Effect of oxygen plasma etching on graphene's mechanical and electrical properties

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Abstract. This paper reports a study of the effect of oxygen plasma etching on the mechanical and electrical properties of chemical vapor deposited (CVD) multilayer graphene. By means of scan probe microscopy (SPM), it was found that the defects were initially induced to the top graphene layer by oxygen plasma etching, which plays an incentive role in further etching. Oxygen plasma bombarding on surface of graphene enhanced the surface roughness, as well changed the tribological properties. The results of electronic transport measurements show a decrease in mobility with the increase of etching duration. These findings are valuable for studying the effects of plasma etching on graphene, and modifying the physical properties of graphene through artificially generated defects.

Keywords: Graphene, Oxygen plasma etching

1. Introduction

Due to its excellent physical properties [1-5], graphene has drawn significant attention in electronic, chemical, biochemical and mechanical applications [6], such as high-speed transistors, DNA sequencing [7,8], and biochemical sensors. In order to expand its applications in technology, efforts have been tried to modify the band structure (semimetal) of graphene. Oxygen plasma etching on multilayer graphene has been taken to study the effects on the mechanical and electrical properties through changing the energy gap between conduction and valence bands [9]. Oxygen plasma etching has become a topic of intense research in the past years [10-14].This process is isotropic that particles attack the wafer from all angles. As well, plasma treatment, especially oxygen plasma treatment with high chemical reactivity to carbon has become an effective way for the modification of carbon based on materials to alter their nano-structures and properties. In this study, we explore the effect of oxygen plasma etching of chemical vapor deposited (CVD) graphene on Si/SiO_2 substrate over different durations.

Graphenes were initially produced with chemical vapor deposition (CVD) using copper as a substrate. Then they were transferred onto a Si substrate with a 300nm SiO_2 buffer layer. Optical microscope was used to confirm and identify that graphene has been transferred successfully. By carefully tuning the time of the oxygen plasma etching, we studied the effect of oxygen plasma etching on graphene. The durations of oxygen plasma etching were selected as 10 seconds, 30 seconds, 60 seconds and 180 seconds, individually. Atomic force microscopy (AFM, Veeco multiMode) was used to explore the morphology and defects on multilayer graphene. Influence of oxygen plasma etching on mechanical properties of graphene was discussed. By comparing four cases of the etching

duration, we analyzed the etching effect on electrical properties of graphene taking advantage of the electrostatic force microscopy module of AFM and ferroelectric analyzer (TF Analyzer 2000). Based on the experimental results, we discussed how oxygen plasma interacted with graphene and how the electrical properties were affected. A conclusion was drawn in the end.

2. Experimental

Silicon with a top layer of oxide is generally used as substrate for various graphene devices due to easy optical identification of the sample. In this study, multilayer graphene produced by chemical vapor deposition (CVD) on copper were transferred to silicon substrate with thermally grown oxide layers (300 nm). Optical microscope was used to locate and identify graphene samples. Before oxygen plasma etching, all samples were cleaned with acetone rinse for 5 minutes in order to remove tape residues and other organic contaminations. Plasma cleaner (PDC- M) with oxygen plasma source was used to etch multilayer graphene under the following parameters: oxygen flow rate of 400 sccm (standard cubic centimeter per minute), the RF power of 150W and pressure of 0.37 Torr (50pa). Etching process durations include 10 seconds, 30 seconds, 60 seconds, 180 seconds.

After the treatments, atomic force microscopy was taken to present the morphology and thicknesses of the samples. Taking advantage of the force imaging mode of AFM, the tribological features of graphene were investigated. A combination of electrostatic force microscopy (EFM) and ferroelectric analyzer module (TF Analyzer 2000 FE-Module) was used to characterize the electrical properties of graphene treated by oxygen plasma etching.

3. Results and Discussion

By analyzing the surface scan images, the average thickness of multilayer graphene is obtained as shown in figure 1. It is found that the thickness of graphene decreases versus etching duration, from initial thickness of 8.4nm approximately to 0.6nm of graphene treated by 180s oxygen plasma etching. Etching rate seems to decreasing with etching duration.

We have realized that the morphology of graphene changes with the oxygen plasma etching as well as roughness and thickness of graphene. While what interests us more is how the oxygen plasma interacts with graphene. To explain the question, we must further understand the mechanisms of oxygen plasma interacting with the remaining graphene sheets after the transient etching process. There are two possible etching mechanisms including isotropic etching and anisotropic etching [15]. If single sheet of graphene removed by oxygen plasma is isotropic, the degree of etching should be identical on a graphene sheet regardless of graphene defects and edges. When a single atomic layer is removed from the top, a single or a couple of chains of atoms at the edge will also be removed. The reason is removing one carbon atom from the top sheet of graphene will need enough energy to break three bonds, but at the edges or defects, only one or two bonds need to be broken due to the existence of dangling bonds. So the energy needed to break C-C bonds at the edges or defect is lower than other parts on graphene obviously [16]. And etching mechanisms must choose the lower energy-requiring method. That means the isotropic process is not likely to happen in this study. For an anisotropic etching, there are usually two methods, anisotropic vertical etching (layer-by-layer) and anisotropic horizontal etching (direct etching from edges or defect to inside) [15].

Unfortunately, we cannot distinguish the removal situation at the edge or defect by using optical microscopy or atomic force microscopy (AFM) due to limitation of the resolution of these instruments. Nevertheless, the modification behavior of surface morphology versus etching time provides useful information helping us with understanding the detailed etching mechanism. For the anisotropically horizontal etching mode, the etching rates at the graphene edges and defective area are anticipated to be higher than those at other intact regions due to the fact that oxygen plasma tends more likely to interact with carbon atom located at the edges/defects of graphene. In addition, this oxygen plasma will react with atoms at exposed edges/defects, regardless of their layer position. This results in the defective regions of the top graphene sheet enlarging, and further generates larger defective areas on the lower layers. While in anisotropic vertical etching, oxygen plasma will interact with graphene

layer by layer. The defective regions of the top sheet will not expand. The surface morphology and the defective region size are not expected to change much during the etching in the case of anisotropically vertical etching. In the experiments, roughness of graphene decrease versus etching process, implying an un-expanded defect region. These results suggest that the removal of graphene by oxygen plasma is most likely anisotropically vertical etching, i.e., layer by layer etching mechanism is preferred. So it is possible to use oxygen plasma etching to change the property of top-layer graphene without affecting interior structure.

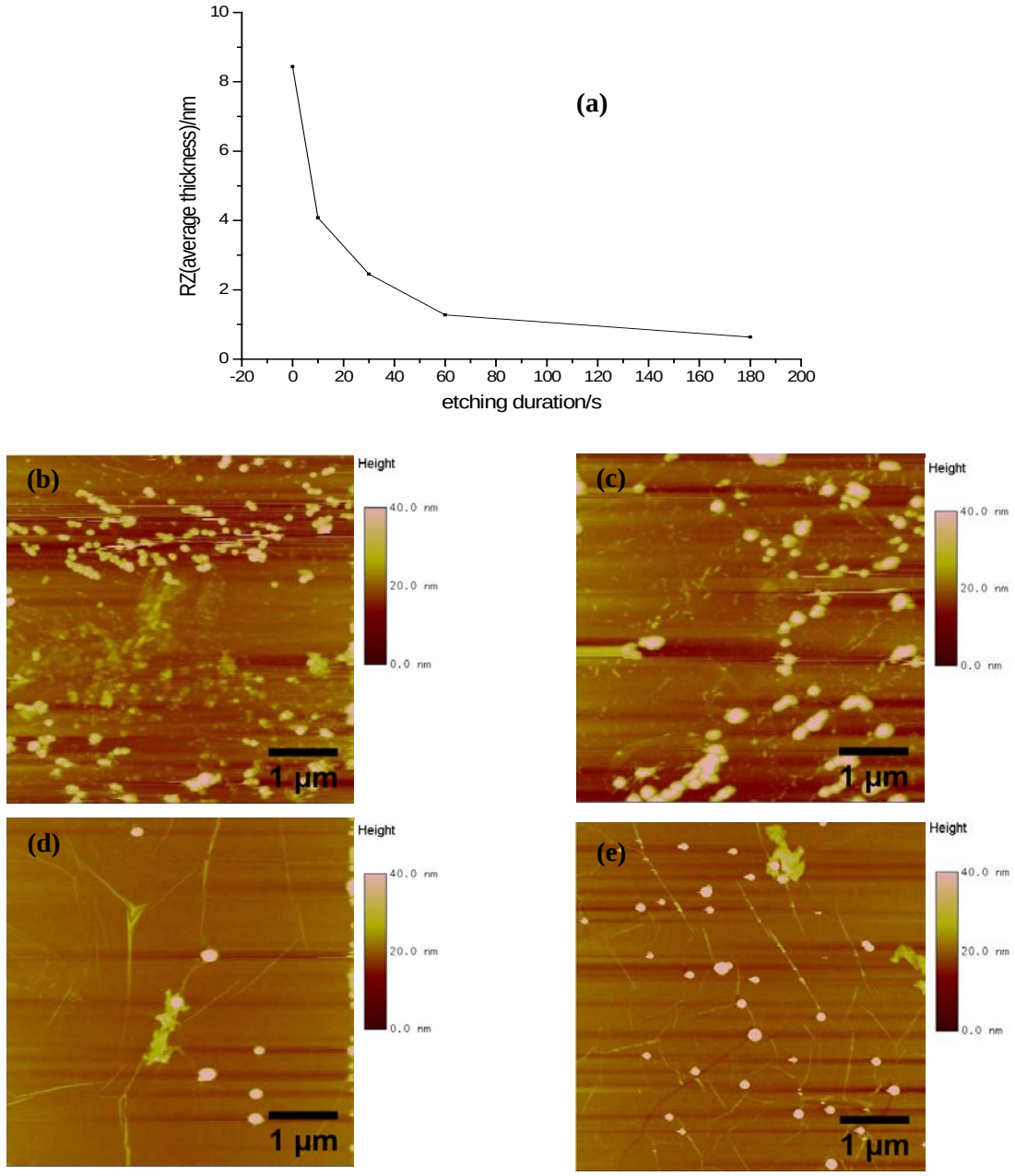

Figure 1. (a) Variation of the average thickness of graphene with the decrease of the cumulative etching time. (b) ,(c) ,(d) and (e) AFM images of graphene being etched with oxygen plasma after (b) 10 seconds ,(c) 30 seconds ,(d) 60 seconds and (e) 180 seconds.

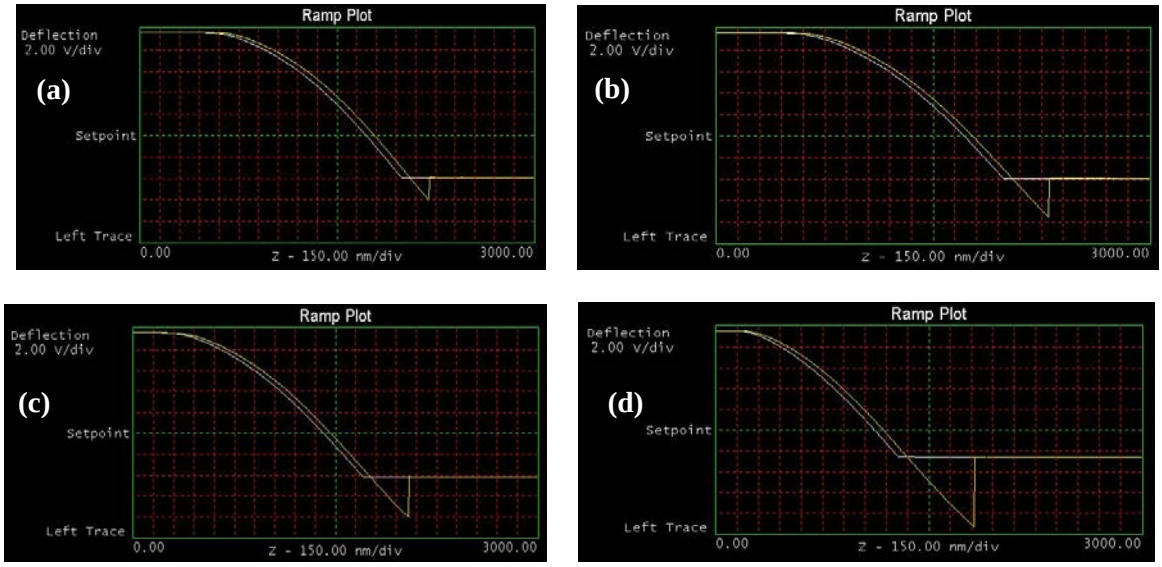

Figure 2. Images show the tracks of pinpoint on etched graphene surfaces with different etching durations (a)etching duration is 10 seconds (b) etching duration is 30 seconds (c) etching duration is 60 seconds .(d) etching duration is 180 seconds. Pinpoint distance of lateral is 3μm.

For purpose of measurement of mechanical properties influenced by oxygen plasma etching, force calibration of AFM has been performed. Figure 2 shows tracks of pinpoint on etched graphene surfaces with different etching durations. The friction force can be extracted from these data (diMutlimode SPM Instruction Manual 004-210-000) [17], as shown in figure 2.

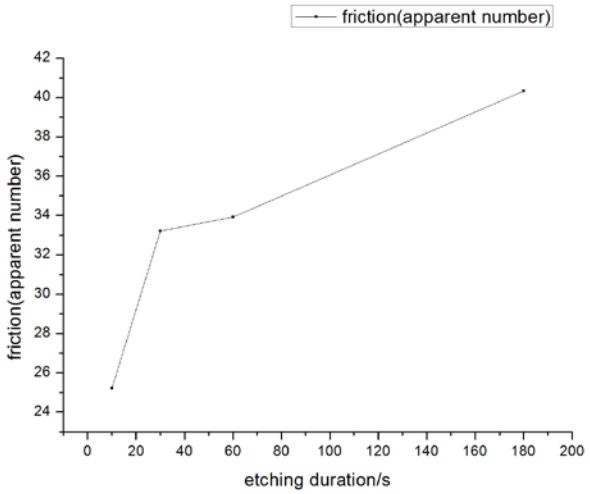

Figure 3. Friction force on graphene being extracted from SPM image cycles as a function of duration of oxygen plasma etching.

It is found that the surface friction decreases with the etching duration. We contribute this phenomenon to puckering effect, taking into account of bending stiffness and in-plane rigidity. The degree of the puckering on graphene and the resulting contact area will depend on the bending stiffness of graphene, as a thinner sample has lower bending stiffness and more thereby puckers [18], leading to a larger contact area and higher frictional force. When graphene layers increases, both the bending stiffness and the in-plane rigidity will be increased, causing a lower puckering degree. Due to this reason, the friction on graphene intends to increase with the decrease of numbers of layers of graphene. This may explain the increase of friction on graphene with the oxygen plasma etching duration, as shown in figure 3. It should be noticed that when number of graphene layers exceeds five layers, friction on graphene will approach friction on graphite [17, 19] where friction is much less

related to puckering effect, or the friction is rarely sensitive to graphene layer numbers. According to the variation behavior of friction versus etching duration, friction does not change much within 60s etching, probably due to the lower decrease in the numbers of layers of multilayer graphene. With increase of etching time friction increases sharply, indicating a thinner graphene where puckering effect plays an important role on friction.

To further explore the electrical property of graphene treated by oxygen plasma etching , electrostatic force microscopy (EFM) has been used to present electric domains of graphene, as shown in figure 4.

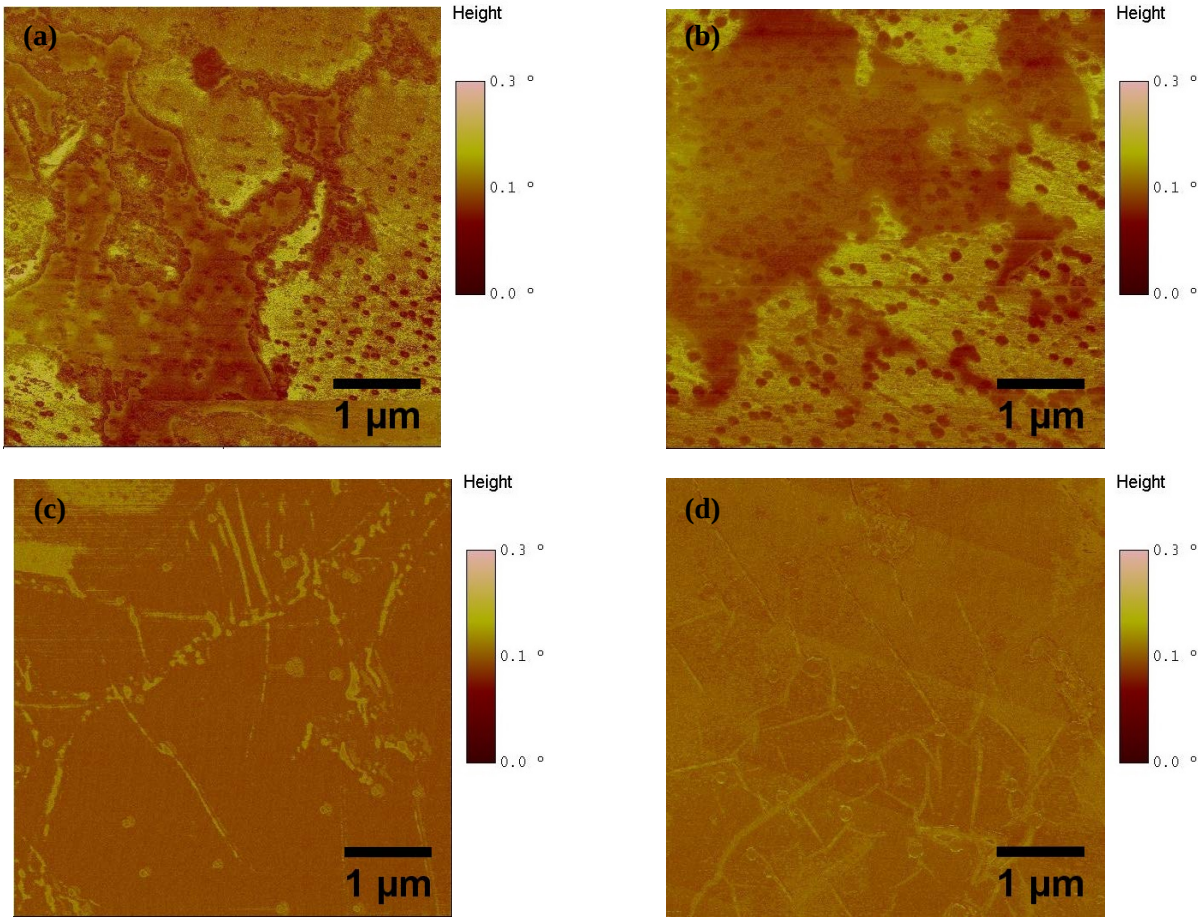

Figure 4. EFM images show the distribution of electric domains for graphene samples treated by different etching time (a) 10 seconds, (b) 30 seconds, (c) seconds and (d) seconds. Height of EFM images represent the surface electric potential when applied a voltage as the brightness of images.

Figure 4 shows the distribution of electric domains for samples treated by different etching time. The brightness represented the surface electric potential when applied a voltage. It can be seen that both the brightness and bright areas decrease with the etching time, indicating a decrease of surface electric domain size with oxygen plasma etching duration, which might be attributed to the fact that oxygen plasma etching reduces the quantity of free electrons or holes on the graphene surface. Oxygen plasma bombardment on the surface of graphene brings more defects on the top layer. Defect expanding reduces movement of the free electrons or holes resulting in a decrease of electric domains [20]. Nevertheless, the electric domain distribution does not appear to be much different when etching time is over 60s.

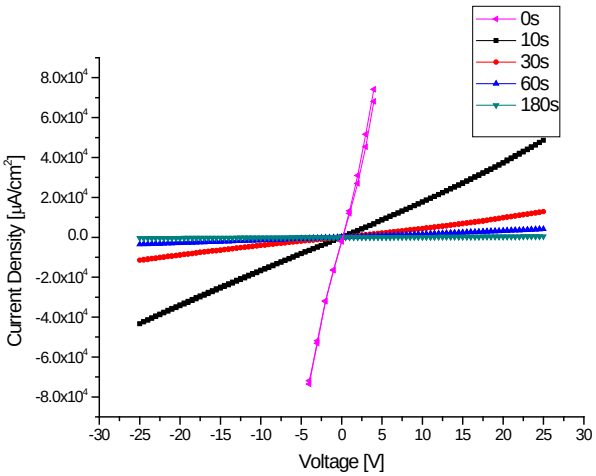

Figure 5. The I-V characteristics for different cumulative plasma exposure, different color of the lines show the different I-V characteristics for different cumulative plasma exposure.

In order to further characterize electrical properties of graphene treated by oxygen plasma etching, we measured the electrical conduction of multilayer graphene using ferroelectric analyzer (TF Analyzer 2000). The I-V characteristic curves are presented in figure 5 for samples with etching duration of 10s, 30s, 60s and 180s, individually. For all samples, a linear relationship is well established between the electric current and applied voltage, besides that the conductivity decreases with the etching duration. As a matter of fact, one of the main purposes to perform oxygen plasma etching on graphene is a try to induce semiconductor characteristic. In this study, the ohmic contact characteristic of graphene does not seem to be broken by oxygen plasma etching. The decrease of conductivity with increase of etching time is due to the reduction in numbers of layers of graphene.

4. Conclusions

This paper reports a study of the effect of oxygen plasma etching on the chemical vapor deposited (CVD) graphene. It is suggested that an anisotropically vertical etching mechanism happens for the oxygen plasma etching on graphene. The oxygen plasma etching increases the graphene surface friction based on puckering effect. The results provide a post-synthesis approach to change the properties of graphene and the possibility of producing the graphene thin films carrying expected properties including monolayer graphene.

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