Nanoscale anodic oxidation on a Si(111) surface terminated by bilayer-GaSe

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Abstract

Nano-scale oxide patterns were fabricated on a bilayer-GaSe terminated Si(111) surface using an atomic force microscope (AFM) in air. The Si(111) surface regularly terminated by bilayer-GaSe is very stable in air, although it can be oxidized through the electrochemical reaction when positive sample bias voltage is applied between the surface and a conductive cantilever tip of AFM. It has been revealed that higher sample bias voltage, slower tip velocity and/or higher ambient humidity produce wider and/or thicker oxide protrusions. Then, nano-scale oxide patterns as narrow as 50 nm have been successfully drawn on the terminated surface by adjusting these experimental conditions. These oxide lines can be etched away by dipping the sample into aqueous HF solution, and nano-scale grooves can be fabricated on the bilayer-GaSe terminated Si(111) surface.

KEYWORDS

Atomic force microscopy, Etching, Oxidation, Silicon, Gallium selenide, Silicon oxides

1. Introduction

For the last decade, there has been growing interest in the successful use of scanning probe microscope (SPM) as a versatile tool for the fabrication of nanometer-scale novel devices on solid substrates [1, 2]. For example, oxide lines induced by atomic force microscope (AFM) tip on Si substrates have been used as etch masks to fabricate a nm-scale metal-oxide-semiconductor field-effect transistor (MOSFET) [3], or a side-gated FET [4]. In many cases of the nano-scale Si-oxide formation using SPM, hydrogen-passivated Si surfaces have been successfully used, because this surface is relatively stable in air. Then nano-scale anodic oxidation reaction (anodization) occurs locally on the surface just under the conductive SPM tip apex, where adsorbed water capillary exists, when positive bias voltage is applied to the H-terminated surface against the tip [5-9]. However, the H-terminated Si surface is easily oxidized in humid ambient [10], which will restrict the application of this surface in air.

Recently, we found that a bilayer-GaSe terminated Si(111) surface (hereafter abbreviated to 'BGS' surface) is very stable against heating and oxidation under the ultrahigh vacuum (UHV) condition [11, 12]. It is also reported that this surface was not oxidized even after exposed to ambient air for one month [13]. The structure of a BGS surface is shown in Fig. 1 [14, 15]. This surface can be fabricated by depositing one monolayer (ML) Ga on a clean Si(111) surface and successive annealing in a Se flux at 500 ~ 600°C [11, 12, 14, 16], or by evaporating bulk GaSe onto the clean Si(111) surface at 550°C [13, 15]. In this structure half of a unit layer of bulk GaSe is bound well with the ideal Si(111) surface, although 2.2% mismatch exists between the lateral Si-Si interval (0.384 nm) and the lattice constant of a GaSe crystal (0.376 nm). Thus, the BGS surface is as inactive as the cleaved

surface of bulk GaSe free of the active dangling bond.

Then we tried to fabricate nano-scale oxide patterns on the BGS surface by the anodic oxidation reaction under the AFM tip. It has been found that nano-scale oxide lines can be fabricated also on the BGS surface. In this paper we report the dependence of height and width of these oxide lines on the bias voltage, tip velocity and humidity. We will also show a preliminary result of the etching of oxide patterns in aqueous HF solution.

2. Experimental

The BGS surface was formed in an UHV chamber with the base pressure of 3×10^{-8} Pa [11, 12]. Boron-doped *p*-type Si(111) wafers (1 ~ 10 Ωcm resistivity) were used as the substrates. A clean Si(111) surface was obtained by the direct current heating process; heating at 600°C for 12 h, repeated flash heating from 850°C to 1250°C, fast cooling to 850°C. Then the sample was cooled down to 520°C at 2°C/min with irradiating a Ga flux onto the surface. Intensity of the Ga flux measured by a nude ion gauge type monitor was 8×10^{-7} Pa. At 520°C, totally 1 ML equivalent Ga atoms (1 ML ≈ 7.8×10^{14} atoms/cm^2) were deposited onto the clean Si surface. Then the surface was irradiated with a Se flux at the substrate temperature of 520°C to form the BGS surface. Typical intensity of the Se flux was 2×10^{-4} Pa.

Nano-scale anodization of the BGS surface was performed in air at room temperature (20 ~ 25°C) using a commercial AFM unit (SPI-3800/SPA-300, Seiko Instruments Inc.). Au-coated Si cantilevers were used to draw anodized patterns. Mean radius of curvature of the tip apex was about 20 nm. Dependences of width and height of the drawn lines on the

bias voltage, tip velocity and relative humidity were investigated, and the size measurement was performed using the same AFM unit and cantilevers as the anodization. The relative humidity was controlled by introducing a mixture of dry N_2 and ambient air into an airtight bag in which the AFM instrument is placed. The height of the drawn line was determined from the cross-sectional AFM image by measuring the length between the baseline and the maximum of the section. The full width at half maximum of the sectional image was used as the width of the drawn line. In addition to these local-oxidation experiments, scanning Auger spectroscopy was investigated using a commercial apparatus (SMART-200, ULVAC-PHI, Inc.) to check the chemical composition of fabricated patterns.

3. Results and discussion

Fig. 2 indicates a typical result of the local anodization using the conductive AFM tip. In this case the sample bias voltage and the tip velocity was set to +8 V and 250 nm/s, respectively, and four oxide lines as long as 5 μm were fabricated with rotating the scan direction by 45°. This AFM image was measured using the same cantilever as that for the local oxidation. As shown in the figure, there are parallel bunched steps and wide terraces on the BGS surface, which are typical structures for the Si(111) surface cleaned by the direct current heating. There are many islands on step terraces, and both surfaces of islands and terraces are anodized. These islands have a same height with one step edge, so we conclude that they are bilayer-Si islands whose surfaces are as well terminated by bilayer-GaSe as step terraces. We think they are formed during the change of the surface structure from the beginning 7×7 reconstruction to the final bilayer-GaSe termination.

Details about the nano-scale structure of the BGS surface is described elsewhere [12].

Protrusive lines are formed regardless of surface corrugation of the BGS surface, just because the AFM cantilever was moved in the constant force mode to keep constant the spacing between the BGS surface and the AFM tip. However, the real value of the tip-surface interval is not yet known. It was revealed by the scanning Auger electron spectroscopy measurement that more oxygen and silicon atoms, and less gallium and selenium atoms appear in the fabricated lines than the surrounding BGS surface. Therefore it is suggested that these protrusions are SiO_x-rich complexes, in which oxygen atoms are supplied from the adsorbed water between the BGS surface and the AFM tip apex.

Fig. 3(a) shows an AFM image and its cross-section measured for oxide lines drawn on the BGS surface with different sample bias voltages. During the oxidation processes tip velocity was set to 300 nm/s, and relative humidity was 38 %. The height and width of these lines as a function of the bias voltage is plotted in Fig. 3(b). Under the present condition the oxidation occurred at higher bias voltage than +4 V, and both line width and height linearly increased along with the sample bias voltage.

Fig. 4 shows an AFM image and its cross-section (a), and a plot of line height and width measured for oxide lines drawn with different tip velocity (b). During the oxidation processes sample bias voltage was set to +6 V, and relative humidity was 38 %. Although the line height linearly increases when the tip velocity becomes slower, the line width does not increase so much. This anisotropic dependence suggests that the oxidation reaction uniformly occurs in the water capillary below the AFM tip at any tip velocity. The fast tip velocity produces a lower oxide line with a certain width determined by the diameter of the water capillary. When the tip velocity is slow, oxides can be accumulated along the vertical

direction and a higher oxide line can be fabricated. The width of oxides, however, does not become wider because the diameter of the water capillary is hardly affected by the present change of the tip velocity.

Fig. 5 shows plots of line width (a) and height (b) of oxide lines fabricated at three different sample bias voltages as a function of the relative humidity. During the oxidation processes the tip velocity was fixed to 300 nm/s. At higher relative humidity the line width becomes wider, but the line height doesn't show any distinct change. As mentioned above, the local oxidation is performed under the constant force feedback mode. Then it is expected that the separation between the surface and the AFM tip is constant. The height of the water capillary, therefore, is not so changed even at the high relative humidity, while the width of the capillary becomes wider with generating a wider oxide line.

In order to investigate the reactivity of these oxide lines fabricated on the BGS surface, a preliminary experiment of the chemical etching was performed in aqueous HF solution. Fig. 6(a) shows an AFM image of oxidized lines fabricated on the BGS surface in the manner mentioned above. After the local oxidation the sample was dipped into a 2% aqueous HF solution for 1 min at room temperature, rinsed in ultra-pure water for several seconds, dried by N_2 gas blow and observed by AFM again. As indicated in Fig. 6(b), two oxide lines were removed through the etching processes, and grooves were fabricated just at the same position. Auger spectroscopy measurement has proved the existence of the almost same amount of Ga and Se on the surface after the aqueous HF treatment. Therefore we conclude that the BGS surface is stable against the dilute aqueous HF etching, and only oxides produced by the anodization was removed. From this experiment it is also revealed that the anodic oxidation has proceeded beneath the BGS surface as deep as several

nm, just in the same scale of the height of anodized lines.

After the removal of local oxides using the aqueous HF solution, the surface inside of the groove is supposed to be terminated by hydrogen atoms, although rest of the substrate surface is still covered with bilayer-GaSe. If this sample is introduced into UHV and heated at the temperature around 450°C, these terminating hydrogen atoms inside the groove will desorb [17-19]. However, the rest BGS surface remains unchanged, because the BGS surface is stable against the heating around 500°C in UHV [12]. Namely, only the surface inside of the nano-scale groove will have active dangling bonds. Then it will be possible to fabricate nano-scale patterns of a different material by adsorbing foreign atoms into the active grooves. Detailed experimental results and discussions about the etching of nano-scale oxides on the BGS surface, and the fabrication of nanostructures of a foreign material, will be described elsewhere [20].

4. Conclusions

We have fabricated nano-scale oxide patterns on a bilayer-GaSe terminated Si(111) surface by the anodic oxidation reaction using a conductive AFM tip in air. It has been revealed that higher sample bias voltage produces wider and thicker oxide protrusions. The change of the tip velocity resulted mainly in the change of the oxide line height, while the change of the relative humidity principally changed the oxide line width. By adjusting these parameters, nano-scale oxide patterns as narrow as 50 nm have been successfully drawn on the BGS substrate. These oxide lines can be etched away by dipping the sample into dilute aqueous HF solution, and nano-scale grooves were fabricated on the BGS surface.

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Figure captions

Fig. 1 A schematic view of a Si(111) surface terminated by bilayer-GaSe.

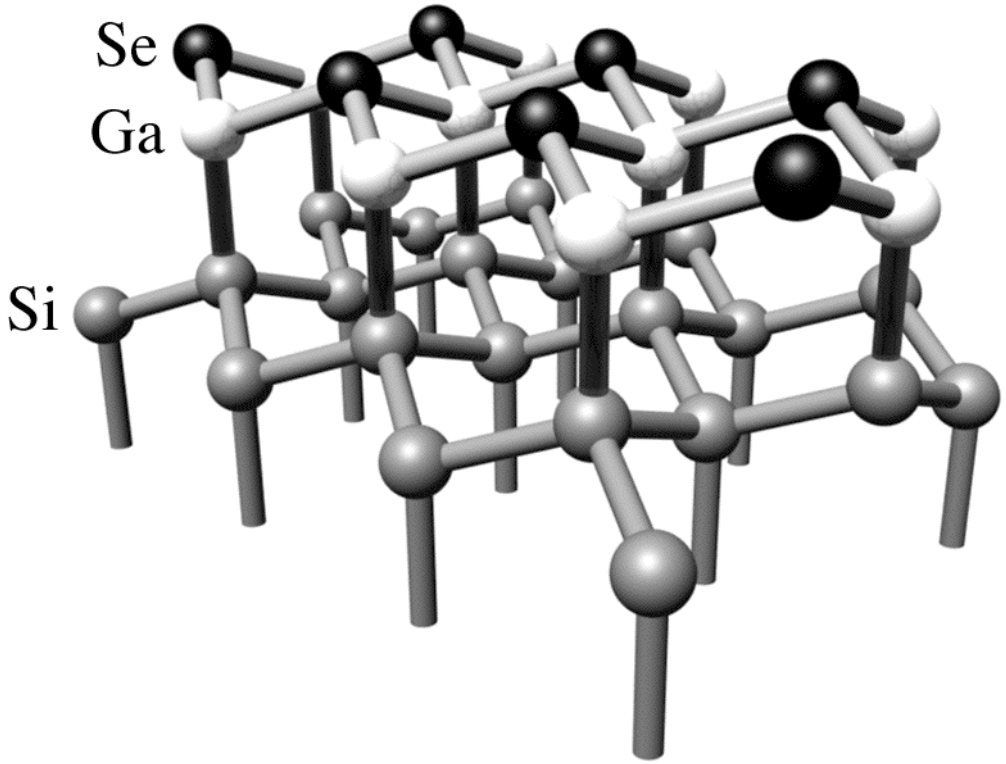
Fig. 2 An AFM image (5 μm × 5 μm) of typical oxide lines drawn on a BGS surface by the AFM anodic oxidation process in air. Sample bias voltage: +8 V, tip velocity: 250 nm/s.

Fig. 3 (a) AFM image and its cross-section measured for oxide lines fabricated on the BGS surface with different sample bias voltages. During the oxidation processes the tip velocity was 300 nm/s, and the relative humidity was 38 %. (b) The height (λ) and width (ð) of oxide lines plotted as a function of the sample bias voltage.

Fig. 4 (a) AFM image and its cross-section measured for oxide lines fabricated on the BGS surface with different tip velocity. During the oxidation processes the sample bias voltage was +6 V, and the relative humidity was 38 %. (b) The height (λ) and width (ð) of oxide lines plotted as a function of the tip velocity (10, 30, 100, 300 … 30000 nm/sec).

Fig. 5 Plots of line width (a) and height (b) of oxide lines fabricated at three different sample bias voltages (+5, +7, +10 V) as a function of the relative humidity. During the oxidation processes the tip velocity was fixed to 300 nm/s.

Fig. 6 AFM images of oxide lines fabricated on the BGS surface (a), and after the etching in 2% aqueous HF solution for 1 min (b).



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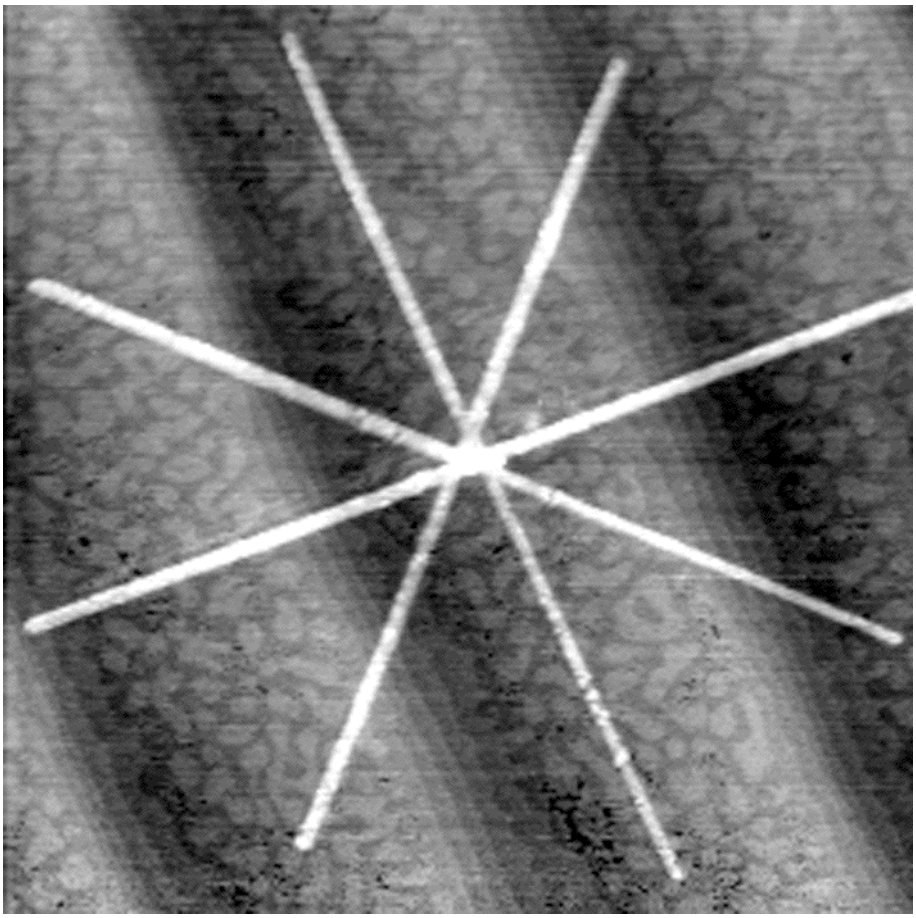
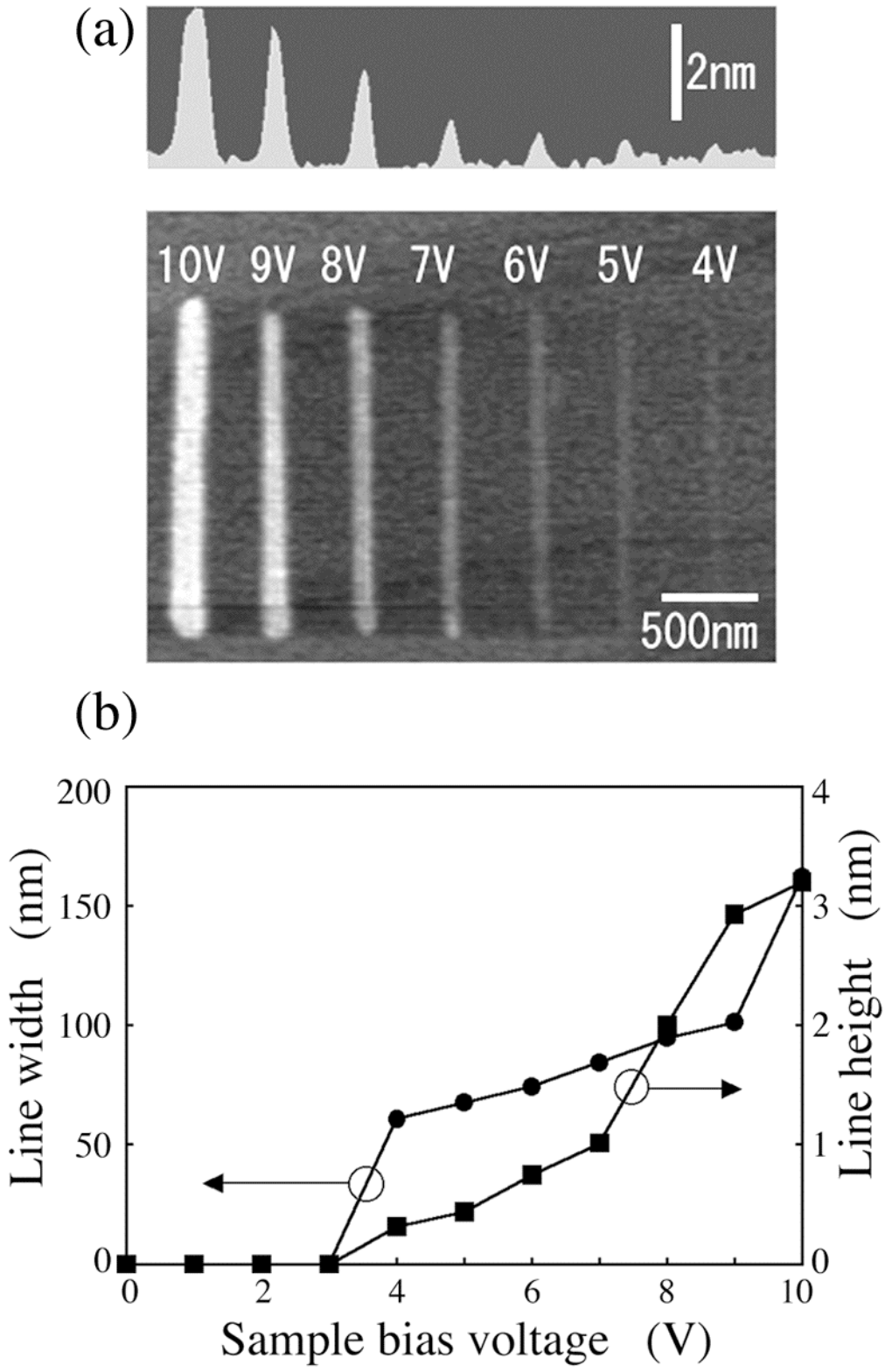


Fig. 2 K. Ueno et al.



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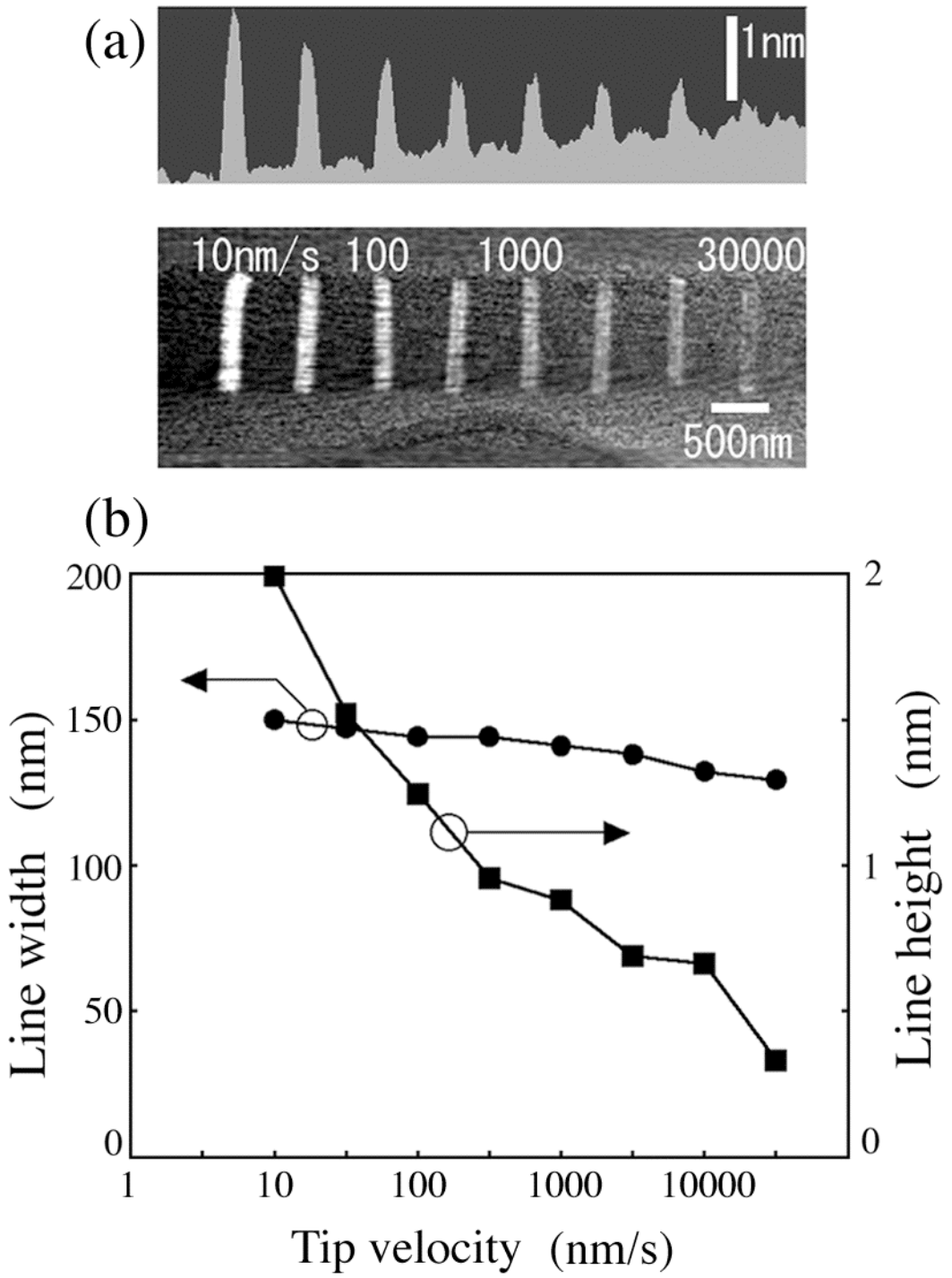

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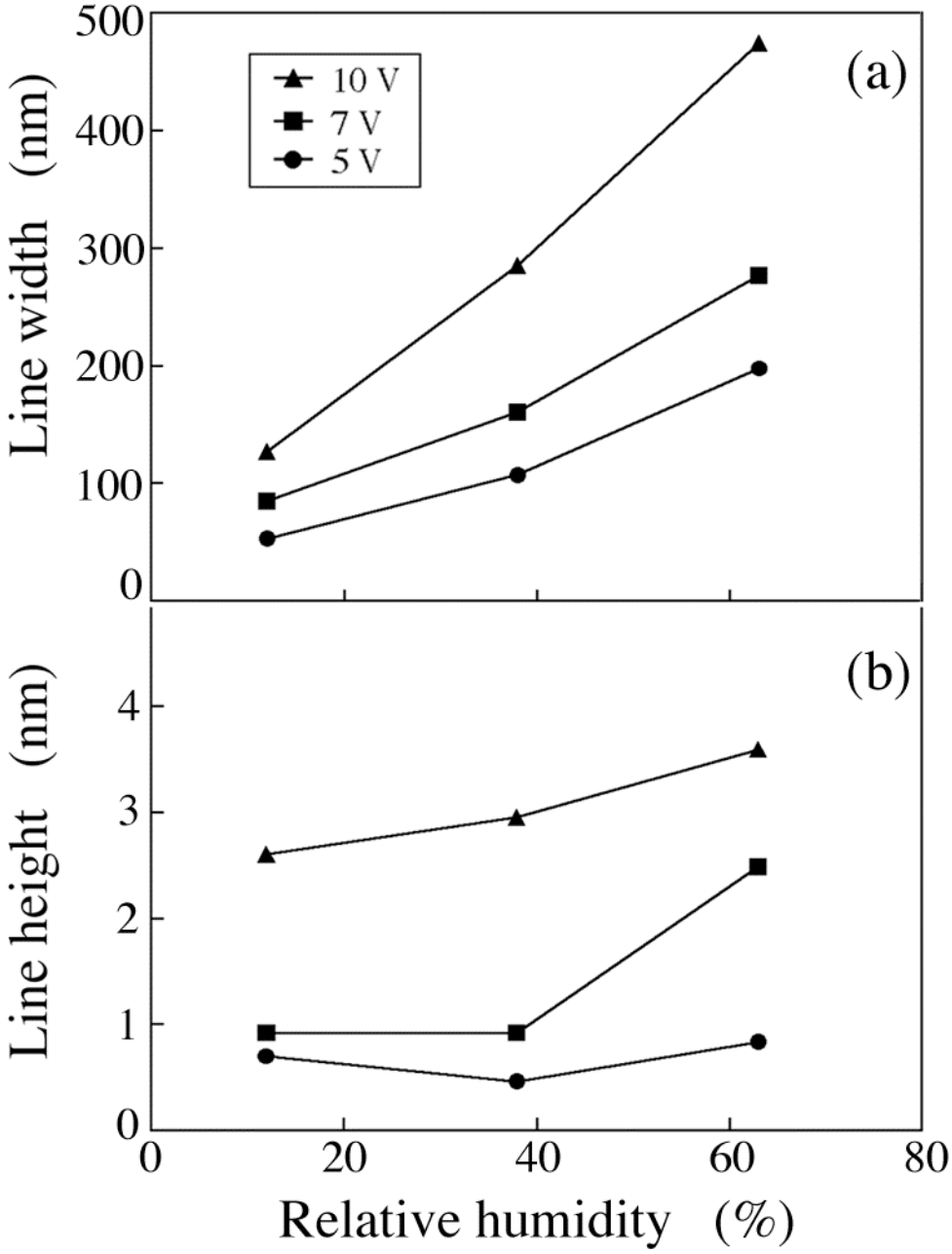

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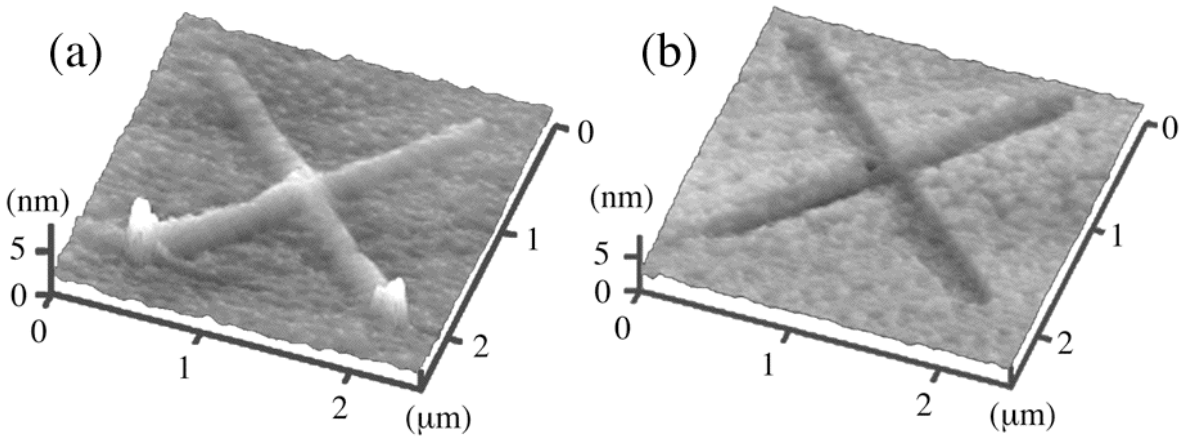

Fig. 6 K. Ueno et al.