# Large effect of etchant on electrical performance of transferred CVD graphene

Ting-Wei Chen<sup>1</sup>, Ya-Ping Hsieh<sup>1\*</sup> and Mario Hofmann<sup>2</sup>

 <sup>1</sup> National Chung Cheng Univ. Graduate Institute of Opto-Mechatronics Chiayi, 62102, Taiwan
Phone: +886-5-2720411-33603 E-mail: <u>yphsieh@ccu.edu.tw</u>
<sup>2</sup> National Cheng Kung Univ. Department of Material Science and Engineering Tainan, 70101, Taiwan

### Abstract

Destructive removal of copper catalyst is a required step in the transfer of graphene to target substrates. We here investigate the impact of different types of copper etchants on the performance of graphene-based transparent optical conductors. Two etchants (Ammonium persulfate and Iron (III) chloride, that are commonly employed in graphene transfer, showed significant differences. Using ammonium persulfate as etchant resulted not only in a decrease of graphene sheet resistance by 3 times but also enhanced the mobility twofold. This effect is attributed to the adverse effect of n-type dopants in FeCl<sub>3</sub> etchants.

## 1. Introduction

Chemical Vapor Deposition is the most promising method to produce graphene at high quality and large quantity. In this process, a catalyst substrate (most commonly copper) is used to convert a carbon precursor into graphene. In order to isolate thus synthesized graphene from the metallic catalytic substrate, an etching step is required to removes the catalyst. The most common etchants are ammonium persulfate (APS) [1-3] and FeCl<sub>3</sub> [4-6]. While differences in morphology such as residue [7] and cleanliness [8] have been reported, no conclusion as to the effect on graphene electrical performance have been reached. For example, it is unclear if the previously observed n-type doping of Chlorine residue is an advantageous or detrimental feature of FeCl<sub>3</sub>. On the one hand, n-type carriers could introduce a parallel conduction channel through ambipolar transport. As a results, however, the presence of charged impurities could deteriorate the carrier transport.

We here demonstrate the threefold enhancement in performance of graphene-based transparent optical conductors (TOCs) by simple variation of the etching process. These results were found to be very repeatable and the origin of this enhancement will be discussed

## 2. Experiment

Copper foil (99.8%, Alfa-Aesar, no. 13382) was first electrochemically polished in  $H_3PO_4(85\%)$  electrolyte and then rinsed with DI water, isopropyl alcohol and finally dried in a stream of dry nitrogen.

Graphene was grown at 1000 °C for 30 minutes with flow ratios of  $H_2$ :  $CH_4 = 20:1$  at a total pressure of 9 torr.

For characterization of electrical properties and Raman spectroscopy,  $1 \text{ cm}^2$  graphene samples grown on copper

ware transferred onto quartz or  $SiO_x/Si$  using a polymethyl-metacrylate (PMMA) layer as mechanical support and removing copper foil by ammonium persulfate(APS) (ADEKA corp. 99%) : DI water=1:5 or FeCl<sub>3</sub>(He Cheing chemical corp. 40%): DI water=1:7. Sheet resistance was then measured using a 4-point probe in van-der-Pauw geometry. Raman measurements were performed in a home-build Micro-Raman system using a 532nm laser excitation source.

The Figure of Merit (FOM) was calculated from the equation proposed by De. et al. [9] for graphene-based TOCs.

### 3. Result and Discussion

The graphene transferred with different etchant on Si- $O_x/Si$  were first characterized with Optical Microscope as shown in Figure 1. Both images shows the transfer is complete and the graphene surface is clean with only little and unavoidable PMMA residue (white spots) present.



Fig. 1 The graphene OM picture for two different etchant. (a)APS etchant, (b)FeCl<sub>3</sub> etchant.

To understand the difference in properties of graphene transferred by both etchants, Raman spectra were taken. More than 10 data points were randomly taken for the two differently transferred graphene samples. The intensity ratio of D-band and G-band (denoted as D/G) was also analyzed from both samples (Figure 2(a)). Both samples exhibit a low D/G ratio (<0.05) which indicates the high quality of both transfer steps.

Significant differences in the position and shape of the Raman 2D-band is found for samples transferred by APS and FeCl<sub>3</sub> (Figure 2(b)), indicating large differences in doping[10] [11]. The difference in width is found to originate from a double-peak structure (inset Figure 2(b)).

Recent reports [7] [12] have shown that that residue from  $FeCl_3$  etchant would cause n-type doping. The coexistence of n-type and p-type regions could explain the observed double-peak structure of the 2D band since both regions would contribute to the Raman signal.

We now turn to investigate the carrier transport in both sample types. When comparing the extracted Hall carrier concentration and Hall mobility, we find that devices from each sample type follow an inverse proportionality as expected from charged impurity scattering (Figure 3(a)). The comparison between the two samples, however, reveals that FeCl<sub>3</sub> samples of similar carrier concentration exhibit much smaller mobilities.



Fig. 2 (a) Raman  $I_D/I_G$  ratio of graphene, (b) Raman 2D peak for APS and FeCl<sub>3</sub> transferred samples.

This discrepancy originates from issues in the Hall measurements in the presence of both n- and p-type carriers. The commonly employed formula for extracting the carrier concentration from Hall-effect measurements fails for ambipolar transport and has to be replaced by [13]

$$R_{H} = \frac{E_{y}}{J_{x}^{B}} = \frac{p\mu_{H}^{2} - n\mu_{e}^{2}}{e(p\mu_{h} + n\mu_{e})^{2}}$$
(1)

The opposing effects of n-type and p-type carriers result in a very small Hall resistance that could be mistaken for a high carrier concentration and leads to an underestimation of the carrier mobility.

We investigate the contribution of ambipolar transport to our sample by introducing the ratio of Hall resistance and the square of Sheet resistance:

$$\frac{R_H}{R_S^2} = ep\mu_H^2 - en\mu_e^2 \quad (2)$$

This ratio will be small if n-type and p-type carriers occur at similar densities and move with similar mobilities but it will be large if either carrier type is dominant. We find that the ratio is significantly smaller for FeCl<sub>3</sub>-transferred (0.8  $\Omega^{-1}$ ) than for APS-transferred graphene (5 $\Omega^{-1}$ ).

We therefore conclude that ambipolar transport is indeed occurring in FeCl<sub>3</sub>-transferred graphene at comparable carrier concentrations and mobilities for n-type and p-type conduction in agreement with previous findings[12].

This finding is surprising in light of the differences in sheet resistance between the two types of samples. Ambipolar transport should result in lower sheet resistances since both carriers contribute to the conduction but the ambipolar FeCl<sub>3</sub>-transferred graphene( $1600\Omega$ ) exhibits much higher sheet resistances than APS-transferred graphene ( $480\Omega$ ). This behavior indicates that the p-type and n-type carrier mobility of FeCl<sub>3</sub>-transferred samples is significantly lower than in APS-transferred samples.

Finally, the figure of merit (FOM) for transparent optical conductor applications were calculated for both transferred samples and compared (Fig. 3c). The FOM is found to be much higher transferred from APS compared to  $FeCl_3$ .



Fig. 3 The electrical performance of graphene. (a) carrier concentration vs. mobility, (b) sheet resistance for both sample types, (c) Figure of Merit for both sample types

#### 3. Conclusions

In conclusion, we found that the choice of etchants in the graphene transfer process plays an important role for the electrical performance of CVD grown graphene. The undesired residue from FeCl<sub>3</sub> etchant was found to deteriorate both mobility and sheet resistance and results in a low FOM. On the contrary, APS etchant shows excellent electrical performance and clean surfaces under microscopy. These findings are of importance for future development of graphene-based electronics.

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- [1] S. Bae, et al. Nature nanotechnology (2010) 574-8
- [2] G. Yang, et al. Physical chemistry chemical physics : PCCP(2013) 1798-801
- [3] M.S. Boutilier, et al. ACS nano (2014) 841-9
- [4] M.H. Kang, et al. IET Circuits, Devices & Systems (2015) 39-45
- [5] V.P. Verma, et al. Applied Physics Letters (2010) 203108
- [6] N. Jain, et al. Electron Device Letters, IEEE (2012) 925-7
- [7] G. Lupina, et al. ACS nano (2015)
- [8] X. Liang, et al. ACS nano (2011) 9144-53
- [9] S. De, et al. ACS Nano (2010) 2713-20
- [10]L.L. Zhang, et al. Energy & Environmental Science (2012) 9618
- [11]S. Das, et al. Journal of Materials Chemistry (2012) 20490
- [12]Y. Yu Wang, et al. Applied Physics Letters (2013) 052103
- [13]S. Kasap Hall effect in semiconductors (2001)