High-Mobility Graphene Nanoribbons Prepared Using Polystyrene Dip-Pen Nanolithography

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ABSTRACT: Graphene nanoribbons (GNRs) are fabricated by dip-pen nanolithography and polystyrene etching techniques on a SrTiO3/Nb-doped SrTiO3 substrate. A GNR field-effect transistor (FET) shows bipolar FET behavior with a high mobility and low operation voltage at room temperature because of the atomically flat surface and the large dielectric constant of the insulating SrTiO3 layer, respectively.

Graphene nanoribbons (GNRs, where graphene is a mono-layer of graphite) have attracted much attention recently because of their novel electronic and spin-involved properties. In particular, a GNR with a narrow width and atomically smooth edges is a promising candidate as a field-effect transistor (FET) with fast switching speed and high carrier mobility for next-generation electronics.

The fabrication of GNRs has been demonstrated using various techniques such as lithographic patterning, chemical, sonochemical, unzipping nanotube, cyclodehydrogenation, local thermal reduction, electrochemical reduction, and organic wire mask methods. Jiao et al. recently demonstrated high-quality GNR FETs on a SiO2/p-doped Si substrate with a mobility up to 1500 cm2/(V·s). Nevertheless, the surface roughness and low dielectric constant (low-k) of SiO2 may limit the quality of GNR FETs in terms of high mobility and low bias operation of a back gate, respectively. Therefore, insulating materials with both an ultraflat surface and high-k are required for high-quality GNR FETs.

Dip-pen nanolithography (DPN) is a powerful technique to fabricate nanostructures such as nanowires and nanodots with precise control of their position and size. The combination of DPN and etching techniques with polystyrene (PS) can provide a new method to fabricate GNRs in a controlled way. In this Communication, we demonstrate a scalable, high-quality GNR FET fabricated on a SrTiO3/Nb-doped SrTiO3 substrate using a PS DPN method.

GNRs were deposited by a mechanical exfoliation method on epitaxial SrTiO3 thin films deposited by pulsed laser deposition techniques using a commercially available 1-in.-diameter SrTiO3 target. Five-nanometer-thick SrTiO3 thin films were evaporated on conducting Nb-doped SrTiO3 substrates (Nb doping level of 1 wt% and resistivity of 0.001 Ω·cm) by pulsed laser beams at a base pressure of about 10−7 Torr. The temperature of the samples and oxygen partial pressure were maintained at 800 °C and 0.1 mTorr, respectively. To prepare an atomically flat surface of the Nb-doped SrTiO3 substrates, the SrTiO3 substrates were etched in a dilute HF solution and annealed at 1000 °C for 1 h.

Figure 1 shows a schematic of the sequential PS DPN processes used for the fabrication of the GNRs. PS nanorods were deposited by a DPN method onto an exfoliated graphene sheet on a SrTiO3/Nb-doped SrTiO3 substrate (Figure 1a). A Si3N4 DPN tip with a radius of less than 10 nm and a PS toluene solution were used. The speed of the DPN tip was 50–300 nm/s, and the widths of the corresponding PS nanorods were 150 to 30 nm (see Supporting Information). The PS nanorods were dried and annealed in a vacuum oven for 90 min at 40 °C and for 30 min at 120 °C, respectively. Note that the glass transition temperature of the PS nanorods is about 100 °C. Figure 1b shows the process of exposure to oxygen plasma to remove the graphene sheet except for the GNR pattern covered with PS nanorods. The power and exposure time of the oxygen plasma were 80 W and 30 s, respectively, at an operation pressure of 10 mTorr. As the PS structures are more resistant to oxygen plasma than the graphene sheet, only PS nanorods and the GNR below remained on the substrate after oxygen plasma exposure (Figure 1c). Finally, all of the PS nanorods were removed by successive serial sonication processes using acetone, ethanol, and distilled water. Thereby, only GNRs were formed on the substrate (Figure 1d).

Figure 2a shows an atomic force microscopy (AFM) image of a graphene sheet on a SrTiO3 substrate where the lateral stripes indicate the roughness of the surface of the SrTiO3 substrate (a surface roughness of 0.2 nm). The graphene sheet (light milky color), whose edge is underlined by a dotted line, covers the upper part of the image window. The graphene sheet was confirmed to be single-layered using Raman spectroscopy, as shown in Figure 2b, where the only Raman shift peak was observed at about 2700 cm−1. Multilayer graphene sheets show not only a main peak but also satellite peaks in the Raman shift peak area. Figure 2c,d shows AFM images of PS nanorods (white), which had widths down to 30 nm, made by the DPN method on the graphene sheet and GNRs (light milky color) with widths down to 25 nm covered by the PS nanorods, respectively. Using the etching processes described above...
with oxygen plasma and chemicals, the GNRs were well formed according to the designed PS pattern.

A FET with a GNR channel was formed on a SrTiO$_3$/Nb-doped SrTiO$_3$ substrate with vertical (sample A) and parallel (sample B) orientations with respect to terrace edges using the DPN method (Figure 3a,b), where the conducting Nb-doped SrTiO$_3$ substrate was used as a back gate. A source (drain) electrode consisting of a Pb nanodot and a Au nanowire were made by DPN processes. For ohmic contact between the GNR and the Au nanowire as the source (drain), a Pb nanodot was predeposited at the left (right) end of the GNR using the DPN method with a PbCl$_2$ solution, solidified in a vacuum oven at 40°C for 60 min, and annealed at 200°C for 30 min. Two Au nanowires over the Pb nanodots were formed using the DPN method with a AuCl$_4$ solution, solidified in a vacuum oven at 40°C for 60 min, and annealed at 250°C for 30 min. Figure 3c,d shows AFM images of a GNR labeled with sample A without and with the corresponding source and drain, respectively. In Figure 3d, the larger dot of the source (drain) connected with the left (right) end of the GNR indicates a Pb/Au dot.

Figure 4a shows a schematic side view of a GNR FET where the GNR channel is connected to the source and drain. Here, the SrTiO$_3$ substrate and Nb-doped SrTiO$_3$ substrate are used as an insulating layer and a back gate, respectively. The white dotted lines indicate the graphene boundary.

Figure 4b shows bipolar FET characteristics of the current $I$ as a function of the applied gate voltage $V_g$, where the conduction carrier is an electron (hole) for a positive (negative) $V_g$.

Hereafter, we estimate an average mobility $\mu_{n(h)}$ in the GNR channel, where $n(h)$ indicates an electron (hole). The average mobility of $\mu_{n(h)}$ is about 3150 ($\pm$2740) cm$^2$/V·s at 300 K. We used the formula

$$\mu_{n(h)} = \frac{g_{n(h)}L}{2WV_{sd}C_g}$$

where $g_{n(h)}$ is the differential conductance ($=dI/dV_g$), $L$ is the channel length of the GNR, $W$ is the width of the GNR, $V_{sd}$ is the applied voltage between the source and drain, and $C_g$ is the average conductance with respect to $V_g$, which is derived from numerical data. Note that the maximum mobility $\mu_{n(h)}$ in the GNR channel is about 4900 ($\pm$4000) cm$^2$/V·s at 300 K, where $g_{n(h)}$ in the above formula is replaced by the differential conductance $g_m$ (which is derived from numerical derivative).
In conclusion, we fabricated a graphene nanoribbon field effect transistor on a SrTiO$_3$/Nb-doped SrTiO$_3$ substrate by combining dip-pen nanolithography and polystyrene etching techniques. The GNR FET demonstrated bipolar FET behavior with a high mobility and low operating voltage due to the ultraflat surface and large dielectric constant of the insulating SrTiO$_3$ layer, respectively. We want to emphasize that the combination of the DPN and polystyrene etching techniques makes it possible to fabricate the scalable, high-quality GNR FET arrays.

**ASSOCIATED CONTENT**

Supporting Information. S1, nanorod width as a function of the dip-pen speed; S2, cross section of the SrTiO$_3$ surface; S3, cross section of the GNR; S4, current—voltage characteristics for various gate voltages; S5, complete refs 18, 20, and 21; S6, FET performance of sample B. This material is available free of charge via the Internet at http://pubs.acs.org.

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