# IR, VIS, AND UV LASER LIGHT IRRADIATION OF AMORPHOUS CARBON FILMS

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***ABSTRACT***

Coherent laser irradiation of amorphous carbon films formatted on Si substrate by ion beam deposition (IBD) and plasma enhanced chemical vapor deposition methods (PECVD) were analyzed in this work. a-C:H films have various sp3/sp2 phases ratio and different quantity of hydrogen, so they were conditional called as diamond like (DLC) (IBD formation method, quantity of H = (25 – 35) % , hardness by Vickers (HV) = 15 – 25 GPa) and graphite like carbon films (PECVD method, H < 20 %, HV = 6 – 12 GPa).

Films were irradiated with nanosecond Nd:YAG laser (Ekspla NL301G) at the first (1064 nm; 6 ns), the second (532 nm, 4.2 ns) and the fourth (266 nm, 3 ns) harmonic by scanning or repeating (10 pulse to one point) regime. The same power was in both regimes, intensity was increased to the threshold of ablation. Irradiation by the first laser harmonic with the power density (30 – 70) MW/cm$^2$ stimulates minor increasing of graphite phase. The peaks at ~ 800 cm$^{-1}$(intensive) and at ~ 970 cm$^{-1}$ (weak) showed SiC formation. Formation of carbides was observed at the second and superior harmonics irradiation when intensity of irradiation is low (< 10 MW/cm$^2$). Graphitization becomes more intensive when intensity of radiation increased and films transform to the glass carbon and nano/micro crystallite compound at intensive ablations regime (second harmonic~ 24 MW/cm$^2$). Ellipsometry measurements show not only the reduction but also high dispersion of film thickness. Micro relief analysis showed that film swelling proceeded during the graphitization process.

**Key words:** amorphous carbon films, laser irradiation.

## *INTRODUCTION*

Amorphous carbon films are perspective materials for many applications because of their unique optical, mechanical, electrical, and chemical properties. The physical properties of plasma-deposited amorphous hydrogenated carbon (a-C:H) films are determined by carbon sp3/sp2 bonding ratio and by hydrogen content [1-3].

Depending on the type of predominating bonds, the a-C:H films are divided into three groups: (i) diamond-like carbon (DLC) with sp3 bonds, (ii) graph-

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ite-like carbon (GLC) with sp2 bonds, and (iii) polymer-like carbon (PLC) with sp3 bonds and a high concentration of hydrogen. The hydrogen concentration and hence the physical properties of a-C:H films can be varied by laser irradiation because of the energy of bonds C-H (and C-C) is considerably smaller than that of C=C or C≡C bonds. In general, the effect of laser irradiation on DLC films is determined by superposition of three processes: graphitization, spallation, and evaporation, that are characterized by different threshold intensities [4]. The laser-induced graphitization of the surface layer has the lowest threshold and causes the changes of material properties. Among these changes, a noticeable reduction of the mass density is the 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 lead to the formation of characteristic surface profiles. The effect of multilevel spallation in DLC films manifests itself in peeling and removal of one or more layers, whose lateral size is comparable with irradiated area and the thickness is much less than the film thickness [4].

The aim of the present work was to study 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 sp3 bonds were discussed.

### *METHODS OF SAMPLE MANUFACTURING AND ANALYSIS*

Amorphous carbon films of a thickness up to 250 nm were formed on Si (100) and (111) wafers by applying a direct ion beam deposition method at room temperature. The substrates were degreased by immersing twice for 10 min in a chemically pure dimetilformamide. The substrates were cleaned for 1 to 10 min by hydrogen plasma before deposition. The films were formed from pure acetylene. The following deposition conditions such as ion energy 700 eV, ion current density ~ 0.12 $mA/cm^2$, pressure below $10^{-2}$ Pa, deposition duration 30 min were used. The details of deposition procedure were presented elsewhere [5,6].

The samples were irradiated in a scanning mode with the step of 25 μm, and pulse to one point by a q-switched YAG:Nd laser ((Ekspla NL15100TH) with pulses repetition rate of 12.5 Hz.

The hydrogen concentration was determined by elastic-recoil detection using a 2.4 MeV 4He2+ beam. The optical properties of laser-irradiated a-C:H films were studied by Raman scattering (Yvon Jobin), infrared (Perkin Elmer) spectroscopy, null- ellipsometry (Gaertner L117). The Rutherford backscattering spectroscopy and elastic recoil detection measurements indicated that the films consist of carbon (73 at.%) and hydrogen (27 at.%). These films are attributed to the typical diamond-like carbon (DLC) films. The properties of films before and after laser irradiation by first harmonic are shown in Table 1.

The IR-laser irradiation at both 35 mw/cm$^2$ and 70 mw/cm$^2$ intensities led to an insignificant graphitization of the DLC films. The formation of the SiC started at the interface between the substrate and the films. The presence of the sic phase was confirmed by the appearance of the peaks at 800 cm$^{-1}$ and 960 cm$^{-1}$ in the RS spectra. However, despite the graphitization and SiC formation, the films had good adhesion with the substrate. The microhardness of the laser-irradiated thin films decreased slightly with the increase of the energy density (*Table 1*). The irradiation with infrared light did not change the films' structure, and the films still remained as DLC. The ellipsometric calculations were performed with or without the SiC layer depending on the rs results. The irradiations with the first harmonics led to a lower refractive index and thicker DLC and SiC layers (*Table 1*). These results indicate that the graphitization process of films was initiated.

**Table 1** – The conditions of irradiation (λ – wavelength, laser intensity) and characteristics of the films' refractive index (n), extinction coefficient (k), film thickness (d), microhardness (HV).

| Sample | λ, nm | Irrad. int. MW/cm$^2$ | Model | n | k | $d_{DLC}$, ($d_{GC}$) Nm | $d_{SiC}$, nm | HV, GPa |
|---|---|---|---|---|---|---|---|---|
| B4 | - | - | DLC/Si | 2.41 | 0.16 | 145 | - | 23 |
| B4-1 | 1064 | 70 | DLC/SiC/Si | 2.36 | 0.27 | 169 | 50 | 17 |
| B4-2 | 1064 | 35 | DLC/SiC/Si | 2.13 | 0.4 | 165 | 10 | 19 |

The DLC films were found to be more sensitive to the VIS (532 nm) and UV laser irradiation (266 nm). The dispersion of film thickness showed that evaporation and surface swelling took place, and the transformation of sp3/ sp2 conditioned. When the intensity of irradiation is >1 MW/cm2, the Si and C diffusion also took place and caused the formation of the high intensity SiC peaks in the Raman spectra (at 800 cm−1and 960 − 1000 cm−1, respectively). Simultaneous processes, such as spallation and phase conversion, stimulated transformation of the sp3 bond to the sp2 bonds and the DLC films to the graphite-like carbon/glass carbon.

**Table 2** – The conditions of irradiation (λ-wavelength, laser intensity), ellipsometry data and the fitting parameters of the Raman spectra

| Sample | λ, nm | Irrad. int. MW/cm$^2$ | D, cm$^{-1}$ | ΔD, cm$^{-1}$ | G, cm$^{-1}$ | ΔG, cm$^{-1}$ | $I_D/I_G$ | n | k |
|---|---|---|---|---|---|---|---|---|---|
| B4 | | | 1312 | 228 | 1540 | 172 | 0.4 | 2.41 | 0.16 |
| B4-1 | 1064 | 70 | 1322 | 254 | 1545 | 159 | 0.6 | 2.36 | 0.27 |
| B4-2 | 1064 | 35 | 1365 | 314 | 1546 | 160 | 1.06 | 2.13 | 0.4 |
| | 532 | 24 | 1346 | 95 | 1598 | 86 | 1.33 | 1.9 | 0.11 |
| | 266 | 42 | 1385 | 171 | 1584 | 111 | 1.23 | 2.47 | 0 |

The RS spectra of DLC films were fitted to determine the D and G peaks position, the full width at half-maxima of the D (ΔD) and G (ΔG) bands, and the integral intensity ratio between the D and G peaks (ID/IG) (*Table 2*).

The Gaussian fitting results demonstrated that the G peak narrowed (86 and 111 $cm^{-1}$) and shifted to the higher wave numbers (58 and 44 $cm^{-1}$), and the (ID/IG) ratio increased. The films can be called a mixture of DLC/GLC with the glassy carbon phase inserts [2,7].

### CONCLUSIONS

The investigations showed that thin DLC films are resistant to IR-laser irradiation (1.16 eV). Irradiation by the first harmonics of a Nd:YAG laser stimulated formation of SiC and a slight hydrogenization of Si at the interface region. The films' graphitization and formation of the SiC clusters took place by increasing the photon energy.

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