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Ricciardella, Filiberto; Vollebregt, Sten; Boshuizen, Bart; Danzl, F.J.K.; Cesar, Ilkay; Spinelli, Pierpaolo; Sarro, Pasqualina Maria

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Filiberto Ricciardella^{1,4} , Sten Vollebregt¹ , Bart Boshuizen² , F J K Danzl³, Ilkay Cesar³, Pierpaolo Spinelli^{3,5} and Pasqualina Maria Sarro¹

¹ Department of Microelectronics, Delft University of Technology, Feldmannweg 17, 2628 CT Delft, The Netherlands

² Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

³ ECN-TNO Solar Energy, Petten, 1755 LE, The Netherlands

⁴ Universitaet der Bundeswehr Muenchen, Institute for Physics, EIT 2, Werner-Heisenberg-Weg 39, 85577 Neubiberg, Germany

⁵ Saule Technologies, 54-427 Wroclaw, Poland

E-mail: filiberto.ricciardella@gmail.com

Keywords: large-area synthesis, transfer-free process, chemical vapor deposition, multi-layered graphene, polymer-free transfer medium

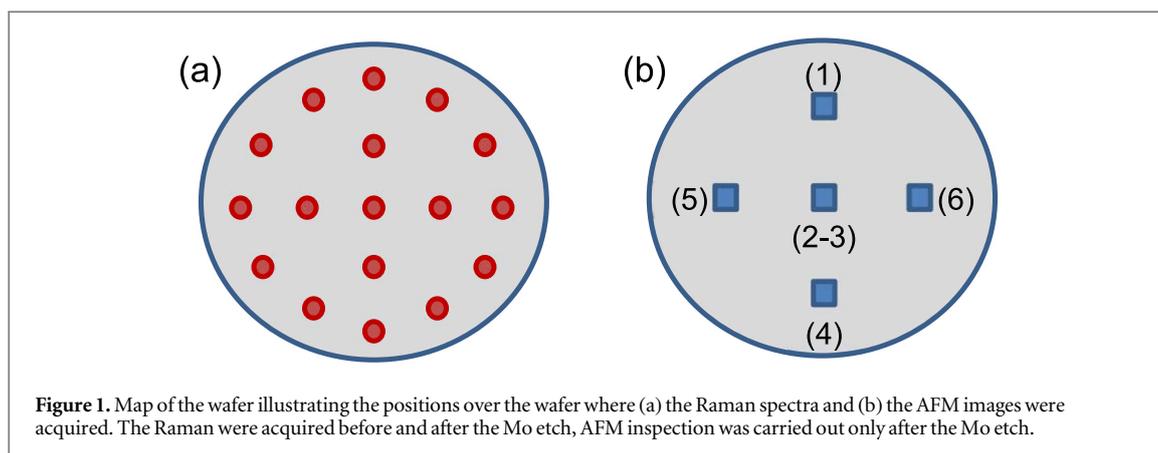
Abstract

Chemical vapour deposition (CVD) has emerged as the dominant technique to combine high quality with large scale production of graphene. The key challenge for CVD graphene remains the transfer of the film from the growth substrate to the target substrate while preserving the quality of the material. Avoiding the transfer process of single or multi-layered graphene (SLG-MLG) has recently garnered much more interest. Here we report an original method to obtain a 4-inch wafer fully covered by MLG without any transfer step from the growth substrate. We prove that the MLG is completely released on the oxidized silicon wafer. A hydrogen peroxide solution is used to etch the molybdenum layer, used as a catalyst for the MLG growth via CVD. X-ray photoelectron spectroscopy proves that the layer of Mo is etched away and no residues of Mo are trapped beneath MLG. Terahertz transmission near-field imaging as well as Raman spectroscopy and atomic force microscopy show the homogeneity of the MLG film on the entire wafer after the Mo layer etch. These results mark a significant step forward for numerous applications of SLG-MLG on wafer scale, ranging from micro/nano-fabrication to solar cells technology.

1. Introduction

The development of scalable graphene deposition method has been a task urgently pursued by researches working in the graphene field [1–4]. Over all the emerging and industrial applications where graphene is involved, it is crucial to have high quality graphene available on large area and suitably deposited on insulating substrate [5]. Out of the established methods for the graphene synthesis [6, 7], chemical vapour deposition (CVD) has emerged as the dominant technique to combine high quality with large scale production as compared to the mechanical exfoliation of highly oriented pyrolytic graphite and epitaxial growth on silicon carbide (SiC) [8–12]. So far, CVD has enabled the synthesis of the largest areas of graphene, although on flexible foils [13, 14]. On rigid substrates, the Wang's group [15] as well as Rahimi and co-workers [16] have grown the material at wafer scale using germanium (Ge) or Cu as a catalyst, respectively. Besides Ge, transition metals or combination of transition metals are typically adopted as catalysts during the CVD growth to synthesize the carbon-based material [17–21].

Despite the significant progress on growing graphene even at the wafer-scale, the key challenge for CVD-grown graphene remains to transfer the film from the growth substrate to the target substrate while preserving the quality of the material [22–24]. The transfer is the unavoidable step associated to the CVD process in order to achieve practical applications. On the other hand, the transfer is the stage of the entire process which can more severely degrade the graphene film by introducing damage, polymer contamination and wrinkles [25–28].



Up to now, plenty of wet [22, 29–31] and dry [23, 27, 32–37] methods have been employed for the transfer of single and multi-layered graphene (SLG-MLG), although most of the proposed solutions are overall applied on areas of few centimetre squared or need intermediate polymer-based transport media.

The direct synthesis of graphene onto the target substrate, such as SiC or other dielectrics substrates, could overcome the transfer step [23, 38–40]. The synthesis usually is assisted by plasma or very high temperature. In case of plasma assisted deposition, the quality of the material can be adversely affected, while the growth by high temperature can severely limit the choice of the substrates [41]. Moreover, the high cost of the SiC substrate and of the process itself hinders the spread of the growth on SiC.

Here we report on a simple, fast and convenient method to release MLG entirely on the 4-inch where MLG was grown. Although a few other groups obtained SLG-MLG at the wafer scale [22, 32, 36], the films were still transferred to the target substrate. Based on the approach introduced in this paper, we completely get rid of any transfer medium (for instance polymer based), while obtaining MLG on an entire 4-inch wafer. The growth and target substrate are the same, thus avoiding any transfer from the two substrates, reducing the possibility to degrade the film and enabling the direct integration of graphene-based devices at large scale [42]. This outcome represents a remarkable step forward compared to the method we reported in our previous works [43–46]. In those papers, we dealt with areas of patterned MLG of hundreds μm^2 which we fabricated using several steps in the lithographic process. In this paper, we present areas of hundreds cm^2 obtained without any complex fabrication process. Last but not least, the lithographic process required to employ quite aggressive compounds, such as the N-methyl-pyrrolidone solvent to remove the photo-resist used to fabricate the micrometric structures. The application of the method hereby presented only requires hydrogen peroxide (H_2O_2) as etching solution, de-ionised water and no costly lithographic steps.

As catalyst metal, we used a molybdenum (Mo) film, a CMOS compatible metal, in order to overcome the disadvantages presented by copper [47]. Once the sacrificial Mo layer was etched, the terahertz transmission near-field imaging (TNFI) showed that the MLG film thoroughly lies on the oxidized silicon wafer (SiO_2/Si). Raman spectroscopy (RS) and atomic force microscopy (AFM) further proved the homogeneity of the MLG film over the entire wafer.

2. Experimental sections

2.1. Material preparation and characterization

Silicon wafer covered by a 90 nm-thick film of thermally grown SiO_2 were used as base substrate. On top of the oxidized Si wafers, a Mo layer (50 nm) was sputtered at 50 °C using a SPTS Sigma DC magnetron sputter coater from a target having purity equal to 3N5. Then, MLG was grown by CVD in an AIXTRON BlackMagic Pro in Ar and H_2 mixture under the pressure of 25 mbar, at 935 °C for 20 min, using 20 sccm of methane (CH_4) as carbon precursor.

In order to etch the Mo underneath MLG and release the film on Si/ SiO_2 , we covered the wafer with a puddle of H_2O_2 solution concentrated at 31% (vol.) (D-Basf). After 5 min, de-ionised water was used to dilute the H_2O_2 puddle. Finally, we dried and heated up the wafer for 5 min at 100 °C.

We investigated the MLG-based wafer through a Renishaw inVia Reflex spectrometer before and after the Mo etching. The tool, equipped with a He-Ne laser ($\lambda = 633 \text{ nm}$) and a 50 \times objective with a numerical aperture of 0.50, was used in back-scattering configuration. As representative of the full area, we acquired 17 spectra on the wafers, as reported in figure 1(a).

Once the Mo film was etched, we inspected the surface morphology of MLG by atomic force microscopy (AFM) employing a ND-MDT NTEGRA AURA set-up. A poly-Si HA-NC cantilever having tip radius less than

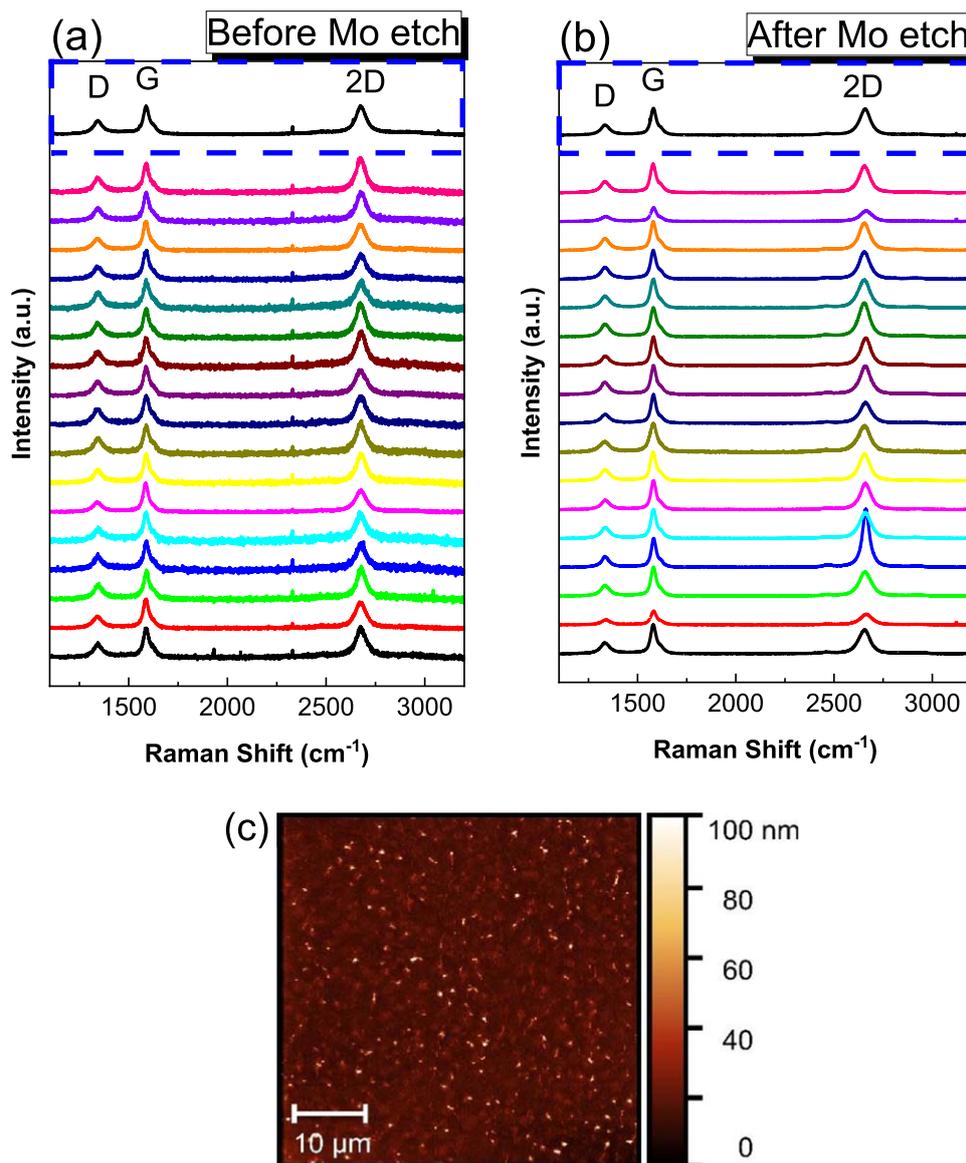


Figure 2. Raman spectra captured over the wafer before (a) and after (b) the Mo etch on the positions draw in figure 1(a). All spectra are normalized to the G band's intensity. (c) Example of AFM image captured on spot (2) labelled in figure 1(b). The area scanned on that spot was $2500 \mu\text{m}^2$.

Table 1. Average values of Raman parameters determined on the investigated wafer before and after the Mo etch.

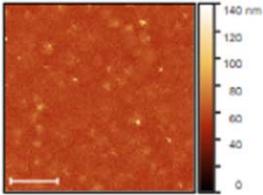
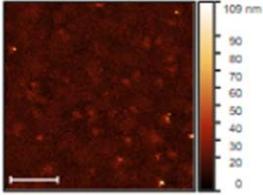
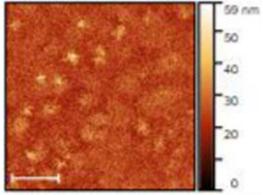
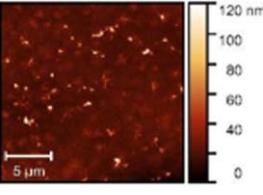
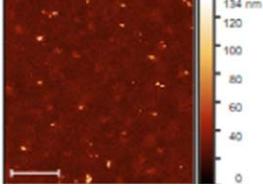
Before etch			After etch		
I(D)/I(G)	I(2D)/I(G)	FWHM(2D) [cm^{-1}]	I(D)/I(G)	I(2D)/I(G)	FWHM(2D) [cm^{-1}]
0.50 ± 0.10	1.00 ± 0.14	70 ± 6	0.40 ± 0.05	1.02 ± 0.32	60 ± 7

10 nm was used in semi-contact mode at a rate of 0.60 Hz. To map the wafer, different spots (figure 1(b)) having area of $2000 \mu\text{m}^2$ were scanned acquiring 256 lines per spot.

Finally, we carried out the terahertz near-field imaging (THz-NFI) to scan the entire 4-inch area after releasing MLG on the Si/SiO₂ wafer. The TeraSpike TD-800-X-HR (Protomics GmbH) tool was used in transmission mode, as described elsewhere [48]. The microprobe was placed at a distance of tens of microns from the substrate.

We performed x-ray Photoelectron Spectroscopy (XPS) to examine the presence of any residues underneath the MLG film after the Mo etch. The XPS measurements were carried out in a K-Alpha system by ThermoFisher. The x-ray gun used an Al K α source with a power of 36 W. The spot size of the gun is approximately $770 \times 380 \mu\text{m}^2$.

Table 2. Values of the roughness and corresponding AFM images collected over the wafer, as highlighted in figure 1(b). The scale bar reported on the images is 5 μm .

Position	Roughness R_a [nm]	AFM image
#1	2.8	
#3	2.7	
#4	2.6	
#5	3.2	
#6	2.9	

3. Results and discussion

Figures 2(a), (b) displays the Raman spectra captured on the wafer before and after the Mo etch, respectively. In both panels, the spectra enclosed in the dashed rectangles represent the spectra averaged from the 17 points. The most prominent bands in all spectra (figures 2(a), (b)) are located at around 1350, 1580 and 2700 cm^{-1} and named as D, G and 2D. The bands are attributed to the disordered mode (D), graphitic mode (G) and overtone of D (2D), respectively. The intensities of the bands, indicated as $I(D)$, $I(G)$ and $I(2D)$, and the full-width at half maximum of the 2D band ($FWHM(2D)$), are used to roughly estimate the number of layers and the quality of the material [49, 50].

Before the Mo etch, the average values of both $I(2D)/I(G)$, i.e. the ratio between the intensities, and $FWHM(2D)$ show that the material mostly consists of MLG (table 1). The nature of the MLG is confirmed especially by the absence of any shoulder in the 2D peak at lower wavenumbers and the ratio $I(2D)/I(G) \sim 1$ [49, 50].

The average ratio $I(D)/I(G)$ indicates the presence of some defects in the material [43, 46, 47, 49, 50]. In this letter, we mostly showed the power of the transfer-free process. Further refinements of the synthesis parameters are ongoing aimed at substantially reducing the presence of defects originating from the growth on Mo. After the

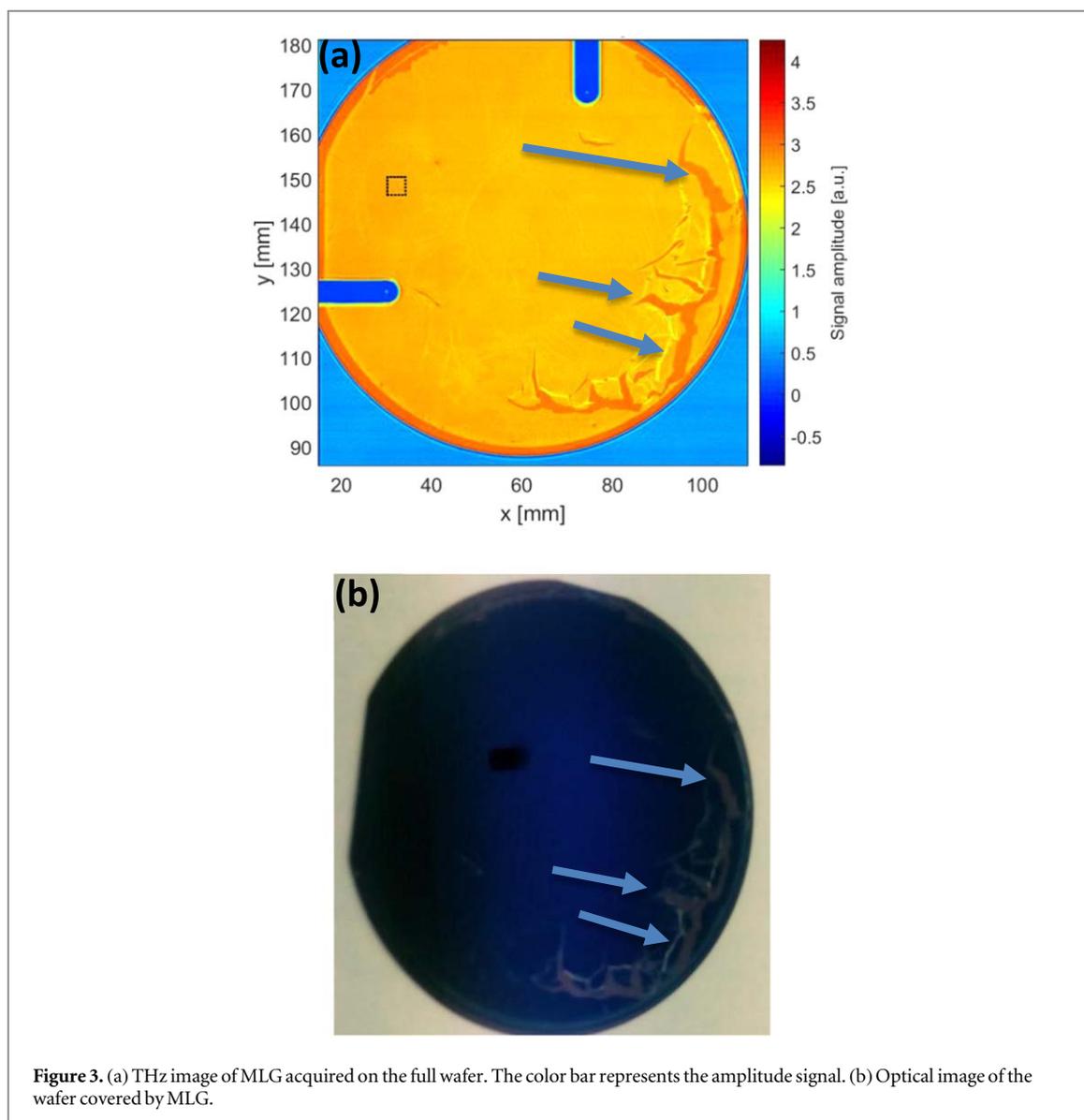


Figure 3. (a) THz image of MLG acquired on the full wafer. The color bar represents the amplitude signal. (b) Optical image of the wafer covered by MLG.

Mo etch, we found out that the three parameters show values still comparable with those before the etch, within the error margins (table 1).

These outcomes firstly highlight that the quality of the released MLG film on Si/SiO₂ substrate is not affected significantly by the Mo etch. The results also provide with an estimation of the homogeneity of the Raman spectra over the entire wafer.

To prove the overall homogeneity of the film over the wafer, the AFM analysis and particularly the roughness was considered a useful parameter. Figure 2(c) shows the area scanned on spot (3) indicated in figure 1(c). The roughness of the film (~ 3 nm) obtained on this position is representative of the values determined over the wafer, as reported in table 2.

The roughness determined from the spots indicated in figure 1 confirms the homogeneity of the MLG film, the maximum variance of the roughness over the wafer being roughly 23%. The average thickness of about 10 nm [51] could indicate the nature of the material more similar to the ultra-thin graphite. However, the presence of multi-layered structures is confirmed by the Raman spectra, as reported in previous report [46].

The rare spikes having higher thickness (~ 100 nm) can likely be attributed to some residues trapped underneath or on the film, most probably drops of water and particles.

To further address the homogeneity of the released MLG film, the wafer was scanned using THz mapping. The amplitude shown by the colour scale in figure 3(a) is proportional to the transmittance of THz radiation through the specimen. A homogenous signal is thus directly related to a homogenous layer, as shown by the light orange color spread over the wafer (figure 3(a)). Therefore, the map of the recorded signal clearly illustrates the wafer covered by the film. The coverage of the wafer is indirectly confirmed by the small darker orange parts on the right side of the wafer, indicated by the blue arrows. Those cracks and wrinkles, even visible in the optical

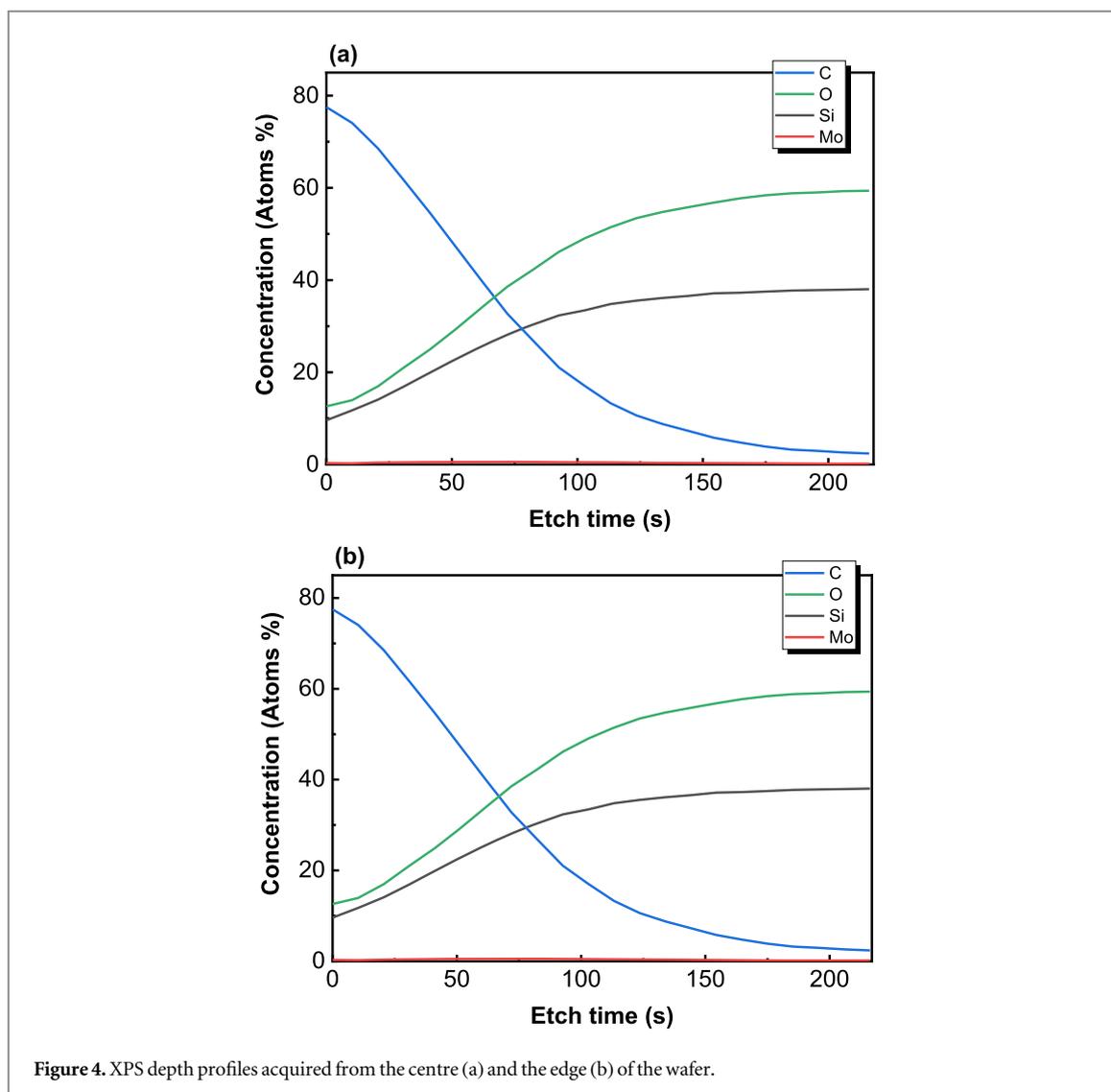


image (figure 3(b)), show parts of the bare substrate in contrast to the lighter parts which represent MLG. It is worth to note that the uncovered area (roughly 4%) is negligible compared to the full wafer. It is very likely that optimizing the transfer-free process, especially during the dilution of the H_2O_2 puddle by water, will reduce considerably the uncovered area of the wafer.

Finally, we verified that the sacrificial Mo layer was definitively removed by the etching solution. Figure 4 reports the profiles captured from two points, in the centre and edge of the wafer.

Both panels in figure 4 show that during the milling by the Ar ion the concentration of Mo atoms (red line) in the film is very likely lower than the XPS resolution [52] (<0.1 atomic %) or also null, as showed by energy-dispersive x-ray spectroscopy (EDX) [43]. Diving deeper into the sample, while the concentration of Mo atoms keeps to be null, the concentrations of O_2 (light blue line) and Si (red line) atoms increase. The SiO_2 layer is indeed immediately reached by the x-ray due to the nanometric thickness of MLG. These outcomes definitively confirm the reliability of our release approach, showing that the H_2O_2 solution can etch away the Mo layer without affecting the MLG layer. Further tests are ongoing to verify the reliability of the approach on SLG-FLG and different thicknesses of the catalyst layer. Also, optical and electrical characterizations of the material will be presented elsewhere.

4. Conclusions

We presented an original method to obtain a 4-inch wafer thoroughly covered by MLG avoiding any transfer step and any transfer medium after the growth by CVD. The MLG grown on Mo layer catalyst was released on the same SiO_2/Si wafer simply etching the catalyst layer in H_2O_2 solution. MLG film was proved to be homogenous on the entire wafer while preserving the quality of as-grown material. No detectable residues of Mo were found underneath the MLG. The introduced transfer-free approach definitely shows that the transfer step

can be overcome for CVD-grown materials on large-scale substrates. In addition, this transfer-free method paves the way to the large-scale fabrication of devices on the growth substrate by CVD graphene.

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Author contributions

F.R. ideated and performed the experimental activity, analyzed data and wrote the paper. F R and S V conceived the idea of the paper. B B performed the XPS characterization. F J K D, K C and P S performed the THz measurements. P M S supervised the manuscript. All authors provided their own contribution in writing the manuscript.

ORCID iDs

Filiberto Ricciardella  <https://orcid.org/0000-0002-9669-5649>

Sten Vollebregt  <https://orcid.org/0000-0001-6012-6180>

Bart Boshuizen  <https://orcid.org/0000-0002-3413-8839>

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