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Charge transfer in the fullerene C_{60}-few layer graphene system and the existence of negative photoconductivity

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The electrical conductance of few layer graphene during thermal evaporation of fullerene C_{60} as well as the conductance under illumination of this bilayer junction is reported. We obtained few layer graphene films by chemical vapor deposition technique, and then C_{60} was thermally evaporated on these films. We found an increase in conductance of few layer graphene during the thermal evaporation of C_{60} and a kind of negative photoconductivity when the bilayer junction was under illumination. We observed that at low light intensities few layer graphene is p-type doped, and we propose that its behavior changes to n-type for high light intensities. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4902055]

Graphene, a zero band gap semiconductor material, has attracted a lot of interest in different areas of science, this is because of its interesting properties such as high room temperature electron mobility, very high thermal conductivity, and high optical transmittance.[1] But those properties are in conflict with many applications,[2] mainly in opto-electronics. Because of that many efforts have been focused in opening a band gap or shifting the Fermi level of graphene. One of these routes to modify graphene is through chemical functionalization,[3] this process changes its carrier concentration and graphene remains highly conductive.[3] Other possible way to modify electrical properties of graphene is by electrochemical top gating.[4] Graphene is very sensitive to the environment due to its monoatomic thickness, and hence its physical properties can be modified by a substrate.[5] Finally, modulation of the optical transmittance of multilayer graphene by means of temperature has also been demonstrated.[6]

On the other hand, fullerene C_{60} is another carbon material that exhibits interesting optical properties. C_{60} is a semiconductor and photoconductive material[7,8] and also is a good electron acceptor.[9,10] Due to the last property, C_{60} enhances p-type graphene whereas it weakens n-type graphene when it is deposited on graphene.[11] Other authors[12] found that C_{60} molecules, which were thermally evaporated on graphene surface, produced a negligible charge transfer. In order to get insight on the interaction of C_{60} with graphene and few layer graphene, in this work, we study their electrical properties where C_{60} is thermally evaporated on few layer graphene films to form a bilayer system. Additionally, Raman spectroscopy is used to study the charge transfer between these two materials.

We obtained carbon films grown by Chemical Vapor Deposition (CVD) onto copper substrates. Copper foils of 0.5 cm × 0.5 cm and 25 μm thickness were inserted into a 2.5 in. quartz tube; the furnace was heated to 1000 °C with flowing 70 sccm H_2 at ambient pressure. These conditions were maintained during one and a half hour to anneal copper, after this time a gas mixture of 138 sccm H_2 and 11 sccm CH_4 was flowed for 30 min. Finally, flowing CH_4 was cut off and the furnace was cooled to room temperature in the hydrogen atmosphere. With these conditions, we obtained carbon films which are a mixture of single and few layer graphene (from two to five layers), which we denominate as FLG. After cooper foil was dissolved, FLG film was transferred on glass substrates for electrical measurements. Two parallel silver strips one millimeter apart were evaporated on top of FLG to form ohmic contacts. Using a Knudsen cell into an evacuated chamber at a pressure $\sim 3 \times 10^{-6}$ Torr, C_{60} powder (purity > 99.5%, MER Corporation) was evaporated on top of FLG film while sheet resistance was monitored *in situ*. After C_{60} deposition, the samples were transferred to a different chamber for electrical characterization as a function of temperature in darkness as well as under illumination in vacuum conditions ($\sim 10^{-4}$ Torr). White light was provided by a tungsten lamp and color filters were used for illumination. To avoid any photovoltaic effect in the junction, opaque electrical contacts made with silver paste were used in these experiments.

FLG films were transferred on top of SiO_2(306 nm)/Si substrate for Micro Raman spectroscopy characterization with and without C_{60}. Raman characterization was performed using a Nicolet Almega XR Spectrometer and 532 nm laser excitation, and 1 mW of laser power in order to avoid heating effects. Monolayer and bilayer graphene zones were selected for this characterization.

In Figure 1(a) sheet resistance as a function of C_{60} thickness is shown. Sheet resistance was monitored in darkness, while C_{60} was deposited continuously. It initially decreases and remains almost constant after about 75 Å, which may indicate a characteristic length for diffusion of charge carriers in C_{60}. The decrease in sheet resistance probes that C_{60} affect the carrier concentration of FLG. Figure 1(b) shows the conductance of the system (C_{60}/FLG) as a function of temperature, in darkness, and under illumination. When the

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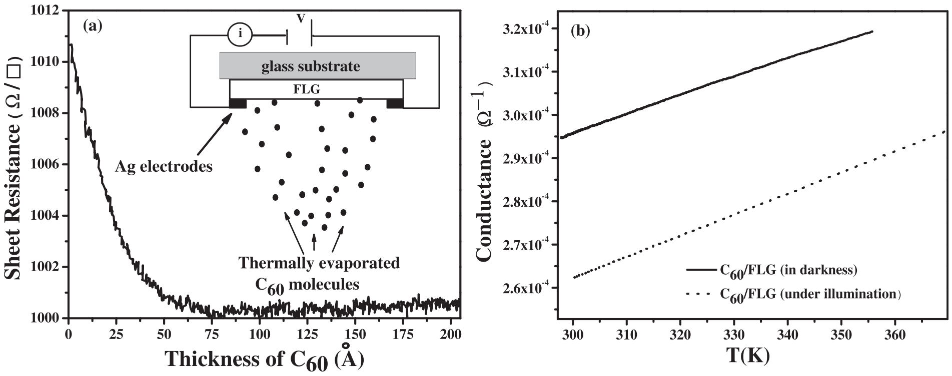

FIG. 1. (a) Sheet resistance of FLG film as a function of C_{60} thickness measured at a fixed bias voltage of 10 mV. (b) Conductance of C_{60}/FLG system as a function of temperature, in darkness and under illumination using an Argon laser at 514 nm of wavelength and 10 mW.

system is under illumination, conductance decreases in contrast to the commonly observed photoconductive behavior of many semiconductors.[13] In both cases, in darkness and under illumination, conductance increases with the increase of temperature. It should be noted that in the coplanar configuration of electrodes used in the present experiments, the measured electrical characteristic mainly corresponds to FLG because the electrical conductivity of the C_{60} layer is orders of magnitude less than that of FLG;[8] that is, the electrical current only flows through the FLG film.

In order to explain the observed behavior, we propose the following scenario. Due to the fact that C_{60} has a high electronegativity, it is a good electron acceptor.[14] Hence, under direct contact of C_{60} and FLG, electrons diffuse to C_{60} creating holes in graphene. Being graphene initially p-type, the increase of hole population makes its conductivity to increase, as observed in Figure 1(a). On the other side, when the system was illuminated electron-hole pairs were created in the C_{60} layer, and we believe that some of these photoelectrons diffuse to the FLG film destroying holes; this process makes the population of holes in FLG to decrease.

The final result is that under illumination the conductivity of graphene decreases, and this effect may explain the experimental result observed in Figure 1(b); which can be classified as a kind of negative photoconductivity.[13] Steady state conductance of the system as a function of light intensity is presented in Figure 2. The interesting observation is that for low intensity the photoconductivity is negative and it changes to a positive photoconductivity regime at higher intensities. To discard the existence of any photocurrent generated in the junctions, a control experiment with zero voltage bias in the device was performed. We should mention that the same phenomena are observed using IR-filtered white light.

To get additional information we made Raman spectroscopy, which has been used to study charge transfer in doping processes in graphene.[4,15,16] In Figure 3, Raman results are shown. In these measurements, we used different thickness of C_{60}: 21, 66, 77, and 100 Å. In Figure 3(a), Raman spectra of C_{60} (21 Å), monolayer and bilayer graphene before and after deposition of C_{60} are presented. The Raman signal becoming from C_{60} is very weak, but it is clearly enhanced when it is on graphene, this effect is probably due to the so called Graphene Enhanced Raman Scattering (GERS).[17] One of the two high-energy Hg modes of C_{60}, the Hg(7) mode labeled by an asterisk in C_{60}/graphene spectrum, is clearly distinguished only when C_{60} was on graphene. Due to the enhancement of the pentagonal pinch mode Hg(8) at about 1566 cm^{-1} the position of G peak of graphene (Pos(G)) could not be distinguished in many cases. The position of 2D peak (Pos(2D)) of monolayer and bilayer graphene in both cases upshifts after deposition of C_{60}. Change in Pos(G) is small (inset of Figure 3(b)), but we found a systematic shifting of around 2 cm^{-1} which is comparable with that observed in Ref. 18. The longest upshifting for the 2D band was observed for the thinnest layer of C_{60}, see Figure 3(b), which is about 20 cm^{-1}. It should be noted that Raman characterization (not presented) of exfoliated graphene and bilayer graphene show similar behavior to that for CVD material reported in Figure 3. The intensity ratio of 2D and G peaks of graphene (I(2D)/I(G)) is also sensitive to carrier concentration.[4] After deposition of C_{60} on n-type graphene the I(2D)/I(G) tends to increase while in the case of a p-type graphene this ratio decreases.[11] We observed small decrease in these ratio from 2.9 to 2.6 before and after deposition of C_{60}. Then, the decrease in I(2D)/I(G) and the upshifting of Pos(2D) suggest that we are obtaining p-type graphene.

Finally, let us visualize the present problem as if graphene were the material in contact with C_{60} in terms of the shifting of the Fermi level (E_F). It was established that the addition of charge carriers leads to a shift in E_F.[4] E_F of ideal graphene is located in K points, where valence and conduction bands meet in the Dirac point (Figure 4(a)). On the other

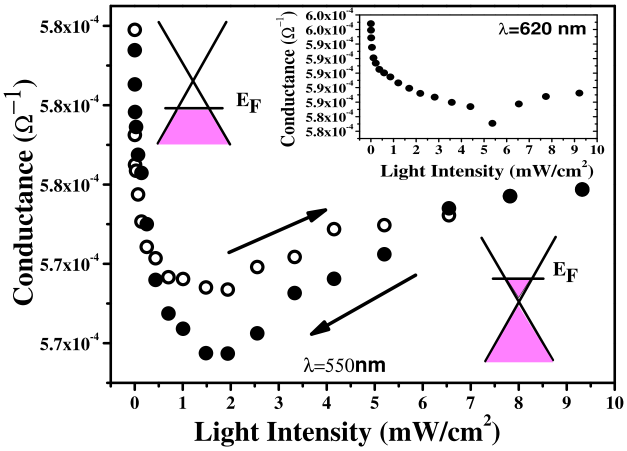

FIG. 2. Conductance of C_{60}/FLG system as a function of light intensity, and schematic energy band diagram showing the position of Fermi level for low and high light intensities. In this case, a green filter centered at 550 nm was used. The arrows indicate the direction in which the light intensity was varied. For the results presented in the inset, a filter centered at 620 nm was used.

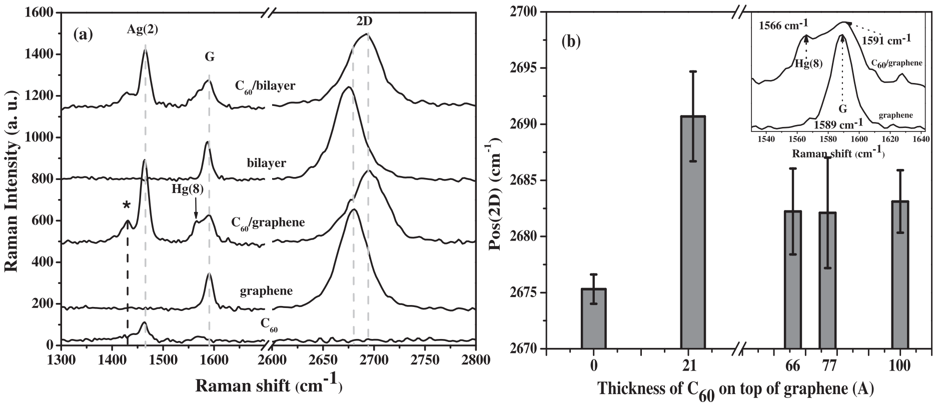

FIG. 3. (a) Raman spectra of graphene, bilayer graphene, C_{60}, C_{60}/graphene, and C_{60}/bilayer. (b) Position of 2D peak of graphene with different thickness of fullerene C_{60}. The inset shows the position of G peak of graphene with and without C_{60}.

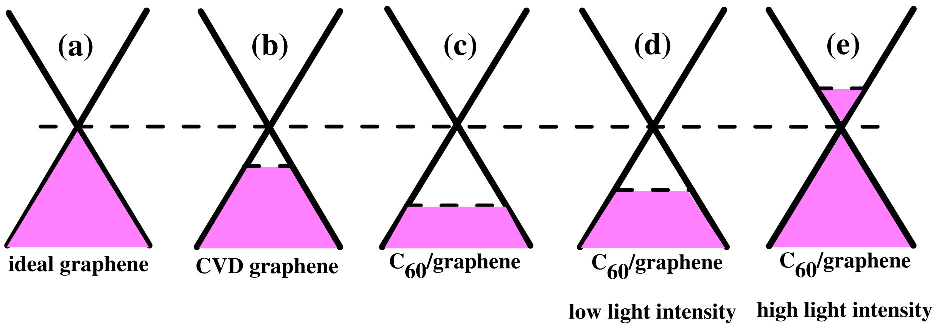

FIG. 4. Schematic of energy bands and the Fermi level shifting in graphene.

hand, it is known that CVD grown graphene is normally p-doped, due to residuals from the etching, washing, and transfer processes.[19] Thus, E_F is below the Dirac point in CVD grown graphene (Figure 4(b)). When C_{60} is put in contact with graphene, the conductance of the last increases, this effect can be explained if E_F shifts below the pristine CVD case because at lower energies the density of states is higher (Figure 4(c)). Under illumination, the photo-generated electrons in C_{60} diffuse to graphene producing an upshifting of E_F to energies where density of states decreases in the valence band (Figure 4(d)); which makes the electrical conductance to decrease. If the intensity of illumination is enough, the injected electrons to graphene make E_F to upshift to the conduction band (Figure 4(e)), and hence the conductance passes through a minimum and finally increases, as observed in Figure 2. This means that under illumination graphene becomes p-type doped for low intensities and n-type for higher intensities, as is shown schematically in the energy band diagram in Figure 2.

In summary, we have shown that the electrical conductance of FLG film increases during the thermal evaporation of C_{60} and it decreases when the resulting system C_{60}/FLG is under illumination. When the light intensity was varied, we observed that for low light intensities FLG became p-type doped and changed to n-type for higher light intensities. p-type doping in graphene and bilayer graphene was confirmed using Raman spectroscopy. We believe that the present findings may be useful for the design of devices using the C_{60}/graphene system for optoelectronic applications.

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