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Hole doping of graphene supported on Ir(111) by AlBr₃

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In this Letter we report an easy and tenable way to tune the type of charge carriers in graphene, using a buried layer of AlBr₃ and its derivatives on the graphene/Ir(111) interface. Upon the deposition of AlBr₃ on graphene/Ir(111) and subsequent temperature-assisted intercalation of graphene/Ir(111) with atomic Br and AlBr₃, pronounced hole doping of graphene is observed. The evolution of the graphene/Br-AlBr₃/Ir(111) system at different stages of intercalation has been investigated by means of microbeam low-energy electron microscopy/electron diffraction, core-level photoelectron spectroscopy and angle-resolved photoelectron spectroscopy.

The precise control over the electronic structure of graphene is essential for practical applications of graphene-based devices. One central problem is that the remarkable electronic properties of graphene are highly affected by ambient conditions, hence graphene typically cannot be utilized in applications “as is”, but has to be modified in a controllable way. In fact, a great potential of graphene for gas sensing technologies exists since adsorption of gas molecules affects the type and the number of charge carriers in graphene and hence noticeable changes in the conducting properties occur.¹ On the other hand, certain graphene based device applications, such as graphene-based field-effect transistors (FETs)² or integrated circuits for nanoelectronics,^{3,4} may require well-defined conducting properties of graphene in order to show stable performance.^{5–7}

Fortunately, the conspicuous response of graphene to contact with foreign active species can be turned into a beneficial control of the electronic structure of graphene. Adsorption of active molecular or atomic species on graphene is known to result in charge transfer to or from graphene, so-called *surface transfer doping* (STD).⁸ Adsorption of such species as ammonia, ethanol,¹ alkali metals^{9,10}, and aromatic molecules with electron-donating groups¹¹ results in electron doping (*n*-doping), while NO₂,^{1,12,13} halogen-containing molecules,^{14–17} Bi, Sb, and Au atoms,¹⁸ MoO₃¹⁹ and F₄-TCNQ²⁰ act as acceptors causing hole doping (*p*-doping) of graphene. However, since the adsorption of these doping agents involves the graphene surface, the stability and performance of such systems under ambient conditions can be limited. Hence, systems employing graphene as a protective layer for the doping agents are of great interest.

This is only possible if these doping agents are placed at the graphene-substrate interface, i.e. *intercalated* under graphene.^{21,22} The *n*-doping of “monolayer graphite” by intercalation of alkali metals was first demonstrated in 1994 by Nagashima *et al.*,²³ and *n*-STD induced by alkali-metals intercalation in graphene and graphite has been studied in detail since then.^{9,10,24–27} Conversely, the *p*-doping of graphene with intercalated materials remained less explored until recently, when it was shown that it is possible to achieve a pronounced hole doping upon intercalation of graphene with fluorine²⁸ and chlorine.²⁹ Here we generalize the use of metal halides for *p*-doping of graphene, by studying aluminum bromide as an electron acceptor and intercalation agent. We show that it is possible to intercalate graphene/Ir(111) with a mixture of AlBr₃ and Br and to achieve a pronounced doping of graphene, comparable to the case of fluorination or chlorination.

The LEEM, CL PES and ARPES experiments were performed at the MAX-IV laboratory (Lund, Sweden) using beamlines I311, D1011 and I4, respectively. The kinetic energy resolution was ~ 125 meV for the core-level PE spectra and better than 50 meV for ARPES; the LEEM spatial resolution was better than 10 nm. All experiments were performed under the same conditions, with a base pressure in the experimental chambers better than 5×10^{-10} mbar. Graphene overlayers were prepared *in situ* following the conventional recipe of propene thermal decomposition, the details can be found elsewhere^{30,31}. Anhydrous AlBr₃ (powder, from Sigma-Aldrich) was deposited on graphene/Ir(111) *in situ* by thermal evaporation from a W crucible using a commercial evaporator (Omicron EFM 3). The amount of deposited material was controlled by the flux monitor of the evaporator and is used as a measure of the sample *exposure* to the molecular beam – the flux is expressed in nA·s.

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In Fig. 1(a)-(d) we show a sequence of LEEM images revealing the evolution of the graphene/Ir(111) sample upon consecutive deposition of AlBr_3 . The first deposition step of AlBr_3 ($\sim 1 \times 10^5$ nA·s at 75°C) results in formation of irregular-shaped bright patches, occupying ~ 10 % of the sample area (Fig. 1(a)). These patches tend to multiply and grow upon further AlBr_3 deposition ($\sim 2 \times 10^5$ nA·s, 75°C), which is shown in Fig. 1(b), until they cover as much as $\sim 95\%$ of the sample surface at $\sim 6 \times 10^5$ nA·s of AlBr_3 at 75°C (Fig. 1(c)). The emergence of bright areas in LEEM images points to the change in the electron reflectivity properties of the sample hence modification in its electronic structure. The electron reflectivity versus energy of the incident electron beam for graphene/Ir(111) together with the corresponding LEED pattern (top-right) is shown in Fig. 1(e), and is characteristic for the dark area in Fig. 1(a)-(c). It has a broad minimum around an electron energy of 7.5-8.0 eV³² which explains the dark appearance of graphene/Ir at these electron energies. The electron reflectivity curve from the bright patches of the sample, shown in Fig. 1(f) drastically differs from that of graphene/Ir(111) on the top panel (e). First, the main reflectivity minimum is sharpened and shifted by 2.5 eV to lower electron energies. Second, there is another reflectivity minimum at electron energy ~ 2.5 eV, which can be attributed to a signal from freestanding graphene.³³⁻³⁵ The μLEED pattern shown in the top-right corner of Fig. 1(f) was taken from bright patches of the sample surface of ~ 1.5 μm size. It reveals a simple six-spot “graphitic” diffraction pattern, with no satellite spots, characteristic for the moiré pattern of graphene/Ir(111) visible on the inset in Fig. 1(e). Based on these facts it is natural to assume that the bright islands in the LEEM images are graphene regions intercalated with AlBr_3 and/or its derivatives. In Fig. 1(a)-(c) it can be seen that intercalation occurs predominantly at graphene grain boundaries. The typical grain size can be deduced from a granular structure of partially intercalated graphene shown in Fig. 1(c) and is ~ 1 μm . In order to perform a complete intercalation of the graphene overlayer, high exposures and post-annealing are required. In Fig. 1(d) a completely intercalated graphene/ AlBr_3 /Ir(111) system is shown which is obtained after exposing of graphene/Ir(111) to $\sim 6 \times 10^5$ nA·s at 75°C and post-annealing to 350°C . After complete intercalation, a LEEM contrast is observed, which is uniform across the entire field of view, and even the network of grain boundaries is barely visible. A reflectivity curve similar to that depicted in the inset of Fig. 1(f), and a graphitic μLEED pattern indicates a complete and uniform intercalation. Note that the amount of intercalated material does not grow linearly with the bromine coverage (Fig. 1). Intercalation starts slowly at low exposures, accelerates once it has started, and slows down again approaching the saturation.

In order to get a better understanding of the interfacial chemistry in the graphene/bromide/Ir(111) intercalation system we have performed systematic PES studies

of the C 1s, Al 2p and Br 3d core levels at different AlBr_3 exposures. Upon deposition of AlBr_3 and subsequent annealing, the C 1s photoemission (PE) spectra (not shown) demonstrate very similar behavior to that of the graphene/Cl/Ir(111) intercalation system.²⁹ However, broadening and splitting of the C 1s core level are much smaller now than for the graphene/Cl/Ir(111) system due to a smaller electronegativity of bromine as a doping agent.

In Fig. 2 we show the evolution of the Al 2p and the Br 3d spectra upon consecutive deposition of AlBr_3 on graphene/Ir(111) at $\sim 75^\circ\text{C}$. A deposition of a relatively small amount of AlBr_3 results in the formation of single-phase AlBr_3 on top (Fig. 2(a)). The dominating $3d_{5/2}$ component of the Br 3d spin-doublet is situated at a binding energy (BE) of 68.2 eV and is separated by ~ 6 eV from the Al $2p_{3/2}$ at 74.2 eV. One has to be cautious when determining detailed stoichiometric ratios from core level intensities due to photoelectron diffraction effects and structure dependent cross section variations.³⁶ However, we find that the ratio of the total peak areas is consistent with a stoichiometry of AlBr_3 , and keep this ratio nearly constant upon further deconvolution of the Al 2p – Br 3d PE spectra. The formation of Al_2Br_6 (same composition stoichiometry) can be ruled out, because no splitting of the Br 3d PE signal into characteristic *bridge* and *terminal* components³⁷ has been observed. In this first stage there is neither evidence for intercalation of graphene nor (from LEED) for formation of a crystalline aluminum bromide phase on top. Therefore we suggest that AlBr_3 is adsorbed on top of graphene in a disordered phase. Through the series of PE spectra, the Br and Al signals from AlBr_3 on top of graphene are indicated with hatched blue and solid light green fill, respectively. Upon the next deposition step ($\sim 1 \times 10^5$ nA·s) the Al 2p and Br 3d PE spectra generally maintain their structure, although several new features appear, which correlate with inception of intercalation processes observed with LEEM. First, there is a new Br 3d spin-doublet shifted by $\sim +0.1$ eV (i.e., to higher BE) from the original Br 3d doublet (at ~ 68.3 eV for its $3d_{5/2}$ component, shown in hatched red color in Fig. 2), which has no counterpart in the Al 2p spectrum. Since the position of this peak is very close to that of bromine in the “on top” AlBr_3 , the chemical state of the Br atoms accounting for this signal is expected to be similar, thus corresponding to a Br-metal bond. Hence we assign the peak at 68.3 eV to atomic Br intercalated under graphene and bonded to Ir. Atomic Br can be formed upon thermal decomposition of AlBr_3 in the crucible or on the sample surface. Second, there is another Br 3d spin-doublet shifted approximately by -1 eV from the original Br 3d doublet (at 67.2 eV for its $3d_{5/2}$ component, solid cyan fill in Fig. 2). We attribute it to intercalated Br_2 or HBr molecules, formed upon thermal decomposition of AlBr_3 in the crucible, because no corresponding signal can be seen in the Al 2p spectrum. The positions of the Br 3d core level in Br_2 and HBr are very close,³⁸ and it is hard

to distinguish between these two species. Finally, there are new doublets in the Br 3d and Al 2p spectra, colored in magenta and dark green, respectively. Those are both shifted by +0.6 eV from the “on top” AlBr₃ signal, and the intensity ratio of these two doublets suggests the AlBr₃ stoichiometry, making it plausible to assign these signals to intercalated AlBr₃. With increased exposure to the AlBr₃ flux, all spectral components grow, but the maximum relative gain is seen for the features assigned to the intercalated species (Fig. 2(c)), in agreement with the LEEM data.

An annealing of the almost completely intercalated sample at 350 °C (Fig. 2(d)) is accompanied by a complete vanishing of the “on top” AlBr₃ signal due to the thermal desorption. Also, a new pair of Br and Al lines appears, separated by ~6 eV (violet and solid grey fill in Fig. 2(d), respectively). The intensity ratio of these lines does not correspond to the stoichiometric AlBr₃ compound, and we assign these signals to a mixture of chemical species, such as radicals AlBr₂⁺, AlBr²⁺ etc., which form upon thermal decomposition of AlBr₃.

The impact of AlBr₃ intercalation on the graphene electronic structure has been studied by ARPES. In Fig. 3 we show the band structure of clean, undoped graphene/Ir(111) (panels (a),(b)) and the corresponding band structure of the brominated (doped) sample (panels (c),(d)), respectively. A full overview bandmap of the undoped graphene/Ir(111) sample was collected, and is displayed as Fig. 3(a), with the important high symmetry points indicated. The cut traced blue in Fig. 3(a) is depicted in more detail in panel (b) of the same figure. It reveals an almost linear dispersion of the graphene π band at the $\bar{K}$ point of the graphene Brillouin zone.³⁹ It is clear from Fig. 3(a),(b) that the Dirac point is positioned almost directly at the Fermi level, which leads to the nearly ambipolar character of charge carriers in graphene, with a trace of hole doping due to the moderate graphene-Ir interaction. Another manifestation of this interaction is the faded replica π bands at around $\pm 0.3 \text{ \AA}^{-1}$ from the $\bar{K}$ point and the minigaps at around 0.75 eV on the main π band (discussed in detail in Ref. 40–42), which are clearly visible in Fig. 3(b).

The bottom panels of Fig. 3 show equivalent data for graphene completely intercalated with AlBr₃ and its derivatives (we used an exposure of $\sim 6 \times 10^5 \text{ nA}\cdot\text{s}$ and post-annealing to $\sim 350 \text{ }^\circ\text{C}$ to ensure a complete intercalation). The overview bandmap represented in panel (c) shows that the structure of the π band remained generally unchanged and undisturbed, although it rigidly shifts upwards i.e. to lower binding energies by some 0.35–0.4 eV. Moreover, the initial sharp bright spot of the Dirac point on the Fermi surface (Fig. 3(a)), becomes a significantly wider circular feature with donut-like intensity distribution after intercalation of AlBr₃ and bromine (Fig. 3(c)). A better understanding of the change in electronic structure caused by bromination can be gained from the ARPES detail shown in Fig. 3(d). The intercalation of graphene with Br/AlBr₃ largely reduces the

graphene-Ir interaction, which is apparent from the vanished interfacial interaction details: neither replica bands nor minigaps are observed upon complete intercalation. On the other hand it is clearly visible that the whole Dirac cone is shifted towards lower BE, leaving the electronic states close to the Dirac point unoccupied. This is equivalent to a downward shift of the Fermi level, or *hole* doping of graphene. The natural reason for this would be an interfacial charge transfer from graphene to the more electronegative bromine, as seen in other graphene/halide interfaces.^{28,29} The value of the Fermi level shift can be determined from extrapolation of the π band above the Fermi level with the assumption that the linear dispersion of the π band remains unchanged upon doping, which gives a value of $\sim 0.35 \text{ eV}$. The doping level of graphene treated with AlBr₃ expressed as a *hole density* can be derived from the Fermi level shift, discussed above, using tight-binding band calculations.^{43,44} From the slope of the dispersion curve in Fig. 3, the value of $\hbar v_F$, where v_F is Fermi velocity, can be estimated as $\sim 6 \text{ eV}\cdot\text{\AA}$ which, together with the Fermi level shift of $\sim 0.35 \text{ eV}$, yields^{18,19,28} a hole concentration of $n_h \simeq 9 \times 10^{12} \text{ cm}^{-2}$ for the brominated graphene (compared to $4.5 \times 10^{13} \text{ cm}^{-2}$ and $\sim 3 \times 10^{13} \text{ cm}^{-2}$ for fluorinated and chlorinated graphene, respectively^{28,29}). This estimation of the doping level in the graphene/AlBr₃/Ir system is consistent with the assumption that the origin of the doping is a charge transfer to the more electronegative halide molecules of the intercalant material, given that electronegativity decreases in the row of halides from fluorides to bromides.

To conclude, we show that *bromination* of graphene can be achieved via *in situ* deposition and subsequent intercalation of Br/AlBr₃. Intercalation of Br/AlBr₃ results in decoupling of graphene from the substrate, which yields a quasi-freestanding graphene suspended on the interfacial intercalant layer. A pronounced hole doping of graphene with area density of around $9 \times 10^{12} \text{ cm}^{-2}$ was observed for the completely intercalated sample. The overall ease of preparation and the controllable doping of graphene intercalated with metal halides, demonstrated here, is attractive for the fabrication of devices utilising graphene’s prized electronic properties.^{2–4} Further, the intercalation of active dopants beneath the surface promises the improved environmental robustness necessary for device applications.⁴⁵

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Figure 1. LEEM study of graphene/AlBr₃/Ir(111) system, with (a)-(c) corresponding to ~10%, ~50%, ~95% (by area) intercalation of graphene with AlBr₃ at 75 °C, respectively, and (d) to ~100% intercalated graphene/Ir(111) at 350°C. Electron energy is 7.5-8 eV, field of view is 20 μm. Panels (e),(f) show electron reflectivity vs. energy for graphene/Ir(111) and graphene/AlBr₃/Ir(111), respectively, collected from ~1.5 μm patches on the sample surface highlighted with circles. The relations are shown with arrows. The insets in the top-right corners of (e),(f) show corresponding μLEED patterns, obtained with an electron energy of 38.6 eV.

Figure 2. Evolution of Al 2p and Br 3d photoelectron spectra upon deposition of AlBr₃ (a-c) and subsequent annealing (d), together with a peak-fit analysis. The photon energy is 150 eV.

Figure 3. ARPES data for pristine (undoped) (a),(b) and doped (c),(d) graphene/Ir(111). Panels (a),(c) show an overview of the graphene π -band dispersion, with the $\bar{\Gamma}$ - $\bar{K}$ direction of the Brillouin zone of graphene indicated (k_y). (b),(d) are the bandmaps in the k_x direction cut through the $\bar{K}$ point of the Brillouin zone. The photon energy is 60 eV.