

INFLUENCE OF LASER HEATING TO THE HYDROGENATED CARBON FILMS

Alfonsas Grigonis^a, Vaclovas Kulikauskas^c, Artur Medvid^b,
Pavels Onufrijevs^b, Živile Rutkūnienė^a and Darius Tribandis^a

^aPhysics Department, Kaunas University of Technology, Studentu 50, LT-3031
Kaunas, Lithuania

^bRiga Technical University, 14 Azenes Str. LV-1048 Riga, Latvia

^cNuclear Physics Institute, Moscow State University, 119899 Moscow, Russian
Federation

Abstract

Amorphous hydrogenated carbon films a -C:H of a thickness up to 450 nm were formed on Si wafers by a direct ion beam deposition method, from acetylene (C_2H_2) and hexane (C_6H_{14}) or a gas mixture of acetylene, hexane and hydrogen. The depth distribution of carbon and impurities were measured by Rutherford backscattering (RBS) technique, the hydrogen concentration was determined by elastic-recoil detection (ERD). The optical properties a -C:H films were studied by Raman scattering (RS), infrared (IR) spectroscopy, null- and spectroscopic ellipsometry (SE). Measurements show, that the laser irradiation leads to graphitization of a -C:H films and formation of glassy carbon. Glassy carbon did not occur in a -C:H films with a higher amount of sp^3 -type C-C bonds.

Keywords: *amorphous hydrogenated carbon films, laser irradiation, optical properties.*

Amorphous hydrogenated carbon films a -C:H of a thickness up to 450 nm were formed on Si (100) and (111) wafers by a direct ion beam deposition method. Before deposition, the substrates were cleaned for 0 to 10 min by hydrogen plasma. The films were formed from acetylene (C_2H_2) and hexane (C_6H_{14}) or a gas mixture of acetylene, hexane and hydrogen. The following deposition conditions were used: ion energy 1000 eV, ion current density ~ 0.12 mA/cm², pressure below 10^{-2} Pa, deposition duration 30 and 90 min. The samples were irradiated in a scanning mode with the step 25 μ m by second harmonic ($\lambda = 532$ nm) of a Q-switched YAG:Nd laser with pulses of duration $\tau = 10$ ns and repetition rate 12.5 Hz. Diameter of the laser beam spot was 2.5 mm at height $1/e^2$. The intensity of laser pulse was varied in the range 1.8 – 10.2 MW/cm².

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by Raman scattering (RS), infrared (IR) spectroscopy, null- and spectroscopic ellipsometry (SE). Morphology was determined by scanning electron microscopy (SEM). RS was taken under the argon laser of 514,5-nm wavelength and 20-mW power excitation at a 2-mm spot size. Data were collected in backscattering geometry tried at room temperature. Distribution curves were fitted with the same Gaussian shapes at a linear background using the least square fitting software. Raman spectra were taken in the range of 400-2000- cm^{-1} but the fitting process was performed for the 1000-1800- cm^{-1} range only. The depth distribution of C and impurities were measured by Rutherford backscattering (RBS) technique using a 2 MeV $^4\text{He}^{2+}$ beam at a scattering angle 160° . The hydrogen concentration was determined by elastic-recoil detection (ERD) experiment using a 2.4 MeV $^4\text{He}^{2+}$ beam energy and with 80° beam-incidence angle to the surface normal. The lavsan filter and silicon detector with 15 keV resolution were applied for particle detection. The results were analyzed by RUMP program. The thickness and refractive and extinction index were measured using automatic rotating-polarizer ellipsometer (Gaertner L115) with He-Ne laser (632.8 nm). IR absorption and reflection spectra were measured in the ranges 100-4000 and 670-4000 cm^{-1} , respectively, by means of a Perkin Elmer spectrometer Spectrum GX.

The film thickness decreases with increasing of hydrogen content in the deposition gas mixture. RBS shows little higher (5-35 %) film thickness. The difference between ellipsometry and RBS was about 5-35 %, which depends on the film thickness and the surface preparation. This fact may be related to the possible hydrogen distribution inhomogeneity, in particular in Si-DLC interface layer. RBS indicated an existence of thin interface layer, which might contain SiC. The ellipsometry calculations were performed for Si/SiH/DLC (with hydrogen⁺ pre-etching before deposition) or Si/SiO₂/DLC (without hydrogen⁺ pre-treatment) systems because optical characteristics of the interface layers were more similar to SiH or to SiO₂, respectively. It should be noted that the deposition rate reduced about 20 % with increasing deposition time from 30 to 90 min. The influence of the hydrogen⁺ pre-treatment to the growth rate (defined by RBS) was minimal (< 8%) in the wide hydrogen gas range (from 0 to 75% of H₂).

An irradiation with a low-intensity laser beam up to $\sim 4 \text{ MW/cm}^2$ resulted in an appearance of grains of size 100-200 nm and a slight increase of a surface roughness up to 10-15 nm. At medium-intensity 5-7 MW/cm^2 of laser beam, large submicrometer-size grains of 50-70 nm in height were developed. The observed process is close to that expected for spallation of surface layers. It should be noted that PLC layers are destroyed at laser intensity lower than those for DLC and GLC films. At highest laser intensity $\sim 10 \text{ MW/cm}^2$, large structural transformations occurred and the grain structure disappeared. The regularities in Raman spectra of laser-irradiated samples depend on the composition of the a-C:H films. At laser intensity (1.8-3.5) MW/cm^2 , weak Raman modes at ~ 1260 and $\sim 950 \text{ cm}^{-1}$ were observed which could be assigned

to diamond nanocrystals and SiC, respectively. At laser intensities higher than 7 MW/cm², Raman spectra were not typical of DLC films. The samples are characterized by a high percentage ($\geq 70\%$) of sp³ bonds in a-C:H films, the shape of Raman spectra for these samples was not significantly changed up to moderate laser intensity, at higher intensity ~ 5 MW/cm², the D-mode decreased with respect to the G-mode and shifted towards lower frequency whereas the position of the G-mode remained almost unchanged. The red-shift of the D-mode could be due to the influence of the mode at ~ 1260 cm⁻¹ attributed to diamond nanocrystals [11] and could indicate the mutual transformations sp² ↔ sp³ between the bonds of different types. In a-C:H films with a larger amount of graphite phase and dominating sp²-type bonds, glassy carbon forms at laser intensities ~ 4 -7 MW/cm². In Raman spectra two modes at 1350 and 1600 cm⁻¹ were distinctly resolved. The irradiation dose necessary for the formation of glassy carbon depends on the amount of sp³ bonds and hydrogen in a-C:H films. At a higher hydrogen amount transformation from PLC to glassy-C occurs at lower laser intensities. The spectral dependence of optical response for silica-coated irradiated samples was explained by the same model of the effective DLC film as for the samples without SiO₂ layer. Summarizing, the structural and optical investigations of laser-irradiated silica-coated a-C:H films formed on Si substrates have shown that the films containing a higher hydrogen content were more sensitive to irradiation of nanosecond laser pulses. The laser irradiation leads to graphitization of a-C:H films and formation of glassy carbon. Glassy carbon did not occur in a-C:H films with a higher amount of sp³-type C-C bonds. As a result of laser irradiation, SiC and diamond-like nanocrystals were also formed. The surface of the initial sample is quiet smooth with a roughness of few nanometers. An irradiation with a low-intensity laser beam up to ~ 4 MW/cm² resulted in an appearance of grains of size 100-200 nm and a slight increase of a surface roughness up to 10-15 nm. As silica layer was transparent for laser light, the absorption by a-C:H layer seemed to be dominant. The changes in morphology allowed one to assume that structural transformations though not significant occurred which could be related to graphitization of the a-C:H film. At medium-intensity of the laser beam 5-7 MW/cm², large submicrometer-size grains of 50-70 nm in height were developed and seemed to be consisted of smaller grains. The observed process is close to that expected from spallation of the surface layers. It should be noted that PLC layers are expected to be destroyed at lower laser intensity than those for DLC and GLC films. At highest laser intensity ~ 10 MW/cm², large structural transformations occurred and the grain structure disappeared. It is reasonable to assume that both spallation and evaporation of material are responsible for the observed pattern.

The carbon and silicon concentrations were changed in a-C:H after growing the oxide layer on the DLC/Si structure. The ERD and RBS analysis show that oxide is not stoichiometric and hydrogen is diffused from DLC layer (27% Si, 67%O, 6%H). Low intensity laser irradiation ($P \leq 3,56$ MW/cm²) slowly changes

the element composition of oxide (31% Si, 62,5%O, 6,5%H) and more influences the changes in the film (before irradiation Si concentration was $\leq 3\%$, after $\sim 10\%$). The profile of Si from SiO₂ layer changed in the RBS spectra after the irradiation and SiC formation can be the condition of that. This spectra show that DLC layer is thinned about 5%-7% after irradiation (hollow between Si from the substrate and Si from SiO₂ decreased). Because ablation of films does not occur in this range of laser intensity, the layer structure transformed and the density increased. It occurs if silicon diffuses into the film and compensates hydrogen deficiency (H removed into SiO₂ or Si) and the quantity of sp³ bonds increases. These results are coincident with the RS measurements showing the small "diamond like" transformation at the low power irradiation.

At the higher power irradiation, laser beam forms channels on the SiO₂/DLC/Si structure surface where element composition depends on the coordinates of the probe point. Profile of RBS spectra and element composition of oxide on the top of the sample B₁P₂ channel after irradiation ~ 7 MW/cm² drastically differed from low power case – the hydrogen removed and the silicon concentration increased to 15%. Oxide is thinned about 20-25% in the channel edge and is non homogeneous. The oxygen concentration decreased and silicon increased there. The carbon layer thinned about three times, so evaporation of amorphous carbon is more intensive than oxide during irradiation. The silicon concentration increased to 40% in the film. So, the perpendicular and parallel to the surface temperature gradient increased with increasing of the power irradiation. The condition of that is heat transport but not the energy distribution in the laser beam. Thin non homogeneous oxide, SiC fragments, and silicon are obtained on the channel bottom where intensity of the beam is maximal. The carbon is not under oxide/carbide layer, but on the surface.

Conclusion

Summarizing, the structural and optical investigations of laser-irradiated silica-coated *a*-C:H films formed on Si substrates have shown that the films containing a higher hydrogen content were more sensitive to irradiation of nanosecond laser pulses. The laser irradiation leads to graphitization of *a*-C:H films and formation of glassy carbon. Glassy carbon did not occur in *a*-C:H films with a higher amount of sp³-type C-C bonds. As a result of laser irradiation, SiC and diamond-like nanocrystals were also formed.

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