Changes in Amorphous Hydrogenated Carbon Films by Ultraviolet and Infrared Laser Irradiation

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Amorphous hydrogenated carbon films were formed on the Si (100) wafers by a direct-ion beam deposition method from pure acetylene and acetylene–hydrogen gas mixtures. The films were irradiated with a nanosecond Nd:YAG laser working at the first harmonics ($\lambda_1 = 1064$ nm), the fourth harmonics ($\lambda_4 = 266$ nm) or with a Nd:YVO$_4$ laser working at the third harmonic ($\lambda_3 = 355$ nm). The films were studied by the Raman scattering, micro-Fourier transform infrared and Fourier transform infrared spectroscopies, null-ellipsometry, optical and scanning electron microscope, and Vickers hardness method. Irradiation by the wavelength $\lambda_1 = 1064$ nm leads to graphitization and formation of the silicon carbide, because of the silicon substrate decomposition. The samples were strongly modified after the irradiation by $\lambda_3 = 355$ nm — the thickness of the films decreased, and silicon carbide was formed. It was observed that nano-structured materials (e.g. carbon nano-onions, nc-diamond) were formed after the irradiation by $\lambda_4 = 266$ nm.

1. Introduction

The effect of laser irradiation on the diamond-like carbon (DLC) films is determined by superposition of three processes: graphitization, spallation, and evaporation (including ablation) [1]. They are characterized by different threshold intensities [1] and their occurence depends on the laser parameters (pulse energy, energy density, pulse repetition rate f, beam shape, and wavelength), the optical (reflectivity, absorption coefficient) and thermophysical (heat capacity, density, thermal conductivity) properties of materials [2, 3]. Controlling those three processes and other parameters, it is possible to create nanostructured carbon-based materials like: nanotubes, carbon nano-onions, nanocones, etc. [1, 2, 4]. In this work the influence of the laser parameters on the a-C:H films properties after the irradiation by a nanosecond pulsed laser will be discussed in detail.

2. Experimental

Amorphous hydrogenated carbon films (a-C:H) were formed on the Si (100) wafers by the ion beam deposition from pure acetylene and hydrogen C_2H_2/H_2 gas mixtures. The thickness d, the refractive index n and the extinction coefficient k of layers were determined using a null-ellipsometer (Gaertner L117, He–Ne laser at 632.8 nm). Ellipsometric parameters of non-irradiated samples were collected from different areas and average values of film thickness and optical constants (n, k) were calculated for each sample. The B4 ($d = 235$ nm,

$n = 2.25$, $k = 0.16$) film was irradiated with a nanosecond Nd:YAG laser, working at the first harmonics ($\lambda_1 = 1064$ nm, $\tau = 6$ ns, $f = 12.5$ Hz) and the fourth harmonics ($\lambda_4 = 266$ nm, $\tau = 3$ ns, $f = 12.5$ Hz). The other sample B3 ($d = 60$ nm, $n = 2.06$, $k = 0.25$) was irradiated with a Nd:YVO$_4$ laser ($\lambda_3 = 355$ nm, $\tau = 10$ ns, $f = 20$ Hz). The diameter of a laser beam spot was 6 mm. Laser irradiation were done at atmospheric pressure at room temperature.

The a-C:H films were studied by the Raman scattering (RS) spectroscopy ($\lambda = 532.3$ nm) in a wave number spectral range of 400–4000 cm^{-1}. The RS spectra for the samples irradiated by λ_1, λ_3 were fitted by two Gaussian--shape lines in the spectral range 1000–2000 cm^{-1}; fitting for the samples irradiated by λ_4 was not made, because of low intensity of the characterizing curves in the spectral range 1000–2000 cm^{-1}. The position of the G band and the full-width at half-maximum ΔG correspond to a crystalline graphite. D peak position and ΔD correspond to the disorder of the sp^2 phase.

The micro-Fourier transform infrared (μFTIR) spectra were collected for the films irradiated by λ_4 in reflection mode using the FTIR spectrometer Vertex 70 coupled with an infrared microscope Hyperion 3000, the MCT single point detector in the spectral range 600–4000 cm^{-1}. A total number of 128 interferograms were collected. The collected spectra of the samples with the 4 cm^{-1} resolution were rationed against a reference spectrum and transferred to absorption values. The FTIR (Spectrum GX, Perkin Elmer) spectra were measured for λ_3 in a reflection mode in the spectral range 650–4000 cm^{-1}.

The surface morphology was analyzed by the scanning electron microscope, SEM (JSM6490LV), the optical microscope (Olympus BX51). The microhardness and

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Young modulus E were measured by the Vickers hardness method, VH (MTS G200 nanoindenter with a Berkovich diamond tip). The crystal size L_a was obtained using equation given by Cançado et al. [5].

3. Results and discussion

The obtained by ellipsometry values of optical constants and film thickness for the samples irradiated by λ_4 ranged in the following intervals: $n = 1.8$–2.7, $k = 0$–0.73, $d = 50$–220 nm; for the λ_3 irradiation: $n = 1.87$–2.10, $k = 0$–0.06, $d = 37$–137 nm; for the λ_1 irradiation: $n = 2.1$–2.4, $k = 0.50$–0.16, $d \approx 170$ nm. These parameters were calculated by means of the program "Film Ellipse" using the most appropriate multilayer models: DLC/SiC/Si (or α-Si).

In the present investigations we used the a-C:H films with a band gap of ≈ 1.4–1.6 eV [6]. Just a small amount of photon energy ($\lambda_1 = 1064$ nm, $E \approx 1.17$ eV) is absorbed by free electrons that transfer the residual energy to a crystal lattice within $\approx 10^{-10}$ s [2]. Such a process leads to the heating of the film and graphitization. The calculated penetration depth of laser light (530 nm) is larger than the film thickness (≈ 235 nm), and consequently, the main part of the energy is absorbed by the silicon substrate ($E_g \approx 1.12$ eV) causing the destruction of the Si–Si bonds. The silicon carbide (SiC) layer ($d \approx 10$ nm) was formed in the interface between the a:C-H film and the silicon substrate because of the diffusion of the silicon into the film. The earlier results have shown that there are no significant changes increasing the irradiation intensity ($35 \to 70$ MW/cm^2) in the a:C-H films [7], only the thickness of the SiC changed ($d \approx 50$ nm). It was observed that nanostructured materials were not formed using λ_1.
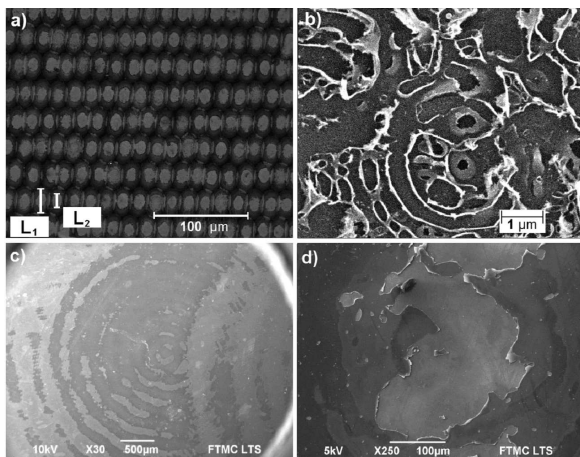

Fig. 1. Surface morphology of the B3 sample after two pulses with 8 MW/cm^2. $L_1 = 25.69$ μm and $L_2 = 15.46$ μm (a), SEM image after irradiation by λ_3 (b); SEM image of the B4 sample after two (c) and four (d) pulses.
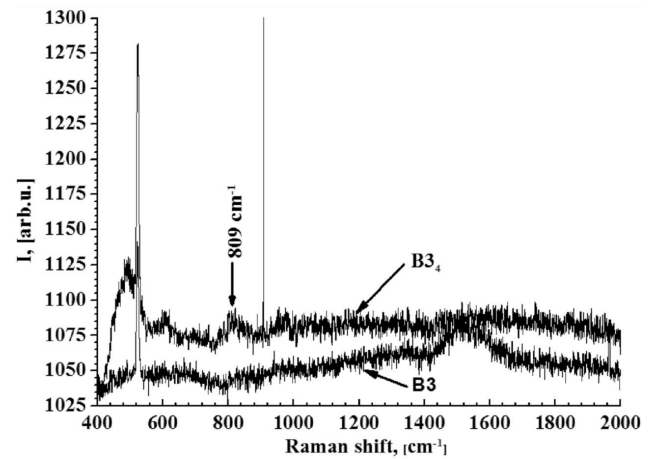

Fig. 2. Comparison of two RS spectra in spectral range 400–2000 cm^{-1} for the non-irradiated B3 sample and the sample B3$_4$ irradiated by eight λ_3 pulses per spot (irradiation intensity of 8 MW/cm^2).
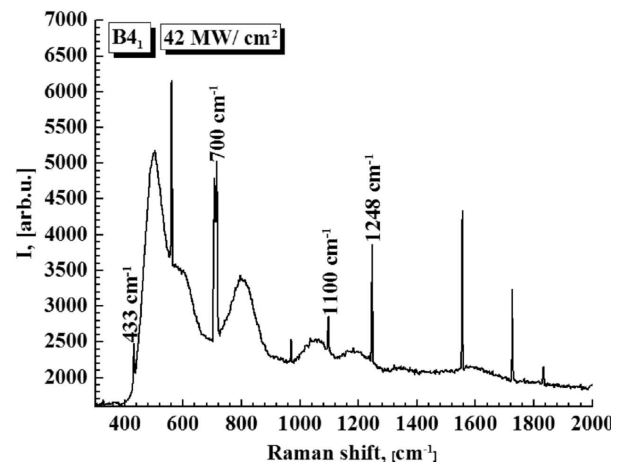

Fig. 3. RS spectra in spectral range 400–2000 cm^{-1} for the B4$_1$ film after four pulse irradiation by λ_4.

The irradiation by the λ_3 laser (355 nm, $E \approx 3.48$ eV; penetration depth ≈ 113 nm) caused ablation of the films that is not homogeneous over the laser beam diameter (Fig. 1a). Moreover, a strong spallation took place (Fig. 1b). The evaporation of the surface occurred and resulted in the decrease of the a:C-H film thickness ($60 \to 45$ nm) and SiC was formed (B3$_4$, ≈ 800 cm^{-1}, Fig. 2) [8, 9]. Increasing the irradiation intensity and pulses number per spot (Fig. 2, Table) the weak bonds (e.g. C–H, C–C) are destroyed leading to hydrogen diffusion into the silicon substrate and evaporation from the film surface. The decrease in the hydrogen content increases the probability to form the graphite layers in the film. Moreover, for the destruction of the C=C bonds more energy is needed — the graphitization process becomes dominating in the a-C:H films as a result (Table): the G peak shifts to the higher wave number position

$1532 \rightarrow 1582$ cm^{-1} and the intensity of the D peak increases. 8 pulses per spot at the irradiation intensity 8 MW/cm^2 leads to ablation of the whole a-C:H surface (Fig. 2). The FTIR results prove it: there were not found any traces of: sp^3 configuration CH$_2$ symmetric (S), asymmetric (A), CH vibrations (sp^3 CH$_2$S, A; CH), sp^3 CH$_3$ A [7].

Fitting parameters of the RS spectra, VH results and main laser irradiation parameters for λ_3.   TABLE

Sample	λ [nm]	Pulses per spot	Irradiat. intensity [MW/cm^2]	D [cm^{-1}]	ΔD [cm^{-1}]	G [cm^{-1}]	ΔG [cm^{-1}]	$I_\mathrm{D}/I_\mathrm{G}$	L_a [nm]	VH [GPa]	E [GPa]
B4	–	–	–	1319	230	1540	169	0.42	45.77	23	209
B3	–	–	–	1288	148	1532	155	0.32	60.08	24	206
B3$_1$		2	8	1256	285	1586	111	1.65	11.65	–	
B3$_2$	355	2	4	1336	268	1582	111	1.58	12.16	–	
B3$_4$		8	8	–	–	–	–	–	–	–	

Not only heating of film surfaces was caused by the λ_4 irradiation (4.67 eV, penetration depth 132 nm), but also graphitization, spallation and ablation processes occurred (Fig. 1c,d). It was observed that a large number of nanostructures was formed after the irradiation: SiC, nc-diamond (Fig. 3, at ≈ 1250 cm^{-1}) [10]; carbon nano-onions [11] were found in the B4$_1$ sample (Fig. 3, at 433, 700, 1100 cm^{-1}) that caused the increase of refractive indices. The results proving the formation of those nanostructures will be discussed in the near future.

Also amorphous phases were strongly expressed: α-Si, SiO$_x$, SiC, trans-polyacetylene ω_1 (trans-(CH)$_x$) C–C stretching mode [12], respectively, $\approx$ 494, 600, 800, 1060 cm^{-1} (Fig. 3).

Main sharp peaks were found at $\approx$ 2849 cm^{-1}, ≈ 2922 cm^{-1}, ≈ 2951 cm^{-1} in the μFTIR reflection spectra for all samples irradiated by λ_4. The first two sharp peaks correspond to the sp^3 CH$_2$S, A and CH, respectively; the third one corresponds to the sp^3 CH$_3$ A. The other functional groups were found for the B3$_x$, B4$_x$ samples irradiated by the ultraviolet laser: C=O, SiC or SiO$_2$, Si-CH$_3$ or sp^2, sp^3 configuration C–C; SiO, S–O and etc. These data prove the formation of SiC and nc-diamond.

It was observed that the hardness decreased ($23 \rightarrow$ 17–19 GPa) after irradiation by λ_1 because the irradiation leads to the decrease of the hydrogen content in the film. HV measurements for the samples irradiated by λ_3, λ_4 were inappropriate, because of the strong changes (reduced adhesion with the silicon substrate, strong fragmentation of the DLC coatings) in the film surface.

4. Conclusions

Weak graphitization and SiC formation in the DLC/Si interface were observed using infrared laser irradiation. The most destructive irradiation took place when the penetration depth was greater than the film thickness. Strong graphitization, spallation and ablation processes were caused by the ultraviolet laser irradiation. SiC layers were created in all samples and the presence of the nanocrystalline fractions (nc diamonds, carbon nano-onions, nc-SiC) was confirmed after the ultraviolet laser irradiation.

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