

# Efficient Reduction and Restoration of Graphene oxide films as a Channel in Field Effect Transistor: Toward Sensor applications

Ryota Negishi<sup>1</sup>, Kazuki, kuramoto<sup>1</sup>, Yasuhide Ohno<sup>2</sup>, Takayuki Nishino<sup>3,4</sup>, Tomohiro Yamaguchi<sup>3</sup>, Kenzo Maehashi<sup>2</sup>, Kazuhiko Matsumoto<sup>2</sup>, Koji Ishibashi<sup>3</sup> and Yoshihiro Kobayashi<sup>1</sup>

<sup>1</sup> Department of applied physics, Osaka University, 2-1 Yamadaoka Suita, Osaka, 565-0871, Japan

Phone: +81-6-6879-4684, Fax: +81-6-6879-7863, E-mail: negishi@ap.eng.osaka-u.ac.jp

<sup>2</sup>ISIR, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka, 567-0047, Japan

<sup>3</sup>RIKEN, Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan

<sup>4</sup>Sanwa Co., 362-1 Izuka, Kumagaya, Saitama, 360-0231, Japan

## 1. Introduction

Chemical and biological sensing using graphene-based field effect transistor (G-FET) has attracted considerable attention because the electrical properties of graphene are highly sensitive to its surface environment [1]. For the sensing application, it is important to establish the fabrication process of G-FET arrays. Reduced graphene oxide (GO) is one of the promising candidates for the channel materials in the G-FET arrays because the large area sheet of graphene is easily obtained by spin-coating method [2]. Recently, Su *et al.* demonstrated the excellent electrical conductivity and carrier mobility of GO flakes reduced by high-temperature alcohol vapors [3]. In this work, we fabricate the reduced GO-FETs (rGO-FETs) prepared by alcohol chemical vapor deposition (CVD) treatment [4], and demonstrate that the rGO films using alcohol CVD treatment are useful for the pH sensor application.

## 2. Experiments

GO (aqueous solution of GO: Graphene Laboratories Inc.) thin films on SiO<sub>2</sub>(320 nm)/Si substrate, were prepared by the spin-coating method. Reduction of GO was carried out under two different conditions: alcohol CVD and Ar/H<sub>2</sub>(3%) annealing at 850 °C for 2h.

Raman spectra were acquired at room temperature using laser excitation of 532 nm with a 100x objective lens (typical spot diameter~1 μm). The mobility of the rGO films was evaluated from source-drain current as a function of gate voltage in the rGO-FET using standard formula [5] described by eq. (1)

$$\mu = \left( \frac{L_{ch}}{W_{ch}} \right) \left( \frac{1}{V_{sd}} \right) \left( \frac{1}{C_g} \right) \left( \frac{dI_{sd}}{dV_g} \right) \dots (1)$$

where  $C_g$ ,  $L_{ch}$ , and  $W_{ch}$  are the gate capacitance, the channel length and the width, respectively. Experimental setup for detecting pH follows the previous report [1].

## 3. Results and discussion

Figure 1(a) shows the Raman spectra obtained from the rGO films prepared by Ar/H<sub>2</sub> annealing and alcohol CVD treatments. The intensity of 2D bands associated with the graphene structure [6,7] increases as the reduction time increases. Moreover, the value of the full width at half maximum (FWHM) of the 2D peak related to the degree of recovery for sp<sup>2</sup> C=C bonds in graphitic structures [8] at the rGO films using alcohol CVD treatment shows lower than that at the rGO films using Ar/H<sub>2</sub> annealing as shown in Fig. 1(b). This result indicates that efficient reduction of GO films occurs by alcohol CVD treatments. Figure 2 shows the relationship of the reduction time and mobility measured at each rGO-FET. Note that the mobility of the rGO-FET prepared by alcohol CVD treatments is higher than that of the rGO-FET prepared by Ar/H<sub>2</sub> annealing. This tendency is in good agreement with previous report [3]. Moreover, the longer reduction time of the GO films shows the higher mobility.

imum (FWHM) of the 2D peak related to the degree of recovery for sp<sup>2</sup> C=C bonds in graphitic structures [8] at the rGO films using alcohol CVD treatment shows lower than that at the rGO films using Ar/H<sub>2</sub> annealing as shown in Fig. 1(b). This result indicates that efficient reduction of GO films occurs by alcohol CVD treatments. Figure 2 shows the relationship of the reduction time and mobility measured at each rGO-FET. Note that the mobility of the rGO-FET prepared by alcohol CVD treatments is higher than that of the rGO-FET prepared by Ar/H<sub>2</sub> annealing. This tendency is in good agreement with previous report [3]. Moreover, the longer reduction time of the GO films shows the higher mobility.

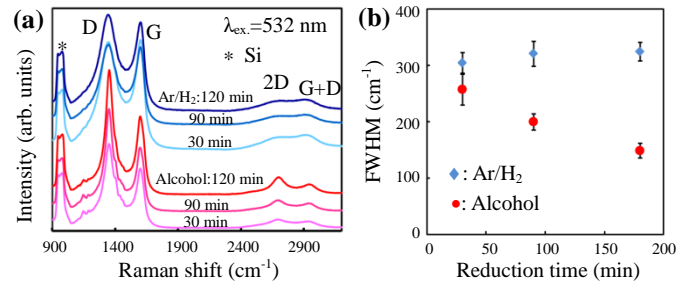


Fig. 1(a) Raman spectra and (b) FWHM of 2D peak obtained from the rGO films prepared by alcohol CVD treatment and Ar/H<sub>2</sub> annealing.

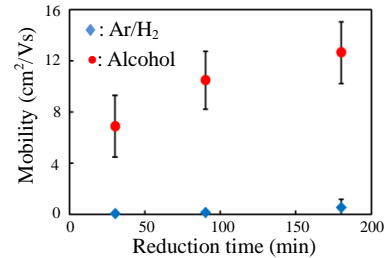


Fig. 2 Reduction time versus mobility of rGO-FETs

Next, we focus on the carrier transport properties in each rGO-FET. Figure 3 compares the temperature dependence of conductance ( $\sigma$ ) for the rGO-FETs prepared by Ar/H<sub>2</sub> annealing (diamonds) and alcohol CVD (dots) treatments. The value of  $\sigma(T)$  is normalized by the  $\sigma$  measured at 300 K. The  $\sigma(T)/\sigma(300K)$  of the rGO-FETs with alcohol shows almost constant value, and this tendency is similar to that of the FET using mechanical exfoliated graphene channel [9]. On the other hand, the value of  $\sigma(T)/\sigma(300K)$

strongly depends on the temperature.

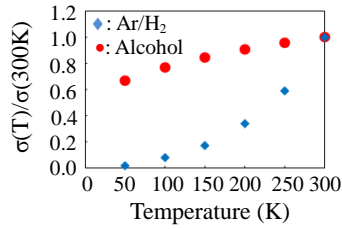


Fig. 3 comparison of temperature dependence of  $\sigma$  at each rGO-FET. Value of  $\sigma(T)$  is normalized by the value at 300K.

Kaiser et al., reported that the conductance of rGO films can be explained by two dimensional variable-range hopping (2D-VRH) through the localized states [10]. In the 2D-VRH model, the  $\sigma(T)$  can be described by eq. (2).

$$\sigma = A \exp\left(-\frac{B}{T^{1/3}}\right) \quad \dots (2)$$

The parameters A and B are expressed by eq. (3) and (4)

$$A = \frac{eR_0^2 v_{ph}}{k_B} \quad \dots (3)$$

$$B = \left(\frac{3}{N(E_F)k_B L^2}\right)^{1/3} \quad \dots (4)$$

where  $e$  is the electron charge,  $R_0$  is the optimum hopping distance,  $v_{ph}$  is the frequency of the phonons associated with the hopping process,  $k_B$  is the Boltzmann constant,  $L$  is the localization length of electronic wave function, and  $N(E_F)$  is the density of states near the Fermi level. Figure 4 is a plot of  $\ln(\sigma_{min})$  as a function of  $T^{-1/3}$ . The solid lines indicate the fitting results on the basis of the 2D-VRH model. From the analysis, we can estimate that the values of the  $L$  in rGO films are 0.47 nm (Ar/H<sub>2</sub> annealing) and 8.12 nm (alcohol CVD treatment). Note that the large localization length of electron wave function obtained from the rGO films prepared by the alcohol CVD treatment indicates that the alcohol treatment leads to the efficient restoration of graphitic structure like a recovery of sp<sub>2</sub> C=C bonds in addition to the reduction. As a result, the rGO-FET prepared by alcohol CVD treatment shows higher mobility compared with that prepared by Ar/H<sub>2</sub> annealing.

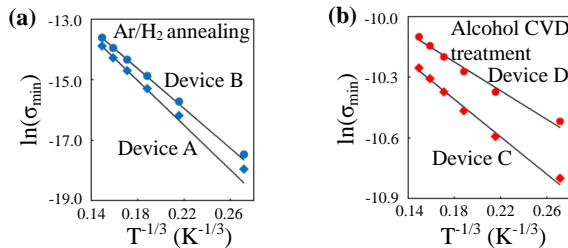


Fig. 4  $\ln(\sigma_{min})$  versus  $T^{-1/3}$  plots of rGO-FETs prepared by (a) Ar/H<sub>2</sub> annealing and (b) alcohol CVD treatment.

We demonstrate that the rGO-FET prepared by the alcohol CVD treatment is used as a pH sensor application. Figure 5 shows a plot of time-dependent source-drain current ( $I_{SD}$ ) for the rGO-FET in pH variation. The  $I_{SD}$  ob-

tained from the rGO-FET prepared by alcohol CVD treatment increases stepwise with pH from 4.0 to 8.2, and the  $I_{SD}$  is virtually constant at each pH value. This result indicates that the rGO channel detects the change of the charge around the rGO surface [1]. Moreover, the variation of  $I_{SD}$  with pH from 4.0 to 8.2 is the almost same value between the rGO-FET (0.3~1.0  $\mu$ A) and the FET (~4  $\mu$ A [1]) with graphene channel prepared by mechanical exfoliation of graphite crystal. Therefore we believe that the rGO-FET prepared by alcohol CVD treatment is useful for the sensor applications.

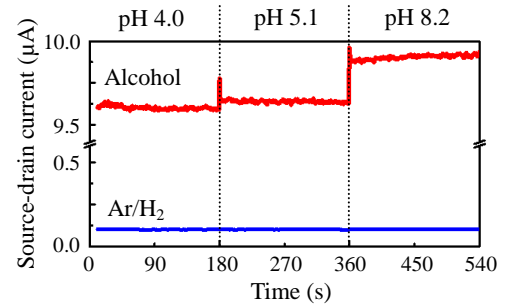


Fig. 5 Source-drain current obtained from the rGO-FETs versus time for pH values from 4.0 to 8.2.

#### 4. Summary

In this study, we fabricate the FET using rGO films prepared by alcohol CVD treatment and Ar/H<sub>2</sub> annealing as a comparison. The 2D band in Raman spectra from the rGO films treated by alcohol shows a sharp peak compared with that from the rGO films by Ar/H<sub>2</sub> annealing. In addition, the mobility in the rGO-FET with alcohol is higher than that in the rGO-FET with Ar/H<sub>2</sub> annealing. From the analysis of the carrier transport properties in the rGO-FETs, we found that the alcohol CVD treatment leads to the efficient restoration of graphitic structure like a recovery of sp<sub>2</sub> C=C bonds in addition to the reduction. We also demonstrate that the rGO-FET prepared by alcohol CVD treatment is useful for highly sensitive electrical sensors.

#### Acknowledgements

This work was partly supported by research assistance from Yazaki Memorial Foundation for Science and Technology in 2012.

#### References

- [1] Y. Ohno, K. Maehashi, Y. Yamashiro, and K. Matsumoto, *Nano Lett.* **9** (2009) 3318.
- [2] Q. He et al., *ACS Nano* **5** (2011) 5038.
- [3] C.-Y. Su, et al., *ACS Nano* **4** (2010) 5285.
- [4] R. Negishi, et al., *Thin Solid Films* **519**, (2011) 6447.
- [5] F. Schwierz: *Nature Nanotech.* **5** (2010) 487.
- [6] A.C. Ferrari, et al., *Phys. Rev. Lett.* **97** (2006) 187401.
- [7] A. Jorio, et al., *Raman Spectroscopy in Graphene Related System*, Wiley-VCH, Weinheim, Germany, (2011).
- [8] B. Krauss, et al., *Phys. Rev. B* **79** (2009) 165428-1.
- [9] R. Negishi, et al., *Jpn. J. Appl. Phys.*, (2012) in press.
- [10] A. B. Kaiser, et al., *Nano Lett.*, **9** (2009) 1787.