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Investigation of the graphene-on-silicon-carbide and CVD graphene as a basis for bioimpedance sensor application

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Abstract

The first results of the bioimpedance technique application to thermo-destructive graphene-on-silicon-carbide will be presented as a basis for biosensor applications as well as the comparison to the CVD-grown graphene.

Introduction

In sensing applications, graphene is attractive as for fundamental physics, as well as for advanced electronics devices and sensors. It has been already reported that graphene-based sensors could detect even individual molecules[2]. Because of biocompatibility of graphene, it is possible to detect glucose, proteins, DNA, or even bacteria.

Currently, the manufacture of Chemical Vapor Deposition (CVD) graphene chips is commercially available. However, the recently developed method of obtaining monoatomic graphene layers by thermal destruction of single-crystal silicon carbide did not reach the commercial level. At the same time, the results of testing thermo-destructive (TDS) graphene as gas analyzers, as well as biosensors for protein molecules, have showed extremely high sensitivity and selectivity to detectable substances[3,4].

Materials

TDS graphene is an epitaxial film that is grown on the surface of a 4H- or 6H-SiC single crystal by thermal annealing in the temperature range 1200 ÷ 1900 °C in a vacuum or in an Ar ambient. Graphene can be grown on C or on Si planes and is a film with 1-3 monolayers or a multilayer film with an amount of layers from 5 to 15 and more[5,6]

To carry out the comparative tests, graphene that was at our disposal was prepared by sublimation of silicon from a semi-insulating on-axis substrate of a 4H-SiC single crystal. Process were carried out in vacuum on Si surface (0001). The specimens were 5 x 5 mm^2 area, Substrate thickness 350 microns.

CVD graphene is created in two steps, the precursor pyrolysis of a material to form carbon, and the formation of the carbon structure of graphene using the disassociated carbon atoms. Both stages of the process requires extreme levels of heat, and therefore metal catalysts must be used to reduce the reaction temperature.

Due to this, the process temperature can be reduced to around 1000 degrees Celsius[7]. For testing, we used CVD graphene films produced by Graphenea Inc. (Spain) deposited on a quartz substrates with a surface area of 10x10 mm^2, and substrate thickness of 525 microns.

Results

To determine the conductivity type of graphene films, the Seebeck method was used. The sensitivity of the device was enhanced by an operational amplifier and permitted us to measure the conductivity type on surfaces with very low carrier concentration. Both graphene samples (TDS and SVD) showed a p-type conductivity that is stable throughout the area. (Fig.1)

Fig. 1. Seebeck method

After annealing in a 1E-4 torr vacuum, TDS graphene retained its original characteristics. CVD graphene stopped demonstrate p-type and conductivity was preserved only on fragmentary areas of the surface. Apparently, the film were ruptured during heating due to the inharmonic characteristics of graphene[8] and in addition partial oxidation and sublimation of carbon atoms in a vacuum medium occurred.

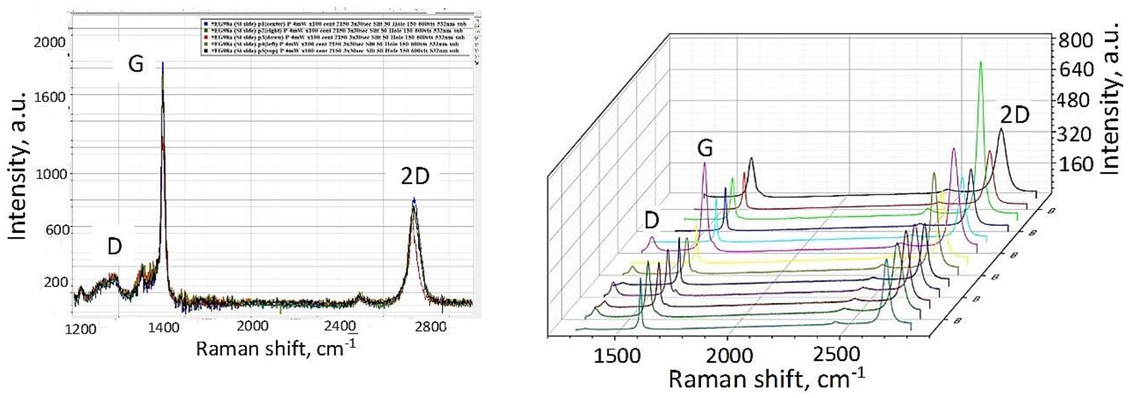

Fig. 2: Corresponding profiles of the Raman spectras for the graphene-on-silicon-carbide (left) and for CVD-grown graphene (right).

RAMAN SPECTRAS. Fig. 2 shows the micro-Raman spectra obtained with Horiba Jobin-Yvon T64000. When analyzing the spectra, the intensity ratio of the D, G, and 2D peaks allows us to conclude that the CVD graphene is reasonably inhomogeneous in terms of deformation, defectiveness, and charge concentration. The thickness of the graphene film is 1-2 atomic layers. There are defects such as domain boundaries. The sizes of domains vary from 60 to 600 nm. Analysis of the spectra for TDS graphene shows a good structural perfection of the film, but the intensity ratio of the IG / I2D peaks indicates that the graphene film is multilayered. At some points, the number of layers reaches 20.

HALL-VAN der PAUW MEASUREMENT. Figure 3 (a, b) show the results of testing on the HMS 3000 (Hall-Van der Pauw). In view of the very high total resistance of graphene films (~ 1-2 kOhm), contact clamps were used for the measurements.

As can be seen from the results of TDS measurements, graphene differs from CVD graphene by carrier concentration by almost an order of magnitude (8.07E13 cm^{-2} and 8.3E12 cm^{-2}). The mobility of carriers in TDS = 219 cm^2 / V*s versus 624 cm^2 / V*s for CVD graphene. The resistivities are related as 3.53E-5 and 1.2E-4 Ohm*cm. Such results confirm the multi-layered structure of TDS graphene. The main contribution to high conductivity is made by the carrier concentration.

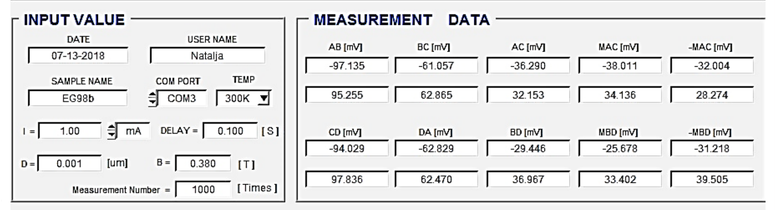

Fig. 3.a. Hall measurement data for TDS graphene.

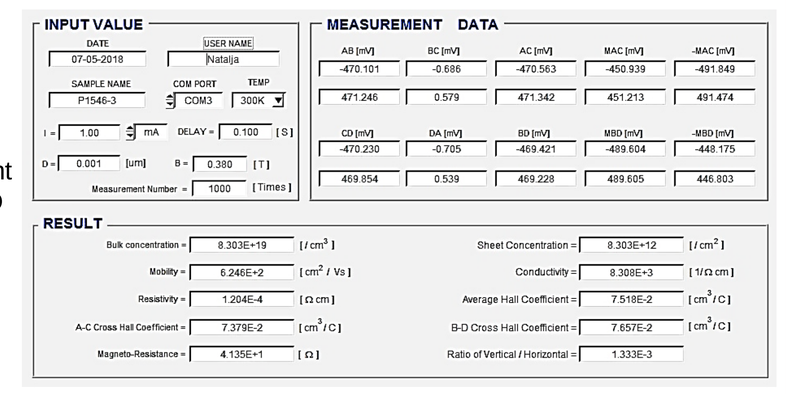

Fig. 3.b. Hall measurement data for CVD graphene.

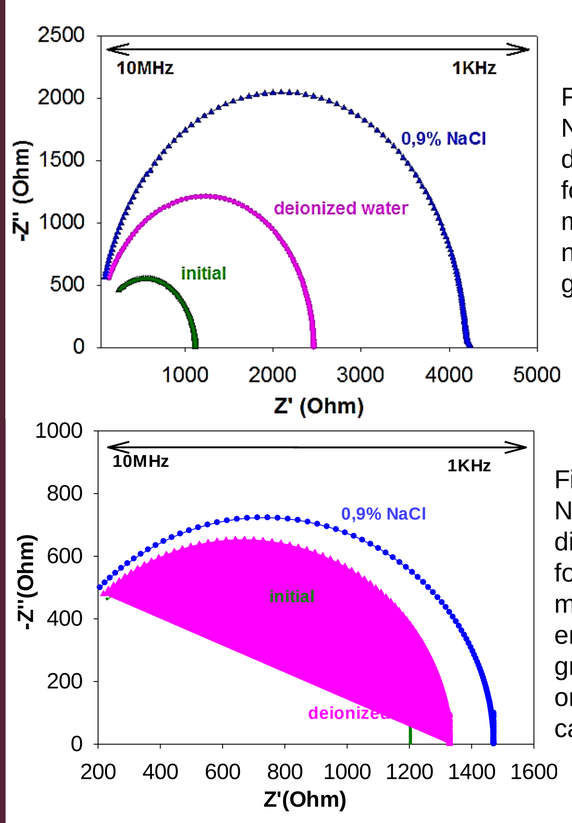

Fig. 4: Nyquist diagrams for EIS measurements of CVD-graphene

Fig. 5: Nyquist diagrams for EIS measurements of graphene-on-silicon-carbide

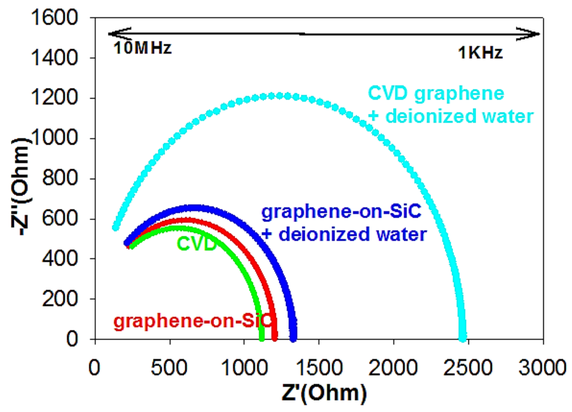

Fig. 6: Nyquist diagrams for EIS measurements of CVD-graphene and graphene-on-silicon-carbide

Fig.7. The Spring Clip Board - SPCB-1

IMPEDANCE MEASUREMENT. However, the key point and the main purpose of testing was to perform impedance measurements of graphene films. Figures 4, 5, 6 show Nyquist plots obtained from TDS and CVD graphene films.

Impedance measurements were performed by the Impedance Analyser of Keysight Technology E4990A within the frequency range from 1kHz to 10MHz. EIS data is presented as a Complex Plane (Nyquist) Plot. Nyquist diagram is just a plot of complex Z values (Ztotal = Z''+ Z'), in which the imaginary part of the impedance Z'', is represented versus the real part Z'.

As can be seen from the Nyquist diagrams, 1 - 2-layer CVD graphene films exhibit higher sensitivity than TDS multilayer graphene structures.

Summary

* The method of impedance measurements applied to graphene films expands the range of possibilities of using the material as sensitive biosensors.
* Monolayer graphene increases the sensitivity of measurements. Multilayer structures have greater reproducibility and multiplicity of use of sensors.
* Based on the results of comparative test tests, it is impossible to draw simple conclusions about the advantages of CVD or TDS graphene due to the inadequacy of the materials compared.

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