Graphene, a single layer of carbon atoms arranged in a honeycomb structure, was first isolated by mechanical exfoliation of graphite in 2004. Intensive research efforts have been devoted to the development of large-scale production methods for device applications in the semiconductor industry, such as the thermal decomposition of SiC (Ref. 2) and chemical vapor deposition (CVD) of hydrocarbons on metal films. To date, graphene as well as its chemical derivatives have revolutionized the physics of low dimensional systems and this has led to many mesoscopic device applications. By taking advantage of surface chemical modifications, it is possible to modify the graphene electronic band structure, such as tuning the Fermi level or controlling the gap size, and hence to manipulate the electronic properties. It has been demonstrated that controlling the type and concentration of charge carriers in graphene films can be achieved by tuning the back/top gate voltage in a field-effect-transistor (FET) device, or via transfer doping by surface modification with strong molecular donor/acceptor molecules, or metal thin films with different work functions, or introducing foreign atoms during the CVD growth processes. In this letter, we report the electrical transport measurements of lithographically patterned mechanical exfoliated graphene in a Hall bar structure before and after molybdenum trioxide (MoO$_3$) modification. Effective non-destructive p-type doping of graphene via surface modification with molybdenum trioxide leads to the downward shift of Fermi level towards the valence band. MoO$_3$ modified graphene retains its high charge carrier mobility, facilitating the observation of quantum Hall effect. In-situ ultraviolet photoelectron spectroscopy studies also show that air exposure of MoO$_3$ modified graphene reduces the doping efficiency. © 2011 American Institute of Physics. [doi:10.1063/1.3609318]

We demonstrate effective non-destructive p-type doping of graphene via surface modification with molybdenum trioxide (MoO$_3$) thin film using electrical transport measurements. The p-type doping via MoO$_3$ modification of graphene leads to the downward shift of Fermi level towards the valence band. MoO$_3$ modified graphene retains its high charge carrier mobility, facilitating the observation of quantum Hall effect. In-situ ultraviolet photoelectron spectroscopy studies also show that air exposure of MoO$_3$ modified graphene reduces the doping efficiency. © 2011 American Institute of Physics.
magnetic field, the Hall resistance develops linearly with the field \( B \) and the charge carrier density is calculated from the Hall resistance slope by:

\[
n = \frac{1}{e} \frac{dR_{xy}}{dB}.
\]

After MoO\(_3\) deposition, the charge carrier density \( n \) reaches \( 1 \times 10^{12} \text{ cm}^{-2} \) with holes as charge carrier, indicating a p-type doping effect and consistent with our previous PES study.\(^{16}\) Based on this charge carrier density, the mobility can be obtained by:

\[
\mu = \frac{L}{W} (enR_{xx})^{-1},
\]

where \( L \) and \( W \) represents the length and the width of Hall bar geometry. Here, the mobility of MoO\(_3\) doped graphene is calculated to be 7300 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 2 K and 6150 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 300 K, respectively. This is slightly lower than the mobility of pristine graphene, which is 8700 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 2 K and 7300 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 300 K. The mobility reduction may be attributed to defect scattering induced by MoO\(_3\) particles on the graphene surface. Nevertheless, the mobility is still large enough for the observation of the quantum Hall effect (QHE) as shown in Fig. 2. Apart from the presence of Shubnikov-de Hass (SdH) oscillations in the magnetoresistance \( R_{xx} \), a prominent plateau and a small plateau are observed in the Hall resistance, which are the hallmarks of the QHE.\(^{21}\) In a two dimensional electron system, the Hall resistance possesses quantized values of \( \hbar/(e^2n) \), where \( v \) is the integer filling factor. However in single layer graphene, the QHE differs from conventional QHE as it shows “half-integer” quantization values expressed as

\[
R_{xy}^{-1} = \pm 4 \left( |n| + \frac{1}{2} \right) \frac{e^2}{\hbar},
\]

where \( n \) is the Landau levels (LLs) index and the four-degeneracy is caused by both the spin and the sublattice degeneracy.\(^{20}\) From this formula, we deduce that the two plateaus observed in the positive magnetic field represent \( n = -1 \) and \( n = -2 \) (corresponding to \( v = -6 \) and \( v = -10 \)), respectively, where the minus sign indicates hole-like LL. The well-defined QH states suggest our graphene samples after doping still retain the high mobility and the unique electronic properties of pristine graphene. This is consistent with the Raman spectroscopy measurements in Fig. 1(b) and confirms the non-destructive nature of the p-doping through MoO\(_3\) surface modification.

As compared with pristine graphene, the positions of the resistance plateaus are shifted to higher magnetic field after MoO\(_3\) modification as shown in Fig. 2(b). The shift is most likely caused by the change in Fermi level (\( E_F \)) position, which is a determinant factor for the positions of QH plateau.\(^5\) In graphene, the Hall resistance \( R_{xx} \) exhibits plateaus when an integer of LL is fully occupied, i.e., the \( E_F \) is located between the \( n \) and \( n+1 \) LL; when \( E_F \) moves across a LL, \( R_{xx} \) jumps by an amount of \( 4e^2/\hbar \). Therefore, the position of the plateau can be adjusted by tuning the \( E_F \) and the LL energy where LL is given by

\[
E_n = \text{sgn}(n) \sqrt{2\hbar v_F^2 |n|B}
\]

For MoO\(_3\) doped graphene, the LL energies are identical to pristine graphene at the same magnetic field. Thus, the shift in QH plateau positions can only be ascribed to the different \( E_F \) before and after MoO\(_3\) evaporation. The MoO\(_3\) modification induced p-type doping shifts \( E_F \) further away from the Dirac point, hence causing the position of QH plateau to move towards larger magnetic field. It has been reported that air exposure can significantly degrade the doping level of MoO\(_3\) modified organic semiconductors.\(^{23}\) To examine the air exposure effect on doping, an \( in-situ \) UPS experiment on MoO\(_3\) modified CVD few-layer graphene was performed. Figure 3 shows the UPS spectra at low-kinetic energy region of 5 nm MoO\(_3\) deposited CVD graphene before and after exposure to air for 2 h, with pristine CVD graphene as a reference. The vacuum level (VL) was measured by linear extrapolation of the low-kinetic energy onset (secondary electron cutoff) in the UPS spectra. After deposition of 5 nm (nominal thickness) MoO\(_3\), the VL showed an upward shift of 2.4 eV, i.e., the work function increased from 4.4 eV (pristine CVD graphene) to 6.8 eV (MoO\(_3\) modified graphene). This is induced by the large work function difference between graphene and the MoO\(_3\) thin film, indicating a large doping effect. However, after 2 h exposure to air, a downward shift of VL by 1.4 eV was observed, and the work function was reduced from 6.8 eV to 5.3 eV. This reduced work function suggests that air exposure can significantly degrade the doping level of MoO\(_3\) modified graphene devices. This can also explain the...
The discrepancy in hole concentration of MoO$_3$ modified graphene from different measurements, i.e., a low concentration of $1 \times 10^{12}$ cm$^{-2}$ from current ex-situ electrical measurements for 5 nm MoO$_3$ modified graphene; while a higher concentration of $7 \times 10^{12}$ cm$^{-2}$ from previous in-situ PES measurements for 0.8 nm MoO$_3$ modified graphene.

In conclusion, using electrical transport measurements, we have demonstrated that surface modification with MoO$_3$ is able to effectively and non-destructively p-dope graphene. The quantum Hall effect in graphene device was observed after MoO$_3$ modification and the p-doping effect was confirmed from the shift of quantum Hall plateaus. The effect of air exposure on the MoO$_3$ induced doping of graphene has been evaluated by in-situ UPS measurements. It is found that the air exposure can significantly reduce the doping level of the MoO$_3$ modified graphene sheet, resulting in a hole concentration of $\sim 1 \times 10^{12}$ cm$^{-2}$ after surface modification with 5 nm MoO$_3$ film. Our results suggest that by developing a suitable encapsulation method, it is possible to achieve higher hole concentration in MoO$_3$ modified graphene devices.

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