Substrate temperature control in a system for deposition of carbon nanostructures at atmospheric pressure

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Abstract. The paper presents a plasma-enhanced chemical vapor deposition system for synthesis of carbon nanostructures on a metal substrate at atmospheric pressure with a system for substrate temperature control. It is realized by using a miniature microwave plasma source with a surface-wave discharge. An important part of the system is the movable target holder which allows adjustment of the distance between the plasma flame and the substrate. The substrate temperature increases during the deposition process due to the heating by the plasma flame. A constant value of the substrate temperature (400 – 700 °C) is essential for the synthesis of various carbon structures. An electronic system with sensors positioned in the holder is designed for measurement and control of the substrate temperature. The substrate temperature is measured in continuous and pulsed modes of the discharge, with the temperature value being controlled by the amplitude, repetition rate and duration of the microwave pulses.

1. Introduction

The unique properties of single-layer carbon nanostructures (graphene), as electrical conductivity, hardness and transparency, are attractive in view of a large number of applications in microelectronics. There exists a wide variety number of carbon nanostructures (nanowalls, nanoflakes, etc.) with multiple graphene layers, which are characterized by high reactivity, and also have great potential for various applications [1]. One of the methods for deposition of carbon nanostructures is the plasma-enhanced chemical vapor deposition (PECVD). Most of the systems for deposition of various carbon nanostructures operate at a low pressure of the neutral gas. In microwave plasma-enhanced chemical vapor deposition systems, the substrates used are sputter-coated with transition metals as catalysts. The conditions are similar to those used for the PECVD growth of carbon nanotubes but with pressure in the processing chamber lower than 1 Torr, when heating of the substrate is necessary. We present a design of a plasma-enhanced chemical vapor deposition system for synthesis of carbon nanostructures at atmospheric pressure with a system for substrate temperature control. It is realized by using a miniature microwave plasma source with a surface-wave discharge. This low-power source produces dense plasma with high neutral-gas temperature [2], which are the main factors for effective decomposition of complex molecules and generation of highly reactive species. The process is carried out in a chamber at a controlled gas mixture of argon, hydrogen and methane. The main part of the
system is the movable target holder which allows adjustment of the distance between the plasma flame and the substrate, thus determining the values of the plasma density and the gas temperature at the substrate surface. The holder contains also a K-type thermocouple in contact with the substrate for temperature measurement. The design of the holder includes also wires for biasing the substrate by a DC voltage. The substrate temperature increases due to heating by the plasma flame. A constant value of the substrate temperature is essential for the synthesis of various carbon structures: nanotubes (400 – 600 °C), nanoflakes (600 – 700 °C), nanowalls [3-4]. We designed an electronic system for precise measurement of the substrate temperature by a K-type thermocouple whereby the temperature can be controlled by a small-size Peltier element. Another manner to control the substrate temperature is used at a pulsed mode of operation of the discharge. The substrate temperature is measured by an electronic system and its value is controlled by the amplitude, repetition rate and duration of the microwave pulses at a fixed distance from the discharge tube end.

2. Experimental set-up and electronic system for measuring the substrate temperature

The experiments were carried out on the set-up presented in figure 1. A miniature microwave plasma source with a surface-wave discharge produces a plasma flame in a dielectric deposition chamber with two metal flanges (top and bottom). A microwave signal at a frequency $f = 2.45$ GHz from an MPG-4M generator (0 – 20 W) is fed to the coaxial surface-wave exciter. The forward and reflected powers are measured from a Pasternack PE2219-30 directional coupler by a HP 437B power meter. The exciter of the surface waves has an outer diameter of 2 mm; its inner conductor is a steel capillary with a diameter of 1 mm. A thin alumina tube is used as a discharge tube because the ceramics can withstand high gas temperatures and has high thermal conductivity. The initial tuning of the source at a frequency of 2.45 GHz is carried out by a Maury 1878C triple stub. The neutral gas-mixture (Ar/H$_2$/CH$_4$) is fed through the steel capillary to the discharge tube. The gas flows are measured by APEX-AX-MC mass-flow controllers.

![Figure 1. Experimental set-up and system for substrate temperature measurement.](image)

The electron temperature and density in the argon gas are estimated by double-probe and optical diagnostics. The results for the plasma parameters at different gas flows and applied power obtained by both diagnostics in the middle of the discharge tube are as follows: plasma density in the range $n_e = 4 \times 10^{20} – 8 \times 10^{20}$ m$^{-3}$ and electron temperature $T_e = 1.6 \pm 0.1$ eV [5, 6]. In the plasma flame, the electron temperature and density and the gas temperature decrease rapidly at a distance of 5 mm. This
is why the copper substrate with dimensions 1.5 mm×1.5 mm is exposed to the plasma flame at 2 mm from the ceramic tube end. The substrate is tightly glued to the thermocouple and fixed to the movable holder. To measure accurately the substrate temperature by a thermocouple, one needs to compensate the error voltage by a reference (cold) junction. The electronic circuit must compensate the changes in the temperature at the reference junction of the thermocouple in order for the output voltage to be an accurate representation of the hot junction measurement. Converting the voltage generated by a thermocouple into an accurate temperature reading is not easy for many reasons: a small voltage signal, a nonlinear temperature-voltage relationship, an error due to the reference junction; also, the thermocouples may pose grounding problems. The small signal requires the use of a high-gain amplifier stage before the analog-to-digital conversion. To measure the temperature of a substrate for deposition of carbon nanostructures in the range of 400 − 700°C, we used a K-type thermocouple (chromel-alumel). This type of thermocouple allows measurement from −200 to 1000°C with an almost invariable Seebeck coefficient − 41.84μV in this wide range of temperature measurement. An appropriate measurement circuit solution when using type K thermocouple is the Analog Devices thermocouple amplifier with cold junction compensation − AD8495ARMZ, which converts the temperature of the thermocouple to a signal voltage with a transfer coefficient of 5mV/°C. This voltage is measured by an Arduino-microcontroller board and fed to a PC; the substrate temperature is thus monitored and displayed. AD8495ARMZ is a fixed gain instrumentation amplifier with thermocouple cold junction compensation on an integrated circuit. The circuit is laser trimmed to match the characteristics of K type (chromel-alumel) thermocouples and amplifies the small thermocouple voltage to provide a 5 mV/°C output. The high common-mode rejection of the amplifier blocks common-mode noise that the long thermocouple leads can pick up.

3. Results for the substrate temperature

The temperature of the substrate is measured in continuous and pulsed modes of operation of the discharge at a gas flow-rate of 250 sccm in a gas mixture Ar/H2/CH4. The result for the substrate temperature dependence on the input microwave power for plasma production is presented in figure 2. These temperatures can be considered as steady-state values, as they are measured after an initial rapid increase with time.

The temperature obtained is in the range 500 − 900°C, which is necessary for deposition carbon nanostructures in gas-mixtures of argon, hydrogen and methane. In the continuous mode, the heating of the plasma source in the chamber is significant, so that it can only operate for a limited period of time without cooling. In a pulsed mode of operation, the source can function for a long period of time without cooling. The temperature dependence on the repetition rate of microwave pulses with an amplitude \( P = 15 \text{ W} \) and a pulse duration \( \tau = 0.435 \text{ ms} \) is presented in figure 3. These temperature values are not sufficiently high for effective deposition of carbon nanostructures. The plasma system operation is very stable at a comparatively low pulse repetition rates; the dependence of the substrate temperature on the pulse duration at 100 Hz was studied (figure 4) at an input power \( P = 20 \text{ W} \). This mode allows one to fix precisely the substrate temperature for a long
period of time by using a temperature stabilized deposition system.

4. Conclusions
A system with a miniature microwave plasma source is designed for deposition of carbon nanostructures at atmospheric pressure. An electronic system is developed for precise measurement of the substrate temperature. The results show that, at a fixed distance of the substrate to the discharge tube, the substrate temperature can be controlled precisely in a pulsed mode of the discharge by varying the pulse amplitude and duration. The distance between the substrate and the plasma flame is optimized in order to obtain temperatures in the range 400 – 800 °C.

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