Gas Sensor Based on Graphene: A Review

R.R. Mistry

Department of Physics, Deogiri College, Aurangabad, India

Abstract: Gas sensors are devices that can detect the presence and concentration of various hazardous gases and vapors through electrical signal. They are widely used in the fields of environmental monitoring. Graphene is a two-dimensional crystal material that has many excellent properties including large specific surface area and high conductivity. These features make it suitable for application for gas sensors. In this paper, introduction of gas sensors and grapheme based gas sensor are firstly introduced, followed by the preparation methods and properties of graphene. Finally, the clear direction of graphene gas sensors for the future is provided according to the latest research results and trends. It provides direction and ideas for future research.

Keywords: Gas Sensor, Graphene, Sensitivity, Response time, Synthesis.

I. INTRODUCTION

The gas sensor which is from a subclass of chemical sensors has found extensive applications in process control industries and environmental monitoring. Bad or Toxic smelling gases frequently encountered in living circumstances such as H_2S and NH_3 as well as hazardous gases used for industrial processes have long been the targets of gas sensors. The detection of the various smells generated gases or dangerous gases from foods or food materials has become increasingly important in food industries. These gaseous components are often present at very low levels and mixed with several disturbing gases. The global issues of energy and environment are increasing the necessity of those sensors which can detect air-pollutants in environments. A gas sensor should posses two basic functions i.e. a function to recognize a particular gas and to recognition into a sensing signal (transducer function) [1]. In many cases, the gas recognition is carried out through adsorption, chemical reactions and electrochemical reactions. The gas recognition by semi conducting oxides is conventionally transducer into a sensing signal through the electrical resistance changes of the sensor elements[2].

Graphene is a two dimensional structure of sp^2 hybridized carbon atoms arranged in a hexagonal structure. The use of graphene in any application begins with the challenge of producing high quality graphene. The quality, size, and structure of graphene films vary with the desired applications[3]. While reduced graphene flakes are needed for composite materials or conductive paints, planar graphene is needed for high performance electronic devices. Graphene based gas sensor has attracted a huge amount of research due to its unique electrical and mechanical properties. With the progress of research on graphene, it is found that the preparation of graphene by mechanical expoliation is poor in repeatability and difficult to precisely control. [4]. To make high quality graphene, how to rapidly prepare large-area, high-quality monolayers and few layers of graphene films has become a subject of extensive research.

II. IMPORTANT PARAMETERS OF GAS SENSOR

Gas sensors are the important components to detection, identification and concentration of gas. The components can transform gas composition and gas concentration from non-electricity to electricity to achieve the measurement of gas [5]. The important parameters of gas sensor measuring performance include the following aspects [6]:

1. Sensitivity

The sensitivity is the measurement of degree of response [7]. Sensitivity is usually expressed as the ratio of the resistance of the gas under test to the resistance in normal air and is denoted by S ($S = Rg/Ra$, where Rg means the resistance of gas sensing materials at a certain concentration of target gas. where Ra means the resistance of gas sensing materials at ambient air atmosphere). The sensitivity of the sensor is that the operating frequency of the device changes with the type and concentration of the gas being detected.

2. Selectivity

Selectivity is the ability of gas sensors to differentiate particular gas in the presence of several gases. The sensitivity of a good sensor to particular target gas should be higher than that of the interfering gas Response time /Recovery Time. The response time and recovery time reflect the response and desorbs speed of the gas sensor to the detected gas. The faster is the speed, the better is the performance.

3. Stability

Stability is the ability of gas sensors to maintain the same output characteristics over a specified period and the measured gas concentration remains unchanged but other conditions change.

4. Repeatability

The test results are consistent when gas sensors are continuously tested in the same test environment. Repeatability can affect the working life of the sensor.

5. Limit of detection (LOD)

The minimum gas concentration that gas sensors can detect is called limit of detection. The concentration requirements of the detection limit will be different for different application areas. LOD is usually defined on the basis of signal to noise ratio (S/N). The minimum concentration can be calculated by signal measured in the low level sample is compared with the signal measured in the blank sample. The detection limit is generally determined by a S/N of 3:1.

6. Working temperature

The working temperature is the temperature at which gas sensor give its maximum sensitivity. The rate of adsorption and desorption of gas depends on the reaction temperature and different sensing characteristics are obtained at different operating temperatures.

III. GRAPHENE BASED GAS SENSORS

Graphene is one-atom-thick sheet of carbon atoms arranged in a honeycomb lattice and the two-dimensional building block for carbon materials. Since its first isolation by Geim and Novoselov in 2004 using micro-mechanical exfoliation method of preparation, so they won the Nobel Prize in 2010 in Physics[8]. Graphene has excellent electron mobility and large specific surface area and it exhibits good gas sensing properties. Graphene material as a p-type semiconductor contains many holes and has pull electron effect in gas atmosphere. Graphene is particularly sensitive to the detection of adsorbed small molecule gases. The unique structure of graphene determines its unique properties, high strength, excellent electrical conductivity and high thermal conductivity and quantum Hall effect can be observed at normal temperature [9].

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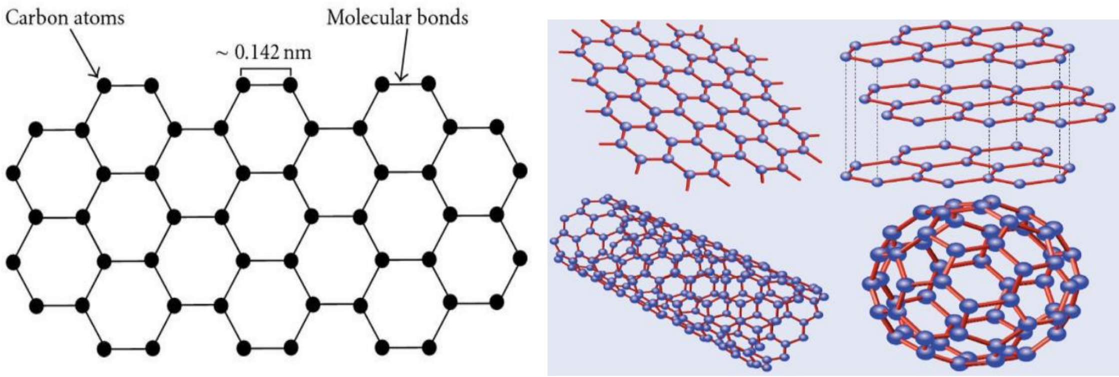

Fig. Ideal Structure of Graphene

Schedin et al.(2007) were studied mechanically stripped graphene for the detection of individual gas molecules [10]. They found that the response of graphene to 1 ppm ammonia (NH3), carbon monoxide (CO), nitric oxide (NO) and water vapor was measured and the change of resistance was recorded.

Dan et al. (2009) found that photolithography fabrication of graphene devices would inevitably leave polymer photoresist on the graphene surface at a thickness of about 1 nm [11]. The residue has a considerable impact on the device's transmission performance and gas sensing. Polymers were chemically doped with graphene and to improve gas sensing performance. This discovery opened the new dimension of graphene gas sensing field.

Hwang et al.(2012) studied the response of graphene to NH3 with different layer number and length-to-width (L/w) ratio [12]. The graphene was prepared from highly oriented pyrolytic graphite (HOPG) through mechanical cleavage proposed a method of preparation of graphene gas sensors by using printing CVD graphene on a silicon wafer to form a regular-shaped graphene silicon wafer and modifying palladium particles on the surface. The sensor prepared by this method has good sensing performance [13].

YanyanWang et al.(2013) studied highly sensitive gas sensor based on graphene/polyaniline hybrid materials [14]. Polyaniline is an organic semiconductor molecule shows excellent performance. The film making process is simple, low cost, work at normal temperature and it is easily compatible with other technologies. It has become a new idea in the research of gas sensors. The graphene and polyaniline combination can exert the advantages of two performance materials and great significance for improving the performance of the sensor.

Huiling Tai et al.(2014) proposed a preparation method of graphene-based ternary composite film gas sensor [15]. The gas-sensitive material is a composite of graphene, metal or metal oxide nanoparticles and conductive polymer compound were used.

Dutta D. et al.(2015) prepared a graphene based gas sensor with two Pd electrodes for sensing H_2 in air [16]. The lowest response and recovery times were obtained in this study.

Shuanglong Feng et al. (2016), 3D graphene flowers (GF) cluster patterns were successfully prepared by using inexpensive homebuilt microwave plasma-enhanced chemical vapor deposition (MPCVD) [17]. The GF sensor achieved a high response of NO2. The sensor also had great recovery characteristic that it took as little as 2 s to reach 90% signal recovery and only 20 s to achieve 100% recovery.

Junyeong Yun et al.(2016) preparted adhered stretchable patterned graphene gas sensor by using integrated micro-super capacitor (MSC) array on the same deformable substrate [18]. The sensor used a stretchable micro-capacitor as a substrate. The sensor worked without electricity, soft, wearable, small and performed well.

Ricciardella F. (2017) prepared the graphene sensing layer by using chemical vapor deposition method on pre-patterned catalyst and then it was eased onto the underlying SiO2 through a completely transfer-free process [19]. The gas sensing sensing area reduced by half with respect to the former one, showed a higher sensitivity upon exposure towards both gases, indicating that the sensitivity can be modulated by varying the geometry of the device exposure area.

Wei Wei et al.(2017) prepared a graphene-based long-period fiber grating surface Plasmon resonance (LPFG SPR) for high-sensitivity gas sensor[20]. A monolayer of graphene was coated onto the Ag film surface of the LPFG-SPR sensor. Which is increased the intensity of the evanescent field on the surface of the fiber, thereby enhancing the interaction between the SPR wave and molecules. This features significantly improved the sensitivity of the sensor.

Jong-Hyun Kim et al.(2017) prepared NH_3 gas sensing with ultra-low energy consumption for fast recovery and a graphene sheet based on a suspended micro-heater [21]. The silicon micro-heater were periodically heated the sensor at a frequency of 1 Hz which is increased the sensor's response time, recovery time, and sensitivity. The sensor showed rapid recovery through heating of the silicon heater. As the temperature increased, the desorption gradually increased by reducing hydrogen bonding.

IV. METHOD OF SYNTHESIS OF GRAPHENE

Several methods are used to synthesis graphene, the common methods of production of graphene have been established, such as mechanical exfoliation, chemical vapor deposition, silicon carbon epitaxial growth method, oxidation-reduction method, etc.

1) Mechanical exfoliation method

Mechanical exfoliation is the earliest method for preparing graphene. Andre Geim et al. (2004), from the University of Manchester, obtained the single-layer, high-purity graphene for the first time by repeatedly peeling flakes of graphite off the platform which were fixed onto a silicondioxide/silicon (SiO_2/Si) substrate using scotch tapes [22].

2) Chemical vapor deposition

Chemical vapor deposition (CVD) method is controllable and widely used in the preparation of graphene. To increase the contact area with the test substance and easier to use in the field of sensors [22,23]. In high-temperature decomposable gases like CH_4 and C_2H_2, carbon atoms are deposited on the surface of the substrate (such as Cu, Pt, Ni, Ru and Ir) by high temperature annealing to form single-layer graphene [24–29]. Somani et al.(2006) prepared first time 35 layers of graphene using thermal chemical vapor deposition [30]. In this method there are two advantages, low cost and simple steps. This method has potential for mass production and environmental friendliness providing a completely new direction for future research. Early in 2009, the B.H. Hong research group in Korea used a silicon wafer deposited with a polycrystalline Ni film as a substrate to prepare large-area and small-layer graphene, and graphene successfully transferred from the substrate, which set off the upsurge of CVD graphene preparation [31]. In the University of Texas at Austin, Xuesong Li et al. prepared graphene on copper foil by a carbon atom chemical vapor deposition method at a temperature of 1000 ^{0}C using a mixed atmosphere of methane and hydrogen (H_2) [32]. The CVD method is considered to be the most promising method for the preparation of high quality, large area graphene. The major disadvantages are high cost, complex production process,; breakage, wrinkle and pollution of graphene and material waste during transfer and inability to control the layer number of graphene produced due to the uncontrollable carbon source.

3) Silicon carbon epitaxial growth method

Epitaxial growth related to the growth of a monocrystalline layer with the same orientation as the substrate on a single crystal substrate and original crystal had been extended outward [33]. The material used for this epitaxial growth was silicon carbide (SiC). The crystal was heated at 1200~1600^{0}C, Si atoms evaporate and C atoms remained was on the surface. Substrate-based epitaxial graphene can be obtained by this method [34]. Berger et al. (2004), from Institute of Technology, Georgia, prepared a graphene thin layer have similar area as the original SiC on the (0001) crystal plane by heating large area single crystal SiC to high [35]. The epitaxial growth method is highly attractive for the preparation of high-quality graphene but some problems in controlling the number of graphene layers and the repeated preparation of large-area.

4) Oxidation-reduction method

The oxidation–reduction method is the most widely applied to achieve large-scale industrial preparation of graphene. The materials used are cheap and the preparation process is simple. In this method firstly prepares the graphene oxide and then removes the oxygen-containing groups on surface of the graphene oxide by thermal reduction or redox reaction [36]. There are three dominant methods preparing graphene oxide: Brodie method, Staudenmaier method and Hummers method [37–39]. Hummers method is wildly used due to its mild reaction conditions, simple and safe operation and less time-consuming and little environment pollution, which is the result of more than sixty years of research by Hummers et al. The oxidant is a mixture of potassium permanganate and concentrated sulfuric acid.

V. CONCLUSIONS AND FUTURE PERSPECTIVE

The future of graphene in the field of gas sensor is undeniably. Due to the special advantages in sensitivity, selectivity and small-size, graphene gas sensors have a good application in industrial and agricultural and environmental monitoring. However, the current large-scale application of graphene still has difficulties. There are two main lacunas. There is no method for large-scale preparation of graphene gas sensors and graphene needs to be further treated to improve its response sensitivity to specific gases. Judging from the current development in research, the improvement of response time, increasing specific surface area by modifying surface and compositing with other nonmaterial's and designing appropriate structure. Improved graphene-based sensitive materials will occupy an important position in the future of gas-sensitive materials and show greater advantages as the research progresses.

REFERENCES

1. Basu S. and Bhattacharyya P.(2012) Recent developments on graphene and graphene oxide based solid state gas sensors. Sens. Actuators B Chem., 173, 1-21.
2. Varghese, S.S.; Varghese, S.H. (2015) Two-Dimensional Materials for Sensing: Graphene and Beyond. Electronics, 4, 651–687.
3. Zhang, S.; Shao, Y.; Liao, H.; Engelhard, M.H.; Yin, G.; Lin, Y. (2011) Polyelectrolyte-induced reduction of exfoliated graphite oxide: A facile route to synthesis of soluble graphene nanosheets. ACS Nano, 5, 1785–1791.
4. Tian, W.; Zhang, X.(2016) A Review of Graphene on NEMS. Recent Pat. Nanotechnol. 2, 10, 3–10.
5. Zhang, X.; Wang, Y. (2013) Research and Development of Gas Sensors Based on Nanomaterials. Sens. Microsyst., 32, 1–5.
6. Wang, T.; Huang, D.; Yang, Z.; Xu, S.; He, G.; Li, X.; Hu, N.; Yin, G.; He, D.; Zhang, L. (2016) A Review on Graphene-Based Gas/Vapor Sensors with Unique Properties and Potential Applications. Nano Micro Lett. 8, 95–119.
7. Sriyudthsak, M.; Teeramongko lrasasmee (2000) A. Radial basis neural networks for identification of volatile organic compounds. Sens. Actuators B Chem, 65, 358- 360.

8. Zhang, S.; Shao, Y.; Liao, H.; Engelhard, M.H.; Yin, G.; Lin, Y. (2011) Polyelectrolyte-induced reduction of exfoliatedgraphite oxide: A facile route to synthesis of soluble graphene nanosheets. ACS Nano**,** 5,
a. 1785–1791.
9. Weitz, R.T.; Yacoby, A. (2010) Nanomaterials: Graphene rests easy. Nat. Nanotechnol., 5, 699–700.
10. Schedin, F.; Novoselov, K.S. (2006) Detection of Individual Gas Molecules by Graphene Sensors. Nat. Mater. 6,652–655.
11. Lu, Y.; Dan, Y.(2009) Intrinsic Response of Graphene Vapor Sensors. Nano Lett. 9, 1472–1475.
12. Hwang, S.; Lim, J. (2012) Chemical vapor sensing properties of graphene based on geometrical evaluation.
a. Curr. Appl. Phys., 12, 1017–1022.
13. Sun, J.; Pan, Z. (2014) A Gas Sensor for CO Concentration Detection. Patent CN104237356A.
14. Wang, Y.; Peng, C. (2013) Gas Sensor Based on Graphene/Polyaniline Hybrid Material and Its Preparation
a. Method.Patent CN102879430A.
15. Tai, H.; Ye, Z.(2014) Graphene-Based Ternary Composite Film Gas Sensor and Its Preparation Method.
a. Patent CN103926278A.
16. Dutta, D.; Hazra, A. (2015) Performance of a CVD grown graphene-based planar device for a hydrogen gas sensor. Meas. Sci. Technol. 26, 115-104.
17. Wu, J.; Feng, S. (2016) Facile Synthesis of 3D Graphene Flowers for Ultrasensitive and Highly Reversible Gas Sensing. Adv. Funct. Mater. 26, 7462–7469.
18. Yun, J.; Lim, Y. (2015) Stretchable patterned graphene gas sensor driven by integrated micro-supercapacitor array. Nano Energy **2015**, 19, 401–414.
19. Ricciardella, F.; Vollebregt, S. (2016) High sensitive gas sensors realized by a transfer-free process of CVD graphene.In Proceedings of the 2016 IEEE Sensors, Orlando, FL, USA.
20. Wei, W.; Nong, J. (2017) Graphene-Based Long-Period Fiber Grating Surface Plasmon Resonance Sensor for High-Sensitivity Gas Sensing. Sensors 17, 2.
21. Kim, J.H.; Zhou, Q. (2017) Suspended Graphene-Based Gas Sensor with 1mWEnergy Consumption. Micromachines, 8, 44.
22. Ji, W.S.; Kitt, A. (2011) Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates. ACS Nano 5,6916–6924.
23. Li, X.; Cai,W. (2009) Evolution of graphene growth on Ni and Cu by carbon isotope labeling. Nano Lett. 9,
a. 4268–4272.
24. Zheng, Y.; Jian, L.; Peng, Z.; Sun, Z.; Zhu, Y.; Li, L.; Xiang, C.; Loic Samuel, E.; Carter, K.; James, M.T. (2013) Toward the Synthesis ofWafer-Scale Single-Crystal Graphene on Copper Foils. ACS Nano **,** 7, 875.
25. Land, T.A.; Michely, T. (1992) STM investigation of single layer graphite structures produced on Pt(111) by
a. hydrocarbon decomposition. Surf. Sci., 264, 261–270.
26. Reina, A.; Jia, X. (2009) Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor
a. Deposition. Nano Lett. 9, 30–35.
27. Marchini, S.; Günther, S.; Wintterlin, J.(2007) Scanning tunneling microscopy of graphene on Ru(0001). Phys. Rev. B, 76, 075429.
28. Coraux, J.; N'Diaye, A.T.; Busse, C.; Michely, T. (2008) Structural Coherency of Graphene on Ir(111). Nano Lett. 8, 565–570.
29. Moriyama, S.; Tsuya, D. (2009) Coupled Quantum Dots in a Graphene-Based Two-Dimensional Semimetal.
a. Nano Lett, 9, 2891–2896.
30. Somani, P.R.; Somani, S.P. (2006) Planer nano-graphenes from camphor by CVD. Chem. Phys. Lett., 430, 56–59.
31. Chen, F.; Quan, Q. (2009) Electrochemical Gate-Controlled Charge Transport in Graphene in Ionic Liquid and Aqueous Solution. J. Am. Chem. Soc.,131, 9908–9909.
32. Li, X.; Cai, W. (2009) Large-area synthesis of high-quality and uniform graphene films on copper foils. Science ,324, 1312–1314.
33. Copel, M.; Reuter, M.C. (1989) Surfactants in epitaxial growth. Phys. Phys. Lett., 63, 632–635.
34. Borovikov, V.; Zangwill, A. (2009) Step-edge instability during epitaxial growth of graphene from SiC(0001).
a. Phys. Rev. B,80, 121406.
35. Berger, C.; Song, Z. (2004) Ultrathin epitaxial graphite: 2D electron gas properties and a route toward
a. graphene-based nanoelectronics. J. Phys. Chem. B,108, 19912–19916. [
36. Zhu, Y.; Murali, S. (2014) Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Adv. Mater. 41, 3906–3924.
37. Brodie, B.C. (2009) On the Atomic Weight of Graphite. Philos. Trans. R. Soc. Lond.,149, 249–259.
38. Staudenmaier, L. Verfahren zur Darstellung der Graphitsäure. Eur. J. Inorg. Chem. (2010), 32, 1394–1399.
39. Hirata, M.; Gotou, T. (2004) Thin-film particles of graphite oxide 1: High-yield synthesis and flexibility of the
a. particles. Carbon, 42, 2929–2937.