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# Fluorinated graphene suspension for inkjet printed technologies

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#### Abstract

The possibility to control the size of the flakes of graphene suspension in the course of their fluorination in an aqueous hydrofluoric acid solution was demonstrated. The effect of the suspension composition, the fluorination time, temperature and thermal stress on the fragmentation process was investigated. The corrugation of suspension flakes, which occurs at fluorination due to a difference in the constants of graphene and fluorographene lattices, leads to the appearance of nonuniform mechanical stresses. The fact that the flake size after fragmentation is determined by the size of corrugation allows the assumption that the driving force of fragmentation is this mechanical stress. This assumption is confirmed by the break of the corrugated layers from flakes under thermal stress. Moreover, fluorination treatment at elevated temperatures (~70 °C) significantly accelerates the fragmentation process. Suspensions of fluorinated graphene with nanometer size flakes are of interest for the development of 2D ink-jet printing technologies and production of thermally and chemically stable dielectric films for nanoelectronics. The printed fluorinated graphene films on silicon and flexible substrates have been demonstrated and the charges in metal–insulator–semiconductor structures have been estimated as the ultra low values of  $(0.5-2) \times 10^{10}$  cm<sup>-2</sup>.

Keywords: fluorinated graphene, graphene suspension, inkjet printed technology, fragmentation process, printed fluorinated graphene films, Ultra LOW charge, silicon and flexible substrates

(Some figures may appear in colour only in the online journal)

#### Introduction

Recently 2D printing technologies have been extended to create the intelligent components and smart systems of printed electronics, such as sensors, thin films transistors, memories, electronic displays, batteries, micro-mechanical systems and other devices of modern electronics [1–5]. Printing processes have attracted great attention due to such features as mask-free patterning, purely additive operation, compatibility with versatile materials, low cost, flexible substrates and scalability to large-area manufacturing.

Printing with inks based on graphene and its derivatives has great potential for applications due to the higher stability of such materials, variable conductivity and high carrier mobility even in the films, obtained from suspensions, the ability to create highly conductive transparent elements, and other unique properties. The choice of printed material is mainly determined by the required physical properties of the printed pattern, such as resistivity, optical transparency, stability to bending and adhesion, etc. Graphene, its derivatives and another 2D materials provide a wide spectrum of properties from conductors to dielectrics [6–9]. In the present study, we have considered graphene based derivatives for dielectric layers or dielectric layers with quantum dots.

Graphene quantum dots (QD, flakes with sizes 1–10 nm) are chemically inert, and when introduced in living cells have good solubility and low toxicity; they are also characterized by stable photoluminescence and good adhesion to various

surfaces [10, 11]. This combination of properties makes them promising for use in optoelectronic devices, sensors, and as markers to visualize biological processes and disease diagnostics (bioimaging). The most commonly used process for obtaining quantum dots is graphene fragmentation at oxidation.

Graphene oxide (GO) is the most known graphene dielectric derivative. The advantages of GO-ink include a wellestablished and cheap technology for GO-suspension production, stability of suspensions in water, the ability to create thin dielectric films and to reduce the graphene oxide to obtain conductive films. The disadvantage of GO is the instability of its properties, when heating over 100 °C or current flow lead to graphene oxide reduction [12–14].

Unlike graphene oxide, fluorographene is the most stable graphene based derivative, with good insulating properties, low dielectric constant ( $\varepsilon = 1.2$ ) [15, 16] and low charge density (~5  $\times$  10<sup>10</sup> q cm<sup>-2</sup>) in the film and at the interface with silicon and other semiconductor substrates [15]. The structural and electronic properties of fluorinated graphenelike systems may be tuned by controlling the fluorination degree, they were studied by the first-principle calculations [17, 18]. The prospective properties make fluorinated graphene very promising for dielectric and protected coatings. Previously, we have found it possible to create partially fluorinated graphene flakes by means of suspension treatment in the aqueous solution of hydrofluoric acid (HF) [15]. Moreover, we have detected a significant reduction in the size and thickness of the graphene flakes during the fluorination process [15].

Printed technologies require thin (one or a few monolayers) and small (lateral size of 50–400 nm) graphene flakes; and the particle size should be approximately 50 times smaller than the diameter of the printer nozzle [5, 19, 20]. The lateral size of flakes in suspensions can be reduced by centrifugation and filtration [21]. However, these procedures significantly reduce the overall concentration of flakes in solution. Therefore, the search for new ways to create suspensions with nanometer flakes of graphene, including other types of modified graphene (dielectric derivatives), is necessary for the development of 2D ink-jet printing technologies.

In this work, we study the influence of technological parameters (content of graphene in suspension, flake size, temperature) on splitting and fragmentation of the graphene flakes during their fluorination. The mechanism is found to be based on the appearance of corrugated surfaces due to fluorination, and, as a consequence, non-uniform mechanical stresses. The non-uniform mechanical stresses result in consistent breaking of the corrugated elements from flakes (formation of small 20–80 nm fragments) and formation of cracks in the large flakes. First, the printed insulating films on silicon and flexible substrates and in metal–insulator–semiconductor structures from fluorinated graphene are demonstrated and characterized.



**Figure 1.** Photographs of pristine and fluorinated graphene suspensions (a) and the fluorinated graphene inks used for printing (b).

#### Samples preparation and research methodology

The objects of our study were the graphene suspensions and thin films from these suspensions, deposited on a silicon substrate. Graphene suspensions were obtained with the use of organic solvent dimethylformamide (DMF) and ultrasound treatments [22, 23]. The used suspensions had composition from 0.5 to 3 mg ml<sup>-1</sup> of graphene in the DMF.

To fluorinate the suspension treatments in 3% aqueous solution of hydrofluoric acid (HF) were used [15, 25]. We have taken the same volumes of the suspension and the HF solution for fluorination. The proof that this treatment really leads to fluorination of the graphene and multigraphene flakes is presented in [15, 25–27]. The evidences of fluorination are based on the reversible transition from conductive to insulating state, the high temperature stability (~450 °C), the vanishing of all peaks in Raman spectra, the dielectric constant 1.2 for films from fluorinated suspension, the appearance of C-F and C<sub>2</sub>-F related peaks in x-ray photoelectron spectra, and the transparency of fluorographene suspension. These properties correspond to fluorinated graphene in contrast to oxide graphene. The transparency of fluorinated suspension is demonstrated in figure 1.

The characteristic time of fluorination was 60-80 days, after which the process of fluorination practically stopped. As a result a suspension with partially fluorinated flakes was obtained. Films from functionalized suspensions were created by applying drops of the suspension on the substrate. After applying the suspension on the substrate, the samples were dried, washed with deionized water to remove residual hydrofluoric acid and organic components of suspension and then re-dried to remove water. An aqueous solution of HF present in the suspension removed the natural oxide on the surface of the substrate. It is important to note that the aqueous solution of hydrophilic fluorinated graphene fairly spreads on the surface of silicon, whereas almost all DMF remained in the area of the drop application. As a result it was possible to divide the region of localization of DMF and films of fluorinated graphene and to obtain thin (10-40 nm) continuous films of fluorinated graphene on a silicon surface [15].

For electrical measurements, contacts to films were created by silver alloy coating or by gold sputtering. Consequently, structures of metal-insulator-semiconductor (MIS)



**Figure 2.** AFM (a) and TEM (b), (c) bright-field images of films with different degrees of fluorination: (a) 10 days and (b), (c) 100 days of fluorinating treatment, respectively. Arrows in (a) mark flakes splitting. The arrow in (b) marks a layered separation of large flakes of arbitrary shape. (c) Crack in a large flake (marked by an arrow).

Au (Ag)/fluorinated graphene/Si were obtained, and properties of the fluorinated graphene as a dielectric film were examined.

To study the properties of the samples the following experimental methods were used: atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and measurements of capacitance-voltage characteristics. The scanning microscope Solver PRO NT-MDT was used to obtain AFM images of the film surfaces, to determine their thickness and to study the structure. AFM measurements were performed in contact and semicontact modes. To produce images of the surface we used the scanning electron microscope JEOL JSM-7800F; the primary electron energy was 2 KeV. Structural characteristics of the films were studied using transmission electron microscope JEM-2200FS with accelerating voltage of 200 kV. For capacitance-voltage measurements the E7-20 immitance meter was used.

#### Functionalization of graphene suspension flakes

Using microscopy (SEM, TEM and AFM) we investigated the evolution of the surface of films, created from suspensions, and variation of the characteristic flake size in suspension, depending on fluorination time, and composition of fluorinating solution. As a result, we have identified the key factors of controllable reduction of the flake size and, thus, modification of the physical parameters of films, fabricated from suspension.

It should be emphasized that the original (prior to fluorination) size of the suspension flakes according to the AFM was  $0.5-1.5 \mu$ m, the thickness of the flakes varied within the range from a monolayer (0.35 nm) to 70 nm, and a large number of flakes had a thickness of more than 20 nm. Treatments in an aqueous solution of hydrofluoric acid led to a gradual decrease in the thickness and size of the flakes in suspension. Figure 2(a) presents the image of the film surface at the initial stage of fluorination. Splitting of medium-sized

flakes into plates with thickness of 2–3 monolayers is clearly seen.

TEM study of the film structure was realized after suspension deposition onto the mirror surface of the foil, preprepared by chemical etching of standard silicon substrate that was epi-ready. Figures 1(b) and (c) show bright-field images of the flakes, observed in the film of fluorinated suspension with treatment duration of ~100 days. This suspension is characterized by a nonuniform distribution of flakes along the surface of the substrate and the predominance of flakes with sizes up to 70 nm in the clusters. In such clusters, sites with clear layering are often observed (figure 2(b)). Relatively large flakes have the form of polyhedra with sharp straight edges, formed by splitting the particle along cracks into smaller pieces (figure 2(c)). However, in the film there are fine flakes with circular shape and lateral sizes of ~20 nm.

SEM and AFM studies show that the thickness of films, obtained from 100  $\mu$ l of the suspension deposited by the drop on the silicon substrate, decreases with increasing fluorination time: 150 nm after 25 days; 80 nm after 40 days; 60 nm after 60 days. The surface relief of the films also decreased accordingly from 70 nm to 2 nm. The change of the films' relief, as follows from AFM data, is primarily due to the decrease of the characteristic thickness of the suspension flakes.

Figures 3(a)-(c) show images of films of fluorinated suspensions with difference graphite content (from  $0.04 \text{ mg ml}^{-1}$  to  $0.3 \text{ mg ml}^{-1}$ ) after 100 days of fluorination. For a film of suspension with graphite content of  $0.04 \text{ mg ml}^{-1}$  we could observe a network of corrugated areas with the width of the network lines of 40-80 nm. As a result, the suspension flakes are separated by a network into the regions with dimensions of 200-400 nm. Figure 3(b) shows the most effective fragmentation of the lakes, when breakage of the suspension elements into flakes of two sizes of 200-400 nm and 20-80 nm occurs. Larger flakes are visible in the figure, and smaller ones form the lower sublayer in the film and are clearly visible in the area closer to the edge of the film, obtained from drop. Further increase in the concentration of graphite in suspension leads to the formation of fully corrugated surfaces of the flakes (figure 3(c)). Nanorelief is



**Figure 3.** (a)–(c) AFM images of the surface of fluorinated graphene films from the suspensions with different graphite content after 100 days of fluorination: (a) 0.04 mg ml<sup>-1</sup>, (b) 0.12 mg ml<sup>-1</sup>, (c) 0.16 mg ml<sup>-1</sup>. (d) Efficiency of the suspension flakes fragmentation under mechanical stresses, depending on the graphite content (where *d* is the average size of flakes after fluorination,  $d_0 = 1.2 \mu$ m—the original average size of flakes). (e), (f), (g) Schematic representation of the fragmentation process. (h), (i) Dependence of the lateral size and thickness of multilayered graphene flakes in suspension with optimum composition of 0.16 mg ml<sup>-1</sup> on fluorination time.

formed during fluorination due to the difference in the value of constants of fluorographene and graphene lattice ( $\sim 1\%$ ) [28], when with increasing degree of fluorination the mechanical stresses accumulate, deforming the fluorinated layers and forming a corrugated surface. At that, fragmentation of flakes practically does not occur, however it is possible in case of additional mechanical or thermal influence on the suspension (see below).

The efficiency of splitting was assessed by the comparison of particle sizes before and after fluorination  $d_o/d$ . Figure 3(d) shows the dependence of  $d_o/d$  on the mass content of graphene flakes in fluorinated suspension. The appearance of the maximum in figure 3(d) corresponds to the suspension with graphite content of 0.12 mg ml<sup>-1</sup>. For the selected composition with the most effective process of flakes fragmentation the change of the particle size was investigated depending on the time of fluorination. Figures 3(e), (f), (g) give schematic representation of the fragmentation process which leads to appearance of flakes with lateral size of 20–80 nm. We have also suggested that the repeated fragmentation within the corrugated network during fluorination leads to segmentation of flakes on the parts with dimensions of 200–400 nm inside the network. Segmentation most likely proceeds through cracks formation in the network lines with reduced thickness.

Figures 3(h), (i) show the dependence of the lateral size of the flakes and their thickness on fluorination time for the composition of  $0.12 \text{ mg ml}^{-1}$ . It is seen that the process of flakes fragmentation may be divided into several stages—up to 20 days, from 20 to 80 days and over 80 days. These intervals correlate with changes in electrical properties of the films, obtained from suspensions. About 20 days' treatment was required for the transition of films from a conducting to insulating state that was determined by reaching a constant

**Table 1.** Specific values of fixed charge density  $Q_{\rm f}$ , calculated on the flat band voltage, determined from the capacitance-voltage characteristics and the state density  $D_{\rm it}$  at the interface with silicon, obtained from the difference between the middle-gap and flat band voltages.

Substrate	Time of HF treatment	20 days	40 days	60 days	80 days	150 days
Si Si	$Q_{\rm f},  {\rm cm}^{-2}$ $D_{\rm it},  {\rm cm}^{-2}$	$(5-6) \times 10^{11}$ $(3-5) \times 10^{11}$	$\begin{array}{c} 1  \times  10^{11} \\ 5  \times  10^{10} \end{array}$	$5 \times 10^{10}$ (1-3) × 10 <sup>10</sup>	$\begin{array}{c} (26) \times 10^{10} \\ 2 \times 10^{10} \end{array}$	$(5-7) \times 10^{10}$ $(3-5) \times 10^{10}$

capacitance in the mode of accumulation of main carriers in the semiconductor at capacitance-voltage measurements (formation of metal-insulator-semiconductor structures). During fluorination for 20 to 80 days the insulating properties of the films improved. According to the measurement of voltampere and capacity-voltage characteristics, in this time interval of the suspension treatment, there was a decrease of the drain current through the films and the charge density in the films and at the interface with the silicon substrate. Further increase of treatment time in the aqueous HF solution (over 80 days) resulted in some degradation of film properties: (weak increase in current through the films and the value of charges in the film). According to XPS after 80-100-days fluorination, oxidation of flakes begins. Table 1 presents the values of the charge density in the film Qf and at the interface D<sub>it</sub> with silicon. As it may be inferred from the table, the minimum values are observed during the fluorination within 60-80 days. Increase in thickness of the films obtained from fluorinated suspension (repeated applying of suspension drops on the substrate) did not lead to an increase in charges. It should be also noted that the values  $\sim 5 \times 10^{10} \,\mathrm{cm}^{-2}$  are extremely low values of the charges in the dielectric films that make fluorinated films attractive for use in modern micro- and nanoelectronics.

As it is obvious from figures 3(h), (i), in the first stage of fluorination of graphene suspensions there is the most intense breakdown of the flakes, and the specific rate of the flakes splitting is ~16.3 nm day<sup>-1</sup>, whereas the speed of reduction of the lateral dimensions is  $34.5 \text{ nm day}^{-1}$ . With increasing degree of fluorination, the size and thickness of flakes stop changing, i.e. the process of breakdown almost stops. This may be due to the fact that for the breakdown of the flakes there is a need in mechanical stresses that are higher than that in the crushed flakes. According to XPS data, with increasing treatment time (over 80 days) the process of oxidation, leading to further reduction of the lateral size of the suspension flakes, becomes visible. The particles' thickness at oxidation, as it is seen in figure 3(i), does not change.

#### Factors determinant for suspension fragmentation

In the course of the study the influence of the following factors on the degree of fragmentation and the rate of the suspension flakes' fluorination was investigated: utilization of a suspension centrifugation (change in initial size and amount of flakes and possible introduction of defects), temperature of fluorination process and additional treatment (non-stationary thermal effects). It is important to note that heating and suspension centrifugation may produce mechanical stresses accelerating the fragmentation process in suspensions flakes.

#### Effect of the suspension centrifugation

To study the influence of initial size of flakes on the rate of the fluorination the suspension was centrifuged. During centrifugation defects can also be formed in large flakes. The rotation frequency of the drum in the experiment was  $\sim 10\,000$  rpm, which allowed separating the finer flakes for fluoridation. It was found that the centrifugation of flakes leads to acceleration of the fluorination and fragmentation processes. AFM and SEM-images of the surface in figure 4 were obtained on the films from the suspension, subjected to centrifuging for 15 min and 30 min. Increase of centrifuging time reduces the amount of flakes and their average size. It is apparent that the flakes in figures 3(a) and 4(d) undergo similar processes (fragmentation of flakes and appearance of corrugated network), and that their fragmentation happens faster after centrifugation. It is important to note that the use of centrifugation speeds up the process of fluorination approximately 2-3 times compared to non-centrifuged suspension. Thus, the insulating films are obtained not in 20, but in 8 days.

### The effect of temperature on the fragmentation of flakes in suspension

The influence of heating on the rate of flake fragmentation was investigated. Heating of the fluorinated suspension to a temperature of ~70 °C for 3 h was found to lead to disintegration of all flakes into small particles with size of 20–80 nm. The view of the film surface before and after heating is shown in figures 5(a), (b). It is clear that the size of the small flakes in figure 5(a) approximately coincides with the period of corrugation in figure 5(a). It is assumed that the increased temperature in combination with mechanical stress on the corrugated surfaces have stimulated the disintegration of the primary flakes into much smaller ones. The similar treatment of non-corrugated (non-fluorinated) flakes did not lead to any pronounced fragmentation effect.

Non-stationary thermal treatment influence on the film already obtained from the suspension was studied in the following experiment. Figure 5(d) shows the AFM images of film surface, produced from fluorinated suspension and most clearly demonstrating the formation of corrugation on the surface. Then the film was subjected to non-stationary heating

#### **Treatment duration**



**Figure 4.** SEM and AFM (insets) images of the films created from suspension depending on the centrifugation time and fluorination time: (a), (b) 15 min and (c), (d) 30 min of the centrifugation at 10 000 rpm, (a), (c) 7 and (b), (d) 21 days of fluorination. The initial concentration of the suspension was  $0.12 \text{ mm s}^{-1}$ . The scale bars of (a)–(d) are 1  $\mu$ m.

when the sample was placed in boiling water (figure 5(e)). Comparing the AFM images, one can see that the film relief after thermal quenching is smoothened by removing corrugated elements from the surface. Schematic images of the processes of flakes disintegration and relief smoothing are shown in figures 5(c), (f).

The fluorographene inks were created with the use of the approach discussed above and the thin films were printed on silicon and flexible polyethylene terephthalate (PET) substrates. FG flakes have the lateral sizes ranged within 20-100 nm and the thickness of 0.4-1.5 nm. The characteristic time of inks preparation (including fluorination process) was about 8 days. The optical image of graphene oxide lines with a different number of printed cycles with a layer of FG printed on top of the left half of the wafer from the line marked with arrows is given in figure 6(a). The FG layers on the PET substrate are presented in figure 6(b). An AFM image of the FG layer on PET and the profile near the edge of FG film is demonstrated in figures 6(c), (d). FG layer thickness can be estimated as ~17 nm. The metal-insulator-semiconductor (MIS) structures were then created for the films on Si substrates and the capacitance-voltage (C-V) measurements were performed (figure 6(e)). The fixed charge density in film  $Q_{\rm f}$  and at interface  $D_{\rm it}$  with silicon extracted from these measurements give the values of  $(0.5-2) \times 10^{10} \text{ cm}^{-2}$ . It is worth mentioning that the  $Q_{\rm f}$  and  $D_{\rm it}$  values extracted from *C–V* characteristics in the case of printed films are even lower than that for FG films created from drops (see table 1). The reason for it is in a higher degree of solution purification for organic additives in case of the inks. The current—voltage curves measured in vertical (insert in figure 6(e)) and lateral (insert in figure 6(f)) configurations are presented in figure 6. In the last case very low current was observed in the FG film. In the case of vertical measurements the strong increase in current at voltage more then 0.3 V (electrical field intensity >1.7 × 10<sup>5</sup> V cm<sup>-1</sup>) is most likely connected with carrier tunneling through the film. Generally, high perspectives in the use of fluorinated graphene for printed technologies are demonstrated.

#### Discussion

Summarizing the data given above, we state that in addition to fluorination two main results of graphene suspension treatment in the aqueous solution of HF can be obtained: (1) formation of a corrugation network, which breaks the surface of the flakes into circular regions with a characteristic size of  $\sim 100-400$  nm, or (2) corrugation of the entire surface of the flakes. The typical size of corrugation in both cases is 20–80 nm. In the first case under optimal conditions (certain content of suspension and time of treatment), the breakdown



**Figure 5.** Temperature effects on the surface of the films obtained from fluorinated graphene suspension. (a), (b) AFM image of the surface of the films, obtained from suspensions (graphene content is  $0.16 \text{ mg ml}^{-1}$  and fluorination time is ~100 days) before and after treatment of the suspension with added aqueous solution of HF at T = 70 °C for 3 h, (c) schematic image of the alleged collapse of the suspension flakes at an elevated temperature. (d), (e) AFM image of the film surface (the content of graphene is  $0.04 \text{ mg ml}^{-1}$  and the fluorination time is ~100 days) before and after thermal quenching in boiling water, (f) schematic representation of the influence of thermal quenching on the corrugated flakes of the film.

of larger flakes into smaller ones with two characteristic sizes ~100-400 nm and 20-80 nm can be performed. It suggests the existence of at least two mechanisms of size reduction of the flakes. In the second case under optimal conditions (the use of enhanced temperature) allows for producing flakes with a single size of 20-80 nm. As noted above, the formation of nanorelief (corrugation) on the flake surface occurs due to the difference in the values of constants of the graphene and fluorographene lattice and accumulation of mechanical stresses under increased fluorination degree. If stresses become large enough and exceed some threshold value, or in case of other stimulating factors (stationary and non-stationary thermal processing), the corrugated regions break off from the flakes, forming fine flakes with the size of 20-80 nm and thickness from one to few monolayers. The continuation of the fluorination in these conditions leads to a gradual reduction of the size of the suspension flakes. In the case of network forming a mechanically induced detachment of corrugated elements leads to the refinement of flakes in the network area, and, apparently, leads to the breaking of flakes into circular regions with a characteristic size of ~100-400 nm.

Let us compare the fragmentation effects under fluorination with the known effect of fragmentation of the suspension flakes during graphene oxidation. In the oxidation model proposed by Pan [12] it was shown that the formation of bonds between carbon atoms and oxygen-containing functional groups C=O, C-OH and COOH results in occurrence of mechanical stresses in the layers of graphene and multilayered graphene. Consequently the nanorelief of films is formed and, hence, the interlayer distance increases, and the possibility of breakage of double C=C bonds in the layers appears. The authors managed to divide the processes of vertical and lateral distribution of oxidation inside the multilayered graphene films. The speed of oxidation front propagation was estimated: lateral oxidation rate was ~150 nm s<sup>-1</sup>, and the vertical was ~15 nm s<sup>-1</sup>. The ratio of these values determines the aspect ratio of fragments, to which the original flakes break up as a result of their chemical oxidation.

The characteristic rate of the flakes' fragmentation and splitting in the case of fluorination, as estimated above from the data of figures 2(h), (i), is ~16.3 nm day<sup>-1</sup>, and the rate of the lateral size decrease is ~34.5 nm day<sup>-1</sup>. Based on the above figures and the model, one might expect the appearance of flakes with aspect ratio of ~0.2. However, in our case flakes with the size of 20–80 nm (average size 50 nm) form at a thickness of ~2 nm. These flakes with the aspect ratio of



**Figure 6.** (a) Images of graphene oxide printed layers (4, 6, 10, 16 printed cycles) with an additional FG layer (8 cycles) printed on top of the left half of the wafer; the boundary of the FG layer is slightly seen in the image and for better visualization it is marked with arrows. (b) FG printed layers (10 cycles) on the PET substrate. An AFM image (c) and height profile (d) near the edge of the FG film printed with the use of inkjet printer FUJIFILM Gimatrix DMP-2831 on the PET substrate (10 printed cycles). (e) The capacitance–voltage curve measured at frequency 1 MHz for Ag/FG/Si structures. (f) The current–voltage curves measured in lateral (1) and vertical (2) configurations. The sketches of current–voltage measurements in vertical and lateral configurations, correspondingly, are presented in the inserts of (e) and (f).

~0.04 do not correspond to the ratio of the penetration rates of fluorination fronts. So, in our case another mechanism of fragmentation works; it is suggested to associate with the appearance of nonuniform mechanical stresses at corrugation forming and breaking along the lines of maximum stress. This is also furthered by the changes in mechanical properties of fluorinated graphene, which becomes more brittle compared to graphene.

According to our model proposed in [15], flake splitting and fragmentation are due to the penetration of the HF solution in the interlayer distance. This process begins when the solution penetrates into flakes vertically along the domain borders. As a result, corrugation at the edges of the flakes occurs first, then a network or a fully corrugated surface form, and only later the fragmentation of flakes takes place. It is obvious that for the multilayer graphene flakes the breaking off of corrugated areas creates additional space for the vertical penetration of the hydrofluoric acid solution, which stimulates the next step of fluorination, the formation of corrugation and fragmentation of the lower layers.

It was experimentally proved that fragmentation of the suspension flakes includes several processes. An alternative fragmentation mechanism may be a collapse of the flakes due to the presence of microcracks. In our case, most clearly this effect is observed when using centrifugation. Apparently, this treatment is a source of microcracks, especially given the fragility of fluorinated graphene. But most likely, this is not the only source of microcracks. Another mechanism of microcracks formation proposed in [29] for the case of graphene oxidation is based on the weakening of bonds between central atoms of the suspension flakes as a result of functionalization of their edges by hydrogen H and oxygen-containing groups = O, OH, COOH. Taking into account the spin state of atoms and passivation of edge atoms of carbon in the flake, an unexpectedly strong effect of bond weakening between the central carbon atoms was discovered [24]. Such weak bonds form 'the channels' (topological channels) that may be centers of the emergence of nanocracks in graphene. The role of this mechanism of fragmentation should increase with decrease in the flake size. The similar effect of the interplay between defects and fluorine ions, the formation of graphene quantum dots and the influence of fluorination degree were investigated by density functional theory calculations [17, 18]. The same mechanisms are likely responsible for the successive fluorination of the suspension flakes, which starts with edge atoms in the flake and, then, covers a larger area.

As is shown in table 1 and obtained for printed layers, films of fluorinated graphene suspensions have characteristics that give perspective for applications; these are the low fixed charge in the film, the density of surface states at the boundary with the semiconductor and high strength of the breakdown field. It was shown that  $Q_f$  and  $D_{it}$  remain consistently low for a wide range of treatment times on different semiconductor substrates and are practically independent of the film thickness. All these factors make films obtained from fluorinated suspensions promising for a wide range of applications. In combination with the stability of fluorographene properties and the possibility to obtain thin and fine suspension flakes such suspensions give perspective for 2D inkjet printing technologies and creation of dielectric layers and coatings in different heterostructures.

#### Conclusions

Analysis of the results of splitting and fragmentation of multilayered graphene flakes in suspension during fluorination in aqueous solution of HF allowed proposing possible mechanisms of these processes. It is assumed that the formation of inhomogeneous mechanical stresses in corrugated, partially fluorinated graphene plays a key role in splitting and fragmentation of multilayered graphene flakes. The assumption is based on the observed correlation between the size of corrugation on the surface of the flakes and size of flakes after splitting and fragmentation. It is also assumed that in the case when corrugated regions form only the network (a lower degree of fluorination), cracks are nucleated in the flakes due to the fragility of fluorinated graphene and a weakening of C-C bonds near the fluorinated areas. We have found the ways to control the rate of flakes disintegration (stationary and pulse heat treatment), and additional factors that accelerate or modify the aspect ratio of the obtained flakes (modifying the suspension composition, centrifuging of the suspension, and additional oxidation). The fluorinated graphene inks were created and FG films were printed and the MIS structures were characterized. The charge in the FG film  $Q_{\rm f}$  extracted from capacitor-voltage measurements has the values of  $(0.5-2) \times 10^{10} \text{ cm}^{-2}$ .

Generally, FG suspensions are very promising for the creation of thin insulating films in heterostructures, protected coatings and 2D inkjet printing technologies.

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