Fluorination as Effective Method for Tuning the Electromagnetic Response of Graphene

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Fluorinated graphene (FG) has been obtained by a fluorination of thermally exfoliated graphite fluoride C_2F layers using a gaseous mixture of BrF_3 and Br_2 at room temperature. Comparative study of electromagnetic (EM) response of thin FG films after recovering their conductivity via different methods is presented in microwave (GHz) and terahertz (THz) frequency ranges. We discovered that fluorination can be used as promising tool for producing tunable EM interference (EMI) shielding materials, combining reflective and absorptive layers.

1. Introduction

Graphene is carbon two-dimensional honeycomb lattice demonstrating outstanding optical, electromagnetic and mechanical properties. Being "pristine," graphene is zero band gap semiconductor, which makes difficult to use it for AC applications, that is for the realization of graphene-based high-frequency ballistic devices as well as the design of graphene-based integrated circuits capable of fully utilizing its unique electronic properties. One of the simple ways to influence the electronic "fingerprints" of graphene, and thereby its electromagnetics, is chemical modification via oxidation,[1] hydrogenation,[2] and fluorination.[3] Next thermal decomposition of functional groups and intercalated molecules creates the pressure, which overcomes the Van der Waals attractions between the layers.[4]

Recently, we demonstrated that nano-thin conductive carbon and graphene films could be highly absorptive ability at certain thickness which is inversely proportional to their conductivity.[5–10] The idea of this communication is to present a tunable EMI shielding layer based on fluorinated graphene.

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Due to the possibility to open and more importantly to vary the band gap in graphene with covalent modification by means of fluorine, currently fluorinated graphene (FG) attracts huge interest for many practical applications. It is known that fluorographene, CF, is a dielectric material with an optical bandgap of 3 eV.[11] There are various methods for preparing FG such as treatment of the material in a gaseous atmosphere (F_2, XeF_2, BrF_3, ClF_3)[12] or plasma, fluorination at room temperature and atmospheric pressure in an aqueous solution of hydrofluoric acid (HF).[13]

In present work, it is demonstrated that the recovery of graphene film conductivity through the simple methods, that is chemical reduction of FG in hydrazine-hydrate vapour and heat treatment in vacuum leads to the changing of AC conductivity level and thereby to changing its EMI shielding ability.

2. Experimental

2.1. Materials

Few-layer graphene sample has been obtained by a thermal expansion of a bromine intercalation graphite fluoride compound in a quartz reactor at 800 °C in ambient atmosphere. The temperature was chosen based on the thermal decomposition data for such kind of the fluorinated graphite compounds.[14] Detailed characterization of the exfoliated product is given in Ref. [15].

Fluorination of the graphene sample was conducted by BrF_3 vapors at room temperature. Graphene powder was put in a Teflon flask with perforated wall and placed in a hermetic Teflon reactor containing solution of BrF_3 (10 vol.%) in Br_2 for several days. Thereafter, the flask content was dried in a nitrogen flow to remove the non-reacted species. This fluorination procedure gives the samples with an approximate C_2F composition.[16]

Scanning electron microscopy (SEM) with a LEO-1455 VP microscope was used for structural characterization of materials. SEM image of the obtained FG particles is presented in **Figure 1**.

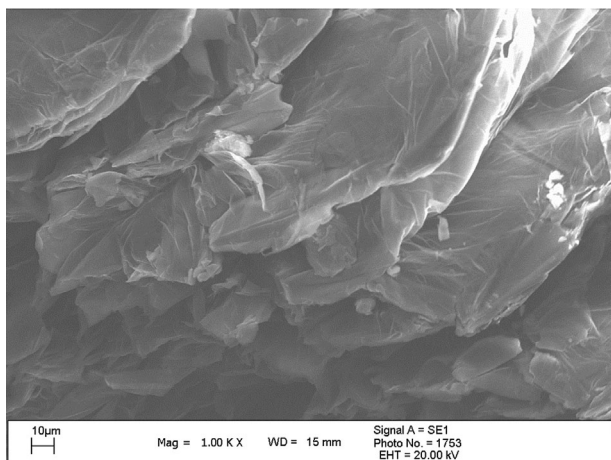### 2.2. FG Films Preparation and Characterization

FG powder was put into a vessel containing 20 ml of toluene and treated in an ultrasonic bath at 100 W and ambient temperature for 1 h. After ultrasonic treatment we obtained a

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Figure 1. SEM images of FG particles.

stable brown-colored FG suspension. Resultant concentration of FG in toluene was 0.2 mg ml^{-1}.

Thin FG films have been produced using spin-coating procedure. The prepared suspension was dropped onto the quartz substrate, which was rotated at 5000 rpm for 750 and 2250 s. In order to measure the EM properties in microwave frequency range using the very simple technique, the size of the quartz substrate was $7.2 \times 3.4 \times 0.5$ mm. The FG suspension easily spread over the surface of the substrate to form a thin continuous film (**Figure 2**).

There are several ways of recovering the conductivity of the modified non-conducting CF films such as irradiation by electron beam,[17] heat treatment in a vacuum and by the action of hydrazine-hydrate vapor.[18,19] In present work, in order to change the fluorine concentration the following two methods were used:

1. Chemical reduction was made by a direct treatment of FG films with 1% hydrazine-hydrate vapor during 10 min.
2. Thermal treatment of FG samples on dielectric substrates in a vacuum (10^{-6} Torr) at 550 °C for 10 min.

In order to investigate the influence of fluorine concentration and film thickness to the resulting EM response, the samples with two different thicknesses have been produced (denote as "thin" and "thick"). The film's thickness was measured by a stylus profiler (Veeco Instruments, Dektak 150, Tucson, AZ, USA) with an accuracy of 1.5 nm. The thickness was averaged over ten different points with the variation ± 3 nm (see **Table 1**).

To control the level of fluorine after each treatment the element analysis of films was carried out using energy-dispersive X-ray (EDX) spectroscopy. The EDX analysis detected 1.82 and 9.71 wt.% of fluorine in initial "thin" and "thick" FG films, respectively (Table 1). The content of fluorine in the films slightly decreased after the hydrazine-hydrate treatment and it dramatically decreased to 0.55 and 1.11 wt.%, respectively, after the film annealing.

Raman scattering was further used to analyze the quality of graphene layers. Measurements were performed by Raman spectrometer Nanofinder HE (LOTIS TII, Belarus-Japan) with a 600-lines mm^{-1} grating and 532-nm laser excitation. It is well known that three main futures are usually observed in
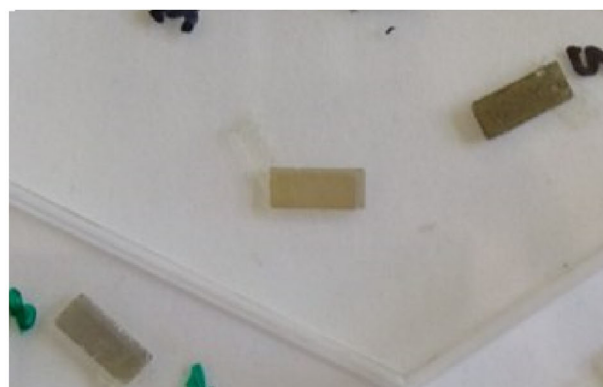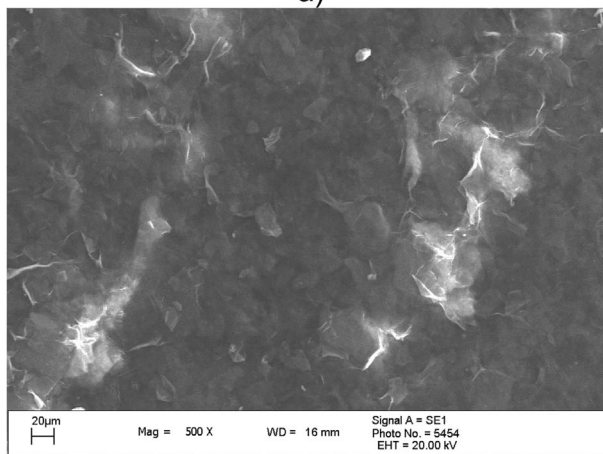
Figure 2. (a) Optical image of FG thin film on a quartz substrate. (b) SEM image of film's surface.

graphite-based materials: D and G bands located at ~1341 and ~1585 cm^{-1}, respectively, and 2D band located at ~2680 cm^{-1}. The Raman spectra of investigated samples after normalizing to the intensity of G band (~1585 cm^{-1}) are presented in **Figure 3**. Note, as it was demonstrated in Ref. [20], additionally, the weak shoulder D' (1620 cm^{-1}) band is usually observed in Raman spectra of fluorographene. This band indicates of a coexistence of conjugative carbon-carbon bonds and sp^3-hybridized carbon atoms covalently bonded with fluorine. As it can be seen, significant D band, associated with disorder-induced symmetry-lowering effects, is typical for FG. Let us note that not only defect regions contributed to the intensity of D band, its value also depends on the flake size.

The relevant quality of graphitic materials can be estimated using the intensity ratio of D band (I_D) and G band (I_G). In our case, before treatment, the ratio I_D/I_G is 0.98 and 1.02 for "thick" and "thin" samples, respectively, which means a decrease in the average size of the sp$_2$ domains upon reduction of FG. The relative intensity I_D/I_G increases up to 1.03 and 1.57 for "thick" and "thin" samples exposed to hydrazine-hydrate vapor. Note, in the case of "thin" film after annealing and hydrazine-hydrate treatment the intensity of the second-order 2D peak also increases indicating the evolution of the structural and electronic properties of our samples.

Table 1. Fluorine concentration of FG films and their AC conductivity (at 600 GHz)[a].

Thickness (nm)	F (wt.%), before treatment	F (wt.%), after annealing	F (wt.%), after treatment with HH	σ_{AC} (10^3 S m^{-1}), after annealing	σ_{AC} (10^3 S m^{-1}), after treatment with HH
50	1.82	0.55	1.73	40.05	44.40
120	9.71	1.11	6.87	89.01	28.93

[a] No significant frequency dependence in a wide frequency range was observed (30 GHz–1 THz), which is inherent to all graphene-like samples (see Ref. [10]).

2.3. Electromagnetic Characterization

The microwave measurements were carried out by scalar network analyzer R2-408R (ELMIKA, Vilnius, Lithuania) in 26–37 GHz frequency range (Kα-band). The EM response of investigated samples was measured as ratio of transmitted/input (S_{21}) and reflected/input (S_{11}) signals. The experimental setup is described in details in previous work.[5] Reflection (R), transmission (T), and absorption (A) are calculated from the measured S-parameters as $R = S_{11}^2$, $T = S_{21}^2$, $A = 1 - T - R$. The THz transmission spectra are collected with THz time-domain

Figure 3. Raman spectra before and after treatments of (a) "thin" FG films and (b) "thick" FG films. All spectra were normalized on the intensity of G band. Fluorescent background was subtracted from the spectra.

spectrometer T-SPEC Ekspla (Lithuania). The measurements details can be found in Ref. [9].

3. Results and Discussion

As it follows from our undertaken study the frequency-dependence of measured S-parameters for FG films does not show any features, for example, absorption peak or strong frequency dependence within the selected frequency range, therefore all results are presented at one frequency (30 GHz).
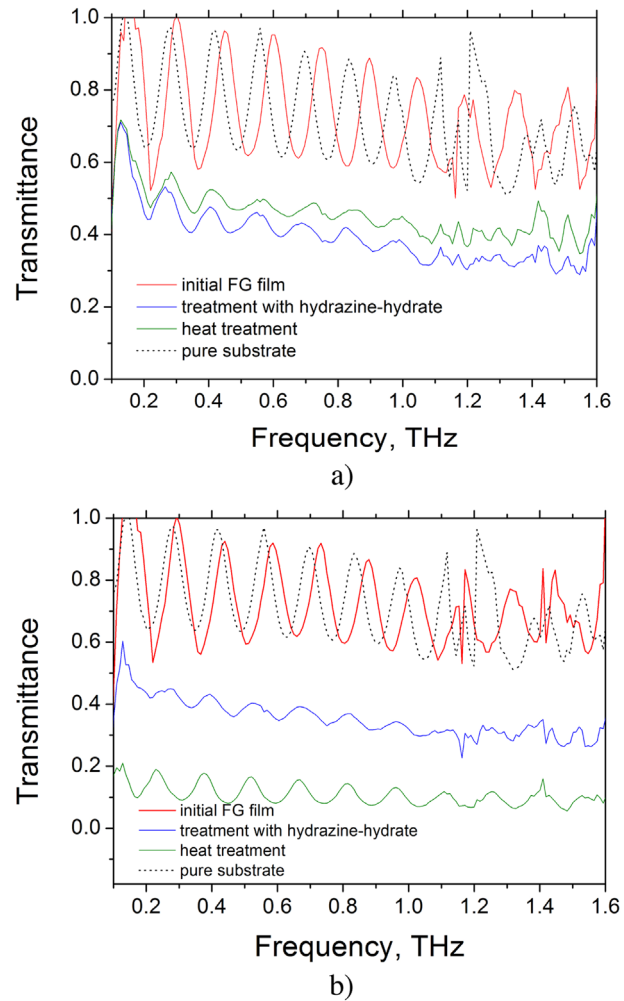
As one can see from **Figure 4**, the FG films before treatment are almost transparent for microwave radiation ($T \sim 75\%$ and $T \sim 78\%$ for films with thickness 50 and 120 nm), whereas after treatment with hydrazine-hydrate vapor the transmission coefficient (T) decreases to the level 62 and 54% for "thin" and "thick" samples, respectively. Such behavior can be explained by an increase of the absorption ability (A) of such structures. In particular, the absorptance of "thick" films increases up to 30% after treatment with hydrazine-hydrate and up to 35% after annealing.

In contrast, after 10 min annealing in vacuum the transparency decreases up to 59 and 18% for films with thickness 50 and 120 nm, respectively. The main contribution to the EM attenuation comes from reflection. Moreover, sample with larger thickness provides the higher reflectance ability ($R \sim 48\%$). At the same time, the absorption of EM radiation is also significant (22 and 34% for "thin" and "thick" films, respectively). This indicates that after some annealing time a transition to the conductive state is observed, indicating a change in the fluorination degree of samples (its decreasing). On ist turn, it means that graphitic regions with different defects are formed after annealing because of removal of fluorine atoms. As it was already mentioned in the introduction section, for every conductive material there is the optimal thickness, which is inversely proportional to its conductivity for which 50% of absorption might be achieved. The larger the conductivity, the smaller the thickness, which is necessary for 50% absorption. For instance, for CVD graphene of average quality one needs 4–7 layers,[8,9] that is 10–15 nm in thickness; the optimal thickness for graphite is 100 nm,[6] for pyrolytic and glassy carbon it corresponds to 75 nm.[6,10] Since for 120 nm film of FG 34% of absorption is reached, it means that optimal thickness is approx. 160 nm, and conductivity of annealed FG is slightly smaller than conductivity of graphite.

The transmittance of FG films on quartz substrate in THz frequency range is presented in **Figure 5**. For comparison, the transmittance spectrum of pure quartz is also presented (dot curve). It is important to note that the observed frequency dispersion is due to the effect of interference on a quartz substrate and small shift of interference peaks is related to the difference in thickness of quartz substrate. Some absorption
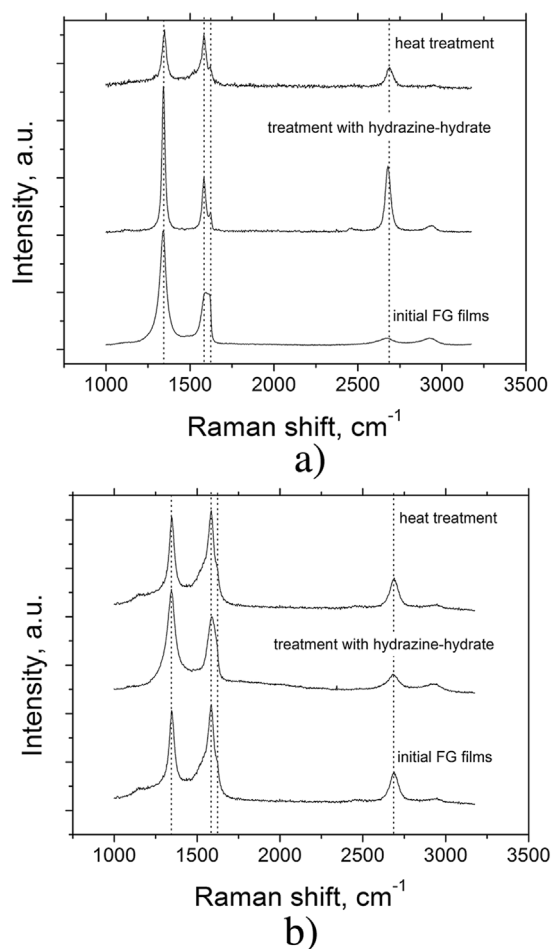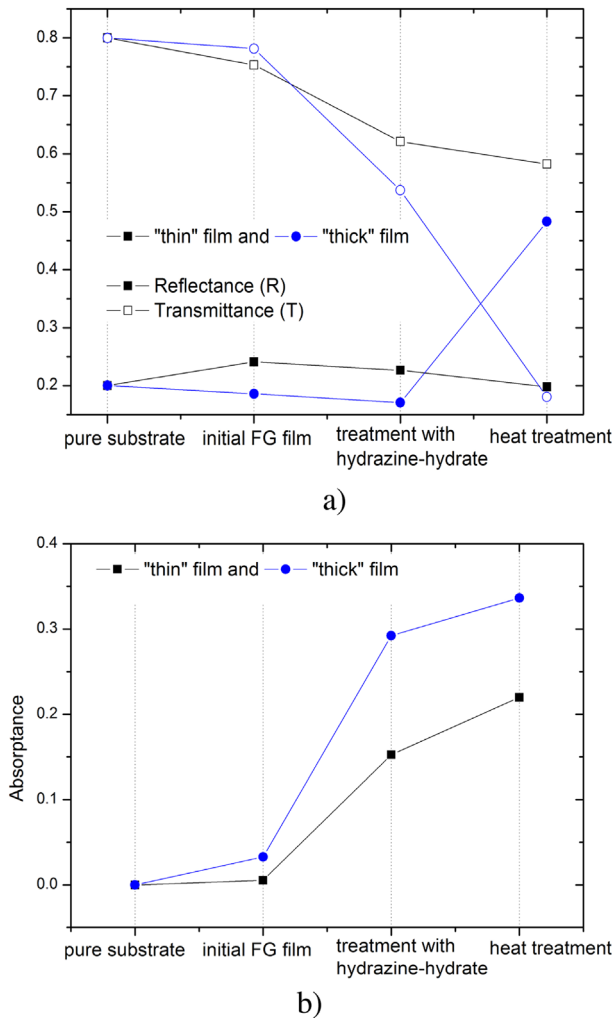
Figure 4. Reflectance (R), transmittance (T) (a) and absorptance (A) (b) of "thin" and "thick" FG films at 30 GHz after the film annealing in vacuum and treatment with hydrazine-hydrate vapor.

Figure 5. Terahertz transmittance spectra of "thin" (a) and "thick" (b) FG films before and after treatment.

feature, close to 1.1 THz, is observed in transmission of initial FG films and film treated with hydrazine-hydrate, corresponding to the residual water, presented in these samples, peculiarities, whereas at heat treated samples they disappear together with water removal due to the annealing.

As it follows from Figure 5, initial FG film is transparent for THz radiations (~80%) that indicate the dielectric properties of such kind materials. At the same time, the annealing of "thick" FG film leads to strong reduction of the transmittance level from 80 up to 10%. For samples after treatment with hydrazine-hydrate vapor the transmission coefficient is reduced up to 40%. It should be noted that the effect of hydrazine-hydrate treatment does not dependent on the film thickness which indicates that only surface layer of films is reduced in this way. This conclusion is in agreement with EDX results (see Table 1).

The effective thin films conductivity (see Table 1) was extracted from the experimental data using the procedure

detailed elsewhere.[6,21] In the numerical calculation, the dielectric permittivity of pure quartz was set as $3.8 + 0.025i$. As it was mention above, the initial FG films are transparent for microwave and THz radiation which, in turn, results in calculations difficulties to extract precisely the dielectric permittivity of such films with pronounced dielectric properties (for conductive film of the same thickness the absorption would be significant, see Ref. [10] for the task statement details).

From comparison of the calculated results and film's elemental analysis the following conclusion can be made:

- Annealing of FG leads to more effective reduction of such kind of material and development of conductive surface layer.
- Hydrazine-hydrate can be used as a reductant, but the effectiveness of such a treatment depends on the film thickness. In particular, the conductivity of "thin" film is the same after annealing and hydrazine-hydrate treatment. In contrast, in case of "thick" films the conductivity of samples after annealing increases three times.

4. Conclusions

We demonstrated that using various methods of recovering the conductivity of thin FG films by regenerating graphene from graphene fluoride, such films can provide different levels of absorption/reflection of EM signal. These characteristics can be easily changed by varying the films thickness or treatments duration, providing a way to tune the electromagnetic characteristics at microwave and THz frequency ranges. Summarizing, we can conclude that along with polymer composites comprising graphene (see Ref. [21–23]), such thin films can be very suitable materials for producing effective absorbers, electromagnetic shielders, for design of high-frequency power detectors and sensors for microwave and THz radiations.

Conflict of Interest

The authors declare no conflict of interest.

[1] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228.

[2] D. C. Elias, R. R. Nair, T. M. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, K. S. Novoselov, *Science* **2009**, *323*, 610.

[3] R. R. Nair, W. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H.-M. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N. Grigorenko, K. S. Novoselov, A. K. Geim, *Small* **2010**, *6*, 2877.

[4] M. Cai, D. Thorpe, D. H. Adamson, H. C. Schniepp, *J. Mater. Chem.* **2012**, *22*, 24992.

[5] P. Kuzhir, A. Paddubskaya, S. Maksimenko, T. Kaplas, Yu. Svirko, *Nanoscale Res. Lett.* **2013**, *8*, 60.

[6] K. Batrakov, P. Kuzhir, S. Maksimenko, A. Paddubskaya, S. Voronovich, T. Kaplas, Yu. Svirko, *Appl. Phys. Lett.* **2013**, *103*, 073117.

[7] P. Kuzhir, N. Volynets, S. Maksimenko, T. Kaplas, Yu. Svirko, *J. Nanosci. Nanotechnol.* **2013**, *13*, 5864.

[8] K. Batrakov, P. Kuzhir, S. Maksimenko, A. Paddubskaya, S. Voronovich, P. Lambin, T. Kaplas, Yu. Svirko, *Sci. Rep.* **2014**, *4*, 7191.

[9] K. Batrakov, P. Kuzhir, S. Maksimenko, N. Volynets, S. Voronovich, A. Paddubskaya, G. Valusis, T. Kaplas, Yu. Svirko, P. Lambin, *Appl. Phys. Lett.* **2016**, *108*, 123101.

[10] P. Kuzhir, A. Paddubskaya, N. Volynets, K. Batrakov, T. Kaplas, P. Lamberti, R. Kotsilkova, Ph. Lambin, *J. Nanophoton.* **2017**, *11*, 032504.

[11] L. G. Bulusheva, A. V. Okotrub, Electronic structure of fluorinated graphene. *New Fluorinated Carbons: Fundamentals and Applications*, Eds: O. V. Boltalina, T. Nakajima. Elsevier, Amsterdam, **2017**, pp. 177–213.

[12] D. E. Ibbotson, J. A. Mucha, D. L. Flamm, *J. Appl. Phys.* **1984**, *56*, 2939.

[13] N. A. Nebogatikova, I. V. Antonova, V. Ya. Prinz, I. I. Kurkina, V. I. Vdovin, G. N. Aleksandrov, V. B. Timofeev, S. A. Smagulova, E. R. Zakirov, V. G. Kesler, *Phys. Chem. Chem. Phys.* **2015**, *17*, 13257.

[14] Yu. V. Fedoseeva, A. V. Okotrub, I. P. Asanov, D. V. Pinakov, G. N. Chekhova, V. A. Tur, P. E. Plyusnin, D. V. Vyalikh, L. G. Bulusheva, *Phys. Status Solidi B* **2014**, *251*, 2530.

[15] L. G. Bulusheva, V. A. Tur, E. O. Fedorovskaya, I. P. Asanov, D. Pontiroli, M. Ricco, A. V. Okotrub, *Carbon* **2014**, *78*, 537.

[16] A. V. Okotrub, N. F. Yudanov, I. P. Asanov, D. V. Vyalikh, L. G. Bulusheva, *ACS Nano* **2013**, *7*, 65.

[17] I. P. Asanov, A. V. Okotrub, A. V. Gusel'nikov, I. V. Yushina, D. V. Vyalikh, L. G. Bulusheva, *Carbon* **2015**, *82*, 446.

[18] A. V. Okotrub, K. S. Babin, A. V. Gusel'nikov, I. P. Asanov, L. G. Bulusheva, *Phys. Status Solidi B* **2010**, *247*, 3039.

[19] M. A. Katkov, V. I. Sysoev, A. V. Gusel'nmikov, I. P. Asanov, L. G. Bulusheva, A. V. Okotrub, *Phys. Chem. Chem. Phys.* **2015**, *17*, 444.

[20] V. Gupta, T. Nakajima, Y. Ohzawa, B. Žemva, *J. Fluor. Chem.* **2003**, *120*, 143.

[21] A. Paddubskaya, N. Valynets, P. Kuzhir, K. Batrakov, S. Maksimenko, R. Kotsilkova, H. Velichkova, I. Petrova, I. Biro, K. Kertesz, G. I. Mark, Z. E. Horvath, L. P. Biro, *J. Appl. Phys.* **2016**, *119*, 135102.

[22] P. Kuzhir, A. Paddubskaya, A. Plyushch, N. Volynets, S. Maksimenko, J. Makutkevic, I. Kranauskaite, J. Banys, E. Ivanov, R. Kotsilkova, A. Celzard, V. Fierro, J. Zicans, T. Ivanova, R. Merijs Meri, I. Bochkov, A. Cataldo, F. Micciulla, S. Bellucci, P. Lambin, *J. Appl. Phys.* **2013**, *114*, 164304.

[23] I. Kranauskaite, J. Macutkevic, P. Kuzhir, N. Volynets, A. Paddubskaya, D. Bychanok, S. Maksimenko, J. Banys, R. Juskenas, S. Bistarelli, A. Cataldo, F. Micciulla, S. Bellucci, V. Fierro, A. Celzard, *Phys. Status Solidi A* **2014**, *211*, 1623.