Electrical properties of the diamond like carbon films irradiated with high energy photons

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Abstract. SiOₓ-containing amorphous diamond like carbon (DLC) is very attractive material for a number of practical applications. DLC films are possible candidates for the formation of passive layers in electronic devices and are used as protective coatings. Both applications are interesting for the construction of medical radiation detectors. Radiation induced structural changes and electrical properties of DLC:SiOₓ films (undoped and co-doped) synthesized at room temperature by means of direct ion beam deposition method were investigated after their irradiation with high energy (E_{max}=15 MeV) X-ray photons. It was found that transparency of the irradiated DLC films was not changed significantly, as compared to initial samples, stating only small increase of the optical band gap in DLC films. However radiation induced changes were dependent on co-doping and film deposition conditions which were responsible for the sp³/sp² ratio and hydrogen content in the investigated films. Analysis of U-I characteristics showed decreasing tendency of the leakage current in the range 0-20 V and especially high dependency of breakdown voltage on the deposited contact area in irradiated films as compared to initial samples. Possible mechanism of radiation induced changes in irradiated DLC films is discussed on the basis of the results of Raman and Infrared spectroscopy.

1. Introduction

Diamond-like carbons (DLC) belong to the group of materials which are attractive for the number of applications due to their outstanding optical, electrical and mechanical properties [1-3]. Properties of synthesized DLC are influenced by deposition conditions and parameters and strongly depend on the ratio of sp³ and sp² bonds and hydrogen content in the material. Incorporation of Si or SiOₓ allows to increase the adhesion of the DLC coating with the Si wafer and to decrease the internal stress and friction coefficient in the synthesized structure, to obtain better thermal stability and to increase the hardness [4].

Electrical properties of DLC films can vary from semimetal to that of wide band gap insulator [5]. However the high density of localized gap states leads to low apparent carrier mobility and significantly degrade the semiconductor properties of materials. It was estimated [6] that the optical band gap of amorphous hydrogenated DLC films deposited from the gas mixture at room temperature...
using hollow cathode method [7] vary in the range of 0.9-4.28 eV and are characterized through high
electrical resistivity. The dielectric constant of these DLC films covers the range of 2.7 – 3.8.
Enhancement of isolating properties is possible via doping of DLC film with SiOx. Isolating properties
of amorphous DLC films together with their tissue equivalence make them promising material as
passive layers or protective coatings in the construction of medical radiation detectors. Assuming that
the modification of the film structure and properties is possible when X-ray photons interact with the
DLC film, there is a need to investigate radiation induced structural changes and properties of the
irradiated materials. However there is a lack of information about the behavior of DLC structures in
radiation fields.

The aim of this work was to investigate electrical properties of the hydrogenated SiOx doped
amorphous DLC films, produced at room temperature using direct ion beam deposition method, before
and after their irradiation with high energy X-ray photons from medical sources with the scope to
apply these films in the construction of medical radiation detectors.

2. Experimental
Amorphous hydrogenated silicon oxide containing DLC films deposited at room temperature on
quartz glass wafers (for optical measurements) and on commercially available crystalline n-Si <111>
wafers (for electrical measurements) from hexametildisiloxane vapor and hydrogen gas mixture by
direct ion deposition method [7] were used for the investigation.

Investigation was performed in two steps. Step A: estimation of the DLC samples with the highest
optical band gap; Step B: deposition of Al contacts with diameters: 1000 μm, 500 μm, and 300 μm
through the mask in electrode beam evaporation equipment CUBIVAP on the top surface of the
samples which indicate the highest optical band gap and formation of the Al-Si-DCL-Al structures for
the investigation of electrical properties. Film preparation conditions are presented in table 1.

| Sample series | Reagents | Pressure, \( \cdot 10^{-2} \) Pa | Ion beam energy, eV | Ion beam current density, μA/cm² | Film thickness, nm |
|---------------|----------|-----------------|-----------------|----------------|-----------------|
| 3             | ((CH₃)₃SiOSi(CH₃)₃+H₂) (1-3) | 800              | 100             | 200            |
| 3-1           | ((CH₃)₃SiOSi(CH₃)₃+H₂ (1-2)     | 800              | 50              | 182            |
| 3-2           | ((CH₃)₃SiOSi(CH₃)₃+H₂)+H₂ (1-2) | 800              | 100             | 180            |

Prepared samples were irradiated with high energy X-ray photons (average energy 10.8 MeV)
generated at the X-ray tube voltage of 15 MV in medical linear accelerator CLINAC (VARIAN).
Total dose of 2 Gy, which is usual for one medical treatment, was delivered to the irradiated structure.

Current-voltage characteristics (U-I) of DLC films were measured by KEYTHLEY 6487
pikoampermeter. Band gap of the investigated structures was derived from the optical transmittance
and absorbance spectra of samples measured by Ultraviolet and Visible Absorption Spectrometer
SPECTCORD UV/VIS.

For the explanation of radiation induced changes in the irradiated samples bonding structure and
optical properties of DLC films were analysed using the results of FT-IR spectrometry performed in
the range from 700 to 4000 cm\(^{-1}\) (spectral resolution of 0.3 cm\(^{-1}\)) by SPECTRUM GX FT-IR (PERKIN
ELMER) spectrometer and the results of Raman scattering spectroscopy obtained by using Spectra
Physics Stablite 2017 argon laser (\(λ = 514.5 \) nm) as a light source for Raman scattering. The Raman
spectra were recorded with a 10 cm\(^{-1}\) spectral resolution in the Raman shift range 900-2100 cm\(^{-1}\).

3. Results and discussions
Investigation of the transmittance and absorbance spectra in UV/VIS range showed that the
transparency of the irradiated DLC films was not changed significantly, as compared to initial
samples, stating only small increase of the optical band gap of DLC films. However radiation induced changes were dependent on co-doping. Estimated values of the optical band gap were around 3.0 eV in investigated samples indicating the highest values for the samples No3: $E_{3E}$=3.25 eV for the initial samples and $E_{3G}$=3.60 eV for the samples irradiated with high energy X-ray photons (figure 1).

![Figure 1](image1.png)

**Figure 1.** Tauc gap of samples No3 before and after the irradiation with high energy X-ray photons.

Current-voltage characteristics (U-I) and conductivity of the initial SiO$_x$ containing DLC films were measured and the influence of the size of Al-contact area was analyzed. Evaluated average breakdown voltages for all investigated structures are presented in figure 2. Differences in breakdown strength of DLC films in Al-DLC(SiO$_x$)-Si-Al structures can be attributed to the internal stress induced via depositing of contacts on the film surface as it was proposed in [4].

After the evaluation of the samples with the best isolating properties and the lowest internal stress, which was additionally influenced by the size of deposited Al-contact area, chosen DLC films were irradiated by high energy X-ray photons and the current-voltage (U-I) characteristics of irradiated samples were measured (figure 3).

![Figure 2](image2.png)

**Figure 2.** Dependence of breakdown voltage on the diameter of the Al-contact area. Inclusion: cross section of the investigated structures.

![Figure 3](image3.png)

**Figure 3.** U-I characteristics of the investigated structure with different size of electrode area: a) Ø 500 μm, and b) Ø 300 μm.

It was found, that the leakage current of irradiated samples was lower within the range 0-20 V as compared to the initial samples, however the conductivity of irradiated samples was one order of magnitude higher than in initial samples. Break down strength was not changed significantly in the irradiated samples with the smallest (Ø 300 μm) diameter of the Al-contact area, however breakdown voltage in samples with larger contacts was dramatically decreased after the irradiation, and indicating enhanced conductivity in investigated structures. Results of investigation are presented in table 2.
Table 2. Electrical properties in Al-Si-DCL-Al structures before and after irradiation.

| Samples   | Film thickness, nm | Exposure dose, Gy Ø 500 μm | Breakdown voltage $U_{\text{min}}$, V | Breakdown strength $E_{\text{min}}$, MV/cm Ø 500 μm | Ø 300 μm Ø 300 μm |
|-----------|-------------------|-----------------------------|---------------------------------------|----------------------------------------------------|------------------|
| Initial 200 | 2                 | ≥ 46.5                      | ≥ 48.2                                | ≥ 2.33                                             | ≥ 2.41           |
| Irradiated ~200 | 2                 | <13.75>                     | <45.1>                                | 0.69                                               | 2.26             |

Possible explanation for radiation induced structural changes in DLC films could be found analyzing Raman and FT-IR spectra of the samples. Shift of the G-peak from 1456 cm$^{-1}$ towards the higher wavenumbers in the Raman spectrum, some changes in the intensity of $sp^3$ peaks revealed from FT-IR spectrum at 2852 cm$^{-1}$ and 2920 cm$^{-1}$ indicates disappearance of the $sp^3$ bonding and the formation of $sp^2$ bonds in irradiated samples. Structural changes are also confirmed by U-I characteristics, which show increased electrical conductivity after irradiation. Possible mechanism of DLC film restructuring is based on ionization process of irradiated material [8]: produced electrons can break the C-H bonds or even C=H bonds, causing rearrangement of film atoms. In this way stronger C-C bonds can be formed and free hydrogen atoms can be released from the films in the form of hydrogen molecules.

4. Conclusions
Investigation of Al-Si-DLC-Al structures showed, that their electrical properties are dependent on the technological DLC film deposition conditions, co-doping during the film deposition and the size of the electrode area deposited on the film surface. It was estimated that the structures with the smallest Al-contact area (Ø 300 μm) exhibited the best isolation properties.

Irradiation of the samples with the high energy X-ray photons had not changed significantly the electrical properties of the samples: with the smallest Al-contact area: most of them were characterized by high breakdown strength (≥50 MV/cm). Increasing of the Al-contact area resulted in dramatically reduced breakdown voltage (≤ 6-8 V) in all Al-Si-DLC-Al structures after the irradiation, indicating increased conductivity of the DLC films.

Investigation of the samples by Raman and FT-IR spectroscopy showed that the radiation induced structural changes of irradiated DLC films are responsible for the modification of the electrical properties.

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