h-BN surface modification by scanning probe microscope

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The study demonstrates the possibility of modifying fragments of hexagonal boron nitride layers by bending them with a probe using a scanning probe microscope. The specific ranges of *h*-BN fragments with a lateral size of about 1 micron have been determined. It was possible to obtain a layer up to 8 monolayers thick from initially thick fragments of *h*-BN by the layer flip method.

Keywords: Hexagonal boron nitride, atomic force microscopy.

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Studies of the properties of two-dimensional (2D) materials are actively conducted over the last decade [1]. Graphene is considered as one of the most famous and studied two-dimensional materials today. A large number of papers [1–3] was devoted to it, however, scientific interest in recent years is shifted towards other two-dimensional materials, for example, transition metal dichalcogenides (MoS_2, $MoSe_2$, $MoTe_2$, WS_2, WSe_2, WTe_2), as well as hexagonal boron nitride (*h*-BN). Currently, van der Waals heterostructures containing thin layers of various 2D materials, including hexagonal boron nitride, are of particular interest. A thin layer *h*-BN (with a band gap of 5.9 eV) can be used as a wide-band barrier [4] between conducting layers (or layers of semiconductor materials) in van der-Waals heterostructure. The formation of such heterostructures is of interest for many applications [5]. In the so-called „assembly" process, materials of a certain thickness are stacked on top of each other using various methods. The most common method of layers depositing onto surface is exfoliation (separation of thin layers from a bulk crystal) [6]. In this case, the thickness of the deposited layers can be tens of monolayers. The possibility of modifying the thickness of these layers and achieving coatings with a thickness of several monolayers are of particular interest. One of the methods that makes it possible to modify thin layers of 2D materials is the method of atomic force microscopy (AFM).

This paper demonstrates the possibility of flip of small-area fragments (also called flakes) of thin layers *h*-BN using probe of atomic force microscope. The main idea is the force action of AFM probe and the subsequent modification of the upper layers connected to the underlying layers by weak van der Waals forces.

The samples under study were split multilayer flakes *h*-BN transferred to the surface Si/SiO_2. The characteristic thickness of the resulting flakes was measured using AFM and ranged from 8 to 30 nm. The total number of layers in such flakes ranged from 12 to 45 (the interlayer distance between the planes *h*-BN is 0.67 nm). The objective of this paper was to develop a method for modifying these flakes with AFM probe in order to obtain thinner flakes.

All AFM studies were carried out under atmospheric conditions using NTegra-Aura microscope (NT-MDT, Russia). The probes of the DCP11 series (TipsNano, Russia) with identical characteristics were used with a radius of curvature of 50−70 nm and a contact rigidity of about 5 N/m. The method of surface modification using an AFM probe consisted of several stages. At the first stage, the selected area is scanned in semi-contact mode and the flake *h*-BN is visualized. Then AFM probe moves to the area that is planned to be bent or moved away (Figure 1, left), and the size of the scanning area is reduced by several times. At the second stage, using the contact mode of AFM operation, the selected area is scanned with a given force F (the optimal value of which was determined in this paper) and the direction of the probe's influence. Selecting the optimal magnitude of force and direction of impact can effectively move (Figure 1, center) or bend the layer (Figure 1, right).

The paper involved a search for the optimal force required to modify the flake. It was found no flake modifications at relatively „small" forces, less than 300 nN. This is due to the fact that the amount of work A_{pr} performed by the probe turns out to be less than the energy of the van der Waals attraction E_{vdw} holding the layers together. The characteristic amount of work performed by the probe is about $A_{pr} = F_{pr}L$. Here F_{pr} — the force of probe pressing to the surface, and L — the size of the flake being peeled off. The characteristic value of the van der Waals attraction energy of layers *h*-BN is $E_{vdw} = E_{bind}N$. Here E_{bind} — specific energy of van der Waals attraction per one pair of atoms in neighboring layers ($E_{bind} \approx 80$ meV/atom [7]), and N — the number of atoms in the flake being peeled off. The characteristic size of peeled flakes was about 1 micron. The value of the van der Waals attraction energy in such flakes, thus estimated, was $E_{vdw} = 0.3$ pJ. Accordingly, the threshold force required to modify the flake was $F_{min} = 0.3\,\mu$N, which is close to the threshold force observed in our experiments.

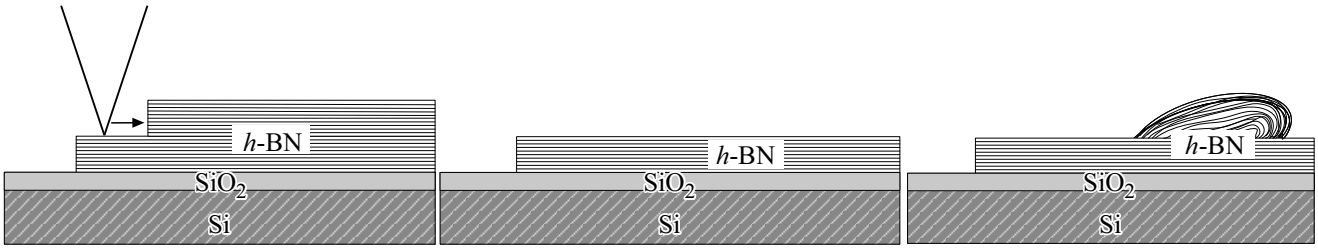

Figure 1. Schematic representation of the technique for modifying multilayer *h*-BN layers using AFM probe. On the left — AFM probe is located next to the multilayer *h*-BN, which is planned to be modified, in the center — the multilayer *h*-BN, completely moved by the probe outside the frame, right — multilayer *h*-BN bent by probe.

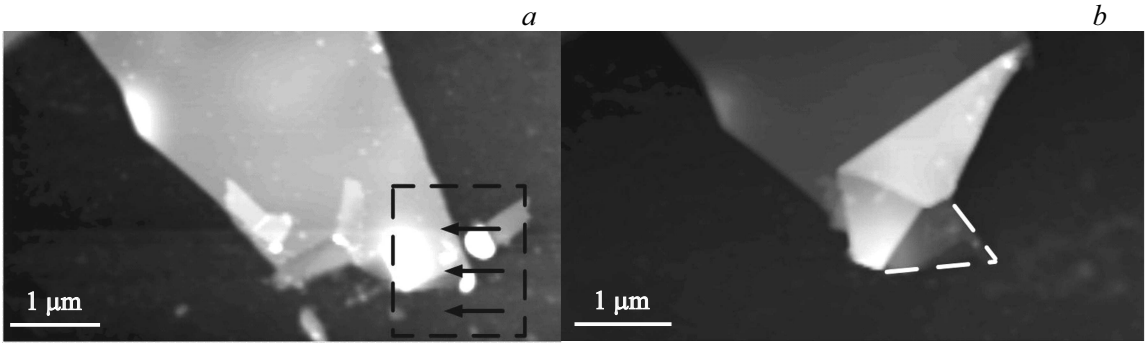

Figure 2. *a* — AFM topography of the initial surface of some flake *h*-BN. The probe area of influence is indicated by a dotted frame, and the direction of action of the force $F = 0.5\,\mu$N — by black arrows; *b* — bent triangular layer *h*-BN. The thin fragment highlighted with a dotted line is the area remaining after the bend.

It is worth noting that the issue of determining the threshold force for flake flip is debatable. It is assumed that the flake flips entirely when contact scanning one of the frame lines. Therefore, in the above estimates of paper A_{pr} we multiply the characteristic force by the size of the flake. However, the exact scenario of how exactly the flake flip occurs is unknown; additional research is needed here. The above estimate should be treated only as a rather rough estimate that does not claim to be accurate. The above estimate also does not take into account the role of lateral forces causing torsional bending of the cantilever. The lateral force is comparable in order of magnitude to the friction force $\sim \mu F_{\text{pr}}$, where μ — friction coefficient. In future studies we plan to study the flake flip mechanism in more detail; this may require numerical modeling of the force interaction of the probe with the flake.

It was also discovered that when the magnitude of the acting force is too large, the probe begins to modify the flake in an uncontrolled manner, leading to the formation of a „lump“ of *h*-BN. The characteristic force at which such modification occurs in our experiments was $F_{\max} = 2\,\mu$N. Thus, the optimal force should be in the range of $F_{\min}$ to $F_{\max}$. In these experiments, the force was chosen with value ($F = 0.5\,\mu$N) close to $F_{\min}$ in order to modify the flake, but at the same time not providing excessive influence on it.

Figure 2, *a* shows the AFM topography of the initial surface of the *h*-BN flake, as well as the probe influence area (dotted frame) and the direction of the force action $F = 0.5\,\mu$N (black arrows in Figure 2, *a*). It can be seen that after the force impact part of the *h*-BN flake was bent (triangular area in Figure 2, *b*). After bending, a thinner fragment of the flake remained on the surface (highlighted by dotted line in Figure 2, *b*), the thickness of which is 5 nm, which is approximately by 2 times less than the thickness of the original flake (12 nm).

Figure 3, *a* shows the AFM topography of another initial flake *h*-BN 15 nm thick and dotted square area of force action. The arrows indicate the direction of the force ($F = 1\,\mu$N). After force action on the film a hexagonal flipped area is visible (black dotted line), and at the bottom there is the substrate (Figure 3, *b*). It is believed that the flipped flake shape *h*-BN may inherit the symmetry of the *h*-BN crystal lattice. The crystal lattice of the honeycomb *h*-BN has hexagonal symmetry and the flipped flake shape can have hexagonal symmetry. In this case, the thinner remaining part of the layer is not observed, i. e. the entire layer appears completely flipped. Thus, it is shown that if large forces are applied to the flake, it will flip entirely.

In all our experiments, it was unable to observe a parallel shift (or rotation) of the layer (Figure 1 in the center). Initially, it was assumed that small flakes could be moved (or rotated) in parallel, like a deck of cards. The impracticability of such modification is due to the fact that when exposed to AFM probe, the force is applied pointwise, and not parallel

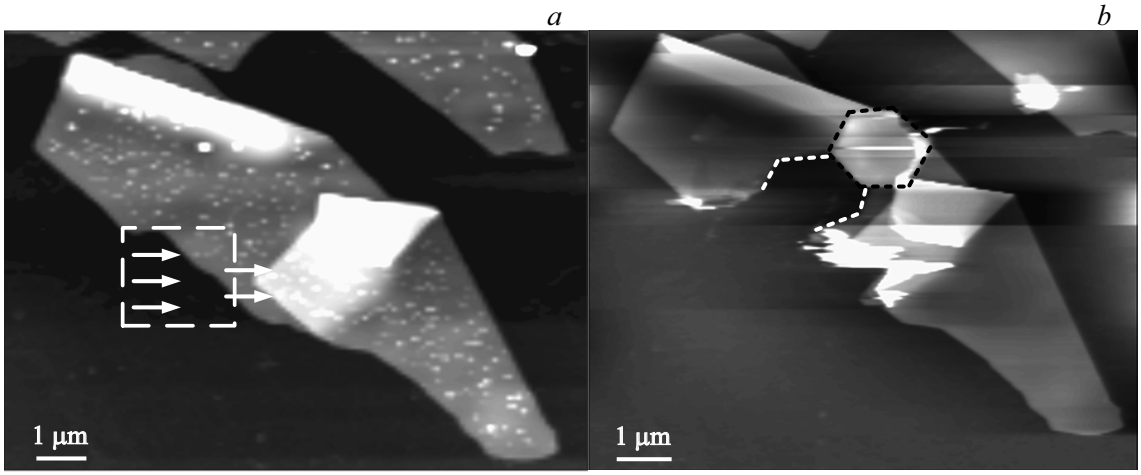

Figure 3. *a* — AFM topography of another initial flake *h*-BN. The area affected by the probe is indicated by dotted frame, arrows indicate the direction of the force ($F = 1\,\mu$N), *b* — hexagonal inverted area (black dotted line), and below — substrate.

along the entire face of the flake. Probably, if used special probes with a large radius of curvature R and act with them on small flakes, the size of which is comparable to R, then it may be possible to move the layers in parallel.

It is important to note that during the flakes modification, a situation was often observed where flipped flake fragments were not tightly pressed to the surface. During flake flip there may be „bubbles" under it filled with air or surface moisture. It is quite difficult to study such flakes. Therefore, in this paper, force „smoothing" of the flakes with AFM probe was performed. To do this, additional scanning was performed in contact mode with low impact forces $F < F_{\min}$, which made it possible to squeeze out foreign material from under the flipped flake, thereby pressing the material more tightly to the substrate. And then scanning was performed in semi-contact mode to visualize the modified flake.

The work function of the original and modified *h*-BN layers was also measured. To do this, using Kelvin probe microscopy, the surface potential of layers *h*-BN was measured, and then the potential was measured on the gauge structure of pyrolytic graphite with a known work function [8]. Based on the difference in the measured values of the surface potential (and knowing the work function of the gauge structure), the value of the work function of the layers under study was determined. The thicknesses of the the obtained flakes were in the range of 5 to 30 nm, and the measured value of the work function for these flakes was almost independent of their thickness and amounted to 5.6 eV [9], which is close to the value of the work function for bulk *h*-BN. This is due to the fact that the size effect of the dependence of the work function on thickness is observed for thinner flakes [8], which could not be obtained.

In conclusion, it is noted that it was able to determine the modes of action of AFM needle on the surface *h*-BN for their modification. The characteristic ranges of permissible impact forces for flipping flakes *h*-BN with a lateral size of about $1\,\mu$m were determined. Parallel shift of layers is not possible in flakes, the dimensions of which are many times greater than the size of the probe-surface contact region. Using the method of layers flip, it was possible to obtain layers with thickness of 8 monolayers from initially thick flakes. In the thickness range from 8 to 30 monolayers *h*-BN, no dependence of the measured work function (5.6 eV) on the film thickness was observed. Further studies will focus on improving the method of controlled modification of *h*-BN flakes, as well as obtaining *h*-BN layers with fewer monolayers.

Conflict of interest

The authors declare that they have no conflict of interest.

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