Nanoscale Fabrication in Aqueous Solution using Tribo-Nanolithography

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Nanoscale fabrication of silicon substrate in an aqueous solution based on the use of atomic force microscopy was demonstrated. A specially designed cantilever with a diamond tip, allowing the formation of a mask layer on the silicon substrate by a simple scratching process (Tribo-Nanolithography, TNL), has been applied instead of the conventional silicon cantilever for scanning. A slant nanostructure can be fabricated by a process in which a thin mask layer rapidly forms on the substrate at the diamond tip-sample junction along scanning path of the tip, and simultaneously, the area uncovered with the mask layer is etched. This study demonstrates how the TNL parameters can affect the formation of the mask layer and the shape of 3-D structure, hence introducing a new process of AFM-based nanolithography in aqueous solution.

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NOMENCLATURE

H_0 = initial height of silicon substrate
H_s = height of silicon substrate at start point of machining
H_e = height of silicon substrate at end point of machining
$H = H_0 - H_e$
d = dissolution before starting machining
α = inclination of slant 3-D nanostructures
W = width of mask layer
P = scan pitch

1. Introduction

Developments in nanoscience and nanotechnology have generated extraordinary interest in the past few years and have raised the necessity for new fabrication processes in the nanometer range to support them. In the most widely used micromachining techniques borrowed from the microelectronic industry, lithography and subsequent pattern transfer are the key fabrication steps. The LIGA process (lithography [Li], electroforming [G], and molding [A]) has been successfully used in the fabrication of electronic parts or molds for injection molding.

Although lithographic methods allow the successful implementation of mostly 2-dimensional structures down to the nanometer scale, the fabrication of structures with 3-dimensional topography has hitherto been an only partly solved challenge. Other significant efforts from bottom-up fabrication processes to top-down processes coupled with contact or non-contact nature have been devoted to engineering functional nanometer range materials and worthy of close attention. Especially, the remarkable challenges related to the 2 or 3-dimensional fabrication in micro- to nano-scale in these days are the electrochemical machining through localized anodic dissolution of a substrate using ultrashort pulse[1,2] and scanning probe microscope (SPM) nanofabrication using sharp cantilever/probe based on atomic force microscope (AFM) and scanning tunneling microscope (STM).

The latter method can be classified into two ways. One is the process of fabricating patterns or structures in contact mode between the cantilever and the substrate by mechanical machining or molecular transportation. Yoshida and Morita[3] developed the mechanical patterning process of mapping images from an AFM using a lab-made micro cantilever for machining. Mirkin and co-workers[4] have shown the novel writing process named dip-pen nanolithography which uses an AFM tip as a nib, a solid-state substrate as paper, and molecules with a chemical affinity for the solid-state substrate as ink. Kolb and co-workers[5] reported the precise positioning of small copper clusters on gold electrode using a copper-deposited STM tip in an electrochemical environment.

The other is the nano-wire or nano-pattern fabrication processes by forming oxide layer or molecules on the substrate in the non-contact mode by tip-induced anodic surface oxidation (electrochemical reaction). These electrochemical patterning study based on SPM were firstly introduced by Dagata et al.[6] Quate and co-workers[7] have shown the process of patterning a series of lines with nanometer range in width using carbon nanotube (CNT)-attached AFM tip developed by Dai[8] using the CVD process. Snow and co-workers[9,10] have shown the possibility of nano-patterning lines below 10nm in width using a metal tip as a tool. In addition, Perez-Murano and co-workers[11,12] have introduced nano-patterning process on Al-coated silicon wafer using a conductive AFM tip in electrochemical environment, and tried to apply this technique to the mass sensor on CMOS. Gwo et al.[13,14] introduced the nano-scale SiO_2 fabrication

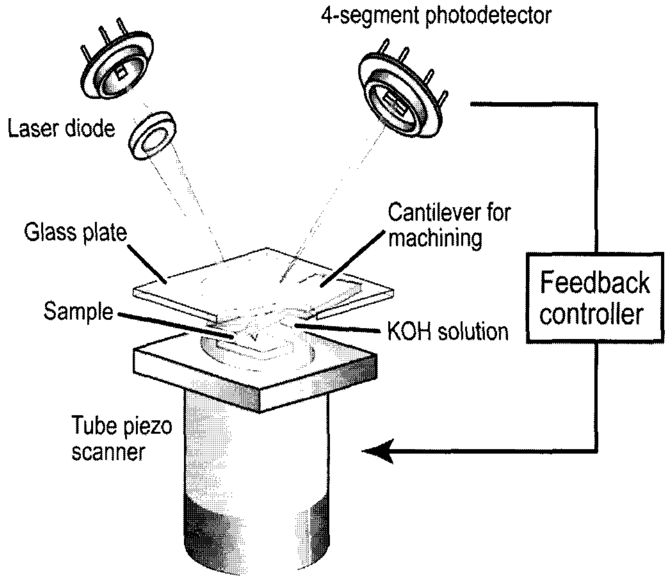

Fig. 1 Scheme of experimental setup for TNL in aqueous solution

process on Si and Si_3N_4 wafer. Other attempts to achieve nano-patterning using maskless methods have been studied by many researchers. Besides conventional electron beam lithography, focused ion beam (FIB)-induced nanolithography,[15,16] proton beam nanolithography,[17] nano imprinting lithography (NIL)[18] have been introduced and showed the possibility of novel nano pattern fabrication processes.

Despite the SPM-based nanofabrication method using non-contact or tapping operations can achieve atomic scale resolution, the low processing speed limits its use because the time constant of the feed back circuit for keeping the tunneling current at a constant determines the maximum processing speed. Additionally, there are some inherent limitations associated with these methods including the need for complex instrumentation, costly fabrication procedures, and time-consuming processing steps. Recently, we reported a new nanofabrication technique, TNL (Tribo-nanolithography), which consists of sequential processes, nano-scratching and wet chemical etching.[19,20,21] The simple scratching can form an amorphous layer on the silicon substrate, which act as an etching mask. Here, we present a simple method of nanometer-scale fabrication of a silicon substrate in aqueous solution based on AFM using a specially designed cantilever with a diamond tip, which facilitates the formation of an amorphous layer (mask layer) on a silicon substrate using processes such as mechanical machining. Owing to their etch resistance to KOH solution, protruding nanostructures with a slope can be fabricated using simultaneous mask layer formation and an etching process.

Table 1 Experimental conditions

Sample substrate	Silicon (100)
Processing direction	<110>
Normal force (μN)	137~673
Speed in Y dir. (nm/s)	39~195
Speed in X dir. (μm/s)	40~200
Pitch of processing line (nm)	39~312
KOH concentration (mass%)	5
Isopropyl alcohol (vol.%)	5
Subsequent etch	1 min with sonication

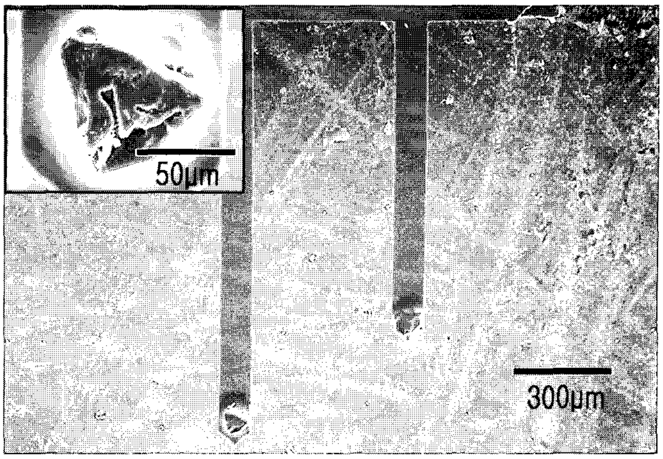

Fig. 2 SEM image of diamond tip cantilever for TNL

2. Experimental Procedure

Undoped silicon (100) wafers were rinsed in acetone and then in deionized water. To remove the air-formed native oxide layer, the samples were then dipped in 5mass% HF for 60 s and rinsed in deionized water again. After mounting the silicon substrate on the AFM stage, the diamond tip cantilever is brought towards it. Then, one drop of KOH solution is supplied through the injector into the space between the diamond tip and the substrate. This drop adheres between the cantilever and the silicon surface during the machining process due to surface tension. All the machining experiments used a 5mass% KOH solution with added isopropyl alcohol[22,23] using a PSIA XE-100 AFM & Shimadzu SPM-9500J2 AFM driven by custom software. Conventional triangular cantilevers with a reflective coating (PSIA 910M-CSC12, force constant of 1.75 N/m & Olympus OMCL-TR800PSA, spring constant of 0.57 N/m) were used in all of the imaging experiments. The processed samples were subjected to additional anisotropic etching with a sonication for 1 min at 24°C using the same KOH concentration to obtain a smoother, uniform surface around the modified area, and to maintain the selectivity of KOH to mask layer.[22] As shown in Fig. 2, the diamond tip cantilever as a tool for TNL is fabricated by the novel fabrication processes using micro-patterning, wet chemical etching and mechanical bonding by manipulator. The developed cantilever on AFM-based TNL apparatus modifies the (100) silicon surface with predefined normal load. Next, the processed silicon sample is etched with sonication in aqueous KOH solution at 24 °C for 5 minutes. After rinsing and drying the sample, the processed part is imaged by a commercial cantilever for imaging under the contact mode AFM. Finally, the etching selectivity with respect to KOH between processed (as an etch mask) and non-processed area shows protruded 2D or 3D nanostructures. Detailed experimental conditions are listed in Table 1.

3. Process Mechanism of TNL in aqueous KOH solution

Fig. 3 illustrates our proposed process of tribo-nanolithography (TNL) in aqueous solution. Wet chemical anisotropic etching of silicon starts when the aqueous KOH solution is added. Then, a mask layer is formed on the silicon substrate when the diamond tip cantilever starts modifying its surface. In studies of the characteristics of this mask layer, we have shown that the mask layer withstands selective anisotropic etching in KOH, but it dissolves in HF solution.[20] Hence, the mask layer stops the etching process on the area modified using the diamond tip, while the untreated surface continues to dissolve. Finally, the difference in the elapsed time of successive mask layer formation along the scanning path of the diamond tip (y-dir in Fig. 3) can fabricate a protruding structure with a slope.

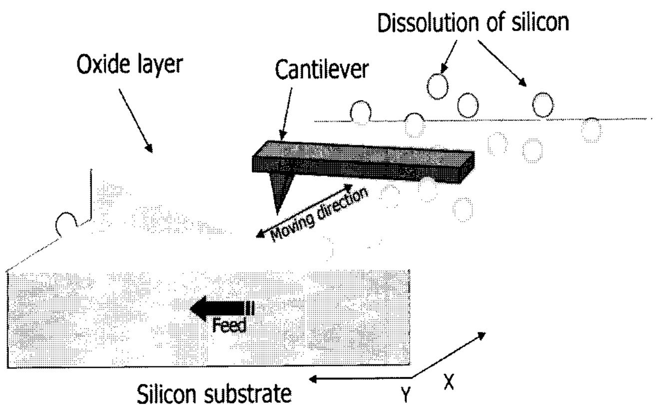

Fig. 3 Process model of TNL in aqueous solution

Fig. 4 illustrates the topographical nomenclature and experimental procedure in TNL process which follows three sequential stages including AFM setting, TNL process in aqueous solution and additional sonication. After approaching the silicon substrate, the slant nanostructure is fabricated by TNL in aqueous process. When KOH solution is added, the silicon substrate keeps dissolving until the diamond tip cantilever starts scratching. Hence, the initially dissolved amount of silicon in height is shown as *d* in Fig. 4 assuming the initial height of silicon substrate is H_0. Other parameters are also predefined in Fig. 4.

4. Result and Discussion

4.1 TNL Processed Surface Analysis

Fig. 5 illustrates the topography of nanostructures prepared using the TNL method in air and aqueous KOH solution. These structures were generated by modifying a 30×15 μm^2 area in air (right) and 5mass% KOH (left) at a scan speed of 40 µm/s in the x-direction and 78 nm/s in the y-direction with a diamond tip cantilever. The silicon amorphous mask layer on the structure surface was not dissolved in KOH solution because the modified area remained protruding after selective anisotropic etching. The structure prepared in air has a uniform height of 42 nm with no slope, while the structure fabricated in KOH is inclined due to the sequential formation of the mask layer. The etching rate of the silicon can also be calculated using the slope. The etching rate is defined as H/t [nm/min], where H is the height variation and t is the total machining time from the start to the end of machining. In this experiment, in 5mass% KOH, the calculated etching rate was $H/t \approx 6\sim7$ nm/min.

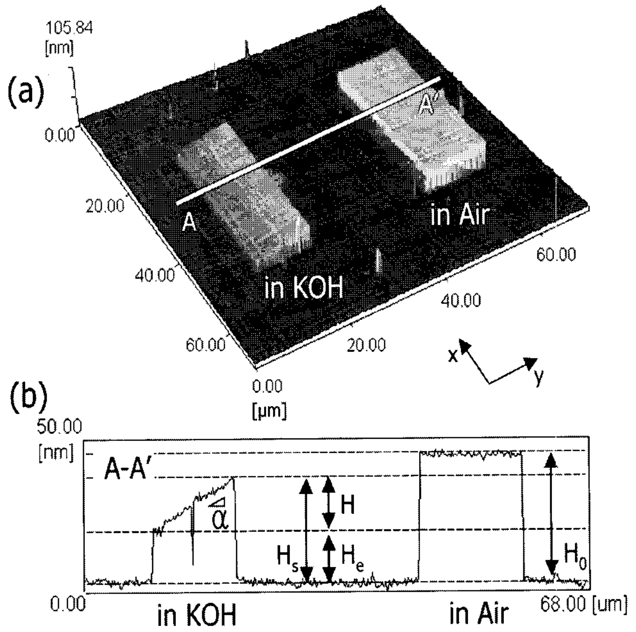

Fig. 5 (a) AFM topography image of nanostructures prepared by the TNL method in aqueous 5mass% KOH solution (left) or air (right), (b) Cross-sectional topography trace of the line marked A-A' in (a)

The slope of the nanostructure gives information on the process of silicon etching during the TNL process in KOH. Moreover, it means that we can control the inclination by changing the scan speed at a constant etching rate. Crystallization of the machined area was analyzed by TEM (Hitachi H-9000UHR III), and the specimen was prepared using an ion milling system. In order to investigate the change of crystallization on silicon surface induced by the TNL, TEM observations of the machined area were done. Cross-sectional TEM images of machined areas prepared using the TNL are shown in Fig. 6. Fig. 6(a) shows a cross-sectional TEM image of the silicon substrate after machining a single line at the normal load of 350 µN. This image shows that the amorphous layer measuring 100 nm in width and 15 nm in depth formed on the machined area. Fig. 6(b) shows the cross-sectional TEM images of the machined area prepared at a scanning pitch of 50 nm. The thickness of amorphous layer was somewhat increased, as can be seen in the Figure. Furthermore, a concave-convex pattern of the silicon crystal structure, which shows the same pitch as the scanning pitch, formed under the amorphous layer. In addition, at a scanning pitch of 50 nm, a dislocation measuring

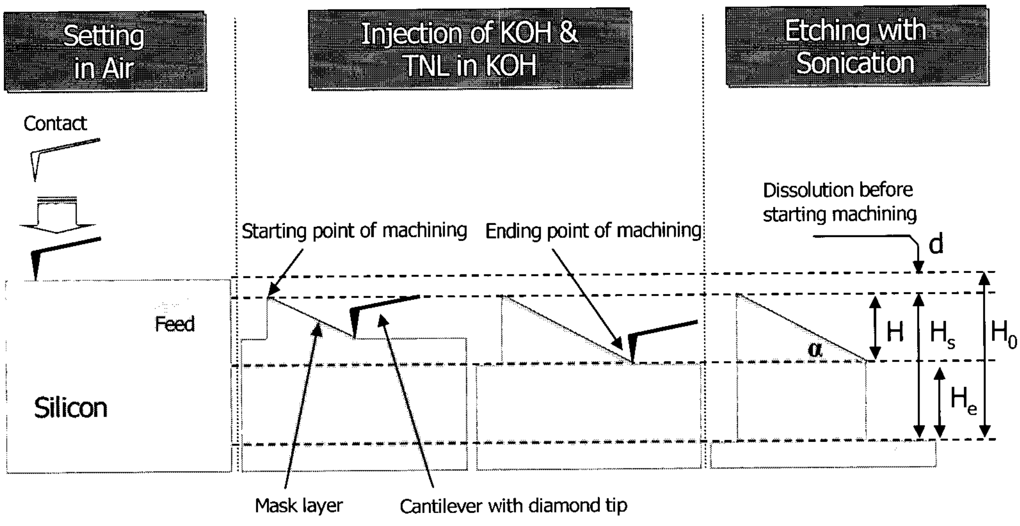

Fig. 4 Experimental procedure and nomenclature

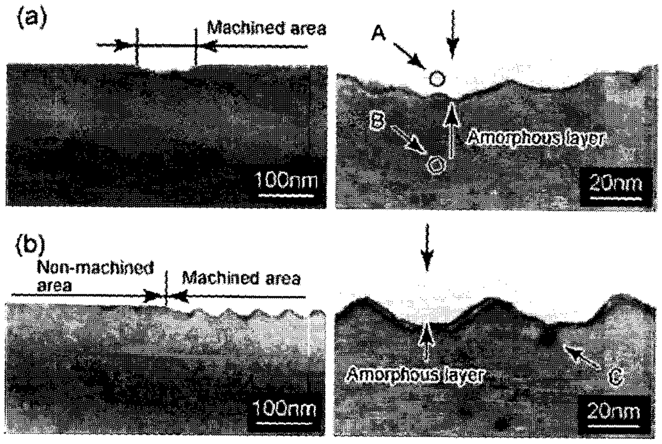

Fig. 6 Cross-sectional TEM images of silicon surface modified by diamond tip cantilever. (a) single line, (b) multiple lines with 50 nm pitch

approximately 5 nm length was observed along the {111} plane of the silicon crystal structure, whereas it could not be observed under conditions of a single line and at a scanning pitch of 100 nm (not shown in this paper, refer Ref. 24). This indicates that dislocations form when the scanning pitch decreases. In the current investigation, dislocations accelerate the etch process in KOH. This finding is contradictory to the characteristics of an amorphous layer which has a masking effect against KOH.

4.2 Inclination Dominating Parameters

In this study, we investigated the shape dependence of nano structures on various TNL conditions. Fig. 7 shows the change in the inclination α of structures at various scanning speeds in the y-direction v_y. It can be seen that the inclination depends significantly on the scanning speed from 39 nm/s to 195 nm/s. The inclination decreases with increasing scanning speed v_y. In the case of low scanning speed, the time lag between the starting and ending time of machining becomes longer. Therefore, there is enough time for a large quantity of silicon substrate to dissolve. As a consequence, a large inclination angle is generated. On the other hand, in the case of high scanning speed, a small quantity of silicon dissolves owing to the insufficient time for etching, resulting in a small inclination angle. The etch rate is constant at 6-7 nm/min at every scanning speed because the KOH concentration is constant. Moreover, this value reflects the rate of silicon etching in a 5 mass % KOH solution. This indicates that the mask layer does not dissolve at any scanning speed. From these results, it can be known that the inclination of the structure is controllable simply by adjusting the scanning speed.

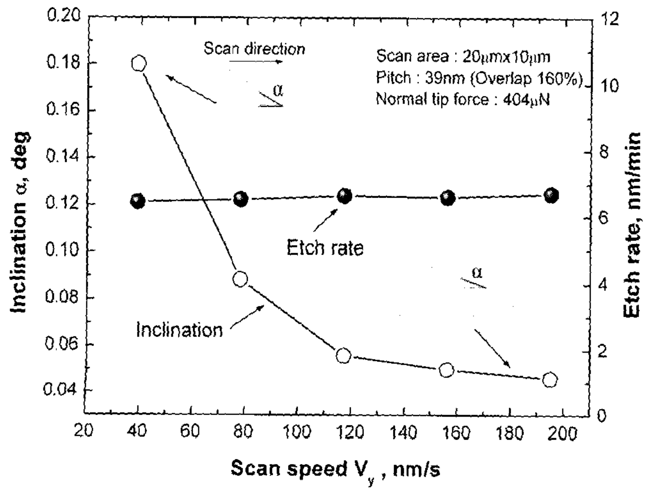

Fig. 7 Change in inclination (α) of the protruding structures generated on increasing the speed in the y-direction, Vy, from 39 to 195 nm/s

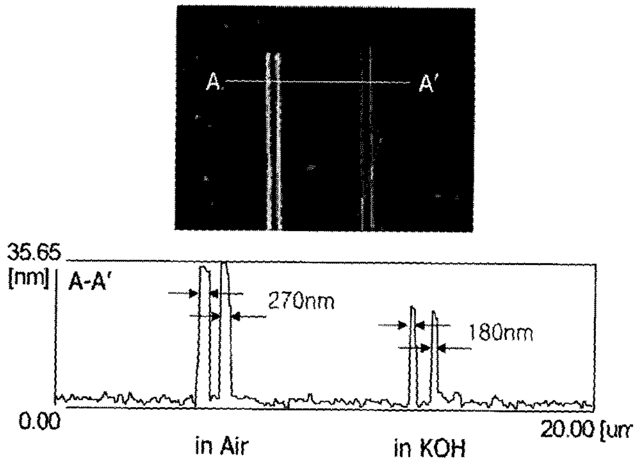

Fig. 8 AFM topography image of bar structures with different width prepared by TNL in air and in KOH

In this experiment, we could control the inclination from 0.05 to 0.18° by changing the scan speed in the y-direction from 39 nm/s to 195 nm/s. To verify the inclination changes and etch resistance variations according to the various scan pitches, it is important to verify the width of the mask layer generated in KOH and in air. Fig. 8 shows an AFM topography and cross-sectional image of line structures machined in air (left) and in KOH solution (right), after subsequent wet etching in 5 mass % KOH for 1 min. It can be observed that the line structure machined in air is higher and wider compared to that machined in KOH solution. This result indicates that a harder mask layer forms on the silicon surface by the TNL in air than in KOH. Additionally, the width of the structure is approximately 270 nm, which shows that 135 nm area from the center of diamond tip can be affected by TNL process in air. This result can be a criterion to predict how dense the mask layer forms on the silicon substrate according to the scan pitch in TNL. The overlap can be defined as:

$$overlap = \left(\frac{W}{P} - 1\right) \times 100(\%) \tag{1}$$

W = width of mask layer

P = scan pitch

From Eq. (1), a mono-mask layer forms on the silicon substrate in the case of TNL with a 270 nm pitch (overlap 0%), whereas a double-mask layer (equivalent to the machining same area twice) forms in the case of 135 nm pitch (overlap 100%).

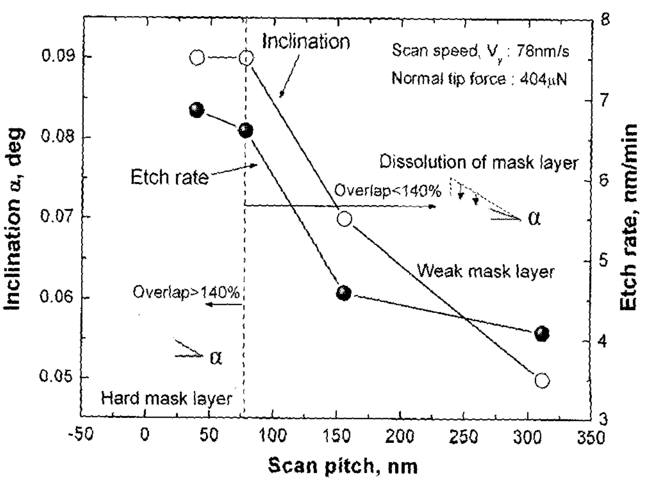

Fig. 9 Inclination (α) and etch rate variation of nano structure as a function of scan pitch

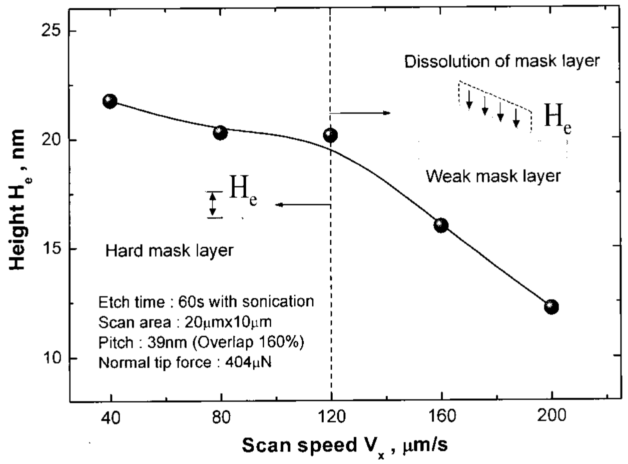

Fig. 10 Height (H_e) variation as a function of scan speeds, V_x

However, the line structure fabricated in KOH shows 180 nm in width, which can be drawn by the smoother surface and lower oxide contamination in KOH solution compared to those in air. Fig. 9 shows the change in the inclination α of structures at various scanning pitches. In the case of the scanning pitch lower than 76 nm (overlap 140%), the inclination value remains constant, which indicates that a hard mask layer forms below 76 nm pitch (overlap>140%). Conversely, the inclination starts to decrease in the case of scanning pitch over 76 nm (overlap<140%). The reason for the decrease in the inclination angle is the dissolution of the mask layer, which is caused by low transition ratio of crystal silicon to amorphous silicon, due to the large scanning pitch. A large amount of silicon crystals are converted to amorphous silicon structure when each scanning pass is superimposed, and consequently, a hard amorphous layer can form on the machined surface.

Fig. 10 shows the height variation of protruded structure H_e as a function of scan speed v_x. H_e is almost constant under 120μm/s in v_x, where it decreases with increasing v_x over 120μm/s. This result can be explained by mask layer dissolution owing to the nonuniformity drawn by the difficulty for diamond tip to trace the silicon surface without skipping in higher scan speeds. Finally, H_e changes as the scan speed becomes higher over 120 μm/s, while it keeps nearly constant under 120 μm/s, in which the mask layer has a higher etch resistance against KOH. Fig. 11 shows the change in the inclination α of structures at various normal loads. It can be seen that the inclination and etch rate are both nearly constant at every normal load. Hence, this result indicates that a hard mask layer forms at any normal load and it has enough etch resistance against 5 mass % KOH solution without any influence on the inclination of the structure. A three-dimensional structure having multiple inclinations was fabricated based on these results as shown in Fig. 12.

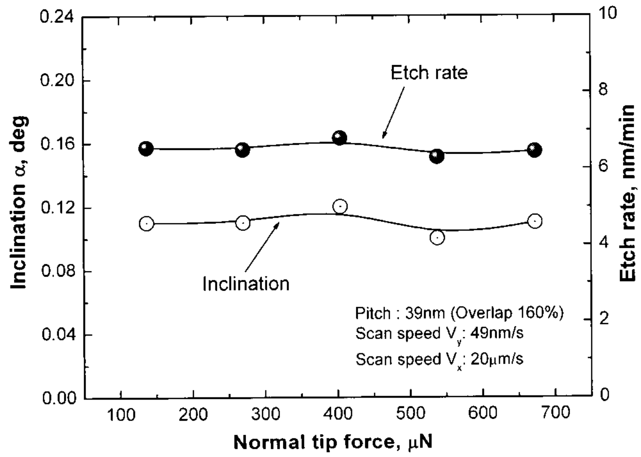

Fig. 11 Inclination (α) variation as a function of normal forces

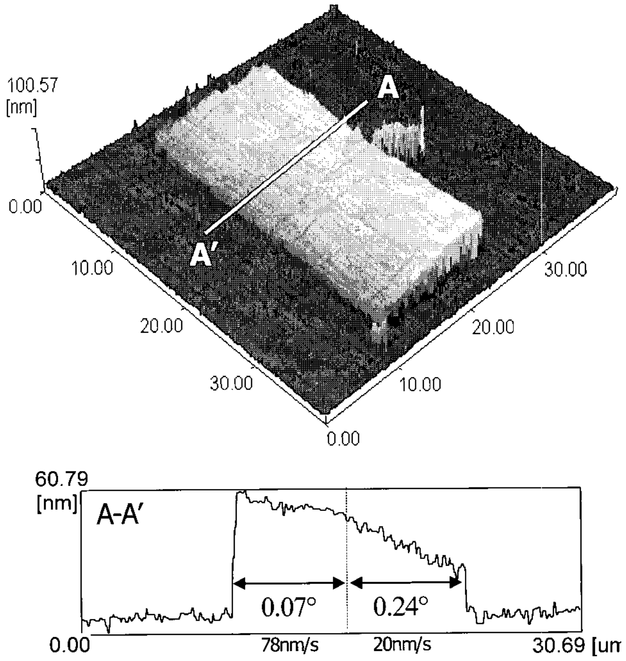

Fig. 12 AFM topography image of slant nanostructure prepared by the TNL method in 5mass% KOH solution

We can control the inclination of the three-dimensional structure from 0.07° to 0.24° by changing the scanning speed v_y from 78 nm/s to 20 nm/s, at a normal load of 400 μN in 5 mass % KOH solution. This image shows that there are no outer disturbances or dissolution of mask layer during the etch processes, and that a smooth (4 nm Ra), slant structure can be fabricated. For further study on TNL via controlled diamond tip cantilever, we have fabricated a pyramidal-shape polycrystalline diamond tip[25] by a novel CVD and wet chemical processes as shown in Fig. 13. Efforts in this direction are underway.

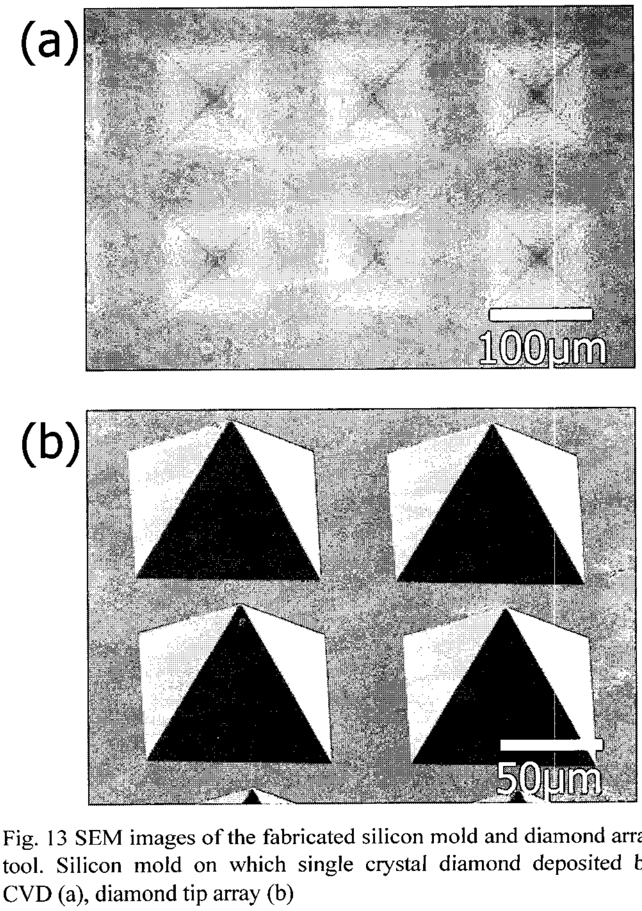

Fig. 13 SEM images of the fabricated silicon mold and diamond array tool. Silicon mold on which single crystal diamond deposited by CVD (a), diamond tip array (b)

5. Conclusions

This study demonstrates a new method of three-dimensional nanofabrication in aqueous KOH solution using the TNL. A slant rectangular three-dimensional structure can be fabricated by this method. Shape dependence of structure on TNL conditions and characteristics of mask layer at various machining parameters are investigated. Hereby, it can be known that the scanning speed v_y is an important factor for controlling the inclination of the structure. On the other hand, scan pitch and scan speed in x-dir is related to the etch resistance of the mask layer rather than the change of inclination. TNL method in solution is a very simple and powerful method for fabricating three-dimensional slant structures based on AFM comparable to those achieved with much more expensive and sophisticated competitive lithographic methods. It can be known that this method introduces the possibilities of nanolithography using conventional mechanical method combined with chemical reaction because KOH wet chemical method can etch structures reliably on the submicron scale.

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