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A New Transfer Technique for graphene Deposited by CVD on Metal Thin Films

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ABSTRACT

Chemical Vapor Deposition of graphene on metallic substrates is one of the most attracting techniques for large area graphene production. The technique widely employed for transferring graphene to other substrates involves deposition of a polymer support with subsequent etching of the metal substrate. Here we report a safer transfer process which requires a two-step polymer deposition. By Raman spectroscopy both the graphene sheets grown on Cu thin films and ones transferred to other substrates have been characterized, showing comparable quality.

INTRODUCTION

Graphene can be obtained by Chemical Vapor Deposition (CVD) by means of a catalytic Cu substrate leading to large area production ideally along the entire surface of the catalyst. The so grown graphene needs to be transferred onto an insulating substrate in order to make electrical measurements or device designing possible. The most popular method for transfer is wet etching of the underlying metal substrate that can be done with ferric chloride, ferric nitrate, or acids such as nitric acid. An improvement of this method is to coat graphene by an insulating and non-reactive polymer like polymethyl-methacrylate (PMMA) or polydimethylsiloxane (PDMS), acting as a support, and then to etch away the growth substrate having this way the graphene-polymer system floating in the etching solution. Finally, graphene with the polymer support is laid onto a desired substrate, e.g. SiO_2, and the support is dissolved in a suitable solvent [1], [2].

Another transfer solution, promising for its industrial implications is the roll-to-roll technique. It has been proposed firstly in 2010 [3] where a 30-inch transfer has been achieved from a Cu foil to a PET film. A similar method, integrating the CVD growth, has also been proposed by Kobayashi et al [4].

Another method leads to avoid the use of a polymeric support layer and to transfer graphene directly on silanized SiO_2 [5].

The transfer process proposed here is inspired by a procedure used in MEMS (Micro Electro-Mechanical Systems) production where an embossed PMMA sample is bonded to another one by applying a high pressure at temperatures nearby the PMMA glass transition [6] By means of spin coating, PMMA layers are deposited onto both the growth and the destination substrates of graphene. This allows for bonding of the two substrates and the successive transfer process.

EXPERIMENTAL

Cu is the transition metal chosen for CVD because the low solubility of C leads to an easier control of graphene growth with respect to other metals such as Ni, Co or Fe. The precursor used in the present work is ethanol due to the low temperature of dissociation, but in principle the method here described can be applied to graphene grown by using different precursors.

In order to propose a technique greatly compatible with the current microelectronics technology, we employed thin films of Cu catalyst [7], instead of the widely used foils

Cu films of 600 nm have been deposited with an electron beam evaporator at a rate of 0.17 nm/s in high vacuum onto oxidized Si substrates (fig. 1a). After evaporation, the samples have been rapidly transferred into a Jipelec JetFirst100C Rapid Thermal CVD (RTCVD) system and placed in high vacuum to prevent Cu oxidation.

The CVD process consists in a heating ramp until 650 °C with a rate of 55 °C/min. An array of halogen lamps allows heating the sample at such rates. This prevents Cu film dewetting, a well-known phenomenon occurring in such systems during the heating stage [8]. Starting from T= 550 °C, a flux of H_2 is provided and maintained also for the following annealing step, in which temperature is kept constant at 650 °C for 5 min. Before the deposition step, H_2 flow is stopped and the system is pumped down to 10^{-2} mbar for 30 s. Ethanol is delivered from a liquid source and deposition is carried out for 5 min at a pressure of 0.9 mbar. Cooling is performed by switching off the heating elements, and eventually, to increase the cooling rate, by fluxing Ar or N_2 in the chamber.

To bond the sample supporting graphene (fig. 1b) to a new sample (Si, in our case), four layers of PMMA (in order to reach a thickness of approximately 600 nm on both substrates) were spun onto both samples. The successive bonding step requires a careful control of the pressure and temperature conditions. For this reason, a press has been designed and realized to be integrated onto a heating hot plate (Torrey Pines Scientific Digital Hot Plate) (fig.2). Four springs with known Hooke constant allow the value of the applied pressure to be determined by measuring their deformation

After curing of both samples, they were put inside the press and heated up to 120°C. A typical bonding recipe requires a pressure of 10 MPa for a time of 1200 s, after which the two substrates are bonded, as elucidated in fig. 1c.

The bonded sample is then split by etching of SiO_2 in a 10% HF solution (fig. 1d), then the sample is immersed in a $FeCl_3$, 1 M solution to etch the Cu film leaving graphene on PMMA, as displayed in fig. 1e.

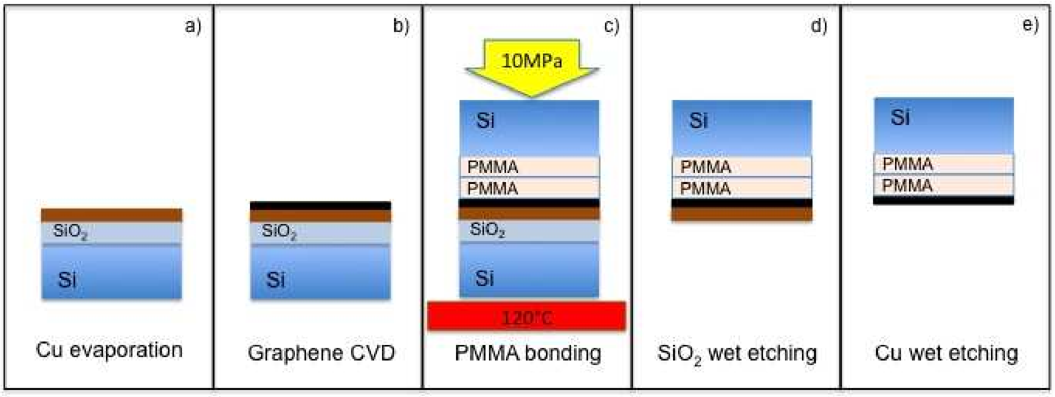

Fig. 1 Scheme of transfer process: a) deposition of Cu (brown) by e-beam evaporation; b) CVD of graphene (black); c) PMMA bonding; d) SiO_2 wet etching; e) Cu wet etching.

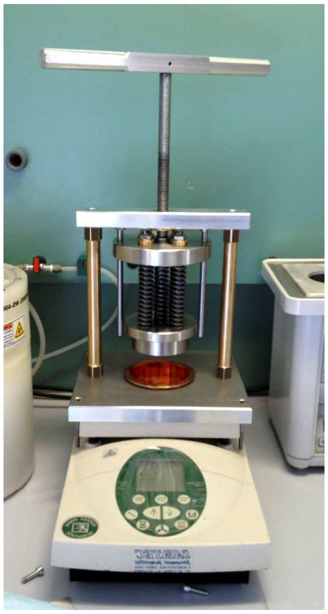

Fig. 2 Press placed on the heater.

Raman characterization has been done on as deposited and transferred samples with a Renishaw InVia Raman spectrometer, equipped with a 442 nm laser (Kimmon IK Series He-Cd Laser). With the chosen laser wavelength, it is possible to characterize directly graphene on Cu avoiding luminescence emission [9].

AFM characterization of transferred graphene has been carried out by means of a Park XE-100 System.

RESULTS AND DISCUSSION

Compared to the standard transfer procedure, the technique proposed allows to avoid the step in which PMMA-graphene floats in the Cu etching solution and so can better preserve the graphene quality. To verify this assumption we compared Raman spectra of graphene taken on some random points on Cu and the destination substrate, respectively.

Raman Characterization

Raman spectra acquired on as deposited graphene are shown in fig 3A. The ratio between the intensity of the 2D peak compared to the G peak gives information about the number of layers [10]. A ratio of about 1.3 suggests the presence of a graphene bilayer.

The same Raman analysis has been performed on transferred samples obtaining similar spectra as shown in Fig. 3B,C. In the case of spectra from transferred graphene, the optical images of the scanned areas are also reported. Spectra of transferred samples, show, in addition to the graphene fingerprints, a clearly visible double peak located at 2950 and 3000 cm^{-1} that can be ascribed to PMMA [11]. It is interesting to note that, even the variations in the relative intensities of the typical (D, G, and 2D) graphene features are fair, suggesting a good layer uniformity, the main differences in Raman spectra are due to the variations in amplitude of PMMA peaks. Moreover, by comparing with the optical images, we note that PMMA peaks are less intense in "stained" regions. A quantitative analysis can be done by calculating the ratio between the intensity of PMMA peak and the intensity of G peak. For point B $(I_G/I_{PMMA})_B=2.5$ while for point C $(I_G/I_{PMMA})_C=0.4$.

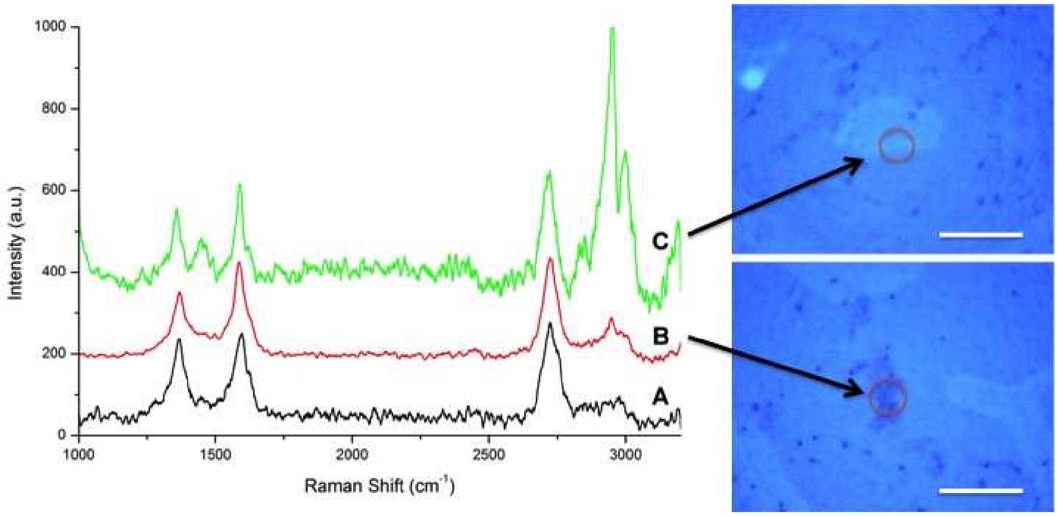

Fig. 3 Raman spectra of graphene on Cu (A) and transferred on PMMA (B and C). In spectrum C, in addition to the peaks around $3000cm^{-1}$, the small peak at $1460cm^{-1}$ is related to PMMA. On the left, optical microscope images of the scanned area are displayed. Scale bars are 20μm.

"Stains" in the micrographs in Fig. 3 are indicative of a difference in the optical contrast. This is confirmed by the micro-Raman analysis, where the laser depth-of focus is very short. To ascertain if the "stains" are due to a weak adhesion of graphene onto the PMMA substrate, we carried out some AFM analysis on selected samples.

AFM Characterization

In Fig. 4 the optical image and the AFM map are shown. The roughness of the PMMA surface is clearly visible in AFM maps. In some regions (not highlighted) the surface topography of PMMA is quite smooth and can be considered as the negative of the Cu surface after graphene deposition. The most interesting part is relevant to the highlighted regions, where “stains” are present, and topography changes showing a different roughness. Since in these regions Raman spectra show also a $I_G/I_{PMMA} > 1$, a possible interpretation is that here PMMA did not adhere well with graphene-on-Cu sample and after Cu etching, the graphene sheet puckers after transfer.

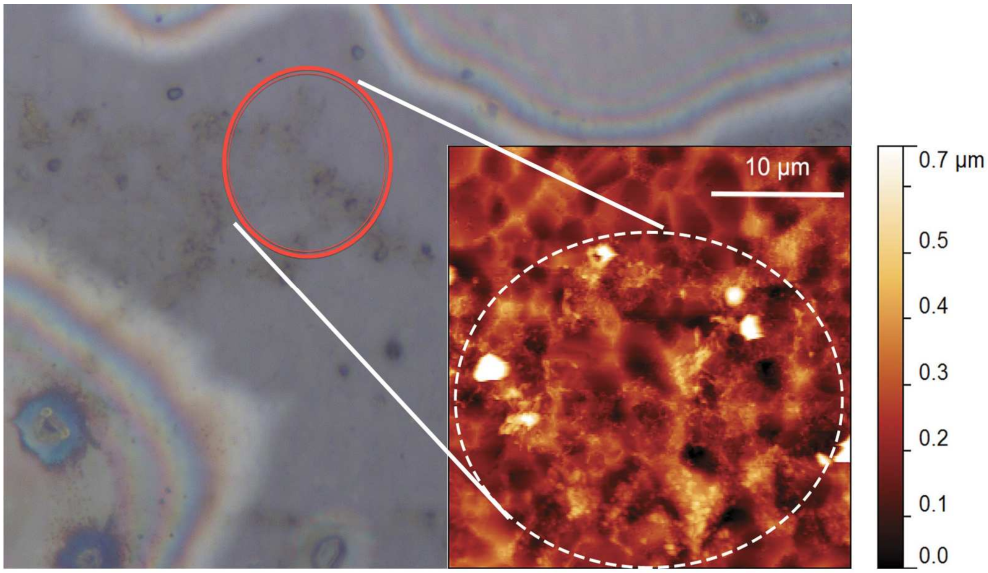

Fig. 4 AFM map of transferred sample and its optical image. In the highlighted zone is visible the corrugation due to graphene growth in deep grooves at grain boundaries present in Cu film.

When dealing with films as catalysing substrates for graphene deposition, the problem of dewetting poses some limitations, e.g. the film thickness, the temperature employed, etc.

A common recipe to avoid hole opening during sample’s heating, is to increase the film thickness up to 500 nm and more. During the dewetting incubation stage, however, deep grooves are formed [8]. When the grooves’ depth equals the film thickness, a new stage, hole opening, starts, and Cu retraction takes place. Then, the employment of relatively thick films does not prevent the groove formation, occurring mainly at grain boundaries.

CVD deposited graphene adheres well to the Cu surface, as it has demonstrated that it can inhibit the motion of Cu surface atoms [12]. On the contrary, the embossed PMMA layer, because of its viscosity, cannot fully penetrate the deep Cu grooves at grain boundaries. Then, after transfer and Cu etching, graphene cannot adhere well with PMMA in the stained regions, then collapses and gives rise to a puckered region. There, the relative Raman intensity of graphene peaks with respect to PMMA is larger. Interestingly, it seems that graphene quality is not affected by such puckering.

It has to be underlined, however, that the puckering problem is not a limitation of our embossing transfer process, but rather related to the poor control of Cu film dewetting during deposition. Strategies to control the Cu atoms motion during high temperature treatment are then needed [9].

CONCLUSIONS

The technique here proposed can be useful for transferring graphene is a safe way. From PMMA graphene can be then transferred on top of an insulating substrate, making it suitable for electrical measurements and realization of devices. Since the flakes have the same shape and relative position than on Cu, this opens up the possibility of pre-pattern graphene directly onto the metal surface and then transfer the same geometry onto the insulating substrate.

The quality of graphene sheets seems not affected by the transfer process, on the contrary we can conclude that the deposition technique needs improvements, in order to reduce groove formation in the Cu films, other than to augment the size of graphene domains.

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