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Intercalation Doping with Metal Chlorides in Low-Temperature-Grown Multilayer CVD Graphene for Interconnect Applications

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Abstract

We demonstrate resistivity reduction of low-temperature (LT) CVD multilayer graphene (MLG) grown at 650°C by intercalation doping with metal chloride. Quality improvement of the LT-MLG and proper selection of metal chloride such as $MoCl_5$ enabled intercalation into the MLG and reduced the resistivity more than tenfold.

1. Introduction

Graphene is one of the most promising candidates for application in LSI interconnects with a view to prolonging the applicability of Moore's law, because of its long mean free path of charge carriers [1, 2]. On the other hand, the density of the carriers in graphene is lower than that in ordinary metals, and can be increased by charge transfer doping. The strong charge transfer doping is obtained in graphite intercalation compounds (GICs) [3].

From the perspective of the LSI process, lower process temperature is preferable in order not to destroy front-end-of-line devices. On the other hand, higher growth temperature is advantageous for MLG quality. Since structure order is required to keep intercalated materials in GIC [4], there is a trade-off between the growth temperature and the doping effect by intercalation. CVD growth temperature of graphene is usually higher than 800°C. We have improved crystallinity of MLG grown at 650°C on a CVD-Ni catalyst on a 300 mm wafer [5]. In this paper, we report intercalation doping experiments in which metal chlorides, namely $FeCl_3$ and $MoCl_5$, were applied for CVD-grown MLGs.

2. Experimental

We prepared MLGs on Ni catalyst by thermal CVD at 650°C, using C_2H_2, H_2 and Ar as source gases. Two types of Ni catalyst were used. Ni layers were prepared by physical vapor deposition (PVD) or metal-organic CVD (MOCVD). Quality of MLG films was analyzed by incident angle-dependent X-ray absorption fine structure (XAFS) analysis and Raman spectroscopy [5]. The Raman spectra provide a measure of MLG quality by the intensity ratio of G-band to D-band (G/D). MLG grown on MOCVD Ni had higher quality (G/D = 29.4) than that on PVD Ni (G/D = 3.4). The MLGs were exfoliated from the Ni catalyst layers by wet etching, and transferred on SiO_2/Si substrates [6]. The transferred MLGs were patterned into 1.5-20 μm-wide strips by photolithography and O_2 reactive-ion etching. They were vacuum sealed in glass ampoules with dopant ($FeCl_3$ or $MoCl_5$) powder. The ampoules were heated to 310°C for 1 day for $FeCl_3$ or to 300°C for 7 days for $MoCl_5$. The doped MLGs were analyzed by Raman spectroscopy, transmission electron microscopy (TEM), and energy dispersive X-ray spectrometry (EDX). The resistance of the MLG strips was obtained by four-terminal measurement using a nanoprobe system.

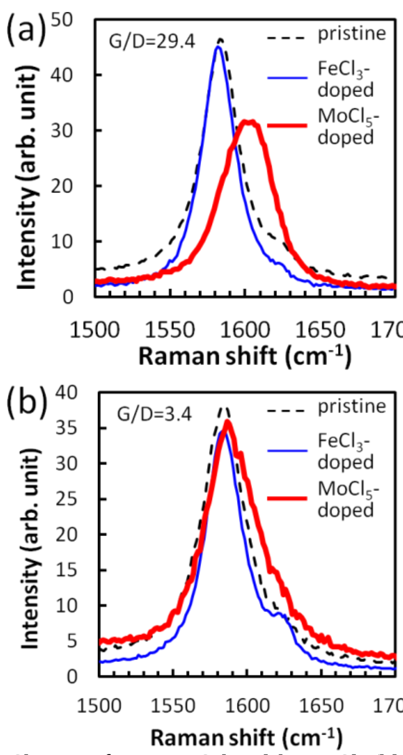

Fig. 1 Change of Raman G band by $FeCl_3$ (blue thin solid line) and $MoCl_5$ (red thick solid line) intercalation in comparison with pristine MLG (black dashed line) grown on MOCVD Ni (G/D = 29.4) (a) and PVD Ni (G/D = 3.4) (b).

3. Results

In the Raman spectroscopy, an upshift of the G band (1582 cm^{-1} in pristine graphite) was observed in the $MoCl_5$-doped MLG grown on MOCVD Ni (Fig. 1). No shift was observed in the $FeCl_3$-doped ones or the MLG grown on PVD Ni. The upshift of the G band is caused by charge transfer into graphene layers from dopant [4]. The elements of the dopant (Mo and Cl) were found in the $MoCl_5$-doped MLG layer by TEM-EDX analysis (Fig. 2). In the MLG, there are two types of regions, each having a different texture: a blue smooth region and a rough region, indicated by A and B in Fig. 3(a), respectively. From atomic force microscopy (AFM), we found that the rough region B is thicker than the smooth region A (Fig. 3(b)). A difference in resistance is also apparent. The sheet resistance of MLG strips (R_{sheet}) shows significant decrease by $MoCl_5$ doping (Fig. 3(c)-(d)). In the thin smooth region A, the resistance reduction exceeds tenfold.

4. Discussions

To obtain the doping effect, dopant must be kept between graphene layers. The ability to do so is strongly dependent on structural order of the host graphite [4]. The XAFS analysis reveals that MLG with higher G/D ratio is more highly oriented [5]. This suggests reasons for more effective doping in MLG grown on MOCVD Ni, especially in the smooth-textured region. The stability also depends on the guest dopant. The stability of GIC with $MoCl_5$ is known to be exceptionally high [7], possibly because of a passive layer of $MoOCl_3$ and/or MoO_3 formed by hydrolysis [8].

5. Conclusions

Intercalation doping is possible even in MLG grown at low temperature. The doping was facilitated by MLG quality improvement and dopant selection. In the case of nanometer-scale MLG interconnect, formation of dense passive layer would be critically important for enclosing dopant.

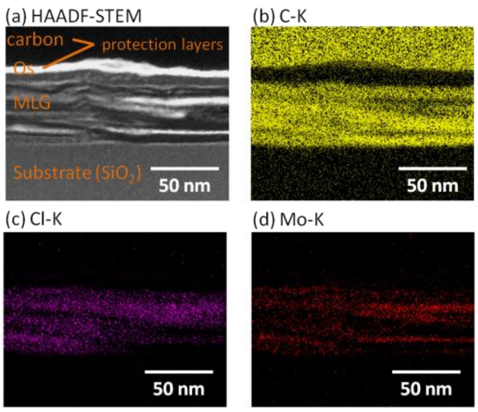

Fig. 2 Cross-sectional elemental mapping of a $MoCl_5$-doped MLG (G/D = 29.4) by TEM-EDX. (a) High-angle annular dark field scanning TEM (HAADF-STEM) image. (b)-(d) EDX mapping images of C, Cl, and Mo, respectively, by K-shell X-ray. Protection layers of Os and carbon are deposited on the MLG film before slicing for the TEM analysis.

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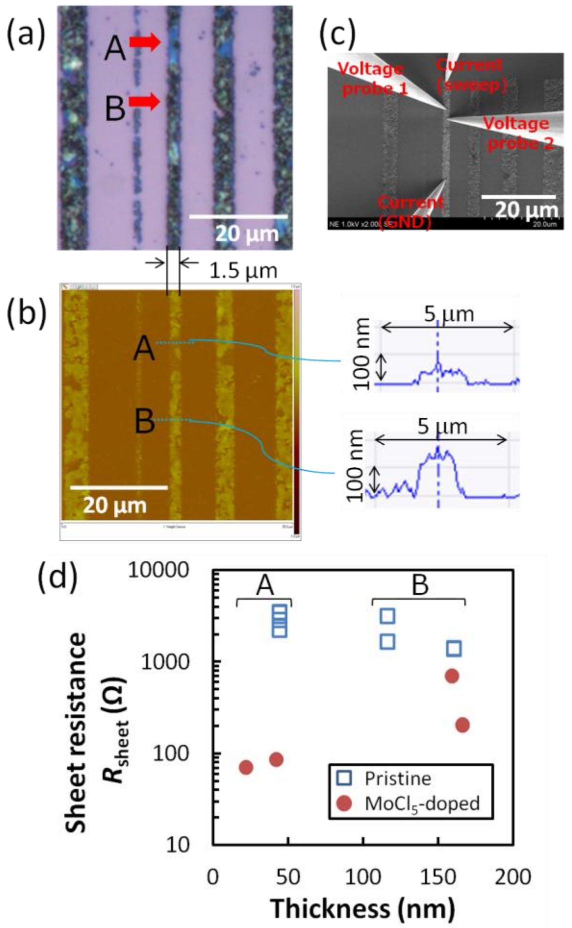

Fig. 3 Resistance measurement of MLG strips (G/D = 29.4). (a) Optical image of MLG strips. Two types of region are indicated by A and B. (b) AFM topograph (left panel) and its cross-sectional profile images for regions A and B (right panel). (c) SEM image of the MLG strip contacted by four probes in the nanoprobe system. (d) Sheet resistance of pristine (squares) and $MoCl_5$-doped (circles) MLG strips as a function of the film thickness.