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CHEMICAL SENSITIVITY OF CARBON NANOFILMS ON DIAMOND AND QUARTZ SUBSTRATES

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INTRODUCTION

Carbon nanotubes and single layer graphene show good potential as chemically sensitive materials[1]. However, when developing chemical sensors on these materials, many technological hurdles in the growth technology and manipulating with nano-objects must be overcome. Focused ion beam written carbon nanowires offer a more controllable technology than that based on carbon nanotubes and graphene[2]. However, high cost of the focused ion beam instruments may be a disadvantage preventing from commercial application of the FIB-written carbon nanosensors. Carbon nanofilms are another nanomaterial promising for sensor applications. Herein, we are reporting a method to obtain chemically sensitive carbon nanofilms on diamond and quartz substrates using high temperature graphitization of diamond surface in vacuum and CVD deposition from methane. Carbon nanofilms on diamond are of special interest because they offer advantages of all-carbon technology and as such are promising for biological and medical applications.

EXPERIMENTAL

Carbon nanofilms were grown on (100) surface of single crystal CVD diamond samples at temperatures 1000 – 1400 °C in vacuum and inert atmosphere. Deposition of carbon films on single crystal quartz substrates cut perpendicular to c-axis was performed in methane atmosphere at temperatures 800 to 1200 °C. A home-made vacuum furnace was used for annealing in vacuum and for deposition from methane. Sample container and heater of this furnace were made of high purity graphite. As-grown carbon films were successively thinned by etching in low power air or oxygen RF plasma.

RESULTS AND DISCUSSION

In-situ measurements of surface conductance of diamond surface were performed on a few samples annealed in inert atmosphere in order to find the onset temperature of the graphitization (fig. 1*a*). It is seen that the conductance induced by heating at temperatures of 980°C and above is irreversible and retains after cooling. The thickness of as-grown carbon films (measured by AFM) may vary from 10 to 100 nm depending on the temperature and duration of annealing, vacuum level, and purity of the inert gas atmosphere. Sheet conductance of the thin carbon films grown in vacuum of 10^{-5} mbar at a temperature of 1200°C for 15 min varied in the range $10^{-5} – 10^{-4}$ S. Thick films grown in vacuum of 10^{-2} mbar for same time showed conductance in the range $10^{-4} – 10^{-3}$ S. Specific resistivity of these films was found to be in the range from 10^{-3} to 10^{-4} Ω·m. This value is much higher than that of graphite ($8·10^{-6} – 15·10^{-6}$ Ω·m) indicating disordered (partially amorphous) atomic structure of the grown carbon nanofilms.

The change in conductance of the carbon films exposed to plasma etching is shown in fig. 1*b*. There are two distinctive regions. At first, the conductance drops linearly with etch-

ing time, and then it reduces exponentially. The linear decrease is attributed to uniform removal of the graphitized layer. After the film has been largely removed, isolated graphitic islands trapped between the surface features are formed (fig. 1*c*). Raman spectra measured on the plasma-etched films reveal D and G bands at 1350 and 1590 cm^{-1} indicating presence of disordered graphitic carbon (no graphene 2D band was detected). With etching, the D and G bands merge into one weak broad band with maximum at a wavenumber of 1450 nm indicating that the very thin plasma-treated carbon nanofilms become completely amorphous.

Thin carbon nanofilms, and especially those etched by plasma, revealed essential chemical sensitivity for gaseous analytes (water, acetone, ammonia, toluene etc.). The sensitivity was measured as a change in conductance during exposure to analyte. The response of the films was different for different analytes and could be positive (increase in conductance, e. g. for water), or negative (decrease in conductance, e. g. for acetone). Fig. 2*a* shows response of thin carbon nanofilms to water vapor present in human breathing and acetone. The normal human breathing even at a distance of 0,6 m can produce a 200 % increase in the conductance of the film. Response and recovery of the conductance is very fast. Fig. 2*c* shows that carbon nanofilm on diamond is sensitive enough to feel in open air at room temperature the evaporation of 1 mm diameter water droplet at distances up to 7 mm.

Though, the exact mechanism of this effect is still not clear, we assume that the chemical response of the carbon nanofilms might be related to polarity of the analyte molecules. Alternatively, the molecules adsorbed on the insulating gap between adjacent conductive carbon islands may provide additional conduction pathways.

In contrast to carbon nanofilms on diamond, the carbon nanofilms as-grown from methane on quartz are more graphene-like rather than amorphous (fig. 3*a*). Raman meas-

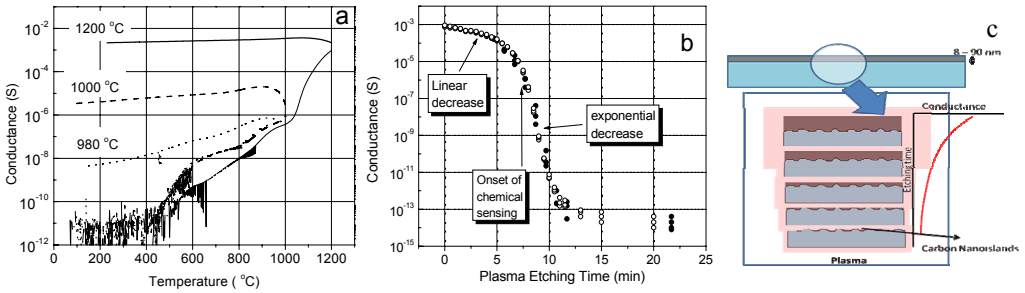

Fig. 1. a – In-situ measurements of surface conductance of diamond samples during the processes of heating and cooling in N_2 atmosphere with different maximum temperatures (indicated on the graph). Rate of cooling/heating was 5 °C/min; *b* – thick carbon nanofilm exhibits linear decrease in conduction at the initial stages of plasma etching and exponential afterwards, whereas thin film shows exponential decrease from the very beginning of etching; *c* – Initially homogeneous carbon film is converted into a random array of graphitic nanoislands after prolonged plasma etching

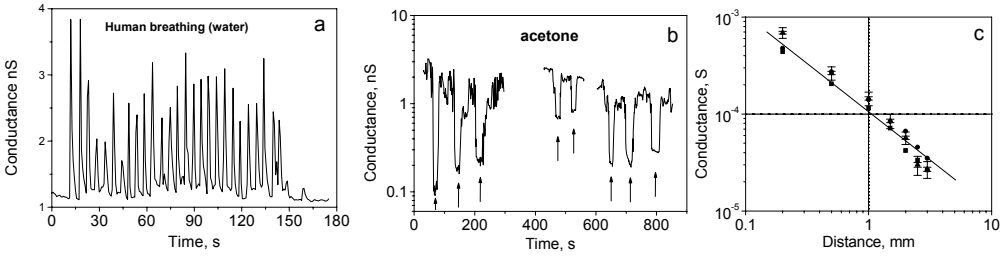

Fig. 2. Conductance of a thin carbon nanofilm exposed to human breathing at a distance of 0,6 m (*a*) and a 1 mm diameter acetone droplet when it is brought to the carbon film at a distance of a few millimeters (shown by arrows) (*b*). Conductance of carbon film when a 1 mm water droplet is placed at different distances to it. The conductance is inversely proportional to the distance

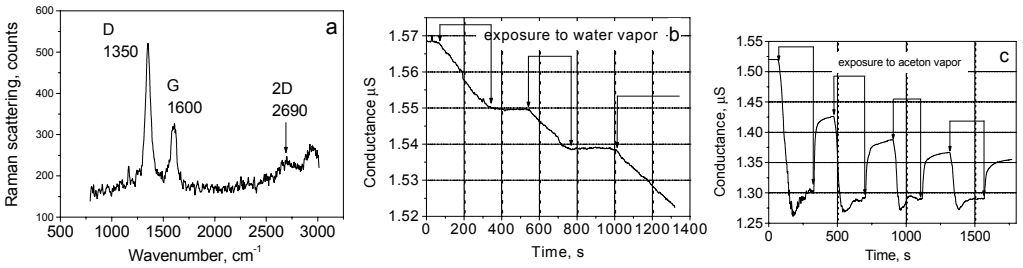

Fig. 3. Raman spectrum (*a*) and change of conductance of as-grown carbon nanofilm on quartz on exposure to water (*b*) and acetone (*c*) vapors. Intervals of exposure are shown with arrows

urements reveal narrow G-band and 2D-band, which are features of graphene. The conductance response of these films to water and acetone is shown in fig. 3*b*, *c*. The conductance linearly decreases with the time of exposure to water vapor and it does not recover after the vapor is removed. In contrast, the conductance of the film decreases sharply in acetone vapor and it restores partially when the film is retracted from the vapor. Thus, the conductance of the carbon nanofilms on quartz is not electronically sensitive to water but sensitive to acetone. However, water vapor may work as an etchant for the carbon films on quartz reducing their thickness and lowering their conductance irreversibly.

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