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Laser induced forward transfer of graphene

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Abstract

Transfer of graphene and of other two-dimensional, materials is still a technical challenge. The 2D-materials are typically patterned after transfer, which leads to a major loss of material. Here we present laser induced forward transfer of CVD grown graphene layers with well-defined shapes and geometries. The transfer is based on photo-decomposition of a triazene-based transfer layer that produces N_2 gas, which propels a graphene layer from the donor to the acceptor substrate. The functionality of the graphene-metal junction was verified by realizing functional bottom contact bottom gate field-effect transistors.

Since the discovery of graphene, many two dimensional (2D) materials with a wide range of exceptional physical properties have been realized.[1,2,3] Due to the interesting physics, the 2D materials have extensively been studied for many opto-electronic applications.[4] Three major bottlenecks, *i.e.* growth, transfer and patterning, have been recognized for the integration of 2D materials into mainstream semiconductor technology. Mechanically exfoliated graphene has so far been the leading material due to its availability for the basic research.[5] The growth of graphene particularly via chemical vapor deposition (CVD) has been the subject of intense research for industrial applications. Graphene transfer and patterning, have also received attention but to a lesser extent. Electronic devices relevant for upscaling, such as graphene field-effect transistors are typically fabricated by transferring CVD-grown graphene onto a secondary substrate using a sacrificial polymeric layer *e.g.* poly(methylmethacrylate) (PMMA). After removal of the PMMA layer, graphene is patterned using photolithography. Electronic devices are then realized by metal deposition onto the patterned graphene. However the conventional photolithography process and metal deposition onto graphene deteriorate the performance of the final graphene devices. Recently, we have proposed an alternative process technology, *i.e.* conformal transfer, wherein lithography and contact deposition on top of the graphene layer were prevented.[6] In conformal transfer, graphene devices were realized by first fabricating the substrate that contains all the device layouts, electrodes and interconnects and then transferring the CVD graphene on top of the structures. The technique is a generic process flow for device fabrications based on 2D-materials. Conformal transfer has been scaled-up to 150-mm wafers with statistically similar devices and with a device yield of unity. It has been shown that physical lamination of the graphene layer on to predefined contacts can readily yield good quality junctions with low contact resistances below 1kΩμm even without any post fabrication treatments. The next natural step for conformal transfer technique is patterning of the graphene layer at the predefined positions while circumventing lithography. Here we present a non-photolithographic-based patterning process.

Laser Induced Forward Transfer (LIFT) is a non-contact printing process.[7] LIFT has originally been demonstrated for the printing of pure metal drops and has been used for transferring a large number of materials in various forms such as ceramic films[8] and OLED pixels.[9,10] The process consists of impinging intense but short laser pulses on the material to be transferred. The ablation process results in gas formation in the material. Releasing the gas propels graphene to a secondary substrate. For a thick organic or metal film, typically a few micrometers, only a thin

section of the film, typically tens of nanometers, for the ablation process is used. As such LIFTing of thin-films like monolayer graphene is not possible. Application of a dynamic release layer has enabled LIFTing of thin films with minimized damages.[11] This release layer is placed between the thin-film and the primary substrate, provides a film with a high absorption at the laser wavelength upon irradiation. The release layer then undergoes a photochemical decomposition at low laser fluence producing gas and the required propulsion for the transfer of the thin-film to a secondary substrate. Triazene-based polymers are good candidates for the release layer.[12,13,14] Triazene is highly photoactive and strongly absorbs in the UV spectrum with a maximum of absorbance around 355 nm[15] making it a good candidate for a release layer. Following its decomposition, triazene polymer releases N_2[16] that acts as the thrust gas for the propulsion of the layer to be transferred. Threshold fluence is rather low and ranges from 16 mJ/cm^2 to 32 mJ/cm^2 for a 248 nm laser wavelength,[15,17] which ensures minimal laser damage on the material to transfer.

Here we present patterned graphene devices fabricated with conformal transfer while preventing photolithography. The graphene films were CVD grown onto a copper foil and then transferred with a PMMA film onto a quartz substrate coated with the release layer. The coated quartz was then used as (primary) donor substrate for the LIFT process. Patterning is achieved by transferring the graphene layer onto individual devices using LIFT. The functionality of the graphene-metal junction was verified by realizing functional graphene bottom contact bottom gate field effect transistors. Efficient conductivity was observed in channel length even up to 100 μm.

Pre-patterned devices were defined on 150-mm Si wafers with 250 nm of thermally grown SiO$_2$ by conventional I-line photolithography. The highly doped *p*-type substrate acts as a common gate. Au electrodes of 150 nm thick were used as the contact metal with 2 nm Ti used as an adhesion layer. Ti and Au were both deposited by sputtering. The SiO$_2$ surface was passivated with hexamethyldisilazane (HMDS) prior to graphene transfer.

The triazene polymer solution is prepared by dissolving the triazene in a 1:1 w/w mixture of cyclohexanone and chlorobenzene. The polymer weight content was 5%-wt. Triazene thin films of 200 nm thick were made by spin coating the triazene solution onto the clean quartz substrate. Triazene films were subsequently baked at 120°C for 15 min to remove the residual solvents. We note that the quartz substrates were cleaned using a cascade of acetone, ethanol, isopropanol, and were exposed to UV-ozone after drying.

Single graphene sheets were grown on copper foils according to procedures previously described in the literature.[18] Graphene was grown on 25 μm Cu foils in a CVD reactor using methane as precursor. Once the growth was complete the graphene was transferred via a wet transfer process by spin coating PMMA (1 wt% solution from toluene) on the Cu foil. The thickness of the PMMA layer was typically a few μm. Then the Cu was etched with a 1 M ferric chloride solution for several hour

s. After etching, the PMMA/graphene was thoroughly washed in deionized water and subsequently transferred to the target substrate. The PMMA/graphene films were floated off in fresh deionized water bath with a submerged substrate. The PMMA/graphene films were very slowly picked up from beneath with a pre-patterned Si wafer or clean glass substrate. To prepare the graphene layer for the LIFT process, a triazene coated quartz substrate was placed over the wet PMMA/graphene/glass with the triazene layer facing the PMMA. The glass slides were subsequently removed by turning the whole stack upside down and submerging again in water, leaving the quartz/triazene/PMMA/graphene in the desired configuration. Both pre-patterned and quartz substrates were baked at 110 °C for 10 minutes following the transfer in order to remove residual water. The PMMA layer was removed using a fresh acetone bath. Subsequently the exposed transferred graphene was washed in a deionized water bath.

We characterized graphene prior to the LIFT process. Graphene was transferred on the pre-patterned substrate by conformal transfer. After washing away the PMMA layer, the transferred graphene was further investigated by scanning electron microscopy (SEM) and Raman spectroscopy, shown in Fig. 1.
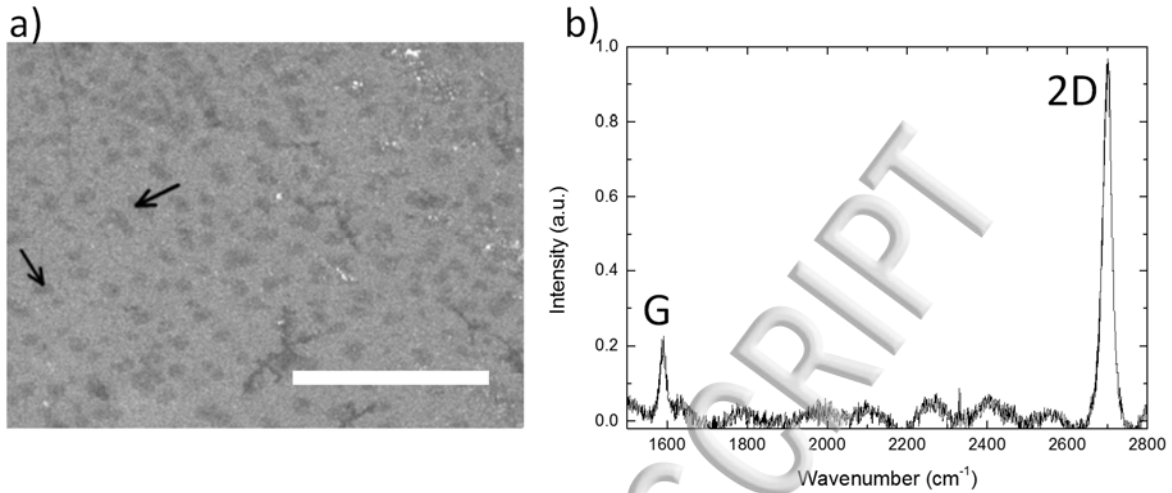
Figure 1. a) SEM image of a graphene layer transferred on to a monitor wafer. Islands of second layer are indicated by arrows. The scale bar is 10 μm. b) Typical Raman spectra of the graphene layer after transfer. Presence of strong 2D and G bands are indicative of mainly monolayer graphene.

The graphene layer is a fully closed monolayer as shown in Fig. 1a. Features like ridges and small disconnected islands of the second layer are inherent to CVD grown graphene. A typical Raman spectrum of the transferred graphene film is given in Fig. 1b. The sharp peaks at 1580 cm^{-1} and 2690 cm^{-1} correspond respectively to the G and 2D peaks, of the monolayer graphene. Hence the graphene used for our work is predominantly a single layer graphene.

Electrical characterization of the graphene FETs were performed in vacuum. Prior to the electrical measurement, the devices were annealed at 150°C in vacuum for one hour to remove any traces of residual water. The conformal transfer is elucidated by the SEM micrograph of Fig. 2a. The cross section shows that the coverage of graphene is conformal and the transferred graphene follows the topography of the patterned substrate. Fig. 2b shows a typical transfer characteristic of graphene FET with channel length and width of 10 μm and 2500 μm, respectively. The FETs exhibit low hysteresis with almost equal electron and hole mobility that amount to 200 cm^2/Vs. The electron and hole field-effect mobility obtained for conventionally transferred graphene are reproducible. We note that since the channel dimension used for the FETs devices are quite large, the electron and hole mobility are affected by the imperfections of the graphene

layer, and are therefore low compared to typical values reported for CVD graphene, wherein channel width of typically a few micron is used.
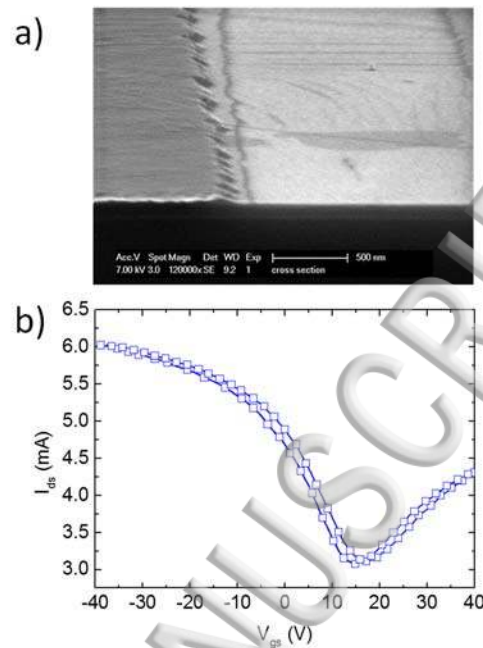
Figure 2. a) SEM cross-section at the contact edge showing the conformal coverage of the graphene over the electrode. b) Transfer characteristics of a typical graphene FET measured at room temperature in vacuum after 1 hour of annealing at 150 °C. Drain bias was 0.5 V.

The LIFT process was investigated using a KrF based excimer laser that generated 248 nm laser pulses of 5 ns. The laser provides a flat top beam. The beam shapes such as square, rectangular or circular are defined by the mask. Here, the beam dimensions were defined by a square mask of 100 μm x 100 μm. Fig. 3 shows the process schematics of graphene LIFT. The first parameter for the successful LIFT is to determine the optimal fluence of the laser beam. The minimum and maximum of the laser fluence is defined by the fluence below which no ablation occurs, or above which the film completely explodes upon laser exposure. The optimal fluence produces a sharp ablation. We determined the minimal and maximal fluence for a triazene layer of 200 nm thick as 30 mJ/cm^2 and 87 mJ/cm^2, respectively; the optimal fluence was 42-54 mJ/cm^2. We note that the fluence can vary slightly due to the non-uniformity of the PMMA and triazene layer. To further reduce the energy needed for transfer, the edges of the 100 x 100 um film were removed on the donor film. The separation distance, or gap spacing, between the donor and the acceptor substrates was fixed at 25 μm.

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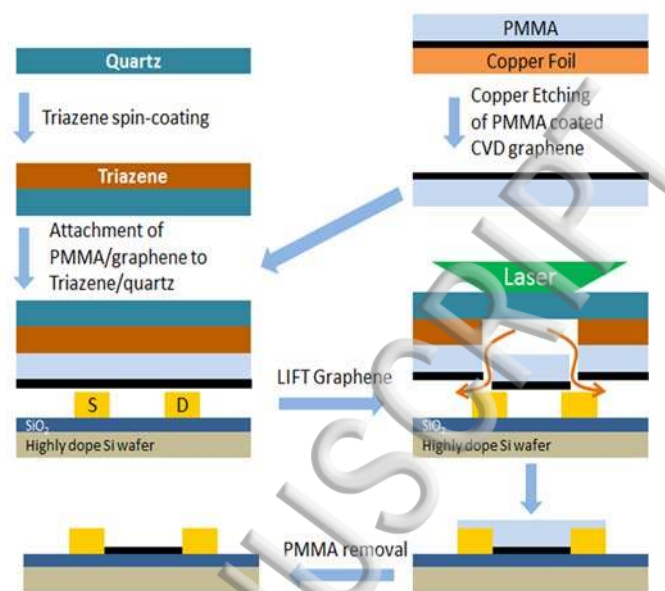
Figure 3. Process flowchart for graphene LIFT. PMMA/graphene LIFTed onto a silicon acceptor wafer. b) A 100×100 µm^2 layer of PMMA/graphene is lifted between two gold patches.

Mere ablation of the PMMA/graphene film does not guarantee a successful transfer to the acceptor substrate. For a successful LIFT, the spacing between the donor and the acceptor substrates is important. When in contact the LIFTed layer tended to stick back to the donor substrate whereas a too large distance (>100 um) increased the chance for the LIFTed layer to fly away and deposit on an undesired spot. Fig. 4a shows an optical image of a PMAA/graphene layer that is LIFTed on a substrate with two square gold contacts with a gap distance of 100 µm. Finally we note that after a successful LIFT, the PMMA layer was washed away as described in the experimental section.

Following the LIFT, graphene devices were transferred to vacuum for the electrical characterization. The graphene layer was annealed at 150°C in vacuum to remove any traces of residual water. Fig. 4b shows transfer characteristics of the graphene transistors. The drain voltage was set as V_D = -0.5 V and the gate voltage swept from +40 V to -40 V and back. The transistor channel length and width were 10 µm and 1350 µm, respectively. The mobility of the LIFTed graphene layer amounts to 10-15 cm^2/Vs for holes and 5 cm^2/Vs for electrons. The field-effect

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mobility was averaged from several LIFTed FETs, and was reproducible. The mobilities are low and therefore not comparable with the commonly reported values for transferred CVD graphene. There are two possible reasons. Firstly, as a result of the large geometrical dimensions of the FET, lower mobilities are expected due to more defects. Secondly, the Au/graphene contact has not received any treatment after the LIFT process. Post processing treatment is needed to optimize and achieve a good contact.[6] Nonetheless, the focus of the work here is to demonstrate the feasibility of the LIFT process for graphene transfer rather than the optimization of the charge carrier mobility of the graphene layer. Finally we note that the LIFT process can also be used for the transfer of graphene on to foils.
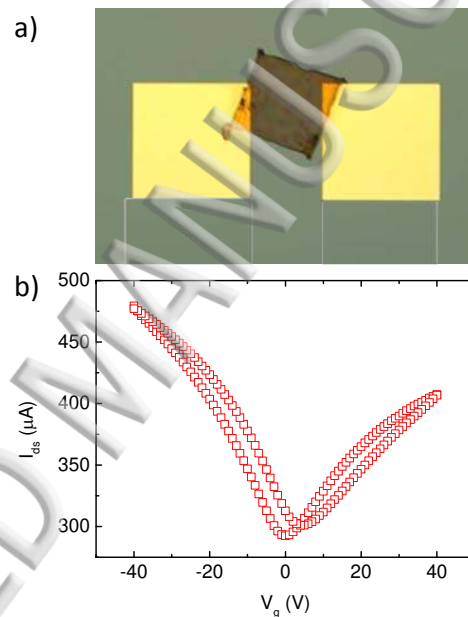
Figure 4. LIFT graphene transistor. a) Micrograph of a graphene layer with rectangular shape transferred on to a SiO2 surface with two Au contact pads. b) Transfer characteristic of a graphene LIFTed transistor.

In summary, we have demonstrated LIFT process as a digital method to transfer graphene from a donor to an acceptor substrate. In combination with the conformal transfer, the LIFT process offers effective transfer for graphene. The method is very economical in terms of the material loss and suitable for transferring graphene to any acceptor substrates. LIFT, as a direct write technique, allows direct transfer of the desired feature without intermediate steps. The LIFT process relies on conventional tools such as excimer lasers that are well scaled up in the display
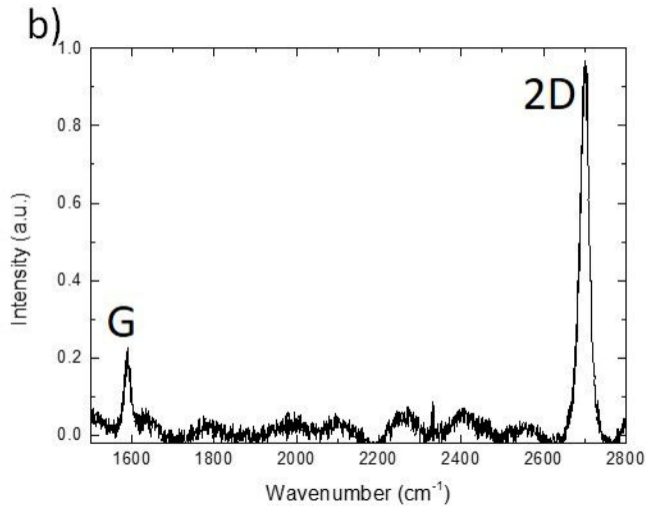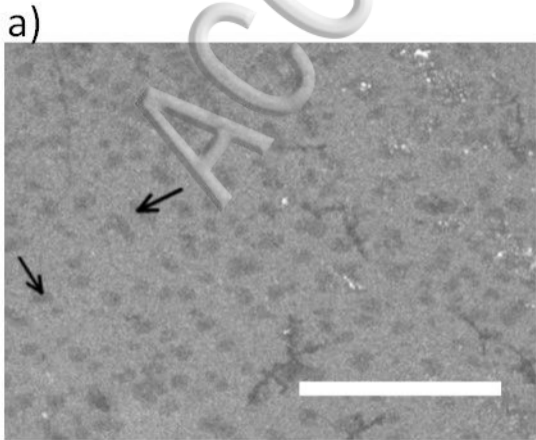
industry[19] and allow well-defined features down to 300 nm. Demonstration of the LIFT of graphene implies that the technique can also be successfully used for the transfer of other 2D-materials.
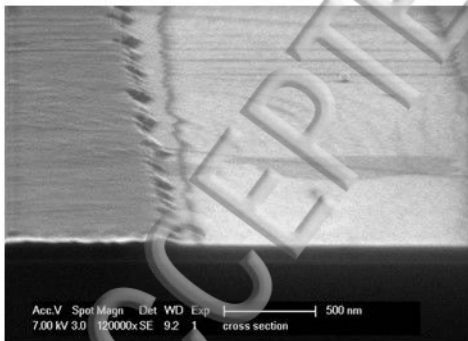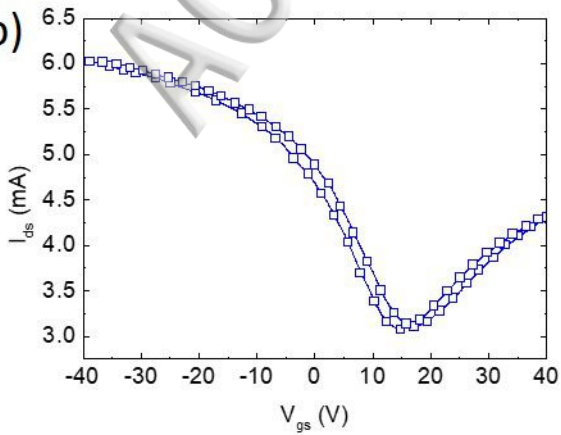
Acknowledgment

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **306** (2004), 666-669.

[2] S. Wang, Y. Si, J. Yuan, B. Yang, H. Chen, *Phys. Chem. Chem. Phys.* **18** (2016), 24210-24218.

[3] S. Wang, Z. Fan, Y. Cui, S. Zhang, B. Yang, H. Chen, *Carbon* **111** (2017) 486-492.

[4] S. J. Han, A. V. Garcia, S. Oida, K. A. Jenkins, W. Haensch, *Nat Commun* **5** (2014), 3086.

[5] S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat Nano* **5** (2010), 574-578.

[6] K. Asadi, E. C. Timmering, T. C. T. Geuns, A. Pesquera, A. Centeno, A. Zurutuza, J. H. Klootwijk, P. W. M. Blom, D. M. de Leeuw, *ACS appl. Mater. & interface.* **7**, (2015) 9429-9435.

[7] J. Bohandy, B. F. Kim, and F. J. Adrian. *J. Appl. Phys.* **60** (1986) 1538-1539.

[8] C. B. Arnold, P. Serra, A. Pique *MRS Bulletin* **32** (2007) **32**, 23-31.

[9] D. P. Banks, C. Grivas, J. D. Mills, R. W. Eason, and I. Zergioti. *App. Phys. Lett.* **89** (2006) 193107.

[10] R. Fardel, M. Nagel, F. Nesch, T. Lippert, and A. Wokaun. *Appl. Surf. Science*, **254** (2007) 1322-1326.

[11] W. A. Tolbert, I.-Y. Sandy Lee, M. M. Doxtader, E. W. Ellis, and D. D. Dlott. *J. Imaging Sci. Technol.* **37** (1993) 411-421.

[12] J. S. Stewart, R. Fardel, M. Nagel, P. Delaporte, L. Rapp, C. Cibert, A.-P. Alloncle, F. Nuesch, T. Lippert, A. Wokaun. *J. Optoelectron. Adv. M.* **12** (2010) 605-609.

[13] K. S. Kaur, R. Fardel, T. C. May-Smith, M. Nagel, D. P. Banks, C. Grivas, T. Lippert, R. W. Eason. *J. Appl. Phys.* **105** (2009) 113119.

[14] J. S. Stewart, T. Lippert, M. Nagel, F. Nesch, and A. Wokaun. AIP Conference Proceedings, **1278** (2010) 789-799.

[15] T. Lippert, L. S. Bennett, T. Nakamura, H. Niino, A. Ouchi, and A. Yabe. *Appl. Phys. A: Mater. Sci. Process.* **63** (1996) 257-265.

[16] L. S. Bennett, T. Lippert, H. Furutani, H. Fukumura, and H. Masuhara. *Appl. Phys. A: Mater. Sci. Process.* **63** (1996) 327-332.

[17] M. Nagel, R. Hany, T. Lippert, M. Molberg, F. A. Nesch, and D. Rentsch. *Macromol. Chem. Phys.* **208** (2007) 277286.

[18] P. Sharma, L. S. Bernard, A. Bazigos, A. Magrez, A. M. Ionescu, *ACS Nano* **9** (2015) 620-625.

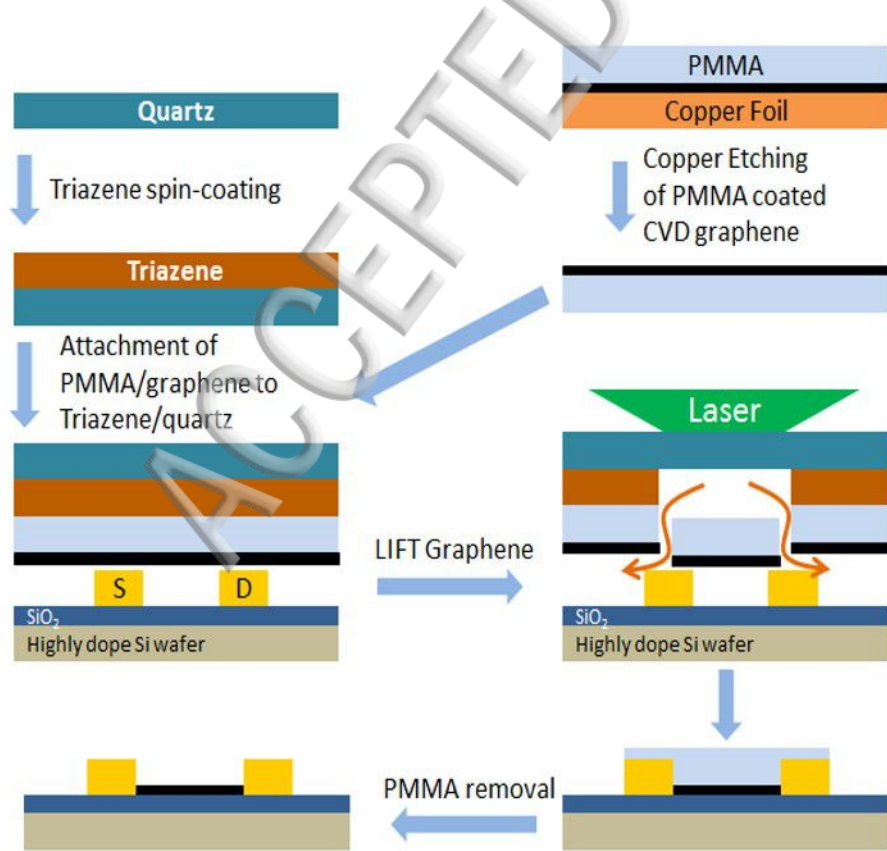[19] R. Pätzel, J. Brune, *Physics Procedia* **41** (2013) 241–248.

a)

Acc.V Spot Magn Det WD Exp   ⊢──────────────⊣ 500 nm
7.00 kV 3.0 120000xSE 9.2 1   cross section

b)

Quartz

Triazene spin-coating

Triazene

Attachment of
PMMA/graphene to
Triazene/quartz

S   D

SiO₂
Highly dope Si wafer

LIFT Graphene

PMMA

Copper Foil

Copper Etching
of PMMA coated
CVD graphene

Laser

SiO₂
Highly dope Si wafer

PMMA removal

a)

b)