Local Modification of Graphite Films by Atomic Force Microscopy

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Graphene has unique properties due to the perfection of its hexagonal crystal structure [1]. It is characterized by low levels of defects and the high mobility of charge carriers [1, 2], which makes it a promising subject of research and makes it possible to improve the performance and reduce the power consumption of devices on its base. However, graphene cannot be practically machined, resulting in the need to find other methods of local changes in the surface properties, including electrical one.

In this paper we present a method for modifying the structure and electrical properties of graphite films by atomic force microscopy [3], which is the basis of the method of local anodic oxidation (LAO).

Electrochemical local anodic oxidation (LAO) film surface of highly oriented pyrolytic graphite (HOPG) with elements of graphene performed by the scanning probe microscope Nanoscope IIID (Veeco, USA), with a block «C-AFM», allowing to apply a potential difference ± 12 V to the "probe-sample" system, using probes for AFM with constant rigidity 1-5H/m and conductive coatings (platinum-iridium PtIr alloy and cobalt coating with chromium sub-layer Co/Cr).

Pre-LAO HOPG scanned to detect possible defects, and then it was carried LAO process by set up the trajectory and speed of the AFM probe along the surface of HOPG, its bend (the pressure of the probe on the sample) and the voltage applied to the system "probe-surface of the sample". The effectiveness of LAO process evaluated using an atomic force microscope to measure height and width of the relief created on the surface (in AFM contact mode)and its conductivity (in C-AFM conducting mode).

LAO process under air conditions represents electrochemical oxidation of the anode, in a system where the cathode is an AFM probe with conductive coating, and an anode is modifiable surface (in this work - HOPG), the electrolyte is the water adsorbed on the surface of the sample, which is the source of oxygen. In case of LAO in a vacuum, sputtering of carbon is due to rupture of the C-C bonds under the influence of an electric current. The process of LAO is affected by resistivity, the tip radius of the probe, its spring constant, resistivity of HOPG and air humidity.

In graphene, carbon atoms are packed in a hexagonal crystalline structure and the process runs stepwise LAO as discontinuity of the valence bonds (C-C). Moreover, its velocity is very high, the oxygen stands out from the water and reacts with the carbon atoms, whereby the surface is deformed, and joined thereto various oxygen-containing groups. It is also possible the complete destruction of the graphene layer.

Thus, there are two possible modifications of the graphite during the LAO process - "sputtering" and "growth" of the material."Sputtering" of graphite is an electrochemical oxidation of the carbon leading to carbon oxides removal from the reaction zone.

"Growth" of the surface is to join of oxygen-containing groups to the HOPG surface under the influence of an electric field, which is achieved at high speeds of the AFM probe along the surface when the break is not all the C-C bond. The result of incorporation of one-atom layer of various radicals and residues of "sputtering" materials into the lattice of graphene is an increase of its size, which is registered as an AFM hills.

It should be noted that LAO’s products “growing” on HOPG, are firmly bonded to the surface and do not collapse under the influence of the probe. "Sputtering" of LAO’s products (oxides and destroyed parts of graphene layer) is rather volatile and they are deposited onto the sample and the probe. Deposition onto the probe is expressed in the deterioration of the conductive

properties of the system, since all the process of LAO’s products (carbon oxides, the surface-modified oxygenated groups, residues and "sputtering" materials) are insulators.

The depth range of "sputtering" of graphite was set experimentally(from 2 to 200 nm). Theoretically, maximum depth is only limited by the duration of the process. The height of the oxide formed is in the range from 0.1 to 2 nm.

References

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