Novel method of large area graphene fabrication

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Abstract. Studying of physical properties of graphene and graphene devices requires fabrication graphene samples of large area. Our fabrication method does not demand special expensive equipment and can be easily implemented. Single-layer graphene flakes with the size up to 200 \( \mu m \) and few-layer graphene flakes with the size up to 2000 \( \mu m \) were obtained by this technique. These flakes can be produced on various substrates including transparent ones. Atomically thin films of other layered materials can be also obtained using this method.

1. Introduction.
Graphene is a unique material, which has a whole spectrum of unusual physical properties. The discovery of graphene by A. Geim and K. Novoselov is a giant step in the development of micro- and nanoelectronics, optoelectronics, high-tensile materials and etc. It’s possible to create in the future a large amount of devices, based on graphene. The main obstacle in the appearance of graphene devices is the following: the methods of fabrication of high-quality graphene flakes are complicated. This makes graphene scarce and expensive. A method described in this paper belongs to the group of graphene production methods by mechanical exfoliation of graphite (scotch-tape technique). One of these methods is the method invented by Manchester group of scientists headed by Andre Geim and Konstantin Novoselov in 2004 which is the prime method for graphene production. In comparison with the other methods of this group the method described in this article has the following advantages:

- **The size of graphene flakes.** The method of graphene fabrication by the mechanical exfoliation of graphite described in [1] allows to receive graphene flakes with the lateral size up to 200 \( \mu m \). The method of reverse graphene exfoliation described in this article allows to increase the size of flakes. The lateral size of single-layer graphene flakes reaches up to 500 \( \mu m \), the few-layer graphene up to 2000 \( \mu m \).
- **The simplicity of graphene fabrication.** This method doesn’t require special equipment, such as plasma reactor [2], MOCVD [3] or HPHT [4] apparata. Furthermore, the size of some flakes allows to make contacts even without electron beam lithography [1].
- **The broad spectrum of substrates.** The reversal exfoliation method allows to receive graphene flakes on various substrates, including the transparent ones. It allows to use graphene's unique optical properties. Graphene produce an unexpectedly high opacity for an atomic monolayer, with a startlingly simple value: it absorbs \( \pi \alpha \approx 2.3\% \) of white light [5], where \( \alpha \) is the fine-structure constant. Thus, it allows to estimate a number of graphene layers measuring absorption coefficient.
2. Fabrication technique.

The technique of graphene preparation, described below, has much in common with the original scotch-tape method invented by Konstantin Novoselov. However, there are quite significant differences between these approaches. Closest to our method is the method described in [6], where graphene is also fabricated using reverse exfoliation technique. The simple scheme of our method is shown at figure 1.

![Figure 1. The scheme of graphene production using reverse exfoliation technique.](image)

The starting material for the production of graphene is highly oriented pyrolytic graphite (HOPG). At the first stage the original HOPG crystal 3 (Fig. 1) is attached to a substrate via an intermediate adhesive 2. As a substrate material is useful, for example, glass, silicon, polikor. As an adhesive 2 could use araldite or adhesive tape with two adhesive surfaces. Next, the surface of a layered crystal 3 must be clean and flat. To do so, the adhesive tape is attached to the surface of a HOPG crystal and then breaks away. If necessary, the cleanup procedure is repeated. Then on the clean surface HOPG crystal the basis substrate 4 is attached with glue 5 (fig.1B). After the glue has cured substrates are separated from each other (fig.1C). If the substrate is transparent, single-crystal fragments 6 (fig.1C), remaining on the substrate 4 may be investigated for the presence of light gray crystals of graphene with an optical microscope. The optical transparency of the corresponding single- or multiple-layer graphene is less than 20%. If the graphite crystals are still thick, the upper layers can be removed using an adhesive tape 7 (fig.1D). Removal of the upper layers occurs as long as at the substrate does not begin to appear single or multi-layer graphene flakes 8 (fig.1E).

3. The results obtained.

Single crystals of graphene, consisting of several layers, obtained as described above, are shown in figure 2. This photo was taken on an optical microscope, Carl Zeiss Axio Imager. Region 1 in Fig. 2 is a film of graphene, which consists of several layers. Area 2 is a section with no adhesive crystals of graphite. The value of light transmittance for a specific area was determined by the brightness of the image by using AxioVision. Change the light transmittance along the segment AB (Fig. 2) shown in Fig. 3. In the transition from area 2 in region 1 the transmission coefficient decreases by about 4%. From this it follows that the region 1 corresponds to approximately two layers of graphene.
Figure 2. Microphotograph of the graphene film on the transparent substrate. Area 1-bilayer graphene, 2-epoxy glue, 3-monolayer graphene, 4-graphite, 5-few-layer (up to 30 layers) graphite.

Figure 3. Transparency of the graphene along the line AB (Fig. 2). The resulting graphene samples were investigated using Raman spectroscopy (RS). Fig. 4 shows the Raman spectrum for regions 3 and 4 (Fig. 2). For opaque graphite (area 4) is observed near the G-line is ~ 1582 cm\(^{-1}\) and 2D-line near ~ 2680 cm\(^{-1}\). To the left of the 2D-line broadening is observed, characteristic of graphite. In addition, the amplitude of the G-line is much greater amplitude of the 2D-line. In area 3 of FIG. 2 2D-line is shifted by ≈ 50 cm\(^{-1}\) to lower frequencies and acquires a symmetric shape. Such a shift and shape of the 2D-lines are typical for single graphene. Also, the monolayer region 3 also indicates small amplitude of G-peak, which is comparable in magnitude to the amplitude of the 2D-line. These facts indicate that the area 3 of FIG. 2 with a lateral size of about 200 μm corresponds to a single-layer graphene. The additional lines appearing for graphene in the G-region, presumably correspond to the Raman scattering of glue by which the graphene is attached to the substrate. More detailed Raman spectroscopy of graphene is described in [7, 8].
4. Conclusion.
Using the method described in this paper, we can obtain monolayer and few-layer graphene samples. The large size of graphene flakes (up to 2000*2000 µm²) allows to produce graphene structures without electron beam lithography. Also, due to the more powerful adhesive ability of epoxy glue we can separate more tightly-bonded materials up to monolayers. One of the major drawbacks of this method is the following: graphene is placed at the thin surface of epoxy glue, which physical properties hinders to change carriers concentration in graphene via the bottom gate. The problem could be solved, for example, by virtue of top gate deposition, for example, ionic liquid gate. At this moment research in that direction is carried out.

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