Resistance-temperature characteristics of CVD and high strength metallurgical graphene

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Abstract: Gas sorption conditions on the graphene surface, as well as their influence on graphene properties, play a significant role when applications are considered. The influence of temperature and pressure on electric properties of graphene were investigated and discussed within this work, which was conducted in order to determine the border values for the sorption and desorption process of hydrogen on the graphene surface. The temperature was changed within the range of 243–373 K. Two types of graphene were used for comparison: one of graphene synthesised by our own method using chemical vapour deposition (CVD) and one of high strength metallurgical graphene (HSMG) in both conducting (cHSMG) and semiconducting (sHSMG) varieties. The characteristics were determined under hydrogen atmosphere in a fitted apparatus under pressure. The overall target material relies on the hydrogen storage of a designed graphene-based composite [1,2].

Keywords: graphene; electrical properties; high strength metallurgical graphene; HSMG.

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1 Introduction

Gas sorption conditions on the graphene surface, as well as their influence on graphene properties, play a significant role when applications are considered. Various methods have been developed recently to manufacture macro scaled graphene sheets. The most common processes are based on the CVD concept and epitaxial growth of graphene on solid substrates [3–12]. Simultaneously, alternative methods have been developed that are based on the control of carbon solubility in solid and liquid forming matrixes [13–15]. Using this last concept, it is possible to grow polycrystalline graphene monolayers with relatively large grains measuring up to 1 mm in diameter that fit conformably together. Consequently, large areas of semi-perfect graphene structures are attainable with a low and controlled number of point and linear structural defects. Such manufactured graphene sheets exhibit extremely high mechanical strength; therefore, they have been called high strength metallurgical graphene (HSMG).

Adsorption of hydrogen to the surface can be performed in two ways: by physical and chemical sorption. It has been shown that a single layer of graphene can engage 3.3% by weight. This value may be doubled for graphene with two sides that can be filled with hydrogen (suspended graphene). For chemisorption, the value is 8.3% by weight [16]. In fact, the value of hydrogen, which manages to attach to the surface of pure graphene, is much smaller. Srinivas et al. [17] study showed that it is possible to join 1.2 wt.% H2. Yuan et al. [18] investigated the absorption of hydrogen on the petals of glucose that was reduced with the use of graphene oxide, or GO. The amount of hydrogen attached in this case was 2.7 wt.%. In most of the presented works, the achieved values do not come close to the limit of profitability designated by the US Department of Energy (DOE), which was 6.5 wt.% for 2010 and 9 wt.% in 2015 [18,19]. The solution to this problem
may be the functionalisation of graphene and graphene planes pillared to allow the hydrogen molecules to move freely between the planes of graphene. Thus, prepared composites can absorb more than 10–12.8 wt.% [16,20]. The work of Kula et al. [1] demonstrated in the simulations and calculations that increase the distance between levels of graphene to 6 Å will be this type of structure (nanocomposite for reversible hydrogen storage). It will have the ability to adsorb 37.3% of hydrogen at a pressure of 10 MPa and a temperature of 250 K [1]. The paper presents the variation characteristics of electrical resistance vs. temperature for different operating atmospheres. The results concerning the behaviour of graphene HSMG are in line with several literature reports [21]. HSMG behaves exactly as graphene obtained from pyrolytic graphite by mechanical exfoliation (it has a negative temperature coefficient of resistance). It is further noted that the method of measuring electrical values working in a controlled atmosphere (composition, temperature, and pressure) excels as a tool for the qualitative assessment of gas sorption on the surface of graphene.

2 Specimens and their characterisation

Two types of graphene were used for comparison in this paper – CVD graphene and synthesised by own method – and HSMG in two options – conducting (c-HSMG) and semiconducting (sc-HSMG). The c-HSMG and sc-HSMG specimens have been obtained using two different processes modes, namely, a low pressure process and an atmospheric pressure process; the method was described in a previous paper [13]. All specimens have been characterised by Raman spectroscopy, SEM imaging and TEM observations with electron diffraction before electrical investigations. The results are presented in Figure 1 (Raman spectra); Figures 2, 3 and 6 (SEM images); and Figures 4 and 5 (TEM pictures and electron diffractions).

Results of characterisation have indicated that all investigated graphene specimens exhibit highly similar Raman spectra (Figure 1). Each spectrum contained 2D and G peaks with an intensity ratio of I(2D)/I(G) from 2.9 (sc-HSMG) to 3.4 (CVD), which confirmed the presence of a single layer defect-less graphene in all specimens [22–24].

Additionally, SEM images (Figures 2(b) and 3(b)) showed the perfect final covering of the forming matrix surface by a graphene single layer coating, which was independent of their different growth mechanisms; namely, these were the dendritic mode for c-HSMG (Figure 2(a)) and the cellular (hexagonal) for sc-HSMG (Figure 3(a)). The graphene sheets formed on liquid metal revealed two different mechanisms for nucleation and growth. In the first mechanism, the growth starts according to the dendritic 2D mode (Figure 2(a)).

The growth of numerous nuclei proceeds notably quickly in certain crystal directions. The longest branches contact and stabilise their random orientations. If the growth rate of the dendrite branches is fast enough, then they can locally overlap even if they crystallise on an absolutely flat liquid metal surface due to crystallographic disorientation (Figure 2(b)). Consequently, the metallurgical graphene grown in this way is also a polycrystalline single layer material. The grains ( flakes) exhibit a random orientation, and few π-bonds exist in overlapping sites.

The alternative mechanism for forming graphene on liquid metal is based on cellular (hexagonal) nucleation and growth (Figure 3(a)). All of the nuclei exhibit a hexagonal shape and are able to move with three degrees of freedom on the surface of the liquid.
metal (including rotation). Therefore, conformable accommodation along hexagon edges occurs when they contact. In this way, perfect hexagonal atoms arrangement can continue between neighbouring flakes (Figure 3(b)); consequently, large monolayer areas of semi-perfect graphene may be formed without any $\pi$-bonds.

**Figure 1** Raman spectra: (a) CVD graphene; (b) c-HSMG and (c) sc-HSMG

**Figure 2** SEM images of grain growth (a) and continuous layer (b) c-HSMG
Figure 3  SEM images of grain growth (a) and continuous layer (b) sc-HSMG

Figure 4  (a) sc-HSMG imaged by TEM and the (b) corresponding electron diffraction pattern, followed by (c) the same pattern with features being assigned

Figure 5  TEM images (a), electron diffraction (b) c-HSMG

The TEM pictures (Figures 4(a) and 5(a)) and their corresponding electron diffraction patterns (Figure 4(b), (c) and 5(b)) identified the perfect hexagonal arrangement of atoms
in the sc-HSMG as well as in c-HSMG specimens. In Figure 4, the graphene membrane can be observed to be locally folded and overlapped; there does not seem to be any damage.

The CVD graphene was not able to exist on the TEM mesh (Figure 6); therefore, these specimens were not investigated by TEM.

Figure 6  SEM images of TEM specimens: (a) CVD graphene and (b) sc-HSMG

3  Experimental technique

The testing equipment for measuring the resistance-temperature characteristics of graphene specimens has been designed, mounted and tested (Figure 7). The equipment consisted of a measurement chamber equipped with the vacuum pump and gas dosing system. Graphene specimens have been located to the measurement table that have been heated or chilled by a Peltier’s modules system with a computer control system. The testing stand enabled the control of the gaseous atmosphere, as well as online temperature and resistance registering.

Figure 7  Scheme of the apparatus for electrical property testing
Investigated graphene specimens have been transferred onto Kapton substrates. Gold connectors have then been deposited to obtain the measurement area of 7 × 7 mm. The resistance of specimens has been measured cyclically in the temperature interval of −20°C to 60°C or −40°C to 20°C. Measurements have been performed in various environments, specifically, air, argon, mixture (Ar + 4% H₂ volume) and at a 1 Pa vacuum. Commercially available gases and mixtures of high purity were used.

4 Results and discussion

First results of preliminary resistance measurements vs. temperature revealed a fundamental difference between the two types of HSMG: that grown through the dendritic mechanism and that formed by cellular mechanism.

The first type shows a positive thermal coefficient of resistivity, which is characteristic for electrical conductors (Figure 8(a)). Therefore, we called this type of graphene c-HSMG. The second type behaves similar to a semiconductor, showing a negative thermal coefficient of resistivity (Figure 8(b)), so this explains why we called it sc-HSMG. The values of the thermal coefficients for c-HSMG, sc-HSMG and CVD graphene have been collected in Table 1. The experimental results are consistent with the literature data. For exfoliation graphene, the results are $-3.7 \times 10^{-3}$ to $-7.1 \times 10^{-4}$ 1/K [21,25] and are comparable with sc-HSMG.

![Figure 8](image)

**Table 1** The experimental results of thermal coefficients. Pressure $p = 1$ Pa

<table>
<thead>
<tr>
<th>Type</th>
<th>Thermal Coefficient [1/K]</th>
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<tbody>
<tr>
<td>sc-HSMG</td>
<td>$-1.7 \times 10^{-3}$ to $-4.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>c-HSMG</td>
<td>$3.5 \times 10^{-4}$ to $4.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>CVD graphene</td>
<td>$1.5 \times 10^{-4}$ to $4.0 \times 10^{-4}$</td>
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The long periods of isothermal heating and cooling have been applied in the next series of resistance-temperature relationship measurements to reveal an impact of gas sorption on the resistivity of various graphene specimens in different gaseous environments. The obtained results have been collected in Figures 9 and 10, which enables a comparison of sorption behaviour for the CVD, c-HSMG and sc-HSMG specimens.
The CVD graphene and c-HSMG specimens, which have been tested under 1Pa vacuum, showed in-phase relationships for temperature and resistance vs. time during cyclic isothermal heating and cooling tests (Figure 9(a) and (c)). The specimens also showed a creeping increase of resistance in each next thermal cycle. This creep behaviour might have been caused by two mechanisms. The first one would be the polycrystalline graphene formatting by structural defect relaxation. The second one would be a gas adsorption from the imperfect vacuum chamber (1 Pa), which would probably be oxygen or/and water vapour. The CVD graphene disclosed quasi proportional growth of resistance
in the following cycles in both the heating as well as cooling stages. This suggests the existence of only one mechanism, namely that the structural defect relaxation probably occurs on the non-conformal grains boundaries. The c-HSMG specimens showed a strong parabolic increase of resistance during the isothermal cooling periods and very weak parabolic recovery of conductivity at the isothermal heating periods, which discloses the susceptibility of c-HSMG to irreversible adsorption of gaseous traces (oxygen and/or water vapour) within the testing conditions.

The sc-HSMG specimens showed anti-phase relationships for temperature and resistance vs. time when they have been tested in the above described conditions (Figure 9(b)). Additionally, we observed a parabolic growth of resistance during isothermal cooling stages and a similar reciprocal decrease during isothermal heating periods. Consequently, the average level of resistance remained at a quasi-constant level. The reason of such behaviour for the sc-HSMG was probably reversible adsorption of the same gaseous traces on the semiconducting substrate.

These interesting properties of the sc-HSMG inspired us to undertake an atmospheric pressure investigation under high purity argon and argon + 4% H₂ environments (Figure 10(a) and (b)). The obtained results confirmed the semiconducting nature of sc-HSMG and its susceptibility to reversible sorption of gases, and the 4% hydrogen addition to the argon atmosphere increased the level of resistance pulses ca. 20 kΩ. Moreover, it changed the character of the cyclic resistance plot visibly toward an increasing parabolic growth of resistance during each subsequent isothermal cooling period, while the resistance value then returned to the initial level during each heating period. In this case, the increasing amplitude of resistance after each heating – cooling cycle also suggests a susceptibility of sc-HSMG to selective sorption of hydrogen from the Ar – H₂ gas mixture. The cyclic return of resistance to the initial level when sc-HSMG has been heated up to 60°C indicates the total desorption of gases.

5 Summary

The three investigated types of single layer graphene, namely, CVD, c-HSMG and sc-HSMG, disclosed various electrical properties and various gas sorption susceptibilities, although each exhibited highly similar Raman spectra and TEM electron diffraction patterns. The CVD and c-HSMG specimens behaved similar to electrical conductors and showed in-phase relationships for temperature and resistance vs. time during cyclic isothermal heating and cooling tests. The sc-HSMG specimens behaved inversely, i.e., they showed anti-phase relationships during the cyclic resistance – temperature test. The CVD graphene specimens did not disclose any gas sorption effects on T-\(\rho\)-\(\tau\) plots instead of those related to HSMG. Most especially, the sc-HSMG exhibited a susceptibility to reversible gas sorption, including selective sorption of hydrogen from the Ar – H₂ gas mixture. We commend the sc-HSMG for further investigation into its application as a functional nanomaterial for future gas sensors [26–32] and/or efficient hydrogen storage systems [33–39].
Resistance-temperature characteristics of CVD

Acknowledgements

The study is financed by The National Center for Research and Development as part of the program GRAF-TECH, project acronym GraphRoll, project title: “Graphene nanocomposite for the reversible hydrogen storage”, agreement number GRAF-TECH/NCBR/07/24/2013.

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