Characterization of Graphene Segregated on Ni

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ABSTRACT

We report a surface segregation approach to synthesize high quality graphene films on Ni under ambient pressure. Graphene films were segregated from Ni surfaces by carbon dissolving at high temperature and cooling down with cooling rates ~10 °C/s. Transmission electron microscopy and Raman spectra studies indicated that these graphene films have high quality crystalline structure and controllable thickness. Graphene films were transferred to insulating substrates by wet etching and were found to maintain their high quality. Electronic properties of the graphene layers were also explored.

Keywords: graphene, segregation, transfer.

1 INTRODUCTION

Graphene [1] has attracted tremendous recent interests as an electronic material with exceptional properties that may enable a new generation of nanoelectronics and functional devices. However, the large-scale synthesis of a high-quality graphene remains a significant challenge and represents the bottleneck for its application in post-silicon electronics. Recently, more efforts have been made to synthesize graphene films through surface segregation on metals, especially on polycrystalline Ni substrates [2-4]. Ni has several advantages in synthesis of graphene films by the surface segregation, such as enough carbon solubility, limited carbide phase, and high surface mobility of carbon atoms [5]. In this article, we report our recent work on the synthesis and characterization of graphene films on polycrystalline Ni substrates.

2 EXPERIMENTS

In our experiments, polycrystalline Ni foils with thickness of 0.5 mm and purity >99.99% from Alfa Aesar were cut into 5×5 mm^2 pieces, followed by a mechanical polish. Precursor gases were CH_4:H_2:Ar=0.15:1:2 with a total gas flow rate of 315 sccm and pressure at 1 atm and H_2 was introduced 1 hour before the CH_4 and Ar. Carbon dissolution time is 20 min at 1000 °C. Samples were cooled down by mechanically pushing the sample holder to a lower temperature (in the range of 30–500 °C) zone in Ar atmosphere. Cooling rates were monitored by a thermocouple on the sample holder. The cooling rate ~10 °C/s was employed for segregating graphene films. The structural characteristics of graphene formed on Ni substrates were studied by transmission electron microscopy (TEM) and Raman spectroscopy excited by an Argon laser operating at 514 nm.

Transferring graphene from metal substrates to insulators is a critical step for realizing electronic applications. In this research, two methods were employed for transferring graphene films from Ni substrates to insulator. In the first method, polymerized siloxane was used as the media to transfer 5×5 mm^2 graphene as grown on a Ni substrate to a glass plate. After graphene synthesis on Ni, a thin layer of silicone was applied on the graphene film, then covered with a glass plate to form a four layer sandwich structure (Ni/graphene/ polymerized siloxane /glass). After a 24 h cure, the silicone rubber was solidified and the Ni substrate was etched away with diluted HNO_3 solution. In the second method, the Ni substrate with as-grown films is placed in an acid solution, where the graphene film detaches from Ni and floats on top of the liquid surface. The film can then be simply skimmed out by the insulator substrate onto which it is transferred.

To characterize the electronic properties of the transferred graphene films, we have patterned them into relatively large-size Hall-bars with multiple contact electrodes (Cr/Au). The devices were fabricated by standard optical lithography, plasma etching and metal deposition. We have performed field effect (transistor) measurements at various temperatures, where the heavily doped Si wafer is used as the back gate.

3 RESULTS AND DISCUSSIONS

Samples for TEM were prepared by detaching the graphene films from Ni in HNO_3 solution, followed by rinsing with de-ionized water. The films float on water owing to the hydrophobic nature of graphene. The films, found to be almost transparent, can nonetheless be distinguished from water by their different reflectivity. Copper grids with Famvar films were used to skim out the graphene films, which were then dried in air naturally. In Fig. 1a, the red dash lines highlight edges of a graphene film, with step features that can be attributed to graphene cracking along certain crystalline directions. The selected area electron diffraction (SAED) pattern along [001] direction clearly shows the graphite lattice structure, and typically 3–4 layers of graphene were observed at the wrinkles and edges of the films as shown by the high resolution TEM (HRTEM) image

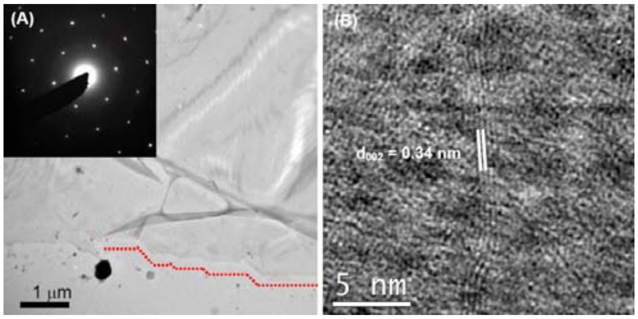

Figure 1: TEM images of graphene. (a) Low magnification image with step shaped edges, highlighted by red dash lines. Inset shows the SAED pattern of the graphene film. (b) HRTEM image of wrinkles in the graphene film, apparently of 3–4 layers.

In Fig. 2, the blue curve is the Raman spectrum acquired from the graphene segregated on Ni surface with a cooling rate of 10 °C/s, the red curve is the spectrum acquired from the polymerized siloxane with two peaks around 2900–3000 cm^{-1}, and the black curve is that from the transferred graphene. Characteristic features in the spectra of the pretransferred graphene are maintained in the spectra of the post-transferred graphene. Polymerized siloxane peaks can also be seen in the spectra from the transferred graphene on the glass plate, probably because the graphene layer is so thin that the Raman signal from the polymerized siloxane can be detected.

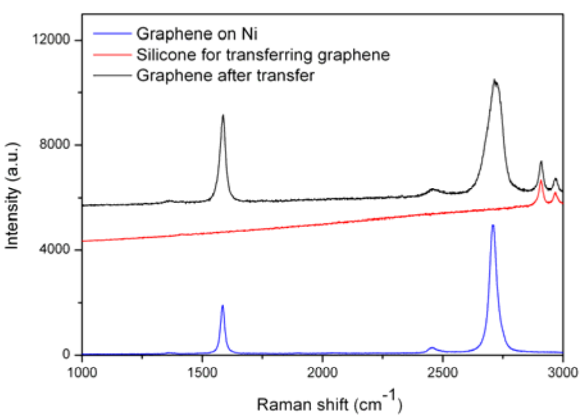

Figure 2: Raman spectra of segregated carbon at Ni surface with different cooling rates.

Fig. 3 shows 4-terminal resistance measured in a device at low temperature (T = 10 K), where the back gate voltage (V_{gate}) is varied between -40 V to 50 V. An ambi-polar field effect is evident, where the resistance can be modulated by ~20%, with its peak ("charge-neutral point") occurring at ~10 V. Similar field effects are observable up to room temperature, though at low T, larger range of V_{gate} can be accessed without gate leakage.

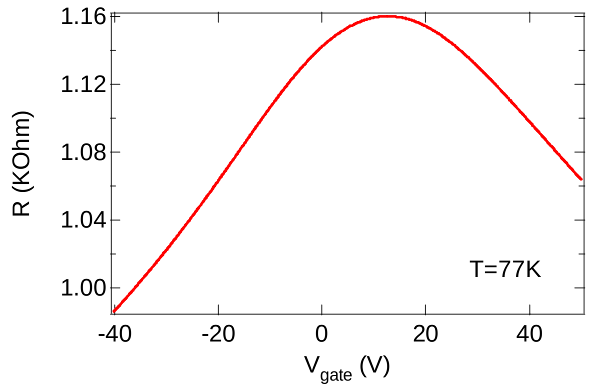

Figure 3: Four-terminal resistance as a function of back gate voltage V_{gate}, showing the electric field effect.

4 SUMMARY

We synthesized few-layer high quality graphene films in large area and transferred them to insulator substrates. The graphene films keep their high quality after the transfer, which was confirmed by TEM and Raman spectrum. These film shows the electric field effect.

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