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# Influence of ion and electron irradiation on properties of diamond-like carbon films

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Diamond-like carbon films, deposited by direct ion beam deposition method using $C_6H_{14}$ and mixture of $C_6H_{14}$ and $H_2$ and were irradiated by low energy electron and ion beams, have been investigated by Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and electrical measurements. The variation of the D- and G-line peak position and integrated intensity ratio ($I_D/I_G$) in the Raman spectra has shown that these films are amorphous with mixture of $sp^2$ and $sp^3$ bonds. It has been found that with increasing substrate temperature during deposition time the DLC films are more graphite-like, and with increasing hydrogen content $sp^2$ clusters are smaller and more disordered. The ion irradiation has more modified surface layer. Electron irradiation of the samples coated by $SiO_2$ can heat the sample because of big current densities and with electric break-down phenomenon can increase $sp^3$ bonds concentration and decrease disorder of diamond clusters.

**Keywords**: DLC films, Raman spectroscopy, ion bombardment, electron irradiation.

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## I. Introduction

Carbon due to its three different bonding configurations ($sp^1$, $sp^2$, $sp^3$) can change its properties from amorphous carbon to diamond and graphite [1-4]. The diamond and diamond-like carbon (DLC) are used in many applications because of their outstanding characteristics: high thermal conductivity, high optical transparency (from IR to nanometer wavelength region), high hardness, low friction and wear, chemical inertness (corrosion resistance in alkali and acid), biocompatibility. Owing to its good electrical properties such as low dielectric constant, wide band gap, and large breakdown field, diamond has also attracted a lot of attention as a promising candidate for high-temperature and high-power devices [5]. In addition to the continued lasting interest in diamond as a protective material (protective antireflection films in windows, optical components, and solar sells, protective coating for magnetic recording media, and hard disks, electrical insulation for chip cooling, and protective coating for reduction of wear and corrosion), recent interest was also focused on its possible applications as a field emitter for displays and other vacuum devices [6,7]. An important processing step in fabrication of microelectronic devices is a reliable and controllable etching procedure. Dry etching of diamond and diamond-like carbon creates

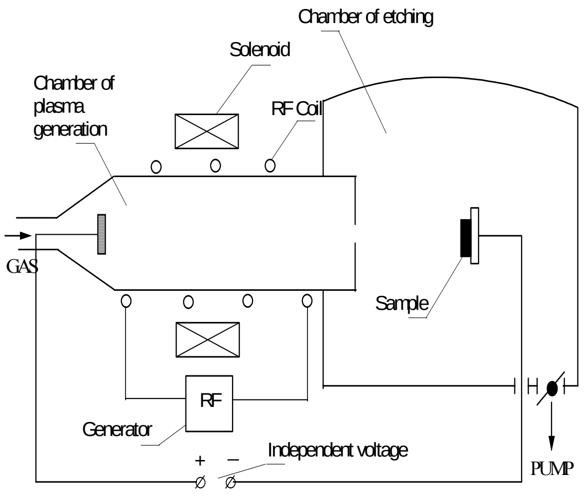


Fig.1. The scheme of two chamber plasmatron system.

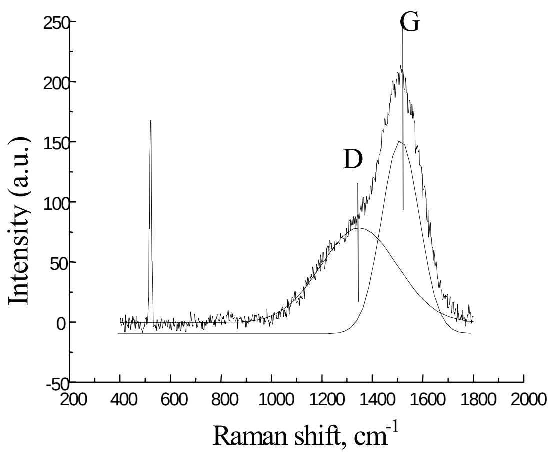


Fig.2. The Raman spectrum of DLC films deposited from $C_6H_{14}$.

damaged surface layer [8]. That is why it is important to investigate not only deposition methods of diamond and diamond-like carbon films but also structural and property changes due to irradiation [9-12].

## II. Experimental

In this paper we report data of depositions of DLC films and irradiation of these coatings using low energy electrons and Ar ions. Using direct ion beam deposition method, amorphous hydrogenated carbon films were deposited on silicon (100), (111) to a thickness of 450 nm. The films were produced from a) $C_6H_{14}$ and b) mixture of $C_6H_{14}$ and $H_2$. During deposition the sample temperatures were ~15°C or 200°C, the ion energy was 1.5-1.8 keV, the ion current density was ~0.12 mA/cm$^2$ under ~10$^{-2}$ Pa, the deposition duration was from 40 to 150 min. Some of the samples were coated by $SiO_2$.

The surface composition was measured by X-ray photoelectron spectroscopy using Kratos Analitical XPS analizator (Al, $K_\alpha$-1253.6 eV). Raman spectra were collected to determine the structure of carbon films. The excitation light was 514.5 nm of argon laser. Elipsometry was used to determine thickness and refraction index of DLC films using automatic rotating-polarizer type ellipsometer Gaertner L115 with He-Ne laser (632.8 nm). Electric properties were measured in Si-film-Metal system. The surface morphology was observed by scanning electron microscopy (SEM).

The bombardment of DLC films with Ar ion beams and electrons was carried out in two-chamber plasmatron system (Fig. 1).

This method differs from the traditional RF diode system and allows to decrease the re-emission of sputtered materials and to irradiate the sample by very low energy ions and electrons.

The generator power was 3.0 kW. The bias voltage of the samples with respect to the plasma varied from 20 to 700 V, gas pressure in the working chamber was from 0.1 to 10 Pa, the current densities of ion and electron flux toward the samples were (0.02 – 3) mA/cm$^2$ for ions and (4 – 6) mA/cm$^2$ for electrons.

## III. Results and discussion

The DLC films deposited from $C_6H_{14}$ on Si (111) and with temperature of 15°C were 300 nm of thickness with electrical resistivity of 0.2 MΩ×cm and index of refraction was 2.3. The atomic densities of these films according XPS data were 91 at% for carbon, 8 at% for oxygen, and 1 at% for silicon.

Raman spectra of these films are shown in Fig. 2.

They are typical for DLC [13,14]. We have had a broad peak in the 1100-1700 cm$^{-1}$ range that is centered at 1521 cm$^{-1}$. The peak at 520 cm$^{-1}$ corresponds to the silicon substrate [15]. This peak suggests that DLC films are transparent (small amount of sp$^2$ bonds). The asymmetrical broad peak is fitted by two Gaussian profiles centered at 1521 $cm^{-1}$ corresponding to G-line assigned to scattering by optic-zone center phonons of graphite and 1324 $cm^{-1}$ corresponding to the D-line assigned to scattering by disorder-activated optic zone edge phonons [16]. The position of the G- and D-line and the integrated intensity ratios ($I_D/I_G$) have been correlated with $sp^2/sp^3$ bonding ratios [14] and graphite crystal size [18]. Robertson and O'Reilly have proposed the model where amorphous carbon films consist of clusters of 3-fold coordinated $sp^2$ carbon embedded in $sp^3$ bonded matrix [19]. D- and G-line positions are different from the main Raman bands of diamond (1333 $cm^{-1}$) and graphite (1580 $cm^{-1}$) and they also indicate the disorder in $sp^2$ clusters and the increase of $sp^3$ bonds, respectively [20]. In our case (1521 $cm^{-1}$), it means that we have hydrogenated DLC film with high $sp^3$ concentration (see table 1).

After irradiation by Ar ions (energy was 700 eV, ion current density - 2 $mA/cm^2$, irradiation time 20 seconds), the integrated intensity ratio changed a little (it increased only till 0.87) but position for G-line (1521 $cm^{-1}$) remained without changes (Fig. 3). By increasing time of bombardment from 30 seconds to 1 minute, $I_D/I_G$ increased to 1.31. G- and D-band positions tuned to higher energy 1527 $cm^{-1}$ and 1360 $cm^{-1}$. It indicates smaller size and higher disorder of graphite cluster and the increase of $sp^2$ bond.

The changes of resistivity (0,2 MΩ×cm) were not great.

In the same conditions, DLC films were deposited on Si (100) from $C_6H_{14}$ + 1.5 $H_2$ mixture. The thickness of the film was 320 nm, refraction index - 2,4.The Raman spectra were different from described above (Fig. 4).

The positions of D- and G-bands were 1375 $cm^{-1}$ and G 1550 $cm^{-1}$ and $I_D/I_G$ - 1.60. It means that hydrogen reduces size of graphite islands. Ion treatment did not changed optical properties of DLC films ($I_D/I_G$ increases only from 1.60 to 1.67). Electrical properties were changed five times (from 0.4 MΩ×cm to 2 MΩ×cm). We suggested that ion irradiation made only intensive modification of surface layer.

Further we investigated temperature

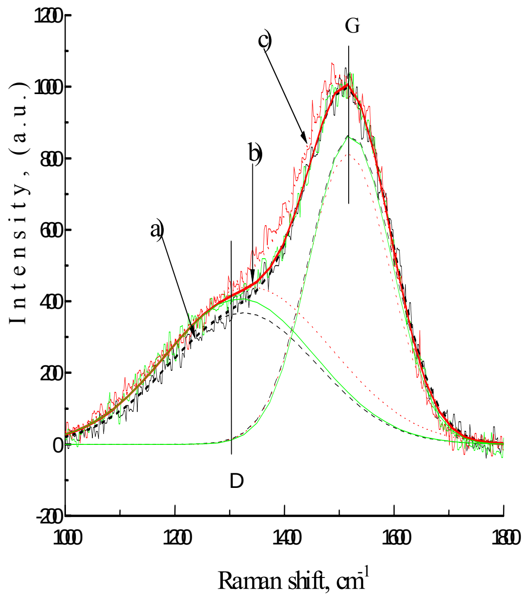


Fig. 3. The Raman spectra of DLC films deposited from $C_6H_{14}$ and irradiated by Ar ions. a) without any treatments, b) 700 eV, 2 $mA/cm^2$, 20 s, c) 700 eV, 2 $mA/cm^2$, 30 s.

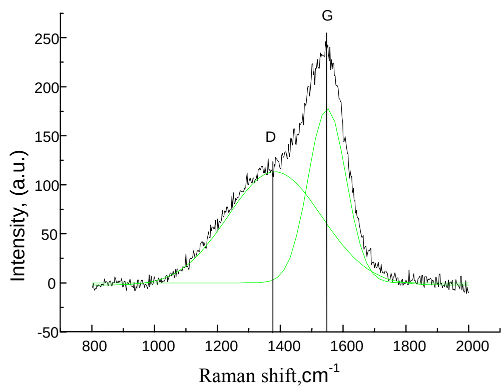


Fig 4. Raman spectrum of DLC films deposited from $C_6H_{14}$ and $H_2$.

influence to the properties of DLC deposited in the same deposition conditions but with substrate temperature of 200°C. The Raman spectra of these films were very different from described above (see Fig 5). The index of refraction was the same. The Raman spectra has shown that with increasing substrate temperature during deposition G-line position tuned to position of crystalline graphite (from 1555 to 1584 $cm^{-1}$) and $I_D/I_G$ ratio increased (from 1.28 to 2.00). Electrical properties increased to 5,2 MΩ×cm. It indicates that we

Table 1. The features of Raman spectra

| Conditions of DLC films deposition | Ion and electron treatment | $I_D/I_G$ | Position of G-line, $cm^{-1}$ | Position of D-line, $cm^{-1}$ |
|---|---|---|---|---|
| $C_6H_{14}$ | - | 0.75 | 1521 | 1324 |
| $C_6H_{14}$ | 700 eV, 2 $mA/cm^2$, 20 s | 0.87 | 1521 | 1319 |
| $C_6H_{14}$ | 700 eV, 2 $mA/cm^2$, 30 s | 1.08 | 1517 | 1337 |
| $C_6H_{14}$ | 700 eV, 2 $mA/cm^2$, 1 min | 1.31 | 1527 | 1360 |
| $C_6H_{14}$ + 1.5 $H_2$ | - | 1.60 | 1550 | 1375 |
| $C_6H_{14}$ + 1.5 $H_2$ | 700 eV, 1.7 $mA/cm^2$, 2 min | 1.67 | 1548 | 1383 |
| $C_6H_{14}$ + 1.5 $H_2$ (200°C) | - | 2.00 | 1584 | 1373 |
| $C_6H_{14}$ + 1.5 $H_2$ (200°C) | 700 eV, 1.5 $mA/cm^2$, 2 min | 2.12 | 1583 | 1379 |
| $C_6H_{14}$ + 1.5 $H_2$ (200°C); $SiO_2$ | - | 2.54 | 1575 | 1388 |
| $C_6H_{14}$ + 1.5 $H_2$ (200°C); $SiO_2$ | 300 eV, 4 $mA/cm^2$, 15 min, (Irradiation of electron) | 1.65 | 1576 | 1391 |
| $C_6H_{14}$ + 1.5 $H_2$ (200°C); $SiO_2$ | 700 eV, 1.5 $mA/cm^2$, 2 min, (Irrad. of ion) | 2.42 | 1577 | 1394 |

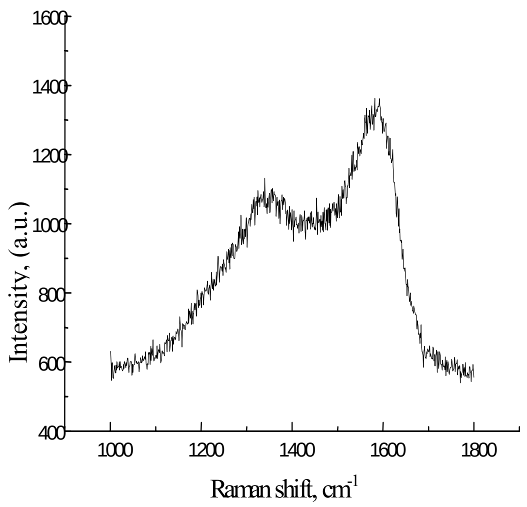


Fig. 5. The Raman spectra of DLC films deposited from $C_6H_{14}$ and $H_2$ and substrate temperature 200°C.

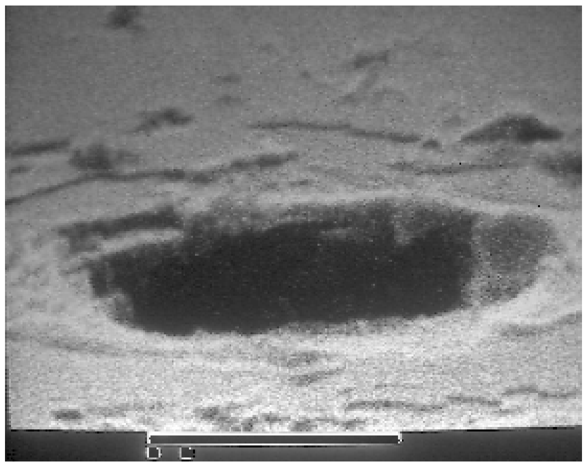

Fig. 6. Typical SEM micrograph of the electrical breakdown of the films after deposition coated by $SiO_2$.

have coatings more graphite-like with high $sp^2$ bond concentration but $sp^2$ islands are very small and disordered. Ion irradiation made these DLC films more amorphous ($I_D/I_G$ increased from 2.00 to 2.12 and specific resistivity - from 5.2 MΩ×cm to 10 MΩ×cm). These changes indicate that ion treatment changed only the surface layer.

The bigger changes were observed in the electron irradiation of the samples coated by $SiO_2$ after deposition. As we see in Fig. 6, the SEM has shown clear fingerprint of electric

Table 2. Comparison of diffraction data

| Lonsdaleite | | Observed phase | |
|---|---|---|---|
| d | $I/I_0$ | d | $I/I_0$ |
| 2.19 | 100 | 2.15 | 100 |
| 2.06 | 100 | 2.03 | 100 |
| 1.92 | 50 | | |
| 1.26 | 75 | 1.26 | 80 |
| 1.17 | 50 | 1.2 | 50 |
| 1.075 | 50 | | |

breakdown. The positions of D- and G-line are the same (1388 and 1575 $cm^{-1}$) but $I_D/I_G$ decreases to 1.65. Electron irradiation can heat the sample because of big current densities with electric breakdown phenomenon and can increase size $sp^3$ bonds concentration disorder of diamond clusters. Electronographic data show polycrystalline phase characteristic to lonsdaleite (Table 2).

## IV. Conclusions

Ion irradiation of DLC films makes graphite clusters more amorphous.

The size of graphite islands and ion treatment decrease and disorder of these clusters increases with increasing hydrogen content.

The DLC films are more graphite-like with increasing substrate temperature during deposition time.

Electron irradiation can heat the sample because of big current densities with electric breakdown phenomenon and can increase $sp^3$ bonds and decrease disorder of diamond clusters.

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## Вплив іонного і електронного опромінення на властивості алмаз-подібних вуглеводних плівок

А.Григоніс, М.Шілінскас, В.Копустінскас, В.Шаблінскас

Методами Раманівської спектроскопії, рентгенівської фотоемісійної спектроскопії, скануючої мікроелектронної мікроскопії і електричними вимірюваннями досліджено алмаз-подібні вуглеводні плівки, осадженні направленим іонним пучком з використанням $C_6H_{14}$ і суміші $C_6H_{14}$ і $H_2$, які опромінювались слабо енергетичними іонними та електронними пучками. Варіація позиції піку D- і G-лінії і співвідношення інтенсивності ($I_D/I_G$) в Раманівських спектрах показала, що ці плівки є аморфними із $sp^2$ і $sp^3$ орбіталями.

Встановлено, що з збільшенням температури підкладки під час осадження АПВ-плівки більш графіто-подібні, і з збільшенням вмісту водню кластери зменшуються і розупорядковуються.

**Ключові слова**: АПВ плівки, Раманівська спектроскопія, іонне бомбардування, електронне опромінення.