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Bias-assisted atomic force microscope nanolithography on NbS$_2$ thin films grown by chemical vapor deposition

Hunyoung Bark$^{1,3}$, Sanghyuk Kwon$^{2,3}$ and Changgu Lee$^{1,2}$

$^1$ SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggido, Korea
$^2$ School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggido, Korea

E-mail: peterlee@skku.edu

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Abstract
Niobium disulfide, one of the metallic transition metal dichalcogenides, has a high potential as an electrode material for electronic devices made of 2D materials. Here, we investigated the bias-assisted atomic force microscope nanolithography of NbS$_2$ thin films synthesized by chemical vapor deposition. We analyzed the lithographed pattern using Raman spectroscopy, transmission electron microscopy and friction force microscopy. These analyses showed that lines having various widths and thicknesses could be generated using the lithography technique by simply varying the scan speed and applied voltage. These analyses also revealed that the NbS$_2$ film transformed from a layered crystalline structure into an amorphous structure upon being lithographed. By generating four line segments forming a square and measuring $I/V$ curves inside and outside of the square, the electrical properties of the lithographed material were characterized. These analyses indicate that NbS$_2$ became hydrogenated and an insulator upon being lithographed.

Keywords: atomic force microscopy, lithography, niobium disulfide, chemical vapor deposition (CVD), conductor, 2D material

(Some figures may appear in colour only in the online journal)

1. Introduction
The splendid properties of graphene have given rise to significant interest in atomically thin two-dimensional (2D) materials [1–3]. Such thin materials have also been made from transition metal dichalcogenides (TMDCs) such as MoS$_2$, WSe$_2$ and NbS$_2$, and have attracted great attention due to their properties, which are distinct from those of graphene [4]. Many studies have in particular examined semiconductor TMDCs such as MoS$_2$ and WSe$_2$ because of their exotic electronic and optoelectronic properties derived from their atomic thickness [4–6]. For instance, high mobilities of up to several hundred cm$^2$ V$^{-1}$ s$^{-1}$ have been observed for MoS$_2$, and high-performance photodetection for WSe$_2$ and atomically thin PN junctions have been reported for MoS$_2$ and WSe$_2$ [7, 8]. However, there have been few reports on metallic TMDCs, even though metallic TMDCs have the practical potential to be used as electrode materials for 2D semiconductors since their atomic structures are similar to those of semiconductor TMDCs [9, 10]. NbS$_2$, one of the metallic TMDCs, is an important material in this regard because it is expected to form Schottky barrier-free contacts with semiconductor TMDCs [11].

To date, the above-mentioned TMDCs have usually been patterned by applying conventional electron-beam lithography along with plasma etching [12, 13]. However, the standard electron-beam lithography process uses poly(methyl methacrylate) (PMMA), which leaves polymeric residues on the samples [14]. Furthermore, plasma etching introduces defects in
the sample and changes its chemical composition [15]. On the other hand, scanning probe microscopy (SPM) is a promising alternative for patterning various materials at the nanoscale [16].

Atomic force microscope (AFM) nanolithography, in particular, has shown great potential for fabrication of nanodevices [17, 18]. This technique can be used to make nanometer patterns with high resolution [19]. Moreover, it can be performed in the ambient environment, hence allowing in situ device measurements and examination, and offering a resist-free process, thus avoiding contamination of the sample by eliminating several fabrication steps such as polymer coatings needed in conventional lithographies [20, 21]. AFM lithography already has been used to build nanoscale electronic structures for traditional semiconductors and metal surfaces, especially to silicon [22–24]. The technique has also been applied to manipulate graphene and MoS2 [25, 26]. Masubuchi et al produced graphene nanoribbons using AFM lithography and Byun et al analyzed hydrogenation and oxidation of single-layer graphene by the AFM lithography [27, 28].

Since graphene is highly conductive, and the electric bias-based AFM lithography of graphene was found to not be so challenging, Donarelli et al attempted AFM lithography on the MoS2 surface by applying a bias voltage through an AFM tip [25]. However, applying this technique to TMDCs is difficult because of their low conductivity levels. Hence, the quality of the lithography with MoS2 was poor and a well-ordered pattern was not generated when this method was used [25]. Applying AFM lithography is also challenging with metallic TMDCs, because of their relatively low conductivity levels, for example compared with that of graphene. Hence, it is necessary to find appropriate conditions in order to develop the bias-assisted lithography technique for these materials.

In this report, we describe applying AFM lithography to NbS2 thin films grown by chemical vapor deposition (CVD). We made patterns on the NbS2 film using a biased-AFM tip in atmospheric conditions. Furthermore, the NbS2 films before and after application of the lithography were analyzed by using Raman spectroscopy, transmission electron microscopy and various SPM methods.

2. Methods

Because it is difficult to exfoliate only a few large-area thin layers of NbS2 from a bulk crystal, the CVD method was used to synthesize the NbS2 thin film on a 300 nm thick layer consisting of SiO2 thermally grown on a silicon substrate heavily doped with boron. A 1 nm thick layer of niobium metal was deposited on the 300 nm thick SiO2/Si substrate and sulfurized with H2S gas in a tubular quartz chamber as reported previously [29]. The thickness of the synthesized NbS2 film was 3 nm (±1 nm). The synthesized films were characterized by x-ray photoelectron spectroscopy (XPS) using a K-alpha (Thermo UK) system with a monochromated Al Kα x-ray source, by transmission electron microscopy (TEM) using a JEM ARM 200F (JEOL) microscope operated at an acceleration voltage of 200 kV and equipped with an energy-dispersive x-ray (EDX) spectroscope, and by Raman spectroscopy using an NT-MDT Ntegra AFM-Raman spectroscope with an excitation wavelength of 532 nm. XPS was performed to determine the binding energy values of niobium and sulfur and the chemical composition of synthesized NbS2 film, and TEM/EDX was used to analyze the crystallinity of the NbS2. We also applied Raman spectroscopy to analyze pristine NbS2 flakes that were mechanically exfoliated from bulk NbS2 crystals (purchased from HQ Graphene) by the conventional scotch-tape method, and then transferred to a heavily doped p-type Si substrate with a thermally grown 300 nm thick SiO2 layer. The Raman spectroscopy result of pristine NbS2 flake was used to compare with Raman spectra of synthesized NbS2 films.

Atomic force microscope nanolithography was performed by using a Seiko Instrument AFM with an environmental enclosure to keep the humidity constant. The noncontact (tapping) mode was used for imaging and the contact mode was used for lithography and for measuring friction and current. A conductive silicon tip, NSG01 (NT-MDT), was used for both contact and noncontact modes. A positive bias voltage was applied on the AFM tip and the sample was grounded by attaching silver paste.

Figure 1. Characterization of the synthesized NbS2 thin film. (a) Raman spectra of the synthesized NbS2 and pristine NbS2 flake. (b) X-ray photoelectron spectrum (XPS) of the synthesized NbS2. Inset images show Nb 3d peaks (left) and S 2p peaks (right). (c) High-resolution transmission electron microscopy (HRTEM) image of the synthesized NbS2. The scale bar indicates a length of 5 nm. Inset shows a diffraction pattern of the area imaged with TEM.
Figure 2. Patterns generated on the NbS2 thin film by bias-assisted AFM lithography. (a) Schematic diagram of the AFM lithography setup. (b) AFM topography image and (c) phase image of lines written by applying various scan speeds at a constant dc bias of +10 V. Inset in (b) shows the AFM line profile. (d) AFM topography image and (e) phase image of lines written by applying various dc voltages at a constant scan speed of 1 µm s⁻¹. Loading force of the tip and the RH were kept at constant values of 5 nN and 40%, respectively, during the lithography. All of the scale bars in figure 2 indicate 5 µm.

3. Results and discussion

Raman spectra of the synthesized NbS2 thin film and the pristine NbS2 flake are shown in figure 1(a). Two major Raman modes, E2 and A1, were observed. Both the synthesized NbS2 and pristine NbS2 showed E2 and A1 peaks at about 329 and 386 cm⁻¹, respectively. These two peaks were found to be within a few reciprocal centimeters of the Raman peaks of NbS2 reported in the literature [30–32]. The peak at 300 cm⁻¹ in the synthesized NbS2 came from the SiO2 underneath the NbS2 layer; the thickness of the synthesized film, being only 3 ±1 nm, was apparently too thin to block the generation of the SiO2 Raman peak. Figure 1(b) shows an XPS spectrum of the synthesized NbS2 film. Six peaks, including C 1s, S 2s, Nb 3d, S 2p, Si 2s and Si 2p, were observed to have binding energy values ranging from 50 to 350 eV. Binding energies were calibrated using C 1s (254.88 eV) as the reference. The left inset shows a magnified view of the Nb 3d₅/₂ and Nb 3d₃/₂ peaks and the right inset shows a magnified view of the S 2p₁/₂ and S2p₃/₂ peaks. The peak positions for the Nb 3d₅/₂, Nb 3d₃/₂, S 2p₁/₂ and S 2p₃/₂ peaks were observed to be 206.62, 203.82, 163.40 and 162.02 eV, respectively. These Nb 3d peak positions are consistent with those of previous NbS2 XPS reports [31, 33]. The Nb to S ratio was calculated from the areas of the XPS peaks to be 1 to 2.19, closely corresponding to the stoichiometry of NbS2. Figure 1(c) shows a TEM image of the synthesized NbS2 thin film, and the inset image shows the diffraction pattern from the region imaged by TEM. These results confirmed the high crystallinity of the synthesized NbS2 thin film.

Figure 2(a) shows a schematic diagram of the bias-assisted AFM lithography setup. The NbS2 thin film was grounded by silver paste. During the AFM lithography, a positive bias was applied to the AFM tip (cathode) and the NbS2 thin film served as the anode. We generated patterns by using the biased AFM tip in the contact mode on the NbS2 thin film as shown in figures 2(b)–(e). Figure 2(b) shows a topological AFM image of patterned lines produced using different writing speeds, but keeping other parameters constant, including a +10 V bias on the AFM tip, a loading force of 5 nN, and a relative humidity (RH) at 40%. The line widths ranged from 1 to 0.2 µm and the thicknesses from 3±1 to 2±0.5 nm for scan speeds between 1 and 2 µm s⁻¹. The line width and thickness may have depended on the lithographed depth: at high writing speeds (>2 µm s⁻¹), only the region at and near the upper surface was lithographed because of an incomplete reaction of H2O with NbS2; in contrast, the entire depth of the NbS2 was transformed at low speeds (<1 µm s⁻¹) (figure 2(b)). The line width could be controlled not only by adjusting the scan speed, but also by adjusting the voltage: increasing the voltage from +2 to +10 V resulted in an increase in the line width (figure 2(d)). Figures 2(c) and (e) show phase images of the patterned lines. Phase detection microscopy (PDM) is a powerful tool for identifying materials since it can be used to obtain an image showing how surface mechanical properties such as stiffness, softness and adhesion change between the tip and surface, which all may cause a phase lag. The phase image of figure 2(c) shows the transformation of NbS2 thin film resulting from the lithography. The lines produced at different voltages appeared to have been well drawn according to the topological AFM image (figure 2(d)), but the phase image of figure 2(e) showed that NbS2 was actually not lithographed so well at voltages less than +6 V. Before using the CVD-grown NbS2, we had tried this technique with NbS2 flakes exfoliated from single crystalline bulk material. It was not easy to find flakes thinner than a few nanometers, and any such thin flakes were too small in area for this kind of systematic study. Note that the reaction did not occur for flakes thicker than several nanometers even at the maximum voltage (10 V), most probably because of high resistance. In the case...
of pristine NbS$_2$, the current flows in vertical stack direction of the layers, thus the resistance is supposed to be high due to the anisotropy of electrical properties of stacked materials [34]. For our CVD-grown NbS$_2$, however, the resistance in vertical stack direction was low because the film was thin. Hence, the bias assisted lithography could be easily realized.

The lithographed NbS$_2$ was also analyzed by carrying out Raman spectroscopy, cross-sectional TEM imaging, and EDX. Figure 3(a) shows Raman spectra before and after the lithography. The $E_2$ and $A_1$ Raman vibrational modes disappeared as a result of the lithography (figure 3(b)) showed the film to have a crystalline layered structure and a thickness of around 3(±1) nm. The atomic percentages of Nb and S in this film were measured using EDX to be 32% and 67%, respectively. After lithography, however, the NbS$_2$ thin film became amorphous (i.e. non-crystalline), and its thickness increased to around 5(±1) nm (figure 3(c)). The Nb and S atomic percentages also became 84% and 16%, respectively. The Raman spectroscopy and TEM results together confirmed that the NbS$_2$ thin film was transformed to another material. Regarding this transformation, note that an application of a bias voltage to an AFM tip has been previously shown to cause water meniscus naturally formed between the tip and the sample to become dissociated into H$^+$ and OH$^-$ ions [35]. In our case, we applied a positive bias voltage to the AFM tip during the lithography, so H$^+$ ions may have become attached to the NbS$_2$ thin film, and may have thus hydrogenated the NbS$_2$. It is, however, challenging to determine whether such hydrogenation occurred because hydrogen atoms are difficult to detect, and there is little information currently available about hydrogenated NbS$_2$. Hence, further work needs be carried out to completely identify the transformed material [27].

We also examined the surface properties of the patterned NbS$_2$ by measuring its topological root mean square (RMS) and by carrying out friction force microscopy (FFM). FFM yields relative friction values, because certain parameters of the experiment, such as load force, torsional constant of the tip and the AFM laser position on the tip, have great effects on the friction force. But since the friction coefficient is sensitive to surface roughness, the results of FFM provide an effective indicator of changes in such roughness. To characterize surface conditions, we measured the topological roughness RMS values and the friction forces of a 10 by 10 µm area of untreated NbS$_2$ and that lithographed at +10 V and 1 µm s$^{-1}$ (figure 4(a)). The RMS values of the untreated and lithographed areas were 0.5 and 1.8 nm, respectively. Figure 4(b) shows an FFM image including a boundary between NbS$_2$ (blue line) and patterned area (red line). All of the scale bars indicate a length of 1 µm.

![Figure 3](image3.png)

**Figure 3.** Changes in an NbS$_2$ thin film after bias-assisted AFM lithography. (a) Comparison of Raman spectra of the film before and after lithography. (b) Cross-sectional TEM image of an untreated NbS$_2$ thin film. (c) Cross-sectional TEM image after the lithography. The scale bars in both panels indicate 5 nm.

![Figure 4](image4.png)

**Figure 4.** Topography and friction of the NbS$_2$ thin film. (a) AFM topography image. (b) FFM image. (c) Line profile of boundary between NbS$_2$ (blue line) and patterned area (red line). All of the scale bars indicate a length of 1 µm.
Electrical properties of the lithographed film were also characterized. A part of the NbS₂ thin film was isolated, as shown in figures 5(a) and (b). A square-shaped set of lines was patterned at +10 V and 0.1 μm s⁻¹ on an NbS₂ thin film, and figure 5(a) shows the corresponding topological image. The PDM image, in figure 5(b), confirmed that NbS₂ was transformed along the patterned line. After the lithography, the electrical current was measured at each of the four points shown in figure 5(a) by contacting each such point of the NbS₂ thin film with the AFM tip, and the results are shown in figure 5(c). Points 1 and 2, outside the square pattern, showed a current, but there was no electrical flow at points 3 and 4. These results showed NbS₂ deformed in the above-described manner to be an electric insulator. It is essential to alter electrical property from the lithography and the above-described bias assisted lithography process transformed the entire depth of the NbS₂ film from a conductor to an insulator. On the other hand, the current between the AFM tip and the NbS₂ film showed rectifying characteristics. It was difficult to pattern the NbS₂ film with negative biases even at the minimum voltage (−10 V) because the current level was too low under a negative bias voltage. This issue may have arisen from the Schottky barrier between the silicon tip and NbS₂, which have both semiconducting and conducting properties depending on the phase of the material. Such an energy band alignment between the synthesized NbS₂ thin film and silicon substrate needs to be further investigated.

4. Conclusion

In this report, we described the technique to form patterns on NbS₂ thin films using bias-assisted AFM lithography. The relationships between various characteristics of a drawn line and AFM lithography parameters such as voltage and writing speed were explored. How the NbS₂ was transformed by the lithographic patterning was analyzed using Raman spectroscopy, TEM, FFM and measuring the current of the isolated pattern. Raman spectra and cross-sectional TEM images showed that the initially crystalline NbS₂ film became amorphous and thicker after being lithographed, and analysis of relative friction forces showed that its surface became rougher. A square pattern generated by the lithography was shown to be electrically isolated, indicating the lithographed film to be an insulator. This lithography technique should be of considerable practical use for thin films synthesized from NbS₂ together with other TMDCs, since it enables easy, clean and precise patterning of 2D electronic devices. The results and analysis of this work suggest that the technique could be used with other 2D metallic materials for diverse device applications.

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