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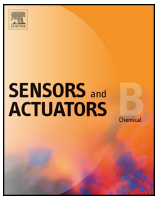

Growth of graphene-like films for NO_2 detection

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ABSTRACT

Chemical vapor deposition of graphene-like (GL) films (nano-crystalline graphite films) from methane on single crystal quartz substrates is reported. The GL films have been characterized by means of Raman spectroscopy, atomic force microscopy and electrical measurements. The thinnest GL films obtained so far have a thickness of 1.5 nm, a relatively rough surface structure and an electrical conductivity in the range of 20 kΩ/□. The high chemical sensitivity of GL films has been demonstrated by measuring the change of their conductance during exposure to a NO_2-containing atmosphere. The optimal electrical conductance, high chemical sensitivity as well as the simple growth method make the GL films promising for practical applications as a chemically sensitive material.

1. Introduction

In the recent decades, carbon nanomaterials have attracted considerable attention of researchers and engineers due to their unique physical/chemical properties and possibility of application in different areas including nanoelectronics, molecular filters, transparent electrodes, touch screens, novel catalysts, optical modulators and chemical sensors [1].

At present, the most widely used chemical sensors are those based on metal-oxides, which do require high working temperature [2]. Conducting polymer sensors are an alternative to metal oxides. They do work efficiently at room temperature, but suffer from long-time instability and irreversibility [3].

Chemical sensitivity of highly crystalline carbon nanostructures like graphene and carbon nanotubes (CNTs) are under extensive study. Usually graphene and CNTs are obtained by chemical vapor deposition (CVD) growth in the presence of metal catalysts [1,4,5]. Attempts to avoid the use of the metal-catalysts led to the development of the catalyst-free CVD growth of graphene on SiC [6] and on sapphire [7]. In both cases, however, the practical utilization of graphene is very limited to the specific substrates like SiC or sapphire capable to withstand very high temperatures. Thus the direct growth of graphene on different insulating substrates including oxidized silicon at temperatures low enough to be compatible with the silicon microelectronic technology is still a challenge to be met.

In contrast to the high quality graphene, the graphene-like films, and especially amorphous carbon nanofilms, can be deposited without a use of a catalyst at much lower temperatures. However, chemical sensitivity of graphene-like and amorphous carbon films have not been studied systematically so far. There are a few reports on chemical sensitivity of amorphous carbon films prepared by direct carbon sputtering, followed by annealing at high temperatures [8]. Those films revealed reasonable chemical response to different analytes, yet their low conductance (in the order of nS) made them unsuitable for the use as practical electronic chemical sensors. Some data on the physical properties of graphene-like films grown by CVD method on Si and SiO_2 substrates has been reported in [9].

In the present communication we introduce graphene-like films directly grown on quartz by CVD from methane in graphite chamber and show that they have fairly good electrical and optical properties and, what is more important, they possess high chemical sensitivity. The favorable physical and sensing properties in combination with the simplicity of fabrication make graphene-like films a material particularly attractive for applications in chemical sensorics.

2. Materials and methods

Graphene-like films were grown in a specially designed vacuum furnace, the working chamber of which was made of high purity graphite and could be controllably filled with gas. The substrates

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were single crystal quartz plates of size 4 mm × 4 mm × 0.5 mm. The large surfaces of the plates were cut perpendicular to the *z*-axis and polished to a roughness of Ra < 1 nm (commercial product of MTI company). Before the processing in the growth furnace, the substrates were cleaned by ultrasonication in acetone and ethanol.

After loading the substrate, the furnace was evacuated to a pressure < 10^{-5} mbar. At this pressure, the container was heated to a temperature of 800–1200 °C for 10 min for degassing. After that, the chamber was filled with methane (ultra-high purity grade) to a pressure ranging from 5 to 8 mbar. Pressure was measured with two gauges Omega DPG 3500B-2000MBARA and Adixen ACC-2009. Mutual calibration of the gauges allowed the pressure measurements with absolute accuracy of 50%. Inspite or rather poor absolute accuracy, the relative accuracy and reproducibility of the pressure measurements were high and the growth process was easy to reproduce.

Raman characterization of the films was performed at room temperature using a spectrometer with laser excitation at a wavelength 632.8 nm in confocal regime. The surface topography of the deposited films was analyzed by an AFM (atomic force microscopy) instrument VEECO Dimension 3100 in intermittent contact mode. For the electrical measurements, Van der Pauw structures of size 100 μm × 100 μm were prepared by standard lithography and argon ion etching. The electrical contacts were made by deposition of Cr (5 nm) followed by deposition of Au (60 nm) in a sputtering setup working at a pressure < 10^{-6} mbar. The Hall-effect measurements were performed in magnetic field ranging from −0.38 to 0.38 T. Optical absorption measurements were performed at room temperature in a spectral range from 200 to 900 nm on the samples with carbon film on one side.

Nitrogen dioxide NO_2 was used to test the chemical sensitivity of the grown films. This gas was chosen for the reason that nitrogen oxides are listed by the US Environmental Protection Agency (EPA) as the major air pollutants. In particular, EPA has established safety standards for NO_2 exposure to be 53 and 100 ppb (part-per-billion) for annual- and hour-average, respectively [10] (note that the USA ambient annual average is currently 10–30 ppb [11]). At the same time, the US National Institute for Occupational Safety and Health recommends that workers at a working place are not to be exposed to NO_2 at concentrations greater than 1 ppm (part-per-million) [12]. Based on this concentration–time criteria, we consider the detection of 1 ppm concentration of NO_2 in 30 min as the minimum sensitivity requirement for practical NO_2 sensor.

Fig. 1 shows the schematic diagram of the set-up used for the measurements of chemical sensitivity. An aluminum thick-wall box with electrical and gas feedthroughs served as the measuring chamber. The samples were placed in the chamber on a teflon holder and electrically contacted with carbon paint and tungsten needles. Keithley 4200-SCS source-measurement instrument was used for two-probe measurements of conductance of the films. The voltage applied during the measurements was 1 V. The level of electrical noise was about 0.1 nA. Ultra high purity nitrogen was used as an inert atmosphere and the carrier gas. A constant nitrogen flow F1 of about 1400 ml/min was maintained during the whole duration of measurement. NO_2 was produced in bottle B by decomposition of 70% nitric acid solution in water. We assumed that at room temperature, the saturated pressure of HNO_3 vapor and H_2O vapor over the surface of 70% nitric acid solution is about 4 mbar (a concentration of 4000 ppm) and about 6.7 mbar (a concentration of 6700 ppm) correspondingly [13]. In order to maintain this concentration stable, the bottle with acid was kept at a constant temperature. Decomposition of nitric acid is described by the reaction: $4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$ and the flow F2 caring NO_2 was actually a mixture of nitrogen, nitrogen dioxide, water vapor and oxygen. We assumed full decomposition of HNO_3 vapor before the gas entered the measuring chamber. Flow F2 could be controlled in the range from 23 to 85 ml/min allowing the variation of the concentration of NO_2 in the measuring chamber from 65 to 230 ppm. During the reference measurements, bottle B was kept empty, or was filled with water. Chemical sensitivity experiments were being performed for one month. No significant change in the response of the film to the analytes was observed during this time. Thus the carbon film showed no degradation of its chemical sensitivity.

In order to check the influence of UV light on the chemical sensitivity of the films, four UV light-emitting diodes working at a wavelength of 405 nm were placed in the measuring chamber at a distance of 1 cm above the sample.

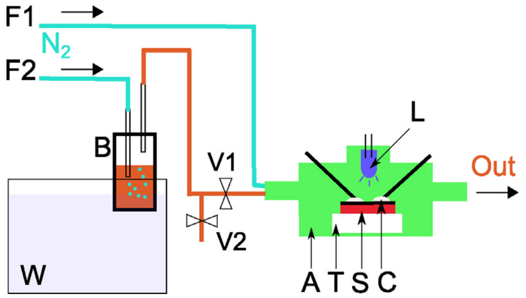

Fig. 1. Setup for the measurement of chemical sensitivity. F1 and F2, two channels of gas flow to produce gas mixture; V1 and V2, valves; W, water cooler for stabilizing temperature of bottle B; B, bottle with analyte; A, measuring chamber; T, teflon holder; S, sample; C, carbon paint contacts, L, four UV light-emitting diodes. For constant bubbling, V1 is open while V2 is closed.

3. Results and discussion

3.1. Characterization of the films

At the early stages of the deposition process, surface of the quartz substrates remains not conductive. With the growth time, the surface became conductive and when the uniformity of conductance over the film area was better than 50%, we assumed that a uniform carbon film had been grown. A qualitative measure of the film thickness was its optical transparency, which was assessed as white-gray contrast seen in optical microscope in transmitted light at the boundary between the bare substrate and the substrate with the deposited film. The thinnest films could be grown at different parameters. The typical parameters, however, were 25–30 min growth at a temperature of 1200 °C and a pressure of 6 mbar.

In order to measure the film thickness, the film edges obtained by mechanical wiping of part of the film from the substrate, were studied by AFM imaging. The height of the step formed between the bare substrate and the carbon film surface was taken as the film thickness (Fig. 2). The thickness of the thinnest films measured this way was about 1.5 nm. These films were almost completely transparent and their roughness was comparable to that of the substrate (about 0.5 nm).

Representative Raman spectra of the studied carbon films are shown in Fig. 3. It is seen that the spectra of the films grown for 30 and 90 min are dominated by well developed D, G and 2D bands, the D and G bands being well resolved.

The evolution of the Raman features with the growth temperature was studied on the thinnest films. We did not observed significant change in conductance. However, Fig. 3 (inset) shows that the intensity ratio of the D and G bands $I(D)/I(G)$ has a maximum at a temperature of 1000 °C.

According to the model discussed in [14] the ratio $I(D)/I(G)$ shows a broad maximum when plotted as a function of the atomic order changing from amorphous to well crystalline. Thus we