



Doping graphene thin films with metallic nanoparticles: Experiment and theory



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ABSTRACT

Precise doping of graphene at nanoscale resolution is vital for a number of applications in nanoelectronics and sustainable energy. Although large metallic contacts are presumed to move the Fermi level of graphene above or below the Dirac point, little has been done to study these effects when graphene is in contact with nanoscale metallic objects of specific sizes and concentrations and to investigate if such phenomena are associated with some forms of doping as in conventional semiconductors. As a case study we determine here the local effect of copper nanoparticles (Cu-NPs) on the Fermi energy of graphene domains in large-area graphene thin films. Tight-binding calculations corroborate our Kelvin-probe force microscopy experiments indicating that the Fermi level shifts in the presence of Cu-NPs (corresponding to 0.2 eV at 20% graphene area coverage by Cu) which break the electron-hole symmetry of graphene due to its weak Van der Waals interactions with Cu even in the absence of chemical bonding and charge transfer, in contrast to previous predictions for large and flat metallic contacts.

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1. Introduction

In order to utilize graphene-based materials in nanoelectronics and sustainable energy applications, it is of paramount importance to establish physical relationships between their fabrication conditions and electronic performance. Modeling the effects of the incorporation of specific heteroatoms and impurities in graphene is a typical example of such a requirement. It is well known that the electronic properties of graphene can be tailored via substitutional doping or by chemically bonding specific functional groups to the graphene layer [1–5]. However, substitutional doping and functionalization also lead to additional undesired effects, because the alteration of graphene through chemical bonding significantly affects its electronic structure near the canonical point, which is responsible for the exceptional carrier mobility in graphene-based materials [6]. Chen et al. demonstrated that the carrier mobility

decreases with increasing dopant density in graphene that was substitutionally doped with potassium, as a result of the scattering of π -electrons in graphene from potassium centers [5].

Controlling the electronic structure of graphene flakes by assembling metallic structures on their surface is another promising direction of research for tailoring their electronic properties, with significant applications in the fabrication of batteries [7], supercapacitors [8], fuel cells [9] and other devices for electronics and energy applications [10,11]. Using first principle calculations, Giovannetti et al. [12] showed that the electronic band structure of graphene can be altered by applying metallic layers on its surface. They demonstrated that this effect is strongly dependent on the specific type of metal being used, with the formation of strong chemical bonds that may significantly alter the band structure of graphene near the Dirac point in the case of some specific metals (such as Co, Ni, and Pd). However, for other metals (Cu, Al, Ag, Au, and Pt), weak bonding only caused shifts in the graphene Fermi energy, which resulted in the doping of this material without significant alteration to its band structure. The distinct behavior of different metals was attributed to differences in their work function relative to graphene [12].

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While the work of Giovannetti et al. pointed out at an attractive avenue for producing doped large-area graphene thin films while limitedly altering their electronic band structure near the Dirac point, assembling metallic layers on top of graphene sheets is not viable for practical applications for which access to the graphene surface is required [7–11]. To this end, the use of nanoparticles of specific metals, including gold [13] and copper [14,15], has been explored for graphene-based devices. However, the roles of the size, shape and concentration of these nanoparticles in affecting the microscopic properties of the resulting nanocomposite systems have never been investigated in detail. For instance, it is not clear if the increase in electrical conductivity that has often been observed in graphene layers decorated with metallic nanoparticles [16] is due to some form of substitutional doping, like in crystalline materials, or to other effects. Furthermore, it is unclear if the specific location at which a metallic nanoparticle is positioned (e.g. at the center of a graphene flake, or near an edge with a specific conformation) is important in affecting the electronic structure and electrical properties of the system [17,18].

In this paper we will investigate the electronic structure and the Fermi energy shifts at the nanoscale in transparent and conducting graphene-based thin films formed by collections of few-layer graphene domains that have been decorated with copper nanoparticles (Cu-NPs) [19] at different diameter and surface area coverage. We will develop a theoretical model at the tight-binding level in order to understand the Fermi level shifts and changes in electrical conductivity that we observed using scanning Kelvin-probe force microscopy (SKPFM) and electrical conductivity measurements.

2. Experimental

Transparent and conducting graphene-based thin films were deposited onto Si(100) and glass substrates using the vacuum filtration method originally invented by Wu et al. [20] for single-wall carbon nanotubes, adapted by Eda et al. [11] for graphene oxide and further developed by Sharifi et al. [21] for surfactant-exfoliated thin films based on few-layer graphene platelets. This fabrication procedure yields graphene-based thin films very similar to those being currently investigated for several large-area applications in electronics and sustainable energy [22,23] and, therefore, offers a realistic benchmark for fundamental studies of their doping mechanisms. Graphite powder (Aldrich, 332461) is used as a starting material for this fabrication process and to obtain graphene-based suspensions in water. In order to be exfoliated and produce few-layer graphene platelets, graphite was ultrasonicated for 24 h in a 3:1 H₂SO₄:HNO₃ mixture, then mildly oxidized in Piranha reagent (H₂SO₄:H₂O₂ = 4:1) and subsequently dried prior to further use. Due to the very low degree of oxidation, this process yields material that is significantly less oxidized than “reduced” graphene oxide commonly prepared using the Hummers' or similar methods [11,21]. 6 mg of the resulting material were suspended for 4 h in a 0.6 g/L aqueous solution of RNA extracted from *torula utilis* (Aldrich) which acts as a non-ionic surfactant and promotes graphite exfoliation [21]. The slurry was left to sediment overnight at 2 °C in a beaker. The top three-quarters of the beaker content were then centrifuged at 6000 rpm for 1 h and the supernatant, largely consisting of well dispersed single- and few-layer graphene flakes, was collected and used for graphene-based thin-film deposition.

The thin-film deposition process basically consists of four steps: i) 5 mL of water suspension of graphene flakes and RNA are vacuum-filtrated through a 220-nm pore size nitrocellulose filtration membrane (Millipore) which leads to the deposition of graphene flakes on the membrane if sufficiently small amounts of

diluted suspensions are used to prevent re-aggregation of the flakes; ii) the filtration membrane loaded with graphene flakes is subsequently transferred onto the requisite substrate and dried under load in a vacuum desiccator; iii) the filtration membrane is etched in consecutive acetone and methanol baths, leaving behind a random distribution of graphene domains and RNA aggregates on their substrate; and iv) the samples were annealed at 550 °C for 5 h to remove RNA and, also, completely reduce them. Extensive characterization, including atomic force microscopy (AFM), scanning electron microscopy (SEM) and Raman spectroscopy was previously used to investigate these films, resulting in >50% clean graphene flakes with less than 5 layers [21].

To decorate graphene-based thin films with Cu-NPs, we introduced them into an ultra-high vacuum radio-frequency (RF) magnetron sputtering chamber (base vacuum $\sim 10^{-7}$ mTorr) attached to a nitrogen-filled glove box (VAC Nexus II) to allow for direct transfer, storage and manipulation of samples with no oxygen exposure [19,22]. The sputtering system is complete with a process gas flow meter (Omega F900) and RF matching network (RF VII). RF sputtering of Cu was carried out from a high purity target (>99.99%) and using argon as a process gas. Two different sets of identical graphene thin films were thus decorated with Cu-NPs. The first set, obtained by varying the annealing temperature from 200 °C to 550 °C at a constant annealing time of 4 h, yielded different Cu-NP diameters as shown in Fig. 1(a)–(d). The area coverage could be kept relatively constant within this set of samples by also adjusting the volume of Cu deposited on our graphene thin films via different thicknesses of the sputtered copper layer. The second set, obtained by varying the annealing time from 1 h to 4 h at a constant annealing temperature of 550 °C, resulted in different copper area coverage on the graphene surface at a relatively constant Cu-NP diameter of about 20 nm. In both cases, non-annealed Cu films formed a semi-continuous system of interconnected Cu particles [22] and the subsequent annealing process in the contiguous glove-box was a critical step for obtaining well-isolated Cu-NPs [19,22]. For comparison, control Cu-NP samples were also deposited and annealed on indium tin oxide (ITO) thin films (15 Ω/□ sheet resistance, Aldrich) in the same system described above. Four-point probe electrical characterization of the samples (Signatone S725 probe station) indicates a strong increase in electrical conductivity of each film upon its decoration with Cu-NPs. Optical transmittance data are included as [Supplementary material](#).

SKPFM measurements were performed at room temperature using a Witec Alfa 300S AFM system integrated with a Kelvin-probe force accessory that includes a waveform alternate current (AC) generator, a stabilized direct current (DC) voltage supply, a lock-in amplifier (Stanford Research Co.) and a proportional-integral-differential feedback control loop. AFM and SKPFM scans are simultaneously recorded with this equipment that is housed in a nitrogen-purged compartment, in which capsules containing the samples are directly transferred from the glove box. During SKPFM measurements, the local contact potential difference V_{CPD} between the tip and the sample surface [23] can be expressed as

$$q \cdot V_{CPD} = \varphi_{tip} - \varphi_{sample} \quad (1)$$

where $q = 1.6 \cdot 10^{-19}$ C is the elementary charge and φ_{tip} and φ_{sample} indicate the work functions of the tip and the sample, respectively. Their difference corresponds to the difference between the Fermi levels within the two systems. For our SKPFM experiments, a platinum-coated conducting AFM tip with $\omega_0 \approx 75$ kHz resonance frequency (Nano Sensors Inc.) was used.

SKPFM is based on small electrostatic forces that are created between a conducting AFM tip and the sample when the two

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