Suspended graphene on germanium: selective local etching via laser-induced photocorrosion of germanium

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Abstract

The implementation of graphene in nanoelectromechanical systems and electronic applications requires not only techniques to fabricate high-quality monolayers, but also methods to process these layers. Nondestructive processing is especially challenging in the case of fragile suspended graphene membranes. In this work, we present a direct writing method for graphene grown on germanium that yields suspended layers without the need to transfer the graphene layer. To this end, we employ laser-induced photoelectrochemical etching which is highly selective and dissolves only germanium leaving the graphene layer intact. Only a focused continuous wave laser beam and water (or an aqueous solution) are required for the etching to proceed. Raman spectroscopy measurements were performed \textit{in-situ} to monitor the etching process. These measurements reveal a dramatic increase of the graphene-related Raman bands as the graphene layer detaches from the substrate. This substantial increase indicates that the commonly observed weak Raman signal for graphene on germanium is not an inherent material property but is due to the interaction of the germanium substrate with graphene. Together with the established graphene growth on germanium, the presented direct writing method builds a complete toolbox for graphene membrane-based applications.

1. Introduction

The search for the most appropriate substrate for graphene growth is still ongoing and of key importance for possible future applications of graphene in nanoelectromechanical systems (NEMSs) and electronic applications. An ideal substrate should be compatible with current silicon-based complementary metal-oxide semiconductor technology, which allows for the integration into well-established standard fabrication processes. However, this integration has been strongly hindered by the difficulties of growing graphene directly on silicon. Attempts to perform such growth show that it leads to SiC precipitates \cite{1, 2}. In order to be able to grow graphene on silicon, buffer layers need to be applied \cite{3}. Germanium is an excellent buffer due to a very low carbon solubility \cite{2, 4}. This low solubility together with the compatibility with silicon-based technology renders germanium a very suitable graphene growth substrate. Indeed, successful wafer-scale growth of high-quality graphene on germanium has already been achieved \cite{2, 4–15} and it has been shown that graphene grown on germanium with different crystallographic orientations shows different properties and surface morphologies \cite{5, 6, 16, 17}. Moreover, in contrast to chemical vapor deposition (CVD) growth of graphene on copper, the graphene layer is directly grown on a semiconducting layer, avoiding metal contamination \cite{2, 18}. 

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An important aspect that can strongly influence the properties of graphene layers grown on germanium is the role of germanium oxide. Contrary to silicon, for which the native oxide is very difficult to dissolve, germanium oxide readily dissolves in water [19, 20]. It has been shown, for example, that the removal or growth of interfacial germanium oxide strongly alters the characteristics of graphene on germanium [19, 21]. On the other hand, it has been reported that graphene grown directly on germanium by CVD hinders the oxidation of germanium [11, 22], however, it can occur due to imperfections on the nanoscale [23–25].

In this work we present an approach that uses the solubility of germanium oxide to our favor. We developed a direct writing method to selectively etch germanium underneath graphene, without damaging the graphene layer. This way one can directly etch shapes into the germanium substrate and obtain suspended graphene. This technique could prove very useful for graphene nano-membrane production as it is straightforward, cheap and can be applied on the wafer scale.

2. Results and discussion

In order to harvest the full potential of graphene on germanium, for example for NEMS, dedicated etching techniques have to be developed. In this work we present a technique that relies only on water (or an aqueous solution) and a focused continuous-wave laser beam, yet at the same time offers a very high etching selectivity.

We first discuss the photoelectrochemical processes at the germanium/water interface without graphene coverage to describe the basic etching mechanism. Light-controlled decomposition of semiconductors has been studied in detail [26–28] but in our case two additional aspects are crucial. First, the sample is illuminated by a micrometer-sized laser spot, which leads to the creation of electron–hole pairs in a small, confined area. Second, no electrical contact to the germanium substrate was made, thus the experiments are performed with a floating potential (electroless setup). The laser illumination leads to an accumulation of photogenerated holes at the surface of the exposed area. These holes take part in the dissolution of germanium [29–31]. Germanium is oxidized and the resulting germanium oxide is dissolved in water, facilitating effective removal of the etched material. Since no external current source is connected, electron and hole currents have to be equal. The compensating electron current is provided by the whole sample area that is not illuminated. In this region electrons are injected from the sample to the solution. The illuminated region hence forms a virtual anode and the surrounding dark area a virtual cathode [31]. The large surface ratio between the illuminated and not-illuminated regions allows to obtain large hole current densities responsible for the observed effective etching, compensated by small electron current densities in the large surrounding area [29]. Scanning electron microscopy images of germanium etched in deionized water are presented in figure 1. The structures were written directly into crystalline bulk germanium without using any photoresist or etching agent. Figure 1(a) shows a static exposure without moving the stage, yielding an etched hole of sub-micrometer size. Panel (b) presents a two-dimensional pattern, written by moving the stage in $x$- and $y$-directions with the same dwell time for each point. Figure 1(c) shows a similar stage movement as shown in (b), but with different dwell times allowing to etch arbitrary three-dimensional shapes. Such a three-dimensional processing is difficult to achieve with conventional lithography-based etching techniques, which renders the developed method attractive for many applications.

Now we move to the case of germanium covered by graphene. In order for the etching to proceed, germanium has to be illuminated and at the same time be in contact with the aqueous solution. For an ideal graphene layer, no water should penetrate underneath graphene and reach the substrate, hence no etching is expected. However, recent works show that

![Figure 1](image-url) Scanning electron microscope images of photoetched bulk germanium. (a) Single point exposure resulting in sub-micrometer sized holes (scale bar: 400 nm). (b) Two-dimensional etch pattern obtained by moving the stage 500 nm between the consecutive etch steps (scale bar: 4 $\mu$m). (c) Three-dimensional structures obtained by using different dwell times. The obtained staircase like structure is about 10 $\mu$m deep (scale bar: 5 $\mu$m).
Figure 2. Three-dimensional illustration of the setup used for the direct-writing etching process. A laser is focused by a water-dipping objective to selectively etch germanium without affecting the graphene layer. This etching process directly yields suspended graphene membranes.

despite the general passivating nature of graphene [11, 22], corrosion occurs at the nanoscale [23–25]. These observations imply that if defects are present in graphene, water can penetrate germanium on the nanoscale [23–25]. The experimental setup used to study the behavior of graphene on germanium upon laser illumination in aqueous solutions is presented as a three-dimensional schematic drawing in figure 2. The laser light is focused on graphene grown by CVD on germanium on a silicon substrate. The sample is then immersed in a 50 mM NaCl solution (compatible with biological applications) and illuminated by a 633 nm continuous wave laser (laser power \(\sim 3\) mW) through a water-dipping objective, yielding a laser spot smaller than 1 µm. At this excitation wavelength, above the direct bandgap of germanium, the penetration depth of light is about 100 nm [33]. Figure 3(a) schematically illustrates such an etching process.

In order to study the evolution of the etching, the outcoming light was collected by the same objective and analyzed in a Raman spectrometer. The chemical specificity of Raman spectroscopy allows us to gain valuable information in-situ. Figure 3(b) shows consecutive Raman spectra measured as indicated in the sketch of figure 3(a). The first spectrum shows a typical Raman spectrum for germanium with a prominent peak at 300 cm\(^{-1}\) and second-order peaks at 550–600 cm\(^{-1}\) [34]. After about 1000 s another band emerges at around 400 cm\(^{-1}\), which can be attributed to Si–Ge [35]. This Si–Ge contribution stems from the material at the Si/Ge interface. Upon further etching the germanium signal decreases in intensity and a silicon peak appears at 520 cm\(^{-1}\), gaining in intensity. A hole through the germanium epilayer has been etched and the laser now illuminates the silicon substrate. The thickness of the germanium epilayer was 3 µm in this case. Note that the germanium signal does not vanish entirely as there are always contributions of scattered light from the sidewalls of the etched hole. The etching process is highly selective. In this structure only germanium is decomposed. In fact, prolonged exposure of a silicon substrate immersed in water under the same conditions did not show signs of decomposition. The resulting high selectivity is desirable for many applications in semiconductor processing, especially for NEMS. In this case, silicon acts as an etch-stop layer and the germanium layer can be regarded as a sacrificial layer. Figure 3 shows that the etching was possible despite the graphene coverage, which implies that there must be a significant amount of defects for this sample that allow the water to reach germanium. One method to assess the defect contribution is Raman spectroscopy. The Raman evolution of the graphene bands obtained for another etching process under the same conditions is shown in figure 4. Please note that the D band is out of the spectral windows for these measurement, but a D’ band is clearly visible. To monitor the temporal evolution of the signal we have to perform static measurements without moving the grating, which did not allow to cover the full spectrum in this measurement. Additional measurements showing the evolution of the D and G band can be found in the supplementary information (available online at stacks.iop.org/2DM/8/035043/mmedia).

At the beginning, the Raman spectrum is barely visible, due to the weak Raman signal of graphene on germanium. Although it is difficult to compare different Raman measurements from different publications in terms of intensity, there is one indicative feature,
i.e. the intensity ratio of the graphene Raman peaks to the Raman peak of nitrogen in air ($\sim 2330 \text{ cm}^{-1}$). For graphene on germanium, the Raman intensity must generally be rather weak, as the characteristic graphene bands are only a few times larger or similar to the intensity of the Raman peak from nitrogen in the air [7, 14, 17, 22, 24, 32, 36].

For exfoliated graphene or graphene on SiC, the Raman signal of graphene is much more intense and the nitrogen peak is generally barely visible on that scale.

Figure 4 shows that already after about 50 s of illumination the Raman signal increases dramatically. We ascribe this sharp increase to the underetching of the graphene layer. This explanation is in agreement with post-process Raman mapping that will be presented in figure 7. Graphene decouples from the substrate and forms a freestanding membrane. This observation clearly shows that the low Raman intensity of graphene on germanium is not inherent to this kind of graphene, but is related to the interaction with the underlying substrate. Graphene on germanium builds a Schottky junction with an effective charge transfer across the graphene/germanium interface [37, 38], which vanishes as soon as the substrate is etched away. Moreover, it has been shown that the large refractive index of germanium can influence the detectable emission intensity, which could also explain the increase in intensity [39].

Besides the apparent increase in Raman signal, the evolution in figure 4 could also be used to extract further information on strain and carrier concentration via a detailed analysis of the G and 2D band positions. However, our measurements show that the evolution of the Raman peak positions varies from point to point on the sample (see supplementary information for more spectra), which makes it very difficult to extract a common behavior for static, time-resolved measurements. Please note, that a statistical, post-process Raman mapping analysis is possible and will be presented in figure 8.

The etching itself is a complex dynamic process that depends on many parameters such as the formation and dissolution of germanium oxide underneath graphene, local changes in strain during the delamination of graphene or changes in carrier concentration of graphene due to changes in the surrounding solution. All of these parameters can influence the Raman peak positions, which can explain the observed differences.

An important aspect which, however, can be extracted from the time resolved evolution is that prolonged laser exposure is not changing the G to D' intensity ratio ($I(G)/I(D') \sim 2$). Also for larger laser powers, no increase in defect-related Raman bands is observed with time (see supplementary information). Instead, the D band intensity seems to depend rather on the initial presence of defects. As already mentioned, the presence of such a defect contribution to the Raman signal is commonly observed for graphene on germanium [4, 13, 14, 32].

In order to further show that the etching technique can not only be used in a static way but also to write a pattern, a scan across the edge of a freshly cleaved sample was performed. To stabilize the graphene during the exposure, a 100 nm thick layer of PMMA was deposited on top of the substrate. Figure 5(a) presents a sketch of the experiment, with the sample being immersed in deionized water. The laser remains in place, and the sample is moved underneath using a high precision stage. Figures 5(b)–(d) show the optical microscope images taken in the spectrometer at different stages of the etching process. As a result, a well-defined line can be etched into the substrate.

When a stabilizing PMMA layer additionally covers graphene, the germanium passivation is enforced
and no water reaches the substrate. Indeed, in this case we do not observe any etching effect inside the sample. However, despite the additional passivation with PMMA, germanium is always in contact with water at the boarders of the sample which enables photoetching at the edges. Hence, when starting a scan from the edge of the sample a pattern can be drawn as shown in figure 5. The etched trench provides access of water to the point of laser illumination. A scan in opposite direction will not lead to an etched trench, since no etching occurs inside the sample. To illustrate this effect, a video showing a scan in the opposite direction, starting from inside the sample is presented in the supplementary information. The lack of etching without water access indicates that the etching is due to a photochemical effect and not related to possible thermal effects due to laser illumination.

In order to further study the suspended graphene, the sample has to be removed from the water. In this process, the surface tension and capillary effects may lead to a damage of the graphene membrane. However, due to the stabilizing PMMA layer, the sample can be removed without damaging the membrane. Next, the PMMA has to be delicately washed away, which is performed in an acetone bath. The sample is then dried in a critical point dryer to minimize surface tension effects. A scanning electron microscope image of a resulting membrane is shown in figure 6. Graphene clearly spans over the whole under-etched germanium trench and is firmly attached to the sidewalls. A facet-like appearance of the germanium substrate next to the suspended layer, typical for Ge(001) [17, 40], can also be observed. Raman mapping of the same membrane is shown in figure 7(b). The underetching of graphene leads, as in the case of the static measurement (figure 4), to a dramatic increase in Raman response. The false-color map indicates a strong 2D Raman signal only in the underetched region. Figure 7(c) presents two Raman spectra for different points. The purple spectrum is taken on the membrane, whereas the green spectrum is measured on the pristine germanium substrate. The decoupling from the substrate is evident and leads to the observed strong increase in signal.

To further study the influence of the photoelectrochemical germanium etching on graphene, we performed Raman mapping measurements on the graphene membrane and in a region far from the etched area that has not been exposed to the laser. Figure 8 presents the results of Lorentzian fits to the G and 2D band in these regions.

Using such statistical results, it becomes possible to separate the influence of doping and strain, which both affect the G and 2D band energies [41]. The solid black lines indicate changes in strain for which we assumed $\Delta \omega_{2D}/\Delta \omega_G = 2.2$ [41]. The parallel thinner solid lines are offset by a hole carrier concentration of $\Delta n = 5 \times 10^{12}$ cm$^{-2}$. The dashed gray lines mark G and 2D band variations caused by changes in hole concentration (slope: $\Delta \omega_{2D}/\Delta \omega_G = 0.7$) [41]. The thinner dashed parallel lines are offset by a change in strain of 0.1 %. As values for undoped, freestanding graphene we assumed $\omega_G^{0} = 1580$ cm$^{-1}$ and $\omega_{2D}^{0} = 2671$ cm$^{-1}$ [41–44], where the 2D value was corrected for the employed laser wavelength (532 nm) [45]. The black circles correspond to measurements on the membrane and the blue squares were recorded in the unexposed, germanium supported region. The latter region shows a rather large scattering of points, which can be understood by the influence of both doping and strain variations. Most of the points align in agreement with a variation of strain, but with a slightly larger slope than the drawn black lines. Here, we use a mean value for the slope, but real values depend on the direction of strain in relation to the armchair and zig-zag axes and can be much larger [41]. Despite the large variation, most of the points are in the region of compressive strain, which is typical for graphene.
on germanium [8, 9, 32, 36]. Changes in doping are also observed, with a few scattered points that significantly differ from the main trend. The statistical mean values for the supported region are 1601.8 ± 2.8 cm⁻¹ for the G band and 2696.9 ± 5.9 cm⁻¹ for the 2D band, marked by an orange square in figure 8. These values translate into a compressive strain of about −0.2% and a carrier concentration of about \( n_{\text{supp}} = 7 \times 10^{12} \text{ cm}^{-2} \) when assuming hole conductivity in good agreement with earlier Raman studies of graphene on germanium [6, 8, 17, 32, 36]. The results for the etched graphene membrane are very different. Upon etching the strain relaxes and the points become less scattered. In fact, the points align well with the trend indicated by the gray dashed line, which corresponds to the G and 2D band shifts caused by changes in hole doping, based on which we assume the sample to be p-type. The differences in doping can be explained by residual germanium, germanium oxide or PMMA on the membrane. The SEM image (figure 6) shows some brighter regions on the membrane, which could be associated with this local variation in carrier concentration. The statistical values for the suspended regions are 1591.0 ± 2.5 cm⁻¹ for the G band and 2680.0 ± 1.9 cm⁻¹ for the 2D band, marked by a red circle in figure 8. These values correspond to a very slight compressive strain of about −0.04%, which, within the accuracy of the performed analysis, can be regarded to be strain free. The extracted carrier concentration of \( n_{\text{mem}} = 5 \times 10^{12} \text{ cm}^{-2} \) is lower than in the supported graphene on germanium region.

### 3. Conclusions

We show that germanium can be effectively photoetched by a continuous wave laser beam in deionized water as well as aqueous NaCl solutions without the need to contact the sample electrically. These findings were employed to develop a highly selective etching method for germanium. This method, applied to graphene grown on an epilayer of germanium on silicon, allows us to directly write trenches into the germanium substrate, leaving graphene and silicon untouched. The so-prepared graphene membranes show a dramatic increase in Raman signal, which indicates that the commonly observed low Raman intensity of graphene on germanium is not inherent to the growth method, but is caused by a strong...
interaction of the graphene layer with the germanium substrate. A Raman mapping analysis of the suspended graphene shows strain relaxation and a lower carrier concentration in comparison to unetched regions. The presented work provides the proof of concept that it is possible to directly write suspended graphene structures into graphene on germanium, which holds great prospect for NEMS applications as this method is simple to implement, safe, clean and cheap and can be applied to samples on the wafer scale.

4. Experimental section

4.1. Graphene CVD growth

The graphene layers were synthesized by the CVD method on a 3 μm thick (100) germanium epi layer deposited on a silicon wafer (Ge/Si substrates were supplied by IHP GmbH). Prior to the graphene growth, germanium substrates were annealed in pure hydrogen atmosphere for 30 min at a temperature of 895 °C. During the process of graphene deposition we sustained the growth temperature of 905 °C and Ar/CH₄ mixture in the ratio of 100:1 at 800 mbar.

4.2. Membrane exposure and Raman measurements

The static exposure was performed using a Horiba T64000 Raman spectrometer with a He–Ne laser (633 nm) at a power of about 3 mW. A Nikon water-dipping objective (40×, NA 0.8) was used to focus the laser. The objective was directly placed into a 50 mM NaCl solution (deionized water + NaCl – ACS grade). The trench etching was performed using a Renishaw inVia Raman spectrometer and a 532 nm laser with a laser power of about 30 mW in pure deionized water (≈18 MΩ cm). The same water-dipping objective was used. The Raman mapping of the membrane was performed using a Renishaw inVia Raman spectrometer and a 633 nm laser for figure 7 (532 nm in the case of figure 8) with a laser power about 1 mW focused using a 50× (NA 0.75) objective.

4.3. Stabilizing polymer and drying

PMMA (MicroChem) was deposited by spin coating and dried on a hot plate at 180 °C for 60 s. After removing the sample from the water the PMMA was washed in acetone. The sample was consecutively dried from acetone using a Leica EM CPD300 critical point dryer. In this process, acetone is first replaced by liquid carbon dioxide which is then brought to its critical point from where it transits into the gaseous phase, minimizing issues related to surface tension.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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