Abstract—The defect integration of Reduced Graphene Oxide (RGO) sheets based on dielectrophoretic (DEP) assembly has been experimentally studied in this paper. Then an Atomic Force Microscopy (AFM) based mechanical cutting method is firstly proposed to form line defects in RGO sheets. Based on these two methods, the experimental studies of the effect of line defects on RGO are explored. The electric transport measurement results show that the resistance of the defected RGO generally increases due to the Anderson localization, which provide a solid prove to the theoretical studies of the influence of defects on the electrical properties of RGO.

I. INTRODUCTION

Graphene has attracted tremendous attentions worldwide in recent years [1, 2]. Although graphene based FET [3, 4], gas sensors [5], solar cells [6] and so on have been successfully demonstrated and exhibit amazing novel properties, the structural defects induced by fabricated in experiment will significantly affect the electronic properties of these devices. Therefore, a study of defects in graphene is critically important. In the past phase of research on defects in graphene, many attentions have been concentrated on theoretical studies [7-13]. However, the direct observation of these topological defects in graphene is quite limited [14-16]. Especially the experimental study of the effect of defects on graphene, so far there is one published work [17]. In this work, defects were introduced by wet chemical treatment, which is not controllable. Wet chemical treatment is not able to induce defects in specific location and other locations without damage. In addition, the current-voltage measurement process is quite complicated. At the outset, graphene sheets are electrically contacted with an Omniprobe nano-manipulator inside a focused ion beam/scanning electron microscope (FIB/SEM). Then the tip of the manipulator is maneuvered to make contact with the graphene sheets. All the movements should be carefully monitored in real time by continuously scanning the electron beam in the FIB/SEM. In this paper, the effect of line defects on RGO sheets has been experimentally integrated. To approach this goal, two methods have been developed.

Firstly, we should assemble GO sheets to the electrodes. Dielectrophoresis (DEP) has emerged as a powerful technique for the selective deposition or directed movement of micro- and nanoscale objects in nonuniform electric fields. It has been applied to assembly of nanoparticles [18], carbon nanotubes [19], DNA [20], and cells [21]. Recently, graphene and GO sheets have been successfully assembled by DEP [22-25]. Therefore, we will also use this sample method to assemble GO sheets to the electrodes. Then, line defects will be induced in the GO junction.

To date, several line defects inducing methods have been proposed, such as Catalytic Cutting Technique (CCT), SPM based Electric Field Tailoring Technique (SEFTT), Energy Beam Cutting method (EEC) and so on. CCT uses nanometer-sized metal particles (nickel [26], Fe [27]) or non-metal particles (SiO$_2$ [28]) as a knife that cuts with nanoscale precision in hydrogen atmosphere at high temperatures. The main shortcoming of this method is that the cutting process is not controllable, and it is very difficult to cut graphene into desired geometries by this kind of method. SEFTT mainly includes two techniques: AFM based anodic oxidation [29] and STM based lithography [30]. When cutting graphene with the SEFTT method, the fabrication result highly depends on the thickness of the water film on the samples. The slightly change of the environment may lead to an unpredicted cutting result. In addition, the size of the electric field generated by SPM is often much bigger than the tip diameters, so it is very difficult to obtain high manufacture precision with the SEFTT technology. The EEC method includes ion beam lithography [31], plasma etching [32], and electron beam etching [33] and so on. But all these technique not only require extremely expensive instrument, but also are easy to damage or dope the graphene samples. In this paper, an AFM based mechanical cutting method is firstly...
developed to introduce line defects in RGO. This method is highly controllable and simple to be performed. It needs not any strict conditions and can be carried out in ordinary environment.

II. MATERIALS AND METHODS

A. Graphene Oxide Sample

Stable aqueous dispersions of graphene oxide (GO) was obtained from Institute of Metal Research (IMR), Chinese Academy of Sciences. The original solution is characterized by a Multimode AFM (Veco Inc., Santa Barbara, CA, USA) operated in tapping mode(Fig.1a). As shown in Fig.1a, the concentration of the original solution is larger. GO layers overlap and form folds. Therefore, the original aqueous GO solution was diluted by 1:1 and then sonicated for 10 minutes at 59Hz in the Ultrasonic Oscillator (SK5210LHC). One drop of 2μl diluted solution is drawn using a pipette with range from 0μl to 2μl and then dropped on the freshly cleaved mica. The prepared sample has been dried at room temperature and then imaged in tapping mode with AFM. Fig.1b shows a tapping-mode AFM image of the GO sheets, along with their height analysis(Fig.1c). More than 90% of the sheets were monolayer GO, the height of which is ~1nm. This height is similar to monolayer GO sheets heights reported in previous studies [34, 35].

B. Dielectrophoretic Assembly and Reduction of Graphene Oxide

A small drop (0.5μl) of the aqueous GO solution was placed onto a chip pipette with range from 0μl to 2μl. Then a sinusoidal potential difference (5-10Vp at 1MHz) was applied to the bias electrode by an arbitrary function generator (Escort, EGC-3230). After 10-40s the generator was switched off, the droplet was dried at room temperature. Then the chips were characterized by AFM. At last, GO sheets were reduced by chemical reduction. The chips with GO sheets bridged gaps were dipped in 55% hydroiodic (HI) acid for 3-5 minutes at 100 °C[36], which is performed by IMR.

Fig.2 depicts a schematic of the DEP setup. The electrodes used here were fabricated by standard photolithography and lift-off techniques. The gold electrodes have a thickness of 40nm and a gap of 1-2.5μm between them. The thickness of SiO2 is around 285nm, as depicted in Fig. 3.
C. Formation of Line Defects by AFM

The line defects were induced by AFM scratching techniques. The tip is scanned under strong loading forces to remove the substrate or resist. Normal antimony doped tips (type: MPP-11100-10 with a radius of 8-12nm) with a normal spring constant 40 N/m (Veeco Company), the structure as shown in Fig.4. In contact mode, using open-feedback mode, GO sheets were cut automatically with NanoMan software of AFM by setting different deflection setpoints, which adjust the cutting force, as shown in Fig.5.

Fig.4 The image of tapping tip MPP-11100. (a) Probe cantilever. (b) Probe tip. The cantilever width $w$ is 35 $\mu$m and length $l$ is 25 $\mu$m. Tip height $h$ is 25 $\mu$m, and the thickness of the cantilever $t$ is 4 $\mu$m.

III. Results

Fig.6 shows formation of line defects in GO sheets by AFM nanocutting. The tapping tip MPP-11100 of the AFM has been moved in contact mode with a constant deflection setpoint. The width of the resulted trench can be seen in Fig.6d, which is around 45nm. The width here is full width at half maximum. This is because that the width measured by AFM is usually wider than the true width of the sample.

Fig.7a presents the tapping-mode AFM image of GO sheets deposited by DEP along with their height analysis (Fig.7b). The thickness is around 16nm. After assembly, the chip of GO sheets bridged gaps was reduced by chemical reduction, as shown in Fig.7c. It can be seen that the chip become more clearly than before reduction. The reason is that the chip is dipped in HI acid for several minutes and the impurity is washed away. Fig.7d shows the thickness is down to about 7nm. Current-voltage (I-V) measurements at room temperature and ambient condition have been presented (Fig7e). The total electrical resistance, consisting of the sheet and contact resistance, decrease from $R = 173.8 \, \text{M$\Omega$}$ to $R = 221 \, \text{k$\Omega$}$. Good Ohmic contacts are verified by the linear relationships.

The effect of line defects on the electrical properties of the RGO junction has been investigated. After reduction, line defects were induced by cutting using an AFM. Then current-voltage measurements were performed. It’s found that all RGO devices show electrical performance degradation after defects induced, which are consistent with the theoretical prediction as shown in Fig.8. In Fig.8a and Fig.8b, when a horizontal line defect was formed in the RGO sheet, the resistance is from 397.4 k$\Omega$ down to 1.9730 M$\Omega$. When a vertical line defect was introduced, the resistance increases from 61.2 k$\Omega$ to 194.5 k$\Omega$ as shown in Fig.8c and Fig.8d.
Fig. 6 Height images of GO after cutting on mica in AFM tapping mode. (a) Scan size: 11.3 μm×11.3 μm. Data scale: 30 nm. (b) Scan size: 6.9 μm×6.9 μm. Data scale: 20 nm. (c) Scan size: 8.0 μm×8.0 μm. Data scale: 50 nm. (d) Scan size: 6.4 μm×6.4 μm. Data scale: 30 nm. (e) Scan size: 5.8 μm×5.8 μm. Data scale: 30 nm. (d) The blue line indicates the width of the trench in (e) is 45±0.2 nm.

Fig. 7 Current-voltage measurement of the junction before and after reduction. (a) AFM image of GO junction before reduction. Scan size is 10.0 μm×10.0 μm and data scale is 150 nm. (b) The height trace of (a), displaying the sheet thickness in the channel is around 16 nm. (b) AFM image of GO junction after reduction. Scan size is 10.0 μm×10.0 μm and data scale is 200 nm. (d) The height trace of (a). The thickness is down to 5.0 nm. (e) I-V measurement of the GO junction before and after reduction, exhibiting an electrical resistance from $R=173.8 \Omega$ down to $R=221 \ k\Omega$. 

1077
In conclusion, we report a DEP based deterministic way to assembly GO into the gap of micro-electrode with controllable layers. These results make high-quality and controllable assemblies of graphene based nanodevices become possible, which may lead to a rapid development for pushing the application of graphene into the real world. In addition, an AFM based mechanical cutting method is firstly developed to form defects in RGO sheets. The amazing advantage of this method is that it can realize massive fabrication through the parallel multi-tip technology, which makes it possible to fabricate defects in graphene at low cost and high efficiency, opens a way to large-scale nanomanufacture. Furthermore, the effect of line defects on RGO sheet has been experimentally investigated based on these two methods, which shows that most of the resistance increases with the introduction of defects. This is the first experimental report to show the influence of introduced defect on the electronic properties of RGO, and provide a solid prove to the theoretical studies.

REFERENCES

