Effect of grain orientation on properties of diamond/graphite metasurface fabricated by laser direct-write

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Abstract. We report on the correlation between the optical properties of the laser modified region with the crystallographic orientation of the irradiated surface. Graphitized structure is formed on CVD polycrystalline diamond surface after laser (KrF, $\tau = 20$ ns, $\lambda = 248$ nm) irradiation. The thickness of the graphitized layer is analysed by transmission electron microscopy and by decreasing the intensity of the diamond line in the Raman spectra. It is found that the change of optical properties of modified layer depends on its thickness and the maximum thickness formed on the grain with orientation $\{111\}$. Simulation of transmittance of diamond/graphite metasurface confirms the variation of the graphitized layer thickness.

1. Introduction

Advances in technology of chemical vapour deposition (CVD) of polycrystalline diamond allow to obtain samples up to a millimeter thick and up to 100 mm in diameter. Different elements of photonics and electronics [1, 2] has been produced by laser induced graphitization of the surface [3-4] and bulk [5-7] of diamond. But the effect of crystal orientation of a diamond on the properties of modified area is not well studied. It is explained first of all by the use of surface graphitization of diamond for applications which does not need precise laser processing, for example for fabrication of two-dimensional diamond detectors with a size of one pixel exceeding 200 $\mu$m [8]. However for planar elements of photonics even for the THz range, when the lateral size of a single structure becomes comparable with that of a certain crystallite, the effect of crystal orientation becomes crucial. In this paper we investigate the correlation between the diamond grain orientation and the thickness of laser-induced graphitized layer by means of a Raman spectroscopy and examination of the cross section of the modified area with the help of transmission electron microscopy (TEM). Numerical modelling of transmittance of diamond/graphite metasurface confirms the variation of the thickness of graphitized layer.
2. Experimental

Experimental details of the laser direct-write technique, used to fabricate graphitized structures, and measurements of the transmittance spectra of the continuous layer (4x4 mm) and grid (width of 15 µm and period of 30 µm) can be found in our recent work [9]. A dual-beam scanning electron microscope FEI Versa FEG equipped by Hikari EBSD Camera was used for the morphology and grains orientation characterization. Diffraction patterns were acquired at 20 kV accelerating voltage and 4 nA beam current. The thickness of the graphitized layer on a diamond surface was analysed by TEM on a lamella prepared by the focused ion beam technique (FIB). Investigation of the laser induced graphitization of diamond surface was performed using a Raman spectrometer (Lab Ram HR800) in micro configuration. The probe beam wavelength was $\lambda_0 = 473$ nm.

![Figure 1](image_url)

**Figure 1.** (a) EBSD map of crystallite orientation on the diamond surface with graphitized ribbons; (b) Bright field TEM image of graphitized layer cross-section on the diamond grains with different orientation; (c) Raman spectra of the modified area on diamond grains {111}, {101} and {001} orientation.

3. Results and discussion

To study the correlation of the properties of a laser graphitized diamond layer with the diamond grains orientation, we obtained a grain orientation map using electron backscatter diffraction (EBSD) of the sample surface (figure 1a). The indexed ribbons in figure 1a correspond to the diamond, and the graphitized ribbons look like non-indexed pixels. A TEM lamella for the top layer thickness analysis was cut from the area marked by black arrow (figure 1a) is presented in figure 1b. The area on the surface was chosen so that two grains with different orientations of {001} and {111} were represented on the cut. The boundary between the two crystallites is clearly visible in figure 1b. The difference in the thickness of the graphitized layer at different grains is also evident: $d_{111} \approx 580$ nm on the orientation {111} and $d_{001} \approx 380$ nm on the orientation {001}.

The thickness of the graphitized layer on crystallites oriented along the three main planes in diamond was analyzed by Raman spectroscopy. The corresponding spectra are shown in figure 1c. The spectrum of the original diamond was also recorded, but not shown in the figure, because the intensity of diamond line, located at 1332.5 cm$^{-1}$, was much higher than the maximum value observed in the spectra for the graphitized surface. Intensity of the diamond peak in the spectra varies depending on the orientation of the crystallite. Similar result was observed in our recent work devoted to the diamond/graphite detectors of ionizing particles, but the orientation of diamond grains was unknown [10].

If we assume that the optical properties of the graphitized layer remain unchanged when passing from one diamond plane to another, but depend only on its thickness, then the ratio of the thicknesses $d_i/d_{max}$ can be estimated from the ratio of the intensities of the diamond line $I_{de}$ in the modified region. It may readily be shown that this ratio is defined as the $\frac{\log I_{de}}{I_{de}/I}$, where $I$ is an intensity of the diamond line from untreated area. The minimum value of the intensity of the diamond line was recorded while passing through a graphitized layer on a crystallite with orientation {111}. Hence, the maximum thickness $d_{111}$ of the modified layer is formed along the {111} planes. For the thicknesses of
layers formed on crystallites with orientations \{001\} and \{101\}, the coefficients of 0.69 and 0.52 are obtained, i.e. \(d_{001}/d_{111} = 0.69\) and \(d_{101}/d_{111} = 0.52\). The result of the analysis of Raman spectroscopy correlates with the ratio of thicknesses of \(d_{001}/d_{111} = 380/580 = 0.66\), obtained from electron microscopy.

So the thickness of graphitized layer depends on the grain orientation of the diamond and the question how to model optical properties of the diamond/graphite metasurface arises. The electromagnetic response of laser modified layer is unknown; we use Drude model to estimate it [9]. The only important parameters in modeling are thickness \(d\) and DC conductivity \(\sigma\) of the graphitized layer. The conductivity of the graphitized area with the size of 4x4 mm is controlled by the thickest part of the modified layer. So we used the maximum thickness of 580 nm for numerical simulation of the transmittance of continuous graphitized area on the diamond surface that is shown in figure 2a.

To calculate the optical properties of graphitized diamond structure with accounting for multiple reflections we employed the rigorous coupled waves analysis (RCWA) in form of the optical scattering matrix [11]. A good agreement between the simulated and measured results is observed and the best fit value is \(\sigma = 305 \, \Omega^{-1} \, \text{cm}^{-1}\). However, a modelling of transmittance of the graphitized grid, acting as a THz beam polarizer, with the same parameters \((d = 580 \, \text{nm} \text{ and } \sigma = 305 \, \Omega^{-1} \, \text{cm}^{-1})\) did not show a good agreement with the experiment. The comparison of measured and calculated transmission spectra in linear polarizations perpendicular (p-) and parallel (s-) to grid is presented in figure 2b. For p-polarization, the calculated transmissivity is only slightly higher than the experimental one, but for s-polarization the difference is significant. The best match is achieved by decrease of \(d\) to the value of 350 nm. In this case one can see a good agreement between the experiment and simulated results. This can be attributed to the fact that the DC conductivity of the ribbon is controlled by its smallest cross section. When the size of the certain grain is comparable with the width of the ribbon, a single diamond grain with the smallest thickness of graphitized layer is enough to control the conductivity.

![Figure 2](image.png)

**Figure 2.** (a) Calculated (red curve) and experimental (black dots) transmittance spectra of the diamond plate with thickness of 578 µm and graphitized layer with thickness of 580 nm; (b) Calculated (curve) and experimental (black dots) transmittance spectra of periodic graphitized grid on the diamond surface for different polarizations of probe beam.

4. **Conclusions**

In conclusion, we have demonstrated the correlation between the grain orientation of CVD polycrystalline diamond and the thickness of laser-induced graphitized layer on it. Raman spectroscopy and STEM technique indicate that the maximum thickness of the modified layer is formed on the surface of the crystallite orientation \{111\}. Simulation of the diamond/graphite metasurface transmittance proved to be quite sensitive to the thickness of structures, and different
thickness of graphitized layer was used for continuous area and grid to achieve a good agreement with experiment.

5. Acknowledgments
This work was supported by RFBR (16-32-60179), by the Competitiveness Enhancement Program of the MEPhI and by Federal Agency of Scientific Organizations under Agreement 007-GZ/Ch3363/26. The theoretical part of this work was supported by Russian Science Foundation (Grant No. 16-12-10538).

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