Technologies of microsystem technique and nanosensorics

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Abstract. Present article deals with microsystem technology and nanosensors. We covered the properties and synthesis technology of Carbon Nanomaterials. The detailed discussion has been made on synthesis of Carbon Nanotubes by thermal chemical vapour deposition (CVD) while reduced graphene oxide by modified Hummers method. Further, as grown Carbon nanomaterials have been used for developing optical detector for visible to near infrared range and Nitrogen Dioxide gas sensor.

Keywords: Microsystem technique, Carbon nanomaterials, optical detector, gas sensor

Introduction

Appearance and development of lithographical technologies for semiconductor microelectronics led to successful exploitation of these technologies as for fabrication of integrated electronics devices with high degree of integration as for fabrication of devices and systems of photonics [1], micromechanics [2], microfluidics [3] etc. The concept of MEMS (microelectromechanical systems) or MOEMS (microoptoelectromechanical systems) has been developed. For instance, this concept could be used for development of analytical instrumentation in integrated implementation. In [4] the realization of gas chromatograph on the base of such approach is considered. Such systems are especially perspective for on-board use due to small sizes and wide functional capabilities.

1. Technologies of microsystem technique

The increase of lithographical systems resolution till tens of nanometers allowed developing NEMS (nanoelectromechanical systems) as well as nanophotonics devices with capabilities unreachable in before. The use of high-resolution lithographical systems allows to fabricate diffractive optical elements for UV and X-ray ranges of electromagnetic spectrum as well as optical structures with relief minimal feature size much less than wavelength [1]. For computer simulation of such subwavelength microstructures rigorous light theory methods should be used [1]. The character of interaction of electromagnetic wave with periodic subwavelength structure is giving opportunity to describe this structure as a layer of some new material (metamaterial) with any specific electrical and magnetic properties [1]. Developed methods for solution of direct and inverse tasks for such subwavelength
structures are allowing to design and to model metamaterials with pre given features for different ranges – from UV to terahertz. However, further development of methods and technologies for microsystem technique devices fabrication demonstrated limitations of approach based on the use of lithographical methods [5]. The technology of lithography was developed for solution of microelectronics tasks, therefore this technology oriented to fabrication of planar or two-dimensional structures. The necessity of multilevel structures formation (or structures with continuous profile) and 3D structures for photonic [1] and microsystem devices determined the development of direct writing technologies (maskless technologies) such as focused ion beam technology (FIB) [6] [see figure 1], high-resolution laser ablation, micromilling [7] etc.

The development of nanomaterials and 2D materials opened up new possibilities in the field of microsystem technique. Particularly, miniature sensors of chemical composition [8] and physical quantities sensors [9] with high sensitivity and selectivity were designed.

2. Nanomaterials and 2D materials for sensorics

The current epoch of materials science is initiated by the invention of electron microscopes. Electron microscope gave the opportunity to land on the field of nanomaterials. In 1991, the invention of Carbon Nanotubes (CNTs) gave further acceleration to the research of nanomaterials [10]. The sp² hybridized, hollow cylindrical structure of carbon atoms (CNTs) shows the unique and superior electronic, optoelectronic and mechanical properties [10,11]. The major extraordinary properties of CNTs including high current transportation capability, high electrical as well as thermal conductivity, high surface area and the high value of tensile strength (100GPa) as well as Young’s modulus (1TPa) makes CNTs strongest material among in so far materials invented. Apart from mentioned properties of CNTs, its flexibility, light absorbing ability as well as nonlinear optical characteristics make CNTs suitable materials for the applications in aerospace, energy storage and harvesting, shielding for electromagnetic as well as microwave, optical detectors, gas sensors and many more. Above mentioned properties and applications motivate us to work on the synthesis of CNTs and CNTs based optical and gas sensors [9, 12]. For synthesizing CNTs, chemical vapour deposition, arc-discharge and laser ablation techniques are used. Among all mentioned techniques, CVD provide best quality and selective CNTs, that’s why in our work, CVD technique is used for CNTs growth. The single walled (SWNTs) and multi walled (MWNTs) CNTs have been grown by utilizing different parameter of CVD system. The CNTs have been deposited on SiO₂ coated silicon substrate with taking iron as catalyst materials. The mixture of Argon and hydrogen (90% and 10%) was used as carrier gas and acetylene used as carbon source gas. The self made thermal CVD system is used for growing CNTs [13-14].

To make electrical analysis of as grown CNTs, two gold electrodes have been deposited on two side of sample (see figure 2). For investigation of photodetection properties of as developed sample, sample was illuminated by 532nm wavelength green laser beam. When the laser beam fall on the sample then the resistance of sample start to decrease sharply. And after few second the decrement in resistance stop and then the laser light has been switched off [see figure 3]. After switching of laser light the resistance of sample sharply increased and reached its primary value. The change in resistance is indicates that CNTs is very sensitive for light beam. When the laser beam falls on CNTs then CNTs...
absorb photons from laser beam and hence electron-hole pairs generation procedure took place in valance band and when as generated electrons get sufficient energy from laser beam then the electron start to jump in conduction band from valance band; which resulted in decrement of resistance of sample. That is possible reason behind the photodetection process of CNTs. We developed power dependent optical detector for detection of 532nm laser source. In that sensor when the power of laser increases then further decrement in resistance of sample has been observed. The sensing property of sensor is analysed for the range of power from 0.8W to 2W of laser beam. After small level manipulation, as developed sample also useful for detection of Nitrogen dioxide gas (NO$_2$) gas. To detect NO$_2$, the polyethylenimine (PEI) functionalised SWNTs has been used, rest sample fabrication steps are same as mentioned above. The feature of SWNTs is p-type in atmospheric conditions [15-17]. In the case when NO$_2$ gas interacts with pristine SWNTs, the gas molecules withdraw electron and thus, upsurge the majority carriers, which reduces the resistance actively [18-19]. The strong bonding of carbon–carbon in SWNTs overcomes their reactivity and inhibit their detecting effectiveness. The carbon nanotubes chemical reactivity has been increased due to the increase in structural defects [19-20]. A limited number of gas molecules adsorbed during exposure on the Pristine SWNTs because of fewer defects on the surface. Further defects i.e. elimination of carbon atoms, breaking of C=CC=C bonds on the sidewalls and on the ends of SWNTs are created owing to the PEI functionalization process. The defects created due to the functionalization on SWNTs surface is occupied by the functional groups, such as amine groups which further expedites the adsorption of NO$_2$ gas molecules. The increase in charge transfer between NO$_2$ gas molecules and SWNTs can be associated with the adsorption of additional NO$_2$ gas molecules on the SWNTs sensor. This led to a generous change in the resistance of the sensor (see figure 4). So, there is an enhancement in the sensitivity of the PEI functionalized SWNTs NO$_2$ gas sensor. Further, the amount of functional group and the type of functional group attached to the surface determines the degree of improvement in the sensitivity of SWNTs. It was found that there is an insignificant influence of moisture on the specific gas sensing response of the sensor. The baseline resistance of the sensor does not have sensible variation under the exposure of relative humidity. The high sensitivity of the developed functionalized sensor towards strong electron-withdrawing particles can be attributed to the PEI functionalization of SWNTs. In comparison to pristine SWNTs, the SWNTs-PEI functionalized gas sensor exhibited a higher sensitivity of 37.00% at room temperature.

We also developed reduced graphene oxide (rGO) based sensor for IR range of solar spectrum. Reduced graphene oxide (rGO) is one of the most widely used materials in optoelectronics and photonics today. Recent researches show that rGO has a natural energy gap. Its width can be adjusted by the control of graphene oxide reduction degree [21]. Calculations shows that the graphene band gap changing can expand the operating spectrum of photodetectors based on it to the far infrared and even to the terahertz range.

Films of reduced graphene oxide were fabricated using known Hummers method. The mixture of materials – flaky graphite/NaNO$_3$ was prepared in weight ratio of 2:1. It was put into a beaker with 98 wt. % H$_2$SO$_4$ at 15 °C to obtain a suspension. Then, KMnO$_4$ powder was gradually added into the suspension with continuous stirring. Its mass was 3 times as much as the mixture one.
The subsequent process included 3 steps. The first was the low-temperature reaction in which the mixture temperature was keeping below 20 °C for 2 hours with constant stirring of the suspension. After complete potassium permanganate dissolution followed the mid-temperature reaction: the mixture temperature was maintaining at 35°C for 30 minutes. Finally, it was the high-temperature reaction – distilled water was slow added into the mixture for cooling and 15 minutes later, hot water and 30% hydrogen peroxide was added. The received suspension was filtered through the filter paper for a qualitative analysis, and the solid mixture was washed with weak hydrochloric acid and distilled water, and dried in a vacuum oven. After that, silver electrodes were applied to make contact for analyzing the sample for optical detection application.

The photodetection properties of sample were analysed under the illumination of IR lasser beam (CO2-laser; wavelength of 10.6 μm) for different laser beam power (1W-3W). Similar to above discussed CNTs based photodetector, the resistance of rGO film based sensor varies under illumination of IR radiation. The change in resistance of sensor was found increases with respect to radiation power. The decline in the resistance of sensor is more and faster than the case of CNTs based detector. The experiment were repeated for many time and in every cycle same type of results have been observed, which shows the that as developed sensor is very stable and providing reproducible outcomes.

The resistance change was observed at the radiation exposure over the entire power range up to 3 W. Also, it has been observed for rGO based optical detector that the response of as developed sensor varies linearly for entire range of used IR radiation power (1W-3W).

To provide the sensitive element operation, it's necessary to observe the resistance recovery up to a value not less than 0.9 of the initial one in the absence of laser radiation. Resistance was not regained to a value above 0.9 of the initial one at the power more than 2 W. The recovery time increases with laser beam power growing quite significantly, i.e. from several seconds up to 1.5 min. The rGO film irreversibly loses its properties at the high power of incident laser beam. High sensitivity, fast response and dependence of the relative resistance drop on the incident beam power close to the linear characteristic of rGO-based films discover the possibility of their application as far IR radiation sensors.

**Conclusions**

The development of nanomaterials and two-dimensional materials with new functional features as well as new technologies of microsystem technique opened up new possibilities in the field of sensorics and analytical systems.

**Figure 3:** Power dependent optical sensing for 532nm laser beam.

**Figure 4:** Change in the behaviour of the SWCNT sensor with the increment in functionalization duration. It is clearly observable from graph that the response of NO$_2$ sensor increased up to 900sec functionalization of SWNTs with PEI and further increment in functionalization duration decreases the response of sensor.
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References
[1] Soifer V A, Gavrilov A V, Golovashkin D L, Doskolovich L L, Dyachenko P N, Khonina S N, Kotlyar V V, Koval’ev A A, Nalimov A G, Nesterenko D V, Pavelyev V S, Shuyupova Y O and Skidanov R V, Diffractive Nanophotonics 2014 CRC Press, Taylor&Francis Group, CISP, Boca Raton.
[2] Verma P, Pavelyev V S, Volodkin BO, Tukmakov K N, Reshetnikov A S, Andreeva T V, Fomchenkov S A and Khonina S N 2014 Computer Optics 40 668.
[3] Wang X Li, Zhu Y and Fang Q 2012 Journal of Chromatography A 1246 123.
[4] Platonov I, Platonov V, Agaфонов A and Pavelyev V 2018 AIP Conference Proceedings 1989 030011.
[5] Moreau W M, Semiconductor Lithography, Principles, Practices, and Materials 1988 Springer.
[6] Tukmakov K N, Volodkin B O, Pavelyev V S, Komlenok M S and Khomich A A 2012 Bulletin of the Samara State Aerospace University (Russia) 7 112.
[7] Pavelyev V S, Miklyaev Y V, Imgrunt W, Bolshakov M V, Kachalov D G, Soifer V A, Aschke L and Lissotschenko V 2010 Proceedings of SPIE 77160.
[8] Kumar S, Pavelyev V, Mishra P and Tripathi N 2018 Sensors & Actuators: A. Physical 283 174.
[9] Pavelyev V S, Tripathi N, Mishra P, Mezhenin A V, Kurenkova Yu G and Sovetkina M A 2018 Journal of Physics: Conference Series 1096 012127.
[10] Iijima S 1991 Nature 354 56.
[11] Tripathi N, Pavelyev V and Islam S S 2018 International Nano Letters 8 1.
[12] Sharma P, Pavelyev V, Kumar S, Mishra P, Islam S S and Tripathi N 2020 J. of Materials Science: Materials in Electronics 31 4399.
[13] Tripathi N and Islam S S 2017 Applied Nanoscience 7 125.
[14] Fukumaru T, Fujigaya T and Nakashima N 2015 Scientific Reports 5 51.
[15] Geier M L, McMorrow J J, Xu W, Zhu J, Kim C H, Marks T J and Hersam M C 2015 Nat. Nanotechnol. 10 944.
[16] Takenobu T, Takano T, Shiraishi M, Murakami Y, Ata M, Kataura H, Achiba Y and Iwasa Y 2003 Nat. Mater. 2 683.
[17] Kumar D, Kumar I, Chaturvedi P, Chouksey A, Tandon R P and Chaudhury P K 2016 Mater. Chem. Phys. 177 276.
[18] Evans G P, Buckley D J, Skipper N T and Parkin I P 2014 RSC Adv. 4 51395.
[19] Terrones M and Terrones H 1996 Fullerene Sci. Technol. 4 517.
[20] Crespi V H and Cohen M L 1997 Phys. Rev. Lett. 79 2093.
[21] Zaaba N I, Foo K L, Hashim U, Tan S J, Liu and Voon C H 2017 Procedia Engineering 184 469.