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Welcome Message

Conference Information

Program at a Glance

Table of Contents

Author Index

IEEE Catalog Number: CFP13NAN-CDR
ISBN: 978-1-4799-0675-8

13:30-13:45	ThC5.1
Feasibility Study for Development of a Carbon-Based MEMS/NEMS Using HOPG and a MEMS Fabrication Process, pp. 1018-1021.	
Sone, Junji	Tokyo Pol. Univ.
13:45-14:00	ThC5.2
A Hands-On Laboratory for Teaching Microfabrication, pp. 1022-1025.	
Marti, James	Univ. of Minnesota
Sibakoti, Mandip	Univ. of Minnesota
Jalali, Mayam	Univ. of Minnesota
Campbell, Stephen	Univ. of Minnesota
14:00-14:15	ThC5.3
Single Layer Graphene Nano-Patterning Based on Local Anodic Lithography in Ambient Conditions, pp. 1026-1029.	
WU, XUAN	MEMS and Nanotechnology Lab. School of Mechanical Systems
Lee, Dong-weon	Chonnam National Univ.
14:15-14:30	ThC5.4
Fabrication of Large-Scaled Synergetic Silicon Nanowire Arrays Using Metal-Assisted Chemical Etching for Solar Cell Applications, pp. 1030-1033.	
Liu, Chien-Ting	National Taiwan Univ.
Hsueh, Chen-Chih	National Taiwan Univ.
Subramani, Thiyagu	National Taiwan Univ.
Lin, Tzu-Ching	National Taiwan Univ.
Lin, Ching-fuh	National Taiwan Univ.
14:30-14:45	ThC5.5
AC Electrodeposition and Plasmonic Properties of Silver Nanowires in Porous Anodic Alumina Templates, pp. 1034-1037.	
Alemu, Negash	State Key Lab. of Solidification Processing, Northwestern
Chen, Fuyi	State Key Lab. of Solidification Processing, Northwestern
Zhang, Jinsheng	State Key Lab. of Solidification Processing, Northwestern
14:45-15:00	ThC5.6
Growth of ZnO Nanowires on Flexible Polyimide Substrates, pp. 1038-1041.	
Gao, Yongji	Peking Univ.
Zhang, Shouldhe	Peking Univ.
Zhang, Haixia	Peking Univ.
15:00-15:15	ThC5.7
Fabrication of Aperiodic Subwavelength Nanostructures by Grayscale Interference Lithography (GIL), pp. 1042-1045.	
Choi, Hyungryul	Massachusetts Inst. of Tech.
Kim, Jeong-Gil	Massachusetts Inst. of Tech.
Barbastathis, George	Massachusetts Inst. of Tech.
15:15-15:30	ThC5.8
Embedded Seal Cavity Preparation Technology Based on the Zirconia, pp. 1046-1049.	
LI, CHEN	north Univ. of china

ThD1	Jade I
Nanomaterials: Nanomaterial/nanoparticles Synthesis III (Oral Session)	
Chair: Wang, Xinnan	North Dakota State Univ.
Co-Chair: Tao, Xinyong	Zhejiang Univ. of Tech.
16:00-16:15	ThD1.1
Electrochemical Studies of Carbon Coated LiFePO4 Doped with Tungsten, pp. 1050-1053.	
Arava, Hanu	Texas State Univ.
Fang, Hui	Sam Houston State Univ.
Zhang, Lu-Lu	Huazhong Univ. of Science and Tech.
Liang, Gan	Sam Houston State Univ.
Hill, Jacob	Sam Houston State Univ.
16:15-16:30	ThD1.2
Two-Stage Model of Quantum Cones Formation on a Surface of Semiconductors by Laser Radiation, pp. 1054-1057.	
Medvids, Arturs	Riga Tech. Univ.
Onufrijevs, Pavels	Riga Tech. Univ.
Dauksta, Edvins	Riga Tech. Univ.

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Single Layer Graphene Nano-Patterning Based on Local Anodic Lithography in Ambient Conditions*

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***Abstract*—In this paper, a systematic study of single layer graphene nano-patterning based on local anodic oxidation (LAO) lithography has been carried out using the atomic force microscope (AFM). Process parameters such as tip scan rate, applied tip bias voltage and their relationship to pattern sizes for local oxidation of graphene sheet were observed and optimized. Graphene oxide with minimum width of 49 nm was realized using the LAO technique in ambient condition. The results indicate that higher scanning rate and lower bias voltage are desired to increase the resolution of nano-patterns, which is significantly important for fabricating graphene-based nanoscale electric devices.**

I. Introduction

Graphene, a single atomic layer of graphite, has received much attention as one of the best alternative materials for next generation semiconductor devices, due to its excellent mechanical (~1.0 TPa) and electrical (200,000 $cm^2v^{-1}s^{-1}$) properties [1]–[4]. Consequently, nano-patterning techniques to form graphene surfaces into any desired shape possess a profound significance for nanodevice applications [5], [6]. In this case, a combined process of electron beam (EB) lithography and O_2 plasma etching was developed to make graphene-based nano-devices [7], [8]. Unfortunately, when nanodevices are processed by a combination of EB lithography and O_2 plasma etching, the physical properties of the graphene can be affected by the scattering effect. These were caused by the damage within the lattice and the roughly etched surface of the graphene, at a level higher than the atomic level [9]. To solve these problems, local anodic oxidation (LAO) lithography using atomic force microscope (AFM) was utilized for the fabrication of graphene nanodevices based on semiconductors [10], [11].

A local anodic oxidation (LAO) method based on AFM has been suggested as a new graphene patterning method [12]–[14]. The advantages of the LAO method include its abilities to pattern a surface to nanometer resolution and to characterize the fabricated nano-device after the nano-patterning process. Also, this method eliminates several process steps, such as photolithography and etching etc. Further, the method does not affect the physical properties of graphene material during the patterning process, because the process is carried out in an ambient environment, through an electro-chemical reaction only. Neubeck *et al.* [15] have reported the result of scanning probe lithography on graphene. They also employed the LAO technique to avoid any contamination of graphene surface during the patterning process. An interesting point to notes is the fact that applying LAO technique to graphene resulted in either etching lines or creating a stable oxide. However, the process parameters have large influence on the created graphene oxide nano-pattern, which directly decide the resolution of nano-pattern [16]. Therefore, to study and optimize the process parameters during graphene oxidation is quite significant for nano-patterning technology.

In this paper, we conducted local anodic lithography on the graphene surface by contact-mode AFM in ambient environment. Different scan rate and tip bias voltage was utilized to investigate the relationship between the process parameters and the growth size of graphene oxide. Based on the optimization of process parameters, various patterns of graphene oxide with nanoscale was realized on the surface of a CVD single layer graphene. The resolution of the graphene oxide line was down to 49 nm.

II. The Synthesis of Graphene Oxide by LAO

Graphene oxide (GO) is covalently functionalized graphene with oxygen-containing functional groups which consists of a cluster of sp^2-hybridized carbons in a sp^3-hybridized carbon matrix [17]. Owing to its insulating characteristic and pronounced mechanical properties, by integrating with graphene, GO has been regarded as a base material for next-generation thin and flexible electronic and optoelectronic devices [18]–[20]. Therefore, to fabricate nano-patterned GO on graphene surface using LAO technology is quite significant for various nanoscale applications.

During the LAO, a relative humidity is necessary, which can provide a thin water layer between the AFM probe and the graphene surface. When a negative DC bias voltage is applied to the AFM tip, as Fig. 1 shows, the oxides grow on graphene surface which act as an anode. There is a threshold voltage at which the anodic oxidation starts. A high electric field ($E > 10^7$ V/m) can decompose water molecules adsorbed on graphene surface into ions (e.g., H^+, OH^-, and O^{2-}). Negatively charged oxygen-containing radicals (e.g., OH^- and O^{2-}) can be attracted to the anode and contribute to the formation of surface oxides and also to the successive growth of the oxide underneath [21]. In this way, we could create nanopatterned graphene oxide on the graphene surface, which can be used to fabricate nanoscale electric devices.

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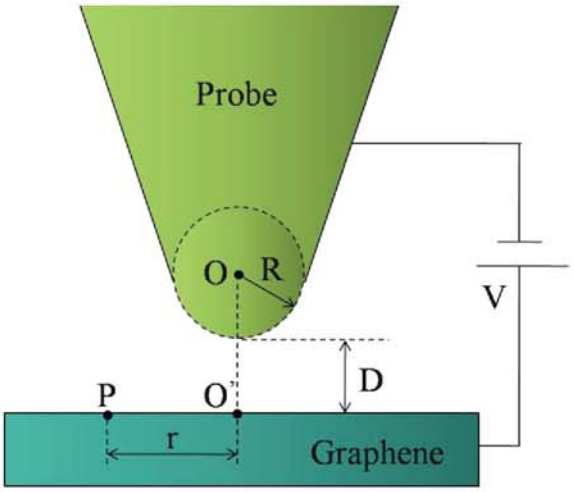


Fig. 1. Schematic of local anodic lithography on graphene surface.

According to the dimension of the AFM probe based on electric field emission theory, the electric field intensity of point P on the graphene surface can be expressed as [22]:

$$E(r) = E_O \cdot [1 + (\frac{r}{R+D})^2]^{-\frac{3}{2}} \quad (1)$$

where E_O is the electric field intensity at the point O' on the substrate (it is the projection of point O); R is the radius of the AFM tip; D is the distance between AFM tip and the graphene surface. We can obtain E_O using the following formula:

$$E_O = V \cdot \frac{R(R+2D)}{D(R+D)^2} \quad (2)$$

where V is the bias voltage applied on the AFM probe.

Therefore, the distribution of electric field intensity on the graphene surface can be achieved. Since we used a contact mode to conduct LAO, the distance D is 0.5 nm. Additionally, the radius of AFM probe is 35 nm in our experiment. Based on these parameters, the distribution of electric field intensity around the AFM tip with different bias voltage is drawn in Fig. 2. It can be seen that a near position to the tip and higher bias voltage can lead to higher electric field intensity, which is more beneficial for graphene oxide generation. In the experiment, the scanning point can be considered as the nearest position to the tip. For this reason, the scanning trace possesses the highest electric field intensity compared with other area, which could ensure that only the scanning trace can generate graphene oxide nanopattern during the AFM probe scanning in LAO.

Based on the above theoretical analysis, a series of experiment were developed to optimize the process parameters during graphene nano-patterning.

III. Experiment and Results

In the experiment, a commercial graphene chemical vapor deposition (CVD) single layer graphene on 285 nm-thickness SiO_2 substrate (Graphene Supermarket, USA) was used for LAO lithography. The LAO lithography was performed in

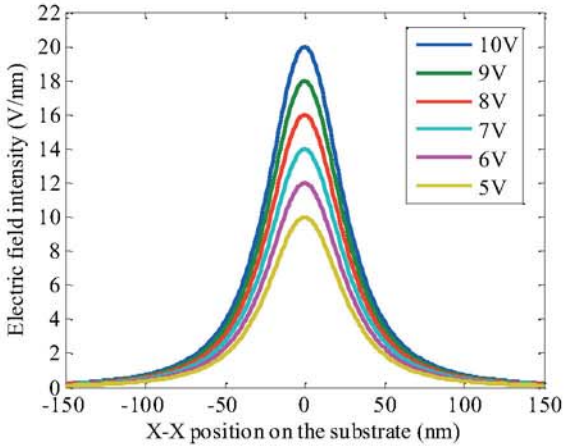


Fig. 2. The distribution of electric field intensity around the AFM tip.

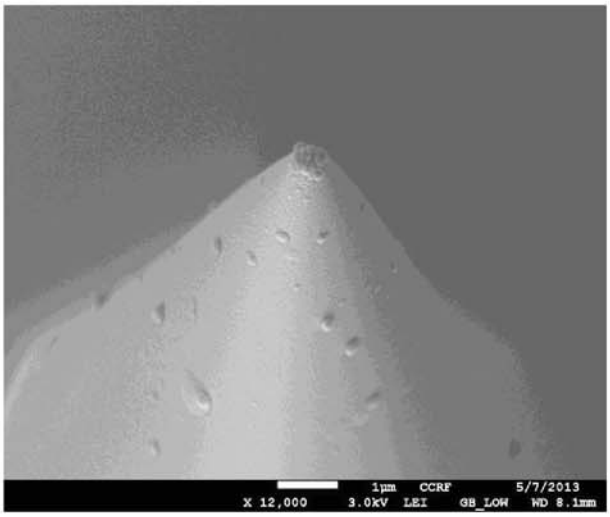
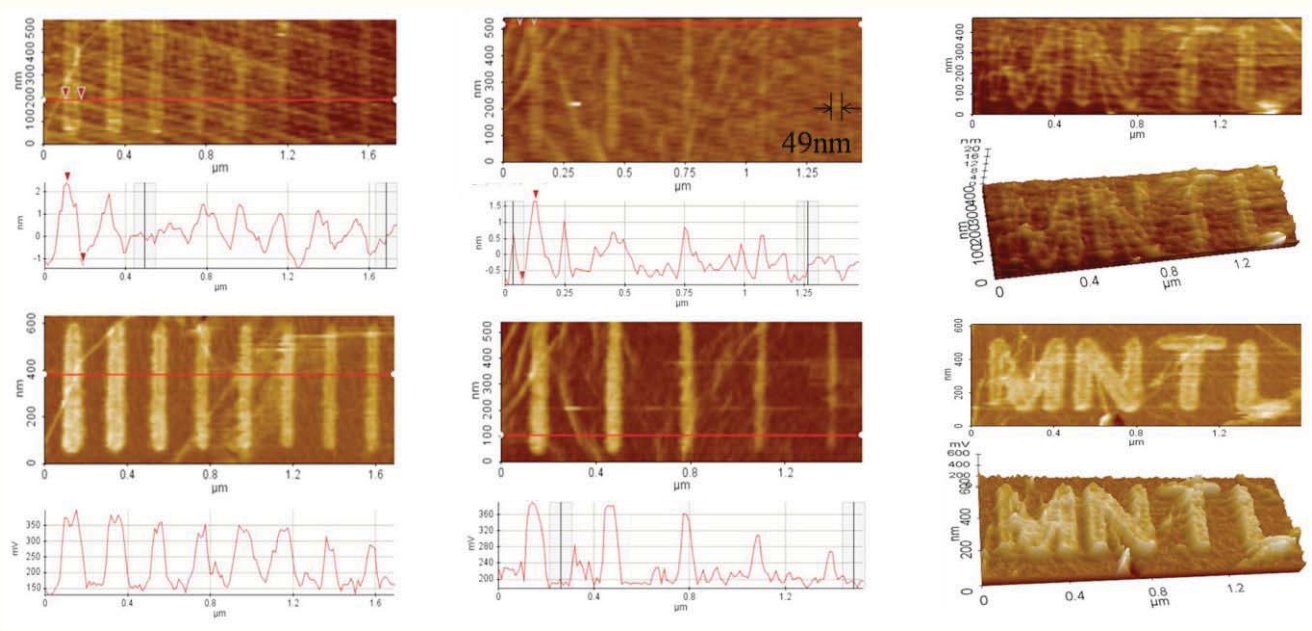


Fig. 3. FE-SEM image of the AFM tip (cantilever type: NSC36/Ti-Pt-3M-C).

25℃ ambient air by contact-mode AFM (XE-100, Park systems, USA). A NSC36/Ti-Pt-3M-C cantilever was applied to conduct the experiment. The spring constant and resonant frequency of the conducting Si cantilever was 0.6 N/m and 170 kHz, respectively. In order to achieve the AFM tip condition, the FE-SEM image of the cantilever probe was captured, which is shown in Fig. 3. The wear condition of the AFM probe is quite important for LAO. Since if the probe has been wear seriously, the increase in the radius of the tip will directly decrease the electric field intensity on the graphene surface. In addition, if the probe attached some contaminations or oxide residue, it will be difficult to generate new graphene oxide on the graphene surface during LAO.

A relative humidity was maintained between 42% and 45% by a humidity controller during the experiment, which is a necessary condition for the creation of graphene oxide [23]. It should be noticed that the scan rate will directly change the reaction time [24], and the bias voltage will has large influence on the electric field intensity of the tip according to our analysis in the above part. Therefore, we mainly focused



(a) (b) (c)

Fig. 4. (a) The influence on the graphene oxide with different scan rate. From left to right: 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 μm/sec, respectively (humidity: 45%, bias voltage: -10 V). Top: 2D topography image; bottom: 2D lateral force image (b) The influence on the graphene oxide with different tip bias voltage. From left to right: -10, -9, -8, -7, -6 V, respectively (humidity: 42%, scan rate: 0.01 μm/sec). When the bias voltage was below -6 V, clear graphene oxide pattern cannot achieved. Top: 2D topography image; bottom: 2D lateral force image. (c) Certain pattern drawing of the graphene oxide, characters "MNTL" (humidity: 45%, scan rate: 0.02 μm/sec, applied tip bias voltage: -10 V). Top: 2D & 3D topography image; bottom: 2D & 3D lateral force image.

on these two process parameters in the experiment: scan rate and tip bias voltage.

A. *Different Scan Rate*

As shown in Fig. 4 (a), in a relative humidity of 45 % and bias voltage of -10 V, different scan rates were utilized to observe the size change of graphene oxide. Eight lines were drawn with different scan rate. The scan rate from left to right is: 0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14 μm/sec, respectively. From the topography analysis image we can notice, as the increase in the scan rate, which means the decrease in reaction time, the height and width of the graphene oxide decrease. Additionally, the friction decrease as the increase in scan rate, which is shown in the bottom lateral force analysis image. Since the width of the graphene oxide reduced when we increase the scan rate, this also increases the resolution of nano-pattern.

B. *Different Tip Bias Voltage*

After the optimization of tip scan rate, we conduct experiment with various tip bias voltage. As can be seen in Fig. 4 (b), with a relative humidity of 42 % and scan rate of 0.01 μm/sec, five lines was drawn with different tip bias voltage. The applied bias voltage on AFM probe from left to right is: -10, -9, -8, -7, -6 V, respectively. According to the topography analysis image, we can see that the height and width of the generated graphene oxide decrease along with the decrease in tip bias voltage, which also confirmed our theoretical analysis about the distribution of electric field intensity. The friction also decreased as the decrease in tip bias voltage which shown in the lateral force image. It means that after LAO oxidation,

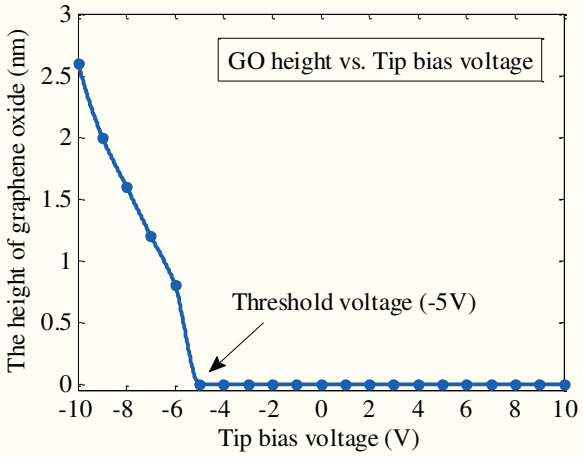


Fig. 5. The relationship between the applied tip bias voltage and the height of created graphene oxide. Voltage polarity was also changed, when applied a positive bias voltage on the AFM probe, there was no graphene oxide generation. And the threshold voltage for graphene oxide growth in LAO was -5 V.

the friction of graphen oxide is much higher than that of graphene. In this experiment, a series of nanostructures were created, with a minimum height of 0.8 nm and a minimum width of 49 nm, respectively. This provided a high resolution for the nano-patterning on graphene surface. It should be noticed that there has a threshold voltage for graphene oxide creation. In our experiment, when the applied tip bias voltage was below -6V, the nanopattern of graphene oxide cannot be achieved. Therefore, aiming at clear nanopatterned graphene oxide, when we carry out the LAO lithography on graphene

surface, the bias voltage applied on the AFM tip should be always at over -6V.

We also change the polarity of bias voltage applied on the AFM tip to observe the graphene oxide generation. However, when the polarity of bias voltage on AFM probe was positive, there was no graphene oxide can be observed. The relationship between the height of nanopatterned graphene oxide and the applied tip bias voltage is drawn in Fig. 5. In the curve, we took average height value of different points on each line shown in Fig. 4 (b) as the height of graphene oxide under different bias voltage.

C. Certain Nano-Pattern Drawing

Based on basic experiments, a certain nanopattern of characters "MNTL" was successfully formed on the graphene surface. We utilized a scan rate of 0.02 μm/sec and -10 V tip bias voltage in order to achieve better resolution. As shown in Fig. 4 (c), the graphene oxide was generated according to the scan trace. It can be seen that the nanopatterned graphene oxide was quite uniform and clear on the graphene surface. In this way, the height and width of the graphene oxide can be controlled by varying the scan rate and tip bias voltage during one oxidation process. Since the bias voltage can be changed during one LAO lithography process, which means the height of different point on a graphene oxide line can be changed. This also provided a possibility to fabricate simple three-dimension nanostructures on the single layer graphene.

IV. Conclusion

In this paper, we presented an optimized method to generate nanopatterned graphene oxide on the CVD single layer graphene sheet. Theoretical analysis was carried out to achieve the distribution of electric field intensity around the AFM probe. Local anodic lithography was conducted on a CVD single layer graphene sheet in the ambient conditions with a relative humidity between 42% and 45%. The two process parameters: scan rate and tip bias voltage was optimized, respectively. A nanopattern with a minimum height of 0.8 nm and a minimum width of 49 nm was achieved. Based on the optimization of the process parameters, a certain nanopattern characters "MNTL" was successfully obtained. The results confirmed that size and friction of nano-patterned graphene oxide can be generated well in the ambient conditions with the optimized parameters, which could be used to fabricate nano electric devices and even simple three-dimension structures for various applications

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