Sensors and Actuators A 280 (2018) 8–13

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Epitaxial graphene thermistor for cryogenic temperatures

Sırrı Batuhan Kalkan, Serap Yiğen, Cem Çelebi*

Quantum Device Laboratory, Department of Physics, Izmir Institute of Technology, Izmir 35430, Turkey

ARTICLE INFO

Article history:
Received 17 May 2018
Received in revised form 10 July 2018
Accepted 13 July 2018

Keywords:
Epitaxial graphene
Encapsulation
NTC thermistor
Low-temperature

ABSTRACT

The thermal responsivity of monolayer epitaxial graphene grown on the Si-face surface of semi-insulating SiC substrate is investigated as a function of temperature below 300 K. The measurements showed that adsorption/desorption of atmospheric adsorbates can randomly modify the electrical characteristics of graphene which is indeed undesirable for consistent temperature sensing operations. Therefore, in order to avoid the interaction between graphene layer and adsorbates, the grown graphene layer is encapsulated with a thin SiO_2 film deposited by Pulsed Electron Deposition technique. Temperature dependent resistance measurement of encapsulated graphene exhibited a clear thermistor type behavior with negative temperature coefficient resistance character. Both the sensitivity and transient thermal responsivity of the SiO_2/graphene/SiC sample were found to be enhanced greatly especially for the temperatures lower than 225 K. The experimentally obtained results suggest that SiO_2 encapsulated epitaxial graphene on SiC can be used readily as an energy efficient and stable temperature sensing element in cryogenic applications.

1. Introduction

Graphene has been considered to be a promising 2D material for the realization of new generation microelectronic and optoelectronic devices with planar architecture owing to its high charge carrier mobility [1], large surface-to-volume ratio [2] and excellent optical transparency [3]. Besides, superior thermal conductivity (TC) of graphene, reaching a value of about 5300 W/m.K [4,5] at room temperature, has motivated researchers to explore the potential use of this 2D material also in temperature sensor technology. The 2D planar structure allows graphene to be directly implanted to integrated circuits as a functional temperature sensing element. However, the restrictions due to sophisticated lithography techniques [6], subsequently low temperature sensitivity and slow response speed of bare graphene [7–9] are the main constrains for the development of graphene based thermal sensors.

The transfer process and substrate choice play an essential role for graphene based temperature sensors. The defects and residues created during the transfer process for chemical vapor deposited (CVD) graphene and as well as relatively low TC of underlying substrates [10] such as silicon dioxide (SiO_2) (1.3 W/m.K) [11] and silicon nitride (SiN) (4 W/m.K) [12], greatly hinder the transient thermal responsivity of graphene layer. In contrast to CVD graphene, epitaxial graphene (EG) is ease of production on silicon carbide (SiC), which plays into our hands with a large TC of around 300 W/m.K [13] when compared to these low TC materials as a substrate: Silicon atoms evaporate from SiC surface at high temperatures and carbon atoms that are left on the surface forms the graphene layer. Therefore, single atom thick EG can be grown readily on SiC's polar surfaces (Si-face and C-face) without need of any transfer and/or sophisticated deposition processes like CVD and sputtering that are the most commonly used techniques to produce metal, semiconductor or ceramic based conventional thermistor devices.

Previous studies showed that extremely large surface-to-volume ratio of graphene leads to undesirable electrical instabilities when it is integrated as a functional component in electronic or optoelectronic devices operating under atmospheric conditions [14]. The adsorbates like O_2 and H_2O in air serve as surface trap states and sequential adsorption/desorption of these molecules drastically alter the electronic transport characteristics of graphene via charge transfer doping phenomenon. In the case of bare graphene exposed to these atmospheric gases, heating and/or cooling process is expected to promote further the adsorption/desorption of these above mentioned adsorbates which may cause abrupt variations both in the electrical and thermal conductivities of graphene [15,16]. Thus, the conductivity of graphene is strongly influenced by the atmospheric gases and humidity fluctuations as it should depend only on temperature variations. This causes different conductivity values for the same temperature,

* Corresponding author.
E-mail address: cemcelebi@iyte.edu.tr (C. Çelebi).

https://doi.org/10.1016/j.sna.2018.07.028
0924-4247/

which must be avoided. Therefore, for stable and reliable temperature sensing operations, the interaction of graphene with the surrounding adsorbates should be necessarily prevented, for example, by encapsulating or passivating the graphene layer with an appropriate material. However, all the graphene based thermistor type sensors investigated in earlier studies do not comprise any encapsulation protection [6–9].

In this work, we report the thermal response of monolayer EG that was grown on a single crystal semi-insulating (SI) SiC substrate by high temperature vacuum annealing process. In order to avoid adsorbate induced possible variations in the charge carrier dynamics of graphene, the adsorbates already stuck on bare epitaxial graphene (BEG) in air were removed by UV light exposure under vacuum conditions. The UV exposure process is necessary to ensure stable and repeatable temperature sensing operations that relies only on the intrinsic thermal and electrical characteristics of the graphene layer itself. Adsorbate free graphene layer were encapsulated with a thin SiO_2 film deposited by state-of-the-art Pulsed Electron Deposition (PED) technique. The resistance vs temperature (R-T) measurements showed that SiO_2 encapsulated epitaxial graphene (EEG) is a typical negative temperature coefficient (NTC) material which exhibits rapid electrical resistance increase with temperature decrease. We have also found that the encapsulation of graphene yields reversible thermal sensing operations unlike BEG samples. Transient thermal responsivity measurements implied that SiO_2 encapsulated EG on SiC can be used readily as a temperature sensing element especially for low temperature applications.

2. Experimental

Monolayer epitaxial graphene is grown on the Si terminated face of a (4 mm x 10 mm) SI 4H-SiC substrate annealed at an elevated temperature of 1450 °C for 20 min in a UHV chamber ($\sim 2 \times 10^{-10}$ mbar). Prior to the graphene growth, SiC substrate degassed at 600 °C over night and then the temperature is raised to 1100 °C for about 10 min to remove the native oxide layer. During the growth experiment, the temperature of the sample was measured remotely by using an optical pyrometer with ±1 °C resolution. At the growth temperature of 1450 °C, the Si atoms sublimate from SiC surface into vacuum and left behind C atoms forms the graphene layer by mimicking the hexagonal lattice structure of underlying SiC crystal. To verify the growth of epitaxial graphene and as well as to determine its thickness, we conducted single point Raman spectroscopy measurements by a green laser with 532 nm excitation wavelength. The details of graphene growth experiments and Raman spectroscopy analysis can be found in our previous studies [17,18].

The morphology of grown graphene layer was characterized by tapping mode Atomic Force Microscopy (AFM) topography measurements. The AFM image of BEG layer (Fig. 1(a)) exhibits typical SiC background based large terraces and graphene related flaky structures appearing with blurry wrinkles lying on these parallel terraces. Small amount of local and darker regions correspond to a few layer BEG flakes. Following the structural and morphological analysis of epitaxial graphene, Cr/Au (3 nm/80 nm) interconnect source/drain pads were deposited thermally on the two sides of the grown layer for conducting two-terminal I-V measurements (see Fig. 1(b)). To promote desorption of adsorbates which were already stuck on graphene in air, the sample was exposed to UV light for a period of 3 h under high vacuum conditions (10^{-5} mbar). The UV irradiation wavelength is specifically selected to be 254 nm since it is energetically sufficient enough to remove the O_2 and H_2O molecules adsorbed by the graphene layer.

After the adsorbate removal process, the sample surface was encapsulated with a 100 nm thick SiO_2 layer by Neocera PEBS-32 PED system. The R-T measurements were conducted using 5 K–300 K Janis cold head optical cryostat equipped with a Pfeiffer Hi-Cube pump station. Lakeshore 331 temperature controller and a calibrated reference thermocouple were used for temperature control and measurements, respectively. In order to ensure good thermal contact and electrical insulation at the same time, low temperature compatible ceramic epoxy was employed for bonding the sample on a Copper (Cu) plate. The Cu plate with the sample on top were mounted on the sample holder of cold head (Fig. 1(d)). The electrical characterizations of the sample were done by using Keithley 2400 Source Meter and Keithley 6220 Picoammeter. The R-T measurements of the sample were conducted under a bias voltage of $V_b = 2$ V.

3. Results and discussion

The I-V characteristics of BEG sample obtained before and after in-vacuum UV light treatment were plotted in Fig. 2(a) The measurements show that room temperature resistance (R_{300K}) of as-grown BEG sample is decreased from ~2.3 kΩ to ~1.2 kΩ after 3 h of UV light exposure. The reduction in the resistance of graphene can be explained as in the following manner. Epitaxial graphene grown on the Si-terminated face of SiC is known to be intrinsically n-type doped due to charge transfer between graphene layer and SiC substrate underneath [19]. The atmospheric molecules such as O_2 and H_2O are adsorbed readily by the graphene layer when it is exposed to air. These adsorbates behave like electron trapping surface states and thus reduce the electron density of n-type epitaxial graphene as schematically illustrated in Fig. 2(b). As the UV light promotes desorption of these adsorbates from the sample surface into vacuum, the trapped electrons are released back to the graphene layer via charge transfer doping mechanism. Therefore, the R_{300K} of adsorbate free BEG becomes lower than that of as-grown BEG measured prior to the UV light exposure process. The R-T characteristics of BEG sample measured before and after UV exposure were compared in Fig. 2(c) and (d). The resistance of as-grown BEG with adsorbates increases almost like exponentially as a function of decreasing temperature (Fig. 2(c)) and resembles to that of a typical thermistor element with NTC character. The overall resistance variation for as-grown BEG was determined to be about 21% for the temperature range between 25 K and 300 K. After the adsorbate removal process with UV light, the R–T characteristics of BEG becomes similar to that of a conventional metal at high temperatures whereas exhibits an upturn at around 150 K (Fig. 2(d)). This peculiar temperature dependent resistance behavior of epitaxial graphene on SiC has been previously attributed to the weak-localization and electron-electron interaction phenomena [20]. It is clearly seen that adsorbate free graphene cannot be used as a thermistor due to the continuous interaction of ambient gases with the graphene layer. The resistance characteristics of bare graphene sensor strongly depends on the partial pressure of the surrounding adsorbates. These random interactions are undesirable for ultimate electrical stability. Our experiments showed that the resistance of graphene can change simultaneously with the adsorption/desorption of electron trapper adsorbates. Thus, the resistance of our fabricated sensor at 200 K becomes the same as the one measured at 130 K due to the parabolic behavior of the R-T curve after UV light illumination (Fig. 2(d)). Therefore, it is of crucial importance to encapsulate graphene in order to stabilize and rectify its temperature sensing capability.

Following the R-T measurements of BEG conducted before and after UV light illumination, the sample was encapsulated with a 100 nm thick SiO_2 layer by using PED technique. For comparison,