## **Band Gap Opening in Graphene**

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## 1. Introduction

Graphene is a two-dimensional, single–layer sheet (with a thickness of only ~0.34 nm) of sp<sup>2</sup> hybridized carbon atoms (covalently bonded to three other atoms). They arranged in a honeycomb lattice. It is the thinnest material in the Universe and the strongest ever measured. Unlike massive charge carriers in common semiconductors, electrons and holes in graphene have not a mass and are Dirac–fermions and obey the linear energy dispersion. Actually, graphene is a zero-band gap 2D semimetal. Graphene has shown ultrahigh intrinsic carrier mobility, up to 200,000–250,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at low temperatures, a room-temperature mobility of ~ 10 000-20 000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was measured. Such mobility is far larger than for any other material. Different synthesis procedures for graphene and graphene oxide have been recently critically and elaborately reviewed. The main approaches are summarized in Fig.1. Detailed discussion of these questions is beyond the scope of my report. I'd like say that there is large progress in the technology of the manufacture of graphene and graphene oxide.

## 2. Band gap in graphene

The valence band and conduction band of graphene look like conical valleys and touch at the high-symmetry points of the Brillouin zone. The energy varies linearly with the magnitude of momentum. The linear dispersion relation leads to zero effective mass near the Dirac-point (Fig. 1).



Fig. 1. (A) Charge carriers in condensed matter physics are normally described by the Schrödinger equation with an effective mass  $m^*$  different from the free electron mass (p is the momentum operator). (B) Relativistic particles in the limit of zero rest mass follow the Dirac equation, where c is the speed of light and  $\sigma$  is the Pauli matrix

Graphene has potential applications in high-speed transistor electronics and integrated circuits. But the lack of an energy gap in its electronic spectra, for example, prevents the use of graphene in making transistors, logic circuit devices, and sensors.

Several methods have been developed to break the lattice symmetry in graphene and open an energy gap. We'll consider several versions of gap-opening. Several efforts have been made to open the band gap of graphene. One possibility to open the band gap in graphene is to use bilayer graphene combined with electric field or magnetic field (see Fig.2).



Fig. 2: The existence of an energy gap between the conduction and valence bands makes possible for graphene to act as a semiconductor. In double-layer graphene, the conical conduction and valence bands meet at a point – the band gap is absent. Electrical fields (arrows) introduce asymmetry into the bilayered structure (bottom), yielding tuned band gap ( $\Delta$ ) that can be selective.

The next strategy to open the band gap of graphene is to introduce a quantum confinement effect of carriers by narrowing the width of graphene to a nanometer scale. Such graphene called nanoribbon (NR). NRs were used as channels in FETs. The band gap since ~30 meV up to ~500 meV and corresponding FETs were reported when NRs were prepared with minimum width ~1 nm – several nm. A direct to indirect band gap transition is possible in NR by the application of an external bias along the width of NR. Epitaxial growth of graphene on the carbon face of SiC under vacuum leads to a gap of  $\approx$ 0.26 eV. This gap originates from the breaking of sublattice symmetry due to the graphene–substrate interaction. Recently, the research group at IBM has demonstrated SiC-based graphene field-effect transistors with a cutoff frequency over 300 GHz, which is very important for nanoelectronics. It is expected that graphene devices will operate in the terahertz frequency range and use for spintronics.

Graphene made on a Cu foil also can have the band gap under the strain. The band gap in graphene can be opened also under infrared laser beam or at high level of humidity (0.26-0.73 eV) etc.

The band gap of bilayer graphene can be opened larger (up to 3.3 eV) by combination of strain (along *z* axis) and electrical field (Fig.3)



Fig. 3 The band gap of the fully hydrogenated bilayer graphene. Here the band gap is a function of the biaxial strain.

Outstanding results are shown on next Fig. 4. We can see here the response of zero-field resistivity  $\rho = 1/\sigma$  of graphene to NO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O and CO in concentration *C* of 1 ppm. As usually, the operational principle of graphene resistive sensors is based on changes in their electrical conductivity due to gas molecules adsorbed on graphene's surface and acting as donors or acceptors. Note that whole surface of graphene as a strictly two-dimensional material is exposed to adsorbates, which maximizes their effect. A low level of excess (1/*f*) noise is typical for this material, a few extra electrons can cause notable relative changes in carrier concentration. The adsorbed molecules change the local carrier concentration in graphene one by one electron, which leads to step-like changes in resistance. Such characteristics of graphene make it possible to increase the sensitivity to its ultimate limit and detect individual dopants. The Hall measurements revealed that NO<sub>2</sub>, H<sub>2</sub>O and iodine acted as acceptors whereas NH<sub>3</sub>, CO and ethanol were donors.



Fig. 4. Sensitivity of graphene to chemical doping. Changes in the resistivity  $\rho$  are caused by graphene's exposure to various gases. The positive (negative) sign of changes is chosen here to indicate electron (hole) doping. Region I – the device is in vacuum prior to its exposure; II – exposure to a 5 litre volume of a diluted chemical; III – evacuation of the experimental setup; and IV – annealing at 150°C.

The dynamic range of detection for graphene sensors may cover from a single molecule to a very high concentration level. Sensor showed rather fast (~10 s) and quite reproducible response to  $CO_2$  at RT and in the concentration range of 10–100 ppm with high sensitivity and low power consumption. The exposure of graphene to ozone dramatically improved NO<sub>2</sub> sensing behavior of the graphene.

#### 3. Field effect transistor sensors made of reduced graphene oxide

The drain current of field effect transistor (FET) depends on gate bias, which we can effectively change upon exposure to different gases. It is shown that such FET sensors demonstrate very high sensitivity with detection capability down to ppb levels or even to single molecule with appreciably fast response time as well as very low noise and cost. The electrical resistance and noise spectra of graphene FET change by some gases (Fig. 5). They demonstrated that vapors of different chemicals (e.g., methanol, ethanol, tetrahydrofuran, chloroform, acetonitrile, toluene, and methylene chloride) led to different effects that can be easily distinguished from the low-frequency noise spectra of graphene. The same phenomena was detected by us earlier for porous silicon gas sensors. There is a change in the characteristic frequency of the Lorentzian noise that is different chemicals. FET sensor can efficiently perform for selective gas sensing without any surface functionalization or fabrication of the device array each to be tuned for a given chemical.



Fig. 5. Noise spectral density  $S_1/I^2$  multiplied by frequency *f* versus frequency f for the device in open air and under the influence of different vapors. Different vapors induce noise with different characteristic frequencies  $f_c$ . The frequencies,  $f_c$ , are shown explicitly for two different gases. The difference in the frequency  $f_c$  is sufficient for reliable identification of different gases with the same graphene transistor. For comparison the pure 1/f noise dependence is also indicated.

Recently, graphene oxide (GO) has received a great attention because it readily exfoliates as single sheets in water and, from these solutions, it is straightforward to produce films. Reduced graphene oxide (rGO) based FET sensors were investigated for NO<sub>2</sub> and NH<sub>3</sub> detection in the low concentration level.

Low concentration NO<sub>2</sub> diluted in dry air starting 1 ppm was detected in reduced grahene oxide (rGO) gas sensors at RT. rGO is both conductive and has chemically active defect sites making it a promising candidate for the sensors allow detecting chemical agents in the ppb range with significantly reduction in noise levels. The 10-100 fold reduction in 1/f noise in rGO sensors were shown over SWNT-based sensors. The noise level in rGO devices strongly decreases with increase in the film thickness. It was shown the important role of noise reduction in the responses to 0.5 ppb 2,4-dinitrotoluene (DNT), a simulant for the explosive TNT. The lower noise levels in the rGO device lead to a notable increase in signal-to-noise ratio. The conductance- based rGO sensors are sensitive to exposures to stimulants of an explosive and the three main classes of chemical warfare agents and nerve agents. Dependence of change in conductivity of reduced GO sensor on the concentration of hydrogen cyanide (HCN) in nitrogen is linear in doublelogarithmic scale since minimal detectable level 70 ppb of HCH:N<sub>2</sub>. Note that the detection of HCN by CNT sensors is unable even at much higher concentration of HCN. In addition, rGO sensor is able detecting other simulants such as organophosphates (i.e., DMMP), and aromatics and alkane derivatives (i.e., DNT and CEES, respectively). The sensitive to DMMP sensor demonstrated in Fig 6. The relatively large number of chemically active oxygen defects opens a possibility of covalent chemical functionalization for increased chemical or biological selectivity.



Fig. 6. (a) the response curve of the chemically reduced graphene sensor to the DMMP vapor under the concentrations of 5–80 ppm and (b) relationship of the response of the sensors with the concentrations of DMMP.

Gas/vapor sensing is possible by use of surface acoustic wave (SAW) devices where the frequency of operation of the sensors changes with exposure to gas molecules. SAW chemical sensors for sensing of H2 and CO at room temperature and at 40 °C, respectively, based on graphene-like nano-sheets deposited on lithium tantalate were reported. The band gap 0.1 eV was opened in such a graphene–LiTaO<sub>3</sub> sensor. The thin graphene layers were produced via the incomplete reduction of GO with hydrazine. The other category of mass sensitive devices, apart from SAW sensors, are bulk acoustic wave (BAW) sensors (graphene based quartz crystal microbalance (QCM) gas/vapor sensors) where the mass is also detected in terms of the corresponding shifts in frequency quite similar to that of SAW sensors. Here a small change in the electrode-mass even down to nano-gram can be detected very efficiently. The mass-sensitive devices like bulk acoustic wave and surface acoustic wave sensors become more and more popular due to their high sensitivity and stability.

Functionalization of graphene by promising for gas detection metal oxide like TiO<sub>2</sub>, ZnO etc. leads to dramatically improving the selectivity aspects. This demonstrated, for example, by us for CNT sensors. For example, we observed synergetic effect in TiO<sub>2</sub>-CNT system -the response to e-butane which was absent for TiO<sub>2</sub> and CNT separately. Such graphene–metal oxide hybrid gas sensors made of ZnO–nanorod–GO were investigated. Detection of ethanol, CO, NH<sub>3</sub> H<sub>2</sub>O<sub>2</sub>, and NO with appreciable selectivity towards electron donor gases like CO and NH<sub>3</sub> revealed that this composite structure would have tremendous potential over ZnO nanorod or GO based gas sensor alone. In addition, this composite sensor is expected to further enhance the sensor

performance because of a larger specific surface area of ZnO nanoparticles on GO islands compared to ZnO alone as a gas sensor.



Fig. 7. The sensitivity of ZnO NRs–a chemically converted graphene thin film sensors to  $H_2S$  gas in (a) oxygen at RT and (c) nitrogen at 270 °C.

Also the ZnO–GO composite sensor is more selective to reducing gases and shows a poor response to oxidizing gases (here NO). The vertically aligned ZnO nanorods with graphene were reported for room temperature detection of  $H_2S$  with high sensitivity (Fig. 7).

## 4. Analysis of experimental results obtained for different graphene sensors

Real situation with parameters of gas/vapor sensors made today from graphene and graphene oxide in not so optimistic as it expected. The best results for the response  $t_1$  and recovery  $t_2$  times are rather satisfactory for resistive and functionalized sensors. Resistive hydrogen sensors working at RT have  $t_1$ ~10-30s, but  $t_2$ ~few min in the detection range 40-8000 ppm and 40 s and 50-60 s in the 0.5-1 % range, correspondingly.  $t_1$  and  $t_2$  are equal to 70-100 s and 200-300 s during NO<sub>2</sub> detection in the range 100-1000 ppm. In the case of the CO<sub>2</sub> detection,  $t_1$  and  $t_2$  were 8 and 10 s in the range 10-100 ppm. The FET detection of ethanol vapors with  $t_1$ =5-10 s and  $t_2$ =30-40 s was reported. Situation with functionalized grapheme-metal oxide sensors at RT is rather good.  $t_1$ =5-6 s and  $t_2$ =2-5 s were reported in the case of the CO<sub>2</sub> and NH<sub>3</sub> detection.  $t_1$  and  $t_2$  are equal to several min- 10-25 min for other reported above graphene sensors detecting NO, H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub> gases and ethanol vapor. No details of parameters of chemical warfare agents and other gases/vapors sensors are available. An additional information about different gas/vapor structures made from graphene and reduced graphene oxide (rGO) is reported.

Note that the development of graphene gas/vapor sensors is in the beginning. We hope that valuable parameters for practice applications of such sensors will be reported in near future.

# 5. Conclusion

The opening of the band gap in graphene is unique phenomenon. It can be used for manufacture of high-speed transistors and sensors. The best surface to volume ratio in two dimensional graphene, every atom of which may be considered as a surface atom, therefore the graphene use has opened up the opportunity the detection of gases and vapors with excellent sensitivity, fast response time, and high stability.

Different types of gas/vapor sensors are considered. Beside resistive sensors, field effect transistor, noise, acoustic wave and functionalized sensors are reported. We discussed possibilities, specific properties and parameters of detection of  $H_2$ ,  $O_2$ , many toxic gases and chemical warfare agents. Sensors mentioned above can work mainly without pre-heating of work body, which is making their use in science and automatics very convenient.

Since the graphene films possess lower resistance (typically in few hundred ohms) compared with the metal oxide–based gas sensors, graphene sensors can be integrated with electronic circuits more suitably.

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