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Different Wavelength Laser Irradiation of Amorphous Carbon

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Coherent laser irradiation of amorphous carbon films formed on Si substrates by ion beam deposition from pure acetylene and acetylene/hydrogen gas mixture is analyzed in this work. The films were irradiated with nanosecond YAG:Nd laser (Ekspla NL301G) at the first (1064 nm, 6 ns), the second (532 nm, 4.2 ns) and the third (355 nm, 28 ns) harmonic by scanning or repeating (10 pulses to one point) regime. Irradiation by the first laser harmonic leads to a minor increase of graphite phase content and shows SiC formation. Formation of carbides was observed at the second harmonic irradiation when irradiation intensity is low (< 10 MW/cm^2). Graphitization became more intensive when power density of irradiation increased and the films transformed to the glass carbon and nano/micro crystallite compound at intensive ablation regime (≈ 24 MW/cm^2). Early ablation starts at irradiation by the third laser harmonic with the intensity of ≈ 8 MW/cm^2 with an increase of Si substrate roughness. Swelling of films was obtained when the sample was irradiated at the third harmonic with 1 MW/cm^2.

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1. Introduction

Amorphous carbon films are perspective materials for many applications because of their unique physical and chemical properties [1–3]. Pulsed laser irradiation offers the possibility of extremely high heating rates in the irradiated spots of the processed material. This rapid energy deposition makes laser-induced phase changes in the amorphous carbon films. Physical phenomena (graphitization, spallation and evaporation) taking place during the laser–matter interaction are characterized by different threshold intensities [4], and strongly depend on the pulse duration [5–7], number of pulses, and the properties of a-C:H films [8–11]. The influence of quantum energy on phase changes of films is not clear [9, 12], so we focus our attention on the influence of different wavelength nanosecond laser irradiation on the properties of diamond-like carbon (DLC) films.

2. Experiment

Amorphous hydrogenated carbon films (a-C:H) were formed on Si (100) wafers by a direct ion beam deposition (IBD) method from pure acethylene and hydrogen/acetylene gas mixtures. The conditions of formation were discussed in previous papers [11, 13]. The obtained a-C:H films were irradiated with a nanosecond YAG:Nd laser (Ekspla NL301G) at the first (1064 nm, 6 ns), the second (532 nm, 4.2 ns), and the third (355 nm, 28 ns) harmonic by scanning or repeating (10 pulse to one point) regime. A diameter of the laser beam spot was 6 mm. The intensity of laser pulse varied for λ_1 in the range of 25–80 MW/cm^2, for λ_2 in the range of 5–25 MW/cm^2 and λ_3 in the range of 1–8 MW/cm^2.

The optical properties of irradiated a-C:H films were studied by the Raman scattering (RS) using an Ivon Jobin spectrometer with a Spectra Physics YAG:Nd laser (532.3 nm, 50 mW, spot size 0.32 mm). The experimental RS curves were fitted by two or four Gaussian-shape lines in the spectral range from 1000 to 1900 cm^{-1}. Infrared (IR) absorption and reflection spectra (Perkin Elmer spectrometer Spectrum GX) were measured in the ranges of 100–4000 cm^{-1} and 670–4000 cm^{-1}, respectively. The thickness, refractive and extinction indices of surface layers were determined using a null-ellipsometer Gaertner L117 operating with a He–Ne laser (632.8 nm). Micro hardness was measured by the Vickers method [14]. The surface morphology was analysed by the optical microscope Olympus BX51.

3. Results and discussion

The films formed from pure acetylene (B1P) and from acetylene/hydrogen mixture (2:1) (B3) were selected as reference samples. Their properties were discussed in previous works [11, 13] and are shown in Table. It was observed that hydrogen addition forms films with larger hardness, lower refraction and extinction indices. It means that the films became more DLC and the content of sp^3 phase increased.

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TABLE

Characteristics of films: ratio of film formation gas mixture, conditions of irradiation (wavelength, laser intensity), carbon/hydrogen ratio in films [11, 13], refractive index (n), extinction coefficient (k), film thickness (d), microhardness (HV).

Sample	Gas	λ [nm]	Laser intensity [MW/cm^2]	C/H [%]	n	k	d [nm]	HV [GPa]
B1P	C_2H_2			73/27	2.25	0.25	235	16
B1P-1		1064	70		2	0.29	196–79	
B1P-2		1064	35		2.4	0.23	195	
B1P-3		532	12		2.1–1.9	0.22	175–145	
B1P-4		532	24		2.2–1.8	0.11	378–111	
B3	H_2/C_2H_2 = 1:2			65/35	2.03	0.14	70	23
B3-1		532	12		2	0.17	80–70	

Laser irradiation of the films by the first harmonic (1064 nm, 1.16 eV) with the medium power density (35 MW/cm^2) showed the decrease of film thickness, which can result from H atoms and CH_x clusters evaporation from the surface. Thickness of films was steady (varied only by about 10 to 15% per surface) but the refraction index decreased and the extinction coefficient increased when the power density of irradiation increased to 70 MW/cm^2. That showed beginning of graphitisation and swelling of films.

Films are more sensitive to laser irradiation by the second harmonic (532 nm, 2.33 eV). Reduction and dispersion of film thickness showed that evaporation and surface swelling followed and the transformation $sp^3 \rightarrow sp^2$ was responsible for it when intensity of irradiation was low (12 MW/cm^2). Si and C diffusion also took place there. Simultaneous processes, such as ablation, spallation and phase conversion-stimulated sp^3 bond transformation to sp^2 (this is the reason for DLC films transformation to glass carbon) proceeded when intensity of irradiation was 24 MW/cm^2. This transformation is clearly observed in the Raman spectra (Fig. 1).

Irradiation by the third harmonic (355 nm, 3.48 eV) resulted in spallation and ablation processes when intensity was 8 MW/cm^2. Processes of bond transformation ($sp^3 \rightarrow sp^2$), spallation and ablation are sensitive not only to irradiation power, but also to the number of pulses per point when quantum energy is the highest. The ablation of film in the spot centre and residue in the periphery after two-pulses shot is shown in Fig. 2. The RS analysis (Fig. 3) confirms graphitisation: the G peak narrowed and shifted 57 cm^{-1} to the higher wave numbers (1585 cm^{-1}). The I_D/I_G ratio increased from 0.38 to 1.38. Films can be called a mixture of DLC and glass-like carbon (GLC), where also glass carbon forms. The analysis of the Raman spectra in the range 400–1800 cm^{-1} showed that the peak of crystalline silicon (521 cm^{-1}) and the wide band at 470–520 cm^{-1} identified as due to hydrogenated nanocrystalline silicon (nc-Si:H) were also obtained. The peaks at 606 cm^{-1}, 800 cm^{-1}

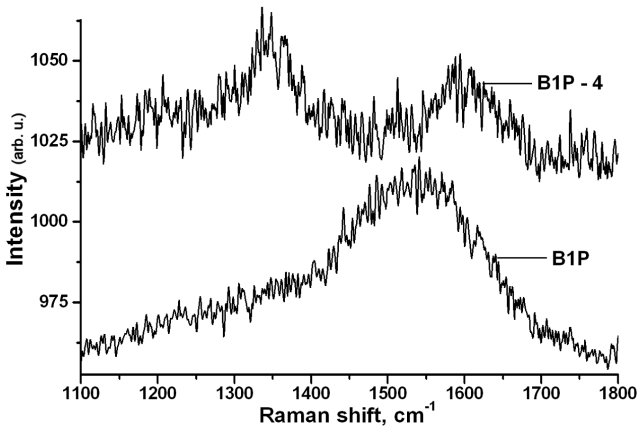

Fig. 1. Raman spectra of B1P sample before and after (B1P-4) irradiation by the second laser harmonic (λ = 532 nm, 24 MW/cm^2).

and the weak peaks in the 900–1000 cm^{-1} range confirm formation of SiOH and SiC (Fig. 3). The intensive irradiation of DLC with UV quanta at 355 nm eliminated hydrogen from the film and stimulated diffusion of silicon and carbon which is the condition of SiC formation. The residue of silicon carbide film is chaotically distributed on the surface after eight pulses shot with 8 MW/cm^2 intensity.

Ablation and intensive evaporation do not start even after 15 pulses shot by the third harmonic with low power irradiation (1 MW/cm^2), but modification of silicon substrate and carbon films proceeded. GLC phase forms from DLC and eventually becomes glassy carbon during the modification process (I_D/I_G increased from 1.15 to 1.34). The narrow G band is shifted by 95 cm^{-1} and the G peak (1590 cm^{-1}) indicates stress in the film. The SiC and SiOH bonds formation confirms that irradiation broke not only C–H but also C–C bonds.

IR transparency decreases ($\approx$ 10%) after intensive (70 MW/cm^2) irradiation by the first harmonic, but it de-

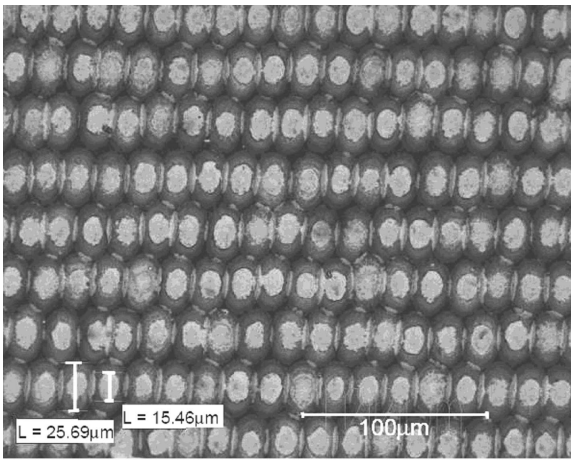

Fig. 2. Surface morphology of B3 sample after two pulses shot irradiation with 8 MW/cm^2 intensity.

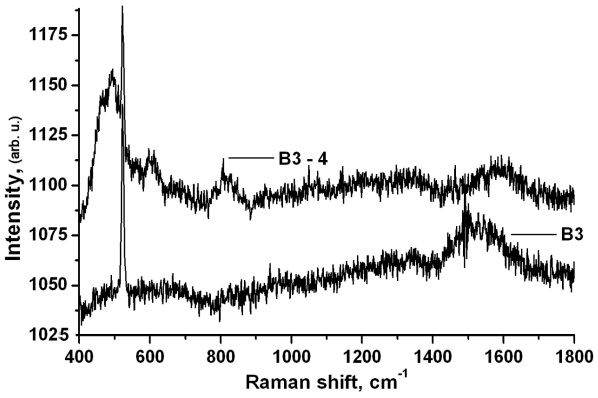

Fig. 3. Raman spectrum of B3 sample before and after two pulses shot irradiation by the third harmonic (λ = 335 nm) with 8 MW/cm^2 intensity (B3-4).

creases from 64.8% (the first harmonic) to 44.5% (the second harmonic) with increasing quantum energy. Higher quantum absorption and photon energy led to more intensive graphitisation although the intensity of the second harmonic was lower (24 MW/cm^2).

Spectral features at 2920 cm^{-1} and 2850 cm^{-1} were obtained in the IR transparency and reflectance (Fig. 4) spectra before and after irradiation. This range was fitted by the Gaussian-shape lines [15]. These features are typical of symmetric (2850 cm^{-1}) and asymmetric (2920 cm^{-1}) sp^3 CH_2 stretching modes.

The reflectance spectra after the third harmonic irradiation (355 nm, 3.48 eV) at different intensities are shown in Fig. 4. A broad minimum at 2100–2000 cm^{-1} associated with SiH and SiH_2 [16] is observed in all spectra. This result confirms the hypothesis that hydrogen diffuses into silicon substrate and/or evaporates from the film during irradiation. The spectral features at 1538 cm^{-1} and 1576 cm^{-1} are observed in the B3-4 and B3-5 samples spectra (Fig. 4). They are typical of asym-

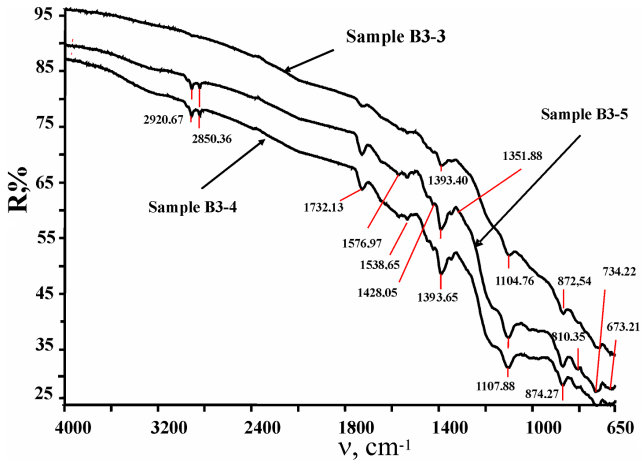

Fig. 4. IR spectra of B3 sample after irradiation by the third laser harmonic (λ = 335 nm). B3-3 samples condition of irradiation — 4 MW/cm^2, 8 pulse shot; B3-4 — 8 MW/cm^2, 2 pulse shot; B3-5 — 1 MW/cm^2, 15 pulse shot.

metric C=C bonds, therefore the effect of irradiation is graphitization. The feature at 1428 cm^{-1} is associated with deformation of CH_2 groups. The dip at 1107 cm^{-1} is characteristic of C–O vibration, also that of Si–O is observed in this frequency range. Silicon oxidation is possible during film ablation and surface layer amorphisation/nanocrystallisation. The spectral features at 874 cm^{-1} and 810 cm^{-1} belong to the C–C bonds and that at 734 cm^{-1} relates to SiH and $SiC/SiCH_3$. Typical vibration of methylene group was blended in the B3-3 sample reflectance spectra. Carbon exists in the sp^2 bonds and vibration of C=O valence bonds practically disappeared, but there are observed spectral features in the 1400–650 cm^{-1} range. The dip at 1393 cm^{-1} showed that CH_3 groups are present in the film. Also the feature at 1104 cm^{-1} associated with Si–O vibration was observed.

4. Conclusions

The measurements showed that the DLC films are not sensitive to irradiation with low energy quanta (1.16 eV). Films graphitization and formation of Si–C clusters or nanocrystallites proceeded with the increasing quantum energy (2.32 eV and 3.48 eV). High photon energy irradiation (3.48 eV) with the intensity higher than 4 MW/cm^2 leads to film ablation whose threshold depends on a number of pulse shots.

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