# MoCl<sub>5</sub> Intercalation Doping and Oxygen Passivation of Submicrometer-Sized Multilayer Graphene

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## Abstract

Intercalation doping in multilayer graphene (MLG) has been improved for the interconnect application in LSI. Retention of dopant up to nanoscale edge of the MLG, which is critically important for nanoscale interconnect, is realized by employing MoCl<sub>5</sub> as a doping material and oxygen gas exposure as a passivation process.

# 1. Introduction

MLG is one of the most promising candidates for application in LSI interconnects, because of its long mean free path of charge carriers [1, 2]. On the other hand, graphene has lower carrier density than ordinary metals. The carrier density can be increased by charge transfer doping. Strong charge transfer doping is obtained by inserting a doping material (intercalate) between graphene layers, forming a graphite intercalation compound (GIC) [3]. Considering the application for nanoscale interconnect, however, leakage of intercalate from edges must be prevented. For this purpose, it is important to select appropriate intercalate material and a passivation process for better environmental stability. Metal chlorides are known to be relatively stable intercalates, even though they deliquesce and are hydrolyzed by water vapor in the atmosphere [4]. To improve environmental stability, we propose utilizing MoCl<sub>5</sub>, which is reported to make very stable GIC [5], as an intercalate with a passivation process involving exposure to pure dry oxygen. We expect that the oxygen partially turns unstable chlorides into stable oxide.

# 2. Experimental

We employ FeCl<sub>3</sub> and MoCl<sub>5</sub> as intercalates [6]. Flakes of MLG were prepared on SiO<sub>2</sub>/Si substrates by the mechanical exfoliation method from highly oriented pyrolytic graphite (HOPG). The substrates were vacuum sealed in glass ampoules with intercalate material (FeCl<sub>3</sub> or MoCl<sub>5</sub>) powder. The ampoules were heated to 310°C for 1 day for FeCl<sub>3</sub> or to 300°C for 2 days for MoCl<sub>5</sub>. The passivation process was conducted by transferring samples from the ampoule into pure oxygen gas without exposure to air. After keeping the sample in oxygen at room temperature, the oxygen was replaced by argon. Then, samples were removed to air. The doped MLGs were analyzed by Raman spectroscopy and scanning transmission electron microscopy with energy dispersive X-ray spectrometry (STEM-EDX).

### 3. Results and Discussions

Figure 1 shows results of Raman spectroscopy analysis of FeCl3- and MoCl5- intercalated MLGs without the oxygen passivation process. G-band peak (~1580 cm<sup>-1</sup>) in pristine MLG splits into three components, G<sub>0</sub>, G<sub>1</sub>, and G<sub>2</sub>, reflecting distribution of intercalate (Fig. 1(a)). As shown in the inset of Fig. 1(a),  $G_0(\sim 1580 \text{ cm}^{-1})$  is from graphene layers that do not have direct contact with intercalate.  $G_1(\sim 1600 \text{ cm}^{-1})/G_2 (\sim 1620 \text{ cm}^{-1})$  is from graphene layers that have contact with intercalate at one or both sides. Degree of charge transfer doping is represented by G peak position ( $\overline{G}$ ), which is defined by the center of mass of  $G_0$ ,  $G_1$ , and  $G_2$  peaks. The  $\overline{G}$  depends on size of an MLG flake and intercalate material (Fig. 1(b)). In FeCl<sub>3</sub>-intercalated MLG flakes whose width in lateral dimension (w) is larger than ~5 µm, G<sub>2</sub> peak is dominant, i.e., intercalates are inserted in most of the graphene interlayer. In this case, the  $\bar{G}$  is around 1620 cm<sup>-1</sup>. When w is smaller than ~5 µm, the  $\overline{G}$  drops off, reflecting degradation of the doping effect, i.e., decrease of intercalate density. In MoCl5-intercalated MLG flakes, the  $\overline{G}$  is higher than that of the FeCl<sub>3</sub> one for  $w \lesssim 4 \,\mu\text{m}$ , whereas it is smaller for  $w \gtrsim 4 \,\mu\text{m}$ . This reflects better retention ability for small size in MoCl<sub>5</sub>-GIC than that in FeCl<sub>3</sub>-GIC. Despite the better retention ability, the  $\overline{G}$  decreases at  $w \leq 4 \,\mu m$  for MoCl<sub>5</sub>-intercalated MLGs. To improve the doping effect in this region, we applied the oxygen passivation process to MLGs with  $w \sim$ 0.5 µm. With exposure of oxygen gas for 1 hour, the G-band has larger Raman shift than that without oxygen exposure (Fig. 2), reflecting improved retention ability.

Retention of intercalate in MLG flakes is observed using elemental mapping by cross-sectional STEM-EDX analysis (Fig. 3). Without the oxygen passivation process, we do not find Mo and Cl within ~30 nm from an MLG edge (circles in Fig. 3(a)). On the other hand, with the oxygen passivation process, we find Mo and Cl in MLG edge region (Fig. 3(b)). In addition, we also find distribution of O in the oxygen-processed sample. This is evidence of partial oxidization of MoCl<sub>5</sub> intercalate, because O<sub>2</sub> itself does not intercalate in graphite. A similar passivation effect by oxygen is expected also in some other metal chlorides, such as NbCl<sub>5</sub>, TaCl<sub>5</sub>, and BiCl<sub>3</sub>, because they are reported to form a passivation layer of their oxide or oxychloride analogues [7, 8].

# 5. Conclusions

We examined the passivation process involving exposure to oxygen gas to improve retention ability of MoCl<sub>5</sub>-intercalated MLG. In the case of the oxygen exposure, larger charge transfer doping and better retention of intercalate are confirmed by Raman spectroscopy and STEM-EDX analysis. Selecting appropriate intercalate material and controlling partial oxidization of metal-chloride intercalate are key techniques to keep intercalate in nanoscale MLG interconnect.

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Fig. 1 (a) An example of Raman G-band peak that splits into three components,  $G_0$ ,  $G_1$ , and  $G_2$ . Inset shows a schematic view of the origin of the components, where lines and spheres represent graphene sheets and intercalates, respectively. (b) G-peak position  $\overline{G}$  as a function of lateral flake size w for FeCl<sub>3</sub>- and MoCl<sub>5</sub>- intercalated MLGs without oxygen passivation process.



Fig. 2 Effect of oxygen passivation for MoCl<sub>5</sub>-intercalated MLG flakes with  $w \sim 0.5 \,\mu\text{m.}$  (a) Raman G-band peak of pristine MLG (dotted) and MoCl<sub>5</sub>-intercalated MLG with/without the oxygen exposure process (dashed/solid). (b) Comparison of distribution of  $\bar{G}$  with and without the oxygen exposure process. Dotted line shows  $\bar{G}$  of pristine MLG.



Fig. 3 Elemental mapping by cross-sectional STEM-EDX analysis of MoCl<sub>5</sub>-intercalated MLG without (a) and with (b) the oxygen passivation process. Distributions of C, Mo, Cl, and O elements are shown (clockwise from the top left in each panel). Areas surrounded by dashed curve represent MLG region. Dotted circles in (a) indicate edge regions from which intercalate materials have gone away.