Massive Seebeck Coefficient of Si/SiO$_2$ Substrate-Supported Graphene Thin Film

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Abstract

Graphene has been used in applications in many fields due to its outstanding electronic, thermal and mechanical properties, since its discovery in 2004. However, having a higher thermal conductivity and lacking of band gap makes graphene unsuitable to use in thermoelectric generators. Several research works have been conducted to reduce the thermal conductivity and introduce a band gap to graphene. However, despite having few theoretically developed studies, experimental work on the thermoelectric properties of graphene are scarce. We deposited few graphene layers on a Si/SiO$_2$ substrate using an ultra-high vacuum thermal evaporator which is a novel and unreported technique to synthesis graphene thin film. Thermally reduced graphene oxide synthesized using a modified *Hummers* method was used as the source material for thermal evaporation. The formation of the thin film was studied by X-ray diffraction and UV-Visible spectrometry. The measured *Seebeck* coefficient of the thin film attained a maximum value of 35.04 mV K^{-1} at room temperature. This is one of the largest *Seebeck* coefficients reported ever.

Keywords: Graphene Thin Film; Thermoelectricity; Seebeck coefficient; Thermal Evaporation; Substrate-supported graphene; Figure of merit; Thermoelectric materials

1. Introduction

Since its discovery back in 2004 [1], Graphene attracted strong interest of the researchers, mainly, in the field of electronics and materials science. Graphene is a, 2-D planar material which carbon atoms are tightly packed to form a hexagonal monolayer having a thickness of only 0.35 nm. Each Sp^2 hybridized carbon is bonded to another 3 carbon atoms using S, Px, and Py orbitals. These hexagonal carbon structures are bonded with each other by σ bonds, forming a very stable hexagonal structure. The remaining Pz orbital, which is perpendicular to the hexagonal carbon plane, make the π bond. The π and π* bands of this corresponding π bond are responsible for the elevated electronic properties of graphene.

The thermoelectric properties of graphene were first studied and reported by Zuev *et al.* [2], Wei *et al.* [3] and Checkelsky *et al.* [4] in 2009. Despite having few theoretical studies [3,5–7], there is little experimental research work reported on thermoelectric properties of graphene. Unlike the freely suspended graphene, graphene supported on a substrate displays different chemical and physical properties. In this paper, we investigate the thermoelectric properties of graphene thin films (GTFs) which are supported on a SiO_2 substrate.

2. Experimental Details

2.1 Synthesis of Reduced Graphene Oxide

Sri Lankan natural vein graphite was used for all the Graphene Oxide (GO), Reduced Graphene Oxide (RGO) and GTF synthesis. H_2SO_4 (99.999%), P_2O_5, $K_2S_2O_8$ (≥99.0%), $KMnO_4$ (≥99.0%), $NaNO_3$ (99.995% trace metals basis), and H_2O_2 (30%) were purchased from Sigma-Aldrich™ and used as received. Modified Hummers method was employed for the synthesis of GO, reported elsewhere [8] and it was thermally reduced to obtain RGO. In a typical experiment, a mixture of 4 g of natural graphite, 12 ml conc. H_2SO_4 and 8 g of P_2O_5 was

prepared and magnetically stirred for 6 hours. After that, another 12 ml of H_2SO_4 was added to the filtrate with 8 g of $K_2S_2O_8$. Then, the mixture was stirred for another 6 hours and added 300 ml of distilled water. The filtrate was air-dried overnight and heated in a furnace at 60 °C for 2 hours. Two grams of pre-oxidized graphite was added to a mixture of 92 ml conc. H_2SO_4 and 12 g $KMnO_4$ and stirred for about 15 minutes. Then, 8 g of $NaNO_3$ was added to the mixture and stirred for 2 hours. After that, 200 ml of distilled water was added and stirred for 15 minutes. Then, 10 ml of H_2O_2 and 560 ml of distilled water were added to the solution. The solution became bright orange color. The filtrate obtained was washed with 10% HCl. The filtrate was dried at 60 °C for 30 minutes and air-dried overnight. Then, the sample was sonicated with 30% H_2O_2 for 20 minutes and the filtrate was dried at 60 °C for 4 hours after washing twice with warm distilled water. To obtain RGO, 0.1 g of GO was heated in an alumina crucible covered with an aluminium foil with pores, for 10 minutes at 350 °C.

2.1 Thermal evaporation of Reduced Graphene Oxide

A tungsten boat filled with 0.1 g of synthesized RGO was heated by applying 100 A DC current in vacuum (~4×10^{-5} Pa) and thermally evaporated onto a Si/SiO$_2$ substrate with an average evaporation rate of 0.5 Å s^{-1}. The thickness of the thin film was measured using quartz-crystal mass-thickness sensor (inside the evaporator). Table 01 below summarizes the conditions used during the thermal evaporation.

Table 01: Conditions used and details of the thermal evaporation process.

Maximum current applied	100 A DC
Pressure inside the chamber	4×10^{-5} Pa
Substrate	Si/SiO$_2$
Temperature of the substrate	Room temperature
Average evaporation rate	0.5 Å s^{-1}

3. Results and Discussion

The formation of graphene was monitored using the UV-Visible spectrometer. Figure 1 show the corresponding UV-Visible spectra of GO and GTF.
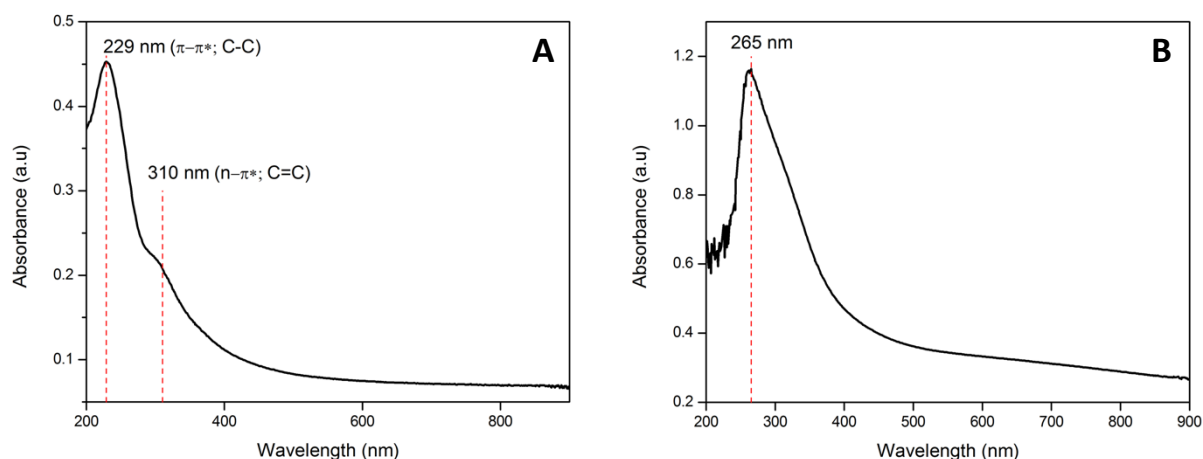

Figure 1: (A) UV-Visible spectrum of GO. The characteristic absorbance peak at 229 nm and the shoulder at 310 nm can be seen. (B) The UV-Visible spectrum of GTF. The absorbance peak which was at 229 nm is red shifted to 265 nm indicating the reduction of GO. Note that the shoulder in A at 310 nm has disappeared in the GTF spectrum.

Two prominent features can be observed in the UV-Visible spectrum of GO. The maximum peak at 229 nm attributed to $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds. The shoulder centered around 310 nm corresponding to $n \rightarrow \pi^*$ transitions of C=O bonds [9]. Similar results were also obtained by Allagui *et al.* [10]. GO was thermally reduced to RGO, and during the thermal evaporation process, it is further reduced to form GTF. The UV-Visible spectrum of GTF is shown in Figure 1(B). The maximum peak observed at 229 nm in the spectrum of GO is red shifted to 265 nm and the shoulder around 310 nm completely disappeared in Figure 1(B). This indicates the removal of intercalated oxygen functional groups, and recovering of electronic conjugation of graphene planes via thermal reduction. These results are consistent with the studies done by Xu *et al.* [11].

The X-ray diffraction studies were conducted at 0.02° per step increment, between 5°-70° using Cu Kα radiation (λ = 0.15418 nm) with a *Rigaku Ultima IV* Diffractometer.
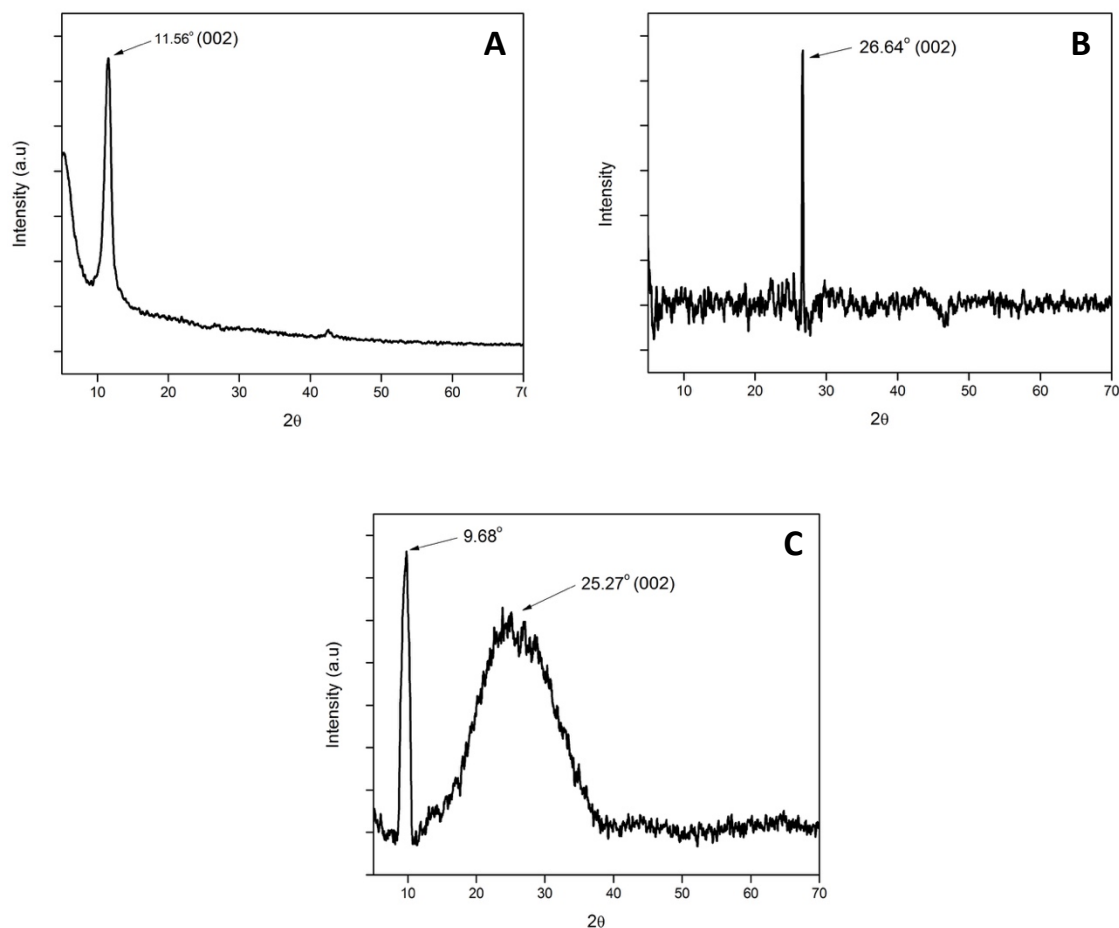

Figure 2: (A) The XRD spectrum of GO. The characteristic peak of GO is seen at 2θ = 11.56°. (B) The peak is then shifted to 2θ = 26.64° in the XRD spectrum of RGO. (C) The broad band seen around the 2θ = 25.67° is identified as the synthesis of graphene. (a.u. = arbitrary units)

Figures 2(A), 2(B), and 2(C) above show the X-ray diffraction patterns of GO, as-synthesized RGO and GTF respectively.

As shown in figure 2(A), typical GO peak at 2θ = 11.56° is visible, which has an interlayer spacing of 0.765 nm calculated using Braggs law;

$$n\lambda = 2d \sin \theta$$

where λ is the wavelength of the X–ray, θ is the scattering angle, n is an integer representing the order of the diffraction peak, d is the interlayer distance. After the reduction of GO to RGO, the peak at 2θ = 11.56° (d = 0.756 nm) shifts to 2θ = 26.64° (d = 0.334 nm) corresponding to (002) plane, as shown in figure 2(B). This d value shift confirms the reduction of GO to RGO, which is supported by UV-Visible spectrum data. Also, this is in good agreement with the previous reported study by Alam *et al.* [8]. The interlayer spacing of GO varying from 0.6 to 1.0 nm depending on the synthesizing process and intercalated species [12]. Having obtained an interlayer spacing of 0.334 nm, we can see that intercalated oxygen functional groups are mostly removed during the thermal reduction and thermal evaporation processes. Since graphene has a 2D structure, as mentioned previously. Therefore, theoretically XRD peaks are not expected from graphene. However, during the thermal evaporation process, since the single graphene sheets are thermodynamically unstable, which makes individual graphene layers to stack together to form a more stable state. This results a broad peak in XRD. The peak centered around 2θ = 25.27° shows the evidence of this stacking phenomenon and it also confirms the formation of graphene which has a structure between amorphous and crystalline structures [13]. Its corresponding interlayer spacing is 0.352 nm, which is only 5% greater than the interlayer spacing in a pristine crystal graphite having true ABAB stacking, which is 0.335 nm [14].

We calculated the number of layers stacked in both RGO and GTF using XRD results by applying the Scherrer's equation with a constant of 0.9 [15]. Table 02 below summarizes all parameters obtained from the XRD analysis. The parameters d, FWHM, H, N indicates the inter layer distance, line broadening at half the maximum intensity, average height of stacking layers and average number of layers, respectively. The calculations show that the RGO initially

stacked a higher number of layers (~381 layers) from which only few layers (1-2 layers) get deposited on the substrate as the GTF.

Table 02: The structural parameters of RGO and GTF obtained from XRD analysis for 002 peaks.

	Reduced Graphene Oxide	Graphene-TF
2θ	26.64°	25.27°
d (nm)	0.334	0.352
FWHM (deg)	0.0642	12.7559
H (nm)	127.2627	0.6387
N	381-382	1-2

A totally new, sharp peak is also observed in the diffraction pattern of GTF at $2\theta = 9.68°$ (Figure 2(C)). This peak corresponding to interlayer spacing of 0.913 nm is very strong and sharp, suggesting long-ranged and highly ordered structure of graphene layers. Dimiev *et al.* [16] studied the formation of GO using Raman spectroscopy and X-Ray diffraction and argued that this peak is due to the originally ordered graphene layers from bulk graphite. We suggest that, during the thermal evaporation process, the some of the remaining oxygen functional groups of RGO intercalate between graphene layers to form long-ranged graphene layered structure which has a larger interlayer distance.

We used a newly developed measurement system to measure the Seebeck coefficient of rhe GTF. A detailed description of the system can be found in the supplementary documents. Figure 3 below shows how the Seebeck voltage of GTF varies with the temperature difference maintained across the thin film. The voltage produced due to the Seebeck effect increases with the temperature gradient. Red line indicates the average plot. The gradient (slope) of the average plot is the Seebeck coefficient of the GTF. Since, the Seebeck coefficient in copper is very low compared to that of graphene its contribution to the overall value is negligible. The

calculated gradient of the plot (Seebeck coefficient) is about 35.046 mV/K (at room temperature), which is approximately 30 times larger than that of the common conventional thermoelectric materials. This value is among the largest Seebeck coefficient values reported
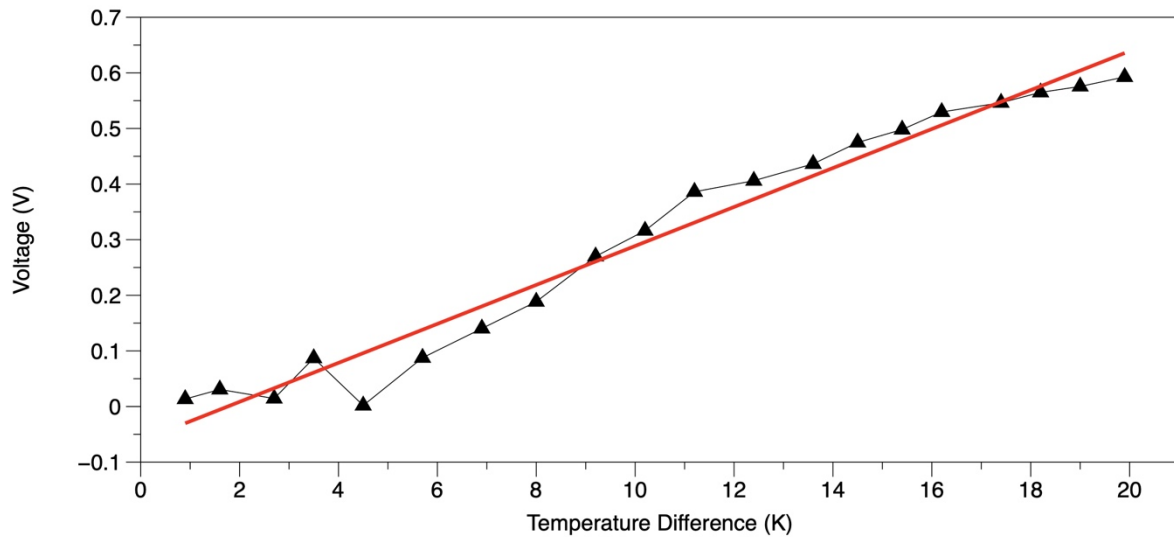
so far. Dragmon *et al.* [17], in their study of graphene thermoelectric device, also reported a Seebeck coefficient in the same range, 30 mV/K.

Figure 03: The induced voltage across the thin film with the applied temperature difference. The slope of the graph yields the Seebeck coefficient.

Unlike graphene in its freely suspended form, the in-plane thermal conductivity of graphene is reduced significantly when it is in contact or supported on a substrate (i.e. Si/SiO$_2$, in this study) [18]. This happens due to the coupling and scattering of graphene phonons with substrate vibrational modes [19]. Suspended graphene has a thermal conductivity ~5000 W/mK. But when it is supported with SiO$_2$ substrate, the thermal conductivity gets reduced to ~600 W/mK due to weak van der Waals bonds formed with the substrate. The phenomenon was clearly described by Seol *et al*. [6] and Prasher [20] in their studies.

In this study, we observed a massive Seebeck coefficient in the graphene-glass system and according to the previous studies, the same system exhibited a low thermal conductivity as explained above. Therefore, it is understood that this system can be used efficiently in thermoelectric applications. The future studies should also investigate the mechanisms of these effects and possible strategies to further increase the Seebeck coefficient and decrease the thermal conductivity of the system.

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Supplementary Documents

Appendix 01. Seebeck coefficient measurement system

A technique was developed to measure Seebeck Coefficient of the GTF as follows. One side of the thin film was heated by connecting to 12V heater. Ultra-thin Copper metallic sticker was

pasted on top of the heater form the thermoelectric couple. Voltage generated was measured using *Keithely 2000* multimeter. Temperature difference between the contact points of the multimeter, on the thin film was measured using *Extech EA15: EasyView™* Dual Input Temperature Datalogger. Voltage data accumulation was done by connecting the multimeter to a PC via GPIB interface and using a MATLAB code developed. The temperature readings were accumulated using *EA15* software. Figure S1 below shows a photograph and schematic diagram of the setup used.
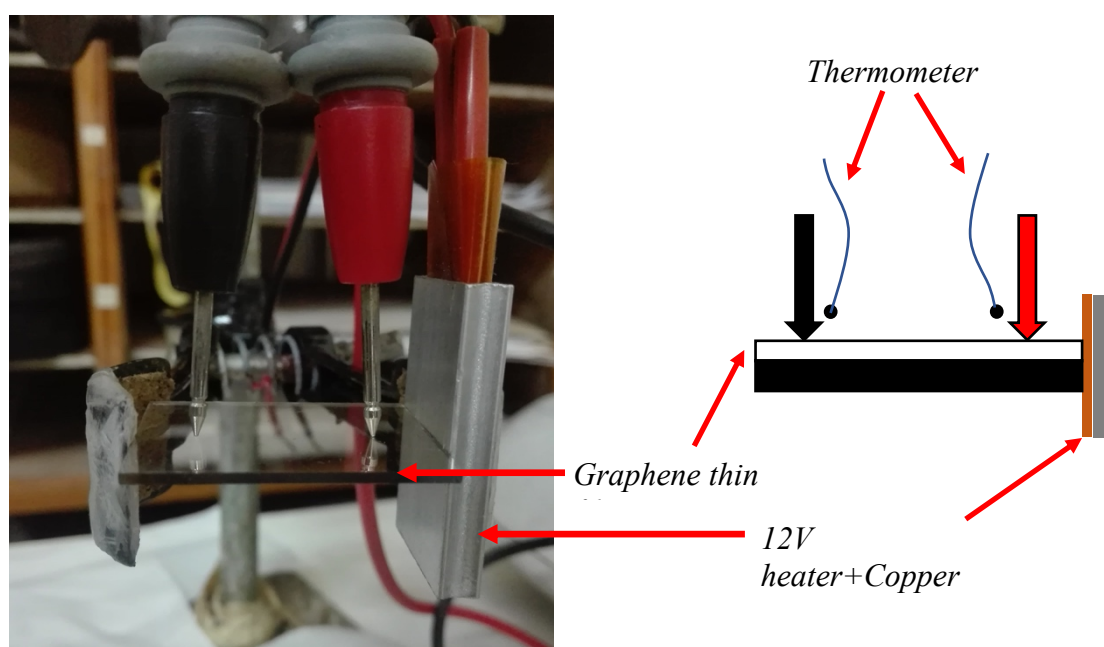

Figure S1: A photograph of the Seebeck measurement system along with the schematic diagram of the same.