# Microdeposition of 3D structure on film surface using micropipette

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A new technique for rapid 3D microstructure preparation using micropipette is investigated. The tool electrode is made by Pt-Ir wire directly inserted into one or several glass micropipettes arrayed together. This electrode is used as anode, and copper plate or indium tin oxide (ITO) film is used as cathode. Both of them are placed in mixed electrolytes of $CuSO_4$ and $H_2SO_4$ for electrochemical microdeposition. To apply voltage between the electrodes, copper microcolumn with controllable diameter and height is successfully deposited into the cathode substrate by lifting the anode in $Z$ direction. Moreover, micropatterns can be made by moving the anode on $XY$ plane, sustaining a gap of a few microns from the substrate. Experiments are carried out to check the feasibility of this method. Microcolumns 50−150 $\mu$m in diameter with aspect ratio (height/diameter) that can be greater than 50 are fabricated. Several copper microcolumns that grow simultaneously are obtained. Moreover, lines with micro-width are also fabricated on ITO film. The experimental results indicate that this method is simple, fast, efficient, and can be mass-produced. It can be widely used for micro/nano deposition and processing.

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Micro/nano technologies are recognized as one of the key technologies that dominate the 21st century. In engineering and science, new microfabrication processes have been investigated worldwide[1,2], including bulk micromachining technology[3], surface micromachining technology[4], X-ray deep lithography, electroform molding, X-ray deep lithography, electroform molding, plastic molding (LIGA) technology[5], bonding technology, sacrificial layer technology, and so on. Localized electrochemical deposition (LECD) has excellent advantages, including its great variety of machinable materials, no macroprocessing force, good surface quality, no internal stress, being mass-produced, and three-dimensional (3D) processes. It has broad application prospects in the field of microfabrication, particularly in precision machining of certain difficult-to-machine metals and their alloys, or in microstructures that have special requirements regarding processing quality and performance[6−9].

Since electrochemical deposition using microelectrodes was introduced in 1995[10], numerous studies have been carried out. A variety of microstructures have been deposited by changing the electrolyte composition and concentration, adjusting the applied voltage and gap between the electrodes, and controlling the movement of the microelectrode[11,12]. El-giar *et al*. added some organic additives in electrolyte for micro column fabrication with smooth surface, and tried to deposit column with smaller diameter[13]. Yeo *et al*. discovered that, when microelectrode was rotated, hollow micro column was generated and the micro pipe was made with this method by LECD[14]. Some deposited products have been obtained; however, electrochemical micromachining is still a rising technology, and much more work needs to be done in many respects.

In this letter, by using a specially designed microelectrode, a new technique of rapid 3D microstructure preparation based on LECD is investigated. The new microelectrode is made by directly inserting Pt-Ir wire into either a single or several glass micropipettes arrayed together. Copper plate and indium tin oxide (ITO) film were used as substrate for electrochemical deposition, microcolumns from 50 to 150 $\mu$m in diameter were fabricated, and their aspect ratios (height/diameter) could be greater than 50. Several synchronously growing copper microcolumns were obtained. Moreover, lines with micro-width were also fabricated on ITO film.

LECD was based on the cathodic reduction of metal ions dissolved in electrolyte under localized electric field. The concept of microstructuring by LECD is shown in Fig. 1. When connecting a microelectrode to the (+) power source terminal and the substrate to the (–) power source terminal, the chemical reactions occuring at the anode and cathode in mixed electrolyte of $CuSO_4$ and $H_2SO_4$ are expressed in the following Equation. Anodic reaction at the end of microelectrode causes oxygen bubbles and electrons, and reduction reaction at the cathode substrate results in copper deposition. With the restriction of the glass micropipette, the electric field is limited to a local region between the anode and the substrate, which results in a reduction reaction that could only occur in this region. Confined deposition is thus produced.

$$\begin{aligned} &H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}O_2 \uparrow, \\ &Cu^{2+} + 2e^- \rightarrow Cu \downarrow . \end{aligned} \quad (1)$$

During deposition processing, a tiny gap is kept between the electrode and the substrate to effectively reduce the adverse effects of stray corrosion and enhance localization of anodic dissolution, so as to improve the machining accuracy. However, a too-small processing

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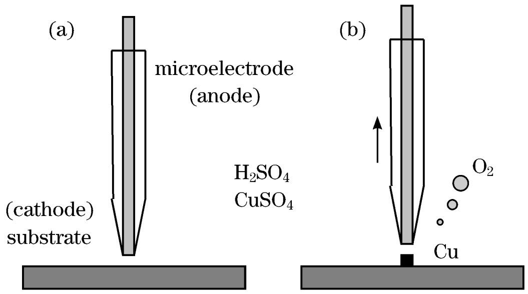


Fig. 1. Schematic of LECD process.

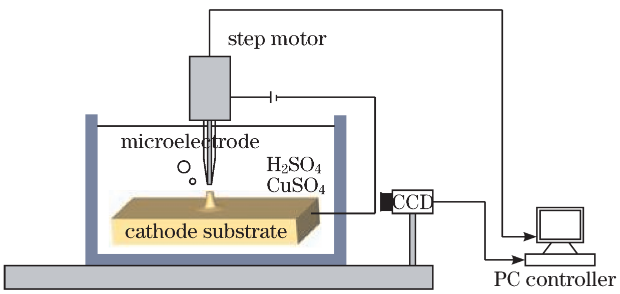


Fig. 2. Schematic of experimental setup.

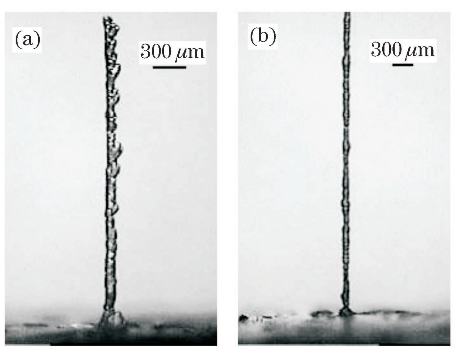


Fig. 3. Cu microcolumns deposited by (a) manual control and (b) automatic control.

gap could lead to some problems. For instance, the product of electrolysis is hard to discharge and easy to silt and adhere to the electrodes, which affects the normal process or even causes the structure to short circuit. Moreover, the phenomenon of microspark discharge is also prone to occur and bring about an uncontrollable discharge ablation, negatively affecting the machining accuracy and surface quality. Via theoretical analysis and experimental verification, a 5-$\mu$m gap during the deposition processing was determined to be the most appropriate. When the microelectrode made by several micropipettes arrayed together is used in LECD, every gap should be maintained at approximately 5 $\mu$m.

As shown in Fig. 2, experimental equipment consists of direct current (DC) power supply (0−5 V), step motor (MTS202, BOIF), microelectrode comprising Pt-Ir wire inserted in glass micropipettes, electrolyte pool, charge coupled device (CCD) monitoring system, and personal computer (PC) controller. The required diameter of Pt-Ir wire is 225 $\mu$m, and its bottom should be in the same plane with the micropipette port. A 100-$\mu$m-thick copper plate (purity 99.99%) and a 300-nm-thick ITO film (both 10 × 10 (mm) in size) are used as substrate, with the ITO film being laid on a piece of 3-mm-thick glass. After some experimental studies, the mixed electrolyte of 0.5 mol/L $CuSO_4$ and 0.4 mol/L $H_2SO_4$ is selected as the most appropriate. The acidic solution could prevent bonding of $OH^-$ with $Cu^{2+}$ because sufficient protons exist in solution with low *pondus hydrogenii* (PH), and the quantity of copper ions is maintained; therefore, acidic $CuSO_4$ solution presents a good condition for copper deposition. Meanwhile, to improve machining precision, stray electrochemical corrosion should be small and the conductivity of electrolyte low, which means the concentration of electrolyte should also be low.

Experiments were carried out to check the feasibility of this new method. The fixed system is shown in Fig. 2. Through CCD, the initial gap between the microelectrode and substrate was observed and adjusted. The switches of the electrical source and the step motor were then turned on. When the voltage value fluctuates along the entire vicinity of 0 V, it can be confirmed that the anode withdrawal speed is equal to the deposition rate. As a result, the gap remains unchanged, and the deposition processes is in steady state.

Figure 3 shows the microscopic image of Cu microcolumns made by manual and automatic control. The initial gap was adjusted to 5 $\mu$m. Experiments were conducted in the voltage range from 2 to 4 V with step of 0.5 V. Control of deposition process is almost impossible when applied voltage exceeds 3 V because of the violent reaction. Considering this, a voltage of 3 V was applied in the experiments. The voltage was observed by a multimeter to ensure the stability of deposition process. It is indicated that deposition has stopped when the voltage remains at 3 V.

As shown in Fig. 3(a), the Cu microcolumn diameter is 130 $\mu$m and its height is 3 mm. The aspect ratio has also reached 23. As it is manually controlled, the withdrawal speed cannot be controlled accurately, which leads to unideal structural characteristics of the deposited product (e.g., surface texture is rough). After some experimental studies, LECD is carried out by automatic control at the most appropriate withdrawal speed of 1 $\mu$m/s to improve its uniformity. As shown in Fig. 3(b), characteristics of the deposited column are best when the applied voltage is 3 V and withdrawal speed is 1 $\mu$m/s; the shape of column is uniform and its aspect ratio is greater than 50 with a diameter of 100 $\mu$m. When the speed exceeds 1.6 $\mu$m/s, deposition cannot process successfully because the microelectrode withdrawal speed is much faster than the deposition rate.

If the microelectrode is replaced by two-micropipette array for LECD, double Cu microcolumns can be fabricated synchronously. The experiments were also carried out with 3 V and 1 $\mu$m/s. Figure 4 shows that both of the columns are 100 $\mu$m in diameter and 1.5 mm in height. Thus, the repeatability and uniformity of deposited results is satisfactory. If the number of micropipettes is increased, more columns could be fabricated simultaneously. Therefore, this new technique of rapid 3D microstructure preparation could mass-produce the columns effectively.

LECD can also be applied to other materials such as

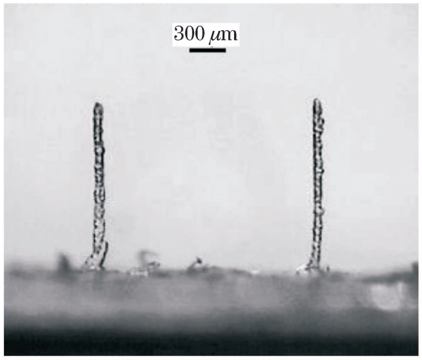


Fig. 4. Double Cu microcolumns deposited synchronously.

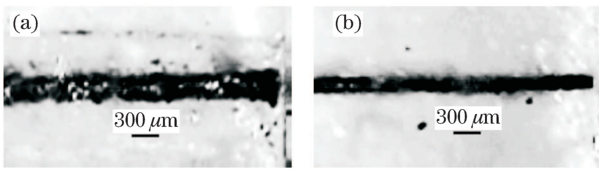


Fig. 5. Microlines made at different motion speed. (a) 125 $\mu$m/s and (b) 200 $\mu$m/s.

the semiconductor substrate. After applying a voltage of 2 V, microlines can be formed by moving the anode on $XY$ plane. The microscopic images of microlines fabricated on ITO film are shown in Fig. 5. Width of the line is 380 $\mu$m, as shown in Fig. 5(a), at a motion speed of 125 $\mu$m/s. The line in Fig. 5(b) is 240 $\mu$m at the speed of 200 $\mu$m/s, while both of the lengths are 4 mm. Hence, LECD is a technique not only for conductors, but also for semiconductors. In addition, if the diameter of the Pt-Ir wire decreases or motion speed increases, lines with smaller width would be obtained.

Moreover, using this method, 3D microstructures with arbitrary shapes could be fabricated by simultaneously moving the microelectrode on the $XY$ plane and upward in $Z$ direction.

In conclusion, with a specially designed micropipette, a new technique of rapid 3D microstructure preparation is successfully investigated. Microstructures such as Cu microcolumn with high aspect ratio, array of columns, and microlines with good uniformity are fabricated with this method. The aspect ratio of Cu microcolumns can be greater than 50, with diameter range of 50−150 $\mu$m. Microlines with 240 $\mu$m width is deposited onto ITO film. The experimental results indicate that this method is simple, fast, efficient, and can be mass-produced. More complex microstructures and wider applications will be further discussed in future studies.

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