

# Direct transformation of a resist pattern into a graphene FET through interfacial graphitization of liquid gallium

Yosuke Miyazawa<sup>2</sup>, Ryuichi Ueki<sup>1,2</sup>, Mio Sasaki<sup>2</sup>, Takeshi Saito<sup>3</sup>, and Jun-ichi Fujita<sup>1,2</sup>

<sup>1</sup>PRESTO JST, Japan Science and Technology Co., Kawaguchi, Saitama 332-0012, Japan

<sup>2</sup>Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan

<sup>3</sup>AIST, Nanotube Research Center, Tsukuba 305-8565, Japan

Graphene is a promising material for electronic devices with high mobility and a tunable band gap; however, large-area production and controllability of a nanoscale channel structure is strongly required for future electronics applications. While many graphene devices are fabricated by etching exfoliated graphene and/or graphene films grown by the chemical vapor deposition (CVD), we found that an extremely thin resist pattern on silicon dioxide can be directly transformed into a graphene field effect transistor (FET) channel through interfacial graphitization of liquid gallium. These patterned graphene FETs show p-type field effect conductance characteristics and a maximum conductance modulation of 16% against an applied gate voltage range from  $-100$  to  $+100$  V at room temperature.

Although carbon is insoluble in gallium, we have found that liquid gallium is a good catalyst for graphene at the liquid–solid interface [1]. Figure 1 shows high-resolution transmission electron microscope (HR-TEM) images of a graphene film fabricated using a free-standing amorphous carbon film deposited on a Formvar resin film. Specimen preparation for TEM observation was performed as follows: Amorphous carbon with a certain thickness was deposited on a Formvar film by laser ablation. An amorphous carbon film was stamped on a liquid gallium surface and annealed at  $1000$  °C for 30 min under vacuum at about  $5 \times 10^{-4}$  Pa. Then the film was removed from the liquid gallium surface and the gallium was removed by soaking in dilute hydrochloric acid. The HR-TEM image of a 15-nm-thick graphitized film is shown in Fig. 1(a). The graphene stacking structure was observed at the edge of the folding part, and only about 2 nm of the outermost surface was graphitized. The graphene structure was wavy and had short continuity. There were, however, 4–6 graphene layers through the film. The crystallinity of graphene remarkably improved with a decrease in the initial amorphous carbon thickness, as shown in Fig. 1 (b) and (c). Annealing at  $1100$ °C produced the best graphene crystallinity, as shown in Fig. 1 (d). Raman spectra of 15- and 8-nm-thick films had broad G and D peaks and no 2D peak. In contrast, an almost pure graphene film fabricated using the smallest amount of amorphous carbon showed a clear 2D peak and well-separated D and G peaks (Fig. 2 (d)). We fabricated two types of graphene FETs: one was an FET channel made from a graphene fragment that was graphitized from a floating carbon film on gallium (Fig. 3(I)), and the other was a graphene channel made by direct graphitization of a resist pattern on silicon dioxide (Fig. 3(II)). A droplet of liquid gallium was placed on a resist pattern to fully cover the channel and was graphitized at  $1000$ °C under vacuum. Ti/Au was deposited for source and drain electrodes with about  $50$   $\mu\text{m}$  separation using a stencil mask. Typical FET characteristics measured by a back-gated FET configuration are shown in Fig. 4(I), and gate-voltage-dependent conductance showed p-type field effect characteristics, as shown in Fig. 4(II). The conductance modulation ratio observed at (a) 15-nm-thick film which means about 13 nm of amorphous carbon remained was very small at about 0.9 %, but the modulation ratio improved up to 6.7 % and 16% for (b) 8-nm-thick and (c) almost pure graphene sheet films. The maximum modulation ratio up to 40% was observed in a graphene fragment (d) that was annealed at  $1100$ °C. Decreasing the initial carbon thickness effectively improved the modulation ratio, where the remaining amorphous carbon presumably screened the gate electric field and suppressed the conductance modulation. The leakage current flowing into the amorphous carbon layer also deteriorated the modulation ratio. The graphene channel directly fabricated from an NEB resist pattern also shows FET characteristics having a modulation ratio of 2% in (e) with a channel

thickness of 15 nm after graphitization and 16% modulation in (f) with channel thickness of about 4 nm. We believe that the reduction in the initial thickness of amorphous carbon and/or resist thickness reduces the graphene layers to a single graphene layer and improves the FET characteristics. In addition, our direct graphitization technique for resist pattern is a new method for graphene device production and presumably has the potential to produce large scale integrated devices.

## REFERENCES

[1] J. Fujita, R. Ueki, Y. Miyazawa, T. Ichihashi, *J. Vac. Sci. Technol. B.* 27, 3063 (2009)

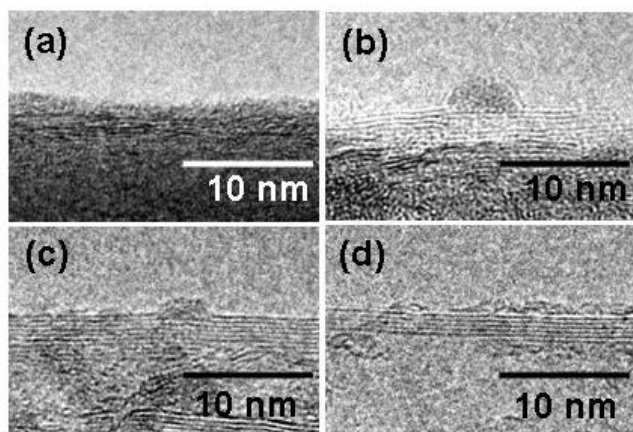


Figure 1. HR-TEM image of (a) a 15-nm-thick film, (b) an 8-nm-thick film, (c) almost pure graphene sheets annealed under vacuum at 1000 °C (d) and at 1100 °C.

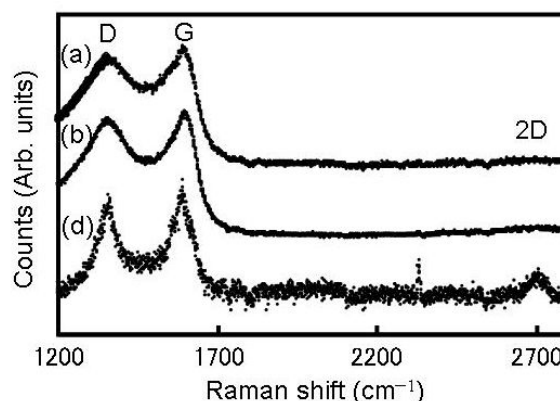


Figure 2. Raman spectrum of (a) a 15-nm-thick graphene film, (b) an 8-nm-thick film annealed at 1000 °C, and (d) almost pure graphene sheets annealed at 1100 °C.

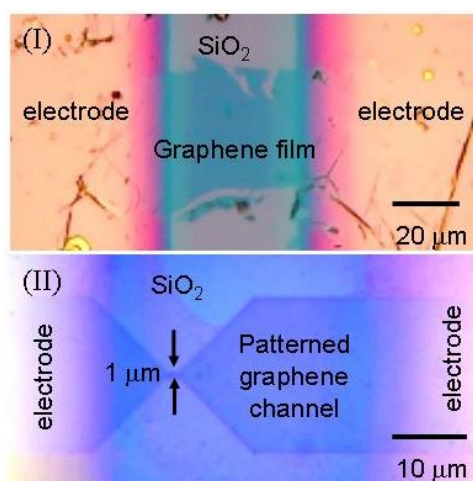


Figure 3. (I) Optical microscope image of FET channel made from a graphene fragment that was graphitized with a floated carbon film, (II) graphene channel made by a direct graphitization of a resist pattern

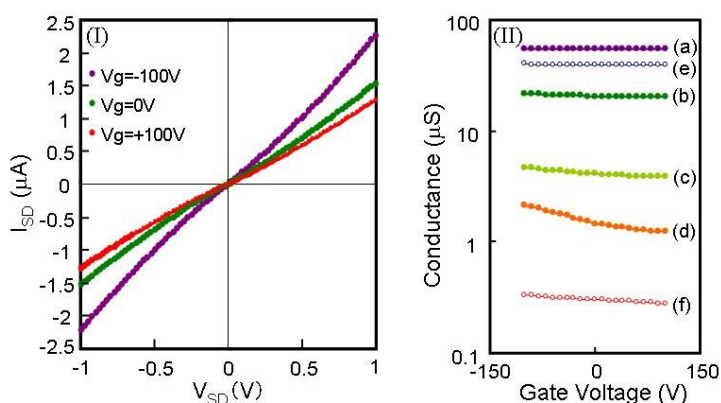


Figure 4. (I) I–V curves measured between source and drain electrodes. (II) Conductance modulation by gate voltage of (a) a 15-nm-thick film, (b) an 8-nm-thick film, (c) almost pure graphene sheets annealed at 1000 °C, (d) and at 1100°C, (e) a 15-nm-thick NEB resist pattern, (f) and a 4-nm-thick NEB resist pattern