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# Study on the possibility of graphene growth on 4H-silicon carbide surfaces via laser processing

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## Abstract

The main aim of this work is to obtain carbon-based materials such as graphene, few layer graphene (FLG) and graphite by thermal decomposition of 4H - silicon carbide (4H-SiC) polar surfaces.
This process takes place annealing SiC at temperatures ranging from 1000°C to 1600°C, in UHV conditions or in inert atmosphere.
This range of temperatures could be attained by thermal annealing in quartz tube furnaces or rapid thermal processes. Even the reactors commonly used for SiC epitaxial growth were successfully employed.
We used a laser-assisted annealing process for the silicon carbide graphitization.
Experimental characterizations were performed by Field Emission Scanning Electron Microscopy (FESEM), Raman spectroscopy and X-rays Photoelectron Spectroscopy (XPS).Raman analysis show that laser annealing proven effective in order to obtain a graphitic phase on the C-face of 4H-SiC samples. A nano crystalline graphitic phase was obtained on the C-face of 4H-SiC samples when an Argon atmosphere was used in the process chamber during the laser annealing. This environment permitted a better control on the Si sublimation from the 4H-SiC surface during the annealing. Moreover, on the same samples the possible presence of graphene was detected by XPS and Raman analyses.A nano crystalline graphitic phase was obtained on the C-face of 4H-SiC samples when an Argon atmosphere was used in the process chamber during the laser annealing. This environment permitted a better control on the Si sublimation from the 4H-SiC surface during the annealing. Moreover, on the same samples the possible presence of graphene was detected by XPS and Raman analyses.

**Keywords:** Annealing, Graphite, Laser processing, Silicon carbide.

## 1 Introduction

In the recent years many research groups reported on the possibility to obtain different carbon-based phases on the silicon carbide surfaces by thermal decomposition of silicon carbide. This is a semiconductor widely known for its superior properties with respect to Si. In particular SiC is characterized by a wide band gap and an elevated thermal conductivity, high breakdown field and electron drift saturation velocity.Thus, the 4H hexagonal polytype of SiC (4H-SiC) can be considered as a semiconductor of choice when power electronic devices capable to operate with high temperatures and high frequencies are needed [1].The use of SiC in connection with graphene, graphite or even carbon nanotubes (CNTs) can be an interesting way to exploit the properties of these material. In particular, graphene is often referred to as a 2D material constituted by a single sheet of carbon atoms closely packed in a flat monolayer [2]. This monolayer is the basic building block for other carbon – based materials, such as carbon nanotubes and graphite. Graphene is a gapless semiconductor, widely studied for its outstanding electronic transport properties. Graphene can be obtained on silicon carbide (SiC) surfaces using epitaxial growth or thermal annealing [3-5].In many cases a stacking of few layers of graphene (FLG) has been found as a result of epitaxial growth or annealing processes [6]. The experimental evidence of the presence of a graphene monolayer instead of FLG can be provided by Raman and X-ray photoelectron

spectroscopy [7].Thermal decomposition of the SiC polar surfaces (known as „Si-face“ and „C-face“) can be useful also for the growth of graphite thin layer needed for the formation of metal/SiC ohmic contacts [8-11].Finally, CNTs can be directly grown on 4H-SiC surface by chemical vapour deposition (CVD), with the possibility to obtain integrated SiC-CNT structures capable to dissipate the heat developed during the operation of SiC-based Schottky barrier Diodes (SBDs) [12].

Different laser annealing process parameters (such laser power, frequency, velocity of the laser beam scan) were studied, in order to decompose both the 4H-SiC Si- and C-faces.A commercial, high peak pulse energy DPSS laser system (Micro-la) was employed in this study.Experimental characterization of the annealed samples was made by standard Field Emission Scanning Electron Microscope (FE-SEM), Atomic Force Microscopy (AFM), Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

## 2 Experimental

### 2.1 4H-SiC substrate preparation

A 4H-SiC n-type, 4°off-axis commercial wafer with a 5 µm thick, n-type epilayer ($N_D$=8.5 x $10^{15}cm^{-3}$) was purchased from Cree Research Inc (Durham-NC).

The wafer was diced in square (7 x 7 mm) and cleaning was performed using boiling acetone and isopropanol. After $N_2$ drying, the samples were dipped in a $H_2SO_4$:$H_2O_2$ (3:1 in volume) solution rinsed in deionised water. Native oxide was then removed by a commercial buffered oxide etch solution. Rinses in deionised water and $N_2$ drying completed the cleaning process.

Samples were loaded in a ultra-high vacuum (UHV) process chamber equipped with a system to introduce inert gas (Ar) and a deep-UV (DUV) silica glass window. Base vacuum level chosen for this experiment is ≈ $1\times10^{-7}$ Torr, while the partial Ar pressure can be controlled in the range from $7\times10^{-5}$ up to 100 Torr.

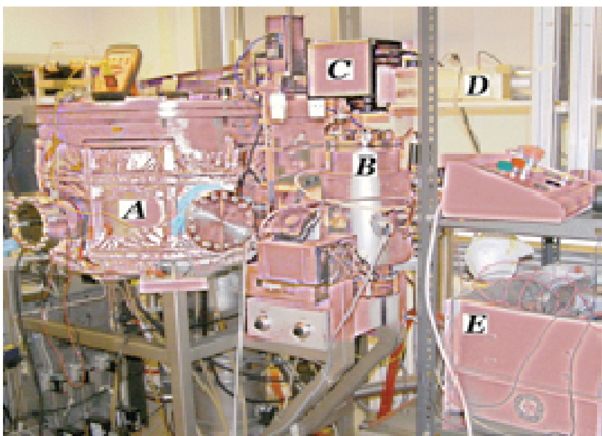


**FIGURE 1:** Experimental set-up used for the laser annealing process

### 2.2 DPSS laser ablation system set up

The laser processing system employed for SiC laser annealing experiments is composed by a:

- Ultra high vacuum chamber in which SiC samples are loaded (**Fig. 1**-A and B)
- DPSS laser system produced by Microla Optoelectronics (**Fig. 1**-D and E);
- Galvanometric scanner head (**Fig. 1**-C)

In order to produce a surface microstructuration on SiC, a DPPS laser system made by Microla Optoelectronics (MLQ-20 series) was used. This DPSS laser system has an end-pump configuration. Pumping system gives a maximum pumping power of 45W with a 808nm wavelength. An optical fibre with a core of 600 µm transports the pumping signal into the resonator. The active medium is a Nd:$YVO_4$ crystal doped 0.3% Nd. This laser has an output wavelength of 1064 nm linearly polarized with a maximum power density of 1300 W/$cm^2$ in continuous wave mode. It can be used also in q-switching mode with a 1-200 kHz range of frequency. The shortest pulse width is 8 ns (**Fig.2**).

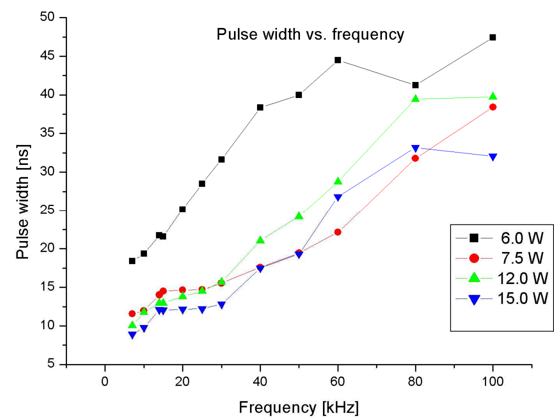


**FIGURE 2:** Characterization of MLQ20 pulse width

A galvanometric head was used to drive laser beam to the samples to be processed. In order to focalize the laser beam on the SiC substrate, two different focusing θ-lenses were used. The values of the focal length employed were 100mm and 254mm. The laser beam spot diameter found at the focus point was 15µm when the focal length of 100mm was employed; for what concern the 254mm focal length, a spot diameter of 40µm was obtained.

With the support of Zemax simulator (**Fig. 3**), we simulate laser beam dimensions in different points of optical path for every θ-lens configuration. With the aim to obtain a characterization of interaction between the laser and SiC substrate, two series of samples were prepared. Two different laser beam dimensions were used: 20 µm using 100mm focal length and 45 µm with 254 mm focal length.

In the first series of experiments, 16 SiC samples were annealed with a laser power of 15 W. Frequency values were ranging from 5 to 40 kHz, and the laser beam velocity was 1 or 5 cm/s, in order to study the laser beam-material interaction and the environment conditions on SiC annealing process. An increment of

pressure was recorded during annealing, probably due to sublimation and evaporation from SiC surfaces.

8 SiC samples were processed exposing the Si-face to the laser direct beam, while the remaining 8 samples were laser annealed on the C-face, with the aim to investigate the effect of the laser annealing on the two SiC polar surfaces.

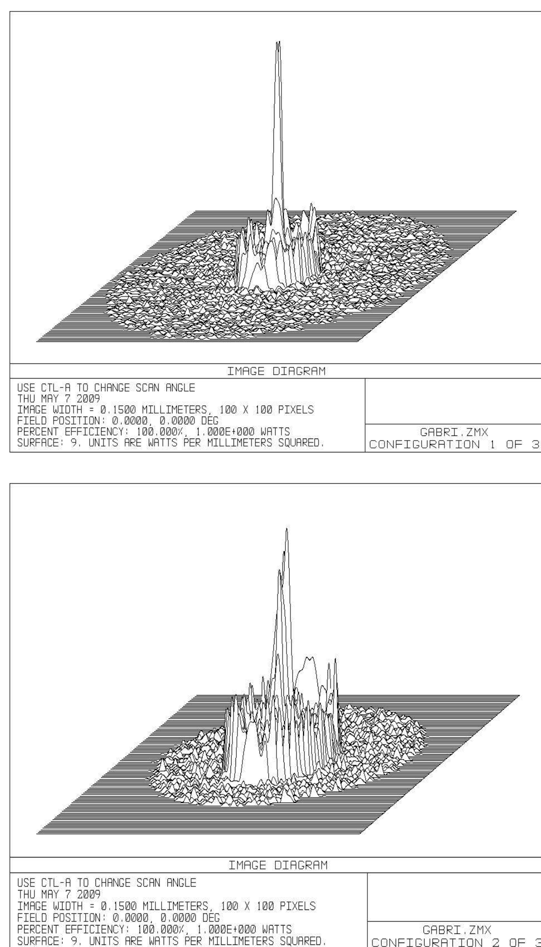


**FIGURE 3**: Zemax simulation of the optical system with 100 mm (top) and with 254 mm (bottom) focal lengths.

Only the samples processed on the C-face in the first series showed the presence of highly disordered graphitic phase, therefore in the second series we performed the annealing experiments only on that polar surface of 11 SiC samples.

An Ar partial pressure ranging from 0.1 to 2 Torr was used during the annealing, in order to control the Si sublimation rate from the SiC surface [13].

Two laser power values were tested in the second series, namely 10 and 15 W. Different working frequencies such as 30 and 40 kHz were employed, and working speed values were 0.8 and 3 cm/s. The interaction time between the laser and the SiC sample was increased substantially from the first series to the second one, by repeating the laser pattern 30 times.

Annealing temperature profiles were monitored ex-situ, shining the laser beam on a self-fabricated laser-welded N-type micro-thermocouple providing a maximum working temperature of 1300°C. The heating rates values for the two different focal length employed in the first and in the second series were obtained by linear fit of the initial annealing step over 1s.When the 100mm focal length was employed, a heating rate of 1015±25 K/s was calculated, while for the focal lenght of 240mm, a heating rate of 740±20 K/s was obtained.

The morphological characterization of the processed samples was performed by a Carl Zeiss Supra 40 Field Emission Scanning microscope.

MicroRaman analysis was performed using a Renishaw spectrophotometer in backscattered configuration, employing a laser beam (514.5 nm) with a power of 5mW.

XPS spectra were acquired using a PHI 5000 Versa Probe X-ray photo electron spectrometer, equipped with a simultaneous charge neutralizator system (in order to avoid electric charge build-up during XPS analysis on semiconductors).

## 3 Results and discussion

On the samples belonging to the first series, the laser annealing treatments have etched the semiconductor surface (**Fig.4**).

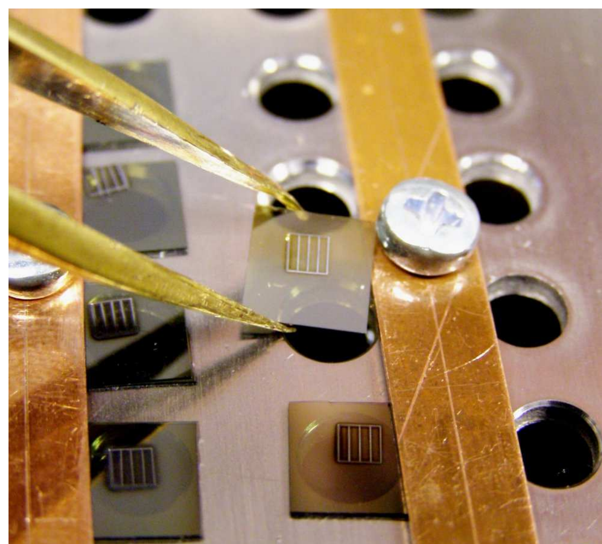

**FIGURE 4**: image of the processed samples after the annealing treatment; a clear etch of the surface is visible.

An uncontrolled Si sublimation has occurred, and a substantial amount of sputtered material can be found externally to the etched region.

The sputtered material is mainly constituted by silicon oxide, as pointed up by Energy Dispersive X-ray analysis (EDX).Etch depth and the amount of sputtered material shown an increase with increasing laser frequencies

This effect is more evident on the samples processed on the Si-face. Moreover, in the etched region EDX analyses showed a substoichiometric Si concentration

A better SiC morphological quality and a high quality of graphene islands on the SiC surface after SiC

thermal decomposition can be obtained reducing the Si sublimation rate from the surface. Thus, an Ar overpressure was employed during the laser annealing process. Si sublimates from the SiC surface at temperatures exceeding 1500 °C when Ar overpressures are present, while in UHV Si sublimation takes place at 1150 °C [13].

Power, frequency and velocity of the laser beam spot on the SiC surface were varied in the second series of samples, with the aim to avoid the etching effect observed on the samples of the first series. The most interesting effect of the laser annealing was observed on sample 2_11, processed with a laser power of 10W, frequency 30 kHz, beam spot velocity 0.8 cm/s and Ar pressure of 2 Torr.

No etch of the surface was observed in this case.

A 100 µm wide region constituted of crystalline silicon was observed in central zone of the pattern created by the laser beam scan on the SiC surface. At the edges of this central region, symmetrical bands with the presence of different particle size and composition were detected. EDX analysis shows elevated concentrations of C in the band immediately adjacent to the central region. Silicon oxide is the main constituent of the external bands (**Fig. 5**).

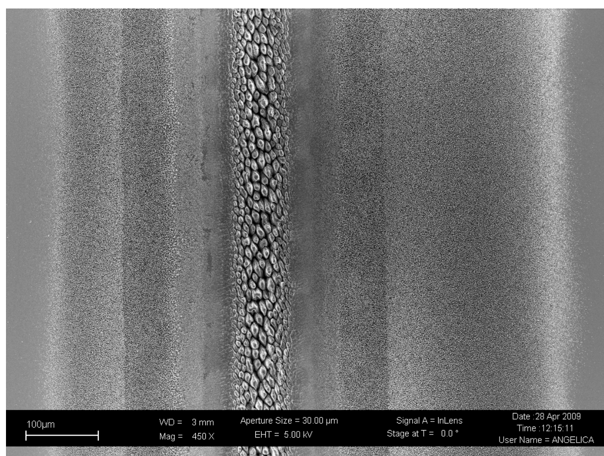


**FIGURE 5**: FESEM image of the sample 2_11 after the annealing process.

Raman spectroscopy was chosen because with this technique it is possible to differentiate between graphene and graphite.

Graphene layers Raman spectrum is composed by the D peak at 1345 cm$^{-1}$, the G band at 1580 cm$^{-1}$ and the 2D band at 2670 cm$^{-1}$. The 2D band width can be used to determine the number of layers of graphene [14].

Raman analysis was then performed with the aim to investigate the possible presence of C phases due to the C atoms rearrangement after the Si sublimation.

Raman spectra acquired on the etched regions of 4 samples representative of the first series are reported in **Fig 6**.

Broad bands characteristic of an amorphous and nanocrystalline matrix were found. In particular, in the range 400-600 cm$^{-1}$ we note a peak at 520 cm$^{-1}$ (due to the LO mode of microcrystalline Si), and a broader band centered around 480 cm$^{-1}$ (due to Si-Si optical modes of an amorphous phase). In the range 700-900 cm$^{-1}$, we found a peak at 782 cm$^{-1}$(ascribed to the 4H-SiC TO mode), and a broader band due to Si-C optical modes of an amorphous phase [15]. The most promising region is in the range 1100-1800 cm$^{-1}$, where vibrational modes due to sp$^2$ bonded C atoms rely [14]. An increase in the C-C content is detected on samples processed on the C-face, respect to Si-face ones. Furthermore, D and G bands are clearly distinguished only on sample 1_16. 2D band was not detected, because of the absence of ordinated crystalline C-C phase.

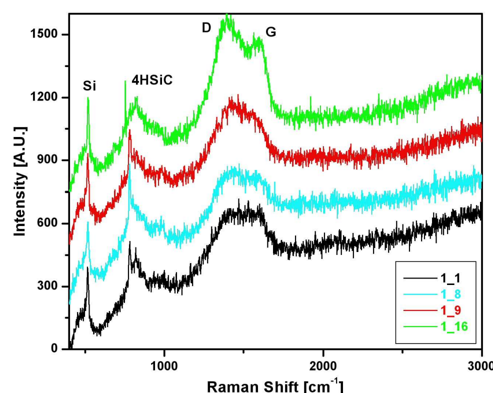


**FIGURE 6**: Raman spectra of selected samples of the first experimental series.

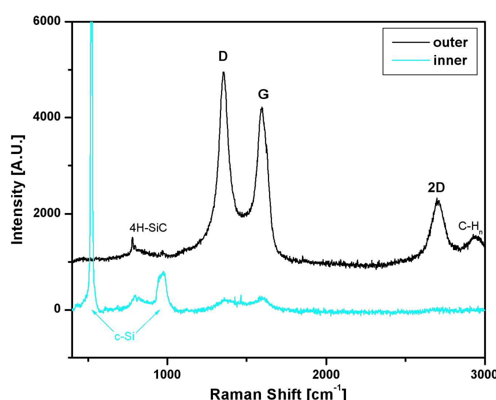


**FIGURE 7**: Raman spectra acquired on inner and outer regions of sample 2_11.

The Raman spectra of the inner and the outer region of sample 2_11 are reported in **Fig.7**. The inner region exhibits a very sharp peak due to crystalline Si. The presence of crystalline Si is in agreement with FESEM and EDX analysis. 4H-SiC related peaks and the D and G bands have low intensities in the central zone. On the other hand, the characterization performed out of the central region of sample 2_11 shows D and G bands more sharper than those of other samples.Most importantly, the 2D signal is perfectly visible. The corresponding Raman shifts are respectively 1356, 1596 and 2705 cm$^{-1}$. These values are in overall good agreement with those reported by other research group

that investigated the growth of graphene layers by SiC thermal annealing [13]. The 2D band FWHM of sample 2_11 is around 80-90 $cm^{-1}$, while for a monolayer of epitaxial graphene on SiC, this value is usually in the range from 37 to 60 $cm^{-1}$. Ni et al. found similar values for epitaxially grown two layers graphene (95 $cm^{-1}$), suggesting that few layer graphene could be present on our samples [14].

XPS spectra were acquired on the most promising samples characterized by Raman spectroscopy, both on laser annealed regions and on non processed regions.

In the samples 1_10 and 1_16 it is possible to observe an increase in the amount of graphite formed during the annealing treatments, by monitoring the change of C1s core level peaks. An increase of the intensity of this peak in the annealed area with respect to the non-annealed area was observed, confirming the presence of C graphite in the etched area.

The intensity of the C1s core level peak in the etched area of the sample 1_16 with respect to the non-annealed area show a substantial increase in comparison to the other samples.

The binding energy (BE) of 284,82 eV can be related to the presence of C in graphitic phase.

On the sample 2_11 the XPS spectra confirms the presence of a C graphitic phase (BE= 284.33 eV) and there is a peak at 285.16 eV (**Fig.8**). This binding energy is related to the presence of graphene by other authors [13,16].

In conclusion, XPS analyses were in good agreement with the results obtained by means of Raman and FESEM.

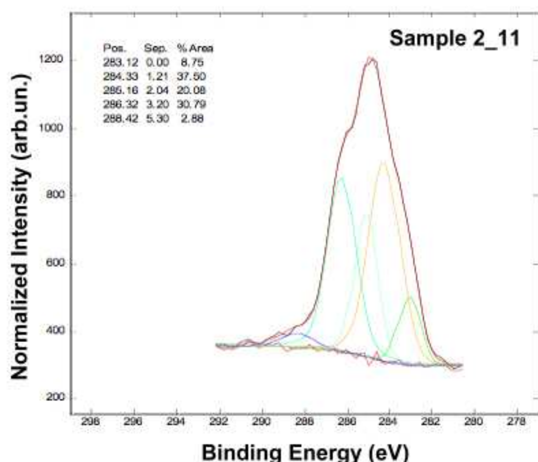


**FIGURE 8** XPS C1s core level peak of sample 2_1.The peak centred at 285.1 can be attributed to C graphene.

## 4. Conclusion

SiC laser annealed samples were prepared and characterized, with the aim to obtain a correlation between process parameters and the presence of C phases such graphene, FLG and graphite. Different values of the laser power, frequency, beam spot velocity and repetition rate were tested, taking into account the presence of two different SiC polar surfaces with different thermal decomposition behaviours

Finally, annealings were done in UHV condition or with an Ar inert atmosphere.

An undesirable, marked etch of the SiC surface was observed on the samples processed in the first series, after the annealing treatments. Only on SiC C-face a disordered graphitic phase was obtained.

In the second series of experiments, an excessive Si sublimation was avoided using an Ar atmosphere, thus avoiding the etching effect. The presence of a nanocrystalline graphitic phase, but also the possible presence of graphene was detected by Raman and XPS performed on a sample belonging to the second series.

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