Oriented Graphitic Carbon Films For Hydrogen Gas Sensors

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Abstract— **An oriented graphitic nanostructured carbon film has been employed as a conductometric hydrogen gas sensor. The carbon film was energetically deposited using a filtered cathodic vacuum arc with a -75 V bias applied to a stainless steel grid placed 1cm from the surface of the Si substrate. The substrate was heated to 400 °C prior to deposition. Electron microscopy showed evidence that the film consisted largely of vertically oriented graphitic sheets and had a density of 2.06 g/cm^3. 76% of the atoms were bonded in sp^2 or graphitic configurations. A change in the device resistance of > 1.5% was exhibited upon exposure to 1 % hydrogen gas (in synthetic, zero humidity air) at 100 °C. The time for the sensor resistance to increase by 1.5 % under these conditions was approximately 60 s and the baseline (zero hydrogen exposure) resistance remained constant to within 0.01% during and after the hydrogen exposures.**

I. INTRODUCTION

Hydrogen gas concentration of more than 4% in air is highly explosive and therefore adequate safety monitoring equipments must parallel the development of hydrogen fuel cell technology [1, 2]. This has led to increased interest in devices which can effectively monitor the concentration of hydrogen gas in air. Hydrogen gas sensing has been demonstrated by functionalized carbon nanotubes (CNTs) [3, 4] and graphene [5, 6]. These materials offer reasonable sensitivity and low power consumption and importantly, they can offer these attributes at room temperature, thereby simplifying the construction of sensor chips and associated circuits. Recently, the ultimate in sensitivity has been achieved using graphene. Single molecules adsorbing to and desorbing from graphene flakes have been detected [5].

To date, the mechanism of hydrogen sensing of nanostructured carbon films are not well understood. It has been reported that both molecular hydrogen physisorbtion and atomic hydrogen chemisorbtion caused changes in the hybridization of different atomic bonding and therefore in the film properties [7].

Whilst functionalized CNT and graphene sensors have demonstrated high performance, their preparation methods typically include the manipulation of individual sheets/tubes, precluding compatibility with large-scale silicon device processing. In addition, there are still significant challenges precluding the large scale production of CNTs having the necessary orientations and properties for sensing applications. Obtaining graphene monolayer films with adequate dimensions for sensing applications is also hard to achieve as most methods rely on mechanical exfoliation, a method which lacks scalability [8].

Carbon films can be prepared with a wide variety of mechanical properties and electrical resistances of the films [9, 10]. The physical and electrical properties of these films could be varied by several orders of magnitude simply by selecting different substrate bias voltages [11].

Oriented graphitic carbon films show great potential for applications including heat electrical sinks, interconnects, sensors and other nano-devices [12]. Fabricating these types of films usually requires energetic deposition. By applying a voltage directly on the substrate holder the energy of the ions can be altered. This is usually the case for Filtered Cathodic Vacuum Arc (FCVA) deposited films [13, 14]. In a FCVA deposition system the energetic condensation processes enabled by the high degree of ionization [15, 16]. However, the application of bias to the low conductivity substrates can cause substrate damage and/or defects in the resulting film.

The aim of this work was to produce a hydrogen sensor from an oriented graphitic carbon film prepared without substrate bias (to avoid damage to the substrate by charging/discharging).

II. EXPERIMENTAL

The carbon film was energetically deposited from a 70 mm high purity graphite cathode within the FCVA

deposition system (Fig. 1). The deposition conditions for the C film were: Arc current = 73 A, arc voltage = 28 V, substrate temperature = 400 °C and the substrate remained at floating potential. A stainless steel gird was mounted in front of the substrates with 11 mm separation (Fig. 2). The grid was biased at -75 V to produce a nanostructured carbon film consisting of a high density of graphitic sheets aligned perpendicular to the substrate [11]. A lift-off process was used to reduce the Pt/oriented C film to the dimensions required for the gas sensor. Finally, 30 nm thickness Pt contacts pads were deposited onto the oriented carbon films using a Precision Etching Coating and Etching system (PECS).

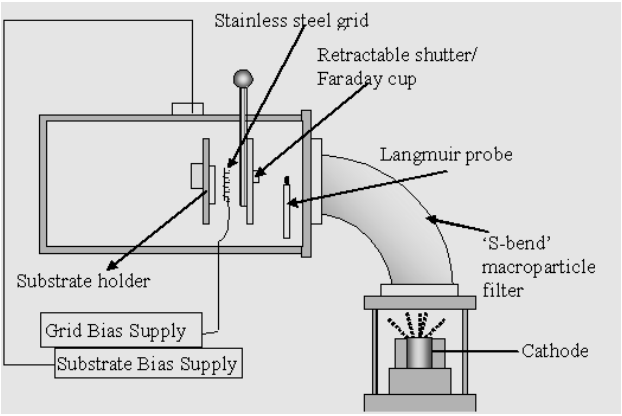

Figure 1. Schematic diagram of the biased grid and sample holder within the FCVA deposition system.

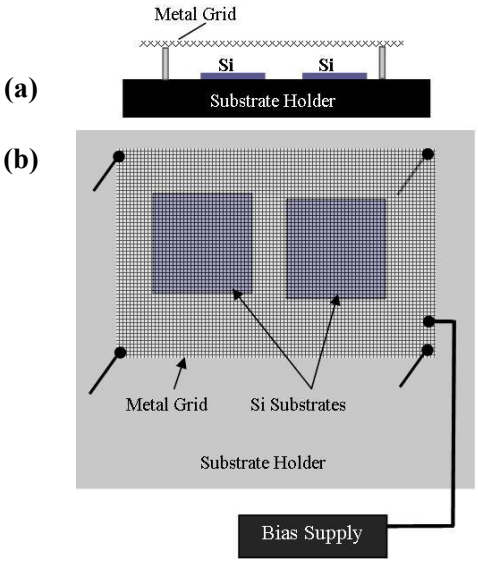

Figure 2. Schematic (a) cross section and (b) plan viewdiagrams of the substrate holder and the grid.

Transmission Electron Microscope (TEM) samples were prepared after chemically etching the Si and SiO_2 layers beneath the carbon layer using 48% hydrofluoric acid (HF) solution. Small pieces of the carbon film and substrate were first floated on nitric acid (HNO_3) solution so that the Si/SiO_2 layers were in contact with the solution. A few drops of HF were then added slowly to start the etching process. Carbon film fragments (containing Au flakes from the electrodes) remained and floated on top of the solution when the etching was completed. The floating carbon layer was then collected using a needle and placed in de-ionised (DI) water to remove the acid and a Cu grid was used to catch the floating carbon flakes. Microstructural characterization was carried out in a JEOL 2010 TEM operating at 200 kV. In addition to imaging, Energy Electron Loss Spectroscopy (EELS) was performed.

Gas sensing performance measurements of the sensor were conducted using a computerized multi-channel gas calibration system (Fig. 3). The sensors were placed in a test chamber. The operating temperature was controlled by an alumina micro-heater in direct contact with the sensor. The performance of the sensor was analyzed with respect to temperature and different concentrations of hydrogen. These concentrations were in the range of 0.06 to 1%, at a constant volumetric gas flow rate of 200 ml/min. *I-V* measurements were carried out using a Keithley 2602 current source unit.

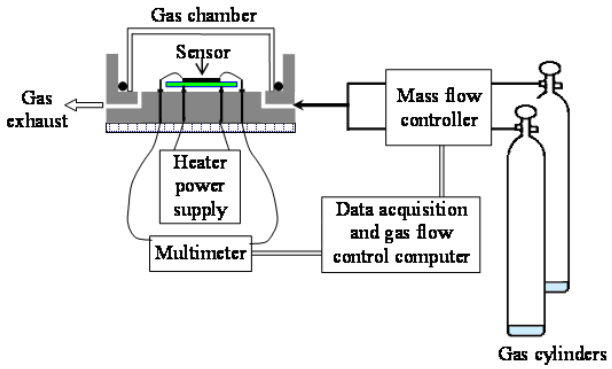

Figure 3. Schematic diagram of gas sensing test apparatus.

III. Results and Discussion

Fig. 4 shows (a) a high resolution TEM and (b) a selected area diffraction pattern from the carbon film. The results showed that the carbon film had a low density of 2.0 g/cm3 with 76 % of the atoms bonded in sp^2 or graphitic configurations. The selected area diffraction pattern was taken from the carbon film and shows strong graphitic {002} reflections. Previous work [9] has revealed

that films with this type of microstructure consist a largely of vertically oriented graphitic sheets.

Fig. 5 (a) shows a schematic view depicting the vertically oriented carbon sheets within the carbon film on the Si substrate. Fig. 5 (b) shows a schematic of the sensor fabricated by depositing Pt contacts using PECS.

The dynamic performance of the sensor at 100 °C in the presence of various indicated hydrogen concentrations in synthetic air is shown in Fig. 6. Percentage change in resistance (sensitivity) of the sensor after exposure to different hydrogen concentration at 100°C is shown in Fig. 7. Sensitivity was measured to be 1.5% upon exposure to 1 % hydrogen gas (in synthetic, zero humidity air) at 100 °C. The time for the sensor resistance to increase by 1.5 % under these conditions was approximately 60 s.

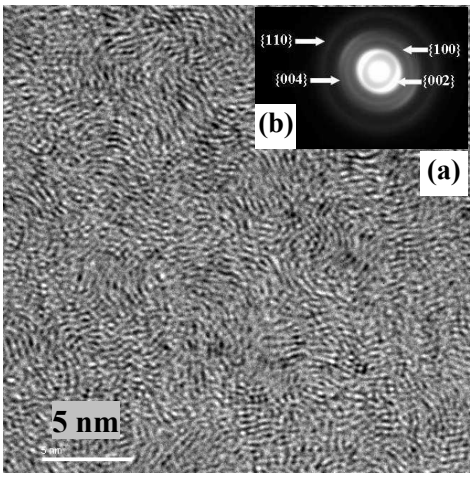

Figure 4. Schematic(a) High resolution TEM image and corresponding (b) selected area diffraction pattern from the carbon film prepared at 75 V bias and a substrate temperature of 400 °C using grid.

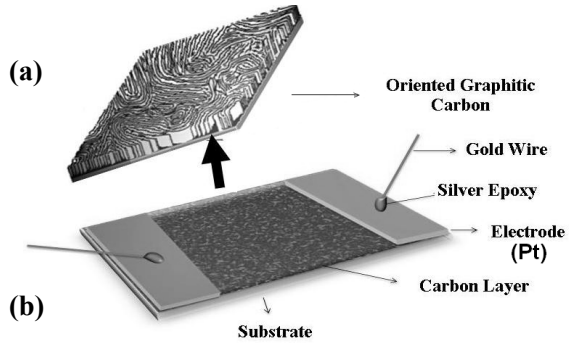

Figure 5. Schematic diagrams of the (a) oriented carbon film and (b) fabricated sensor with Pt contacts.

The sensor sensitivity increases linearly with the increase of hydrogen concentration. Repeatability of the sensor responses was measured after exposing to 0.25% hydrogen twice during the test sequence (Fig. 6) and it was observed that the sensor response magnitude was the same for both cases. It was also observed that the baseline (zero hydrogen exposure) resistance remained constant to within 0.01% during and after the exposure tests.

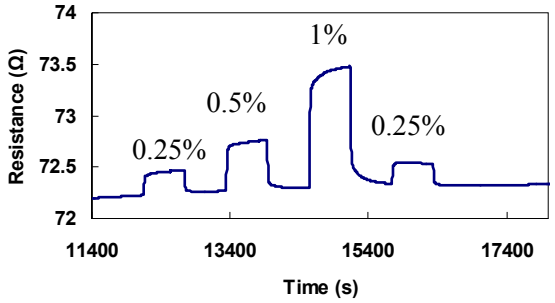

Figure 6. Dynamic responses of the sensor in the presence of various indicated hydrogen concentrations in synthetic air at 100 °C.

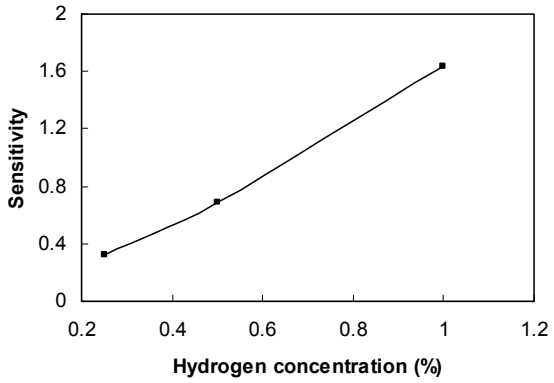

Figure 7. Percentage change in resistance(sensitivity) upon exposure the sensor to different hydrogen concentration at 100 °C.

IV. CONCLUSION

An oriented graphitic nanostructured carbon film was deposited on Si substrate using a biased grid in a FCVA deposition system. It was shown that this method is suitable for the deposition of oriented films on poorly conductive substrates. The film was used to make a conductometric hydrogen gas sensor. The sensor sensitivity increases linearly with the increase of hydrogen concentration therefore the oriented graphitic sensor has the potential for industrial hydrogen sensing applications.

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