MODIFICATION OF AMORPHOUS a-C:H FILMS BY LASER IRRADIATION

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Amorphous diamond-like hydrogenated carbon films a-C:H were formed on Si wafers by a direct ion beam deposition method from acetylene or a gas mixture of acetylene and hydrogen. The samples were irradiated in a scanning mode by second harmonic (wavelength $\lambda = 532$ nm) of a Q-switched YAG : Nd laser. The effect of laser irradiation was studied by Raman and infrared spectroscopy and spectroscopic ellipsometry. The changes in the optical spectra of the samples with different H amount were investigated in the dependence on laser intensity. Experimental data were interpreted taking into account the structural transformations of a-C:H films.

Keywords: amorphous diamond-type carbon films, laser irradiation, optical properties

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1. Introduction

Amorphous carbon films are promising materials for many applications because of their unique optical, mechanical, electrical, and chemical properties [1]. The physical properties of plasma-deposited amorphous hydrogenated carbon (a-C:H) films are determined by carbon $sp^3/ sp^2$ bonding ratio [1] and by hydrogen content [2].

Depending on the type of predominating bonds, the a-C:H films are divided into three groups: (i) diamond-like carbon (DLC) with $sp^3$ bonds, (ii) graphite-like carbon (GLC) with $sp^2$ bonds, and (iii) polymer-like carbon (PLC) with $sp^3$ bonds and a high concentration of hydrogen. As the energy of bonds C–H (and C–C) is considerably smaller than that of C=C or C≡C bonds, the hydrogen concentration and hence the physical properties of a-C:H films can be varied by laser irradiation. In general, the effect of laser irradiation on DLC films is determined by superposition of three processes: graphitization, spallation, and evaporation, which are characterized by different threshold intensities [3]. The laser-induced graphitization of the surface layer has the lowest threshold and causes the changes of material properties. A noticeable reduction of material density is most important for the surface morphology, as it leads to a pronounced surface swelling. Two other processes, spallation and evaporation, cause the material removal and result in characteristic surface profiles. A multilevel spallation in DLC films manifests itself in peeling and removal of one or more layers in lateral size comparable with irradiated area and thickness less than the film thickness [4].

Modelling has shown [5] that an increase of laser pulse duration from femto- to nanoseconds resulted in the development of stratified graphitization layers of DLC into the sample bulk. In nanosecond laser processing, thermal gradient parallel to the interface was less than perpendicular gradient by orders of magnitude due to a small thermal diffusion distance and large dimensions of the laser beam as compared to the thickness of a melted DLC layer. This quasi-stationary laser annealing [6] is a one-dimensional problem, in which the structural transformations of a-C:H films depend on temperature, decreasing from the surface towards the bulk. Thus, the laser-modified surface layer appears to be non-uniform in depth. The surface swelling, which is attributed also to the change of film structure, is observed at slightly higher laser intensity than the drop of chemical resistance and presumably requires stronger structural transformations. At quasi-stationary annealing, the graphitization threshold of 500°C was evaluated for various a-C:H films whereas the sublimation...
temperature for graphite was as high as 4000 °C [7]. To authors’ knowledge, the influence of hydrogen amount on phase transitions and optical properties of a-C:H films has not been as yet investigated.

The aim of the present work was to study the optical properties of laser-irradiated a-C:H films. The critical values of irradiation for essential structural transformations were estimated. The corresponding changes in bonding and concentration of $sp^3$ bonds were discussed.

2. Experimental

Amorphous hydrogenated carbon films a-C:H of a thickness up to 250 nm were formed on Si (100) and (111) wafers by a direct ion beam deposition method at room temperature. The substrates were degreased by immersing twice for 10 min in a chemically pure dimetilformamide. Before deposition, the substrates were cleaned for 1 to 10 min by hydrogen plasma. The films were formed from acetylene or a gas mixture of acetylene and hydrogen. The following deposition conditions were used: ion energy 1000 eV, ion current density $\geq 0.12$ mA/cm$^2$, pressure below $10^{-2}$ Pa, deposition duration 30 min. The details of deposition procedure were presented elsewhere [8]. The parameters of initial samples, i.e., non-irradiated a-C:H films on Si, were discussed in [9].

The samples were irradiated in a scanning mode with the 25 µm step by second harmonic (wavelength $\lambda = 532$ nm) of a Q-switched YAG: Nd laser with pulses of duration $\tau = 10$ ns and 12.5 Hz repetition rate. Distribution of intensity in the laser beam was close to that for one mode. Diameter of the laser beam spot was 2.5 mm at 1/e$^2$ intensity height. The intensity of laser pulse was varied in the range of 1.8–10.2 MW/cm$^2$.

The depth distribution of C and impurities were measured by Rutherford backscattering (RBS) technique using a 2 MeV $^4$He$^{2+}$ beam at a scattering angle 160$^\circ$. The hydrogen concentration was determined by elastic-recoil detection (ERD) experiment using a 2.4 MeV $^4$He$^{2+}$ beam. The optical properties of laser-irradiated a-C:H films were studied by Raman scattering (RS), infrared (IR) spectroscopy, null- and spectroscopic ellipsometry (SE). RS was investigated using Ar laser beam ($\lambda = 514.5$ nm, 20 mW) with a 2 mm spot size. Experimental RS curves were fitted by two Gaussian-shape lines in the spectral range of 1000–1900 cm$^{-1}$. IR absorption and reflection spectra were measured in the ranges of 100–4000 and 670–4000 cm$^{-1}$, respectively, by means of a Perkin Elmer spectrometer Spectrum GX. The thickness and refractive index of surface layers were determined using automatic rotating-polarizer null-ellipsometer Gaertner L115 operating with a He–Ne laser (632.8 nm). Spectroscopic ellipsometry studies were performed by means of a photometric ellipsometer with rotating analyzer in the range of 1–5 eV [10].

3. Results and discussions

3.1. Structural studies

Figure 1 illustrates the surface morphology of initial and laser-irradiated DLC/Si samples. As is seen, the surface of the initial sample is quite smooth with a roughness of few nanometres (Fig. 1(a)). An irradiation with a low-intensity laser beam (up to $\geq 4$ MW/cm$^2$) resulted in an appearance of grains of 100–200 nm size and a slight increase of a surface roughness up to 10–15 nm. The changes in morphology allowed one to assume that structural transformations, though not significant, occurred and could be related to graphitization of a-Si:H film. At medium intensity of laser beam (5–7 MW/cm$^2$, Fig. 1(b)), large submicrometre-size grains of 50–70 nm in height had 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 ($\geq$10 MW/cm$^2$), 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.

3.2. Raman scattering and IR spectroscopy

Figure 2 presents the results of RS studies. As is seen, two main Raman modes D (at $\sim 1360$ cm$^{-1}$) and
Fig. 2. Raman spectra of B1P2 sample (a) before and (b) after irradiation by laser at 10 MW/cm² intensity.

G (at 1560 cm⁻¹) were observed. The regularities in Raman spectra of laser-irradiated samples depend on the composition of the a-C:H films. At laser intensity of 1.8–3.5 MW/cm², weak Raman modes at ~1260 and ~950 cm⁻¹ were observed which could be assigned to diamond nanocrystals and SiC, respectively [11]. At laser intensities higher than 7 MW/cm², Raman spectra were not typical of DLC films.

The samples (B1P3) obtained at a relatively low hydrogen content (~35%) are characterized [9] by a high percentage (≥70%) of sp³ bonds in a-C:H films. The shape of Raman spectra for these samples was not significantly changed up to moderate (1.8–3.5 MW/cm²) laser intensity. At higher intensity of ~5 MW/cm², the D mode decreased with respect to the G mode and shifted towards lower frequency (by about 10–20 cm⁻¹) 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 [12] and could indicate the mutual transformations $sp^2 \leftrightarrow sp^3$ between the bonds of different types. In addition, a possible formation of SiC (~950 cm⁻¹) should also lead to an increase of sp³ bonds as well as an increase of Si amount in a-C:H films [13]. This assumption is in agreement with previous data [3, 7].

In a-C:H films with a larger amount of graphite phase (B1P2) and dominating sp²-type bonds [11], glass carbon forms at laser intensities ~4–7 MW/cm². In Raman spectra two modes at 1350 and 1600 cm⁻¹ were distinctly resolved (Fig. 2(b)). In typical glassy carbon the D mode is stronger than the G mode [14]. 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 (sample B1P1) a transformation from PLC to glassy C occurs at lower laser intensities. However, a further small increase of laser intensity leads to an intensive spallation.

An irradiation with a laser beam of low intensity (1.8–3.6 MW/cm²) has led to a slight (2–7%) decrease of transmittance, though reflectance spectra remained almost unchanged (Fig. 3). At laser intensity higher than 3.6 MW/cm², the reflectance decreased with respect to the spectra of non-irradiated sample. The reflectance decrease after irradiation was frequency-dependent, especially towards longer wavelengths. At the same time, an increase of the valence vibration modes was observed at ~2850 and 2920 cm⁻¹ as well as that of deformation modes at 1400–1500 cm⁻¹, which have been attributed to methyl. However, the band at 1500–1700 cm⁻¹ assigned to the vibrations of C=C bonds increased simultaneously. Therefore it is reasonable to assume that as a result of irradiation, hydrogen either evaporated or migrated joining free carbon bonds increasing hence the amount of CH₂ in sp³ hybridization. However, this process did not lead to the increase of DLC amount as the transformation of carbon in sp³ bonds into sp² bonds was more probable at increased temperature of a-C:H film. The films with higher hydrogen content were more sensitive to laser irradiation.

3.3. Spectroscopic ellipsometry

The optical properties of untreated a-C:H films were investigated by reflectance [15] and ellipsometric [9] techniques. The optical response was usually interpreted in the model of the effective film. It was found that in the case of thin (70–100 nm) a-C:H films the dielectric function was close to that [16] of amorphous carbon (a-C) films and was characterized by a
significant contribution of $sp^2$ sites. In the case of thick films, the dielectric function spectra were approximated by the contribution of Lorentzian lines. The dielectric function was shown to be dependent on the growth technology and was well described by the Tauc–Lorentz model [17]. The characteristic energy of a single Lorentzian line $E_0$ increased in a series of thick DLC samples indicating an increased contribution of $\sigma \rightarrow \sigma^*$ transitions in $sp^3$ sites.

A typical feature of the investigated optical spectra (Fig. 4) was the interference pattern disappearing at high irradiation intensities. Analysis showed that the interference pattern was mainly caused by the SiO$_2$ layer, the thickness ($\sim$690 nm) of which did not change significantly during irradiation up to the high laser intensities. It should be noted that the sample B1P3 was most stable and a small-amplitude interference pattern was still noticed at the laser intensity of 7.1 MW/cm$^2$. This experimental observation can be explained by non-homogeneity of irradiated layered structure and the roughness of the interface between DLC and substrate.

Fig. 3. IR reflectance spectra of irradiated sample B1P3 with respect to non-irradiated sample at laser intensities of 3.8 MW/cm$^2$ (1) and 5.1 MW/cm$^2$ (2).

Fig. 4. Experimental (points) and modelled (curves) spectra of ellipsometric parameters for sample B1P3 irradiated at 4.75 MW/cm$^2$. 

![Graph](image-url)
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 SiO\textsubscript{2} layer [9, 15]. By solving the multilayer model using the transfer matrix technique [10], the dielectric function of the irradiated a-C:H films was determined (Fig. 5). At low radiation density (2.4 MW/cm\textsuperscript{2}) the dielectric function $\varepsilon(E)$ of thin DLC film was close to that for a-C [9]. At higher radiation density (4.8 MW/cm\textsuperscript{2}) the contribution of this DLC film was approximated by three Lorentzian lines and the spectra of effective $\varepsilon(E)$ (Fig. 5) were interpreted as broadened $\varepsilon(E)$ for a-C:H. At the highest laser intensity (7.1 MW/cm\textsuperscript{2}) the effective dielectric function was modelled by glassy carbon [18] with increased density. It should be noted that glass-like materials are usually formed [19] at the laser irradiation with pulses of $10^{-7}$ s duration and 10 MW/cm\textsuperscript{2} intensity. As a whole, the interpretation of ellipsometric data is in a good agreement with the model of laser-induced graphitization [20] and structural changes [21] of DLC films under laser irradiation.

For another thin sample B1P1 the regularities in the change of DLC layer upon laser irradiation were similar to those described above. The interference pattern was observed up to laser intensities $\sim$4 MW/cm\textsuperscript{2}. It is interesting to note that at $\sim$7 MW/cm\textsuperscript{2} the interference pattern has been masked in the range 1.0–3.5 eV, though it has been still observed in a higher photon energy region of 3.5–5.0 eV. This observation indicated that a-C:H film was strongly affected by laser irradiation whereas silica layer was still not completely destroyed for this sample. The spectra of ellipsometric parameters for the sample irradiated at the highest laser intensity are presented in Fig. 6. As is seen, the interference pattern due to silica layer is absent and the contribution from a-C:H layer dominates in the optical response. The experimental data were well described by the model of Lorentzian-type oscillators assuming the presence of two, upper and lower, a-C:H layers of 23 and 17 nm thickness, respectively. The change of the dielectric function $\varepsilon(E)$ of a-C:H layers under the influence of laser radiation is illustrated in Fig. 7. As is seen, the shape of $\varepsilon(E)$ for non-radiated sample is close to that for a-C [16]. At low intensity laser irradiation,
the absorption edge of a-C:H films was broadened indicating an increase of the contribution due to the $sp^2$ sites, i.e., by an initiated graphitization process. At highest intensity two contributions to the optical response could be clearly noticed. The first contribution with the peak at 3.7 eV was close to that due to $sp^2$-bonded C atoms in diamond film and the second one with maximum at 4.4 eV originated from glassy carbon [18].

The ellipsometric data for a thicker a-C:H layer ($d = 204$ nm) coated by $\sim 660$ nm thick SiO$_2$ film and formed on Si-substrate are presented in Fig. 8 at a low laser intensity. It should be noted that according to fitting results, the silica film was dense, in agreement with reference data [22]. The contribution of a-C:H film to optical response was well approximated by that of metastable amorphous carbon films with a high ($\sim 76\%$) percentage of diamond like component and with a porosity of up to 26%. The dielectric function of a-C:H film obtained from fitting procedure of ellipsometric measurements for sample irradiated by various laser intensities is shown in Fig. 9.

When the laser intensity was increased up to $3.6$ MW/cm$^2$, the experimental data for sample B1P2 (Fig. 9) could be fitted by model calculations taking into account the inhomogeneity of a-C:H film. However, the spectral dependence of $\varepsilon(E)$ for a-C:H film was still in agreement with the accepted model. At

![Fig. 7. Dielectric function of DLC film in the sample B1P1 irradiated at different laser intensities. $L_1$ and $L_2$ are the data for upper and lower parts of DLC layer, respectively.](image)

![Fig. 8. Experimental (points) and modelled (curves) spectra of ellipsometric parameters for sample B1P2 ($d = 204$ nm) irradiated with laser intensity of $3.6$ MW/cm$^2$.](image)

![Fig. 9. Dielectric function of a-C:H film in the sample B1P2 irradiated at different laser intensities. Curves $2a$, $3a$ and $2b$, $3b$ are the data for upper and lower parts of a-C:H layer, respectively.](image)
high laser intensity the $\varepsilon(E)$ spectra changed significantly. A possible graphitization of the DLC film could be responsible for the increase of $\varepsilon(E)$ values at lower photon energies, while the contribution at 3.6–4.5 eV can be assigned to the formation of glassy carbon and $sp^2$-bonded C atoms in diamond [18].

4. Summary

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 $sp^3$-type C–C bonds. As a result of laser irradiation, SiC and diamond-like nanocrystals were also formed.

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References


AMORFINIŲ a-C:H DANGŲ MODIFIKAVIMAS LAZERIO APŠVITA

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Santrauka

Joninių spindulinių nusodinimo metodu acetileno bei acetileno/vandenilio mišiniuose ant silicio pagrindo buvo suformuotos amorfinës hidrogenizuotos panāšios į deimantą anglies dangos (a-C:H). Apšvitai koherentines šviesos kvantais naudotas YAG:Nd impulzinis lazeris, kurio impulso trukmė 10 ns, paskirstojimų dažnis 12,5 Hz, spindulio skersmuo 2,5 mm, skanavimo įtakos 25 μm, apšvitos galia 1,8–10,2 MW/cm². Lazerio apšvitos įtaka buvo tirta Ramano, infraraudonosios spektroskopijos bei spektrinės elipsometrijos metodais. Tyrimai parodė, kad, esant skirtingoms vandenilio koncentracijoms dangose, jų optiniai spektrai kinta priklausomai nuo lazerio intensyvumo. Didžiausius pokyčių dėl koherentinės spinduliuotės poveikio turinčios daug $sp^2$ ryšių, t. y. daug grafito fazės; jos savo savybėmis artimos panašioms į grafitą anglies dangoms. Esant tam tikrai apšvitos galiai, kuri priklauso nuo to, kiek vandenilio dalyvauja sudarančių šią fazę, šios dangos virsta stiklo anglimi. Taip pat nustatyta, kad lazerio spinduliuotė gali sukelti SiC bei į deimantą panašų kristalų susidarytą dangose.