



Study of nitrogen doping of graphene via *in-situ* transport measurements

Rong Zhao^a, Tareq Afaneh^a, Ruchira Dharmasena^a, Jacek Jasinski^b,
Gamini Sumanasekera^{a,b,*}, Victor Henner^{c,d}

^a Department of Physics and Astronomy, University of Louisville, Louisville, KY 40292, USA

^b Conn Center for Renewable Energy, University of Louisville, Louisville, KY 40292, USA

^c Department of Theoretical Physics, Perm State University, Perm 614990, Russia

^d Department of Mathematics, Perm Technical University, Perm 614990, Russia

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ABSTRACT

Here we report *in-situ* monitoring of electrical transport properties of graphene subjected to sequential and controlled nitrogen plasma doping. The nitrogen is presumed to be incorporated in to the carbon lattice of graphene by making covalent bonding as observed by the swinging of the sign of the thermopower from (initial) positive to (eventual) negative. Electrical transport properties for nitrogen-doped graphene are believed to be governed by the enhanced scattering due to nitrogen dopants and presence of localized states in the conduction band induced by doping. Our results are well supported by Raman and XPS results.

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1. Introduction

As a novel nanomaterial with a single sheet of carbon atoms arranged in a honeycomb lattice, graphene has attracted strong scientific and technological interests [1] since its discovery in 2004 [2]. The fascinating properties of graphene, such as extremely large carrier mobility [3], high thermal conductivity [3], tunable band gap [4] and quantum Hall effect [5], have led to its great application potentials in the devices such as transistors [6], rechargeable lithium ion batteries [7], ultra-sensitive sensors [8] and supercapacitors [9]. We have previously reported *in-situ* electrical properties of graphene during covalent functionalization with oxygen [10], hydrogen [11] and fluorine [12]. However, substitutional doping of carbon in graphene with appropriate elements can change the physical and chemical properties of graphene in a more dramatic way leading to important device manufacturing. Among all these different doping, nitrogen doping of graphene is expected to introduce additional n-type carriers in graphene systems which is crucial for applications in high frequency semiconductor devices [13] and enhanced catalysis for energy

conversion and storage [14–17].

Numerous approaches have been proposed to synthesize nitrogen-doped graphene, including nitrogen-containing precursors in chemical vapor deposition (CVD) [18,19], thermal annealing of graphene oxide in ammonia [20] and N₂/NH₃ plasma treatment [21–23]. In this work we present *in-situ* electrical transport properties of graphene during plasma assisted nitrogen doping.

2. Experimental

Graphene was synthesized by chemical vapor deposition on copper foils using CH₄ gas and transferred to Si/SiO₂ or glass substrates as described in [24,25]. Electrical transport studies were performed on graphene transferred onto glass substrates. Two Chromel (KP/Au – 7 at% Fe (Au:Fe) thermocouples and a platinum resistive heater were utilized for thermopower measurements. Two additional copper wires were used for simultaneous 4-probe resistance measurements as described in Ref. [26]. A custom-designed split ring capacitively coupled RF plasma system (13.56 MHz, max. power 600 W) was used at room temperature to generate nitrogen plasma. Plasma exposure time was established by *in situ* monitoring of the change in resistance and thermopower of the sample. For low-temperature measurements, a chip carrier

* Corresponding author at: Department of Physics and Astronomy, University of Louisville, Louisville, KY 40292, USA.

E-mail address: gusuma01@louisville.edu (G. Sumanasekera).

supporting the graphene sample was transferred to a closed cycled refrigerator (Janis Research Co. CCS-350ST-H) which can be cooled down to a base temperature of ~ 8 K. The sample-containing refrigerator column is enclosed by an electromagnet (LakeShore model EM4-CV 4-in. gap, Horizontal Field) capable of producing magnetic field which can be swept between -1 and $+1$ T. All the samples used for transport measurements and Raman/XPS characterization were subjected to nitrogen plasma under identical conditions. We placed two samples each for XPS and Raman in addition to the sample used for transport study. All the samples were kept in close proximity to ensure they undergo similar plasma treatments. The Raman spectra were collected using an InVia Renishaw Raman spectrometer with the excitation wavelength of 632 nm. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a MultiLab 3000 VG Thermo Scientific surface analysis system. Mg K α (1253.6 eV) radiation was used as the excitation source, and the measurements were performed at room temperature and under ultrahigh vacuum conditions at pressures in the 10^{-9} Torr range.

3. Results and discussion

Fig. 1(a) shows the nitrogen plasma in operation gently exposing graphene sample. Fig. 1(b) and (c) show the *in-situ* time evolution of R and S of the graphene during two successive nitrogen doping processes. The graphene sample was carefully exposed to the nitrogen plasma of 25 W for a short period of time (~ 60 s) at a gas flow rate of 15 standard cubic centimeters per minute (sccm) and the pressure was ~ 200 mTorr, the plasma was then turned off and the monitoring of the change in R and S was continued. Extreme care was taken in order to not inflict any damages to the sample during the process. Sample was at the floating potential.

Pristine graphene is typically p-type due to the residual species (e.g., oxygen and water molecules) adsorbed on the surface of graphene. This ambient p-type behavior has been identified as due to electrochemically mediated charge transfer mechanism between a redox couple in humid air and the Fermi energy of graphene [27–29]. In our previous work on hydrogenation and fluorination [11,12], we studied the functionalization effects on degassed sample in order to minimize the influence the effect of oxygen. But in the case of nitrogen doping, we were interested on the effect of substitutional doping of graphene with nitrogen which has less profound effect on the functional groups such as oxygen. Further, the conditions used in this study (high pressure and low temperature) are not sufficient for effective degassing.

During the first nitrogen doping process, R was found to increase from its initial value of $\sim 880 \Omega$ to $\sim 950 \Omega$ and saturate.

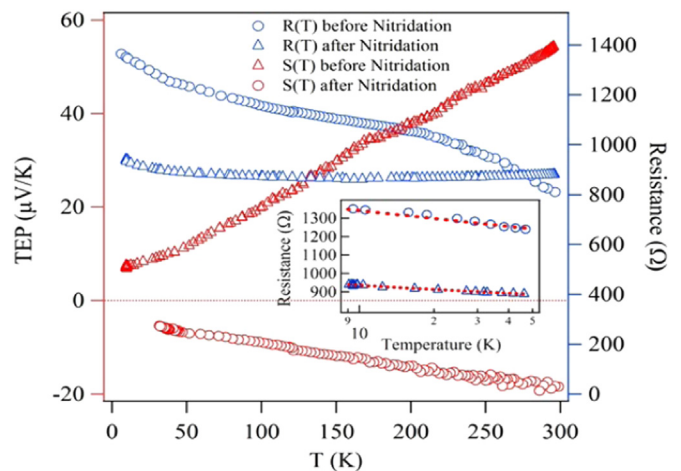


Fig. 2. Temperature dependence of Resistance (right axis) and Thermopower (left axis) of graphene before and after nitrogen doping. Inset: low temperature (below 50 K) resistance behavior with logarithmic temperature axis.

During this period, S was found to decrease from its initial value of $\sim +42 \mu\text{V/K}$ (p-type) down to a $\sim +19 \mu\text{V/K}$ (still p-type) and saturate. During the next nitrogen doping process, R continues to decrease down to a saturated value of $\sim 790 \Omega$ while S reverses its sign and saturates at a value of $\sim -19 \mu\text{V/K}$. This confirms n-type doping of graphene due to the nitrogen atom incorporation into graphene. The nitrogen doping effectively modulates the electrical properties of graphene by shifting the Fermi level above the Dirac point.

Fig. 2 shows the temperature dependence of S (left axis) and R (right axis) for the pristine and nitrogen-doped graphene. For the pristine graphene, $S(T)$ remains p-type throughout the entire temperature region with a nearly linear behavior, while $R(T)$ shows weak temperature dependence at high temperatures and increases at low temperatures. Nitrogen-doped graphene remains negative and shows linear $S(T)$ behavior while $R(T)$ increases with lowering T throughout the temperature range. The pronounced $R(T)$ dependence of nitrogen-doped graphene can be attributed to the enhanced scattering due to nitrogen dopants and presence of localized states in the conduction band induced by doping. The inset in Fig. 2 shows the low temperature behavior of the resistance for both samples with logarithmic temperature axis. Both resistance curves show obvious logarithmic dependence at low temperatures. Generally, a two-dimensional system in the weakly localized regime exhibits logarithmic temperature dependence of resistance [30].

Fig. 3a shows the MR data for pristine and nitrogen-doped graphene at 8 K. The negative MR was observed for both samples

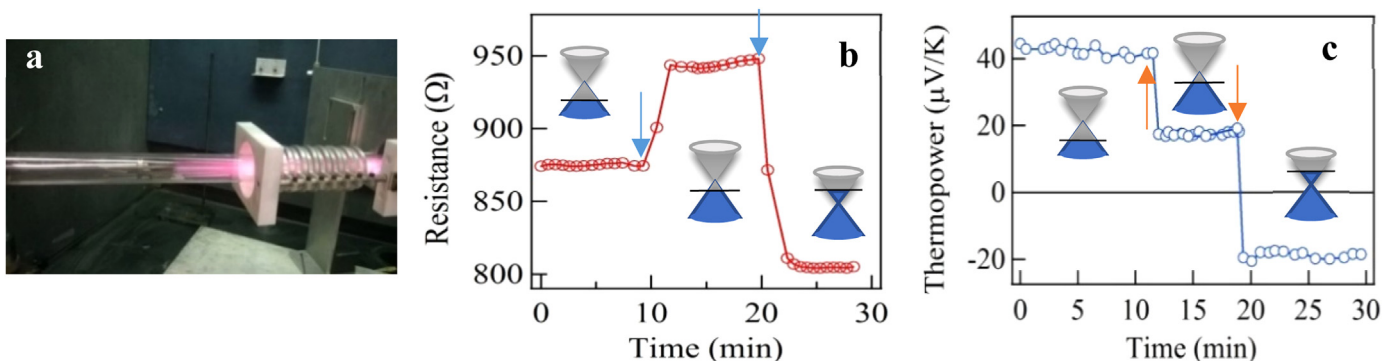


Fig. 1. (a) Nitrogen Plasma in operation. In situ time evolution of the (b) resistance, $R(t)$ (c) thermopower, $S(t)$ during nitrogen doping. The arrow heads represent the initiation of intermittent plasma.

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