A new wet etching method for black phosphorus layer number engineering: experiment, modeling and DFT simulations

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***Abstract*—This paper reports the successful atomic layer patterning of 2-dimensional Black Phosphorus (BP) and the simulation of the etching process by Density Functional Theory (DFT) method. The wet etching process can etch selected regions of few-layer black phosphorous with an atomic layer accuracy, which provides a feasible patterning approach for large-scale manufacturing of few-layer BP materials and devices. Absorption energies of iodine atoms/molecules at different location of BP layer edge were also calculated by DFT method, shown a vertical etching direction preference which was important for achieving high quality patterns.**

Keywords—Black Phosphorus, atomic layer etching, Density Functional Theory, etching process simulation, absorption energy

I. INTRODUCTION

Two-dimensional (2D) materials have drawn high interests for applications in electronic and photonic devices. They have unique properties such as high carrier mobilities, high on-off ratios, anisotropy, lack of surface dangling bonds, low defect concentrations, high optical absorption, and tunable bandgaps. [1-5] For most 2D materials, the atom layer number greatly affects their energy band structures and electronic transport properties. This made many band-gap-engineering by layer numbers possible. Devices such as Tunneling Field Effect Transistor (TFET) [2] or wavelength-tunable photodetectors/emitters can be relativity easy to fabricate [3-4]. However, on the other side, layer number variation in device fabrication can cause undesired device performance variations. Thus, atom layer number controlling in 2D material devices is a critical issue. Currently, experimental or theoretical reports on atom layer etching processes for the 2D materials are still very rare. [3]

2D black phosphorus (BP) can be viewed as a stack of phosphorus atomic planes with interlayer Van der Waals force, whose direction is along [010] direction. BP has a direct bandgap, which is tunable by its atomic layer number. Here, we present a wet etching method for BP, which could achieve atom layer accuracy and controllability along [010] direction.

II. ETCH EXPERIMENTS AND RESULTS

Iodine was chosen as the etchant in the experiment due to its compatibility with mainstream photoresist and the suitable etch rate range. Since oxygen and water may introduce oxygen defects in BP, we used Isopropyl Alcohol (IPA) and methanol mixture as solvents [5]. Etching depth was measured by an Atomic Force Microscope (AFM). Etching depths with different times and/or concentrations are shown in Figure 1. The relations between the etch depths and etch time/etchant concentrations are linear. The linear fitting lines were shown in Figure 1. From the fitting results, the etching rate along [010] direction was around 0.081-0.101 nm/(min*g/L). Considering that one BP layer is 1.0473 nm thick [6], this etch rate is slow enough to have an atomic layer accuracy. The etch rate can be then modelled as:

$$\mathrm{R} = 0.091 * \frac{C_{I2}}{\frac{g}{L}} \frac{\mathrm{nm}}{\mathrm{min}}.$$

In the above equation, R is the etch rate of BP, and C_{I2} is the concentration of iodine.

It should be noticed that the etch rate was thickness-independent. For example, before etching, the BP sample shown in Figure 2 (a) was not uniform. After etching, the thickness was reduced by 11 nm uniformly across the 20 microns keeping the same profile shape, as measured by AFM (Figure 2 (b)). Due to the very large area to measure and the AFM tip size (around 10 nm), the edge steepness is very hard to be measured by AFM.

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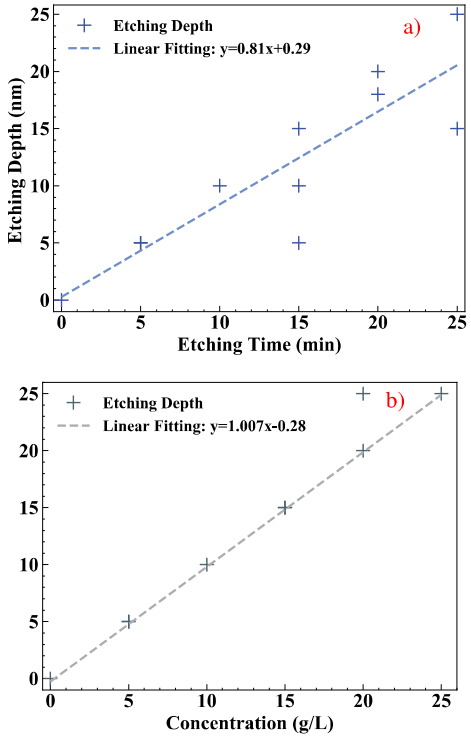

Figure 1. (a) Etching depths vs. different etch times using 10g/L iodine/IPA-methanol solutions. (b) Etching depths after 10 minutes etching vs. iodine concentrations of iodine/IPA-methanol solutions.

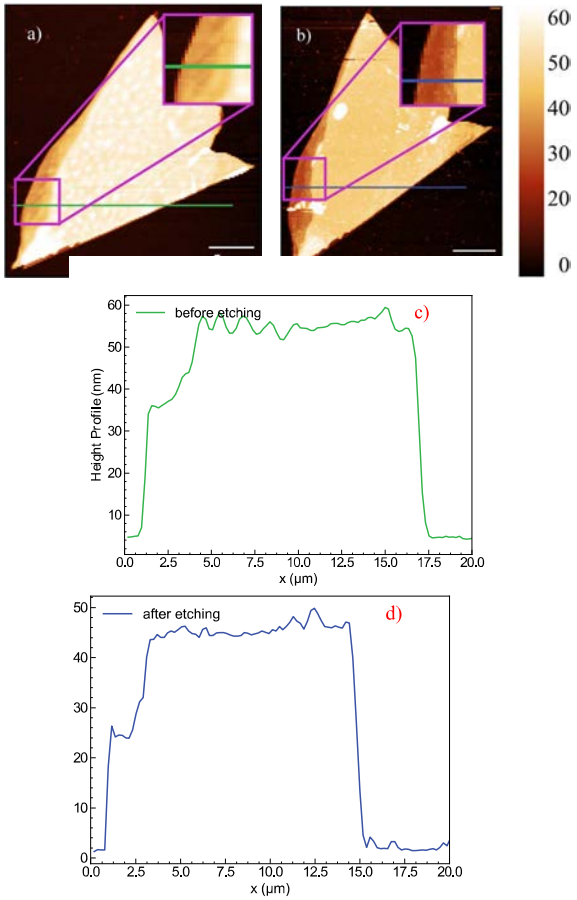

Figure 2. AFM thickness characterization for a BP sample. (a) and (c): 2D and 1D thickness profiles before etching. (b) and (d): 2D and 1D thickness profiles after etching. The etch solution was 5g/L iodine/(IPA-methanol) solution, and the etch time was 20 min.

Samples etched by 10g/L iodine solutions for 10 mins were characterized by Scanning Transmission Electron Microscope (STEM), Raman microscopy, energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) spectra (Figure 3), which showed that there were no iodine remains after the etching process, and the crystal structure were not changed by the etching (Figure 3). Raman spectrum showed the good crystallinity (figure not shown here).

After we developed an etch recipe to control the atom layer numbers, BP patterning with deep ultra-violate lithography and wet etching was investigated. Polymethyl methacrylate (PMMA) was used as the photoresist. A TEM copper grid of 6 μm bar width was used as the photomask. After 12 min etching, we achieved 15 nm thickness difference between the exposed and unexposed region as shown in Figure 4.

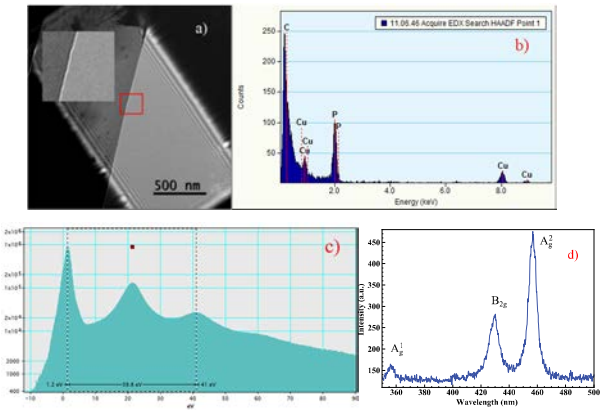

Figure 3. Material characterizations of a sample after etching by a 10 g/L iodine/IPA-methanol solution for 10 mins. a) STEM image and d) Raman spectrum showing a good BP crystallinity after etching. b) EDS data, c) EELS spectrum: showing that no iodine residues left. The carbon peak is from the polycarbonate (PC) film remain on the copper TEM grid.

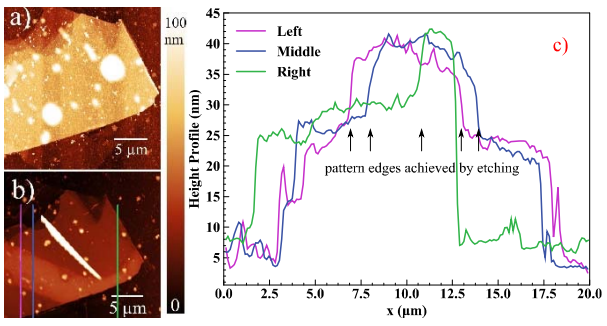

Figure 4. (a), (b) AFM thickness data of the sample before and after patterning. (c) 1D thickness profiles after etching at three locations indicated by the purple, blue and green cutlines shown in (b).

III. DFT Simulation for the Etching Process

Both exfoliation methods and etching can introduce thickness differences thus plane edges. Different from bulk materials which can have defected surfaces, 2D materials normally have defects or dangling bonds on the edges of the layers due to the Van der Waals force structure. Therefore, etching behavior might be different at edge regions compared to other regions. To investigate this problem, Density Functional Theory (DFT) method was used to simulate the etching behavior around plane edges. Specifically, absorption energies for iodine atoms and molecules were calculated as both may exist during the etching processes. It was also of our interest to calculate the absorption energies of iodine atoms/molecules with P atoms laterally and those in the layer below to see which direction is preferred in the reactions.

We used a 4×4×3 BP supercell with half of the first layer removed to emulate a surface edge. Quantum-Espresso [7] software package was used for the calculations.

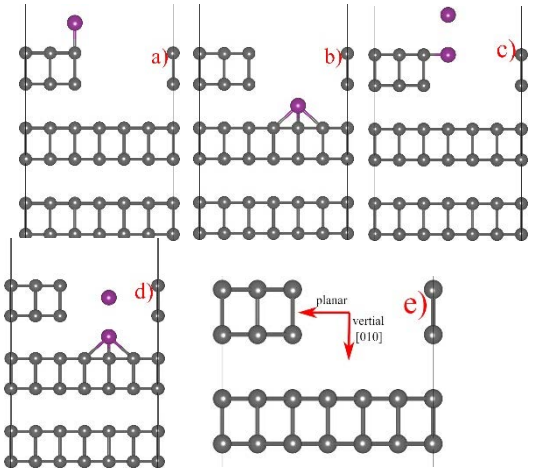

Figure 5. Schematic view from a [001] direction of an ideal BP lattice and the iodine atom/molecule before geometry relaxation. (a): iodine atom on top layer edge. (b): iodine atom on second layer. (c): I_2 molecule on top layer edge. (d): I_2 molecule on second layer edge. (e) Schematic view of the two etching directions.

After a full relaxation, we obtained the lowest total energy for each case. For top layer edge, the absorption energy for iodine atom or molecules were $E_a = 1.06$eV, $E_c = 0.96$eV. While the second layer were $E_b = 1.69$eV, $E_d = 1.52$ eV.

The absorption energies for iodine atom or molecule on the top layer edges are much lower than those on the second layer. This means that iodine atom or molecule tends to attach on the exposed second layer region instead of the exposed edges, which means that the etching direction is [010] direction, the surface normal direction.

The DFT calculations support a vertical etch direction instead of the possibility of an area shrinkage from the edges. This is desired for the use in lithography and patterning of BP, and is consistent with the patterning results shown in Figure 4 (b).

IV. Conclusions

We report a new iodine-based wet etching method for black phosphorus, which could achieve an atom layer accuracy along [010] direction. The etch rate is thickness-independent, and has a linear relationship with the etchant concentration. With this method, a BP pattern with a 15 nm etch depth was successfully fabricated. DFT calculations were used to study the etch behavior around edges. Absorption energy calculations show that iodine atoms/molecules prefer to be absorbed by the layer below the edges, predicting an [010] etch direction.

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