Evaluation of resistance of diamond-like carbon coating to the corpuscular radiation in outer space conditions

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Abstract. The purpose of this work was to research the resistance of thin coatings to the effects of corpuscular radiation, as well as evaluation speed etching of diamond-like films with different content of diamond phase. There were two samples of monocrystalline silicon with DLC coating. To evaluate the resistance, two groups of grooves were etched on each sample. The depth was then measured to calculate a relative etching ratio of DLC coating. The resistance was determined to be four times that of silicon.

1. Introduction
The use of polymers in the structure and devices of spacecraft allows their weight to be reduced, along with their dimensions, thereby increasing their economic efficiency, however, the far lower stability of polymers against open space factors such as vacuum, temperature, and ionizing and particle radiations significantly hinders their wide application. One way to solve this problem is to cover the surfaces of polymers with protective gas tight coatings based on metals and metal oxides [1, 2].

A relatively new trend that is being intensely developed in the recent years is the use of diamond-like carbon (DLC) for the protection of products and materials from various negative factors due to the number of unique properties inherent to those coatings: high mechanical strength, high gas tightness, biocompatibility etc. [3-5]. Over the recent 2-3 years there have been lots of articles in which polymers with DLC layers are considered as promising packaging materials for the food and pharmaceutical industries due to their good gas tightness. This allows one to consider diamond-like coatings as promising for the protection of polymer structures and products used in the open space.

Bashkov et al [6] report on the protective properties of DLC coatings under the conditions of open space, demonstrating their gas tightness under thermal and vacuum impacts, and a tangible reduction in material erosion under the impact of particle radiation. This work is a continuation of the study dealing with the compatibility of DLC coatings in the open space, in particular, study of the stability of these coatings against particle flows that cause etching and erosion of most polymers.

The aim of this work was to develop a method for assessing the stability of thin coatings against ion radiations and the etching rate of diamond-like films with various contents of the diamond phase.

2. Test Materials and Experimental Equipment
Silicon was chosen as the material of the substrates for the application of DLC coatings. This choice was accounted for by the fact that during the impact of ion fluxes on samples the etching of the surface...
layer of different polymers may occur by various mechanisms and at different rates, whereas the etching of single crystal silicon has been well studied and is stable. Furthermore, single crystal silicon is delivered in the form of polished wafers with very high surface purity, while obtaining polymers with comparable surface purity is a complex or potentially impossible task.

In this work samples of DLC coatings were studied that were applied onto 20x20 mm single crystal silicon wafers using the vacuum electric arc method with plasma flow separation and laser arc initiation on an East-01 instrument (OOO NPT, Russia). This coating application method allows synthesizing coatings with high substrate adhesion and provides for a high diamond likeness [7, 8]. The coatings thickness was 170 nm including an adhesive Ti sublayer having a thickness of up to 50 nm.

Before coating, masks were positioned on each sample for forming a window in the coating required for measuring its thickness under a probe microscope. Also this mask was used to form an uncoated area for assessing the impact of the ion flux onto the substrate.

Focused gallium ion beam was used as a source of particle radiation. This radiation was chosen because of the possibility of sharp focusing of the beam and forming a controlled impact area with well-controlled parameters, furthermore, gallium ions are preferable for producing particle radiation because their impact causes physical sputtering of the target material unlike oxygen, nitrogen or fluorine ions that may enter into chemical reactions.

Ion irradiation was provided using the FIB module of the NanoFab-100 ultrahigh vacuum four-chamber nano-technological device (manufactured by CJSC “NT-MTD”, Zelenograd) intended for studying the surface of up to 100 mm diameter wafers under the conditions of ultrahigh vacuum and equipped with a gallium ion radiation source.

2.1. Determination of Focused Ion Beam Impact Parameters

Ion beam impact is achieved by multiple scanning of the selected area with a sharp focused ion beam. The main variable parameters of radiation are acceleration voltage, beam width and number of passes. The acceleration voltage and width control the shape (diameter) of the beam and the energy and density of the ion flux, whereas the number of passes determines the time of impact.

For a known etching ratio, these functions allow the time of exposure to be calculated, which is required for etching to the desired depth. Taking into account the high purity of the materials used and their stable parameters, the etching ratios for a wide range of materials used in microelectronics are well known. For single crystal silicon substrates the sputtering ratio for irradiation with 30 keV gallium ions is well known and is 2.412 [9, 10]. The magnitude of ion current depends on the width and acceleration voltage; it cannot be strictly controlled.

3. Experiment

Each sample was exposed to radiation in multiple areas for which the time of impact varied and hence the depths of the etch grooves also differed. Different grooves depth allowed a more accurate determination of etching rate (stability against impact) and assessing the scatter of etching rates depending on depth. The etched areas were at the boundary between the coating and the pure silicon such that the coating boundary was close to the middle of the etched area. This arrangement provided for:

- Simultaneous and similar impact both on the coating and on the silicon
- Good visibility of etched areas during further probe microscope scanning
- Visible comparison between the etching rates of the silicon and the diamond-like coating

Experimental parameters were optimized during method testing. One of the tasks of the work was to determine the size of the etched area. The following criteria were used for selecting these parameters:

- Specific features of surface topology scanning using the probe method
- Minimizing the effect of back-deposition depending on the small size of the area
- Minimizing the time of exposure to the focused ion beam
Based on these criteria, the sizes of the areas studied in this work were 10x40 µm and 5x20 µm. In our case the maximum time of exposure for the small and the large grooves was 30 and 60 min, respectively. It should be noted that the width of the etch groove varies depending on ion current which is measured during etching.

For the experiment, a 100 µm beam with energy 30 keV was chosen. With these beam parameters, the ion current varied within 50 to 56.5 pA and was measured after each etching with a Faraday cup of the FIB column. At these current magnitudes, the beam diameter at the sample surface is approx. 25 µm which is satisfactory from the viewpoint of etching accuracy requirements.

After ion beam irradiation, secondary ion images of the surface portions were obtained for each sample containing all the irradiated areas. These images allow assessing the sizes and positions of the etched areas and simplify detection in the scanning probe microscope. Figures 1, 2 show the images of samples Nos. 1 and 2.

Data on exposure times for etch grooves of Samples Nos. 1 and 2 are summarized in Table 1.

4. Results and Discussion
A typical image showing the topology of the ion beam irradiated areas is shown in Figure 3. For both of the samples the boundary of the diamond-like coating is well observed, and the impact area has clear limits. Some high peaks in the image are reflections of noise during probe microscope scanning.

Surface analysis of the images shows that silicon etching rate is several times that of the coating rate. For quantitative analysis of the sputtering rate, the average depth of etched areas was measured on the coating and on the silicon. The results are presented as groove depths measured using the probe method as functions of irradiation time, Figure 4.

The plot shows experimental results on etch groove depth in the silicon as a function of exposure time for samples № 1 and № 2 (curves 1 and 2, respectively). In addition, curves 3 and 4 show etch groove depth in the diamond-like coating as a function of exposure time for samples № 1 and № 2, respectively. Depths of each groove for samples № 1 and № 2 are summarized in Table 1.

The depths of the 10x40 µm grooves were close to those arrived at through calculation, and for the 5x20 µm grooves the depths were slightly greater than calculated, however, the difference was within
10%, this being probably accounted for by different ion beam movement velocities which were dependent on the shape and size of the exposed area. The sputtering rate of the DLC coating was several times lower than that of silicon.

**Table 1.** Exposure time and depth for each groove of samples №1 and №2.

| Groove № | Milling time (sec) | Groove depth of sample №1, nm | Groove depth of sample №2, nm |
|----------|--------------------|--------------------------------|--------------------------------|
|          |                    | Si | DLC | Si | DLC |
| 5×20 µm  |                    |    |     |    |     |
| 1        | 60                 | 4  | *a  | *a | *a  |
| 2        | 300                | 46 | 1    | 45 | *a  |
| 3        | 900                | 162| 42   | 172| 45   |
| 4        | 1800               | 360| 150  | 352| 156  |
| 10×40 µm |                    |    |     |    |     |
| 1        | 60                 | *a | *a  | *a | *a  |
| 2        | 300                | *a | *a  | 11 | -5b |
| 3        | 900                | 37 | *a  | 35 | -6b |
| 4        | 1800               | 72 | 17  | 75 | 16   |
| 5        | 3600               | 158| 40  | -  | -    |

*a Groove depth cannot be measured using scanning probe microscopy.

*b Foaming effect.

**Figure 3.** Model of ion irradiated area topology constructed based on the results of probe microscopy studies.
Figure 4. 5x20 um Groove Depth as a Function of Etching Time.

For both samples the dependency of silicon etch groove depths on silicon exposure time are similar and can be approximated with a straight line: that suggests a constant etching rate. Furthermore, the results proved to be almost identical for both samples, which is indicative of the stable repetitiveness of the results.

The diamond-like coating etching rate is also constant. The ‘kink’ in the curve corresponds to the DLC coating / Ti sublayer boundary. At an early stage of etching, both samples exhibited ‘foaming’ of the DLC coating which was especially clearly seen in the 10x40 µm areas and reached 6 nm for sample № 2. This phenomenon has not yet been discussed in the literature and will be further studied.

Diamond-like coatings are an amorphous mixture of allotropic carbon modifications: graphite (sp2-hybridization) and carbon (sp3-hybridization). Because the density of graphite is 1.7 times lower than that of diamond, DLC coatings have quite an inhomogeneous structure from the viewpoint of density which is dependent on the degree of diamond likeness. It is therefore impossible to calculate the coating etching ratio directly, thus, the stability of the DLC coating was expressed as the ratio of the coating etching rate and the silicon etching rate which is calculated using the formula

\[ SR = \frac{h_{\text{Si}}}{h_{\text{DLC}}/t} = \frac{h_{\text{Si}}}{h_{\text{DLC}}} \bigg|_t, \]

where \( SR \) is the ratio of silicon and diamond-like coating etching rates, \( h_{\text{Si}} \) and \( h_{\text{DLC}} \) are the silicon and diamond-like coating etching depths and \( t \) is etching time.

When selecting data for the calculation of \( SR \) one should take into account those etch grooves where the diamond-like coating etching depth is not greater than the coating thickness. This is required in order to exclude grooves in which both the diamond-like coating and the Ti sublayer were etched. Finally, grooves 3, 8 and 9 in sample № 1 and grooves 3 and 8 in sample № 2 were chosen. The value of \( SR \) was 4.1, thus, one can conclude that the diamond-like coating is approximately four times as stable against particle irradiation compared with a single crystal silicon provided that physical sputtering occurs. The results also show that the \( SR \) of the DLC coating of samples № 1 and 2 are similar.

Furthermore, the study showed that for smaller exposure areas (5x20 um compared with 10x40 um) the etching rate at depths of greater than 300 nm does not change due to back-deposition. It is
therefore recommendable to choose 5x20 µm exposure areas during further studies. This will accelerate experiments due to the following reasons:

- Reduction of FIB exposure time
- Reduction of time of scanning probe microscopy studies

One should note that this work dealt only with two coating samples and was mainly aimed at testing the method and choosing optimum parameters of studies. Further studies should primarily target the dependence of etching rate on the degree of diamond likeness and other structural parameters of DLC coatings as well as the effect of coating application techniques.

5. Conclusions

A method for assessing the stability of thin coatings against particle radiations has been developed. The Ga ion irradiation stability of diamond-like coatings applied onto single crystal silicon using the vacuum electric arc method with plasma flow separation has been studied. We show that the Ga ion irradiation stability of the diamond-like coating is 4 times that of single crystal silicon.

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