface properties, such as wettability, chemical potential,

and expansion for energy storage². More in general, in recent years, several efforts have been devoted to investigate the interplay between topographical features of corrugated graphene (correlation length, height, aspect ratio, and bending radius) and the emerging novel physical, chemical and mechanical properties.

The ion beam irradiation of a substrate can produce tailored surface structures at the nanometer scale¹¹. The emergence of the nanostructures is induced by self-organization and has a high degree of universality since similar morphologies can be obtained on semiconducting, metallic, insulating materials using noble gas ions as well as reactive ions. A particularly great effort has been devoted to study the surface patterning by low- (~ 1 keV) to medium-energy (up to 100 keV) ion irradiation of covalently-bonded semiconductors, such as silicon, which promptly get amorphized under ion bombardment¹². In this energy range, for which ions mainly lose energy for nuclear stopping, the typical size of the nano-morphologies is in the range of a few to hundreds of nanometres. By suitably choosing the ion beam parameters/target combination, regular nanopatterns of well-defined periodicity can be obtained, including ripples (see for example Dell'Anna et al.¹³) and semiconductor quantum dots¹⁴. There are different physical mechanisms triggered by ion irradiation that regulate the spontaneous appearance of surface nanopatterns¹⁵, and a complete theory able to predict the specific interplay of these different mechanisms based on the different possible choices of the experimental parameters (ion species, energy and fluence, ion incidence angle, substrate material and temperature) is still missing¹⁶. Therefore, the major part of the abundant experimental and theoretical studies produced in the last three decades has had the long-term crucial aim of obtaining the accurate and precise control of the geometrical and chemical properties of pre-designed ion-induced surface patterns. In fact, it has been shown that ion beam irradiation can be a nano-technological process enabling applications in different fields, such as optics, electronics and magnetism¹⁷. The use of nanorippled surfaces as periodic templates for thin-film¹⁸ and

nanoparticle deposition¹⁹ is particularly promising to tailor specific magnetic or optical properties through the introduction of a spatial anisotropy. Recently, it has been shown that highly regular ion-induced nanorippled surfaces can be transferred onto biocompatible polymeric substrates²⁰ and used in a neural cell adhesion and spatial organization study²¹.

In the present work, nanostructured substrates of rippled or terraced topography were produced on silicon surfaces through ion beam irradiation and subsequently covered with a graphene sheet. The topography of the bare and graphene-covered substrates was analysed by atomic force microscopy (AFM) to relate the different nanostructured substrate geometries to the final out-of-plane graphene deformations. Furthermore, the substrate-induced strain of graphene was studied through Raman spectroscopy. To the best of our knowledge, this is the first study combining the nanostructuration of substrates by ion beam irradiation and a study of substrate-induced graphene corrugations.

MATERIALS AND METHODS

Fabrication of the textured surfaces by ion irradiation

Three (100) silicon wafer pieces of 1x1 cm² area were irradiated at room temperature using a low energy ion implanter (Danfysik A/S Denmark, model 1050) equipped with a gas-fed Chordis ion source. The 1 keV O⁺ beam with flux of $1.1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ was electrostatically raster scanned ($f_x, f_y \sim 1 \text{ kHz}$) full area over the three samples, which were tilted 50° or 55° with respect to the ion beam direction. Ion fluences were $1 \times 10^{18} \text{ ions /cm}^{-2}$ and $2 \times 10^{18} \text{ ions /cm}^{-2}$. A vacuum $< 2 \times 10^{-6} \text{ mbar}$ was maintained in the implantation chamber. For each irradiated sample, the chosen ion beam parameters are outlined in Table 1.

Graphene deposition

Graphene films were synthesized by Graphenea Inc. (San Sebastian, Spain) on copper foils by Chemical Vapor Deposition (CVD) and then transferred through a wet chemical transfer method²² onto the textured S1, S2 and S3 substrates, obtaining in this way samples G1, G2 and G3. The process used polymethyl methacrylate (PMMA) as a temporary graphene-supporting layer that was transferred onto the silicon substrate; the PMMA was then removed in an acetone bath. The Raman measurements did not evidence the presence of PMMA residues.

AFM measurements

Sample topographies were measured before and after graphene deposition by AFM images that were acquired with a scanning probe microscope (Solver Px Nt-MDT Co., Zelenograd, Moscow, Russia) operating in semi-contact mode with a silicon tip having a nominal radius of less than 10 nm. The scan frequency was $f = 0.8$ Hz and the scanning areas were of $2 \times 2 \mu\text{m}^2$ and of $5 \times 5 \mu\text{m}^2$, with a resolution of 1024×1024 pixels. All the measurements were carried out in air at room temperature; to remove image tilts and low frequency distortions possibly induced by the scanner, a third-order surface subtraction was performed on the raw scan data.

An adhesion force map (pull-off) and corresponding surface topography were concurrently acquired from samples S3 and G3 using the Bruker ScanAsist AFM imaging technology in QNM mode (quantitative nanomechanical mapping). Peak force microscopy in tapping mode was carried out using a silicon cantilever (Model: ScanAsist air) with a stiffness of 0.4 ± 0.1 N/m and a diameter of 20 ± 5 nm. The chosen tapping frequency was $f = 7$ KHz. AFM measured the interfacial forces between the tip apex (covered with native oxide) and the silicon- or graphene-textured surface. For each peak force tapping cycle, the tip approached and contacted the surface; subsequently, an attractive force was measured during the tip retraction phase (pull-off)

force measuring the tip-substrate adhesion force). The force-distance spectra were taken by scanning a 500x500 nm² area at a resolution of 256 lines with 256 pixels per line.

Raman measurements

A Raman spectrometer (LabRAM Horiba Jobin-Yvon Ltd) was used for vibrational mode Raman measurements of the graphene-covered samples. A laser of 633 nm wavelength, 5 mW power and beam spot diameter of $\sim 4 \mu\text{m}$ was used in all measurements. Raman spectra were acquired in the 1000–3000 cm⁻¹ range and accumulated for 10 s. Raman spectroscopy measurement was carried out on G1 and G2 samples and the resulting spectra were compared with that of a reference sample, i.e CVD-grown graphene deposited onto a flat Si surface (sample name: Gr-Si-CVD). The spectra were always acquired from surface portions in which the continuity of the graphene film had been previously assessed by optical microscopy and AFM surveys. The peak position and intensity of G and 2D Raman bands were extracted by a Lorentzian fit.

Numerical analysis of AFM topographies

The extraction of the AFM linear cross sections and all the discussed numerical analyses of the AFM topographies were performed running in-house-developed code in Python²³ with the scientific and numerical packages: Numpy, Scipy, Matplotlib. The minimum correlation length l of the surface nanopatterns was estimated from the position of the first peak maximum in the 1D height-height autocorrelation function (ACF), calculated from the AFM images along the projection of the ion beam direction onto the sample surface, identified as the x-direction. For periodic nanopatterns, the x-projection gives the corresponding wave-vector direction and l represents the ripple wavelength λ . To measure the average difference between peak heights and valley depths of the ripples, called mean roughness depth R_z , the maximum vertical distances D_l between the highest and lowest data points within one correlation length and for all the possible lengths l contained in a single x-line scan were calculated and summed to provide

the final R_z average value (more details about this calculation can be found in²⁰). The D_1 histograms were computed together with the corresponding Probability Distribution Function (PDF), calculated with a gaussian kernel density estimation by Scott's method²⁴. To further compare the nanopatterns before and after graphene deposition, the PDFs of the surface slopes in the x- and y-direction were used. For each AFM image, the corresponding 2D gradient was first calculated; its x and y components were used to calculate the 1D gradient distribution functions along the two directions by means of a gaussian kernel density estimation by Scott's method.

RESULTS AND DISCUSSION

AFM analysis: silicon samples

The focus of the next two sections is on samples S1/S2 and G1/G2. S1 and S2 samples were irradiated with different values of fluence and incidence angle. They were appropriately chosen to induce well-known^{13,16} extreme topographical differences on the surfaces, which were in turn used to study the different out-of-plane graphene deformations that they induced.

Figures 1 (a)-(b) illustrate the topography evolution of a silicon surface upon 1keV O ion irradiation when both ion fluence and incidence angle are increased (see Table 1). In Figure 1(a), a periodic rippled pattern has formed on sample S1 with wavevector in the x direction, namely the one parallel to the projection of the ion beam direction onto the surface. These types of nanopatterns are therefore called parallel-mode ripples¹³. The short, medium and long-range regularity is confirmed by the inspection of the corresponding height-height ACF, calculated along the x direction (x-ACF, see Figure 2 (a)), which also provides the fundamental ripple wavelength $\lambda=42.2$ nm (Table 2). In Figure 1(a), a second, weak undulation is visible; it is oriented in the y-direction and has a longer correlation length. Its presence causes the wave-like

background shown in the x-ACF function in Figure 2(a) as well as the poorly-pronounced long-range oscillation in the corresponding y-ACF component. This double structure has been often observed and becomes more and more evident by increasing the ion fluence^{17,25}. In Figure 1(b) the morphology of the silicon substrate S2 has transformed from parallel-mode ripples of S1 into parallel-mode terraces. This is a well-known evolution, which can be observed by increasing the ion irradiation time - and therefore the fluence²⁶, and/or by increasing the ion incidence angle^{13,27}. From an analytical point of view, the terraced topographies develop on the irradiated surfaces when nonlinear contributions cannot be ignored anymore in the equation for the surface height evolution in time²⁶. In the x-ACF of S2 in Figure 2(b), the previous very regular spatial correlation of S1 along the x direction is lost, while the shortest correlation length $l=673.1$ nm is now much larger than the fundamental ripple wavelength in S1, $\lambda=42.2$ nm (Table 2). The loss of regularity causes the x-ACF in S2 to become more similar to its y-ACF than in S1 sample. Also a slightly more pronounced and regular y-ACF long range oscillation is now visible (compare x-ACF and y-ACF in Figures 2(a)-(b)). This is a surface evolution induced by the increasing ion fluence, which more and more defines the first weak corrugation in the y-direction and, eventually (at higher fluence), can form a quasi-periodic undulation, overlaying the parallel-mode nanopattern¹⁷. The observed increase of l with irradiation time or incidence angle is called *coarsening* and was first attributed by Hauffe²⁸ to the sputtering of surface structures by nearby reflected ions. A height profile along the x-projected ion direction is shown for samples S1 and S2 in Figures 3(a)-(b) respectively. A change is ongoing from a sinusoidal-like to a faceted or saw-tooth-like shape, with rear and front sides (with respect to the incoming ions) approaching a normal and parallel alignment to the ion beam direction respectively²⁹. The so-called ion sculpting is universally observed in case of a prolonged non-linear regime and can be attributed to the shadowing of the ripple valleys by the emerging surface heights that impede in this way the ions from eroding the valleys³⁰. The two line scans also allow the understanding of the topographical origin of the increase of the mean roughness depth R_z from S1 to S2,

reported in Table 2. When the linear regime yields, the increase of R_z is exponential while the ripple wavelength keeps constant; at longer times, when the non-linear effects contribute to the pattern evolution, the growth of R_z becomes slower while the correlation length starts to increase. Asymptotically, both R_z and l stabilize with a final reduced order and quality of the surface pattern¹².

AFM analysis: graphene-covered samples

Figures 1(c)-(d) show the AFM topographies of graphene films G1 and G2 transferred onto samples S1 (Figure 1(a)) and S2 (Figure 1(b)) respectively. Figures 3(c)-(d) show the corresponding height profiles along the x-direction. Sample G1 appears to have conformed to the underlying sinusoidal-like S1 nanopattern since it presents a similar ripple-like profile. Accordingly, the G1 x- and y-ACF curves in Figure 2(c) are similar to the corresponding S1 ACFs in Figure 2(a). In x-ACF in particular, a similar long, medium and short correlation range is maintained, and the fundamental ripple wavelength λ in G1 is in fact $\lambda=42.5$, comparable to $\lambda=42.2$ in S1. The reduced range of the x-ACF autocorrelation values in sample G1 as compared to S1 is instead related to the very little decrease of the corresponding mean roughness depth R_z (see Table 2). Therefore, G1 follows along x the same undulation of S1, but on average not entirely from the crests down to the bottom of the valleys; it results instead slightly suspended. To further investigate this aspect, Figure 4(a) shows the PDFs of the vertical distances D_i , calculated from the S1 and G1 AFM topographies. The bell-shaped curves reflect the sufficiently periodic nature of the two profiles, which was already highlighted by the ACFs. The maximum of the two distributions corresponds to the R_z value reported in Table 2. As expected, the distribution of the peak-to-valley heights shifts towards lower D_i values and the corresponding average R_z value becomes slightly lower than in S1.

Figures 3 (b),(d) allow the comparison of the height profiles of samples S2 and G2 along the ion beam projected direction. The saw-tooth-like shape of S2 does not allow a conformal coverage with graphene. As a result, in G2 sample, graphene laid down along the x-direction with a reduced mean roughness depth R_z and with a longer correlation length than in S2 (Figure 2(b),(d) and Table 2). It comes out that in G2 a slower spatial undulation with a reduced out-of-plane amplitude partially disguises the underlying saw-tooth profile. The magnitude of the vertical distances in S2 seems to provide a too moderate interaction to bend the graphene sheet down to a peak-to-valley extension comparable with the S1/G1 case. Accordingly, the percentage decrease (P) of R_z in S1/G1 and S2/G2 is $P_1 = 14\%$ and $P_2 = 32\%$ respectively. In addition, from the x-ACF and y-ACF of sample G2 (Figure 2(d)), it also emerges that the resulting out-of-plane undulations in x and y are more similar in G2 when compared with those in the G1 graphene layer. Therefore, the reduced silicon-graphene interaction of the S2/G2 system causes a more isotropic distribution of graphene corrugations on the silicon substrate as compared to G1. Figure 4(b) shows the PDFs of the vertical distances D_1 calculated from S2 and G2 AFM topographies. The less smooth shape of the S2 PDF, if compared with the S1 PDF, reflects the irregular terraced topography produced by the higher fluence ion irradiation. As expected, the G2 PDF shifts towards lower D_1 values. Some just sketched peaks in the 10-20 nm range are visible in G2 PDF. This result indicates the presence of a few more frequent peak-to-valley height ranges that produce the kind of irregularity visible in Figure 3(d) and the more pronounced oscillation in x-ACFs of Figure 2(d) if compared with Figure 2(b). To summarise, the G2 graphene coverage recovers a higher degree of regularity along x than its S2 silicon substrate and a more isotropic x- and y-distribution of its out-of-plane undulation as compared to the graphene sample G1.

To complete the description, the PDFs reported in Figure 5 present, for each sample, the two distributions of gradients $\partial z/\partial x$ and $\partial z/\partial y$ (z being the height coordinate) calculated along the

x- and y-direction using the data represented in the AFM images of Figure 1. In those figures, the projected ion beam onto the sample surface enters from left to right. Therefore, the slopes of the surface portions facing the ion beam are positive, while the rear faces have negative slopes. In case of an ideal sinusoidal-like rippled pattern, the symmetry of the shape produces the symmetry of the corresponding 1D slope distribution about the axis origin, since each positive slope of the continuous front curve corresponds to an equal but negative slope of the continuous rear curve. In Figure 5(a) the slope distribution along the x-direction has two main symmetric peaks, reflecting some regularity of the rippled pattern; the two maxima correspond to the more present slope angle $\alpha \sim 11^\circ$ in the profile (Figure 3(a)). The symmetry of the distribution curve at smaller slope angles is interrupted since, in the x profile, especially the rear faces present some discontinuity (see Figure 3(a)), which is the first appearance of nonlinear effects, due to the sufficiently high ion fluence used. In the y-direction, the long-range, weak wrinkling is sufficiently symmetric to produce a sharp symmetric slope distribution around the origin. In Figure 5(b) the effects of the ion-fluence increase are shown: the slope distribution in the x-direction becomes asymmetric, with a single prominent peak in the positive range, principally due to the constant slope contribution of the front faces. In the negative range, the contribution from slope angles at larger values than in the corresponding positive range derives from the more structured rear faces of the saw-tooth-like x-profile and can be attributed to the still on-going, nonlinear, ion-sculpting process^{13,29}. The slope distribution along the y-direction is still symmetric but wider and reflects the evolution of the nanostructures towards a quasi-periodic undulations of higher aspect ratio.

The analysis of the changes in the slope distributions after graphene deposition of Figures 5(c)-(d) completes the description of the different out of plane deformations resulting from specific substrate-graphene interaction² induced by the different silicon topographies. Samples G1 of Figure 5(c) shows a predominant, sinusoidal-like wrinkling in the x-direction that reflects the

highly anisotropic S1 substrate; in addition, in G1, the different undulations in x- and y-direction produced the different width of the two slope distributions. Interestingly, the x distribution is more continuous than the corresponding curve of its S1 substrate (Figure 5(a)); this indicates that the suspended graphene smooths the discontinuities, especially of the rear faces of the S1 x-profiles. In the y-direction, the PDF is similar to the corresponding S1 curve, so that a conformal, long-range, weak rippling is confirmed and an asymmetry between the interaction with the S1 substrate along the x- and y-direction emerges, with a consequent asymmetry in graphene deformation. The terraced topographies of sample S2 produce a different interaction with the deposited graphene (Figure 5(d)). The suspended graphene sheet clearly recovers a less asymmetric slope distribution along x, and a sharper, symmetric distribution along y, if compared with the corresponding distributions of its S2 substrate (Figure 5(b)). The reduced negative range of the x-PDF indicates a smoother, less structured rear profile than in S2 and, overall, a more symmetric undulation. Also, the symmetric range of slope values in the y-direction is now reduced. Therefore, this slope-analysis confirms that the graphene coverage of sample S2 produced a smoother and more ripple-like shape in x- and y-direction if compared with the corresponding S2 profiles. Also, the similarity between the x- and y-PDF in G2 increases as compared primarily with S2 but also with G1 (Figures 5(b)-(d)), which indicates a more isotropic distribution of wrinkles than in S2 and G1.

Adhesion force measurements

The AFM peak force working mode allows the recording of the adhesion properties of the tip-surface system in parallel with the topographic data of the analysed surface and, therefore, the investigation of changes in the chemistry of the system³¹.

The adhesion force measurement was carried out on samples S3 and G3 (Table 1); the AFM topography in Figure 6(a) shows the partial coating of the S3 nanopatterned silicon substrate

with the graphene sheet producing in this way sample G3. Sample S3 had been irradiated at the same incidence angle of sample S1 and the same, highest, ion fluence of sample S2. Therefore, as a result, its x-ACF in Figure 7(a) is typical of a parallel-mode rippled pattern with short-medium- and long-range regularity and a fundamental ripple wavelength $\lambda=42.6$ nm (see also Table 2). In the y-ACF, a just-sketched oscillation reveals the presence of the already-here-discussed shallow, long-range undulation in the y-direction of the corresponding topography. The S3 surface is more similar to the one of the S1 rather than the S2 sample since it is known that the increase of the incidence angle reduces the time-range of the linear regime¹³. Therefore, in the prolonged irradiation time changing the topography from S1 to S3, a quasi-linear regime persisted, with the still ongoing, maybe slower growth of the mean roughness depth R_z and a still constant wavelength λ (Table 2). Coherently, the ACF analysis of the G3 topography resembles that of G1 sample: the out-of-plane undulation of graphene G3 has still a dominant auto-correlated component in the x-direction (Figure 7(b) and Figure 2(c)). The mean roughness depth values calculated on S3 and G3 (see Table 2) produces a percentage decrease of the R_z value $P_3 = 26\%$, which is intermediate between P_1 and P_2 values. Therefore, the reduction is due again to the suspended conformation of the graphene layer confined above the periodic ripples. As, an example, the x-line height (topography) profile in Figure 6(c) shows the consecutive z contributions from S3 and G3 and confirms on average the reduction of the peak-to-valley height moving from S3 to G3.

Figure 6(b) illustrates the adhesion force map from the same surface region of the AFM topography of Figure 6(a); it shows the spatial distribution of the adhesion force (nN) acting between the hydrophilic silicon tip and the bare or graphene-covered textured surface when the tip is moving vertically away from the surface. The lateral resolution in Figure 6(b) and the extent of the corresponding adhesion-force interaction depend on the diameter of the tip apex and on the related contact area at the tip-graphene (or tip-silicon) interface; here, a diameter

smaller than the ripple wavelength was intentionally chosen, so that the tip can entirely follow the depth of the through region. The adhesion force profile in Figure 6(c) is acquired from the same x-line scan from which the 1D topography profile was extracted (centre of the image). Both curves in Figure 6(c) show the consecutive contributions of S3 and G3. The reduction of spatial regularity of the 1D force profile of the graphene surface mimics the change of the shape of the corresponding 1D topography scan. The adhesion force profile of the silicon S3 as well as of the graphene sample G3 has maxima and minima values that are shifted of half a period with respect to maxima and minima in the corresponding topography profile (comparison in Figure 6(c)). On both surfaces, the adhesion force decreases on the ripple crests and increases on the ripple valleys. This is due to the larger contact area between the tip and the valleys than between the tip and the crests. However, this analysis did not show an adhesion force that was larger in graphene valleys than in silicon valleys. Therefore, it seems that the suspended graphene layer does not behave like a membrane being deformed under the action of the normal force due to the adhesion of the tip during the retracting movement^{31,32}. We can hypothesize that the aspect ratio λ/R_z is too small for a free graphene deformation during the retraction phase.

Raman measurements

In graphene and more in general in sp^2 carbon materials, the main features in the Stokes Raman spectrum^{33,34} are the G peak at $\sim 1580\text{ cm}^{-1}$, associated with the doubly degenerate zone centre E_{2g} mode, and an especially intense 2D band at $\sim 2657\text{ cm}^{-1}$ that is a second-order overtone of zone boundary phonons. Those phonons give rise to the generally Raman-forbidden D band ($\sim 1388\text{ cm}^{-1}$) only in the presence of atomic defects within the graphene layer, while G and 2D always satisfy the Raman selection rules. D and 2D peak positions are dispersive (dependent on the laser excitation energy). The 2D band shift and the 2D/G band intensity ratio are related to the number of graphene layers^{35,36}. Figure 8 presents the Raman spectrum of samples G1, G2

and of reference sample Gr-Si-CVD measured at 633 nm and plotted after non-flat background subtraction. In sample Gr-Si-CVD the 2D peak is a single sharp Lorentzian with FWHM $\sim 14 \text{ cm}^{-1}$, a signature of a single graphene layer^{36,37}. For samples G1 and G2, the 2D to G intensity ratio $I(2D)/I(G)$ is respectively 1.7 and 1.2, indicating the presence in each sample of a single graphene layer.

In samples G1 and G2, the rippled or terraced substrate induces curvatures in the bidimensional carbon lattice that were deeply investigated in this study through AFM analysis. The G band arises from the in-plane C-C bond stretching of all pairs of sp^2 atoms³³; a tensile strain would therefore reduce the G mode energy, causing a Raman redshift. If the strain is uniaxial, as in the case of bending, a split of the G peak into two separate vibrational components can be observed, one along the strain and the other perpendicular to it^{38,39}. The 2D band also downshifts, but does not split for a small uniaxial strain⁴⁰. In sample G2, the G and 2D peak positions are redshifted as compared to those of Gr-Si-CVD (see Table 3), and the shift of the 2D peak is larger than that of the G peak (37 cm^{-1} vs 23 cm^{-1}). Therefore, the terraced silicon substrate S2 induces a strain in the above graphene layer. In G1 sample, the redshift of the 2D peak (46 cm^{-1}) is larger than in G2 sample, indicating an increasing strain in G1 sample with respect to G2 sample; besides, in G1 sample the split of the G band appears, with a G^+ peak less intense than G^- . The former is perpendicular to the applied strain, while G^- is parallel to it, therefore experiencing a larger mode softening than G^+ (Table 3). This result can confirm the previously discussed AFM analysis, which showed that in G2 the graphene sheet follows the S2 substrate in a less conformal way than G1 sample with S1 sample. In Figure 8, the Raman analysis shows a clear split of the G band in G1 sample but not in G2 sample. Nevertheless, a faint shoulder in the G peak of G2 samples witnesses the non-perfect isotropy, which was already discussed in the AFM data analysis. As a consequence, Raman analysis confirmed that G2 sample has a higher degree of isotropy than G1 sample. The AFM analysis already proved that the directional anisotropy in

the out-of-plane undulation and the P height reduction were respectively higher and lower in G1 sample than in G2 sample, because the different silicon topographies induced a different silicon-graphene interaction with a different resulting degree of graphene suspension and a different resulting out-of-plane undulation both in x- and y-direction.

CONCLUSIONS

This paper discussed the conformality changes of graphene layers deposited onto different nanopatterned substrates. The nanostructures were obtained by irradiating small portions of a crystalline silicon wafer with a broad beam of low-energy O ions. The effects on the topography of the silicon, and consequently of the graphene covering the samples, caused by different choices of the ion fluence and ion incidence angle were studied through an extensive AFM image processing and analysis. The study confirmed that the adhesion energy between silicon and graphene, and therefore the different degree of conformality, was related to the amplitude and correlation length of the substrate undulation. In this study, the more shallow and regular rippled silicon substrate produced a better conformality than the silicon substrate of larger height excursion (one order of magnitude) and poorer nanopattern regularity. In this second case, the percentage of decrease of the amplitude of the graphene undulation was higher, and the presented analysis showed that this more suspended graphene sheet recovered a higher degree of regularity and isotropy in its out-of-plane undulation along the x- and y- direction if compared with its silicon substrate and with the other graphene sample. The AFM peak force adhesion analysis did not evidence a deformation of the suspended portions of graphene due to the adhesion of the tip during the pull-off phase. The different emerging conformality also reflected in the different Raman response of the two graphene samples. This spectroscopic analysis revealed a more intense and uniaxial strain in the more anisotropic and conformal

graphene sheet. The Raman analysis was not able to resolve the strain contributions located on either graphene crests or valleys, because of the laser spot diameter $d \sim 4 \mu\text{m}$. In the next future, we intend, therefore, to apply TERS (Tip Enhanced Raman Spectroscopy) to investigate further the strain induced on graphene by rippled and terraced silicon substrates.

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TABLE CAPTIONS**Table 1:** Irradiation parameters and sample names used in this study.

Bare Si samples	After graphene deposition	Implanted ion species	energy (keV)	Fluence 10^{18} (ions/cm ²)	Incidence angle (°)
S1	G1	O+	1	1.0	50
S2	G2	O+	1	2.0	55
S3	G3	O+	1	2.0	50

Table 2: The minimum correlation length l (or wavelength λ), and the mean roughness depth R_z together with its standard deviation sd are reported for the bare silicon samples S and the corresponding graphene-covered samples G. All the values are calculated along the x-direction. The percentage reduction P of R_z after graphene deposition is reported for the three S/G systems.

	l or λ (nm)	$R_z \pm sd$ (nm)	P (%)
S1	42.2	2.8 ± 0.6	
S2	673.1	25.3 ± 5.4	
S3	42.6	3.1 ± 0.6	
G1	42.5	2.4 ± 0.7	14
G2	802.2	17.1 ± 4.6	32
G3	43.1	2.3 ± 0.7	26

Table 3: The peak positions of the G and 2D bands in the Raman spectra of the reference sample Gr-Si-CVD and the graphene-deposited samples G1 and G2 of Figure 8. For sample G1, the G band splits in two subbands G^+ and G^- : the corresponding peak positions are reported.

	G peak position [cm^{-1}]	2D peak position [cm^{-1}]
Gr-Si-CVD	1609	2685
G1	$G^- = 1588$ $G^+ = 1613$	2639
G2	1586	2648

FIGURE CAPTIONS

Figure 1: $2 \times 2 \mu\text{m}^2$ AFM topographies of (a) silicon sample S1, irradiated with 1 keV O ions and a fluence of $1 \times 10^{18} \text{ ions}\cdot\text{cm}^{-2}$ at 50° ; (b) silicon sample S2, irradiated with 1 keV O ions and a fluence of $2 \times 10^{18} \text{ ions}\cdot\text{cm}^{-2}$ at 55° ; (c) sample G1 obtained by covering S1 with CVD-grown graphene; (d) sample G2 obtained by covering S2 with CVD-grown graphene. The arrows indicate the projection of the ion beam direction onto the sample surface.

Figure 2: 1D height-height ACFs, calculated along the x- and y-direction from AFM topographies of (a) S1 and (b) S2 bare silicon samples and (c) G1 and (d) G2 samples covered with CVD-grown graphene. In each figure, the vertical line shows the position of the first peak maximum in the x-ACF, representing the minimum correlation length l (or wavelength λ). The green curve (the reader is referred to the web version of this article) is the gaussian fit from which the peak position has been extracted. For an adequate calculation of l , the $5 \times 5 \mu\text{m}^2$ AFM scans of samples S2 and G2 have been used.

Figure 3: AFM line scans extracted along the projection of the ion beam direction onto the surfaces, which is horizontal from left to right. (a)–(d): S1, S2, G1, G2 samples. The $5 \times 5 \mu\text{m}^2$ AFM scans of all samples S and G have been used.

Figure 4: Probability distribution function of the vertical distance values D_l calculated from (a) S1 and G1 AFM topographies; (b) S2 and G2 AFM topographies. For an adequate calculation, the $5 \times 5 \mu\text{m}^2$ AFM scans of samples S2 and G2 have been used.

Figure 5: Probability distribution function of the surface slopes in the x- and y-direction of (a)–(d) S1, S2, G1, and G2 AFM topographies. For an adequate calculation, the $5 \times 5 \mu\text{m}^2$ AFM scans of samples S2 and G2 have been used.

Figure 6: (a) AFM topography of the ion irradiated silicon substrate S3 and of an adjacent graphene-covered S3 surface region, namely one surface portion of the G3 sample; (b) adhesion force [nN] map obtained by scanning the same contiguous S3 and G3 surfaces; (c) the superimposition of the topography and the adhesion force profiles of contiguous samples S3 and G3; the two 1D profiles were extracted from the same x-line scan (centre of image) in (a) and (b). The dashed line in (a) and (b) is a guide for the eye, roughly indicating the silicon-graphene transition, which is not straight at this spatial scale.

Figure 7: 1D height-height ACFs, calculated along the x- and y-direction from AFM topographies of (a) S3 bare silicon samples and (b) G3 sample covered with CVD-grown graphene. In each figure, the vertical line shows the position of the first peak maximum in the x-ACF, representing the minimum correlation length l . The green curve (the reader is referred to the web version of this article) is the gaussian fit from which the peak position has been extracted.

Figure 8: Stokes Raman spectra of graphene covered samples G1 and G2 and of reference samples Gr-Si-CVD. The peak centers of G and 2D bands are reported in Table 3. The G2 and G1 spectra are y-shifted of 50 and 100 intensity units respectively for readability reasons. For interpretation of the references to colour in the legend, the reader is referred to the web version of this article.