1. Introduction

Graphene with its unique electrical, thermal mechanical, optical barrier, and chemical properties has aroused widespread interest.\[1–10\] The quantum Hall effect,\[2\] extremely high carrier mobility,\[4\] and tunable work function make graphene an attractive material for the fabrication of electronic devices. Accurate control of the electrical transport properties is considered critical for the development of graphene devices.

Au nanoparticles and films are deposited onto clean graphene surfaces to study the doping effect of different Au configurations. Micro-Raman spectra show that both the doping type and level of graphene can be tuned by fine control of the Au deposition. The morphological structures of Au on graphene are imaged by transmission electron microscopy, which indicate a size-dependent electrical characteristic: isolated Au nanoparticles produce n-type doping of graphene, while continuous Au films produce p-type doping. Accordingly, graphene field-effect transistors are fabricated, with the in situ measurements suggesting the tunable conductivity type and level by contacting with different Au configurations. For interpreting the experimental observations, the first-principles approach is used to simulate the interaction within graphene–Au systems. The results suggest that, different doping properties of Au–graphene systems are induced by the chemical interactions between graphene and the different Au configurations (isolated nanoparticle and continuous film).
In this paper, we deposited Au on the surface of monolayer graphene at room temperature. Using Raman measurements, the electrical properties of Au-doped graphene were investigated, while the structures of Au on the graphene were imaged at a series of deposition stages using transmission electron microscopy (TEM). In this way, the electrical properties of the Au–graphene system were revealed to be dependent on the size and configuration of Au. Based on the above results, field-effect transistors (FET) were prepared, and in situ measurements were performed in high vacuum to systematically characterize the electrical transport in Au–graphene systems. The results suggested that, both the doping type and carrier density of graphene could be tuned by finely controlling the Au deposition. To understand the experimental observations, the first-principles calculations were carried out, and it was found that the charge transfer, and thus, the doping type were closely associated with the interactions between graphene and the different Au configurations. This work may lead to possible applications in graphene-based electronic devices.

2. Results and Discussion

2.1. Raman Scattering Spectra

For investigating the doping effect of different Au configurations, monolayer graphene was synthesized and then transferred onto 285-nm-SiO\textsubscript{2}/Si substrates. The quality and number of stacking layers were evaluated by Raman spectroscopy.\textsuperscript{[24]} The D-peak is almost undetectable, indicative of the absence of a significant number of defects. The 2D band, centered at 2676 cm\textsuperscript{-1} with a full-width at half-maximum (FWHM) of 34 cm\textsuperscript{-1}, shows a symmetric Lorentz shape, and the intensity ratio of G/2D is about 0.35. These features are typical of high-quality, monolayer graphene.\textsuperscript{[25]}

Various amounts of Au were deposited on the graphene surface to investigate the size-dependent interaction between Au and graphene. Raman spectroscopy is highly sensitive to the electronic structure of materials, and we used it to examine the correlation between Au deposition and doping properties. It is an effective method for distinguishing the doping type by comparing the positions of the G- and 2D-peaks between doped and pristine graphene.\textsuperscript{[26]} Because the SiO\textsubscript{2} layer under the graphene film is insulating, its effect on the electron distribution of graphene is not considered here. The evolution of Raman spectrum for graphene with increasing Au amount is displayed in Figure 1, with a comparison to the as-grown graphene. When increasingly decorated by a small amount of Au, the G-peak blue-shifts gradually from 1582 to 1587 cm\textsuperscript{-1} while the 2D-peak red-shifts from 2676 to 2660 cm\textsuperscript{-1} as a function of the increasing deposition time (0 to −40 s), exhibiting typical n-type doping in the low-coverage deposition regime. Reverse shifts from 1587 to 1578 cm\textsuperscript{-1} for the G-peak and from 2660 to 2672 cm\textsuperscript{-1} for the 2D-peak are observed after the deposition time further increases, resulting from a reduction of the n-doped efficiency. As the deposition time increases to 70 s, both the G- and 2D-peak show slight blue-shifts to 1585 and 2682 cm\textsuperscript{-1}, respectively, suggesting a p-type doping. These Raman results indicate the controllable n-type and p-type doping by depositing differing amounts of Au. In addition, the defect-induced D’ band at −1620 cm\textsuperscript{-1} emerges as a shoulder peak of G band at 20 s\textsuperscript{[29,30]} and obviously increases at 40 s (denoted by the black arrow in Figure 1a), then slightly decreases at 60 and 70 s. Considering previous theoretical predictions,\textsuperscript{[17]} we suggest that the evolution of the D’ band in our Raman spectra results from the defects created by the chemical interaction which breaks the translational symmetry of the graphene lattice. It is also responsible for charge-induced renormalization of the electronic and vibrational energies, leading to the broadening of the 2D band. Consequently, the formation of a metal–graphene interface not only results in a redistribution of the electrons, but also to a metal–graphene chemical interaction.

2.2. TEM Morphology

Bright-field TEM images of graphene/Au,\textsuperscript{[29]} corresponding to the deposition times of 10, 20, 30, 40, 60, and 70 s are

![Figure 1](image-url)  
Figure 1. a) The G- and b) 2D-peak positions in Raman spectra as a function of Au deposition time. The black arrow indicates the D’ band position at 40 s.
shown in Figure 2. With short time depositions (Figure 2a–c), the Au atoms assembled into isolated hexagonal nanoparticles,[30] distributing on the graphene surfaces with relatively uniform size and shape. The nanoparticles were imaged in high-resolution TEM (inset of Figure 2a). The sixfold symmetrical lattices have a fringe spacing of about 0.24 nm, thus identifying the (111) crystal planes of Au, and showing the high crystallinity of the Au nanoparticles. The diameters of the nanoparticles are about 20, 27, and 32 nm, with the deposition times of 10, 20, and 30 s, respectively. As the deposition time is further increased to 40 s, where the Raman spectroscopy shift reaches a maximum, the nanoparticles are about 45 nm in size and the morphology has evidently changed to one without a uniform hexagonal shape (Figure 2d). Further deposition coalesces the Au nanoparticles (Figure 2e), leading to a large increase in their size. The G and 2D bands back-shift (deposition time = 60 s) from the critical values in the Raman spectra, suggesting a gradual reduction in the level of n-type doping as the Au nanoparticles are coalescing. Opposite doping occurs when a thin continuous Au film starts to form (Figure 2f); the corresponding G and 2D bands in the Raman spectrum shift to 1585 and 2682 cm$^{-1}$, respectively (Figure 1). The Raman results, in conjunction with the TEM images, demonstrate that the doping type of graphene is clearly related to the configuration of Au deposited on its surface.

2.3. FET Measurements

Raman spectra and TEM images confirm that Au nanoparticles and continuous films produce n- and p-type doping in graphene, respectively. This provides strong motivation to fabricate doping-type-tunable graphene FET devices by controlling the Au deposition on the channel. An optical image of a graphene FET device is shown in Figure 3a and b, and the schematic diagram of the device construction is shown in Figure 3d. The uniform color contrast of graphene indicates uniform thickness. During the in situ FET tests, a 1.0 V direct current was applied between the source and drain, and a variable gate bias, $V_g$, ranging from −100 to +100 V was applied on the bottom of the SiO$_2$/Si substrate. Sequentially, the drain–source current ($I_{ds}$) was monitored as a function of $V_g$ through an electrical feedthrough. As-grown graphene shows p-type behavior in the FET test due to the pre-existing adsorbates (Figure 3c). The $I_{ds}$ increases slowly with decreasing $V_g$. The minimum in the gate-dependent conductivity defines the position of the Dirac point, which does not show up within the measured range. After degassing, the Dirac point moves to near the zero gate voltage, and the electron and hole conductions show much better symmetry in our graphene FET devices. The slope corresponds to the mobility ($\mu$) of charge carriers, which are deduced to be about 1400 and 2000 cm$^2$ V$^{-1}$ s$^{-1}$ for electrons and holes, respectively, based on the equation:[15]

$$\mu = \frac{L}{(WC_g V_{ds})(\Delta I_{ds}/\Delta V_g)},$$

where $L$ and $W$ are the channel length and width, respectively, $C_g$ is gate capacitance per unit area, and $V_{ds}$ is drain–source bias.

Using the same process, three FET devices A, B, and C were prepared for electrical transport measurements. For device A, we used a smaller heating current and longer deposition distance to obtain small isolated Au nanoparticles on the graphene channel (Figure 3e). Figure 4a shows the
gate-dependent drain–source current for various deposition times of Au. The Dirac point shifts toward negative gate voltages from 0 to −6.0 V as the deposition time increases from 0 to 25 s. This is because the Fermi level moves away from the conical Dirac point for the case of graphene contacted with Au nanoparticles, resulting in an effective increase of electron density and hence the n-type doping. For device B, a larger heating current was used to deposit continuous Au films onto the graphene channel (Figure 3f). The evolution of the \( I_{ds} - V_{g} \) curve at a series of deposition times is shown in Figure 4b. In contrast to the case of Au nanoparticles on device A, the continuous Au film, acting as an acceptor on device B, produces p-type doping in the graphene. As a result, the Dirac point shifts from 0 to +11 V as the deposition time increases from 0 to 25 s. The evolution of the hole and electron mobilities for devices A and B are plotted in Figure 4c and d, respectively. It is clearly seen that the hole mobility of graphene gradually decreases from 1960 to 1796 cm\(^2\) V\(^{-1}\) s\(^{-1}\) after p-doping whereas the electron mobility reduces from 1118 to 1075 cm\(^2\) V\(^{-1}\) s\(^{-1}\) after n-doping. The slight suppression of carrier mobility results from the additional impurity scattering caused by the Au deposition.\(^{[31]}\)

Based on the opposite doping types of devices A and B, device C was gradually deposited with Au nanoparticles until a continuous Au film was formed, using the same condition as that for the sample in Raman measurements. The amount of charge transfer was tuned by controlling the deposition time, and the shift of the \( I_{ds} - V_{g} \) curve was systematically monitored by the corresponding FET transport measurements after each deposition. The device was found to be doped stepwise from n- to p-type, as shown in Figure 5a; the Dirac point first shifts to −4, −12, −17, −22, and −26 V, and then gradually shifts back to −25, −24, −20, −16, −8 V, passes through 0 V, and then to +2 and +6 V. The maximum of Dirac point shift corresponds to the frequency shift in the Raman spectroscopy at time, \( t = 40 \) s, likewise the significant change of Au morphology can be observed in the TEM image at this time mentioned above. Hole and electron mobilities based on the deposition time for device C are

![Figure 3.](image-url)  
**Figure 3.** a) Optical image of graphene FET device used for electrical transport measurements, with a channel of 5 mm in width and 1 mm in length. b) Optical microscopy image of monolayer graphene taken from the channel region shown in (a). c) \( I_{ds} \) as a function of \( V_{g} \) taken in high vacuum (\( \sim 1.0 \times 10^{-8} \) mbar). d) Schematic diagram of the FET device construction. e,f) Schematic diagrams of the FET devices with Au nanoparticles (e) and Au films (f) on the channels.

![Figure 4.](image-url)  
**Figure 4.** a,b) The \( V_{g} \) dependent \( I_{ds} \) at various Au deposition times for devices A (a) and B (b). c,d) The deposition-time-dependent hole and electron mobilities for devices A (c) and B (d).
Tuning the Doping Type and Level of Graphene with Different Gold Configurations

Figure 5. a) The $V_f$ dependent $I_{ds}$ at various Au deposition times for device C. b) The deposition-time-dependent carrier densities for devices A, B, and C. c,d) The deposition-time-dependent hole (c) and electron mobility (d) for device C.

plotted in Figure 5c and d, respectively. Although the mobilities of device C are much lower than that of devices A and B, the evolution of the hole and electron mobilities are similar with the two devices that, electron mobility decreases after p-doping while hole mobility decreases after n-doping.

According to the Dirac point shifts, the carrier density can be estimated from the equation:

$$n = C_\text{g} V_\text{Dirac}/e,$$

where $V_\text{Dirac}$ is the Dirac shift relative to that of pristine graphene, and $e$ is the electron charge. The carrier densities as a function of deposition time for devices A, B, and C are shown in Figure 5b. The induced electron concentration is estimated at $-1 \times 10^{12}$ to $-2 \times 10^{12}$ cm$^{-2}$. Minus values indicate a concentration of hole carriers rather than of electron carriers. Based on the expression of the change in Fermi energy:

$$\Delta E_f(n) = \hbar |v_F| \sqrt{2 n},$$  \hspace{1cm} (3)

where the Fermi velocity $|v_F|$ is $1.1 \times 10^6$ m s$^{-1}$; the Fermi energy in graphene can be adjusted between $-0.09$ and $-0.12$ eV, with the sign depending on downshift or upshift. These electrical transport properties allow us to tune the Fermi level of graphene from below to above the Dirac point; that is, the conductivity type and carrier density can be selected by controlling the Au deposition.

2.4. First-Principles Calculations

To interpret the doping effect of Au nanoparticles/film on graphene, the interactions between graphene and different configurations of Au adsorbates were simulated by the first-principles calculations. Based on the optimized models in Figure 6, the equilibrium separations between Au and graphene, the binding energies, and the work functions were calculated, as listed in Table 1. Compared with the graphene–Au film, the graphene–Au nanoparticle system has smaller equilibrium separation and larger binding energy, which also implies stronger chemical interactions.\[17\] Using the calculated work functions and equilibrium distances in Table 1, the band alignments of both contact models are plotted and shown in Figure 7a and b, with the vacuum level and the orginal work function (or Fermi energy) of Au $W_{\text{Au}}$ fixed as a reference. In the graphene–Au particles contact system, the difference between $W_{\text{G-Au particle}}$ and $W_{\text{Au}}$ defines a potential change $\Delta V$ of 0.83 eV, which is mainly generated by the interfacial chemical interaction.\[17\] Compared with the orginal work function of graphene $W_{\text{G}}$, the value $W_{\text{G-Au particle}}$ is lower for about 0.42 eV ($W_{\text{G-Au particle}} - W_{\text{G}} = -0.42$ eV), leading to an upshift ($\Delta E_f$) for the graphene Fermi energy. Hence, the graphene is n-doped by Au particle. As graphene contacts with Au films, $\Delta V$ is only 0.21 eV deduced from the smaller difference between $W_{\text{G-Au film}}$ and $W_{\text{Au}}$. A 0.20 eV increase of $W_{\text{G-Au film}}$ than $W_{\text{G}}$ ($W_{\text{G-Au film}} - W_{\text{G}} = 0.20$ eV) determines a downshift of graphene Fermi energy, and demonstrates that the graphene is p-doped by Au film. It could be found from the two illustrations that the chemical interaction induced $\Delta V$.

Figure 6. a) Top and b) side views of the atomic structures of graphene–Au nanoparticle system. c) Top and d) side views of the atomic structures of graphene–Au film. The gray balls represent the carbon atoms in graphene, while the yellow, green, and purple balls represent the first, second, and third layer, respectively, of the Au atoms adsorbed on top of the graphene, with the [111] direction perpendicular to the graphene surface.
plays a negative role on the work-function-difference-induced electron transfer between Au and graphene. As mentioned above, graphene has stronger chemical interactions with the Au particles, which creates a much higher $\Delta V$ in the graphene–Au particle model than in the graphene–Au film, and causes these two systems to have opposite doping types.

The directions of charge transfer is also confirmed by the effective potentials of the whole systems. The effective potentials between graphene and Au comprises three terms:

$$v_{\text{eff}}(r) = -\int dr' \frac{n^+(r')}{|r - r'|} + \int dr' \frac{n^-(r')}{|r - r'|} + v_{\text{xc}}(r),$$

where $r$ is the atomic radius, the first two terms represent the electrostatic potentials caused by the positive background and by the electronic density, and $v_{\text{xc}}(r)$ is the exchange-correlation potential. Figure 7c and d show the average effective potentials along the [0001] direction for the graphene–Au nanoparticle and film configurations, respectively. The macroscopic averages of each layer were performed using macroscopic average techniques, which allows a general description of the effects of interfacial perturbations.$^{[33,34]}$

In each curve, the left valley represents the potential of Au, while the right valley represents the potential of graphene. As shown in Figure 7c, the effective potential is inclined in the graphene. Driving from the potential difference, the electrons transfer from the Au nanoparticles to graphene, which agrees well with the band illustration of Figure 7a. In contrast, graphene exhibits a relatively higher effective potential when contacting Au film, as shown in Figure 7d. The electrons are inclined to transfer from graphene to the Au film, resulting in a built-in electric field directed to the Au from graphene. The Fermi level will down-shift due to the injected holes, which produces p-type doping in the graphene, and is consistent with the band structure in Figure 7b. These theoretical calculations reveal a close relationship between the doping type and the interactions within the graphene–Au systems; qualitatively our experimental results could be interpreted as graphene being n-doped by isolated Au nanoparticles and p-doped by a continuous film.

3. Conclusion

Au nanoparticles and films were deposited onto graphene surfaces at room temperature. Raman spectra indicated that graphene was n- and p-doped by low and high coverage of Au, respectively. The morphology of Au on graphene imaged by TEM suggested that isolated Au nanoparticles yielded n-type doping while continuous Au films resulted in p-type doping. Accordingly, graphene FETs were fabricated, in which both the doping type and carrier density could be tuned by finely controlling the Au deposition. The interactions between the graphene and Au nanoparticle/film were simulated by first-principles calculations. The results revealed that the different doping properties observed in the experiments were derived from the effective potential difference related to the interfacial interaction within graphene–Au nanoparticle and film systems. This work is of significant importance for graphene band modulation and device design.

4. Experimental Section

The first-principles calculations were performed in the framework of density-functional theory (DFT)$^{[15,36]}$ within the generalized gradient approximation (GGA), using the Vienna Ab-initio Simulation Package (VASP)$^{[37]}$ Calculation models were periodically repeated by an atomic slab consisting of one graphene monolayer.

| Table 1. Calculated equilibrium separations, binding energies, and work functions of graphene (G)–Au nanoparticle/film systems. |
|---|---|---|---|
| | G | Au | G–Au nanoparticle | G–Au film |
| Equilibrium separation $d$ [Å] | 3.10 | 3.58 |
| Binding energy $\Delta E$ [eV] | 4.690 | 5.102 | 0.036 | 0.015 |
| Work function $W$ [eV] | 4.275 | 4.893 | 4.275 | 4.893 |

Figure 7. a,b) The band alignment illustrations of graphene–Au nanoparticle (a) and graphene–Au film (b) systems, using the calculated work functions and equilibrium distances listed in Table 1. The vacuum level and the original work function of Au ($W_{\text{Au}}$) are fixed as a reference. c,d) Average effective potentials in graphene–Au nanoparticle (c) and graphene–Au film (d) systems along graphene [0001] direction.
(128 carbon atoms, lattice constant of 2.46 Å), with a Au nanoparticle or one continuous film located on the top, as shown schematically in Figure 6a and c, respectively. The triangular lattice of Au(111) surface matches the honeycomb lattice of graphene in the unit cells, which was proven to be the most stable configuration of graphene with Au contact.[17] An 18 Å thick vacuum layer was applied for separating the slabs to form a surface. The lateral distance between neighboring particles was about 19.8 Å, which was large enough to avoid the overlap of their electronic states in the periodically expanded model. Au 5ds6s was treated explicitly as valence.[18,19] Ions and electrons interactions were approximated by ultrasoft pseudopotentials, and the plane-wave cut-off energy was set to 330 eV. A (8 × 8 × 1) Monkhorst–Pack mesh was used to sample the Brillouin zone. A conjugate gradient algorithm was used to optimize the structures by relaxing all the atomic geometries,[20,21] with forces on all the atoms converged to within 0.01 eV/Å. Although the part of van der Waals forces between Au atoms and graphene are not involved in DFT calculation, there should be some direct hybridization in our models, especially between Au atoms and graphene, since the lowest layer of Au atoms mostly locate on the T site of graphene.[17,21]

Large-area monolayer graphene was grown by chemical vapor deposition on 25-μm-thick Cu foils (Alfa Aesar, item No. 13382),[22] and transferred onto 285-nm-SiO₂/Si substrates (p⁺ doping, ρ = 0.002–0.005 Ω cm) using a process similar to that described previously.[18,19] We also transferred the as-grown graphene onto 300- mesh TEM copper grids (with lacey carbon supporting films, Ted Pella, Inc.), using the same transfer process. Au deposition was performed in a home-built vacuum system with a base pressure of 10⁻⁶ mbar. A high-purity Au (99.9999%) source was affixed to a tungsten filament in the upper part of the vacuum chamber, and Au could be evaporated by direct current resistive heating to a temperature around 1000 °C. By adjusting the heating current and the distance between graphene and the Au source, the deposition rate, and hence the coverage and size of Au nanoparticles could be controlled. The evolution of Raman spectrum for different deposition states was detected by a confocal microprobe Raman system (WiTec Alpha300, 532 nm excitation laser, −6 mW). The corresponding bright-field TEM images were obtained on a JEOL2010F TEM operating at an accelerating voltage of 200 kV.

For fabricating the graphene FET devices, −500 nm thick Au films were deposited on the graphene surface as source and drain electrodes, and consequently defined a transport channel of 5 mm in width and 1 mm in length between the two electrodes. The FET transport measurements were performed in the vacuum chamber where the graphene FET device was attached to a ceramic heater with a temperature tunable up to 150 °C. Before the deposition and tests, the devices were degassed for 2 h by in situ annealing at 100 °C to eliminate the pre-existing adsorbates (e.g., H₂O, O₂, and/or other molecules), and then cooled down to room temperature. Using a similar deposition process, three FET devices A, B, and C were prepared with controlled heating currents and deposition positions.

Acknowledgements

We appreciate support from the National "973" Program of China (Grant Nos. 2012CB619301 and 2011CB925600), the National Science Foundation of China (Grant Nos. 90921002 and 60827004), and the National Science Foundation (Grant No. 1006350), the Office of Naval Research, SWAN NRI.


Received: March 8, 2012
Revised: June 11, 2012
Published online: July 24, 2012