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Studies on p-TiO_2/n-graphene heterojunction for hydrogen detection

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ABSTRACT

Thermally oxidized p-type Si [resistivity (5–10) Ω cm and ⟨1 0 0⟩ orientation] with oxide thickness of 245 nm was used as the substrate for the deposition of graphene by CVD. The formation of multilayer graphene (MLG) was confirmed by Raman spectroscopy. A heterojunction was fabricated by sol–gel coating of TiO_2 on CVD grown graphene layer. The formation of titanium dioxide was verified by electron dispersion spectroscopy (EDS). The surfaces of TiO_2, graphene as well as p-TiO_2/n-graphene interface were characterized by scanning electron microscopy (SEM). Detail sensor study of the p-TiO_2/n-graphene heterojunction was performed by taking two lateral catalytic metal (Pd) contacts deposited by e-beam evaporation. The response time of 16 s and the corresponding recovery time of 61 s were obtained for 0.5% H_2 in air at 125 °C. The p-TiO_2/n-graphene junction showed selectivity for H_2 compared to methane. The stability study was performed and it showed almost the steady results over a period of 3 days as tested by the discrete measurements. The sensing mechanism was formulated using a simplified energy band diagram.

1. Introduction

Due to the flammable nature of hydrogen gas the detection of trace amount of hydrogen is essential to address the safety concern during its storage. Metal oxides are the most studied materials in the field of gas sensors due to their easy availability, economic viability, and high response toward reducing and oxidizing gases. Amongst the metal oxides, titanium dioxide (TiO_2) is important owing to its high temperature stability and robustness against chemical/corrosive atmosphere. There are many reports on high temperature and high efficiency gas sensors based on TiO_2 [1,2]. The nanostructured TiO_2 surface, obtained by sol–gel technique, reduced the hydrogen sensing temperature [3]. Apart from the oxides, carbon based materials have shown immense potential for gas sensor applications [4]. Graphene, which is a perfect 2D network of carbon atoms, is also a promising material for gas sensor study. The 2D carbon lattice has very high surface to volume ratio, highest thermal conductivity (~5000 W/mK), and electrical mobility ~200,000 cm^2/V s) [5], and these properties are all suitable for any electronic device based applications, including chemical sensors. So, the combination of the two materials i.e. TiO_2 and graphene, may yield a system worth studying for chemical sensors. In 2011, Zhang et al. reported the preparation of graphene and TiO_2 composite structure by using spin coating technique for the use as photo catalytic agent [6]. In 2013, Pan et al. also reported on the preparation of TiO_2/graphene nanocomposite by the hydrothermal method for photo catalytic application [7]. In both the reports, the Hummers' chemical method was employed for graphene synthesis. Further, Fan used TiO_2/graphene nanocomposite as an electrochemical sensor for the detection of adenine and guanine (2011) [8] and for the detection of hydrogen peroxide (H_2O_2) and NADH (2012) [9]. A report on anatase and rutile based n–p composites obtained from the same source (Aldrich) of Titania for carbon monoxide (CO) and methane (CH_4) sensing is available in the literature [10]. The gas response was correlated to the rutile concentration in the composite, and a sample having 75% rutile selectively sensed CO relative to methane. Nanocomposites with oxides like ZnO and SnO_2 were studied for hydrogen sensor response. A selective response for hydrogen relative to CH_4 and CO is reported [11].

Apart from nanocomposites, the reports on gas sensors using heterojunction between two different materials are also available. In 2012, Chowdhury et al. reported the sensing of ammonia (NH_3) gas using organic p-zinc phthalocyanine (ZnPc) and inorganic n-zinc sulphide (ZnS) heterojunction device [12]. The influence of donor (ammonia) and acceptor (oxygen) species on the sensing characteristics was also reported for this organic/inorganic

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heterojunction device. In 2013, Muhsien et al. showed that porous silicon based heterojunction device [n-SnO_2/p-PSi/c-Si] could be used for carbon dioxide (CO_2) and hydrogen (H_2) gas sensor applications [13]. Brilis et al. in 2007, reported very high H_2 response of p-NiO/n-SnO_2 heterojunction device at room temperature [14]. The thin films of p-NiO and n-SnO_2 were grown by adopting two different techniques viz. pulsed laser deposition and chemical vapour deposition respectively. The results revealed that the response of the two layer heterojunction device toward hydrogen was superior to the response of only NiO. Deng et al. used nanofibers of zinc oxide and titanium dioxide to fabricate (ZnO/TiO_2) heterojunction device for ethanol sensing [15]. ZnO and TiO_2 nanofibers were synthesized by electro spinning and hydrothermal growth technique respectively. The ZnO/TiO_2 heterojunction showed higher response (~3 times) than only ZnO and TiO_2 based devices toward ethanol (20–500 ppm). The progress in the nanoscale metal oxide based heterojunction has been reported by Miller et al. [16]. Carbon based heterojunction devices were reported by Gao et al. [17]. The reversed biased device, comprising of amorphous carbon deposited on n-Si substrates by magnetron sputtering, showed very high response to NH_3 at room temperature. Such high sensitivity was attributed to the change in the space charge layer width upon adsorption of NH_3 molecules. The oxide-graphene heterostructures were reported by Shin and co-workers for photovoltaic applications [18].

In this paper we report on the fabrication of TiO_2/graphene heterojunction and the study on the sensor response of hydrogen mixed with air in the temperature range, 75–150 °C. Graphene film was grown on the oxidized silicon substrate by indigenously developed CVD method and the TiO_2 thin film was deposited on graphene by the simple and reliable sol–gel technique. The selectivity and the stability studies have been included in this communication.

2. Experimental

2.1. Graphene synthesis

The multilayer graphene was synthesized by the atmospheric pressure CVD method developed indigenously in our laboratory. A ~300 nm thick Cu film was deposited on the SiO_2/Si substrate by electron-beam evaporation. Hydrogen (H_2) to nitrogen (N_2) gas ratio of 25:500 in SCCM was maintained for 1-h to anneal the catalytic Cu metal film. Graphene was grown at 1000 °C using methane (CH_4) gas (as hydrocarbon source) along with the gas mixture of hydrogen and nitrogen in the ratio 25:5:300 (SCCM) for 8 min [19].

2.2. Deposition of TiO_2 and fabrication of the TiO_2/graphene heterojunction

Sol–gel technique was adopted for the deposition of TiO_2 thin film. The 0.0035 (M) solution of 99.999% titanium (IV) Tetra-Isopropoxide (TTIP) (Sigma–Aldrich) and 0.0217 (M) glacial acetic acid (Merck) were mixed in a round bottom flask and the mixture was stirred vigorously for 15 min in an ice bath. The de-ionized (DI) water was then added drop wise to the stirring solution. The mixture of TTIP, acetic acid and DI water was again stirred vigorously for 1 h at 0 °C to obtain a clear and transparent solution [3]. The solution was kept overnight in the dark condition. The graphene sample on SiO_2/Si substrate was masked to open a defined surface area for TiO_2 deposition. Thereafter, the masked sample was dipped into the prepared solution slowly by using a programmable dip coating unit (Spectrodip-Programmable dip coater, Spektron Instruments Inc, India). The dipping time of the sample for TiO_2 deposition was 10 s. Subsequently, the sample was annealed at 450 °C for 3 h in air ambient. The 2D-XRD analysis confirming the crystallinity of our sol–gel grown TiO_2 thin films is already reported by us [3,20].

2.3. Characterizations

The graphene and TiO_2 films were analyzed by Raman spectroscopy (Model LABRAM DILOR JY Spectrometer, with a 632.8 nm He–Ne Laser source) and electron dispersion spectroscopy (Model JEOL JSM-6390LV) respectively. The FESEM (Model JEOL JSM-6390LV) was used to study the surface morphology of titanium dioxide, graphene and the titanium dioxide/graphene interface. The type of conductivity of graphene and titanium dioxide was determined by hot probe technique.

2.4. Formation of electrical contacts

The palladium (Pd) metal contacts of dimension (2 mm × 2 mm) and thickness 0.2 μm were deposited over graphene and TiO_2 surface respectively using e-beam evaporation technique after carefully masking the device. Fine copper (Cu) wires and the silver paste were used to complete the electrical contacts.

2.5. Sensor setup

The sensor set up consists of the stainless steel tube gas transmission lines fitted with the mass flow controllers and the mass flow meters (Digiflow, USA). A closed corning glass tube (~95.4 cc) with gas inlet and outlet ports is placed coaxially inside a resistively heated furnace with a 4 cm constant temperature zone [1]. A precise temperature controller (with ±1 °C accuracy) and a copper constantan thermocouple are used to measure and control the temperature of the sensor chamber. High purity [hydrogen gas (H_2) 99.998 vol%; methane gas (CH_4) 99.99 vol%; nitrogen (N_2) 99.99 vol% and air (oxygen ~20 vol% and nitrogen ~80 vol%)] were used for the sensing experiments. Prior to the introduction into the sensor chamber, the carrier and test gases were mixed in a mixing chamber of volume ~86.2 cc. The gas on/off was controlled by Swagelok valves, and the switching was done in approximately 1 s. The current–voltage characteristics were studied by a Keithley Pico ammeter (Model 6487, M/S Keithley Instruments).

3. Results and discussions

3.1. Raman spectroscopy

The presence of graphene layer was confirmed by Raman spectroscopy. The Raman spectrum of the graphene film used in this study is shown in Fig. 1. The 'D', 'G' and '2D' peaks are observed at

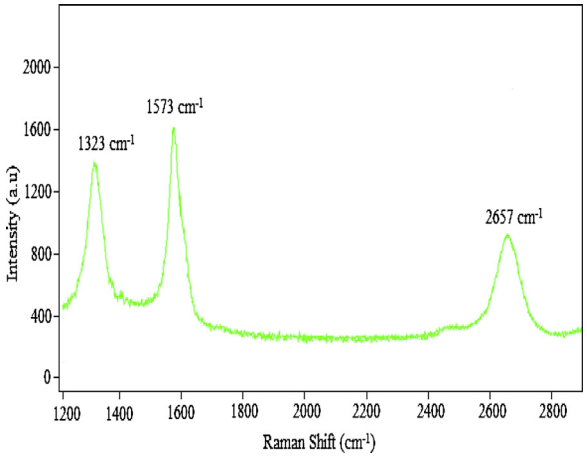

Fig. 1. Raman spectra of CVD grown multilayer graphene thin film.