공학석사학위논문

Micro patterning on cylindrical surface by electrochemical etching using laser masking

레이저 마스킹을 이용한 원통형상의 미세 패턴 전해에칭

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Abstract

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Selective electrochemical etching of stainless steel was achieved by applying laser masking on cylindrical surface. Micro patterned recast layer was formed through ytterbium doped pulsed fiber laser irradiation on the workpiece surface. The micro patterned recast layer can be used as a mask during electrochemical etching process. Since the surface of the workpiece was non-planar, laser masking characteristics were investigated to form uniform mask on the entire surface. To minimize the factors causing non-uniformity of mask formation, galvano line scanning method was applied to laser masking process. Electrochemical etching characteristics were investigated to achieve deeper etched depth. Selective electrochemical etching of stainless steel was conducted in 2 M sodium nitrite electrolyte. The results were observed by scanning electron microscope (SEM) and surface profiles were measured by 3D surface profiler. Through a series process of laser masking and electrochemical etching, micro patterning on cylindrical surface was successfully performed.

Keywords : Micro patterning, laser masking, electrochemical etching,
non-planar.

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Chapter 1

Introduction

1.1 Research background

Micro fabrication technologies for micro patterning have been widely investigated and continuously developed due to its paramount importance in various industries such as electronics, micro-electromechanical systems (MEMS), micro total analysis system (μ-TAS), and miniaturized sensors [1-2]. One of the well established methods and mostly used in the micro patterning is MEMS fabrication process that is based on photolithography techniques. Although photolithographic techniques are suitable for large production, MEMS fabrication process has limitations to be applied to non-planar surface, such as limitation of depth of focus of the source lights [3]. As demands for micro patterning on large area of a non-planar surface increases, such as improvement on tribological performances of automotive or magnetic storage components by fabrication of micro grooves and dimple patterns on the surface, several methods for micro patterning on a curved surface were reported. Nanosecond laser machining has been used for surface texturing or micro patterning on non-planar surface [4]. However, a heat affected zone with possible micro cracks inside the material was generated by nanosecond laser. Micro electro chemical machining (ECM) was used to fabricate micro dimples on cylindrical surface of stainless steel to reduce friction between mechanical components, but the material removal rate was very low in comparison with other machining processes [5]. Relatively faster fabrication of micro patterns was carried out by electrochemical etching using a flexible stencil mask [3]. The flexible PDMS stencil was fabricated by photolithography process and used as a mask on non-planar surface during electrochemical etching. Despite the fact that micro patterns on a large area can be achieved by electrochemical etching, flexible PDMS stencil mask was inappropriate for small size of patterns. Hydrophobicity of PDMS surface makes difficulty for the electrolyte to be filled in the small patterns. Additionally, the process for making the stencil mask requires high cost due to expansive equipments.

To overcome these limitations, a new micro patterning process without a specific mask on non-planar surface is suggested and investigated in this research. Electrochemical etching that has high selectivity and relatively high etch rate was used to fabricate large area of micro patterned surface. Electrochemical etching is generally conducted in conjunction with a photoresist mask that brings complex processing steps, high cost and difficulty to coat uniform patterned mask on the non-planar surface. These limitations could be compensated by laser masking process. The protective layer that is formed through laser masking could be used as a mask during electrochemical etching [2, 6]. Furthermore, the laser masking process brings advantages of fast and low cost for various patterning because the masking process is carried out in the air and does not need photolithography process at all. Thus the fabrication of micro patterning on non planar surface could be conducted in normal experimental condition without any expansive equipment such as clean room and vacuum chamber.

1.2 Research objective and thesis overview

The purpose of this research is development of a new process for micro patterning on non planar surface without a specific mask that makes the whole process complicates and brings high cost due to expansive experimental equipments. To achieve the purpose, a serial process of laser masking and electrochemical etching was presented. Since the workpiece surface is non planar, the laser masking characteristics change along the geometrical surface. Therefore, investigation of factors causing non-uniformity formation of the mask was taken to form uniform protective layer on the entire surface. Also electrochemical characteristics were investigated to control parameters that could achieve proper etched depth of micro patterned surface.

In chapter 2, principles of the two discrete steps: laser masking and electrochemical etching are described. Then, the explanation of experimental system which has been constructed and utilized for the experiments is continued with details.

In chapter 3, the characteristics of laser masking are investigated. The factors causing non-uniformity of the formation of protective layer are also presented. To minimize the factors, galvano line scanning method is applied and results are described.

In chapter 4, the characteristics of electrochemical etching are investigated. Since the formed mask layer cannot be used as a mask permanently because of the breakdown of the layer due to material removal, induced over potential and current density, appropriate parameters are selected to achieve micro patterning that has proper etched depth. Furthermore, results of various v-shape micro patterning have been shown.

Finally, conclusion of this thesis was presented in chapter 5.

Chapter 2

Principle and experiments

2.1 Procedures and principle of micro patterning on non-planar surface

The process of micro patterning on non planar surface consists of laser masking, electrochemical etching and ultrasonic vibration cleaning step as shown in figure 2.1. Through the process, selective electrochemical etching of stainless steel was performed and micro patterns were produced on the cylindrical surface.

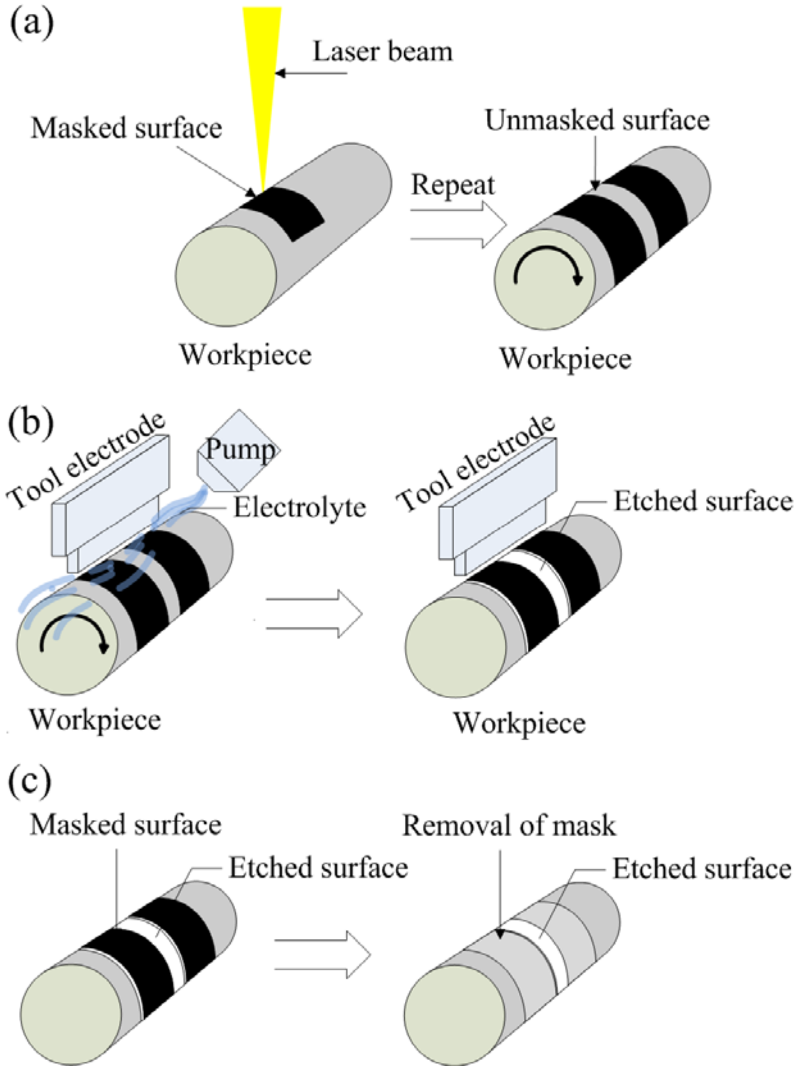


Figure 2.1 Schematic diagrams of the process for micro patterning on cylindrical surface: (a) laser masking, (b) electrochemical etching, and (c) ultrasonic vibration cleaning.

2.1.1 Laser masking

Laser masking is one of the laser material processing that is a thermal energy based, non-contact typed process, which can be flexibly applied for wide range of materials. The laser masking is based on direct writing of pulsed laser beam by laser irradiation as shown in figure 2.1 (a). A common usage of the laser irradiation is the laser marking for the purpose of decorating and various colorizing of the metal surfaces. In the case of metals such as stainless steel or titanium, different colors can be appeared on the irradiated surface area by different laser irradiation conditions [7]. The phenomenon results from light interference due to periodic marks those are formed by laser irradiation and induced oxidation of the metal surface. However, in the recent study, the laser irradiated surface was used as a mask in the electrochemical etching process [6]. Selective electrochemical dissolution of the workpiece was possible without a special mask via the different rates of the anodic dissolution between the laser un-irradiated surface and the laser irradiated surface.

Heating, melting or ablation of substrate materials is determined by the impact of laser power density as a result of the laser irradiation. Melting and vaporization occur in the interaction zone between the laser beam and material as the laser power density exceeds a critical point above the boiling point of material as shown in figure 2.2. the molten material can be ejected from the cavity by the vapor and plasma pressure, but part of the material in liquid-state remains with lead to form recast layer on the surface in high power density (≥10^6 W/cm^2) while the material remains solid state at the heating process with low power density (≤10^5 W/cm^2). Thus, with the controlled laser beam parameters, the amount of material ablation can be minimized and the melting zone that is not removed by thermal energy of laser beam is quickly re-solidified [8]. The formed re-solidified oxidized layer on the surface is called recast layer [2, 9]. As shown in figure 2.1 (a), using laser irradiation, various micro patterned recast layer on the workpiece were formed rapidly, and the patterned layer acted as protective layer like a mask for the selective etching during electrochemical etching step. Figure 2.3 shows SEM images of the formed recast layer on the stainless steel plate. Figure 2.3 (a) is the top view, (b) and (c) are the cross sectional view of the stainless steel by FIB analysis after laser masking.

In the recent study, the oxidation state and phase transformation of the recast layer of the stainless steel were investigated. When the surface is exposed by laser beam, oxide films such as Cr_2O_3, FeO and Fe_2O_3 were formed and also phase transformation from martensite to austenite phase occurred on laser masked surface [6]. This beneficial phase transformation results in passive ability of laser masked surface [10]. The current density of laser masked surface that indicate rate of anodic dissolution was less than that of the unmasked surface and also corrosion resistance was improved due to a low passive current density [6, 11]. Therefore, selective etching was performed because of different rates of anodic dissolution between laser masked surface and unmasked surface [2, 6].

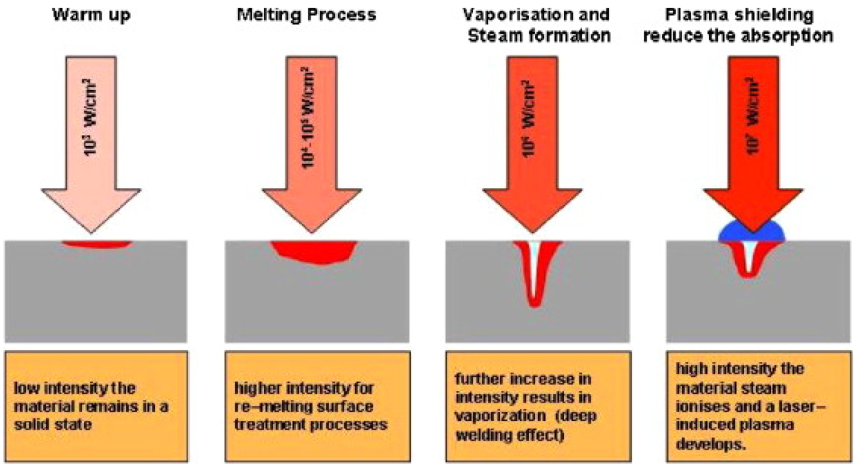


Figure 2.2 The impact of intensity on the effect of the laser beam [12].

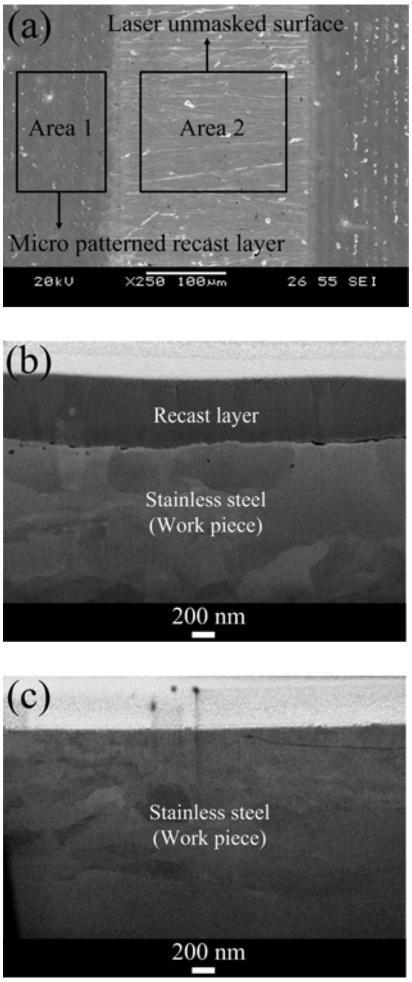


Figure 2.3 The top view and cross sectional view of stainless steel plate after laser masking: (a) SEM image of the top view of the recast layer, (b) the cross sectional view of the recast layer (Area 1) by FIB analysis and (c) the cross sectional view of the un-irradiated surface (Area 2).

2.1.2 Electrochemical etching

Electrochemical etching is a process that removes conductive materials by anodic dissolution with the electrical power support that drives chemical reaction. A variety of metals and highly corrosion-resistant alloys can be machined by electrochemical etching. Electrochemical etching process is based on electrochemistry that is the study of chemical reactions in which ions and electrons cross the electrode interface between a metal electrode and a conductive electrolyte. The process using electrochemistry is generally called an electrode process because the chemical reactions occur at the electrode. When potential is applied to electrodes in electrochemical etching, material removal process that destroys the atomic bonds of the metal is induced by an electrical field in an electrochemical cell [13]. Electrode processes produce inequality in the electric charges of the electrode and the electrolyte, which is called interfacial potential difference that can influence anodic dissolution rate. Kinetics and thermodynamics of electrode reaction are related to potential difference. Potential difference between two electrodes can be easily measured by providing an arbitrary potential difference between two different electrodes when there are two metal-solution interfaces in the electrochemical cell using a voltage source. So with controlling the interfacial potential differences at the electrode, the overall cell voltage can be controlled. In this research experiments, two electrodes that consist of a stainless steel workpiece electrode and a platinum tool electrode were placed in an electrochemical cell. In case of stainless steel that mainly consists of iron (Fe) and chromium (Cr), the electrochemical reactions in electrochemical cell are as shown in Eq. (1) [14].

$$
\begin{aligned}
& Fe \rightarrow Fe^{2+}(aq) + 2e^{-} \\
& Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^{+}(aq) + 2e^{-} \\
& Fe + 2OH^{-}(aq) \rightarrow Fe(OH)_2 + 2e^{-} \\
\text{Anode:}\quad & 2Cr + 7H_2O \rightarrow Cr_2O_7^{-}(aq) + 14\,H^{+}(aq) + 12e^{-} \\
& Cr + H_2O \rightarrow Cr(OH)^{+}(aq) + H^{+}(aq) + 2e^{-} \\
& Cr + 2H_2O \rightarrow Cr(OH)_2^{+}(aq) + 2H^{+}(aq) + e^{-} \\
& H_2O \rightarrow 2H^{+}(aq) + 2e^{-} + \tfrac{1}{2}O_2 \uparrow
\end{aligned}
$$

$$
\begin{aligned}
& 2\,H^{+}(aq) + 2e^{-} \rightarrow H_2 \\
\text{Cathode:}\quad & O_2(aq) + 4\,H^{+}(aq) + 4\,e^{-} \rightarrow 2H_2O \\
& O_2(aq) + 2H_2O + 4\,e^{-} \rightarrow 4HO^{-}(aq) \qquad (1)
\end{aligned}
$$

2.1.3 Ultrasonic vibration cleaning

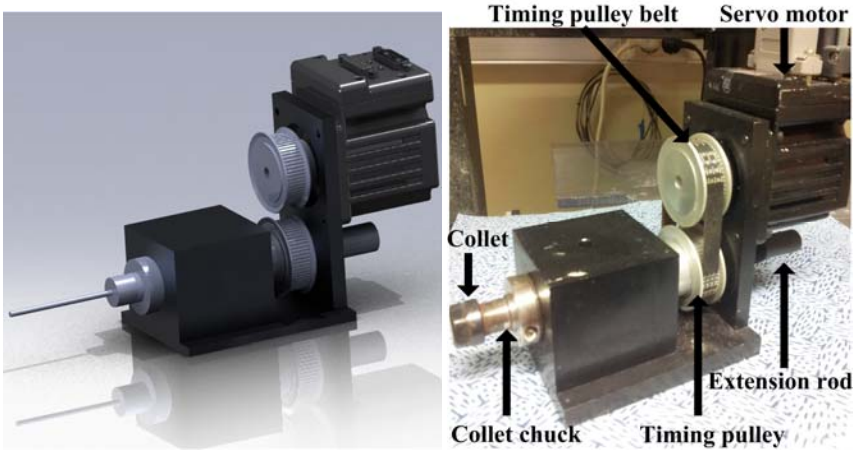
After laser masking and electrochemical etching, selective removal of substrate materials to make micro patterns can be performed. Through ultrasonic vibration cleaning step etching as described in figure 2.1 (c), the sludge and the dissolved recast layer were cleaned away. As a result, micro patterns on stainless steel can be fabricated by selective.

2.2 Experimental setup

The experimental setups for the process consist of a rotary system, a pulsed fiber laser system for laser masking and an electrochemical etching system. Platinum plate was used as a tool electrode and stainless steel 304 rotary shaft that has 3 mm of diameter was used as a workpiece. Surface was observed by scanning electron microscope (SEM) and surface profile of the workpiece was measured by 3D surface profiler (Nano View-E1000).

2.2.1 Rotary system

A new experimental rotary system was constructed to control the rotation speed of a shaft workpiece as shown in figure 2.4. Rotation speed of the workpiece should be synchronized with the laser scanning speed during laser masking step to form appropriate recast layer that can be used as a mask in electrochemical etching step. Also rotation speed of the workpiece should be controlled during electrochemical etching step to achieve micro patterning that has uniform etched depth along the entire area of cylindrical surface of the workpiece. The constructed rotary system consists of 4 major parts; servo motor, collet chuck, timing pulley and extension rod. A servo motor (SM165D, Smart motor) which has advantages of fast response and controllable ability in wide range of rotation speed, was applied to the constructed rotary system. Specification of the servo motor was shown in table 2.1. Generated torque transferred to collet chuck through timing pulley and timing pulley belt. Then the workpiece that is fixed by collet in collet chuck can be rotated with controlled rotation speed by the constructed rotary system. External potential can be applied to the workpiece through extension rod that is connected to the workpiece which is located below the servo motor. The constructed rotary system was placed on X-Y stage that has 0.1 μm of resolution.



(a) Initial design (b) Constructed equipment

Figure 2.4 New experimental rotary system.

Table 2.1 Specification of servo motor

Characteristics (unit)	Value
Input power (VDC)	20 – 48 (max)
Peak torque (N-m)	0.30
Continuous torque (N-m)	0.19
No load speed (RPM)	9000
Nominal power (kW)	0.13
Encoder resolution (ppr)	2000
Voltage constant (V/kRPM)	4.45
Torque constant (N-m/Amp)	0.03
Rotor inertia (10^{-5}kg-m^2)	0.70

2.2.2 Laser masking system

An ytterbium (Yb)-doped pulsed fiber laser from IPG Photonics Corp. that had a 1,064 nm wavelength and a 100 ns pulse length was attached to a Z-axis moving stage for focusing the laser beam, as shown in figure 2.5. The laser masking system consists of three major parts; a fiber module, a collimator head, and a scan head. The pulsed laser beam which is generated from the laser module and passed by the collimator head enters the scan head. Then, the laser beam could be controlled by a galvanometer scanner inside the scan head. A galvanometer scanning system (SCANLAB AG SCANcube® 10) was used for the laser beam to be transmitted flexibly at a high scanning speed. The average power that is provided by the pulsed fiber laser module ranges from 2 W to 20 W and 20 kHz to 80 kHz of pulse repetition rate with 50 μm of spot size of the laser beam. The exact specification of the pulsed fiber laser is appeared in table 2.2. In the laser masking step, stainless steel workpiece that was clamped to the rotary system was irradiated by an ytterbium pulsed fiber laser in the air and micro patterns were created on the surface by the laser beam that is controlled by galvanometer. Table 2.3 shows laser masking condition.

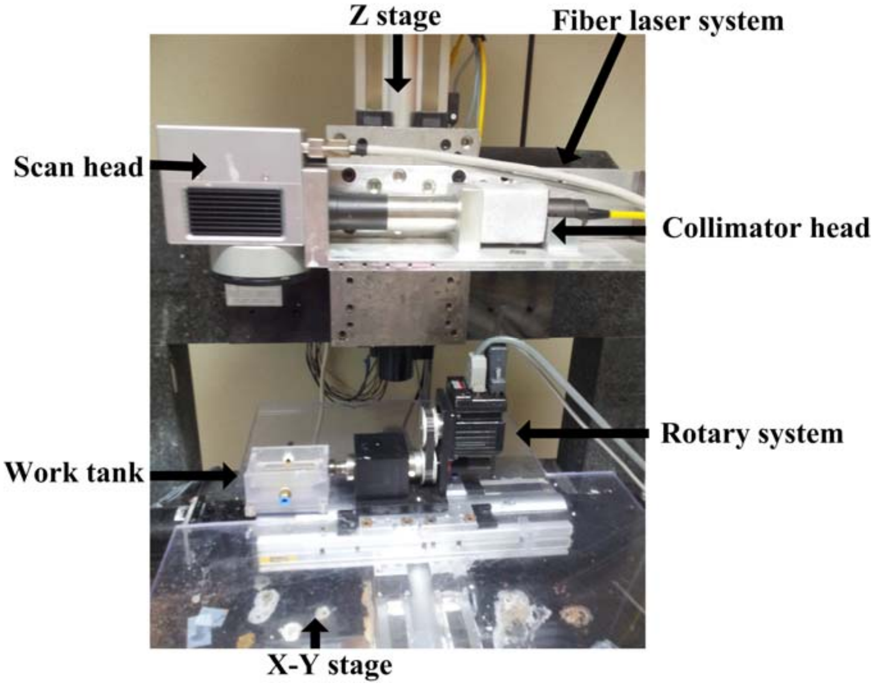


Figure 2.5 Laser masking system

Table 2.2 Main specification of pulsed fiber laser

Characteristics	Min.	Typical	Max.	Unit
Mode of operation	Pulsed			
Maximum pulse energy		1		mJ
Nominal average output power	19	20	21	W
Output power adjustment range	10		100	%
Nominal pulse repetition rate		20		kHz
Pulse duration	80	100	120	Ns
Central emission wave length	1055	1064	1075	Nm
Pulse repetition rate	2		80	kHz
Beam quality, M^2		1.5	2.0	
Output beam diameter	6		9	mm

Table 2.3 Experimental condition for laser masking

Parameter (unit)	Value
Average power (W)	4
Repetition rate (kHz)	80
Peak power density (MW/mm^2)	0.34
Line spacing (μm)	10
Scanning speed (mm/s)	19.6

2.2.3 Electrochemical etching system

After laser masking, the patterned surface of stainless steel was electrochemically etched with continuous supply of electrolyte by circulation pump. Figure 2.6 shows a schematic of system configuration of electrochemical etching. The electrochemical etching system consists of tool electrode which is attached on Z-axis moving stage, work tank, rotary system, electrolyte circulation pump, pulse generator and oscilloscope. Circulation pump of electrolyte was used to eliminate the sludge such as $Fe(OH)_2$ or $Fe(OH)_3$ by flushing electrolyte on the workpiece surface during electrochemical etching. Work tank was placed on X-Y stage that has resolution of 0.1 μm as same as the rotary system. Anodic dissolution of stainless steel was performed in 2 M sodium nitrite ($NaNo_3$) electrolyte and pulse voltages were applied by pulse generator. The gap distance between the tool electrode and the workpiece was kept constant at 200 μm and the tool electrode was scanned above the workpiece that was rotating by the rotary system. The bottom surface of tool electrode was only exposed while the other sides of tool electrode were insulated by enamel. Table 2.4 shows experimental condition for electrochemical etching.

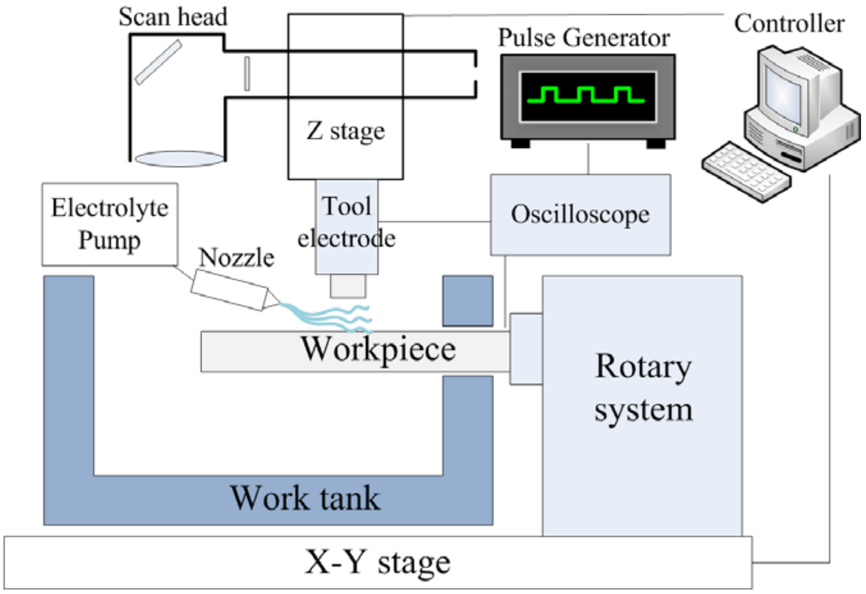


Figure 2.6 Schematic of system configuration of electrochemical etching.

Table 2.4 Experimental condition for electrochemical etching

Parameter (unit)	Value
Electrolyte	2M $NaNo_3$
Pulse on time (μs)	50
Pulse period (μs)	500
Gap distance (μm)	200

Chapter 3

Laser masking characteristics

3.1 Factors causing non-uniformity of the recast layer

Laser masking step is based on laser scanning irradiation over an area of metal surface that transport photon energy into the surface in the form of thermal energy. When the laser beam exposed on the metal surface, the temperature of the surface starts to rise and melting occurs if the surface is sufficiently heated by thermal energy. The melting zone which is not removed by thermal energy of laser irradiation is quickly re-solidified and results in the formation of recast layer on the metal surface [6]. The characteristics of the recast layer are mainly influenced by laser beam parameters that lead to change in laser beam energy [2]. Therefore, it is required to control the laser beam parameters to form appropriate recast layer that can be used as a mask during electrochemical etching. The laser masking characteristics changes due to geometry of the workpiece surface. Since the workpiece is a non-planar, it is important to investigate factors that could change the laser masking characteristics in order to form uniform recast layer over the cylindrical surface.

A rectangle pattern that had bigger width than that of the workpiece diameter was exposed once on the fixed workpiece surface by single step of the laser masking to investigate the laser masking characteristic as described in figure 3.1. As shown in figure 3.2 (a) and (b), recast layer was formed on the surface of the stainless steel shaft workpiece. Coverage area of the formed recast layer was approximately in the angle of 138 degrees as described in figure 3.2 (c). After the laser masking, electrochemical etching was conducted to confirm the ability of the recast layer as a mask. Figure 3.3 shows the result of selectively etched surface by single step masking of the rectangle pattern. The mean etched depth was about 3.5 μm during 5 minutes of etching time. However, no longer etching time was possible because collapse of the recast layer starting from outer parts occurred as shown in figure 3.4 (a) and (b). Figure 3.4 (c) and (d) were enlarged images of collapsed recast layer. Actual coverage area of the recast layer that can be used as a mask in electrochemical etching during 5 minutes of etching time was approximately in the angle of 125 degrees as shown in figure 3.5. This was because of non-uniform recast layer that was formed along the surface according to different laser masking characteristics.

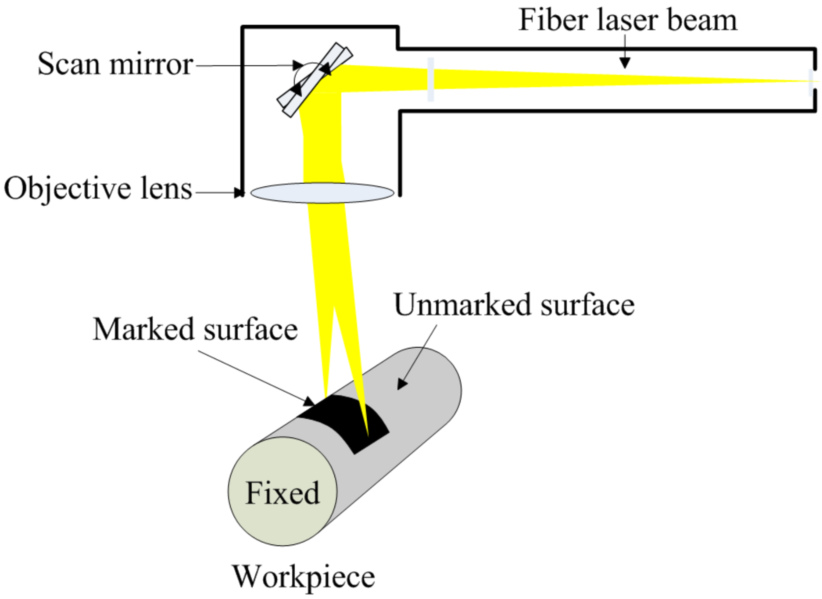


Figure 3.1 Schematic of single step laser masking on fixed workpiece.

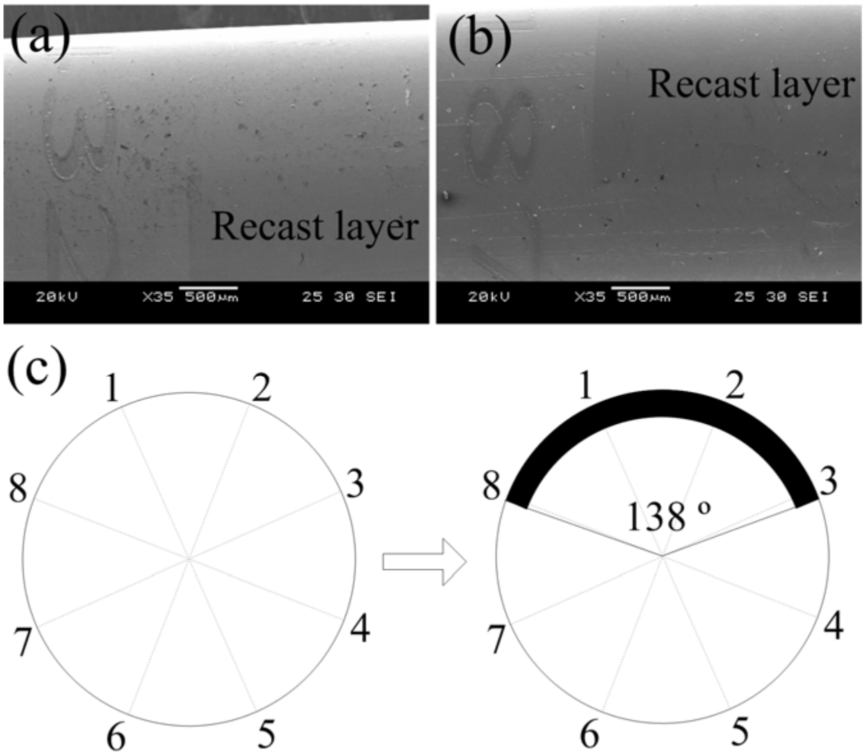


Figure 3.2 Coverage area of recast layer by single step laser masking: (a),(b) SEM images of formed recast layer. (c) schematics of coverage area of laser masking.

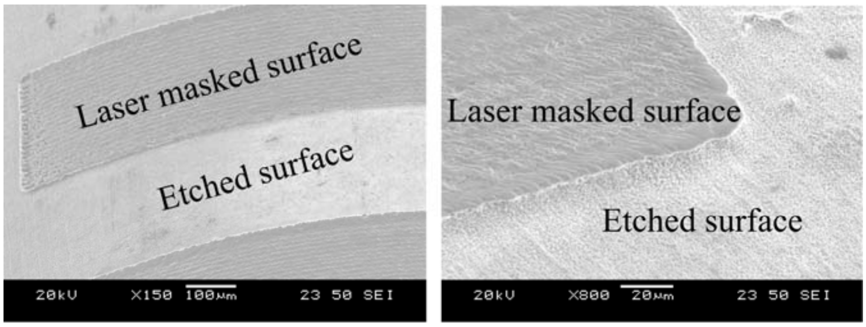


Figure 3.3 SEM images of selectively etched surface by electrochemical etching after single step laser masking.

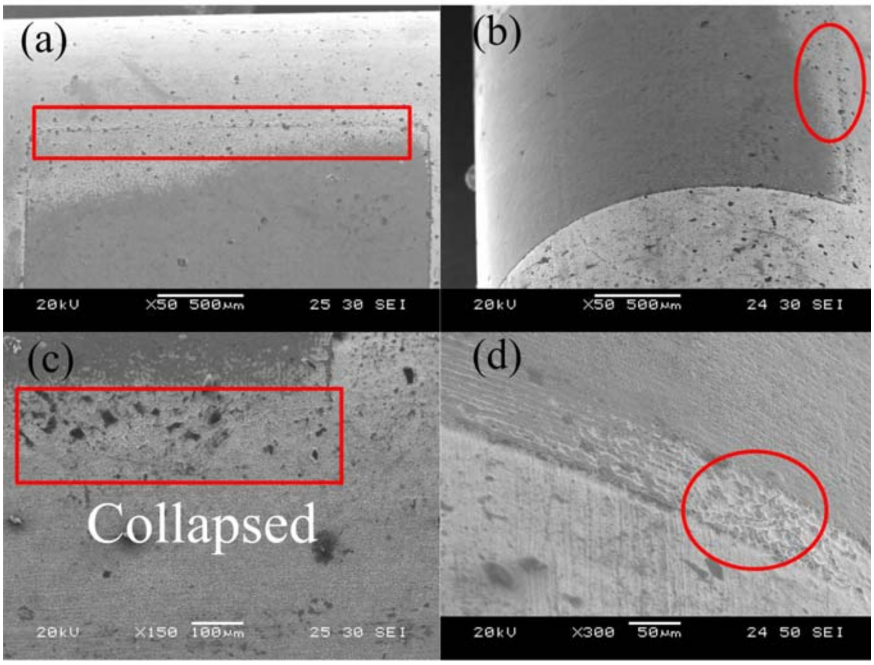


Figure 3.4 Collapse of recast layer: (a), (b) SEM images of collapsed recast layer after 5 minutes etching time, (c) and (d) enlarged images.

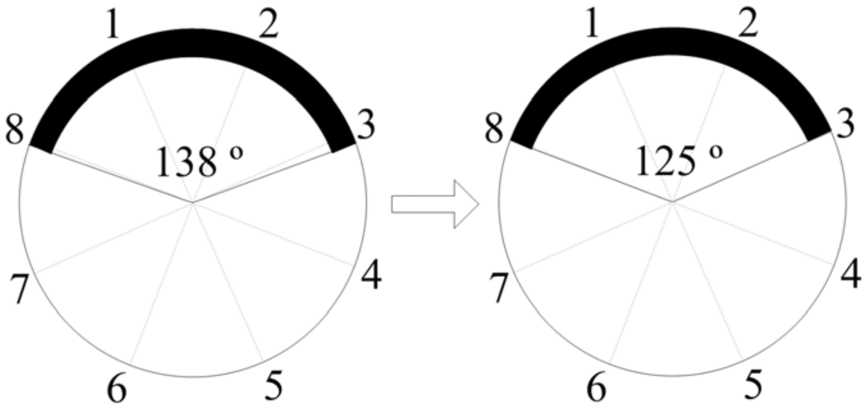


Figure 3.5 Schematics of actual coverage area after collapsed by etching.

There were several factors that cause non-uniformity of the formed recast layer on the cylindrical surface. First of all, focus length was one of the significant factors that changes laser beam energy as shown in figure 3.6 (a). The difference in focus length was increased as the laser beam scanned far from the center of the cylindrical workpiece where the optimal focus length was. To confirm the effect of different focus length of the laser, a simple test was taken. Stainless steel plate was placed at the optimal focus length, second plate was place at 0.8 mm (calculated from 125 degrees) far from the optimal focus length where the collapse occurred after 5 minutes etching time and the third plate was place at maximum difference of 1.5 mm, which was the same as the radius of the workpiece. Figure 3.7 shows the results of the test that the recast layer that was formed on the plate at optimal focus length could be used as a mask in electrochemical etching like in figure 3.7 (a) while the recast layer that was formed even on the plane plate that was placed at 0.8 mm of difference from the optimal focus length partially collapsed as shown in figure 3.7 (b) and no recast layer was formed on the plate that was placed at 1.5 mm of difference from the optimal focus length that was shown in figure 3.7 (c).

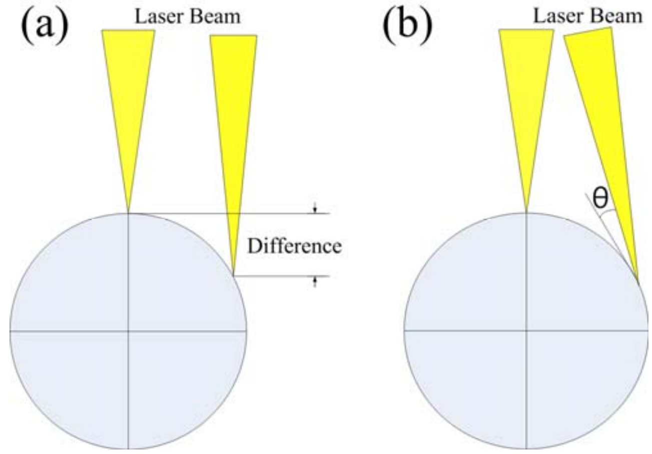


Figure 3.6 Schematics of factors causing non-uniformity: (a) Different focus length, and (b) different incident angle.

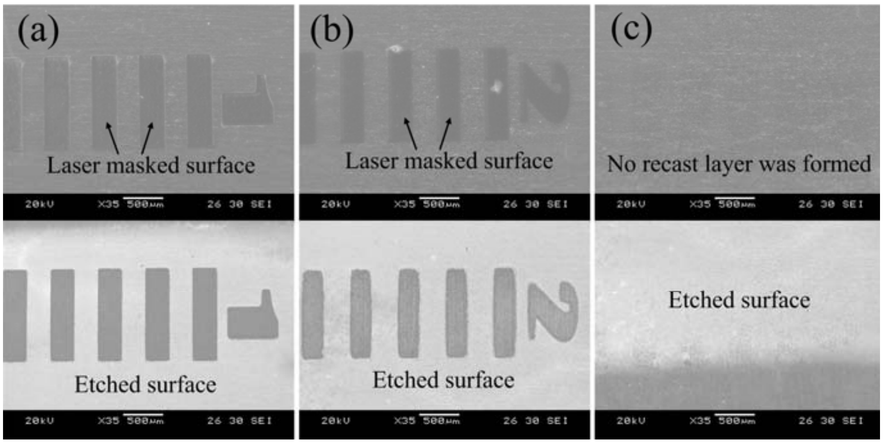


Figure 3.7 The results of the different focus length effect: (a) placed at the optimal focus length, (b) placed at 0.8 mm difference, and (c) placed at 1.5 mm difference.

Another factor that causes the change in the laser masking characteristics is incident angle of the laser beam like shown in figure 3.6 (b). Incident angle of the laser beam changes during the laser masking step because the surface of the workpiece is non-planar. Incident angle of the laser beam decreases as the laser beam scans outward to the center. There are many researches about the investigations of effect of Nd: YAG laser beam energy and incident angle on stainless steel sheet. From the fact that when the incident angle of the laser beam was increased, the spot size of the laser was decreased so as the density of the laser beam energy was increased [15-16]. Therefore, different density of laser beam energy could lead to form non-uniform recast layer along the surface.

Additionally, in practical experiments, there occurs field distortion error of an image during laser masking step as described in figure 3.8. Thus, field distortion error of the laser masking should be compensated by the correction functions to make proper patterns of laser mask [17-18].

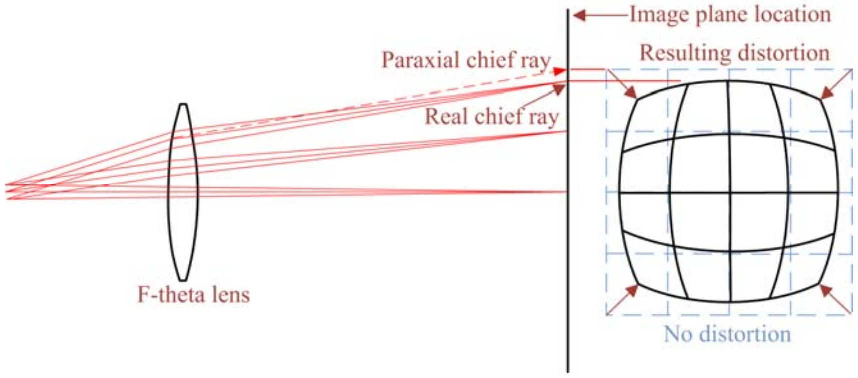


Figure 3.8 Schematic of field distortion error in laser scanning system [19].

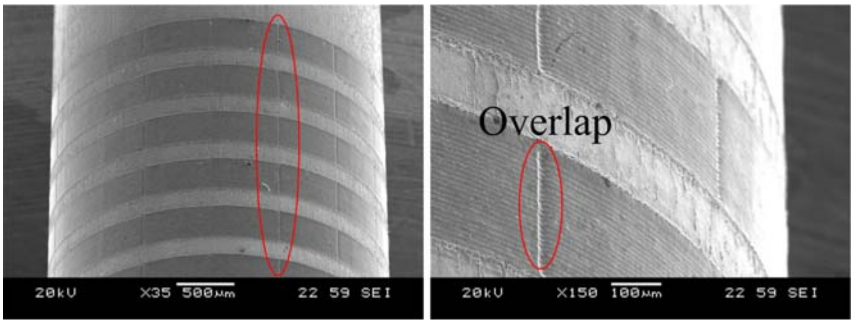


Figure 3.9 SEM images of pattern overlap.

To minimize these factors so as to make uniform recast layer, the pattern that is going to be exposed on the workpiece surface should be minimized. Furthermore, multi-steps with smaller rotation angle in laser masking step are required to make full round patterns on the workpiece. However, even though non-uniformity of the recast layer could be compensated with smaller pattern masking, there were still remaining problems such as pattern overlap as shown in figure 3.9 since the masking process was not continuous.

3.2 Galvano line scanning method

To overcome limitations that were described before in 3.1 section, laser masking method using galvano line scanning was applied to make uniform patterned mask on cylindrical surface of the workpiece. As shown in figure 3.10, line scanning of the laser beam was only exposed on the optimal surface of the rotating workpiece to make uniform mask on the entire surface. As a result, no partial collapse of the recast layer occurred after electrochemical etching and non-uniformity of the formed recast layer that was induced by the factors such as focus length, incident angle and field distortion error could be neglected. Furthermore, transferring the workpiece in X, Y axes with synchronized laser masking, uniform masks with various micro patterns could be performed. Figure 3.11 shows the result of multiple band patterned product that was fabricated by electrochemical etching using galvano line scanning laser masking. Deeper etched depth that was about 14 μm during 15 minutes of etching time could be done through the galvano line scanning laser masking method.

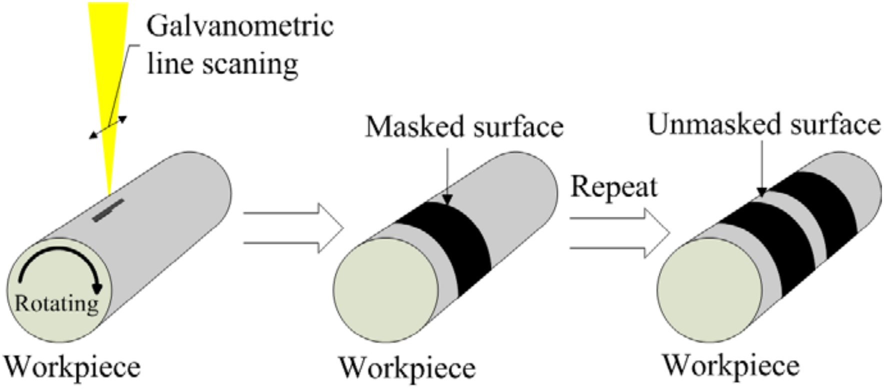
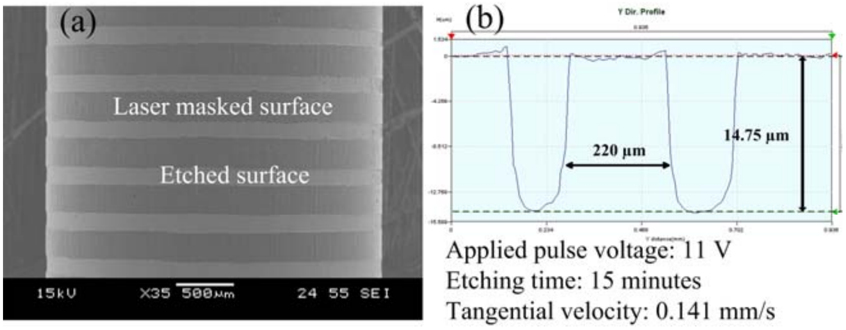


Figure 3.10 Schematics of galvano line scanning laser masking method.



Applied pulse voltage: 11 V
Etching time: 15 minutes
Tangential velocity: 0.141 mm/s

Figure 3.11 Micro patterning using galvono line scanning: SEM image of multiple band patterns, and (b) surface profile measured by 3D surface profiler.

Chapter 4

Electrochemical etching characteristics

Even though there formed uniform recast layer on the workpiece surface, it cannot be used as a mask permanently during electrochemical etching. Induced overpotential and current density could break down the recast layer in a certain electrochemical etching condition. Since the selective etching is due to different rates of anodic dissolution between masked surface and unmasked surface, amounts of material removal from the masked surface also depend on electrochemical etching condition. Therefore, it is important to investigate electrochemical etching characteristics to fabricate micro patterns without collapse of the recast layer.

4.1 Etching characteristics according to pulse voltages

One of a significant parameter that affects electrochemical etching characteristics is an applied pulse voltage. Applied pulse voltages were changed from 10 V to 15 V in the experiments while other values such as pulse period (500 μs), pulse on time (50 μs), etching time (15 minutes) and tangential velocity (0.141 mm/s) were fixed. For each result, left is a SEM image and right is a surface profile that was measure by 3D surface profiler in figure 4.1. Etched depth increased as applied pulse voltages increased as shown in figure 4.1. However, when the applied voltage was over 12 V, partial collapse of the recast layer occurred like in figure 4.1 (c). The result in figure 4.1 (d) shows that when the applied pulse voltage was over 15 V, the recast layer completely removed after electrochemical etching. These results were because of induced increased current density and increased overpotential break down and dissolute the recast layer so the layer couldn't be used as a mask no more during electrochemical etching.

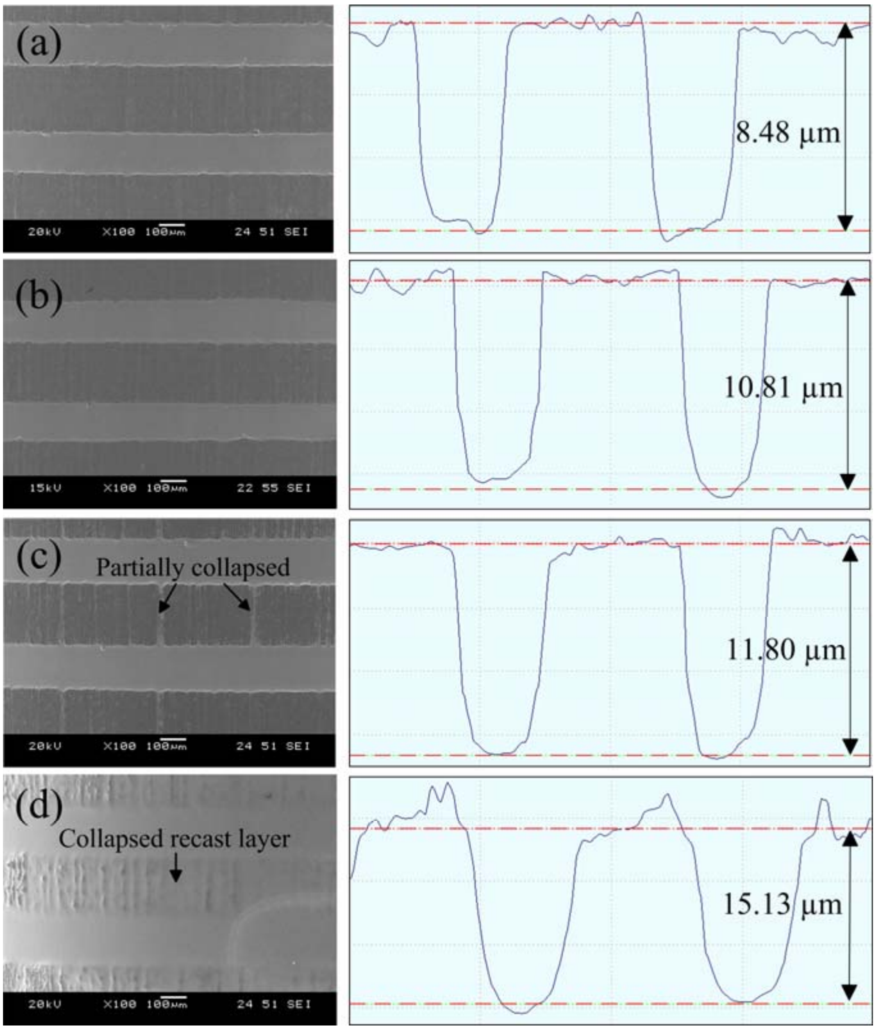


Figure 4.1 Results of SEM images (left) and surface profiles (right) according to different pulse voltages: (a) 10 V, (b) 11 V, (c) 12V and (d) 15 V.

4.2 Etching characteristics according to etching time

Effect of electrochemical etching time has been investigated by many researchers in the field of electrochemical science. As it was predictable, etched depth and porosity increased as etching time increased [20]. To find out the maximum etching time when the failure occurs, etching time was increased 10 minutes to 20 minutes. As a result, similar phenomena were observed when the etching time was over 20 minutes. Partial collapse occurred within excessive of etching time as shown in figure 4.2. The result of surface profile of a to a’ line after 20 minutes of etching time was measured by 3D surface profiler. Even though the rate of anodic dissolution of the masked surface is less than that of the unmasked surface, the amounts of material removal from the masked surface increase as the etching time increases [6]. Accordingly, if the etching time is longer than 20 minutes, the formed recast layer couldn’t be used as a mask no more as shown in figure 4.2.

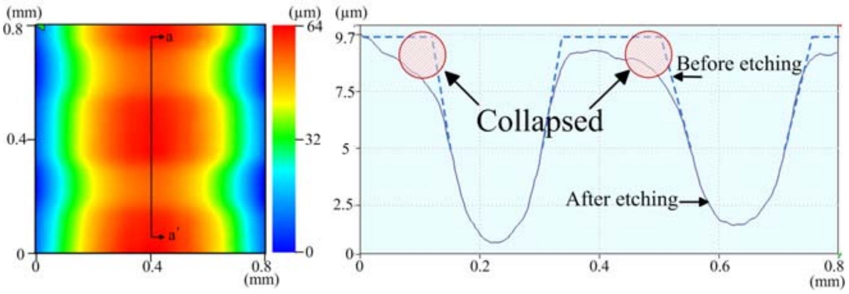


Figure 4.2 Surface profile after 20 minutes etching time.

4.3 Etching characteristics according to tangential velocity

Workpiece was rotated by the rotary system during electrochemical etching process to etch entire surface. Thus the electrochemical etching characteristic according to the rotation speed of the workpiece was investigated. Rotation speed was controlled by tangential velocity of the rotating workpiece. A graph that is described in figure 4.3 shows the results of increase in etched depth as tangential velocity decreases until a certain velocity. When the tangential velocity was too low such as 0.047 mm/s, induced increased current density on unit area due to decrease in tangential velocities would cause removal of the recast layer. Therefore, amounts of material removal from the top surface became larger and relative etched depth decreased.

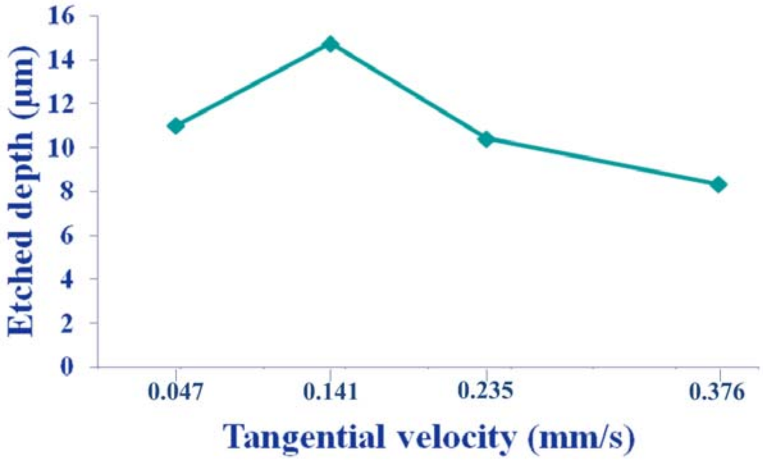


Figure 4.3 Etched depth according to rotation speed of the workpiece.

4.4 Results of v-shape micro patterning on cylindrical surface

Various v-shape micro patterning were produced based on electrochemical etching characteristics. Appropriate etching parameters were selected and selective etching was performed using galvano line scanning laser masking process. Figure 4.4 shows SEM images of the results of various v-shape micro patterning on cylindrical surface. Etching time was 15 minutes with 11 V of applied voltage and 0.141 mm/s of tangential velocity. These kinds of v-shape micro patterns can be applied to a practical example, such as micro grooves on an air kinetic pressure bearing to reduce frictions in magnetic storage disk [21].

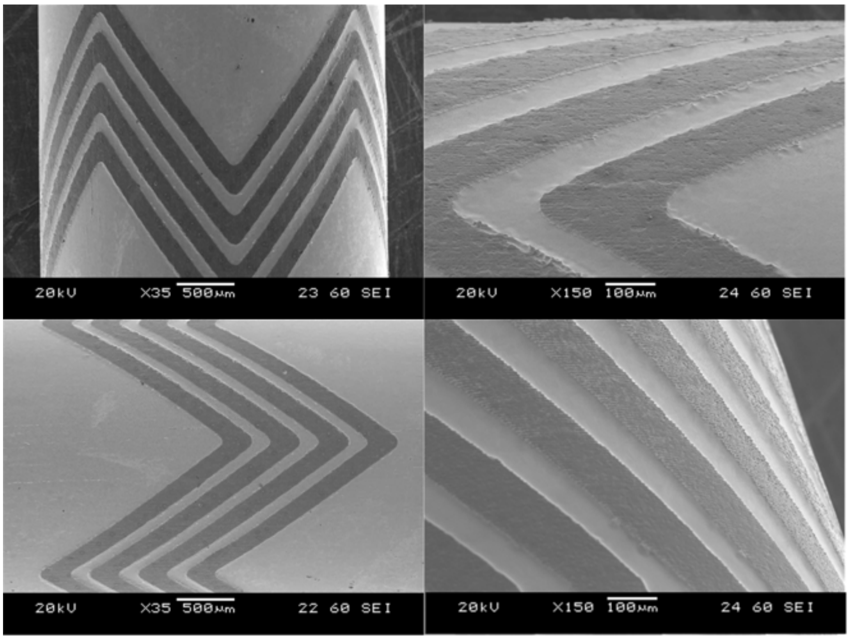


Figure 4.4 SEM images of various v-shape micro patterning results.

Chapter 5

Conclusion

Micro patterning on a non-planar surface was performed successfully by a series process of laser masking and electrochemical etching. Micro patterned recast layer was formed through the laser masking. The formed recast layer had passive ability that leads to different rates of anodic dissolution between unmasked surface and masked surface. Thus the layer could be used as a mask in electrochemical etching process.

From the reasons that the laser masking characteristics change along the non-planar geometrical surface, investigation of factors causing non-uniformity formation of the recast layer was taken. The factors causing non-uniformity such as different focus length, incident angle of the laser beam and field distortion error could be compensated by continuous line scanning at the surface of optimal focus length by galvano line scanning laser masking method. Uniform mask was formed on the entire surface and through the electrochemical etching the micro patterned on the cylindrical surface was obtained. Uniformity of the formed recast layer was improved by galvano line scanning method, no partial collapse occurred. Maximum etching time before the collapse of the recast layer was longer and etched depth also increased from 3.5 μm to 14 μm.

CHAPTER 5. CONCLUSION

Electrochemical etching parameters were controlled to prevent collapse of the recast layer because of the induced large overpotential or large current density that could break down the recast layer. Appropriate parameters were selected based on electrochemical etching characteristics experiments; 11 V of applied pulse voltage, 15 minutes of etching time and 0.141 mm/s of tangential velocity of the workpiece. Various v-shape micro patterning were performed successfully with the selected parameters.

Overall, electrochemical etching using laser masking is fast and simple process that can overcome the disadvantages of existing methods such as complex procedure and high cost of equipments. Consequently, the micro patterning on the cylindrical surface by electrochemical etching using the laser masking can be applied to various fields, especially in surface texturing and micro patterning.

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국문초록

전해 에칭 (electrochemical etching)은 가공속도가 빠르고 표면조도가 좋으며 재료의 강도나 경도에 관계없이 가공할 수 있어 금속의 패터닝 (patterning)에 많이 이용되어 왔다. 금속의 미세 패터닝은 표면 텍스처링 (surface texturing)에 응용되어 기계부품의 마찰 저감 등에 적용된다. 일반적으로 많이 사용되는 포토리소그래피 (Photolithography) 가공법으로 원하는 패턴의 선택적인 가공을 위해서는 감광막 (PR, photo-resist) 을 이용하게되는데 이러한 보호층 역할을 할 수 있는 감광막 마스크 형성은 평면에 비해 곡면에서는 일정한 도포가 어려운 단점이 있다. 따라서 평면이 아닌 곡면에서 선택적인 가공으로 원하는 미세 패턴 형성을 위해서는 패턴형상을 갖는 전극이나 마스크의 제작이 요구된다. 그러나 이러한 방식은 패턴에 따른 전극 혹은 마스크를 매번 제작해야 하는 한계점을 지닌다. 본 논문에서는 이러한 기존의 가공법이 갖는 곡면에서의 미세 패턴형상의 한계점을 해결하고자 레이저 마스킹 (laser masking) 공정을 적용하여 곡면에서의 다양한 미세 패턴형상을 갖는 가공법에 관해 연구하였다. 선택적인 가공물의 용해는 레이저 마스킹과 전해 에칭 과정을 통해 이루어진다. 레이저빔을 시편에 조사함에 따라 형성되는 재응고층이 보호층 역할을 하여 전해 에칭을 통한 선택적인 가공이 가능하였다. 곡면에서 일정한 재응고층 마스크를 형성하기 위해 레이저의 갈바노미터 (galvanometer)에 의한 라인스캔 (line scan)속도와 시편의 회전속도를 동기화 시켜 원하는 영역에 패턴 마스크를 형성하며 전극을 이용한 전해 에칭으로 미세 패턴가공을 성공적으로 수행 하였다. 보

호층으로 사용되는 재응고층의 특성을 보기 위해, 레이저 빔의 조사조건에 관한 실험을 수행하였으며 선택적인 미세 패턴의 제작을 위해 전해 에칭 조건 변화에 따른 특성을 조사하였다. 시편으로는 스테인리스강 (stainless steel 304 rotary shaft)이 사용되었으며 전해액으로는 $NaNO_3$을 사용하였다. 최종 가공된 미세 패턴은 주사전자현미경 (SEM, scanning electron microscope)으로 관찰되었으며 가공 정도는 비접촉 3차원 미세 형상 측정기 (non contact 3D surface profiler)로 측정되었다. 결과적으로 본 논문에서 새롭게 제안된 이 공정은 빠르고 다양한 패턴 형성이 가능한 레이저 마스킹의 장점과 안정한 중성염을 전해액으로 사용하여 상대적으로 친환경적인 전해 에칭의 장점을 갖는 가공법으로 이를 통해 곡면에 다양한 미세 패턴형상가공이 가능하다.

주요어: 레이저 마스킹, 전해 에칭, 라인 스캔, 곡면

학번: 2011-20757

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