All-carbon diamond/graphite metasurface: Experiment and modeling

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We model theoretically the electromagnetic response of a diamond/graphite metasurface, acting as a THz beam polarizer. The response appears to be quite sensitive to the thickness and burial depth of laser-induced graphitized structure, and its simulation is validated by our experiments. Our simulations create a theoretical basis for designing optical elements based on all-carbon metamaterials, fabricated by laser direct-write technique. Published by AIP Publishing.

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Recent achievements in the field of metamaterials and metasurfaces exploit the idea of manipulating the electromagnetic response of matter by means of making compound metal/dielectric or full-dielectric structures with spatial modulation of composition on distances less than the photon wavelength. As a rule, the manufacturing of metamaterials and metasurfaces requires sophisticated technologies of heterostructure growth and nanostructuring. A new approach to THz metamaterial structures is based on a laser direct-write of metal-less graphitic-like structures on the surface of a CVD-grown polycrystalline diamond. This method of diamond modification is very flexible; it allows one to fabricate arbitrary complex graphitized meta-structures on the polycrystalline diamond surface and even buried inside the material bulk, such as demonstrated for IR range (1–14 μm). Compared with the well known direct laser-writing by multiphoton polymerization, our method is really a one-step process to fabricate composite metal/dielectric meta-structures.

The goal of this paper is to develop a theoretical model, allowing us to describe and design diamond/graphite metasurfaces with predictable and controllable electromagnetic properties in the frequency range of interest. To verify our model, we simulate the properties of a graphitized grid on the diamond surface, acting as a beam polarizer for THz range, and continuous graphitized layer on the same substrate. Such structures have been demonstrated in our recent work, also containing the experimental details of the excimer KrF laser direct-write technique to fabricate the graphitized layers and structures on a CVD diamond surface and measurements of the THz transmittance spectra by a submillimeter BWO spectrometer “Epsilon.”

To numerically calculate the electromagnetic response with accounting for multiple reflections, we use so called rigorous coupled wave analysis (RCWA) and optical scattering matrix. The method consists of (i) splitting the structure into layers, homogeneous in the perpendicular direction (five in this case: air, air and diamond, graphite and diamond, and air), (ii) solving Maxwell’s equations in each layer, and (iii) matching the solutions in neighboring layers using Maxwell’s boundary conditions. To improve the convergence of the plane wave decomposition we employ Li’s factorization rules and Granet’s adaptive spatial resolution. This method, in combination with the so called matched coordinates approach, allows us to calculate the optical response of periodically modulated structure with a reasonable accuracy for less than 30 plane wave harmonics per dimension of periodicity.

Important for this method is the knowledge of the dielectric susceptibilities of all constituent materials, as well as of the geometrical parameters of the structure to be simulated. In our case, the constituent materials are polycrystalline diamond and nanocrystalline graphite, produced by direct laser-write of diamond. The dielectric susceptibility of diamond in THz range is well known to be nearly nondispersive. We use in our calculations ε\(_{\text{diamond}}\) = 2.376\(^2\) ≈ 5.65. The response of graphitized diamond is unknown. As in Ref. 7, we use a simple Drude-type model

\[
\varepsilon_G = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)},
\]

where \(\omega_p\) and \(\gamma\) are the plasma frequency and relaxation rate, respectively. Equation (1) takes in the THz range \(\omega \ll \gamma\) a simpler Ohmic form

\[
\varepsilon_G \approx 1 - \frac{\omega_p^2}{\gamma^2} + \frac{i\omega_p^2}{\omega\gamma} = 1 - \frac{4\pi\sigma}{\omega} + \frac{4i\pi\sigma}{\omega},
\]

where

\[
\sigma = \frac{\omega_p^2}{4\pi\gamma}
\]

is the graphitized diamond conductivity. This formula gives a metallic character of the dielectric susceptibility of the graphitized layer (Re \(\varepsilon_G < 0\)) with strong damping, so that

\[
n_G \approx k_G \approx 1,\]

where \(n_G + ik_G = \sqrt{\varepsilon_G}\), provided that \(\omega \ll \gamma < \omega_p\). As can be seen from Eqs. (2)–(4), in our frequency range \(\omega \ll \gamma < \omega_p\) the dependence of the optical response on \(\omega_p\) and \(\gamma\)
disappears if the conductivity $\sigma \propto \omega_p^2/\gamma$ is kept constant. So, the only important parameters are the conductivity $\sigma$ and the thickness $h_G$ of the graphitized layer. The measurement of $h_G$ by a transmission electron microscope on a lamella that has been cut by a focused ion beam has shown a variation of thickness in the range from 350 to 580 nm. The thickness of the laser-induced graphitized layer depends on the orientation of certain grains of a polycrystalline diamond, as it was demonstrated recently by Salvatori et al.\textsuperscript{23} The obtained values of $h_G$ significantly exceed the value of 200 nm measured before\textsuperscript{7} by subtracting the depths of the crater before and after removal of the graphitized layer by thermal annealing. This disagreement can be explained by inefficiency of thermal oxidation to completely remove the modified layer from a diamond surface.

In our modeling of the optical properties, the parameter $\sigma$ was fitted and assumed to be the same for both continuous graphitized area and the grid. Then, the best fit of the calculated transmission spectra to the experiment was achieved for $h_G = 580$ nm in the case of continuous graphitized area and $h_G = 350$ nm for the grid, which corresponds to the maximum and minimum values, respectively, of the graphitized layer thickness in the transmission electron microscope measurements described earlier.

Figure 1 displays the comparison of measured\textsuperscript{7} and calculated transmittance spectra ($T_{\text{exp}}$ and $T$, respectively) for normal THz emission incidence of a diamond plate of thickness $h_D = 580$ µm, covered by a homogeneous graphitized film of thickness $h_G = 580$ nm. For completeness, we also show in Fig. 1 the calculated reflectance ($R$) and absorbance ($A$) spectra. However, for the quantitative analysis, the experimental transmittance spectra are sufficient. The main feature of the measured as well as calculated transmissivity spectra are well defined Fabry-Perot oscillations because of multiple reflections from the both diamond substrate surfaces due to sample transparency. It is seen that the agreement between the numerical calculation and measurement is quite reasonable and the best fit gives $\sigma \approx 305$ $\Omega^{-1}$cm$^{-1}$. In order to check this value, we have measured the DC conductivity using the standard four-contact method in the case of graphitized surface and two-contact method in the case of grating. The measured values were $\sigma_{2D} \approx 200-250$ $\Omega^{-1}$cm$^{-1}$ for the homogeneous graphitized 2D film (assuming the film to be 580 nm thick) and $\sigma_{1D} \approx 390-430$ $\Omega^{-1}$cm$^{-1}$ (assuming the graphitized 1D ribbons to be 15 µm wide and 350 nm thick). The best fitted optical value of $\sigma = 305$ $\Omega^{-1}$cm$^{-1}$ lies between these estimates, which seems to be quite reasonable. A difference of the measured conductivity of the graphitized film and ribbon may be attributed to the fact that their thickness is strongly fluctuating. In the case of ribbons, additionally, their width is fluctuating. The ribbons’ width of 15 µm is comparable with the size of diamond grains, which is in the range of 10–50 µm.

The metallic optical response of the graphitized diamond ensures that the graphitized grid on top of the diamond is expected to work as a linear metallic grid polarizer, which is demonstrated here. The scheme of our structure is depicted in Fig. 2(a), where two periods of the grid structure along the $x$ direction are shown schematically. The period of the grid and width of graphitized ribbons are $p = 30$ µm and $w = 15$ µm, respectively. In order to check these parameters, we characterized the spatial profile of our structure by the white-light interference profilometer Zygo [see the red curves in Fig. 2(a)] and a three-dimensional profile in Fig. 2(b). Such measurements have shown that the graphitized

FIG. 1. Calculated spectra of transmittance $T$, reflectance $R$, and absorbance $A$ (red solid, blue dashed, and green dashed-dotted lines, respectively) of a diamond plate with a homogeneous graphitized film of thickness $h_G = 580$ nm, in comparison with the measured transmission spectra $T_{\text{exp}}$ (black dots). The thickness of diamond is $h_D = 578$ µm in simulation and $580 \pm 2$ µm in the experiment.

FIG. 2. (a) Schematic cross section of the diamond/graphite grid (black dashed-dotted lines) and a typical result of the measurement of the groove depth by means of the white light interference profilometer Zygo (red solid line). Two periods of the structure are shown. (b) Profilometer-measured topographic map of a typical part of the graphitized grating structure. It shows that the graphitized ribbons are immersed deep into the diamond by about 0.8 µm, in agreement with the results of our numerical analysis of their optical response (see in the text below).
ribbons are buried below the level of the untreated surface of the diamond. A part of the graphitized layer can be removed due to the laser-induced ablation, thus forming a groove. The depth of grooves $d$ appeared to be about 800 nm, according to our profilometer measurements, which is in agreement with our spectra fitting, see below.

We simulate the electromagnetic response of the structure with graphitized ribbons assuming their thickness to be $h_G = 350$ nm. The results of the numerical fit of transmittance spectra for the grid polarizer for parallel (s-) and perpendicular (p-) polarization of the incoming beam relative to the ribbons is presented in Fig. 3. One can see quite a good agreement between the simulated and measured spectra in this case. The increase in the spread of experimental data in the frequency range of 36–37 cm$^{-1}$ is due to a decrease in the signal-to-noise ratio in the water vapor absorption bands in the atmosphere.

Note that this nice agreement between the measured and simulated transmittance is achieved assuming the depth of the grooves equal to $d = 800$ nm. Figure 4 shows the comparison of the measured and calculated transmission spectra in linear polarization perpendicular to the grid for the cases of $d = 0$ (panel a) and $d = 2$ µm (panel b). It is seen that, indeed, the agreement worsens, and the value 800 nm is the best fit. It should be mentioned that this value is in agreement with the profilometer data shown in Fig. 2.

For comparison, the simulation of the electromagnetic response of the grid with $h_G = 580$ nm is presented in Fig. 5. The difference between the measured and calculated transmittance spectra is reasonably small for p—polarization. However, for s—polarization the simulated transmissivity spectrum lies below the measured one in all the experimental range. Of course, the degree of polarization (DOP) in the graphitized diamond grid cannot be made so high as in the conventional metal grid polarizers due to a lower conductivity of laser graphitized diamond compared with that of typical metals. However, free standing wire grids are not suitable for applications in strong fields, and diamond-based structures can show a better optical strength. The maximum observed DOP $= (T_{TM} - T_{TE})/(T_{TM} + T_{TE})$ was 54% in our graphitized diamond structure, but it can be raised up by optimizing the structure. For example, as can be seen from the calculated transmissivity in Fig. 5, a simple increase in the graphitized ribbon thickness

![](image1.png)

**FIG. 3.** (a) Calculated spectra of transmittance $T$, reflectance $R$, and absorbance $A$ (red solid, blue dashed, and green dashed-dotted lines, respectively) in linear polarization perpendicular to the graphitized grid, in comparison with the corresponding measured transmission spectra $T_{exp}$ (dots). The period of the grid and width of graphitized ribbons, used in our numerical simulation, are $p = 30$ µm and $w = 15$ µm, respectively. The thicknesses of diamond and graphite parts of the grid and depth of the groove are $h_D = 573$ µm, $h_G = 350$ nm, and $d = 800$ nm, respectively. (b) Same as in panel (a) but for polarization parallel to the grid.

![](image2.png)

**FIG. 4.** (a) Same as in Fig. 3(a), but without groove on the surface ($d = 0$) in the numerical calculation. (b) Same as in Fig. 3(a), but for a deeper groove ($d = 2$ µm) in the numerical calculation.
from 350 to 580 nm raises DOP up to 71%. The last can be done by means of laser pulses with duration $l$ longer than was used in our experiments, because in this case the value of $h_G$ is proportional to $l^{1/2}$. To conclude, we developed a numerical model that allows us to describe and predict the electromagnetic properties of all-carbon metasurface structures. This model is in a good quantitative and qualitative agreement with the experiments for diamond/graphite polarizer, fabricated by laser direct-write.

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