Graphitization and amorphization of textured carbon using high-energy nanosecond laser pulses

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A B S T R A C T
Laser pulses can effectively induce local structural changes and modify the physical properties of carbon allotropes. So far, only graphitization has been demonstrated using low laser energies (< 1 J/cm²). The novelty of this paper is a result of laser-induced amorphization of a highly anisotropic carbon allotrope by using high energy (1.5–15.4 J/cm²) 5 ns, 532 nm Nd-YAG laser pulses. Moreover, cycling phase change, between an amorphous and a crystalline phase, is also obtained by adjusting the pulse energy. However, cycling ability is restricted to a few cycles as a consequence of laser-induced surface damages caused by both high temperatures during and high thermal gradients during and after laser exposure. The occurrence of graphitization or amorphization depends on the amount of solid crystalline seeds during solidification from the melt, which is controlled by the post-pulse temperature of the carbon surface. This study uncovers new applications of carbon allotropes, such as optically-controlled reversible phase-change memories.

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1. Introduction
Carbon allotropes are key building blocks in a wide range of applications as they feature extremely versatile electrical, mechanical and optical properties. This versatility is linked to the variability in their crystalline structure, in particular the sp² (graphite-like) to sp³ (diamond-like) atomic bond ratio or the amounts of sp² clustering and of disorder [1,2].

As a result, numerous research groups have proposed different methods to control the atomic structure of carbon allotropes. Partial control of the atomic structure of carbon thin films can be achieved during deposition by tuning the deposition parameters [3–7] or after deposition by slow thermal annealing in an oven [8–13]. In a more localized manner and to induce rapid changes, beams of electrons [14], ions [15], or photons [16–20] can be used. However, only the application of an electric field in electronic devices has enabled reversible changes, through the formation and rupture of graphitic filaments [21–25]. This has opened the way toward electrically-controlled carbon-based resistive memories [21,24,25].

The continuous development of optical technologies such as the widespread Blu-Ray technique has demonstrated that using photons instead of an electric-field to induce reversible phase changes is of both technological and commercial interest [26].

So far, laser-based phase change experiments have only conducted to graphitization and not to amorphization, hence obstructing further device applications, including optical memories. However, most studies have focused exclusively on a small energy density window, below 1 J/cm², to avoid surface degradations [16–18,20]. As a consequence, surface damages on carbon films have been mostly overlooked, despite their critical impact on applications ranging from crystallization to ablation.
The goal of this paper is to demonstrate optically-induced reversible phase change in carbon. Here, we present a detailed study on the impact of high-energy laser pulses (1.5–15.4 J/cm²) on the crystalline content and surface morphology of two films of textured carbon. This material consists of nano-sized clusters of graphitic planes that are preferentially oriented perpendicular to the substrate, therefore it has attracted a large interest for applications in electronics and thermal management [14,16,17,27–29]. Moreover, as the crystalline regions are separated by amorphous carbon, textured carbon is neither fully amorphous nor fully crystalline, consequently it is highly suitable for the investigation of laser-induced crystallization or amorphization.

We show that laser-induced amorphization of carbon is possible, i.e. the phase change from crystalline to amorphous, can be obtained for sufficiently high energy laser pulses. The reversible phase change can be explained by considering crystallization kinetics and the impact of solid crystallization seeds. This demonstration of reversibility makes the development of phase-change memories feasible: we provide a proof of concept by studying the cycling ability of textured carbon phase change. Critically for carbon laser-annealing applications, we also study the resulting surface state by classifying the surface damages. We show that different surface artefacts appear for different thermal gradients and temperatures.

2. Experimental details

2.1. Preparation of the films

Two thin films of textured carbon [27] are deposited by a Filtered Cathodic Vacuum Arc [30] system on two separate Si substrates for the annealing experiments. The deposition parameters are a bias voltage of −500 V on the substrate, an arc current of 60 A and a pressure in the chamber of 4 × 10⁻⁶ Torr before deposition and a maximum of 10⁻⁵ Torr during deposition. The deposition duration is 9 min for one substrate, 2 min for the second. Using a Dektak XT surface profiler, the two films are found to be respectively 310 ± 120 nm and 110 ± 40 nm thick. We refer to them as “sample A” and “sample B”, respectively.

2.2. Laser-annealing

Annealing is conducted in ambient atmosphere with a 532 nm Surelith I-10 Nd-YAG laser, with energy tunable between 110 and 200 J beam per pulse. Before annealing, the total pulse energy and the non-uniform spatial distribution of the pulses are characterized with a Labmax Top power metre and an Ophir M2-200s beam profiler (see Supplementary Material Section 1). The samples are mounted on a mobile stage normally to the beam at approximately 300 mm from the source and annealed by single pulses. After each pulse, the film is translated normally to the beam by 6 mm to prevent overlap between neighbouring annealed areas. In total, 41 pulses are shot on sample A and 24 on sample B.

2.3. Post-annealing characterization

After laser exposure, the surface morphology of the films is observed with a LEO 1550 Gemini Field Emission SEM.

Bright-field and high-resolution TEM analysis are performed by a FEI Titan TEM at 300 kV. TEM samples are prepared by using a Focused Ion Beam Helios 450 S, at 30 kV for coarse milling, and at 5 kV for final fine milling (to reduce surface amorphization effects by the high-energy Ga ions used in FIB sample preparation).

To characterize the atomic structure quantitatively and non-destructively, Raman spectroscopy is carried out with a WITec 532 nm Raman microscope. The laser is used at low intensity to prevent annealing during characterization [19]. Unless stated otherwise, Raman spectra are acquired roughly at the energetic centre of each annealed spot. Broad G (1580 cm⁻¹), D (1350 cm⁻¹) and T (1060 cm⁻¹) bands are observed. To extract the desired data from the spectra, we use an automated parameter extraction method based on Lorentzian fit (Supplementary Material, Section 2). Moreover, a Bootstrap method [31] is applied to derive the uncertainty range for the extracted Raman parameters, which reaches around 4% on the I(D)/I(G) ratio. The extracted Raman parameter values are interpreted according to the standing framework for strongly disordered graphite, semi-crystalline carbon and amorphous carbon [1,32]: the G peak is associated to bond stretching of sp² atoms. The T band, more commonly monitored with UV Raman spectroscopy [1] but observed in the spectra acquired here, indicates the presence of atoms in sp³ configuration. The spatial variability in the Raman spectra (e.g. due to the position of the beam with respect to the sample) is assessed on the pristine film and found to be much smaller than the observed variations due to laser-annealing (Supplementary Material, Section 3).

3. Results and discussion

3.1. Reversible phase change

As-deposited textured carbon is composed of clusters of graphitic planes perpendicular to the substrate and separated by amorphous regions, as shown by the HRTEM images (Fig. 1 (a)) and the electron diffraction pattern showing the (002) reflection peaks of graphite (Fig. 1 (a) inset).

The Raman spectrum of pristine textured carbon (Fig. 2 (a), inset, bottom spectrum, “as-deposited”) yields the following parameters: I(D)/I(G) = 0.69 ± 0.01; G peak position xG = 1548 ± 1 cm⁻¹; full with at half maximum (FWHM) of the G peak wG = 268 ± 3 cm⁻¹. These values are consistent with a mostly sp² carbon allotrope with up to 20% of sp³ atoms [32].

After laser annealing with increasing energy densities, we observe in both films a continuous increase of the D peak intensity (Fig. 2 (a)) while the width of both the D and G peaks decreases (see Supplementary Material, Section 4). In sample A (respectively sample B), the maximum I(D)/I(G) is reached at 4.3 J/cm² (respectively 2.0 J/cm²), corresponding to a 43% (respectively 15%) increase from the pristine material. These results are consistent with carbon graphitization. Similar graphitization trends have been reported at energy densities below 1 J/cm² [16–19]. HRTEM images of sample A annealed at 4.3 J/cm² show that the structure of laser-annealed textured carbon is composed mainly of graphitic planes (Fig. 1 (b)) that are found to remain mostly perpendicular to the substrate (similarly to the pristine material).

Then, from 4.3 J/cm² upward (respectively from 2.0 J/cm²), the I(D)/I(G) ratio decreases continuously and the peaks broaden. It indicates a continuous evolution from a graphite-like material to a more amorphous carbon. At about 10 J/cm² (respectively 4.3 J/cm²), I(D)/I(G) values reach their initial level (their level in the pristine material). Beyond 10 J/cm² (respectively 4.3 J/cm²), the amorphization trend continues (Fig. 2 (a)): I(D)/I(G) decreases down to 65% (respectively 64%) from the pristine material.

Fig. 1 (c) and (d) are HRTEM cross-sections of sample A after laser annealing with a 14.2 J/cm² pulse. Supporting the Raman data, it is found that most of the carbon layer has become amorphous, except at the C/Si interface where graphitic planes following the Si–C interface are observed (Fig. 1 (d)). The Si layer also appears to be degraded. Though no SiC Raman peaks (at ca. 760 and 960 cm⁻¹) are detected, the presence of SiC at the Si–C interface may not be
excluded, as SiC vibrations have a very small cross-section [1]. By looking at the Raman data on the whole range of energies, it is found that the threshold energies (for graphitization and amorphization) and maximum I(D)/I(G) values are higher in the thicker sample A than in the thinner sample B (Supplementary Material, Section 5). This suggests that volume mechanisms are
involved in the phase change.

Overall the data show that, depending on their energy density, nanosecond laser pulses can trigger either graphitization or amorphization in textured carbon thin films. While laser-induced graphitization of carbon has been reported several times, it is the first time laser-induced amorphization is achieved. The phase change is reversible, as demonstrated when annealing the same spot with alternating high and low energy pulses (Fig. 2(b)). However, the cycling ability is low (3 cycles), hinting at irreversible degradations in the material during laser exposure. To understand the origins of this irreversibility, we carry out an analysis of the surface morphology of the laser-annealed regions.

### 3.2. Laser-induced damages

Previous studies on low energy laser-annealing of amorphous carbon (a-C) report a slight increase in surface roughness [17]. Here, SEM images confirm this trend for pulses between 1.5 J/cm² and 3.9 J/cm² (for sample A). The increase in roughness is due to spherical surface grains, whose density and size increase with increasing pulse energy (Fig. 3, (a) and (b)). In the literature, such grains are attributed to localized melting of the top carbon layer during annealing, followed by air-cooling and rapid solidification [33]. This suggests that the surface of the textured carbon layer reaches its melting temperature at energy densities as low as 1.5 J/cm². Let us remark that the melting temperature of textured carbon has never been measured. However, as it is composed of a mixture of sp² and sp³ bonded atoms [27] with similar cohesive energies [34], the melting temperature of textured carbon is expected to be close to that of graphite (4450 K [35]). Laser-induced melting of graphite has been reported at energy densities as low as 0.6 J/cm² [33,36–40].

To support the hypothesis that the film partially melts at energy densities as low as 1.5 J/cm², we study by numerical modelling the temperature rise in a vertical graphitic film, that is, where the graphitic planes are aligned perpendicularly to the substrate similar to textured carbon. The material is annealed by a 5 ns energetic laser pulse. We use the finite element method with the software Cast3M [41]. We find that at energy densities as low as 0.6 J/cm², the surface temperature rises above the melting temperature (while most of the film remains at temperatures lower than the melting temperature). A detailed discussion of these results is provided in the Supplementary Material, Section 6.

In a small range of energies around 3.9 J/cm², cracks (Fig. 3 (c) and (d)) are observed. They uncover the Si layer locally, so that at crack locations, only Si Raman peaks can be observed. Cracks are known features of nanosecond laser annealing experiments [33] caused by strong thermal gradients in the solid phase. The occurrence of cracks at 3.9 J/cm² thus indicates that at such energy densities, the carbon film is still partially solid and undergoes thermal gradients reaching throughout the layer. The absence of cracks below this threshold suggests that the large thermal gradients remain confined to the surface. The renewed absence of cracks above this threshold suggests that the carbon film is then fully melted. The small energy window for crack appearance can be explained by the high thermal conductivity of liquid carbon (nearly 10 times larger than solid carbon [36]), which fosters the downward diffusion of the heat toward the solid/liquid interface and the fusion of the solid layer. In other words, when the film starts melting homogeneously, full melting occurs very rapidly. Similar processes have been reported during laser-annealing of Si [42]. Interestingly, in the thinner sample only (B) and in the direct vicinity of the cracks, wave-like structures with a roughly 500 nm period are observed (Fig. 3 (d)). Such ripples are common features in laser-annealed crystalline Si films. Appearing when the Si surface temperature is close to its melting point [43], they are attributed to light-induced electronic surface waves (plasmons) and have a period equal to the excitation wavelength when the light direction is normal to the surface [44].

However, ripples have never been reported after laser-annealing of disordered carbon; moreover, at 3.9 J/cm², the carbon layer surface is thought to be significantly above its melting temperature. Consequently, we postulate that the ripples do not appear directly in the C layer, but rather appear in the Si layer around the locations where it is uncovered by the cracked C layer; upon cooling, the carbon melt solidifies around Si ripples, forming the structures observed here. They are not apparent in the thick film as the layer thickness is much larger than the ripple height. This interpretation further entails that at 3.9 J/cm², the Si/C interface temperature is close to the Si melting point (1680 K), while the top carbon layer temperature is above its melting point (4450 K).

When the energy density increases above the cracking

Fig. 3. Features commonly observed at the surface of un-annealed and laser-annealed textured carbon. (a) Smooth un-annealed surface. (b) Increasing roughness at low energy densities. (c) Appearance of cracks. (d) Cracks and ripples that are observed only on the surface of Sample B. (e) Sputtering traces (spheroids and hollow pillars). (f) Explosive boiling traces.
threshold, from 3.9 to 6 J/cm² (sample A), the size and density of the surface grains increase (Fig. 3 (c)). Grain shapes evolve progressively from spherical to anisotropic, yielding full or hollow cylinders (pillars or tubes). The tubes and pillars are attributed to the sudden quenching of the carbon layer at the end of the laser pulse. The different structures (full or hollow cylinders) suggest that the carbon layer boils during the pulse and that bubbles of liquid carbon are frozen at different stages of their vaporization. The hollow cylinders (whose number increases with increasing energy) indicate that some sputtering takes place. This conforms with the literature, which indicates that sputtering occurs when the temperature increases significantly above the melting point [33].

Finally, at even higher energy densities, between 6 and 15.4 J/cm², the surface microstructure shows important matter restructuration, forming deep grooves and ridges. Signs of secondary sputtering (spheroids on the remaining material) are also observed (Fig. 3 (f) for this observation on Sample B). We recall that surface boiling is attained at energy densities as low as 3.9 J/cm², so in this energy range, the surface temperature of the carbon layer is expected to be far above its boiling point. We attribute the matter restructuration to explosive boiling, the main mechanism used in laser ablation techniques [45, 46]. Estimates of temperatures restructuration to explosive boiling, the main mechanism used in laser ablation techniques, expected to be far above its boiling point. We attribute the matter restructuration to explosive boiling, the main mechanism used in laser ablation techniques [45, 46]. Estimates of temperatures restructuration to explosive boiling, the main mechanism used in laser ablation techniques, expected to be far above its boiling point. We attribute the matter restructuration to explosive boiling, the main mechanism used in laser ablation techniques [45, 46]. Estimates of temperatures restructuration to explosive boiling, the main mechanism used in laser ablation techniques, expected to be far above its boiling point. We attribute the matter restructuration to explosive boiling, the main mechanism used in laser ablation techniques [45, 46]. Estimates of temperatures...
Appendix A. Supplementary data

Supplementary data related to this article can be found at http://doi.org/10.1016/j.carbon.2016.04.026.