Thin Solid Films 568 (2014) 6–12

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Graphene-coated quartz crystal microbalance for detection of volatile organic compounds at room temperature

Vu Van Quang [a], Vu Ngoc Hung [a], Le Anh Tuan [b], Vu Ngoc Phan [b], Tran Quang Huy [c], Nguyen Van Quy [a,*]

[a] *International Training Institute for Materials Science, Hanoi University of Science and Technology, No. 1, Dai Co Viet Road, Hai Ba Trung, Hanoi, Viet Nam*
[b] *Advanced Institute of Science and Technology, Hanoi University of Science and Technology, No. 1, Dai Co Viet Road, Hai Ba Trung, Hanoi, Viet Nam*
[c] *Laboratory of Ultrastructure and Bionanotechnology, National Institute of Hygiene of Epidemiology, No. 1, Yersin Street, Hai Ba Trung, Hanoi, Viet Nam*

ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form 21 July 2014
Accepted 22 July 2014
Available online 28 July 2014

Keywords:
Graphene
Chemical vapour deposition
Volatile organic compounds
Quartz crystal microbalance
Gas sensors

ABSTRACT

The detection of volatile organic compounds (VOCs) at room temperature with rapid response and recovery is important for early explosive alarm. Herein, we demonstrate significantly enhanced VOC-sensing properties of quartz crystal microbalance (QCM) coated with monolayer graphene film. The monolayer graphene was firstly synthesized by the chemical vapour deposition (CVD) method on Cu foil and then transferred to the gold electrode of the QCM for VOC-sensing application. The gas-sensing properties of the graphene-coated QCM sensor were examined at room temperature for various concentrations of numerous VOCs, including butanol, isopropanol, acetone, and ethanol. The results revealed that the graphene-coated QCM sensor exhibits the best performance with ethanol gas. The gas-sensing mechanism of the graphene-coated QCM sensor was attributed to the adsorption and desorption of VOC molecules on the defect sites of graphene sheet.

1. Introduction

Graphene is a two-dimensional (2D) material with a single atomic layer of sp^2 bonding carbon atoms, and has attracted a lot of attention due to its outstanding properties, including high mechanical strength, ultraviolet–visible–infrared transparency, carrier mobility, and thermal conductivity [1], which are important for many applications in solar cells, light-emitting diodes, transistors, and chemical sensors [2–6]. Recently, the possibility of using graphene as a highly sensitive gas sensor was reported [7]. It was shown that the increase in graphene charge carrier concentration induced by adsorbed gas molecules can be used to make highly sensitive sensors that even have the possibility of detecting individual molecules. The operational principle of a conductivity-based gas sensor using graphene is similar to that of other solid-state sensors. It is based on a change in their electrical conductivity (σ) in the surrounding environment due to gas molecules being adsorbed on the surface of the graphene and acting as donors or acceptors. Graphene is a two-dimensional crystal with only a surface and no volume, which maximizes the effect of surface dopants. However, graphene is highly conductive and shows metallic conductance even in the limit of zero carrier density [8,9]. Therefore, changing the conductivity of graphene requires the adsorption of a large amount of donors or acceptors; this is one of the main challenges of applying graphene to conductivity-based gas sensors using comb-like electrodes.

Graphene was initially obtained by mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite [10]. Recently, several methods including reduction of graphene oxide and the chemical vapour deposition (CVD) method using Ni or Cu metal as a seed layer have been developed [11–14]. Among these, the CVD method has many advantages such as easy scalability and high quality. Moreover, CVD graphene film easily transfers to arbitrary substrates by a transfer process without intense mechanical and chemical treatments, preserving the high crystalline quality of the graphene samples [14, 15]. In this study, we developed a highly sensitive and reproducible sensor for detection of volatile organic compounds (VOCs) based on CVD graphene coated on the active electrode of a quartz crystal microbalance (QCM). The QCM is an extremely sensitive mass device that can detect the change in mass of a molecule, and thus sensors based on the QCM have high sensitivity and accuracy [16]. QCM-based gas sensors are widely utilized as a result of their robust nature, availability, and affordable interface electronics. In addition, the characteristics of QCM gas sensors invariably depend on the type of sensing film coated on the active electrode. More recently, graphene monolayers have gained prominence as sensitive layers. Graphene has a very high volume–exposure ratio for the adsorption of gas molecules. Thus, the low effective mass coupled with the high surface area makes graphene resonators ideal candidates for mass sensing [17]. Hence, the combination of an extremely sensitive mass device with a very high surface area and no graphene volume promises the possibility of designing high-performance gas sensors with high sensitivity, selectivity, fast response–recovery behaviour, and stable reproducibility.

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[*] Corresponding author. Tel.: +84 9 2661 4028.
E-mail address: quy@itims.edu.vn (N.V. Quy).

http://dx.doi.org/10.1016/j.tsf.2014.07.036
0040-6090/

2. Experimental details

A schematic illustration of the detailed fabrication process of a graphene-coated QCM sensor is presented in Fig. 1. The graphene film was grown on Cu foil by the CVD method. Firstly, Cu foil was treated by annealing in H_2 at 26.6 Pa at room temperature to 1000 °C for 1 h. Secondly, CH_4 gas was then introduced while maintaining H_2 for the formation of graphene. Growth was allowed to occur for 10 min under a total pressure (H_2 and CH_4) of 40 Pa. These steps were conducted automatically with a program so that the growth of graphene films had good reproducibility. As-obtained graphene was transferred on the top electrode of QCM by using poly-methyl methacrylate (PMMA) as the supported membrane. In detail, the graphene-grown Cu foil was cut into small circular pieces with a diameter of 12 mm coated with PMMA, and immersed in an aqueous iron (III) chloride ($FeCl_3$) solution in order to etch away the Cu foil. When the Cu was completely etched away, the graphene supported by PMMA was rinsed in deionized (DI) water several times to remove any etchant residues. The PMMA-supported graphene was then transferred onto the Au-electrode of QCM, which is a commercial QCM made from a 5 MHz AT-cut quartz crystal plate 1 inch in diameter, polished on both sides, with one electrode deposited on each side. PMMA was then removed by repeatedly rinsing with acetone solution and DI water after the graphene was completely adhered onto the QCM device.

The sensing properties of the graphene-coated QCM sensor were investigated using a home-made measurement system. The details of the gas sensing measurement were presented in our previous work [18]. In brief, all measurements were carried out in an air-conditioned room at a constant temperature of 25 °C, and the gas-sensing system and alcohol solutions were also stored at the same temperature. The dry air flowing through the mass flow controller-1 (MFC-1) at a rate of f_1 (sccm-standard cubic centimetre per minute) picked up the vapour from the liquid source. The alcohol vapour was then diluted by the MFC-2 at a rate of f_2 (sccm). The concentration of alcohol vapour was carefully adjusted by the flow rate of MFC-1 and MFC-2 and calculated by the following equation [19]:

$$C(\text{ppm}) = \left(\frac{P_i}{P} \times \frac{f_1}{f_1 + f_2}\right) \times 10^6 \qquad (1)$$

where P is the input air pressure (which is atmospheric pressure in our experiment) in P_a, and P_i is the saturated partial pressure of alcohol solution in P_a obtained by the Antoine equation as follows:

$$\text{Log}P_i = A - \frac{B}{C + T} \qquad (2)$$

where A, B, and C are Antoine constants, and T is the temperature in Celsius (T is 25 °C in our experiment).

The change in frequency of the sensors was monitored by a frequency counter, QCM200, which was connected to a computer system via the software program SRSQCM200. Micro-Raman spectra (inVia Raman Microscope-Renishaw) with an excitation laser wavelength of 633 nm and power of 3 mW and transmission electron microscopy (TEM) (Tecnai G2 F20 S-TWIN) with an operating voltage of 80 kV were used to characterize the quality of our graphene sheet.

3. Results and discussion

The CVD graphene films can be transferred onto lacey TEM grids. The TEM image of the as-prepared graphene film is shown in Fig. 2. The graphene flakes appear to cover several squared micrometres. The TEM image also shows that the graphene film still has many defects due to the synthesis or transfer process. The Raman spectroscopy was carried out at room temperature to characterize the quality of graphene, as shown in Fig. 3. It should be noted that Raman spectroscopy provides a quick and easy characterization of the structure and quality of the as-synthesized graphene. Graphene's electronic structure is uniquely captured by its Raman spectrum, which clearly evolves with the number of layers. Monolayer graphene exhibits defect-induced Raman signals at the G peak of ~1580 cm^{-1} and overtone peak 2D-band at ~2700 cm^{-1}, historically named the G′ peak [20]. In our previous study, the Raman characteristics of Cu foil before and after graphene growth, as well as after transferring onto a silicon substrate, were investigated for comparison. The results indicated that the graphene films remained as a monolayer even after being transferred onto the SiO_2/Si substrate [21]. The Raman characteristics were examined with the SiO_2/Si substrate acquired on regions covered (Fig. 3a) and uncovered (Fig. 3b) by graphene. The appearance of the G-band and 2D-band in the graphene-covered region indicated that the monolayer graphene was grown and transferred onto the SiO_2/Si substrate.

Regarding gas-sensing characteristics, sensitivity and response–recovery time depend strongly on the interaction between the surface of the sensitive layer and the adsorbate molecules. Many dangling bond defects, such as hydroxyl, carboxylic, and carboxylic acid usually exist on the graphene surface. These dangling bond defects can exist above and below the basal plane or the edges of the graphene [22]. It can be clearly seen that the dangling bond defects as well as the functional groups around the vacancy sites or at the tips play a very important role in the sensing properties of the carbon nanotubes gas sensor [23]. Moreover, the defects can be weakly bonded with adsorbate molecules when exposed to target gas [24]. The density functional theory, which describes the adsorption of adsorbate molecules on graphene, was demonstrated in previous reports [22,23]. For each adsorbate,

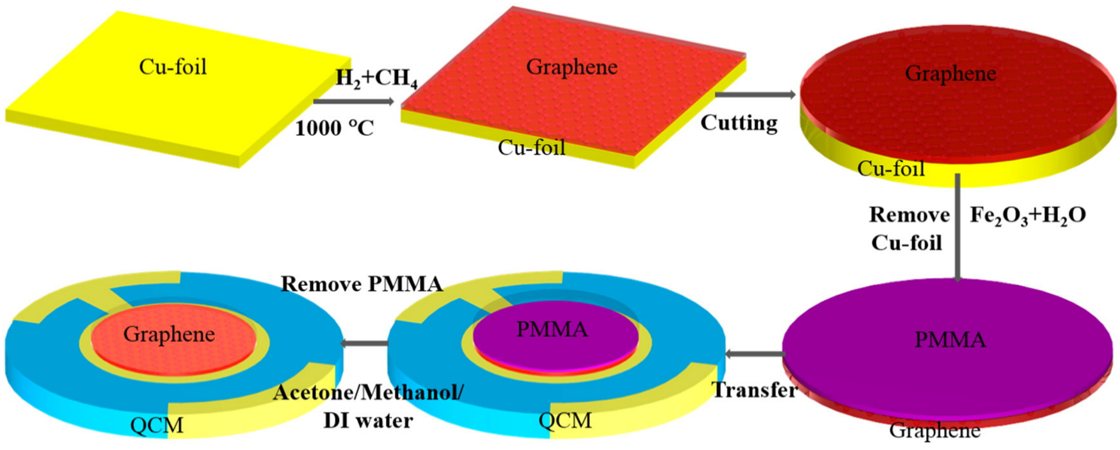

Fig. 1. Schematic diagram of the fabrication process of graphene-based QCM sensor.