Fabrication and Characterisation of Resistive Nanocrystalline Graphite

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***Abstract*—This work demonstrates the feasibility of fabricating resistive nanocrystalline graphite (NCG) on a Si substrate. The NCG film thickness of 9 nm was deposited using metal-free plasma enhanced chemical vapour deposition (PECVD) on a 6-inch p-type silicon wafer. The surface and electrical properties of the resistors produced were investigated. The average grain size of the NCG thin film is 35 nm with 0.8 nm of surface roughness. The electrical characterization of the NCG strips show metal-like behaviour in which the resistance is proportional to the strip lengths. The sheet resistance is found to be 39 kohm/sq which is two orders of magnitude larger than graphene deposited using Chemical Vapour Deposition. This indicates the carrier transport across grain boundaries has a large influence on the overall resistance of the device. However, the nano-sized grains on the NCG material could be used to enhance the sensitivity of the material towards the environment.**

Keywords— nanocrystalline graphite, resistor, plasma enhanced chemical vapor deposition, grain boundaries

I. INTRODUCTION

Graphite and graphene are being increasingly researched for various electronic device applications. Due to their unique material properties, it unveils promising applications in various sensing technology [1-2]. Graphene is also compatible with thin film processes and can be found in devices such as solar cells [3], sensors [4] and switching devices [5]. However, large-scale graphene device fabrication remains challenging.

Recently, nanocrystalline graphite (NCG) material has attracted attention because the film can be deposited on insulating substrates in large scale[6-10]. The film has shown uniformity in terms of electrical and mechanical properties [9]. Different approaches were used to produce scalable NCG film including epitaxial growth [2] and using photoresist [7]. However, the high temperature anneal (>1000°C) in these processes limit the electronic devices application. It was previously demonstrated that the NCG layer can be produced with metal-free plasma-enhanced CVD tool at a temperature of less than 1000°C and the film showed resistive characteristics [6-10]. This indicates the deposition technique is feasible to produce nanocrystalline graphite on a large sized wafer.

NCG has been shown to exhibit good electrical property. It was demonstrated in the earlier work the NCG/p-Si junction exhibited Schottky characteristics with a barrier height of 0.58 eV [10]. In addition, NCG film is used for piezoelectric strain sensing [9,11]. It was found that the piezoresistive sensitivity of the NCG layer is higher than graphene based strain sensor and can be tailored by the grain densities for electro-mechanical and transparent electrodes in flexible electronics. Due to its excellent mechanical properties, NCG-based nanoelectromechanical (NEMS) devices have been demonstrated [11].

The NCG thin film is known to have high amount of defects which consequently affects the film resistivity. Nevertheless, they are suitable for gas sensors and chemical sensor in various applications. Physical properties such as surface roughness and surface morphology play crucial roles to enhance the sensing capability. It was shown that when grain boundaries exist in graphene, the sensitivity increases by ~300 times when gas molecules adsorbed on the surface compared to a single-crystalline graphene [13].

Based on the NCG process [10], we demonstrate the viability of fabricating resistive devices using NCG and p-type silicon. The NCG film was etched and patterned through lithographic process to produce two terminal resistive devices. The electrical characteristics were measured and analyzed to determine the resistance of these devices. It was found these devices exhibit metal-like behaviour in the NCG and the resistance is proportional to the strip lengths. The obtained results are are comparable with few-layers graphene based device [14].

II. EXPERIMENTAL

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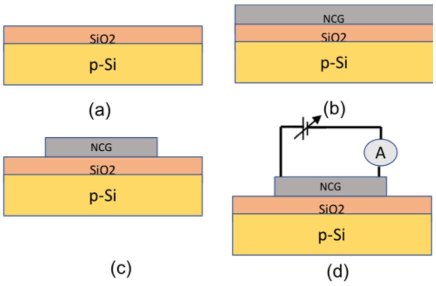


Fig.1. Device Fabrication Process (a) SiO_2 layer deposited on p-Si (b) NCG deposition (c) NCG patterning (d) Schematic of NCG/p-Si resistive device

$$La\ (nm) = (2.4 \times 10^{-10})\ \lambda^4\ (I_D/I_G)^{-1} \quad (1)$$

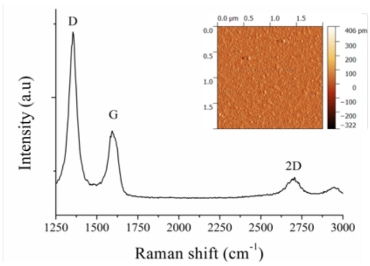


Fig. 2. Raman measurement of the NCG film (inset) AFM image of the NCG surface.

The fabrication started with a 6-inch single side polished p-type silicon wafer. The Boron doped silicon wafer has an average resistivity of 19 Ω.cm. Figure 1 shows the fabrication process of the NCG device.

First, an 200 nm SiO_2 layer was deposited on p-Si using plasma enhanced chemical vapor deposition (PECVD) at deposition temperature of 350^{o}C (Figure 1(a)). Then, NCG films were deposited on these SiO_2 layer (Figure 1(b)) with PECVD. The deposition process was carried out at 750 ^{o}C, gas pressure of 1.5 Torr and RF power of 100 W, using a mixture of hydrogen and methane as the precursors. The thickness of the NCG film was measured to be 9 nm using ellipsometry. The working parameters of the PECVD deposition technique of NCG has been outlined elsewhere [8]. Photolithography was used to pattern the film (Figure 1(c)). The NCG films were etched in oxygen plasma with pressure, power and gas flow set at 100 mTorr, 100 W and 50 sccm, respectively. The schematic of a typical device structure is shown in Figure 1(d).

The NCG film was patterned with widths measured from 30 to 500 µm while the lengths are varied from 20 to 5000 µm. Atomic Force Microscope (Park Systems) was used to measure the surface topography, NCG thickness and surface roughness in a non-contact mode. The structural investigations of the NCG material were achieved using Raman spectroscopy with excitation laser wavelength of 532 nm. In electrical characterization, I-V measurements were carried out using Keithley 4200-SCS semiconductor parametric analyzer. The measurements were performed in ambient room temperature.

III. Results and Discussions

Figure 2 shows the Raman spectrum of the deposited NCG film. There are two signature peaks which can be observed for graphite which are at 1350 cm^{-1} and at 1580 cm^{-1}. The peak at 1350 cm^{-1}corresponds to amorphous carbon (the D band) and the peak at 1580 cm^{-1}corresponds to single crystal graphite (the G band) [3]. The D peak is observed to exhibit high intensity. This behaviour could be due to either small grain sizes or the grain boundaries in the NCG structures. The second order of the D peak which is known as 2D peak is also visible in the Raman spectrum at 2690 cm^{-1}. The presence of a distinct 2D peak is in good agreement with graphene structures formed in deposited films [15]. The ratio of the D and G peaks is accountable for the presence of the grain size of the NCG [15]. The crystallite size (La) of the grains inside the NCG film was calculated using (1) [15];

where λ is the laser excitation wavelength in nm which is 532 nm. From the equation, the average grain size is found to be 35 nm. The inset in Figure 2 shows the AFM topography image of the NCG surface. The root mean square (rms) surface roughness is determined to be 0.8 nm.

Figure 3 shows the images taken from optical microscope and Scanning Electron Microscope, (SEM) of the patterned NCG on SiO_2 layer. Figure 3(a) shows various dimensions of the device which width varies from 30 µm to 500 µm and the device length varies from 77 µm to 5 mm. The bright region is the p-Si area where the NCG in contact with. Fig. 3(b) is the NCG resistive strips on SiO_2/p-Si substrate.

Figure 3(c) shows the resistive device with NCG/p-Si structure. The widths, W and lengths, L are labeled accordingly. Each strip is a single diode with two anode pads. The inset shows the enlarged view of the deposited NCG film on SiO_2 layer. The NCG film thickness is approximately 9 nm. The NCG strips were first measured using direct tungsten needle probes to determine the sheet resistance and contact resistance. Figure 4 shows the I-V plots along the patterned NCG strips with different lengths but fixed width of 30 µm. The NCG strips were located on SiO_2/p-Si substrate. The linear form of the I-V plot indicates the metallic behavior of the as-grown NCG films. The linear plot also indicates good electrical conduction along the nanosized grains.

From these plots, resistance values were determined and were plotted against the NCG strip length as shown in the inset of Figure 4. The contact resistance of 60 kΩ is obtained from linear fitting of the plot. The high contact resistance is due to the direct measurement using the tungsten probe needle on the NCG strips but the device is still able to produce good conductivity. The gradient of this plot is used to calculate the sheet resistance of the NCG film which is governed by (2)

$$R = \rho\ L/(Wt) \quad (2)$$

where ρ is the resistivity, L is the NCG strip length, W is the NCG width and t is the NCG thickness.

Hence, the sheet resistance (R_{sh}=ρ/t) is found to be 39 kΩ/sq. The sheet resistance values are comparable to the 2 k -80 kΩ reported in several work using CVD technique [16-19]. Compared to CVD graphene [20], the sheet resistance of our NCG is two orders of magnitude larger. This indicates the carrier transport across grain boundaries has a large influence on the overall resistance. However, the NCG film from this work shows higher conductivity compared to graphene films made from graphene oxide [21] or chemically exfoliated

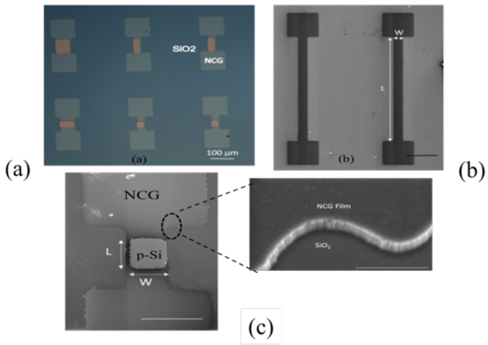
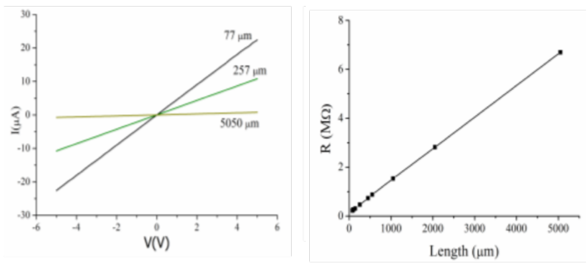


Fig. 3. (a) Optical microscope images of NCG devices with various dimensions, (b) Scanning electron microscope (SEM) image of NCG resistive strip on SiO_2/p-Si layer. Scale bar is 100 µm, (c) SEM image of a single Schottky device structure. Scale bar is 50 µm, (*inset*) Enlarged view of NCG deposition on SiO_2 layer. Scale bar is 500 nm.

graphene [22]. This shows that although the NCG film is less than 10 nm, the lateral conductivity is high as shown earlier. Consequently, this would enable sufficient lateral conductance in the NCG devices.

IV. Conclusions

This paper has demonstrated a simple metal-free fabrication process to fabricate NCG/p-Si resistive devices in wafer scale. The two-probe current-voltage measurements for the NCG strips show excellent metal-like behaviour in the NCG and the resistance is proportional to the strip lengths. The nano-sized grains on the NCG material could be used to enhance the sensitivity of the material towards the environment. Therefore, the NCG/p-Si resistive device show considerable potential for various sensing applications.



(a) (b)

Fig. 4. (a) I-V characteristics of NCG strips with different length (b) Plot of resistance against NCG strip lengths

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