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RECENT ADVANCES IN GRAPHENE APPLICATION FOR ELECTRONIC SENSING

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Abstract: The great interest in graphene is caused by its potential for constructing various sensors exhibiting excellent parameters. The high carrier mobility and the unique band structure of graphene makes it promising especially in the field-effect transistors (GFET) applications. In this article, recent advances of the selected graphene-based sensor applications were presented and the possible directions for further investigations were pointed out.

Keywords: graphene, sensors, GFET, metrology.

1. INTRODUCTION

Graphene is a two-dimensional layer consisting of carbons which are arranged in a hexagonal lattice. It exhibits a number of exceptional properties, such as high electrical and thermal conductivity, outstanding mechanical strength, superior flexibility and a large surface area per unit volume. Although graphene is transparent, it is able to absorb about 2% of light from the visible to the infrared range which is a remarkable optical property for the material with only an atomic layer of thickness. Graphene can be produced by various methods, for instance, by micromechanical exfoliation of graphite, epitaxial growth, chemical vapor deposition or exfoliation of graphite in liquid solvents. Another low-cost choice is to utilize reduced graphene oxide.

Electronic structure of monolayer graphene indicates that this material is a zero-gap semiconductor because the conduction and valence bands meet at the corners of the Brillouin zone. The low energy band dispersion at these points, which are commonly called Dirac points, is linear, revealing that the charge particles in graphene could be treated as massless Dirac fermions moving with an energy-independent Fermi velocity of approximately 10^6 m/s. Because of the zero density of states at the Dirac points, electronic conductivity of graphene is actually very low. However, it could be enhanced by the appropriate doping with electrons or holes to create a material with potentially better conductivity than in the case of the known good metallic conductors at room temperature. It is possible to continuously drive the Fermi level from the valence (conduction) to the conduction (valence) band by applying a gate voltage, resulting in a pronounced ambipolar electric field effect. The bilayer graphene could be regarded as a zero band-gap semiconductor, too, but its electronic dispersion is not linear near the Dirac point. On the other hand, the valence and conduction bands begin to overlap for more than three-layer graphene. The electronic properties of graphene can be easily modified and "tuned", e.g. by chemical doping and functionalization.

In large part, the constantly increasing interest in graphene is caused by its great potential for developing sensors of various types to enable detection of target factors with the much higher accuracy than in the currently used commercial devices. The high carrier mobility and the unique band structure of graphene makes it promising especially in field-effect transistors (FET) applications. The aim of this article is to present recent advances of the selected graphene sensor applications. We would also like to point out the perspective directions of the investigations in the field of graphene-based sensing.

2. SENSING APPLICATIONS

Based on the above-mentioned exceptional features, graphene is a promising candidate as a physically responsive material for sensing devices. One of the most popular solutions in the field of sensing of various stimuli is the use of graphene field-effect transistor (GFET) architecture [1]. GFETs are very attractive due to the simplicity of design and ease in mass production. Additionally, these devices exhibit the inherent capability of signal amplification.

Graphene-based phototransistors have recently attracted significant interest because of their potential application for ultrafast detectors. The gapless nature of graphene and the high carrier mobility result in the efficient transmission of carriers which are almost unimpeded. It was demonstrated that photoresponse for optical intensity modulations up to 40 GHz is possible to be achieved in such devices and the intrinsic bandwidth may exceed 500 GHz [2]. There are some limitations, however, because the photoresponsivity, defined as photogenerated current per incident optical power, of pristine graphene photodetector is low (about 10 mA/W) due to the short recombination lifetime and relatively weak light absorption, so some improvement is necessary. One of the promising solutions is to create midgap defect states by titanium layer introduced into the graphene (Fig.1) which provides electron trapping centers and creates a bandgap. As a result, graphene quantum dot-like arrays were fabricated [3] with the enhanced photoresponsivity in the visible, near-infrared and mid-infrared ranges which reached as high values as 1.25 A/W, 0.2 A/W, and 0.4 A/W, respectively. Similar idea was utilized in a hybrid graphene–PbS quantum dot device with ultrahigh photodetection gain and high quantum efficiency [4]. In this type of construction graphene serves as the carrier transport channel and the colloidal quantum dots are the photon absorbing centres. The light-activated quantum dots generate electron–hole pairs and then the holes are transferred to the graphene layer, leading to the photoconductive current, while the electrons remain trapped in the quantum dots. It was shown that the responsivity is determined by the quantum dot size. In the case of small quantum dots the photoresponsivity could reach up to approximately 5×10^7 A/W.

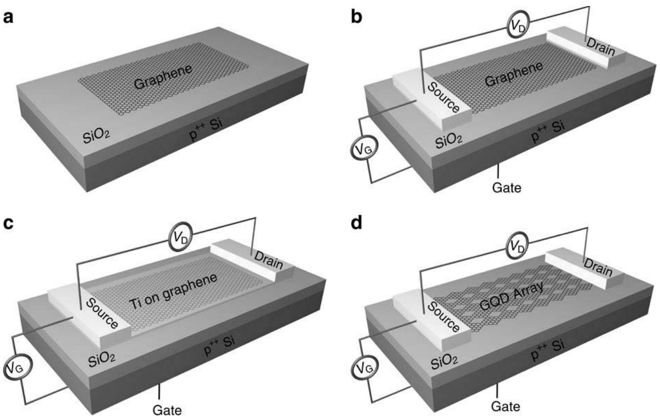

Fig.1. Fabrication process of graphene photodetector: (a) exfoliation of monolayer graphene onto a SiO2/Si substrate, (b) source, gate and drain terminals fabrication, (c) deposition of a thin nm-scale Ti layer by electron-beam evaporation, (d) removal of Ti resulting in the formation of graphene quantum dot-like (GQD) array structure [3]

Graphene used in the field-effect transistor architecture (GFET) could be employed for the detection of radiation-induced charge in undoped semiconductor absorber substrates without the need of the collection of the generated carriers [5]. The detection principle is based on the high sensitivity of graphene to local electric field changes caused by ionization of the electrically biased substrate. The promising performance of GFETs for the detection X-rays, gamma-rays and alpha particles was experimentally demonstrated.

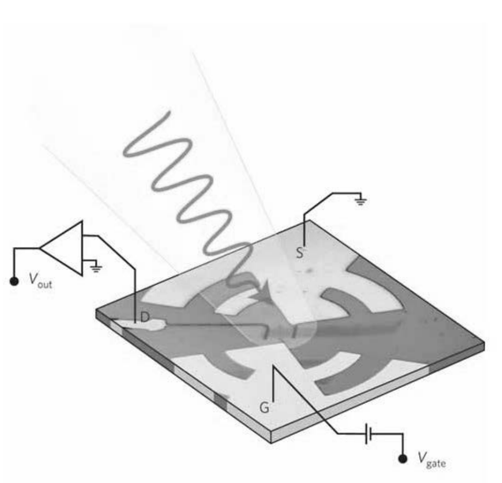

Fig.2. Antenna-coupled GFET-terahertz detector [7]

The phenomena of charge generation and carriers mobility increase with the increased temperature could be employed for the design of the high-sensitive temperature sensors based on a reduced graphene-oxide field-effect transistor [6]. To eliminate the influence of oxygen and humidity on the RGO channel, causing electrical instability, the GFET devices were encapsulated by a tetratetracontane. It was shown, that the prepared sensor had good electrical stability and low hysteresis. The measurements of the channel conductance indicated the high response to the temperature variation with the sensitivity of 6.7 nS/K.

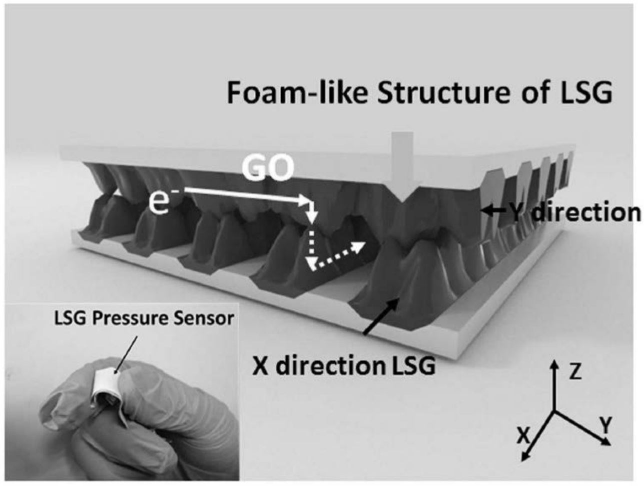

Fig.3. The structure of the pressure sensor based on the foam-like laser-scribed graphene oxide (LSG). Inset shows a flexible LSG pressure sensor in hand [9]

The frequency-independent absorption of graphene combined with its unique electronic structure and high mobility of carriers, allows to efficiently detect electromagnetic signals in the terahertz region at room temperature (Fig.2) [7]. It was suggested in the literature, that graphene devices could be very promising for large-area fast imaging of macroscopic samples.

Strain-induced modifications of electronic band structure are followed by the measureable changes of the electrical properties of graphene and could be a basis for stress sensing applications. Although the pristine graphene structure deformation was firstly proposed for the strain sensors, there are many other ways to get a better sensitivity. One of the most promising ideas is to utilize the imperfection of a large-scale graphene resulting in the appearance of a conductive network between separated graphene sheets [8]. From a macroscopic point of view, the strain response of the graphene network mainly depends on the conductivity between neighbouring flakes which is determined by the overlap area and the contact resistance. Recently, an interesting ultra-sensitive flexible resistive pressure sensor for e-skin application with a foam-like structure based on graphene (Fig.3) has been reported [9]. The sensitivity of the constructed device was 0.96 kPa^{-1} in a wide pressure range (0 - 50 kPa) and it was able to detect the pressing, bending and twisting. It was also shown, that this type of sensor could be used for dynamic pressure measurements with the short response time of 0.4 ms.

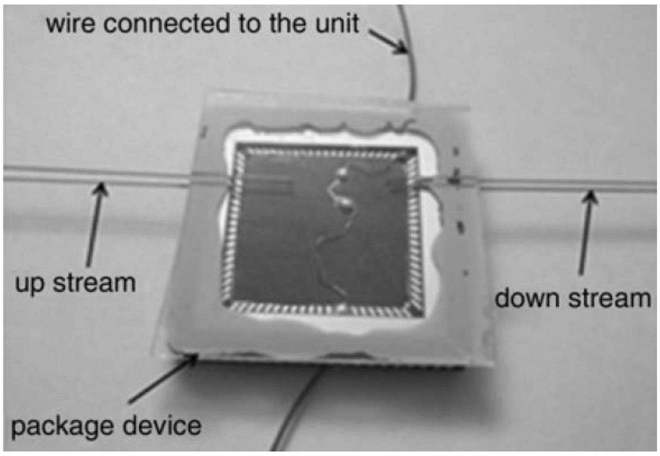

Fig. 4. The sealed graphene-based flow sensor [10]

Graphene could be used in nanoscale flow and temperature sensors (Fig.4) [10], as well. It has a large surface-to-volume ratio and a high temperature coefficient of resistance and, as a result, exhibits low thermal inertia and high sensitivity to temperature variation. What is more, the negative temperature coefficient of graphene enables the self-protection of the sensors and minimizes the sensing errors caused by the current-induced heating. The reported resolution of approximately 0.01 l/min of the constructed flow sensors was achieved by the use of graphene hot wires. Additionally, it was shown, that desired sensitivity and time response can be obtained by optimizing the number of graphene layers, the dimension of the device and the applied voltage.

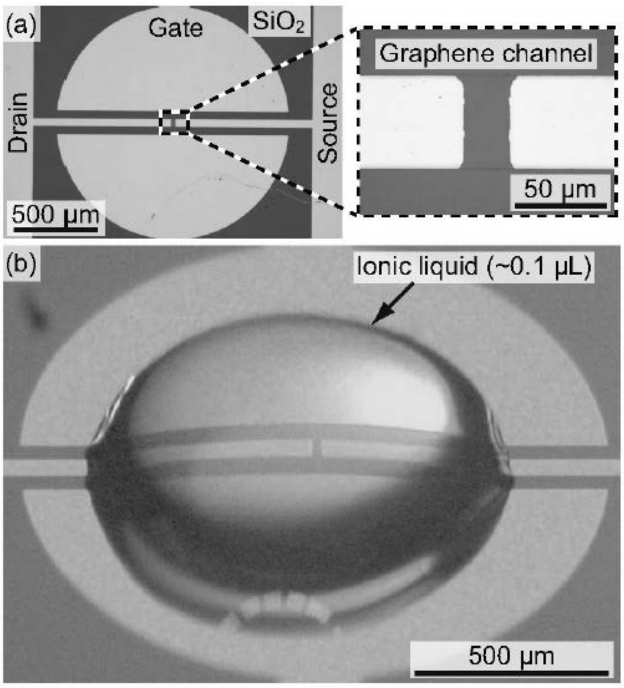

Fig.5. Ionic liquid (IL) GFET gas sensor (a) before dropping IL and (b) after dropping IL [11]

Recently, chemical sensing of gas molecules (e.g. NO_2, NH_3, H_2O) with the use of various graphene devices has been reported. One of them (Fig.5) utilizes an ionic liquid (IL) consisting of organic salts molten at room temperature, which serve as the liquid gate material of the GFET [11]. The general principle of GFET gas sensor is that gas molecules adsorbed on the graphene surface could act as either acceptors or donors influencing the transport current. Noteworthy, graphene gas sensors exhibit low power consumption when compared with the conventional gas sensors, such as the ones based on metal oxide semiconductors, which require heating at temperature of approximately 300 centigrade to enhance their reactivity. In the case of GFET gas sensors, very high sensitivity of the detection (up to 1 ppb) can be achieved at room temperature due to the extremely high conductance and low intrinsic noise of graphene. However, the noticeable lack of electronic identification selectivity of gas molecules, could significantly limit the potential application of graphene for this kind of sensing. To improve the performance of GFET gas sensors, graphene may be functionalized with the "recognition elements" which can interact with the target gases. The modification of graphene structure, such as e.g. nanomesh production, could also increase the selectivity and sensitivity of the graphene-based gas sensors.

3. CONCLUSIONS AND PERSPECTIVE

As it has been briefly reviewed in this article, there is no doubt, that graphene has demonstrated its great potential for electronic sensing applications. However, there are still numerous challenges because the overall performance of graphene-based sensor devices could be affected by various intrinsic or extrinsic factors. The prediction of the designed sensor performance seems to be a crucial issue during the development process, too, because the realization of a prototype is often an expensive and a time-consuming task.

In the nearest future, further simulations followed by the experimental work on graphene field-effect transistors chips, will be carried out in the Department of Metrology and Information Systems at the Faculty of Electrical and Control Engineering, Gdańsk University of Technology [12]. The intensive study devoted to the weak output signal analysis and the processing of signals coming from the arrays of graphene-based sensors, is planned, too.

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Ogromne zainteresowanie grafenem w dużej mierze związane jest z możliwością zastosowania tego materiału do budowy różnego typu sensorów charakteryzujących się doskonałymi parametrami. Bardzo duża ruchliwość nośników ładunku oraz specyficzna pasmowa struktura elektronowa grafenu sprawiają, iż wydaje się on być bardzo obiecującym materiałem, szczególnie do zastosowań w układach pomiarowych wykorzystujących czujniki o architekturze tranzystorów polowych z kanałem grafenowym (GFET). W artykule omówione zostały najnowsze osiągnięcia w dziedzinie badań nad zastosowaniem grafenu w wybranych typach czujników. Wskazano także możliwe kierunki dalszych badań, które mogłyby być realizowane w najbliższej przyszłości w Katedrze Metrologii i Systemów Informacyjnych na Wydziale Elektrotechniki i Automatyki Politechniki Gdańskiej.

Słowa kluczowe: grafen, sensor, GFET, metrologia.