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Electrical conductivity and optical properties of thin carbon films grown by pyrolysis of ethanol–water mixture vapor

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ABSTRACT

A simple, low-cost and safe method to obtain thin carbon films is described. Deposition of graphene-like films on dielectrics, excluding the process of transfer from a metal surface, is of special interest. The properties of carbon nanomaterial are studied. The paper reports the data of electrical and optical measurements, the results of transmission and scanning electron microscopy and Raman spectroscopies. It is found that the growth conditions strongly affect the quality of products. The emphasis is placed on the influence of water content in the feedstock on the properties of the films obtained. An explanation of this influence is proposed.

1. Introduction

Graphene, a remarkable flexible crystal with the thickness of only one atomic layer, is of great interest owing to its extraordinary physical and electrical properties. It is a most promising candidate for future nanoelectronics. Graphene films can serve as field effect transistors [1,2], sensors [3,4], transparent conductive films [5,6], clean energy devices [7,8] and graphene-based fillers [9,10].

The realization of these potential applications requires high-quality and large-area graphene films. Different ways for producing graphene are known, such as micromechanical cleavage of graphite [11,12], liquid-phase exfoliation of graphite [13], oxidation of graphite [14,15], graphene synthesis in a voltaic arc [16], thermal decomposition of silicon carbide [17,18] and chemical vapor deposition (CVD) [19,20]. The CVD growth on transition metal surfaces is particularly advantageous for the preparation of large area and high quality graphene-like film. However the transfer process from metal surfaces is cumbersome and resource intensive. This step increases the production cost and can also cause wrinkle formation. Therefore, the possibility of obtaining graphene-like films directly on insulating surfaces is of great value for technology applications. In recent years, some methods for the growth of graphene-like on SiO_2/Si or other dielectric substrates have been reported [21–23]. Earlier we found that at high temperatures (900–1000 °C) the pyrolysis of ethanol vapors allows obtaining carbon films not only on a catalytic metal surface, but also on dielectric substrates [24]. Moreover, almost all CVD growth methods rely on methane gas as the precursor. Methane is extremely flammable and can form explosive mixtures with air. This led researchers to use ethanol, a low-cost and safe reagent, as a precursor in the growth of graphene films by the CVD method [25–27]. But the presence of water and knowledge on its role are essential for this technology. In this article, we consider these items.

Since the pyrolysis of ethanol–water vapor is obviously the simplest and cheapest means of obtaining graphene-like films on a dielectric surface, namely SiO_2/Si and quartz, we used it in our work. The aim of the paper is to describe the properties of the films obtained by this method. We have also examined the role of water content in the feedstock and demonstrated how the water concentration can affect the properties of films.

2. Material and methods

2.1. Growth of polycrystalline graphene films

The experimental setup is shown in Fig. 1. Graphene-like films were grown in a flow-type quartz reactor incorporated in a CVD apparatus, which included a tube furnace, temperature control system, reagent (ethanol and water) feed system and a vacuum pump. Quartz and SiO_2/Si (270 or 300 nm of thermally grown SiO_2 on a Si wafer) we used as a substrate. The synthesis was carried out in an inert gas flow at a reduced pressure (~10^3 Pa). The feedstock flow rate was controlled by a peristaltic pump and was varied from 2 to 4 ml/h. The water–alcohol mixture (96% ethanol and distilled

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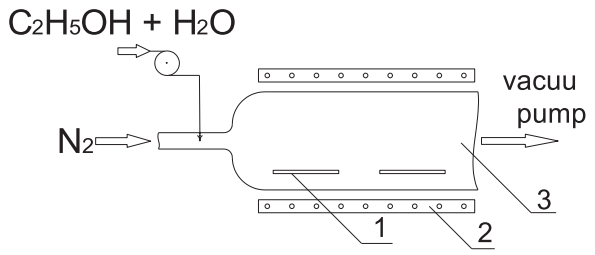

Fig. 1. Schematic of the experimental setup used to grow carbon films from an ethanol–water vapor: (1) substrates, (2) external electric furnace, (3) quartz reactor.

water) was fed directly into the evaporation zone, allowing for consistency between the composition of the feed solution and the ratio of the components of the gas phase. After the deposition process, the reagent feeding was stopped and the reactor was cooled down to room temperature in an inert gas flow (argon).

Synthesis temperature was varied in the range 850–1050 °C. Reaction times from 0.5 to 2 h and the water contents in the initial mix between 20% and 70% were investigated.

2.2. Materials characterization

Two-probe resistance measurements were performed under ambient conditions using a digital multimeter. For this purpose, two copper contacts were deposited on films by vacuum evaporation. Visible absorption spectra were recorded with a Specord 50 spectrophotometer. The transmittance at 550 nm was taken as a reference for comparing different samples.

Transmission electron microscopy (TEM) images were acquired with a JEOL JEM 2000FX TEM system. The morphology of the samples was studied with a ZEISS Evo 50 scanning electron microscope (SEM). Raman spectra were taken with a Bruker Senterra micro-Raman system in the 800–3700 cm^{-1} range under 0.5 cm^{-1} resolution. This instrument was equipped with a 532 nm laser.

Electrical and optical measurements were performed on films deposited on quartz substrate. Other studies were carried out on films deposited on SiO_2/Si substrate.

3. Results and discussion

As was previously shown by our group, even 10% ethanol solution can be used as a reagent for successful deposition of carbon nanowires on a nickel catalyst [28]. This surprising result was repeated in the present study. It was experimentally found that the addition of water to the initial reagent leads to two parallel processes: a catalytic process on the surface of copper producing fibrous carbon structures, and a non-selective non-catalytic process forming a thin carbon film, up to the water concentration of 70%. Properties of the films obtained on copper and quartz substrates at temperatures above 850 °C are comparable, but the structures formed on copper and requiring the transfer complicate the procedure. So, the results below refer only to the non-catalytic deposition on silica substrates.

It was found that an increasing water content in the feedstock increases the transparency of the films produced (Fig. 2), which become ≪darker≫ with increasing synthesis temperatures. The transmittance of the number of layers is not a direct proportionality, so for sufficiently thick graphene films it is more pertinent to use the term ≪optical density≫ (Fig. 2A). A plot of optical transmission versus reagent composition is shown in Fig. 2B for comparison.

Dependence of the sheet resistance on the reagent composition at different synthesis temperatures is shown in Fig. 3. The sheet resistances of the films grown at 950 °C and at 1050 °C varied from 1.5 to 25.5 kΩ/square and from 0.44 to 0.82 kΩ/square,

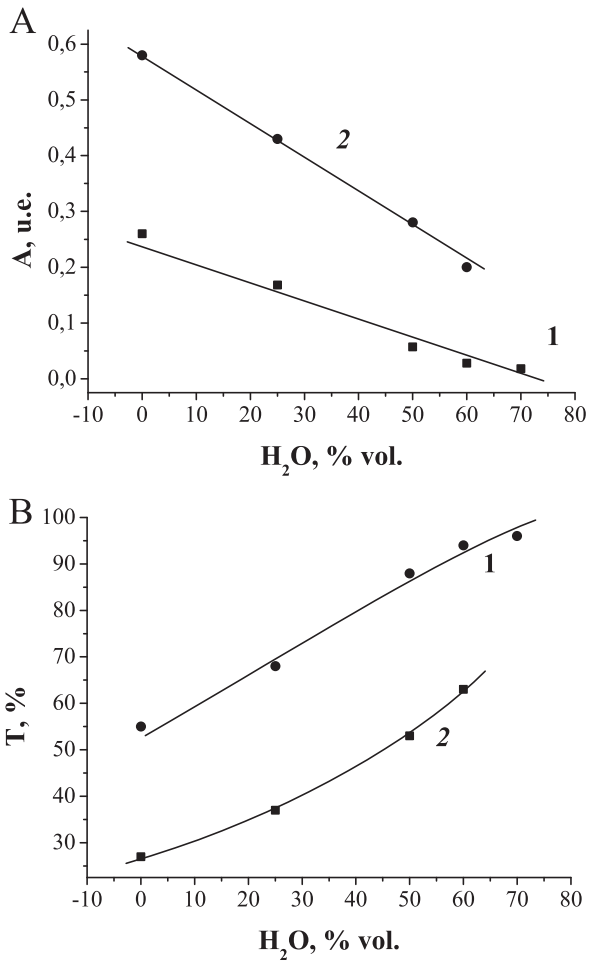

Fig. 2. Dependence of the optical density of carbon films on quartz substrates (a) and transmittance (b) at 550 nm on the reagent composition. Synthesis temperature were 950 °C (1) and 1050 °C (2), deposition time was 30 min.

respectively. So, the carbon structures obtained at high temperatures, possess better electrical conductivity. However, the resistance of the obtained films increases with water introduction into the reaction mixture. A relatively high sheet resistance of the samples will be explained below.

Like temperature growth effect, synthesis duration also influences the properties of films – the kinetic experiments showed that

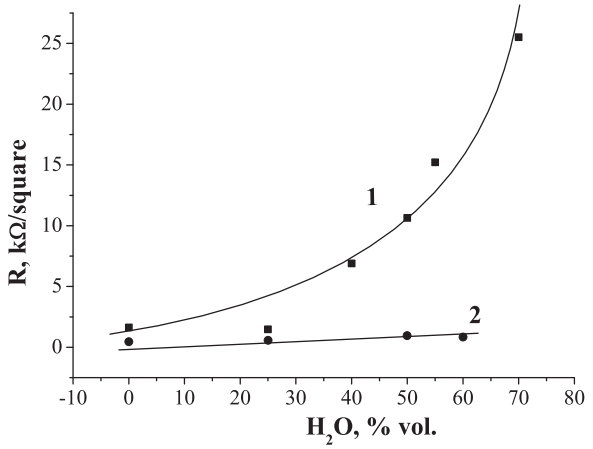

Fig. 3. Dependence of the sheet resistance on the reagent composition. Synthesis temperature was 950 °C (1) and 1050 °C (2), deposition time was 30 min.