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Optical characterization of double-nanotextured black diamond films

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ABSTRACT

Double-nanotextured black diamond films with different geometries were fabricated by double-step femtosecond laser treatments at different split ratios of accumulated laser fluence. A "2D-like" pseudo-periodic nanostructure was obtained for the first time when the split ratio was slightly unbalanced in favour of the first step of the treatment, as inferred by scanning electron microscopy. Raman analysis showed that a residual biaxial stress, composed by a superposition of a tensile and a compressive component, is always present after the laser writing process, and that the two components tend to balance each other in the 2D pseudo-periodic case. Spectrophotometric measurements in the 200–2000 nm wavelength range returned outstanding solar absorptance values for all the fabricated films (reaching the unprecedented value of 99.1% in the "2D-like" structure), launching double-nanotextured black diamond as a possible alternative to black silicon as absorbing layer for high-efficiency solar cells.

1. Introduction

In recent years, irradiation with femtosecond laser pulses turned out to be an efficient technique to improve the optical absorption properties of semiconductors in the visible and infrared wavelength ranges, aimed at producing a new generation of solar cells with enhanced conversion efficiency. The first and most recognized example is "black" silicon [1–3], in which laser pulses induce the formation of micrometer-sized cones on the light-receiving surface, which were demonstrated to dramatically improve solar absorptance due to light trapping by multiple reflections [4]. However, while on the one hand black silicon may represent the perfect material for the fabrication of standard photovoltaic cells, on the other it may suffer from an unacceptable loss of performance in thermionic devices conceived for concentrating solar power systems [5], such as photon-enhanced thermionic converters [6,7], where a low electron affinity is mandatory to increase the emission efficiency.

A material able to combine the outstanding solar absorptance of black silicon with excellent electron emission properties is "black" diamond [8,9], obtained from native transparent diamond by fs-laser surface treatment. Indeed, femtosecond lasers are now widely used also for processing transparent dielectric materials [10] and wide-bandgap semiconductors [11]. Unlike black silicon, irradiation of diamond with fs-laser pulses does not result in the formation of micrometer-sized structures, but of a nanotextured surface with smaller dimensions. In particular, if a linearly polarized beam is used, a one-dimensional LIPSS (Laser-Induced Periodic Surface Structure) is formed with periodicity in the range 80–170 nm, depending on the laser wavelength [12]. Single-nanotextured black diamond films demonstrated to improve absorptance of native diamond both in the visible [13,14] and infrared [15] ranges, due to both light trapping and introduction of energy levels within the semiconductor bandgap, able to interact more efficiently with sub-bandgap photons. The highest absorptance values obtained with single-nanotextured black diamonds are 92–93% in the solar spectrum (300–2500 nm), whereas black silicon micro-structured films easily exceed 95%; this is a clear indication that a 2D periodicity of the laser-induced structure, as

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the one induced in black silicon films, may further enhance optical absorption if compared to the 1D case. In this regard, a preliminary study was performed [16] in an attempt to realize a double-nanotextured black diamond film by using a double-step laser-writing process, where an accumulated fluence equally distributed between the two treatments demonstrated to be effective in improving the solar absorptance of a 1D nanotextured black diamond. However, the process was not able to reproduce a 2D regular nanostructure, due to a non-optimized distribution of the laser fluence delivered to the sample during the two steps of the treatment.

In this work, we make an important step forward for the newborn black diamond technology. We show for the first time that it is possible to obtain a "2D-like" pseudo-periodic surface nanostructure by double-step femtosecond laser-writing process, paving the way to the realization of optimized and regular 2D arrays, similar to the ones fabricated on black silicon. In particular, we introduce here a comprehensive optical characterization (including scanning electron microscopy, Raman analysis, and spectrophotometry) of four double-nanotextured black diamond films fabricated with different split ratios of accumulated laser fluence. Results point out that, when the split ratio of accumulated laser fluence is slightly unbalanced in favour of the first step of the treatment, a 2D array of nanorods can be obtained, allowing for a further significant increase of solar absorptance values, even higher than 99% and comparable to those of state-of-the-art black silicon films.

2. Fabrication of double-nanotextured diamond films

Four freestanding "thermal management grade" CVD polycrystalline diamond samples, with lateral dimensions $10 \times 10\ mm^2$ and thickness 250 μm, provided by Element Six Ltd. [17], were used in this work. Laser treatment was performed in a high-vacuum chamber (base pressure $< 10^{-7}$ mbar) by using a linearly polarized femtosecond pulsed laser beam, produced by a regeneratively amplified mode-locked "chirped-pulse" Ti:sapphire laser (wavelength $\lambda_{fs} = 800$ nm). Pulse duration was 100 fs. Repetition rate was 1 kHz. In order to obtain double-nanotextured films, the focused laser spot scanned the surface in a two-step process: in a first step, namely the *x*-step, the diamond sample was moved along the horizontal axis (*x*) of an automatically controlled micrometric *x*-*y* translational stage, performing a complete scan of the surface in a "bustrophedic" way (*i.e.* following a left-right/right-left serpentine path); then, in a second step, namely the *y*-step, the sample was rotated by 90° and the same "bustrophedic" laser scanning procedure of the first step was repeated. Being the laser beam linearly polarized along *y*-axis in both the steps, the 90° sample rotation was indeed necessary to simulate the interaction of the sample with a laser beam linearly polarized along *x*-axis, in order to obtain spatially crossed LIPSSs derived from the superposition of the two steps of the treatment.

For all the experiments, the same total accumulated laser fluence $\Phi = 5.0\ kJ/cm^2$, which returned the best periodic 1D structures in terms of geometric regularity [8], was used. The total accumulated laser fluence is defined as $\Phi = N\Phi_p$, where *N* is the average number of pulses impinging the surface unit, and $\Phi_p = E_p/(\pi w^2)$ is the single pulse laser fluence, where E_p is the pulse energy and *w* is the circular beam radius on the focal plane. The difference among the four double-nanotexturing processes is in how the total accumulated fluence $\Phi = \Phi_x + \Phi_y = N_x\Phi_p + N_y\Phi_p$ was shared between the two steps of the laser treatment, where (Φ_x, N_x) and (Φ_y, N_y) are the accumulated laser fluence and the average number of pulses impinging the surface unit related to the *x*- and *y*-step, respectively. Table 1 resumes all the parameters considered in the two steps of the laser treatment for four different combinations of Φ_x and Φ_y. The percentages of total accumulated laser fluence delivered to the sample in a single *x*- or *y*-step are defined as $\Phi_{x,\%} = \Phi_x/\Phi$ and $\Phi_{y,\%} = \Phi_y/\Phi$, respectively. For practical reasons, pulse energy was kept constant for all the experiments at $E_p = 3.6$ mJ, corresponding to a single pulse laser fluence $\Phi_p = 7.33\ J/cm^2$, calculated by assuming a laser beam diameter ($1/e^2$ width) equal to $2w = 250$ μm. In this way, the accumulated laser fluence can be simply varied by acting on the laser scanning speed, resulting in a different average number of pulses impinging the surface unit.

Table 1
Experimental parameters of the four different double-step nanotexturing processes performed, where the percentages of total accumulated laser fluence delivered to the sample in a single *x*- or *y*-step are reported as $\Phi_{x,\%}$ and $\Phi_{y,\%}$, respectively.

Sample	Φ_x (kJ/cm^2)	$\Phi_{x,\%}$ (%)	N_x	Φ_y (kJ/cm^2)	$\Phi_{y,\%}$ (%)	N_y
#1	1.89	90	610	0.21	10	70
#2	1.68	80	545	0.42	20	135
#3	1.38	66	455	0.72	33	225
#4	1.05	50	340	1.05	50	340

After the double-step process, all the textured samples were subjected to wet etching in a strongly oxidizing solution (H_2SO_4:$HClO_4$:HNO_3 in the 1:1:1 ratio, 15' at boiling point), followed by ultrasound sonication in deionized water, in order to remove possible non-diamond contents and residual debris.

3. Results and discussion

In the following subsections, the morphological, structural, and optical properties of the four fabricated double-nanotextured black diamond films will be phenomenologically discussed.

3.1. SEM characterization

Morphology of the double-nanotextured surface of the fabricated black diamond films was evaluated by field emission gun-scanning electron microscopy (FEG-SEM, Zeiss mod. Leo-Supra 35). As can be seen from Fig. 1, reporting four representative pictures of the different fabricated structures, the surface morphology strongly depends on the percentage of total accumulated laser fluence delivered to the sample in a single *x*- or *y*-step.

As expected, when almost all the accumulated fluence is delivered in the first step (we recall here that it is always the *x*-step), high spatial frequency ripples are mostly formed perpendicularly to the direction of polarization (*y*) of the laser beam, as in the cases of Fig. 1a and b. The periodicity of the laser-induced structures is about 170 nm, similarly to the case of single-step treatments [8] performed at the same laser wavelength (800 nm). However, we can observe a significant loss of geometric regularity when the accumulated fluence delivered in the second step (*y*-step) is increased from 10% to 20% of the total fluence. Indeed, ripples of Fig. 1a extend in an almost uninterrupted way for quite a long distance (about 3 μm); conversely, ripples of Fig. 1b, although maintaining a good degree of regularity, are less defined, and here and there interrupted by oblique grooves, forming an angle of about 45° with *x*-axis.

The one-dimensionality of the laser-induced nanotexturing is lost completely in the case of Fig. 1c, showing the surface of a sample treated with a split ratio of 66% (*x*) − 33% (*y*). The regular sequence of ripples and grooves is replaced by a high density of nanostructures with various shapes, resembling a 2D pseudo-periodic distribution of nanorods with a length of a few hundred nanometers. Interestingly, the average orientation of nanorods forms an angle of about 45° with *x*-axis, as the direction of the long