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Stability of Graphene doping with MoO_3 and I_2

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We dope graphene by evaporation of MoO_3 or by solution-deposition of I_2 and assess the doping stability for its use as transparent electrodes. Electrical measurements show that both dopants increase the graphene sheet conductivity and find that MoO_3-doped graphene is significantly more stable during thermal cycling. Raman spectroscopy finds that neither dopant creates defects in the graphene lattice. In-situ photoemission determines the minimum necessary thickness of MoO_3 for full graphene doping.

Graphene is a 2D crystal of carbon, in which the atoms are sp^2 hybridized and arranged in a honeycomb structure. This gives rise to its unique band structure and hence to its exceptional physical, electrical and optical properties [1-3]. There is a great interest in utilising these properties in electronics, opto-electronics, lighting, displays and photovoltaics. In electronics, graphene has been proposed for devices such as high frequency RF transistors or resistance standards. In opto-electronics, graphene has great potential to replace indium tin oxide (ITO) as a flexible, transparent electrode [4]. To exploit such potential, research has focused on scalable techniques for synthesis [5-10], transfer [11,12] and doping [13] of graphene. However, despite its very high carrier mobility, due to its unique band structure, the carrier density in undoped graphene is very low, so that doped graphene is necessary to realize its potential. There are various ways to dope graphene, by substitutional doping [14,15], by plasma doping [16], functionalization [17], or by transfer doping [18-27]. Substitutional doping [14] and plasma doping [16] are liable to introduce defects, which lower carrier mobility. Transfer doping is therefore a valuable option, as used in organic semiconductors [28,29]. Since graphene-based transparent electrodes are aimed to be used in touch screen panel displays or solar cell technology, it is critical to assure stability of the dopants at their operating conditions, in particular at relatively high temperatures (50-120˚C). In this report, we study graphene doping by MoO_3 and I_2, compare their stability, and assess their effect on the graphene lattice.

In conventional adsorbate doping, a molecule is adsorbed via a charge transfer between graphene and the adsorbate. In general, this process can easily be controlled and has the advantage of preserving the graphene lattice and its physical properties. Adsorption takes place through weak chemical interactions, thus resulting in relatively minor perturbations in the band structure of graphene. The drawback is that such weak interactions mean that the adsorption is unstable, especially at high temperatures. The stability can be improved by using transition metal oxides such as MoO_3 with high work functions, ~6.8eV. Synchrotron photoemission measurements have shown that MoO_3 gives effective *p*-doping of graphene [24]. Nevertheless, air exposure produces a deleterious effect on MoO_3 films whether evaporated on organic semiconductors [29] or on few-layer graphene [23]. Air exposure lowers the work function of the adlayer, and thus lessens the doping effect. We note that the stability of air-exposed MoO_3-doped graphene has yet to be assessed thoroughly, as well as being compared to other dopants. Here, we evaluate the stability MoO_3 as a dopant for graphene, and compare it to that of I_2 a more conventional adsorptive dopant [20]). We study the variation of graphene conductivity on annealing in vacuum at various temperatures. Our results show that MoO_3-doped graphene is more stable than both I_2-doped and as-transferred graphene. Raman spectroscopy proves that neither doping material induces additional defects into the graphene lattice. By in-situ photoemission spectroscopy, we

determine the minimum necessary thickness of MoO_3 for full graphene doping. As MoO_3 is compatible with microelectronic processing, it is liable of being employed at a large scale production of devices. Altogether, this report represents a step towards ITO replacement by flexible and more common materials.

We use monolayer graphene grown on Cu foils and transferred onto SiO_2-coated Si by a wet transfer process (using ammonium persulphate as etchant) [11]. For doping, we first pre-anneal as-transferred graphene at 200˚C and ~10^{-6}mbar for 30min, and then (following transfer in air of ~1min), we either evaporate MoO_3 from a powder source at ~10^{-6}mbar or dip graphene into a saturated aqueous solution of I_2. Effective doping is confirmed by an increase in the graphene conductivity. To quantify this, we normalize the sheet conductivity of each sample to that of pre-annealed graphene sample. We adopt this base line since the pre-annealing of the as-transferred graphene removes many of the adventitious dopants [30], associated with the transfer process and air exposure. We note, however, that as our electrical measurements are performed in air, the as-annealed graphene (base line) is not completely undoped during conductivity measurements, which may lead to an underestimation of the doping. For electrical characterization, we use an array of 4-terminal devices. First, we deposit Au electrodes by thermal evaporation (Au:Cr 45:5nm). We then transfer graphene on top (covering the Au contacts). Subsequently, devices are patterned using electron beam lithography with UVIII resist and reactive ion etching with oxygen plasma. The graphene channel width is 2μm and the distances between the electrodes are 5/10/5μm, in a 4-probe geometry. Current and voltage are given and read by source–measurement units in ambient conditions. The maximum voltage applied is 0.05V and the currents are in the μA range. The variation of sheet conductivity is the average of >10 working devices.

Fig. 1 compares the conductivity of graphene doped by MoO_3 or by I_2 solution to that of pre-annealed graphene. We observe that the conductivity of the as-transferred graphene drops by ~40% of its original value (base line) after 30min pre-annealing at 200˚C in vacuum (~10^{-6}mbar), Fig. 1(a). The evaporation of ~4nm of MoO_3 results in the conductivity of the pre-annealed graphene approximately doubling, whilst for I_2 immersion the conductivity of the pre-annealed graphene nearly trebles. In terms of absolute sheet resistivity, the average pre-annealed value of ~1210Ω/sq is reduced by MoO_3 to ~600Ω/sq and by I_2 to ~460Ω/sq. Following 30min post-annealing at 300˚C in vacuum (~10^{-6}mbar), MoO_3-doped graphene retains 87±4% of the increased conductivity value, while I_2-doped graphene retains only 19±1% of the conductivity obtained immediately after doping. This significant difference in the sheet conductivity retained following post-annealing highlights the superior stability of MoO_3 as dopant. For a systematic stability evaluation, we post-anneal separate samples with devices (one for each

dopant) at nominal temperatures of 80, 130, 200, and 300˚C for 30min in ~10^{-6}mbar, Fig. 1(b). The stability is now benchmarked against as-doped graphene. We find that post-annealing lowers the conductivity of graphene in all cases, but this reduction is minimal for MoO_3 whilst it is dramatic for I_2, even at rather low temperatures. MoO_3-doped graphene shows a decrease in conductivity of only ~0.3% at 130˚C and ~7% up to 200˚C, while in the I_2 case, it is ~56% at 130˚C and ~72% at 200˚C. These results reveal that I_2-doped graphene is not compatible with current operating temperatures of screen panel displays or solar cell technology. Additionally, we note that MoO_3-doped graphene is more stable than graphene doped by adventitious dopants resulting from air exposure. This implies that MoO_3 makes graphene a more stable conductor, limiting ambient effects on device conductivity. In the case of I_2-doped graphene annealed at 300˚C, not only is the doping effect lost, but the conductivity in fact falls below that of the pre-annealed graphene. This suggests that I_2 not only desorbs (i.e. reducing the doping), but that the graphene itself is further degraded by annealing at this higher temperature.

To assess this potential degradation, we perform Raman spectroscopy of the MoO_3 and I_2 doped graphene, before and after post-annealing at 300˚C, Fig. 2(a). We acquire the spectra using a 514nm laser at ~500µW with a 50× objective (spot diameter of ~1.5µm). Prior to the post-annealing, the MoO_3-doped graphene spectrum has I_{2D}/I_G of ~2.4, a full width at half maximum of ~30cm^{-1} and a negligible D peak, features consistent with high-quality monolayer graphene [22]. The spectrum of I_2-doped graphene also has a negligible D peak, but presents a I_{2D}/I_G of ~1 and the G and 2D peak positions are shifted to higher wavenumbers, which is compatible with more heavily doped, high-quality monolayer graphene [31]. As the D peak is related to the number of defects in the graphene lattice [32], its continued absence indicates the non-destructive nature of both dopants at room temperature. Following post-annealing at 300˚C, a higher background in the region around the D and G peaks is observed for both the I_2 and MoO_3 doped films as well as when a similar treatment is performed on pre-annealed graphene that has not been intentionally doped, Fig. 2(b). The increase of background in this region relates to amorphous carbon formation from decomposition of ambient adsorbants and/or defects induced in the graphene lattice. That this effect is not noticeably enhanced for the doped samples, highlights the non-destructive nature of both dopants at temperatures up to ~300˚C. We note that the Raman spectrum of as-transferred graphene annealed at only 200˚C (i.e. pre-annealed) does not show a similar change, indicating that degradation of the graphene is minimal for annealing up to this temperature. We also evaluate how the conductivity of pristine graphene annealed at 200˚C evolves following subsequent air exposure. We observe that the conductivity recovers almost completely, i.e. >97% of its improved value, within ~24 hours of air exposure. This again indicates that the drop in conductivity during pre-annealing to ~200˚C is related to desorption of adventitious dopants rather than to structural damage of the graphene lattice.

Finally, we comment that for the spectrum of I_2-doped graphene that has not been post-annealed in Fig. 2(a), we have subtracted the photo-luminescence given by I_2. In Fig. 2(c) we show the original spectra of I_2 doped graphene before and after post-annealing. Here we observe the photo-luminescence background disappear after post-annealing and we thus infer the loss of the majority of the iodine upon post-annealing.

To assess at which thickness of MoO_3 the doping of graphene on SiO_2 saturates, we use in-situ X-ray and UV photoemission spectroscopy (XPS and UPS) during MoO_3 evaporation. We perform XPS using an Mg X-ray source ($h\nu$=1253.6eV) and UPS with a Helium lamp (He I, $h\nu$=21.2eV) in normal emission geometry. We detect electrons with an overall energy resolution of ~0.8eV for XPS and ~0.1eV for UPS. For these measurements, we evaporate MoO_3 in situ, at a pressure of ~10^{-9}mbar. For data analysis, the photoelectron binding energy is referenced to the Fermi edge of a polycrystalline Cu foil in electric contact with graphene and the C 1*s* peaks are fitted with Doniach-Sunijc profiles [33] convoluted with Gaussians. The value of the work function as a function of doping is determined by measuring via UPS the Fermi level and the secondary photoelectrons cut-off [34], see Fig. 3(a). The measurements are taken by applying a negative bias of ~9V, which allows the acceleration of the lowest energy secondary electrons into the spectrometer. The work function increases with increasing MoO_3 evaporation from a starting value of ~4.3eV for graphene on SiO_2 until it saturates at ~6.8eV after the evaporation of ~4nm of MoO_3, compatible with the work function of bulk MoO_3. After a week of air exposure, the work function recovers somewhat to a value of ~4.8eV. To understand the effect of the high work function oxide on graphene, we measure the C 1*s* XPS spectra of graphene following pre-annealing and evaporation of different thicknesses of MoO_3, Fig. 3(b). We analyze the C 1*s* spectra by performing a non-linear mean square fit of the data, reproducing the spectra by using at least 4 components, corresponding to C-C sp^2, C-C sp^3, C-O, C=O, respectively at 284.4eV, +1.4eV, +2.4eV, and +4.3eV [12], Fig. 3(c). The sp^2 component is that expected for a graphene layer, whilst the presence of the much weaker sp^3 component can be attributed to the presence of some graphene defects and/or deleterious carbon over the millimeter-scale graphene regions probed, likely resulting from the transfer and pre-annealing steps. C-O and C=O components are not detected in the fit, indicating that the transfer and pre-annealing processes are reasonably successful in removing Poly(methyl methacrylate) (PMMA) residue. As soon as MoO_3 is deposited, the C 1*s* peak maximum shifts towards lower binding energies and its line shape changes. This can be attributed to a rigid shift of the spectrum, due to *p*-doping, and the emergence of a new component associated with the C-Mo interaction. After evaporating 0.15nm of MoO_3, the sp^2 and sp^3 components show a rigid shift of ~0.5eV towards lower binding energies and a new component appears at ~283.3eV, Fig. 3(d). The rigid shift can be attributed to *p*-doping of

graphene, since all photoemission spectra are aligned to the Fermi level. Note that the shift of the C 1*s* peak (band bending) is directly related to the Fermi level variation. The sp^2 peak shifts ~0.67eV towards lower binding energies, from ~284.6eV of the pre-annealed graphene to ~284.0eV with ~4nm of evaporated MoO_3 on top.

In Fig. 3(e) the work function shift is schematically described as the sum of band bending and surface dipole since several constructive and opposite effects can occur at the interface, which can to a first approximation be considered as an overall interfacial dipole [35]. The band bending of the air exposed sample is not included as it is not possible to extract reliable values, given that adventitious C contamination of the MoO_3 surface during ambient exposure leads to an increase in the C 1*s* signal which obscures that arising from the graphene layer beneath. The work function is found to saturate at ~1nm of deposited MoO_3, while the band bending saturates at only ~0.3nm. This indicates that the charge transfer mostly occurs after deposition of a monolayer, i.e. ~0.26nm for MoO_3 [36]. Following air exposure, the work function of the evaporated MoO_3 drops, as previously reported on few-layer graphene [23]. As a consequence the total charge transfer between graphene and the adlayer diminishes, lowering the conductivity. This explains the contrast between the high Fermi energy shift measured in-situ and the ex-situ electrical measurements shown in Fig. 1, in agreement with previous reports [37]. We therefore note that as higher doping levels can be obtained in vacuum, there remains potential to develop techniques that further improve the air-exposed MoO_3 doping. To calculate the Fermi level position with respect to the Dirac cone, we measured the mobility of graphene. We fabricate Hall devices with Van der Pauw geometry, obtaining an average hole mobility of approximately 3300cm^2/Vs and 650cm^2/Vs for undoped and MoO_3-doped graphene respectively. These values correspond to a charge carrier densities of $9.3\times10^{11}cm^{-2}$ and $7.3\times10^{12}cm^{-2}$, and using the relation $E_F(n)=\hbar|v_F|\sqrt{(\pi n)}$ [31], to a Fermi level of -0.12eV and -0.35eV. The doping induces a shift of ~0.23eV, which provides an indication of the bending value expected for air exposed MoO_3-doped graphene, Fig. 3(e).

We find MoO_3 doping to be more stable than that of I_2, especially at relatively low temperatures (<130˚C), which suggests the usefulness of MoO_3 for real device applications. We note that the stability is directly correlated to the sublimation temperatures of both materials. At sub-atmospheric pressures, it is ~600˚C for MoO_3 and below 113˚C for I_2 [38]. This is consistent with the fact that the Raman spectrum of I_2-doped graphene after post-annealing does not show the photo-luminescence background of I_2, Fig. 2(c). In order to interpret our findings, we further study the adsorption of I_2 and MoO_3 on graphene by density functional theory. All calculations are done with plane wave pseudo-potential code Cambridge Serial Total Energy Package (CASTEP), using a Perdew-Burke-Ernzerhof (PBE) style

generalized gradient approximation. Ultra-soft pseudopotential is used with a cut-off energy of 280eV. The van der Waals interactions are included in the Grimme's empirical method. First, one molecule of I_2 is put on a $9.8\times8.5Å^2$ graphene sheet with a periodic boundary condition. The adsorption energy depends on the configuration of the molecule on graphene. We find the adsorption energy is about -0.05eV. This means the molecule could be trapped at some metastable positions with positive adsorption energy. Therefore, the adsorption of I_2 on graphene is purely physical and thus rather weak. Considering thermal effects, it is expected to weaken as the temperature is increased. For comparison, we then study the graphene-MoO_3 interface with different oxide terminations. As the MoO_3 interface could have different ratios of O and Mo (depending on the crystal orientation), we prepare several different poly-crystalline and amorphous MoO_3 models on top of graphene. The binding energy is found to vary between -0.58eV and -0.72eV in the same graphene supercell. Being one order of magnitude larger than that for I_2, the binding energy values for the oxide explain why MoO_3 is more stable on graphene. We thus highlight the promise of using MoO_3 or other dopants with reasonably high sublimation temperatures, to stably dope graphene at operating device conditions, as demonstrated here by our electrical, Raman, and photoemission measurements. Fig. 4 illustrates the doping of graphene using MoO_3 and I_2 and their differing stabilities following post-annealing.

In conclusion MoO_3 and I_2 improve the graphene sheet conductivity without deteriorating its lattice structure. MoO_3-doped graphene is, however, much more stable than graphene doped with I_2 when annealed in vacuum. The difference in stability is remarkable: the relative change in conductivity of MoO_3-doped graphene after a 300˚C annealing is lower than I_2-doped graphene after a 80˚C annealing. Finally, in-situ photoemission spectroscopy shows that MoO_3 dopes graphene strongly on SiO_2 before exposure to air, and is thus of potential use for device applications. Doping with transition metal oxides is a step forward towards reliable and stable graphene-based transparent conductors.

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Figure 1: (a) Relative variations in sheet conductivity after pre-annealing at 200 ˚C (cleaning), doping and post-annealing at 300 ˚C (stability), with pre-annealed graphene as reference. (b) Stability of sheet conductivity for post-annealing at progressively higher temperatures, with the data normalized to the as-doped graphene.

Figure 2: (a) Raman spectra of graphene doped with MoO_3 and I_2, before and after post-annealing at 300 ˚C. The photo-luminescence background caused by I_2 has been removed in the spectrum of the graphene that has not been post-annealed. (b) Raman spectra of pristine graphene before and after annealing at 200 ˚C and 300 ˚C. (c) Raman spectra of I_2-doped graphene before and after post-annealing, with original background.

Figure 3: (a) Variation of the secondary cut-off in UPS spectra, related to the shift in work function.(b) XPS spectra of Cn 1*s* aligned to the Fermi energy. (c) Fitting of the C 1*s* peak after pre-annealing. (d) Fitting of the C 1*s* peak after the deposition of 0.15 nm of MoO_3. (e) Work function shift and band bending versus evaporated thickness of MoO_3.

Figure 4: Model of graphene doping using MoO_3 or I_2 and subsequent annealing. The variation in Fermi energy is represented for each case.