

THERMOELECTRIC POWER OF CVD GROWN GRAPHENE AS SURFACE CHARGE DOPING INDICATOR

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Introduction

Recently graphene has generated a great deal of interest among the researchers worldwide [1]. Physical properties of graphene have already been explored, and fascinating electrical, optical, mechanical and thermal characteristics have remarkably been found well integrated in this intriguing material. Owing to its unique two-dimensional (2D) band structure graphene has been widely recognized as one of the most promising candidates for post Si-CMOS nanoelectronics, while its Dirac-like charge dynamics underlying the appealing material properties provides an ideal platform for fundamental research. In addition, compared with conventional 2D semiconducting systems, such as heterostructures or quantum wells, graphene proves to be more sensitive to its environment, i.e., the supporting substrate and the gases/chemicals adsorbed on the surface. Indeed, as reported by many groups [2-4], annealing graphene in high vacuum or H₂-Ar gas mixture is a key process to achieve high quality devices. In this talk, we present a study of the response of the thermoelectric power (TEP) and the 4-probe resistance of graphene during the process of annealing and exposure to various gases. Availability of large area graphene grown by chemical vapor deposition (CVD) [5, 6] facilitates straight forward TEP measurement by anchoring two miniature thermocouples and a resistive heater on the graphene without undergoing any micro fabrication processes [7]. Use of two extra wires as the current leads can be easily implemented to measure the 4-probe resistance. The measured Seebeck coefficient and the 4-probe resistance provide useful information beyond the traditional electronic transport measurements. In particular, its extreme sensitivity to the particle-hole asymmetry advances the TEP measurement as a sensitive probe to distinguish the absorption mechanism of reactive gases. Our observations hold promise for practical applications of graphene in gas sensing devices.

Experimental

CVD synthesis of graphene: The recipe for graphene synthesis in this work is similar to that in our previous research [6] and Ref. [5]. Polycrystalline Cu foil with thickness of 25 μm and purity >99.8% is used as a substrate. 70 ppm CH₄ as precursor gas is carried by H₂:Ar=1:30 mixture with total gas flow 310 sccm; pressure is 1 atm; and the graphene formation time is 10 min at 1000 °C. After graphene formation, samples are cooled down by mechanically pushing the sample holder to lower temperature zones (room temperature) in Ar atmosphere. Cooling rates (~10 °C/s, an average value from 1000 to 700 °C) are measured by a thermal couple on the sample holder. For transferring graphene to Si/SiO₂ substrates, as-synthesized samples are coated by PMMA using a spinner. The spinning speeds are in range between 500 to 3000 rpm depending on the size of samples. After coating PMMA, samples are placed on an aqueous solution of iron nitrate for etching off the Cu substrate. Afterwards, graphene/PMMA films are scooped out from the solution, rinsed several times by DI water and placed on the Si/SiO₂ substrates. At last, PMMA is removed by acetone.

TEP measurement: After transferring onto Si/SiO₂ substrate, the graphene sample is mounted on a ceramic holder connected to a measurement probe, and then the probe is loaded into a quartz reactor placed inside a tube furnace. Two Chromel/Alumel thermocouples are attached to the sample with small amounts of silver epoxy, and a small Pt resistive heater is placed at one of the ends of the device, as shown in Fig. 1. We use the subtraction method described in Ref. [7] by Sumanasekera, *et al.*, for the TEP measurements. Figure 1 illustrates this method to measure the Seebeck coefficient of the graphene (S_G) at a given temperature. Specifically, we record the thermoelectric voltage $V_1 = (S_G - S_C)\Delta T$ and $V_2 = (S_G - S_A)\Delta T$ as a function of $\Delta V = V_1 - V_2 = (S_A - S_C)\Delta T$, and extract S_G from the obtained slopes during heating and cooling, controlled by sending a current through the Pt heater. Here S_A and S_C are the Seebeck coefficient of the Alumel and Chromel wires, respectively; their values are well documented in the NIST ITS-90 Thermocouple Database. And then, we record the time evolution of S_G during a vacuum annealing/degassing process, followed by the exposure to various gases.

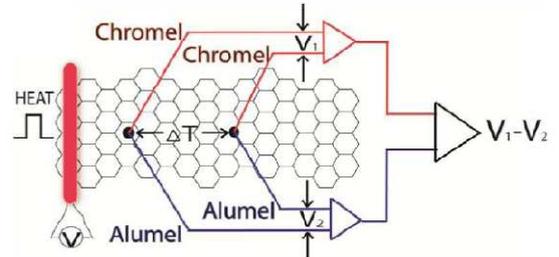


Fig. 1 The circuit schematic of a graphene-based thermoelectric gas sensor. The Pt resistive heater (red) is connected to a voltage source, while the two Chromel/Alumel thermocouples are measured by two nanometers.

Results and Discussion

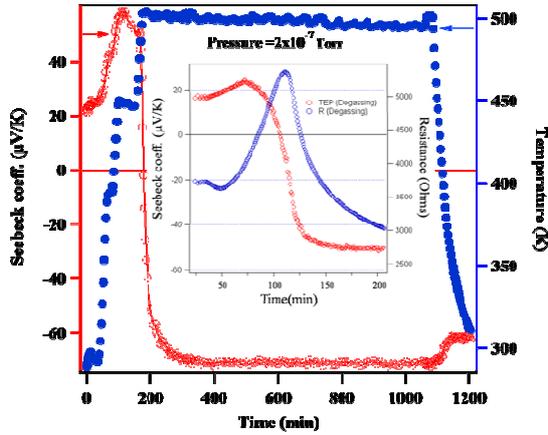


Fig. 2 Main panel: the time evolution of S_G (red) and the temperature (blue) during a vacuum annealing process. Inset: the time evolution of S_G (red) and graphene resistance (blue) during the annealing.

As shown in Fig. 2, S_G changes dramatically from a positive value (p-type) to negative (n-type) when the graphene is annealed at 500 K. Specifically, before the annealing $S_G \approx 23 \mu\text{V/K}$ under ambient conditions, while it becomes to $S_G \approx -60 \mu\text{V/K}$ after degassing and cooling back to room temperature. The total change in S_G is $\sim 400\%$, demonstrating the high sensitivity of the device to gas molecule desorption on the graphene surface. For comparison, the total change in resistance, as shown in the inset of Fig. 2, is $< 200\%$, and it is non-monotonic (increase or decrease in resistance depending on the type of the dominating charge). The observed p-type behavior of graphene on a Si/SiO₂ substrate under the ambient can be interpreted as a result of the electron exchange between the oxygen redox couple in the adsorbed water film and the electronic states of graphene. The corresponding energy diagram is shown in Fig. 3(a), where the work function of graphene is 4.6 eV [8-10] and the chemical potential of the oxygen/water layer lies between -5.66 and -4.83 eV, depending on the pH value of the solution. Since the Fermi level of graphene lies near the redox potential of the oxygen dissolved in the mildly acidic water adsorbed on the SiO₂ surface (which has a work function of 3.03 eV [11]), electrons can readily transfer from the graphene to the oxygen/water layer, as demonstrated in Fig. 3(a).

Finally, after annealing and cooling down to room temperature, the device is exposed to various gases such as N₂O, NH₃ and ambient air. Figure 3(b) shows the time response of the device during the exposure; repetitive exposure-annealing cycles show no “poisoning” effects of the introduced gases (i.e., the device can be annealed back to the same initial state). Figure 3(b) also indicates that N₂O acts as an electron acceptor for graphene, while NH₃ acts as an electron donor. The weak n-type doping induced by NH₃ is consistent with previous works on SWNTs and recent studies on graphene.

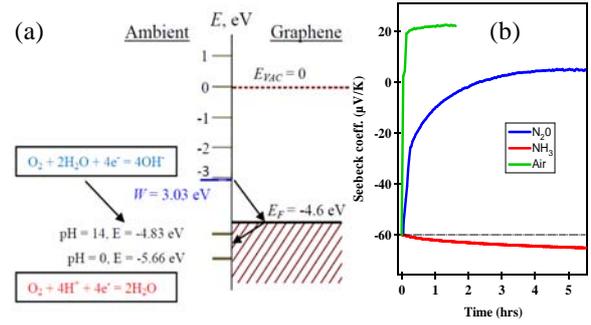


Fig. 3 (a) Energy level diagram of the wafer/oxygen redox couple compared to the Fermi energy of graphene. (b) Time response of S_G for a degassed CVD grown graphene to N₂O, NH₃ and ambient air.

Conclusions

The thermoelectric response of graphene is found to be a sensitive measure of the gas molecule charge doping on the surface of graphene.

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References

- [1] Geim AK. Graphene: Status and Prospects. *Science* 2009;324(5934):1530-1534.
- [2] Ishigami M, Chen JH, Cullen WG, Fuhrer MS, Williams ED. Atomic structure of graphene on SiO₂. *Nano Lett* 2007;7(6):1643-1648.
- [3] Morozov SV, Novoselov KS, Katsnelson MI, Schedin F, Elias DC, Jaszczak JA, Geim AK. Giant intrinsic carrier mobilities in graphene and its bilayer. *Phys. Rev. Lett.* 2008;100(1):016602-1-4.
- [4] Chen JH, Jang C, Xiao SD, Ishigami M, Fuhrer MS. Intrinsic and extrinsic performance limits of graphene devices on SiO₂. *Nat. Nanotechnology* 2008;3(4):206-209.
- [5] Li XS, Cai WW, An JH, Kim S, Nah J, Yang DX, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee SK, Colombo L, Ruoff RS. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* 2009;324(5932):1312-1314.
- [6] Cao HL, Yu QK, Jauregui LA, Tian JF, Wu W, Liu ZH, Jalilian R, Benjamin DK, Jiang Z, Bao JM, Pei SS, Chen YP. Wafer-scale Graphene Synthesized by Chemical Vapor Deposition at Ambient Pressure. *Appl. Phys. Lett.* 2010;96(12):122106-1-3.
- [7] Sumanasekera GU, Grigorian L, Eklund PC. Low-temperature thermoelectrical power measurements using analogue subtraction. *Measure. Sci. Technol.* 2000;11(3):273-277.
- [8] Filletter T, Emtsev KV, Seyller T, Bennewitz R. Local Work Function Measurements of Epitaxial Graphene. *Appl. Phys. Lett.* 2008;93(13):133117-1-3.
- [9] Datta SS, Strachan DR, Mele EJ, Johnson ATC. Surface Potentials and Layer Charge Distributions in Few-Layer Graphene Films. *Nano Lett.* 2009;9(1):7-11.
- [10] Shi YM, Dong XC, Chen P, Wang JL, Li LJ. Effective Doping of Single-Layer Graphene from Underlying SiO₂ Substrates. *Phys. Rev. B* 2009;79(11):115402-1-4.
- [11] Romero HE, Shen N, Joshi P, Gutierrez HR, Tadigadapa SA, Sofo JO, Eklund PC. N-Type Behavior of Graphene Supported on Si/SiO₂ Substrates. *ACS Nano* 2008;2(10):2037-2044.