Graphene Trails on PECVD Hydrogenated Amorphous Silicon Carbide Films SiC-a: H by Laser Writing at Room Temperature

D. J. Feria, M. N. P. Carreño, R. C. Rangel, I. Pereyra
EPUSP, University of São Paulo, P.O. Box 61548, 5424-970, São Paulo, Brazil
deissyferia@usp.br

Abstract—In this work, we present the production of graphene trails by direct 405 nm laser writing at room temperature and atmospheric pressure on hydrogenated amorphous silicon carbide films (SiC-a:H) produced by Plasma Enhanced Chemical Vapor Deposition (PECVD). Graphene trails of approximately 0.6 mm x 4μm were obtained on a-SiC:H by moving the substrate with film in a computer controlled XY table and keeping fixed the laser source. Variations were made in both scanning speed and laser focusing length, identifying a great dependence on the graphene quality with these two parameters. The graphene was characterized by Raman Spectroscopy and best results of graphene quality with these two parameters. The graphene was obtained on a-SiC:H by moving the substrate with a laser of 405 nm wavelength, with an area of 0.6 mm x 4 μm. The electrical measurements show high electrical conductivity, with sheet resistances (R_s) ranging from 0.7 kΩ to 1.3 kΩ per square. Being a fast, efficient and low cost, the technique opens new possibilities of manufacturing approach for microelectronic devices and sensors.

Keywords—graphene/SiC-a, Laser, electrical conductivity

I. INTRODUCTION

Graphene is a two-dimensional material formed by one or few layers of carbon atoms with sp2 hybridization compacted in a honeycomb like hexagonal cell structure [1]. In recent years it has been widely recognized as a promising material for microelectronic devices and sensors due to the exceptional and unique properties gathered in the same material, as high electrical and thermal conductivity, thermal stability and excellent mechanical properties [2]. These characteristics make it one of the most promising nanomaterials in terms of integrated and miniaturized applications in microelectronics[3], optoelectronics[4], in the manufacture of transparent electrodes, storage, sensors of different types [5][6] and also applications in large areas such as energy conversion, solar cells[7], plastics manufacturing or conductive ceramics[8]. One of the main applications reported in recent years with graphene-based electronic devices are electrochemical sensors, basically due to their high electron transport, good compatibility and flexibility[9]. Therefore, several methods have been developed with the aim of obtaining graphene on a large scale or with different characteristics depending on the type of application for which the material is needed, for instance, for composites or films with large area.

Currently there are different techniques for the production of graphene sheets, among them we can mention mechanical exfoliation of Highly Oriented Pyrolytic Graphite (HOPG)[10], chemical exfoliation[11], techniques of chemical vapor deposition (CVD)[12][13] and sublimation of carbides[14]. Particularly the last two techniques have been successful since they allow the formation of large area graphene sheets. However, in the CVD method it is necessary to use a catalytic metal that promotes the breakdown of the used carbonaceous gas molecule, but afterwards it must be eliminated and the graphene film transferred to other substrates, this process ends up being a limitation for applications where a specific pattern or design is required on a surface. In the case of Sublimation of Carbides, the method consists of the growth of epitaxial graphene on Silicon Carbide (SiC) substrates, from the decomposition of a SiC crystal that is subjected to ultra-high vacuum and temperature of 1200 ° C [15] or atmospheric pressure (inert atmosphere) at 1650-2000 °C[16]. Conditions in which superficial silicon atoms start to evaporate, leaving C atoms on the surface that bond together forming the hexagonal graphene network. The latter has the advantage of eliminating the corrosion steps of the metal and the transfer of graphene, allowing the direct use of graphene / SiC as a substrate, but the process becomes costly when it requires the use of SiC blades, ultra-high vacuum and high temperatures, in addition it also has limitations for production in defined patterns.

Another method that recent research has developed is the production of graphene by direct laser treatments on different materials that contain carbon in its composition, such as nickel coated with solid carbon [17], polyimide [18][19], polydimethylsiloxane (PDMS) [20], as thermal reduction of Graphene oxide (GO) to reduced graphene oxide (rGO)[21], among others. Direct growth and graphene design with a defined pattern have the advantage of direct and rapid production of graphene on the surface of different polymers or other carbonaceous materials [22].

In previous works we demonstrated that using the PECVD technique with silane and methane precursor gases (SiH4 + CH4) with certain deposition conditions and RF Power it is possible to obtain highly ordered Hydrogenated Amorphous Silicon carbide films (SiC-a: H) on any material rigid or flexible that withstands temperatures above 300°C.
This advantage facilitates the application of "wearable" sensors to be operated directly from the body. In this work, we manufacture graphene by direct laser writing (laser radiation) patterned at room temperature on the SiC-a: H films mentioned above.

II. EXPERIMENTAL

A. Deposition of SiC-a:H films

For the substrate, were deposited in Corning glass slides at 320 °C by the PECVD technique, with an RF source of 13.56 MHz, two types of SiC-a:H films, the 3680 and 3690-H. In both cases, the gases used for the process are essentially: pure silane (SiH₄), pure methane (CH₄), with the difference that the second type of film is grown with a dilution in H₂ (table 1), which promotes the growth of a more ordered and homogeneous material. The deposition rate is approximately 2.4 nm/ min and 1.6 nm/ min for 3680 and 3690-H respectively, being deposited different thicknesses: 10 nm, 500 nm and 700 nm approximately. The thickness of the deposited films was characterized by profilometer (Tencor Alpha Step 500).

The obtained SiC-a:H preserves some of the interesting properties of crystalline SiC, since with this deposition method, silicon atoms bound preferentially to carbon atoms, forming an order very similar to SiC [24][25].

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>SiH₄ (sccm)</th>
<th>CH₄ (sccm)</th>
<th>H₂ (sccm)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3680</td>
<td>3.6</td>
<td>80</td>
<td>-</td>
<td>320</td>
</tr>
<tr>
<td>3690H</td>
<td>3.6</td>
<td>90</td>
<td>200</td>
<td>320</td>
</tr>
</tbody>
</table>

B. Laser Fabrication of graphene

In this work a continuous 500 mW (fixed power) and 405 nm diode laser impinges onto a sample holder attached to a computer controlled XY table (by Mach 3 software). The layout of the laser tracks are designed in AutoCAD. In this way, the laser scans the SiC-a:H surface with defined geometry and speed, recording graphene lines from the evaporation of Silicon atoms, due to the energy and temperature provided by the laser, see Figure 1. Important parameters were investigated such as different SiC-a:H material with different thicknesses, laser scanning speed and laser focusing depth on the sample. Due to the fast solidification (heating and cooling) of the Substrate and the high speed of the procedure, it is possible to form high quality graphene at an effective cost.

C. Graphene characterization

The produced graphene lines were characterized by optical microscopy, scanning electron microscopy FEI Inspect F50, and confocal Raman spectroscopy (WITEC, Confocal Raman Microscope Alpha300 R) using green laser line (532 nm). The objectives used were 100x and 50x.

Subsequently, for electrical characterization, metallic contacts (Ti /Au) already reported in the literature were deposited with excellent results using electron beam vaporization technique. For the shape of the contacts, shadow masks with 0.5 mm diameter holes spaced apart 2 mm, were fabricated and utilized.

III. RESULTS AND DISCUSSION

The first samples were obtained varying the laser scanning speeds from 50nm / min to 600nm / min in 50nm / min steps, afterwards with the speed that lead to the best results, a series of lines with different distance from the laser focus with respect to the sample surface (figure 2) was made. The best Raman spectrum was obtained for a speed of 500nm / min and focus distance of 250 μm (f >0). The analysis of the Raman bands showed a crystallite size (La) of 22nm and distance between point defects (Ld) of 10nm, which indicates a low amount of defects and a good quality graphene[26]. In addition the I₂D/I₅ ratio [27] and the 2D band shape results can be interpreted, in accordance to recent studies as few-layer graphene[28].
The optical images in fig. 3a. and 3b. (3680 and 3690H respectively) reveal that the 3690H SiC-a: H presented a greater internal stress resulting in the breakage of the film at different points which are shown with red arrows at fig. 3b., therefore the continuity of the graphene lines was interrupted.

The 3680 sample (fig 3a) with a thickness of 500nm provided greater resistance to the temperature provided by the laser, in addition to allowing the formation of continuous graphene and with less disorder, as inferred from Raman spectra. The lines are wavy at the few millimeters scale, but they are clearly parallel, and the wave aspect is attributed to the step motors controlling the XY table.

The effect of the carbide thickness on the quality of the obtained graphene was investigated. For this purpose, two more thicknesses of SiC-a 3680 (64nm and 200nm) were deposited on Corning glass substrates. Graphene was not formed in the smaller thickness, and in the second one, the spectra of the graphene produced showed a considerable increase in disorder.

The 2D band mapping of sample 3680 is shown in fig. 3c and 3d, in which the continuity of graphene (yellow area) is observed. The Raman spectra (figure 3e) obtained from random locations, indicated with red, blue and green crosses in fig. 3d demonstrates that graphene trails are uniform, from the structural point of view, and of high quality. The graphene trails, with an area of approximately 1cm x 4μm, identified in the Raman mapping, can be seen in the SEM image (Figure 4-red arrows) at the borders of each trail.

Onto the graphene trails Ti / Au contacts were deposited at room temperature by electron beam evaporation, with thicknesses of 10nm / 50nm in order to obtain optimal ohmic contacts and a lower percentage of oxidation on contact with the environment. The conductivity results obtained for the graphene trails in different areas showed sheet resistances (Rs) between 0.7 kΩ/sq to 3 kΩ/sq [20][29][30]. These differences in conductivity are attributed to the number of breaks presented in the SiC-a: H film after the laser is applied.

IV. CONCLUSION

A new approach for the direct growth of graphene in large standardized areas was developed. Results from both Raman spectroscopy and electrical characterization showed that previously optimized SiC-a: H films allow the formation of graphene by direct laser writing at room temperature with high conductivity and with good structural properties. From these considerations, these results are quite promising for the development of electronic devices, specifically electrochemical sensors.
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REFERENCES