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Spectroscopic ellipsometric and Raman spectroscopic investigations of pulsed laser treated glassy carbon surfaces

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ABSTRACT

In this study spectroscopic ellipsometry (SE) and Raman spectroscopy are applied to study structural modification of glassy carbon, due to high intensity laser ablation. Two KrF lasers with different pulse durations (480 fs and 18 ns), an ArF (20 ns), and a frequency doubled Nd:YAG laser (8 ns) were applied to irradiate the surface of glassy carbon targets. The main characteristics of the different laser treatments are compared by introducing the volumetric fluence which takes into account the different absorption values at different wavelengths. SE showed the appearance of a modified layer on the ablated surfaces. In the case of the ns lasers the thickness of this layer was in the range of 10–60 nm, while in the case of fs laser it was less than 20 nm. In all cases the average refractive index (n) of the modified layers slightly decreased compared to the refractive index of glassy carbon. Increase in extinction coefficient (k) was observed in the cases of ArF and fs KrF laser treatment, while the k values decreased significantly in the cases of nanosecond pulse duration KrF and Nd:YAG laser treatments. In the Raman spectra of the ablated areas the characteristic D and G peaks were widened due to appearance of an amorphous phase. Both Raman spectroscopy and SE indicate that the irradiated areas show carbon nanoparticle formation in all cases.

1. Introduction

High intensity laser pulses result in extreme conditions when irradiating solid surfaces. High absorption in visible and UV, good focusability of the laser light, short pulse durations lead to high intensities in the top layer of the material and formation of plasma with high temperature and pressure. The material, which remains in the ablation crater, is affected by these high temperatures and pressures. After solidification its structure depends on the formed phase during the ablation, which can be liquid, overheated liquid or in case of femtosecond laser ablation highly excited, solid density ionized material. In this latter case the two-temperature model [1] describes the system, with different electron and lattice temperatures, which relaxes within ps timescale. The cooling rate is an important parameter, which influence the progress of non-equilibrium phase transitions and the final bond types and amorphous/crystalline degree of the solidifying material.

The sp^2 and sp^3 hybridization structure of carbon strongly depends on the condition of the formation, therefore carbon is a good indicator to monitor the relaxation processes, which occur after intense laser pulse – material interaction. Investigations of laser irradiated carbon forms were reported by several groups. Raman spectroscopic investigations of highly oriented pyrolytic graphite (HOPG) surfaces, irradiated by ArF laser, indicated the formation amorphous structure, when fluences were used up to 15 J/cm^2 [2]. Laser shock induced structural modifications as hardening of glassy carbon surface, induced by excimer and frequency doubled lasers was reported in [3,4]. KrF laser ablation of graphite targets by energetic pulses (fluences up to 250 J/cm^2) [5] revealed that spheroid diamond particles were formed besides the appearance of a disordered graphitic layer. The study of ultrafast laser ablation of HOPG showed a reduced heat affected zone and a decrease in sp^3 bonds as pulse length shortened [6]. According with this observation molecular dynamics simulations showed that fs laser pulse excitation in diamond induces a non-equilibrium transition to graphite [7].

In this study different laser sources were used to irradiate the surface of glassy carbon (GC) targets with lower fluence values (up to 1.7 J/cm^2). The effect of irradiation was studied using

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Table 1
Main parameters of the applied lasers.

Laser	Dye-KrF	KrF	ArF	Nd:YAG
Wavelength (nm)	248	248	193	532
Type	Excimer	Excimer	Excimer	Q-switched
Pulse length	480 fs	18 ns	20 ns	8 ns
Fluence range (J/cm^2)	0.14–0.57	0.48–1.72	0.52–1.52	0.85–1.66

Raman spectroscopy and spectroscopic ellipsometry (SE). Raman spectroscopy is a commonly accepted method to distinguish the different carbon bonding structures [8–14]. Our previous study showed that SE also gives the possibility to distinguish different kinds of carbon layers, as e.g. diamond-like or graphite-like amorphous carbon [15]. In the followings we show, that comparison of ellipsometry and Raman spectroscopy results allows easier interpretation of laser induced effects in carbon targets. Furthermore, the introduction of the volumetric fluence [16] as a variable, allows an efficient representation of the optical properties and Raman parameters of the laser modified surfaces.

2. Experimental

Surfaces of glassy carbon targets (Sigradur G plates with 3 mm thickness) were modified by series of laser pulses (from 1 to 20) in air atmosphere using different laser sources. Glassy carbon has a fullerene-related structure. The microstructure consists tightly curled two to four graphene layers which has enclosed micropores of the order of 5 nm in diameter [17]. ArF, KrF, hybrid dye-KrF [18] excimer lasers and a frequency doubled Nd:YAG laser were applied to irradiate the surface. The laser parameters are summarized in Table 1. The beams were focused by a fused silica lens with 50 mm focal length. The surface of the glassy carbon targets was above the focal plane. Due to the spherical aberration of the lens the lateral intensity distribution within the illuminated area was roughly uniform with step like edges. The laser irradiated areas exceeded the spot size of the ellipsometric measurements in all cases.

Changes in the optical properties were followed by a Woollam M2000 rotating compensator ellipsometer. Ellipsometric angles Ψ and Δ were respectively recorded at 60° and 70° angles of incidence in the 250–1000 nm wavelength range. The measurements were carried out with microspot option in order to investigate a homogeneous area from the laser treated surfaces. The measuring spot size along short axis was ~110 μm. The samples were placed on an x–y–z stage and were carefully aligned to guarantee that each laser treated area can be investigated at the same position. For details of evaluation see Section 3.1.

Raman spectra were recorded by a Thermo Scientific DXR Raman Microscope. The excitation source was a frequency doubled Nd:YAG laser (532 nm). The laser beam was focused by a 50× magnification objective onto a ~2.5 μm^2 area with 3× 30 s integration time. The laser power was in the range of 1.5–2.5 mW. The resolution of the Raman spectra was 5 cm^{-1}.

High resolution SEM images in secondary electron mode were recorded to visualize the morphology of the irradiated areas (Hitachi S-4700, operating voltage: 5 kV, magnification: 60,000×).

3. Results

To interpret the results of ellipsometry and Raman spectroscopy corresponding to different laser modifications one has to choose a parameter which determines the effects of the laser pulses having different wavelength and pulse durations. The wavelength determines the absorption penetration depth in GC therefore the heating rate and the temperature of the surface region. The characteristics of the different laser treatments can be described by introducing the volumetric fluence which takes into account the different absorption coefficient values at different laser wavelengths. The volumetric fluence in the followings is given by the fluence multiplied by the absorption coefficient of GC. It describes the energy value absorbed in a unit volume near to the surface.

3.1. SE results

To evaluate the ellipsometric measurements, first the intact GC was analyzed. The measured Ψ and Δ values were evaluated by the general oscillator model [19,20], using the combination of Gaussian and Tauc–Lorentz oscillators. The resulting n and k data were later used as the optical data of the substrate and they were fixed during the evaluation of the laser treated samples. Since the measured ellipsometric angles of the treated areas were close to the Ψ and Δ values of the intact GC sample, a one-layer model was applied to fit the data collected on transformed surfaces, using again the combination of Gaussian and Tauc–Lorentz oscillators. The parameters of these oscillators were initialized based on the fitting of the ellipsometric curves of the intact GC surface ensuring that the resulting ellipsometric angles are close to the measured data. In that way, the model consisted of the GC substrate (n and k values measured on the intact bulk GC), a modified layer and air ambient. We have to note, that this one-layer model provides average n and k values of the top most region of the sample and does not give information on the internal structure of the layer or on the texture of the modified surface. However, application of this model allows a comparison of the effects of different laser treatments and gives an estimation of the depth of the remaining modification.

When plotting the results as a function of the volumetric fluence a clear tendency is observed. Fig. 1 shows the resulting n, k and thickness values of the modified layer as a function of the volumetric fluence for the different laser sources. Results are

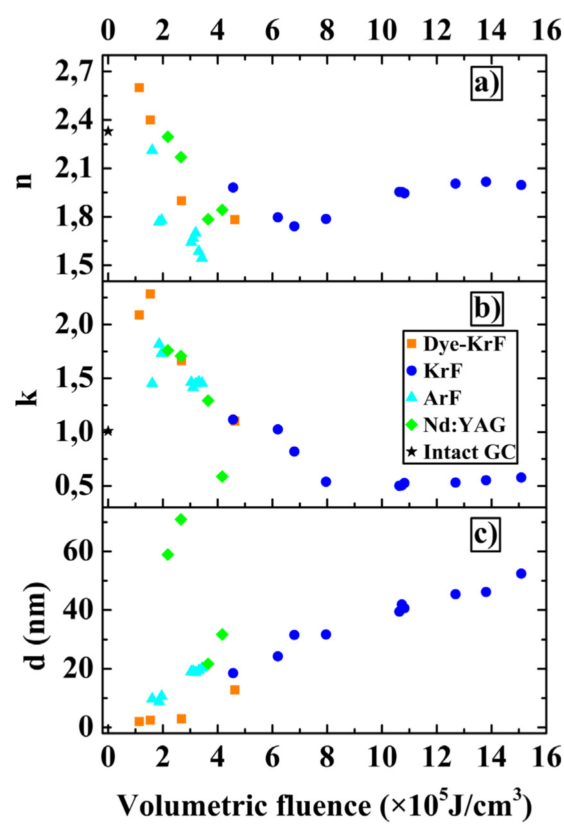

Fig. 1. (a) Refractive index, (b) extinction coefficient at 532 nm and (c) thickness of the modified layers as a function of applied volumetric fluence in case of one pulse treatment.