Pulsed Electrochemical Deposition for 3D Micro Structuring

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In this paper, micro structuring technique using localized electrochemical deposition (LECD) with ultra short pulses was investigated. Electric field in electrochemical cell was localized near the tool tip end region by applying pulses of a few hundreds of nano second duration. Pt-Ir tip was used as a counter electrode and copper was deposited on the copper substrate in mixed electrolyte of 0.5 M $CuSO_4$ and 0.5 M H_2SO_4. The effectiveness of this technique was verified by comparison with ECD using DC voltage. The deposition characteristics such as size, shape, surface, and structural density according to applied voltage and pulse duration were investigated. The proper condition was selected based on the results of the various experiments. Micro columns less than 10 μm in diameter were fabricated using this technique. The real 3D micro structures such as micro spring and micro pattern were made by the presented method.

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1. Introduction

Micro/nano technologies are recognized as one of the most key technologies that dominate the 21st century. In engineering and science, new microfabrication processes have been investigated world widely. Up to now, the most generalized process for microfabrication is the lithography technology and its applications used in semiconductor industry. This process has advantages in mass production and miniaturization. However, it is basically two dimensional process and can be applicable to the specific material such as silicon. Also micro/nano fab including expensive equipments is necessary for the lithography process. Micro mechanical processes such as micro milling and micro drilling are being studied for micro machining of metals. But in mechanical processes, burr generation, tool wear and breakage problems should be solved for microfabrication. Non-conventional machining processes like micro electrical discharge machining (MEDM), micro ultrasonic machining, laser beam machining, and focused ion beam machining make another field of microfabrication method. MEDM has handicap in electrode wear. Micro ultrasonic machining is proper for removal of nonconductive materials as glass and ceramics, but it has disadvantages in complex shape machining and tool wear. Laser beam machining is improper for precise metal ablation and generates heat affected layer on machined surface. Focused ion beam machining and AFM/STM manipulation technique for micro/nano structuring are proper for ultra fine features generation but have drawbacks in long process time, low production efficiency and expensive equipments usage.

Electrochemical process has been developed for metal corrosion and plating. In the 20th century, this process is used to precise die/mold manufacturing with complicated shape, electrolyte in-process grinding and electroplating. In 1986, Bard suggested scanning electrochemical microscopy (SECM) that could observe the micro texture by analyzing the electric signal between micro electrode and an object immersed in electrochemical cell after applying voltage.[1]

In this paper, as one of the applications of SECM for micro structuring, microfabrication method by electrochemical deposition is suggested using micro electrode and metal substrate. By electrochemical deposition, three dimensional micro structure could be made easily on high strength metals. This process has advantages in fabrication time and cost compared with any other microfabrication methods. Also, various materials such as metals, metal alloys, conductive polymer, and semiconductor can be used, and the application field is very wide. In near future, if micro systems are generalized in industry, when needs for micro parts of small quantity with various shapes are increasing, it is expected that micro electrochemical deposition is promising and powerful for micro structuring.

Since electrochemical deposition using micro electrode was introduced in 1995, some research results have been reported about the effects of applied voltage, electrolyte and its concentration on size, shape, and structural characteristics of deposited product.[2] In the previous studies, for localized electrochemical deposition, micro electrode was shielded by glass or wax and DC voltage was applied.[2-6] El-giar added some organic additives in electrolyte for micro column fabrication with smooth surface, and he tried to deposit column with smaller diameter.[3] The porous structure of deposited material was improved applying the ultrasonic vibrations on the electrolyte.[5] Yeo discovered that, when micro electrode was rotated, hollow micro column was generated and using this principle he made the micro pipe by electrochemical deposition.[6] Schuster showed that micro mold could be made by electrochemical machining.

Dissolution region was localized near the micro electrode tip end using ultra short pulses with a few tens of nano second duration instead of DC voltage.[7] Ahn drilled micro holes with 8 μm in diameter on 304 stainless steel using the ultra short pulses without passive layer generation on machined surface using Pt balance electrode.[9]

In this study, by applying the ultra short pulses in electrochemical deposition, micro structures such as micro column, micro spring and micro patterning were fabricated. Also, the effects of pulse conditions and electrolyte concentration on deposition characteristics in size, shape, structural density and surface quality were investigated.

2. LECD using ultra short pulses

2.1 Principles of electrochemical deposition

Electrochemical deposition bases on the cathodic reduction of metal ions dissolved in electrolyte under electric field. Concept of micro structuring by electrochemical deposition can be briefly explained as follows. When connecting Pt-Ir micro electrode to (+) power source terminal and substrate to (-) source terminal, chemical reaction of Eq (1) occurs at the anode and cathode in copper sulfate and sulfuric acid mixture solution. An anodic reaction at the end of micro electrode causes oxygen bubbles, and a reduction reaction at the copper substrate results in copper deposition. (Fig. 1)

$$H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2 \uparrow \quad \text{(Anode)}$$
$$Cu^{2+} + 2e^- \rightarrow Cu \downarrow \quad \text{(Cathode)} \qquad (1)$$

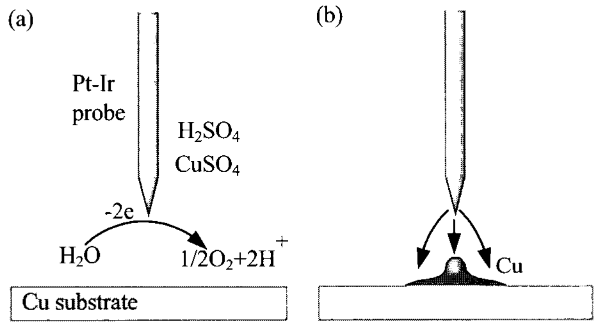

Fig. 1 Schematic diagram of electrochemical reaction at (a) micro electrode and (b) metal substrate

2.2 Electrical double layer and ion migration

As shown in Fig. 2, when voltage is applied between tool electrode and a conductive substrate immersed in electrolyte, electric charges located on the surface of metal electrode and distributed ions in electrolyte make electrical double layer.[8,9] Except only fluoric ion, other anions are adsorbed on metal electrode surface by chemically mutual reaction. This is called specific adsorption, and the locus of the electrical centers of the specifically adsorbed anions is called inner Helmholtz plane (IHP). Cations are hydrated by the water molecules and water molecule also adsorbs at metal electrode surface. Therefore, solvated cations can approach the metal surface only to a distance of about two water molecules size. The locus of centers of these nearest solvated cations is defined outer Helmholtz plane (OHP). The region from metal surface to OHP makes the compact double layer and its thickness is about 3 Å. The region from OHP to ions layer that electrically distributed in bulk electrolyte by charged electrode makes diffuse double layer. The thickness of the diffuse double layer depends on the total ionic concentration in the solution. This electrical double layer has similar properties with that of a capacitor in electrical circuit.

The copper deposition process can be briefly described as follows. Copper ion is moved to diffuse double layer by electrical migration that is caused by polarized metal substrate. Copper ion reaches OHP by diffusion caused by concentration difference, and it is deposited on copper substrate after getting over the activation energy barrier. Then copper ions are crystallized, and structure grows. Fig. 3 shows a schematic diagram of electrochemical deposition process.

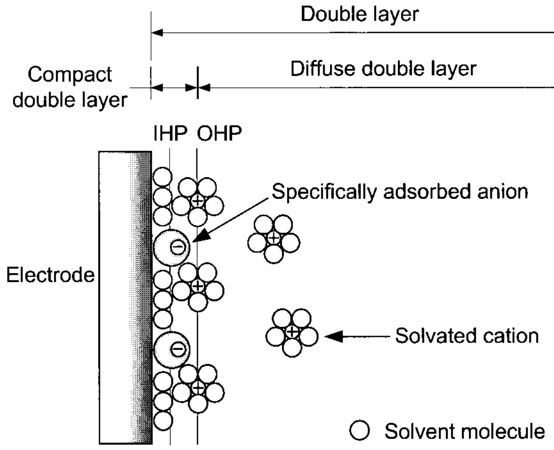

Fig. 2 Electrical double layer

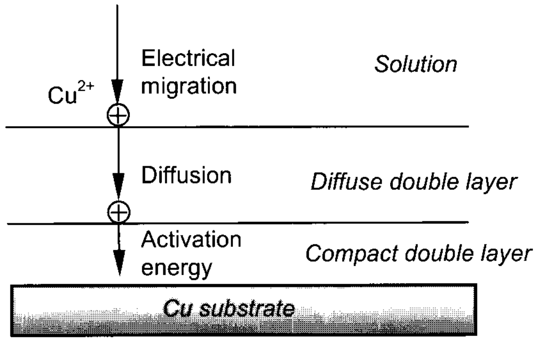

Fig. 3 Cu deposition process through electrical double layer

2.3 Mechanism of LECD by ultra short pulses

To make micro structure by electrochemical deposition, the deposition area should be localized. Up to now, most researchers have used the insulated micro tip for deposition localization.[2-6] After insulating the micro tip with wax or glass, tip end is exposed by mechanical polishing. However, the repeatability of insulation state is poor and the exposed tip shape is not uniform. The insulation film is frequently peeled off by the interruption between micro tip and deposited material. In addition, there is limitation of exposed size.

In this research, with unsealed micro electrode, deposition area was localized using ultra short pulses instead of tip insulation. Ultra short pulses can be applied for localizing the deposition region because double layer has the property of the electric condenser. Capacitance value multiplied by electrolyte resistance value equals the double layer charging time constant in electrochemical cell. This charging time constant varies according to location on electrode surface. The distance between tip end and substrate is closer than that of tip side and substrate. Therefore double layer between the former one is charged firstly and current flows in advance. The pulse is cut off before charging the latter double layer, so the current flow through electrode side is negligible. This means that localization can be achieved without insulation of electrode. If we choose proper pulse duration considering charging time constant of double layer, we can deposit copper on substrate beneath electrode. In this work, deposition characteristics were investigated according to three categories: the existence of electrode insulation, DC voltage and ultra short pulses.

3. Experimental results

3.1 System set-up

As shown in Fig. 4, experimental equipments consist of a pulse generator, a motion controller (PMAC, DELTA TAU), electrochemical cell and the monitoring system. Voltage and current were measured by oscilloscope (300 MHz, Tektronix). CCD vision system (SNU precision) monitored the process of deposition. A 100 μm thick copper plate (purity 99.9 %, Nilaco) was used as substrate with size of 20 mm by 30 mm. Pt-Ir STM tip (Veeco NanoProbe) was used as electrode and its nominal diameter was 40 nm. Fig. 5 is a SEM image of the experimental tip.

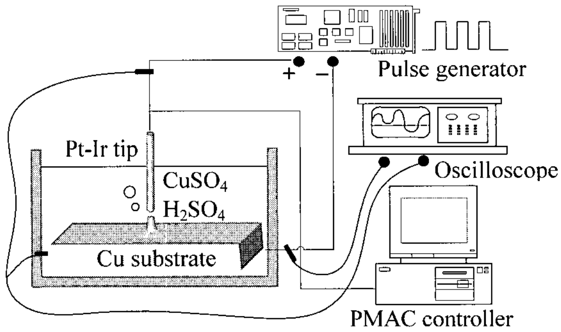

Fig. 4 Schematic diagram of experimental set-up

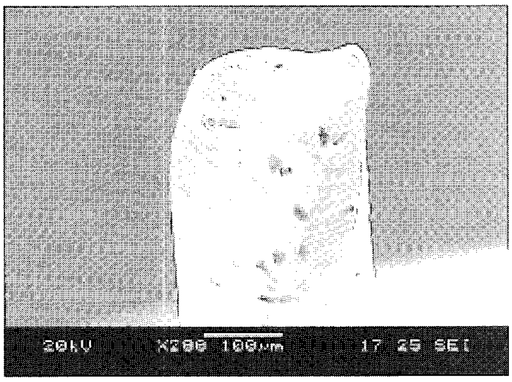

Fig. 5 Pt-Ir STM tip

El-giar reported the effect of the concentration of $CuSO_4$ on the rate of deposition. By changing the Cu^{2+} ion concentration from 0.015 to 1.0 M, they observed that the ion concentration does not affect the structure growth rate. But ion concentration lower than 0.125 M generates rough, spongy, irregular, highly porous and dendritic structures with nodules.[3] In this research, 0.5 M $CuSO_4$ and 0.5 M H_2SO_4 electrolyte was selected after some experimental studies about the concentration of the electrolyte. In H_2SO_4 with low pH, concentration of proton is high. Thus acid solution prevents bonding of OH^- with Cu^{2+} because sufficient protons exist in solution and the quantity of copper ions are maintained. Therefore H_2SO_4 solution makes good condition for copper deposition.

The electrode and deposited structure stuck together during experiments regardless of voltage types or insulation of electrode. Deposited structure grew to the end of electrode, and they stuck together. This phenomenon made short electrical circuit. At this time, even though the electrode was moved upward, the short circuit condition remained. In relation to this sticking, Jansson used an active current limiter to cut current to less than 0.1 mA as soon as voltage dropped due to a contact event.[10] A relay circuit was made to cut current in case of contact. The relay cuts current when A/D converter gave signals from PMAC controller and oscilloscope. Experimental processes can be summarized as follows. After adjusting initial gap between electrode and substrate, voltage is applied. When short circuit occurs, the relay circuit cuts current and electrode is moved a little. Then power is applied and structure grows again.

3.2 Experiments using DC voltage

Electrochemical reaction occurred fiercely when applying DC voltage with non-insulated Pt-Ir tip. At the moment of voltage applied, copper deposition occurred and whole substrate surface was covered with deposited copper layer. Experiments were conducted in the voltage range from 1.5 to 3.5 V with step of 0.5 V. Control of deposition process was almost impossible when applied voltage exceeded 2.5 V because of the violent reaction. The growth rate of deposit was very rapid, so controller often misrecognized the circuit condition as short circuit in spite of current cut off when feed step was less than 1 μm. Considering these results, feed step was fixed with 3 μm in DC voltage experiments.

The reaction did not occur severely when Pt-Ir tip insulated with Apiezon Wax was used. However, insulated part of the tip end was damaged after experiments about 3 times. As shown in Fig. 6, diameter of the column generated with non-insulated tip was 38 ~ 60 μm. The size of column was reduced about 38 ~ 54 % compared with the results using insulated tip. It was guessed that insulated tip was more effective to make a small column under DC voltage condition. In experiments using non-insulated tip, copper was dispersed at once on the whole surface of substrate. In case of insulated tip experiments, copper was also dispersed on the substrate after making one column as average. Surface was smoother than that of deposit grown with non-insulated tip.

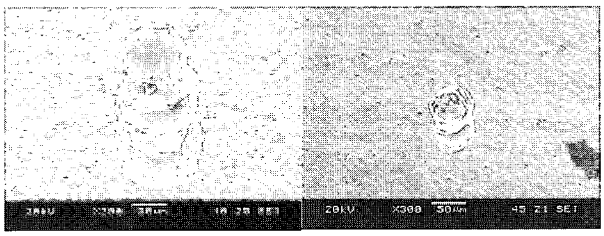

Fig. 6 Cu columns deposited at DC 2.5 V using Pt-Ir tip (a) without and (b) with insulation

3.3 Experiments using ultra short pulses

Size, shape, surface, and micro-structural density of deposited structure were investigated according to electrochemical condition by applying ultra short pulses using insulated or non-insulated tip.

Table 1 Deposition characteristics as functions of applied voltage and pulse duration using non-insulated tip

	3.0 V	3.5 V	4.0 V	4.5 V
250 ns	N/A	N/A	N/A	□
300 ns	N/A	□	□	△
350 ns	N/A	□	◎	△
400 ns	□	◎	◎	◎
450 ns	□	●	●	△
500 ns	□	◎	◎	△
550 ns	□	◎	△	△
600 ns	◎	△	△	△
□	Radius of column base was too big. Copper grains were widely dispersed.			
◎	Copper grains were dispersed a little.			
△	Column was formed with lumpy grains.			
●	Proper condition			

At first, applied voltage and pulse duration with Pt-Ir tip was changed. Z directional feed step of electrode was 1 μm, and total moved length was 25 μm. Experiments were performed at every 0.5 V from 3.0 V to 4.5 V and at every 50 ns from 250 ns to 600 ns. Pulse period was fixed at 1 μs. Experiments were repeated three times at each condition. The repeatability of deposited columns was quite good at the same condition. Experimental results are shown in table 1. At the condition expressed as □, copper grains were widely dispersed, and radius of column base was too big. Deposited column had cone shape. At the condition indicated as △, copper grains were also dispersed, and column was formed with lumpy grains. In most cases, split columns were grown as shown in Fig. 7(b). At ◎ condition, copper grains were dispersed a little, but surface texture was quite rough. At the condition presented as ●, surface quality became excellent and copper dispersion disappeared on substrate. Diameter had not much difference at the base and at the top of column. In this table, N/A means that no columns were deposited. As shown in Figs. 7 and 8, when applied voltage was 3.5 ~ 4.0 V and pulse condition was 450 ns/ 1 μs, diameter of deposited column was the smallest in the experimented range. Surface was smooth, and there were less copper grains on substrate.

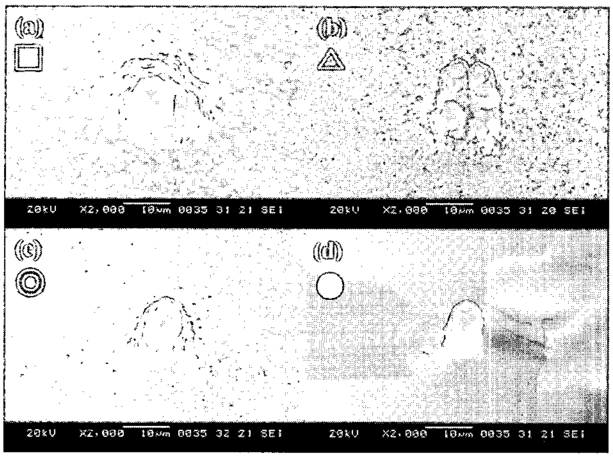

Fig. 7 Columns made at various conditions: (a) 3.0 V, 400 ns/ 1 μs (b) 4.5 V, 450 ns/ 1 μs (c) 4.0 V, 400 ns/ 1 μs (d) 3.5 V, 450 ns/ 1 μs

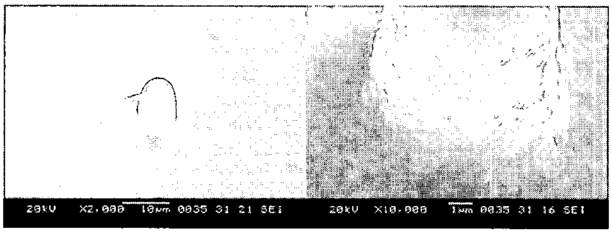

Fig. 8 Column fabricated with 4.0 V, 450 ns/1 μs

Next is the case of applying ultra short pulses with insulated electrode. The experimental condition was the same as that of the previous experiments. The repeatability was checked by fabricating three columns at the same condition except that Z feed step was 1 ~ 3 μm considering growing speed. Table 2 shows the experimental results. As shown in table 2, proper condition might not be found. From the view of column diameter, as shown in Fig. 9, deposited column is smallest when 2.0 V and 400 ~ 500 ns/ 1 μs pulses are applied. It was difficult to make a column with smooth surface under these conditions. We can conjecture that insulation layer and exposed tip apex were not uniform. In this case, copper was scarcely dispersed on substrate because side current flow was blocked by electrode insulation. From the results, it was very hard to make micro structure with insulated tip since insulation quality was not guaranteed including peeled off problem by interference between electrode and deposited material.

Table 2 Deposition characteristics according to applied voltage and pulse duration using insulated tip

	1.5 V	2.0 V	2.5V	3.0V
200 ~ 350 ns	N/A	N/A	△	△
400 ns	N/A	◎	△	△
450 ns	N/A	◎	△	△
500 ns	△	◎	△	△
◎	Copper grains were dispersed a little.			
△	Column was formed with lumpy grains and its shape was dendritic.			

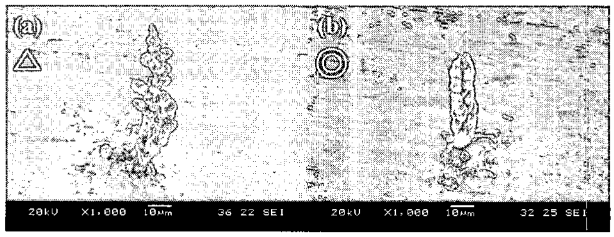

Fig. 9 Columns made with (a) 3.5V, 200 ns/ 1 μs (b) 2.0 V, 450 ns/ 1 μs

4. Micro structuring by LECD

4.1 Micro column

Figure 10 shows the SEM image of micro column array fabricated with 3.5 V and 350 ns/ 1 μs by LECD. Repeatability was good and the shape of column was uniform. Diameter was about 15 μm and height was 80 μm. Any deposited structure was not collapsed after acetone washing and ultrasonic cleaning.

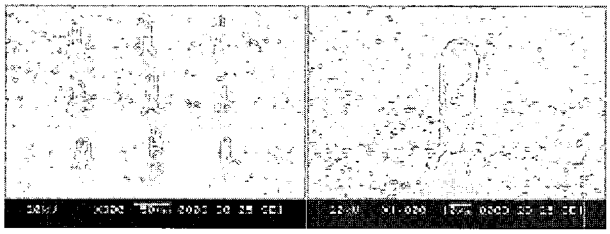

Fig. 10 Column array made with 3.5 V, 350 ns / 1 μs

4.2 Micro spring

If electrode moves circularly on XY plane and upward simultaneously, micro spring can be fabricated by LECD. An insulated tip was used because spring was easy to be affected by the exposed tip side. The experimental condition was fixed with 2.5 V and 450 ns/ 1 μs. Motion was controlled to make spring with 100 μm diameter and 350 μm pitch. The final shape of deposited micro spring is shown in Fig. 11.

Diameter of spring coil was maintained with 10 ~ 12 μm, and deposited shape was uniform. To find the mechanical stiffness of the fabricated spring, the relationship between applied load and displacement was measured using micro stage and precision scale with 10 μg resolution. As shown in Fig. 12, spring constant value is 5.71 N/m. The measured value is overestimated about 20 % compared with macro scale material stiffness of copper. In addition, various pitches were tested from 250 μm to 350 μm. The shape of spring became worse with smaller pitch. Form of spring coil was not uniform, and its shape was dendritic. From the results, it was concluded that LECD using ultra short pulses could be used for fabricating arbitrary shape 3D micro structure.

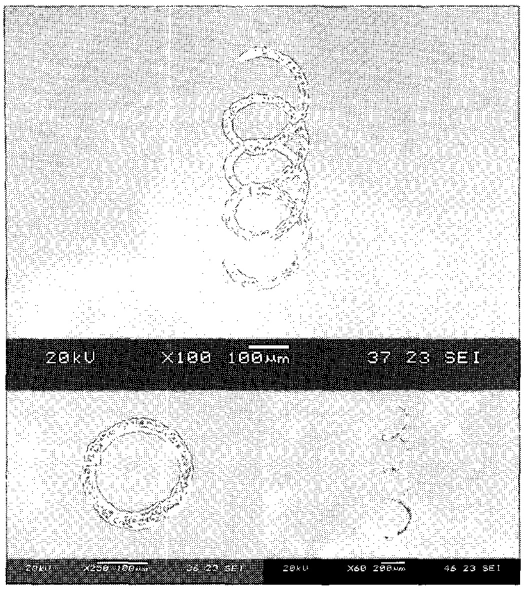

Fig. 11 Spring made with 2.5 V, 450 ns/ 1 μs

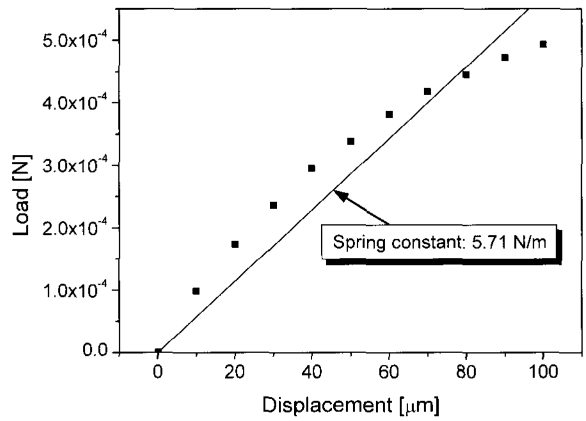

Fig. 12 Spring displacement according to load variation

4.3 Micro patterning

LECD using ultra short pulses can be applied for micro patterning. Micro pattern can be made by moving the electrode on XY plane sustaining gap of a few micro meters from the substrate. In this research, micro patterns such as alphabets and a spiral were written as shown in Figs. 13 and 14. The growth direction of structure was perpendicular to the feed direction of electrode. So, deposition could occur discontinuously.

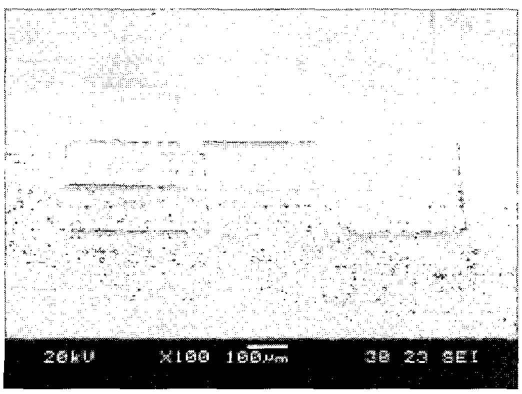

Fig. 13 Image of letters made with 2.5 V, 450 ns/ 1 μs by micro patterning

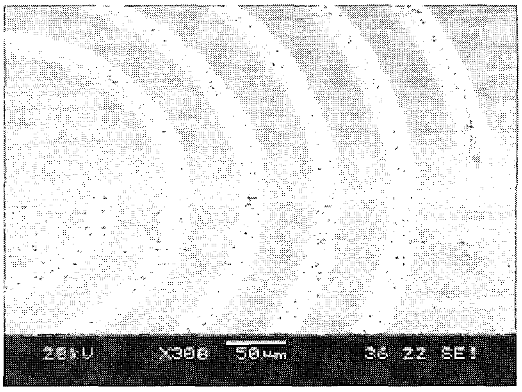

Fig. 14 Image of a spiral with 2.5 V, 350 ns/ 1 μs by micro patterning

To avoid this situation, the electrode was controlled not to touch the deposit. From some basic experiments, the growth time of structure was calculated to set the maximum feedrate. Figure 13 is the SEM image of alphabets 'snu' and Fig. 14 is the image of a spiral. The width of pattern line was 10 ~ 15 μm.

5. Conclusions

Localized electrochemical deposition is a remarkable method for making 3D micro structure easily. This process has advantages in variety of materials and cost efficiency compared with other microfabrication methods. In this work, micro structures were fabricated by applying ultra short pulses with LECD. The effectiveness of this technique is verified by comparison with LECD using DC voltage. Mixed electrolyte of 0.5 M copper sulfate and 0.5 M sulfuric acid solution was used. The proper condition was selected from the results of some experiments. The real 3D micro structures such as micro patterns, micro columns, and micro springs were fabricated by the suggested method.

REFERENCES

1. Bard, A. J. and Faulkner, L. R., "Electrochemical Methods: Fundamentals and Applications," 2nd ed., John Wiley & Sons, New York, 2000.

2. Madden, J. D. and Hunter, I. W., "Three-Dimensional Microfabrication by Localized Electrochemical Deposition," Journal of Microelectromechanical Systems, Vol. 5, No. 1, pp. 24-32, 1996.

3. El-Giar, E. M., Said, R. A., Bridges, G. E. and Thomson, D. J., "Localized Electrochemical Deposition of Copper Microstructures," Journal of the Electrochemical Society, Vol. 147, No. 2, pp. 586-591, 2000.

4. Said, R. A., "Microfabrication by Localized Electrochemical Deposition: Experimental Investigation and Theoretical Modeling," Nanotechnology, Vol. 14, pp. 523-531, 2003.

5. Yeo, S. H., Choo, J. H. and Sim, K. H. A., "On the Effects of Ultrasonic Vibrations on Localized Electrochemical Deposition," Journal of Micromechanics and Microengineering, Vol. 12, pp. 271-279, 2002.

6. Yeo, S. H. and Choo, J. H., "Effects of Rotor Electrode in the Fabrication of High Aspect Ratio Microstructures by Localized Electrochemical Deposition," Journal of Micromechanics and Microengineering, Vol. 11, pp. 435-442, 2001.

7. Schuster, R., Kirchiner, V., Allongue, P. and Etrl, G.,

"Electrochemical Micromachining," Science, Vol. 289, pp. 98-101, 2000.

8. Ahn, S. H., Ryu, S. H., Choi, D. K. and Chu, C. N., "Localized Electro-chemical Micro Drilling Using Ultra Short Pulses," Journal of the Korean Society of Precision Engineering, Vol. 20, No. 8, pp. 213-220, 2003.

9. Paik, W. K. and Park, S. M., "Electrochemistry: Science and Technology of Electrode Processes," Cheongmoongak, Seoul, 2001.

10. Jansson, A., Thornell, G. and Johansson, S., "High Resolution 3D Microstructures Made by Localized Electrodeposition of Nickel," Journal of the Electrochemical Society, Vol. 147, No. 5, pp. 1810-1817, 2000.