CHANGES BY THE ULTRAVIOLET AND INFRARED LASER IRRADIATION IN THE AMORPHOUS CARBON FILMS

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Abstract

Amorphous hydrogenated carbon films (a-C:H) were formed on Si (100) wafers by a direct-ion beam deposition (IBD) method from pure acetylene and acetylene - hydrogen gas mixtures. The a-C:H films were irradiated with a nanosecond Nd:YAG laser (Ekspla NL301G), working at the first harmonics (λ_1= 1064 nm), the fourth harmonics (λ_4= 266 nm). a-C:H films were studied by Raman scattering (RS), micro Fourier transform infrared (μFTIR) spectroscopies; null-ellipsometery, Vickers hardness (VH) method , scanning electron microscope (SEM).

Keywords: *laser irradiation, infrared, ultraviolet, amorphous carbon, carbon onions.*

Introduction

The effect of laser irradiation on diamond-like carbon (DLC) films is determined by superposition of three processes: graphitization, spallation, and evaporation; they are characterized by different threshold intensities [1].

Experimental

Amorphous hydrogenated carbon films (a-C:H) were formed on Si (100) wafers by a IBD method from pure acetylene and acetylene - hydrogen gas mixtures.

The a-C:H films were irradiated with a nanosecond Nd:YAG laser (Ekspla NL301G), working at the first harmonics (λ_1= 1064 nm, pulse duration of 6 ns) and the fourth harmonics (λ_4 = 266 nm, pulse duration of 3 ns). Pulse repetition rate was 12.5 Hz, the diameter of the laser beam spot was 6 mm.

The a-C:H films were studied by RS spectroscopy in the spectral range of (400−2000) cm^{-1} (Ivon Jobin spectrometer). Spectra-Physics Nd:YAG laser (532.3 nm, 50 mW; spot size 0,32 mm) was used as an excitation source. The RS spectra for the λ_1 harmonic were fitted by two Gaussian-shape lines in the

spectral range of (1100 − 1800) cm^{-1}; for the λ_4 harmonic – by four Gaussian-shape lines in spectral range of (1000 − 1800) cm^{-1}. The μFTIR spectra were collected for the λ_4 harmonic in reflection mode using a FTIR spectrometer Vertex 70 coupled with infrared microscope Hyperion 3000 (both from Bruker Optik GmbH) and a MCT single point detector in the spectral range of (600 – 4000) cm^{-1}. A total number of 128 interferograms were co-added. Spectra at a resolution of 4 cm^{-1} of the film were rationed against the reference spectrum and transferred to absorption values.

The thickness *d*, the refractive index *n* and the extinction coefficient *k* of the surface layers were determined using a null-ellipsometer (Gaertner L117) operating with a He-Ne laser (632.8 nm). The microhardness and Young's modulus for the λ_1 harmonic were measured by the VH method (MTS G200 nanoindenter). The surface morphology was analyzed by SEM JSM6490LV (JEOL). Crystal size L_a was obtained from equation formed by Cancado et al.[2].

Results and discussion

Ellipsometric parameters for the samples irradiated by the λ_4 harmonic are: n = 1.8 - 2.7, k = 0 - 0.73, d = (50 – 220) nm; for the samples irradiated by the λ_1 harmonic are: n = 2.1 to 2.4, k = 0.5 to 0.16, d ~ 170 nm. These parameters were calculated by a special program using the most appropriate multilayer models: DLC / SiC / Si (or αSi).

Hardness and Young's modulus for the B_1 and B_2 samples irradiated by the λ_1 harmonic (Fig. 1., Table 1.) respectively are 17 GPa, 206 GPa and 19 GPa, 207 GPa. HV measurements for the samples irradiated by the λ_4 harmonic were inappropriate, because of the strong changes (reduced adhesion with a silicon substrate, strong fragmentation of the DLC coatings and etc) in the film surface.

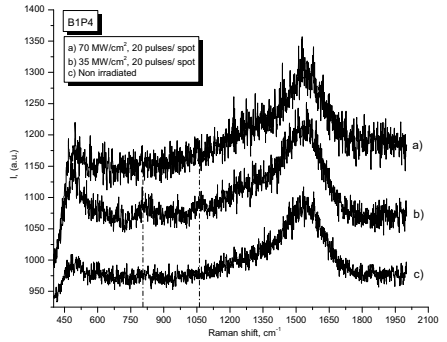

Fig. 1. RS spectra for the films in spectral range of (400 – 2000) cm^{-1}: a) B_1 and b) B_2 films RS spectra after irradiation by the first λ_1= 1064 nm laser harmonic (different irrad. intensity); c) not modified film B;

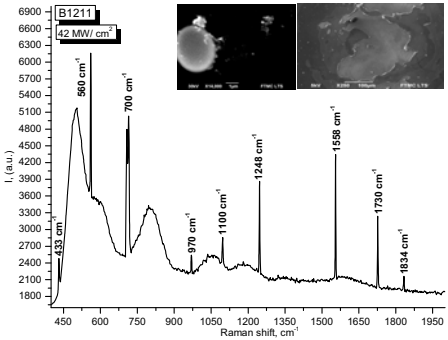

Fig. 2. RS spectra for the B_{1211} film in spectral range of (400 – 2000) cm^{-1} and SEM pictures after the irradiation with λ_4 = 266 nm laser harmonic

Irradiation by the λ_1 harmonic (irrad. intensity 35 MW / cm^2) caused slight changes (Fig. 1. a), proving the ellispsometric parameters and calculation of the L_a (Table 1.), in the film: formation of the amorphous silicon carbide αSiC clusters (Fig. 1. b) ~800 cm^{-1}) [3, 4], the intensity curve of ~ 1060 cm^{-1} is associated with the trans – polyacetylene ω_1 (trans-$(CH)_x$) C - C stretching mode [5]. There are no significant changes increasing the irradiation intensity (35 MW/cm^2 →70 MW/cm^2) in the DLC films, only the intensity of the characteristic curves recorded in the RS spectra (Fig. 1. curve 2) decreases (Fig. 1. curve 1) and the curve shifts to the lower wave number position. The compounds having weak bonds (287 kJ mol^{-1} for the C - CH_3 [6]) are destroyed and decomposed into a "stable" compounds using laser irradiation.

Not only heating of the silicon substrate, film surfaces were caused by the λ_4 laser harmonic irradiation (4,67 eV), but also and a graphitization, spallation and ablation processes occured (Fig. 2. SEM photos). It was observed that after the irradiation by the ultraviolet laser radiation (λ_4) large amount of nanostructures were formed in the films: silicon carbide, nanocrystalline

diamond (Fig. 1. ~1250 cm^{-1}) [7]; carbon – onions just in the B_{1211} sample were found (Fig. 2. (433, 700, 1100) cm^{-1}) [8] and the others, which caused the increase of the refractive indexes.

Table 1 Fitting parameters of the RS spectra and the main laser irradiation parameters

Sample	λ, nm	Pulses per spot	Irrad. inten. MW/cm^2	D, cm^{-1}	ΔD, cm^{-1}	G, cm^{-1}	ΔG, cm^{-1}	$\frac{I_D}{I_G}$	L_a, nm
B	-	-	-	1319	230	1540	169	0,42	45,77
B_1	1064	20	70	1314	203	1538	172	0,39	49,67
B_2			35	1309	199	1541	164	0,40	48,06
B_{351}	266	1	42	1334	135	1569	142	0,65	29,58
B_{1211}		4		1303	134	1529	198	0,59	32,58
B_{1221}		4		-	-	-	-	-	-
B_{241}		8		1364	157	1578	148	1,02	18,85
B_{1F21}		8		1360	83	1591	128	0,39	49,29
B_{411}		10		-	-	-	-	-	-

Also an amorphous phase was strongly expressed (600, 800, 1050, 1200) cm^{-1} (Fig. 2). The amorphous phase characterizing curves were observed in all samples irradiated by the λ_4 laser harmonic, only crystalline structures characterizing curves were changing slightly.

The main sharp peaks were found for all samples irradiated by the λ_4 harmonic at ~2849 cm^{-1}, ~2922 cm^{-1}, ~2951 cm^{-1} wave number positions studying μFTIR reflection spectra. The first two sharps peaks correspond to sp^3 configuration CH_2 symmetric, asymmetric and CH vibrations respectively; the third one corresponds to sp^3 configuration CH_3 asymmetric vibrations. The other functional groups were found for the samples: 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 the silicon carbide and of the nanocrystal diamond. μFTIR experiments for other samples are planned for nearest future.

Conclusions

Significant changes (graphitization, ablation) were not observed after the irradiations by the λ_1 harmonic, only have been observed the variations of characteristic curve intensities and positions. The significant changes showed after the irradiation by the λ_4 harmonic: graphitization, ablation processes were dominating, causing the formation of the crystalline fractions in the films.

References

1. Grigonis, Z. Rutkuniene, A. Medvids The influence of nanosecond pulse laser irradiation on the properties of a-C:H films// Vacuum. ISSN 0042-207X: Elsvier Science, 2008, Volume 82, Issue 11, p. 1212–1215;
2. L. G. Cançado, K. Takai, T. Enoki et al. General equation for the determination of the crystallite size L_a of nanographite by Raman spectroscopy// Applied Physics

Letters. ISSN 1077-3118: American Institute of Physics, 2006, Volume 88, Issue 16, 163106;

3. F.-K. Tung, E. Perevedentseva, P.-W. Chou et al. Structural and spectroscopic analysis of hot filament decomposed ethylene deposited at low temperature on silicon surface// Applied Surface Science. ISSN 0169-4332: NORTH-HOLLAND, 2005, Volume 252, Issue 4, p. 1167–1174;
4. J R Shi, X Shi, Z Sun et al. Structural properties of amorphous silicon-carbon films deposited by the filtered cathodic vacuum arc technique// Journal of Physics: Condensed Matter. ISSN 1361-648X: IOPSCIENCE, 1999, Volume 11, Number 26, p. 5111 – 5118;
5. M. Rybachuk, A. Hertwig, M. Weise et al. Near infra-red optical materials from polymeric amorphous carbon synthesized by collisional plasma process// Applied Physics Letters. ISSN 1077-3118: American Institute of Physics, 2010, Volume 96, Issue 21, 211909;
6. Klaus May , Stefan Dapprich , Filipp Furche et al. Structures, C–H and C–CH_3 bond energies at borders of polycyclic aromatic hydrocarbons // Phys. Chem. Chem. Phys.. ISSN 1463-9084: RSCPublishing, 2000, Issue 22, p. 5084-5088;
7. Saraf, L.V., Bunch, K.J. ; Engelhard, M.H. et al. Variation of Oxygen-to-Carbon Ratio in Oxyacetylene Flame// NANO'08 (2008; Arlington, TX), conference. Nanotechnology, 2008. - Arlington., 2008. p. 813 – 816;
8. G. Davidson Properties of inorganic and organometallic compounds, Volume 37, Athenaeum Press Ltd, 2005, p. 27. ISBN 0-85404-446-9, ISSN 0584-8555.