Measurement and control of the substrate temperature in vertical graphene nanosheets deposition

V Vachkov and Zh Kiss’ovski
Faculty of Physics, St. Kliment Ohridski University of Sofia, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria
E-mail: vachkov@phys.uni-sofia.bg

Abstract. The characteristics of the microwave surface-wave plasma discharge at atmospheric pressure and the control of the gas mixture (Ar/H2/CH4) in the deposition chamber, together with the temperature of the metallic substrate, are important parameters in the processes of deposition of vertical graphene nanosheets. Since obtaining carbon nanostructures necessitates regulating the substrate temperature in the range 550 – 980 °C, we developed an electronic system based on an Arduino Uno microcontroller. It was designed to automatically measure and control the temperature of the substrate heater with the capability of varying smoothly the temperature by a PID-regulator. The measurements were carried out by a K-type thermocouple, whose hot end was placed at the point of measuring the temperature. The resulting thermoelectric voltage was amplified by a MAX 31855 amplifier, followed by processing by the microcontroller and subsequent determination of the temperature. This system offers the possibility of controlling accurately the temperature as required by the regime of deposition.

1. Introduction
The modern methods of depositing graphene structures allow the synthesis of thin layers suitable for many applications in electronics, such as electrodes in supercapacitors and high-sensitivity sensors. Of particular interest are the different types of graphene structures, such as vertical nanosheets, which have a great potential for the implementation of supercapacitors [1]. One of the methods used for depositions of carbon nanostructures is microwave plasma-enhanced chemical-vapor deposition (MPECVD) at atmospheric pressure. The initiation of the processes of methane decomposition is carried out in a microwave surface-waves discharge at atmospheric pressure with a precise control of the gas mixture (Ar/H2/CH4). The process of deposition of nanostructures requires a precise control of the temperature of the metal substrate in the deposition chamber. Maintaining a stationary value of the substrate temperature is essential for the synthesis of various carbon structures, such as nanotubes (400 – 600 °C), nanosheets and nanowalls (600 – 700 °C) [2-3]. Many of the systems for deposition of various carbon nanostructures are working at low pressures, which further complicates the technological process of deposition and presents difficulties in controlling it. In this work, we designed and built a plasma-enhanced chemical-vapor deposition system for synthesis of carbon nanostructures at atmospheric pressure, which includes a system for accurate measurement and control of the temperature based on an Arduino Uno microcontroller, as necessitated by the technological regime of deposition. The metal substrate temperature was controlled within the range of 550 – 980 °C, which is

1 To whom any correspondence should be addressed.
important in view of achieving a high efficiency of the deposition processes and the expected properties of the vertical graphene structures. The system has the capability of varying smoothly the temperature and keeping a certain preset value by means of a proportional-integral-derivative (PID) regulator [4]. The PID control is by far the most widely used way of accurate feedback control. The basic idea behind it is for the controller to produce a signal correcting any deviation from a preset temperature value and adjust appropriately the power supply to the heating element. In the experiments reported, the temperature was measured by a calibrated K-type thermocouple, whose hot end was placed at the point of measuring the temperature, while the cold end was connected to an electronic circuit compensating the temperature difference between the warm and cold end. The resulting thermoelectric voltage was amplified by a MAX 31855 amplifier, followed by processing by the microcontroller and subsequent accurate determination of the temperature [5].

2. Experimental set-up for deposition of vertical graphene nanosheets and microcontroller system for measuring and controlling the substrate temperature

The experiments were carried out on the setup presented in figure 1. The microwave plasma source at atmospheric pressure based on a surface-wave discharge produces a plasma flame in a dielectric deposition chamber with two metal flanges. A microwave signal of frequency \( f = 2.45 \text{ GHz} \) produced by an MPG-4M generator (0 – 20 W) is fed to a coaxial surface-wave exciter. The forward and reflected power separated by a Pasternack PE2219-30 directional coupler are measured by an HP 437B power meter. Because of the high gas temperature, a thin ceramic tube is used as a discharge tube placed in the coaxial exciter. The microwave generator signal fed to the coaxial exciter at frequency 2.45 GHz is tuned by a Maury 1878C triple stub. A neutral gas-mixture (Ar/H2/CH4) is fed through a steel capillary to the discharge tube, with the gas flows being regulated by APEX-AX-MC controllers.

![Diagram of experimental setup](image)

**Figure 1.** Experimental set-up and system for measuring the substrate temperature.

The electron temperature and density in the gas mixture were estimated by optical spectrometry of the argon gas emission, as follows – electron density in the range \( n_e = 4 \times 10^{20} - 8 \times 10^{20} \text{ m}^{-3} \) and electron temperature \( T_e = 1.6 \pm 0.1 \text{ eV} \). In the plasma flame, the electron temperature and density and the gas temperature decreased rapidly within a distance of 10 mm. This was why the nickel-foam substrate with dimensions 5 mm \( \times 5 \) mm was exposed to the plasma flame at 7 mm from the end of the ceramic tube.

The heater was glued to the thermocouple connected to the amplifier. The temperature in deposition chamber was measured and controlled by the setup presented in figure 2; the values
measured were recorded in a text file, as is convenient for further processing and analysis. Measuring precisely the substrate temperature by a thermocouple necessitates the use of an electronic circuit that compensates the changes in the temperature at the reference (cold) junction of the thermocouple, so that the output voltage is an accurate representation of the hot junction measurement. Conversion of the voltage generated by a thermocouple into an accurate temperature reading is not an easy task for many reasons: a small voltage signal, a non-linear temperature-voltage relationship, an error due to the reference junction and problems in grounding the thermocouples. The small signal requires the use of a high-gain amplifier stage before the analog-to-digital conversion. For the purpose of maintaining the substrate temperature in the range of 615 – 650 °C as needed for depositing vertical graphene nanosheets we used a K-type thermocouple. This type of thermocouples allow measurement from –200 °C to 1372 °C with an almost invariable Seebeck coefficient (41.84 μV). An appropriate solution for temperature measurement by a K-type thermocouple is designing an electronic circuit including a MAX 31855 thermocouple amplifier with cold junction compensation to convert the temperature of the thermocouple to a voltage signal which is applied to an Arduino Uno microcontroller (D9, D10, D13 digital inputs) for processing and calculating the actual temperature of the heater element.

The circuit includes a zero-cross detector module, which is a type of voltage comparator used to detect a sine waveform transition from positive to negative values, and an LCD display for visualizing the temperature values measured.

3. Results of the temperature measurements in the deposition chamber
A smooth temperature control is very important in ensuring the efficiency of the deposition processes of vertical graphene structures. Typically, the optimal deposition of graphene structures is achieved in the range temperatures of the metallic substrate between 615 – 650 °C, indicating the need to use a PID controller to maintain the deposition temperature. In this work, the temperature of the substrate was measured in a pulsed mode of discharge operation at a gas flow rate of 185 sccm in a gas-mixture of argon, hydrogen and methane. The control achieved by the system designed and built by us is demonstrated in figure 3, which shows how the preset temperature value is established, in accordance with the technological regime of deposition. Figure 4 presents vertical carbon nanosheets obtained at the temperature of 615 °C.

Figure 2. Electronic measurement and control systems of the substrate temperature.
4. Conclusions
A system was designed and built for deposition of vertical graphene nanosheets at atmospheric pressure by means of a miniature microwave plasma source. An electronic system was developed for measurement and control of the substrate temperature. The results show that the quality of the graphene structures deposited depends strongly on the temperature regime and on the gas discharge conditions. The distance substrate – plasma flame was optimized in order to obtain temperatures in the range 615 – 650 °C needed for efficient deposition.

Acknowledgements
This work was financially supported in part by EU project PEGASUS, NIS-SU No 3257.

References
[1] Ostrikov K, Cvelbarand U and Murphy A 2011 J. Phys. D: Appl. Phys. 44 174001
[2] Ohashi T, Kato R, Takumi Ochiai T, Tokun T and Kawarada H 2012 Diamond & Related Mater. 24 184–7
[3] Malesevic A, Vitchev R, Schouteden K, Volodin A, Zhang L, Van Tendeloo G, Vanhulsel A and Van Haesendonck C 2008 Nanotechnol. 19 305604
[4] O’Dwyer A 2009 Handbook of PI and PID Controller Tuning Rules 3rd Edition (Imperial College Press) 2 4-16
[5] Kiss’ovski Zh, Djermanova N, Mitev D and Vachkov V 2014 J. Phys.: Conf. Series 514 012007