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Three-dimensional Electrochemical Micromachining on Metal and Semiconductor by Confined Etchant Layer Technique (CELT)

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Abstract— **We developed a technology for three dimensional (3D) electrochemical micromachining. The confined etchant layer technique (CELT) has been applied to achieve effective three-dimensional (3D) micromachining on different kinds of metals and semiconductors. This technique operates on the basis of indirect electrochemical process, and is a low-cost technique for microfabrication of arbitrary 3D structures in a single step.**

I. INTRODUCTION

Recently, many novel approaches combined with electrochemical technique have been applied for micromachining. Most of the techniques are limited to two –dimensional (2D) or pseudo-three-dimensional (3D) microstructures with shapes similar to the extrusions from the 2D photolithography mask. As the 3D mold contains much more information than that in a 2D pattern, it needs the innovation of traditional technique for quick replication of truly 3D micro-mold to the substrate. The electrochemical method is considered to be a mild and friendly technique with low pollution to the environment. Several new electrochemical micromachining methods have been proposed recently, such as electro-micromachining using ultrashort pulses, proposed by Schuster et al. [1-3]; localized etching method using a SECM (scanning electrochemical microscope), proposed by Fan and Bard [4-7]; Confined etchant layer technique proposed by Tian et al. [8-13] and electrochemical scanning probe lithography (SPL) methods [14, 15]. Although these methods have a good potential for application, the fabrication of 3D structures in a batch has been only partially realized.

Confined Etchant Layer Technique (CELT) is a promising approach for electrochemical 3D micromachining. This technique can fabricate 3D microstructures on different kinds of substrate. The principle of CELT can be described as follows (Fig. 1). The etchant is generated electrochemically on the surface of a machining tool or a mold with a desired 3D micropattern. A specific scavenger is added to the solution that can destroy the etchant within a very short duration so as to prevent the etchant from diffusing away from the mold surface. Thus, the etchant layer around the mold is kept so thin that its profile takes approximately the contour of the microstructures of the mold. By continuously approaching the mold to the workpiece, the microstructures complementary of the mold are obtained. As a result, the 3D pattern of the mold can be replicated on the etched substrate. The key feature of the CELT is that it is distance-sensitive and this characteristic has allowed the arbitrary 3D microstructures to be replicated on the substrate in a simple process. Another advantage of CELT is that it can be applied to metal, semiconductor and insulator since it is based on the chemical reaction between the etchant and the workpiece.

Till now, we have successfully applied this technique in the micromachining of 3D complex patterns on the metals including Cu, Ni, Ti, Al, NiTi alloy [8] and the semiconductors including GaAs, Si [9-11, 16].

II. EXPERIMENTS

The experimental setup has been described elsewhere [16]. The workpiece was fixed at the bottom of a Teflon cell in the micromachining experiments. An instrument composed of a stepping motor and a piezoelectric tube under computer control could monitor the movement of the mold electrode relative to the substrate to be etched, with a step size from 50 nm to 50 μm.

The metal workpieces to be etched were copper, nickel, aluminum, titanium and nitinol foils with purity of 99.9%. They were polished by alumina powder with different diameters of 2 μm, 1 μm and 0.5 μm successively, then rinsed with water and acetone in the ultrasonic bath, and finally washed with ultra pure water prior to use.

The semiconductor workpieces to be etched were n-GaAs(100) and p-Si(100) wafers (Huajing Electronic Corporation, Wuxi, China). The 300-μm thick GaAs wafer was doped with Si and the carrier concentration n ranged from 1.0×10^{18} cm^{-3} to 4.31×10^{18} cm^{-3}. The 525-μm thick Si wafer was boron-doped, with a resistivity of 0–20 Ω cm. Before mounting in the electrochemical cell, the Si wafer was cleaned with H_2SO_4 and H_2O_2 (4:1), the native oxide layer was removed by dipping in 10% HF solution, and the wafer was then rinsed with ultrapure water. The preparation of the GaAs workpiece was done by simply rinsing with acetone and water.

The mold generating the etchant was used as the working electrode in a three-electrode system. A Pt wire ring surrounding the working electrode and a saturated calomel electrode (SCE) were used as the counter electrode and the

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reference electrode, respectively. The workpiece including metal, semiconductor or insulator was left at open-circuit in the solution.

Three kinds of mold were used in the etching experiments. One has a regular gear-like microstructure on it as shown in Fig. 1 and it was fabricated by bulk silicon etching technique on a silicon wafer. To have an excellent conductivity, a Pt film with a thickness of one hundred nanometers was deposited by RF magnetron sputtering on the mold surface. The second kind of mold was fabricated by an electric-discharge machining (EDM) technique. This Pt–Ir (80% Pt) mold included 3D microstructures made up of grooves tens of micrometers wide, forming the logo "XMU" of Xiamen University, and three hemispherical cavities with diameters of hundreds of micrometers. The third kind of mold was a titanium plate with a hexagonal array of hemispherical cavities (diameter 104.7 μm). This was fabricated by a through-mask electrochemical micromachining technique developed by Landolt's group[17-19]. The titanium plate was attached to the holder in the CELT instrument by conductive silver glue. To make a Pt-covered surface, a 200 nm thick Pt film was also deposited on the mold surface by RF magnetron sputtering.

All the micromachining experiments for the semiconductors and the nitinol were done by controlling the mold so that it was at a fixed distance of a few hundreds of nanometers above the substrate surface. The working procedure was as follows. The mold was brought slowly down until a sudden rise in the force between the mold and the substrate was detected. To protect the mold from crashing, the value of the force must be below 1 mN. The mold was then withdrawn to a fixed position away from the substrate by means of the piezoelectric tube. When the initial distance between the substrate and the mold is small enough and less than the thickness of the CEL, a 3D microstructure can be fabricated on the surface of the workpiece using the CELT mechanism.

The electrochemical parameters were controlled by a CHI 631B electrochemical workstation. The microstructures of the mold and the etched workpieces were characterized with a confocal microscope (Olympus 2000) and an optical microscope (Leica Q550MW).

III. Results

3.1 Electrochemical Micromachining on Metal

3.1.1 Electrochemical Micromachining on Cu, Ni, Al, Ti

Metal can be used as key materials in the microelectronic devices and micromechanical system (MEMS) because of its good electric and heat conductibility as well as excellent mechanical properties. But it is much more difficult to carry out wet etching technique to bulk metals due to its spontaneous corrosion in solution and the easy corrosion on the crystal boundaries. A key issue of using CELT for 3D micromachining on the metal substrate is to select an appropriate etchant and scavenger system.

As copper can be rapidly oxidized and dissolved by metallic cation like Fe^{3+}, Fe^{3+} was electrogenerated on the mold to be used as etchant. The Sn^{2+} was used as a scavenger that can react with Fe^{3+} quickly in the solution to confine the etchant nearby the mold with gear-like complex microstructures as shown in Fig.2 (a). The bipyridine forms complexes with Fe^{2+} or Fe^{3+}, which can improve the corroding ability of Fe^{3+} for Cu. Since $[Fe(bipy)_3]^{3+}/[Fe(bipy)_3]^{2+}$ has a higher redox potential than Fe^{3+}/Fe^{2+}, and contrarily the $[Cu(bipy)]^{2+}/Cu$ has a lower redox potential than Cu^{2+}/Cu. In addition, it can make the corrosion more uniform. The potassium chloride was added to increase the conductivity of the solution and to reduce the ohmic polarization of the solution. Furthermore, the chloride can enhance the corrosion of copper in the acidic solution. Since bipy is easy to form complex compound with Fe^{2+} or Fe^{3+} in the solution, the following process occurs during the micromachining process.

Generation reaction of etchant on the mold surface:

$$[Fe(bipy)_3]^{2+} \rightarrow [Fe(bipy)_3]^{3+} + e \quad (1)$$

Etching reaction of substrate:

$$[Fe(bipy)_3]^{3+} + Cu + bipy \rightarrow [Fe(bipy)_3]^{2+} + [Cu(bipy)]^{2+} \quad (2)$$

Destroying reaction of etchant (or scavenging reaction):

$$[Sn(bipy)]^{2+} + 2[Fe(bipy)_3]^{3+} \rightarrow Sn[(bipy)]^{4+} + 2[Fe(bipy)_3]^{2+} \quad (3)$$

Therefore, the etching solution for the Cu workpiece is chosen to be 0.02 M $FeCl_2$ + 0.01 M KCl + 0.06 M bipyridine (bipy) + 0.1 M $SnCl_2$ + 0.05M HCl. Fig. 2(b) is the microscopic image of fabricated microstructures on Cu substrate. The micromachining was done by controlling the mold potential in a constant current density. The current density was set at 1.25×10^{-2} A·cm^{-2} by a galvanostat to generate etchant on the mold and the etching time is 8 min. Fig.2 (b) shows that a gear-like pattern has been replicated on Cu and the Cu surface has nine slots fabricated on it, which is the complementary copy of nine protruding teeth on the mold surface.

CELT has also been applied to fabricate the gear-like microstructures on Ni, Al, Ti substrate. Figs. 2 (c)-(e) are the corresponding negative patterns of gear-like microstructures that have been fabricated on the substrate. The etching solutions for Ni, Al and Ti contain 0.03 M $NaNO_2$ + 0.01 M KCl + 0.1 M $C_4H_6O_6$ + 0.3M NaOH, 0.05 M $NaNO_2$ + 0.5 M NaOH + 0.2 M $C_4H_6O_6$ and 0.2 M NaF + 0.2 M $NaClO_3$ + 0.1 M $NaNO_2$, respectively. The resolution of micromachining can reach the submicrometer scale, which is the same as the micromachining of Cu.

3.1.2 Electrochemical Micromachining on Nitinol

However, the microfabrication on the alloy like nitinol is more complex than the metal of single component. Nitinol is an alloy composed of near-equiatomic proportions of nickel and titanium. This alloy shows a very high elastic deformation and a shape memory effect, which are not shown by other types of conventional metallic alloys. The excellent mechanical properties of nitinol make its machining extremely difficult. In the experiment, the nitrite is a kind of

precursor that can be electrogenerated into nitric acid on the conductive mold electrode. The nitric acid can etch the Ni component of NiTi alloy. When fluoride is added to the etching solution, the protons generated on the mold can combine with F^- ions to form the weak acid HF. The mixture of HF and HNO_3 can chemically dissolve the NiTi alloy and the etch rate ranges from 0.1 μm/s to 0.5 μm/s with the use of different volume ratios. Meanwhile, the tartrate must also be added into the electrolyte to produce $C_4H_4O_6^{2-}$ as a complex-forming ligand to prevent the precipitates of $Ni(OH)_2$. Thus, the etching solution contained $NaNO_2$, KF, $Na_2C_4H_4O_6$. A basic solution containing sufficient scavenger OH^- was added to react with HF or HNO_3 in order to obtain a very thin CEL. The electrochemical and chemical reactions that take place during the etching can be expressed as follow:

Generation reaction at tip: $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+$ (4)

Heterogeneous surface etching reaction:

$Ti + 6HF \rightarrow H_2TiF_6 + 2H_2$ (5)

$3Ni + 8HNO_3 \rightarrow 3Ni(NO_3)_2 + 2NO + 4H_2O$ (6)

Homogeneous scavenging reaction: $H^+ + OH^- \rightarrow H_2O$ (7)

In the study of micromachining with a complex Pt-Ir mold (Fig.3 a), bearing the logo "XMU", the composition of the etching solution is 1.5 M $NaNO_2$, 0.5 M KF, 0.4 M NaOH, and 0.1 M $C_4H_4O_6Na_2$. The distance between the mold and the nitinol was kept 200 nm and the potential applied to the mold was constant at 1.0 V. After etching with CELT for 200 s, micropatterns complementary to the corresponding patterns on the mold were fabricated on the substrate (Fig.3 b). The precision of duplication could easily reach the micrometer. Before the experiment, the mold was observed with a confocal microscope. Figure 3(a) shows that there were three letters "XMU" and three hemispherical microholes on this 3D mold. After etching with CELT, micropatterns complementary to the corresponding patterns on the mold were observed to have been fabricated on the substrate. On careful analysis of the micropatterns shown in Fig. 3(b), we observed that the microstructure "U" fabricated on the NiTi alloy had a better resolution than the other two letters "X" and "M". The line widths are 21 μm and 23 μm for the two sides of the microfabricated "U" in Fig. 3(b), which are near to those of the corresponding microstructures on the Pt–Ir mold (23 μm and 24 μm).The diameters of the microholes (A–C) were 67 μm, 100 μm, and 68 μm. The diameters of the convex microstructures (A1–C1) were 46 μm, 84 μm, and 63 μm. Therefore, the etching precision for the fabricated microstructures corresponding to A, B, and C can be calculated to be 31.3%, 16%, and 7%. Despite the tilted mold and an error of parallelism between the mold and the workpiece, the precision of machining can also reach the micrometer dimension. At present, the related study to improve the parallelism between the mold and the workpiece is under way in our lab.

3.2 ELECTROCHEMICAL MICROMACHINING ON SEMICONDUCTOR

Silicon is the most important material for MEMS owing to its excellent electronic and mechanical properties. Gallium arsenide (GaAs) is another important compound semiconductor, which is widely used in high-speed and high-temperature components, optoelectronic devices, and force and resonant sensors. The micromachining of these two materials down to micrometer or even submicrometer dimensions is considered to be a key technology in MEMS.

An effective etchant and a suitable scavenger have been chosen to utilize CELT in micromachining. Electrogenerated Br_2 was used as an etchant. In view of the fast reaction between L-cystine and Br_2 used to synthesize L-cysteic acid by organic electrochemistry, L-cystine (RSSR, R = $CH_2CH(NH_2)COOH$) was used in the experiments of 3D micromachining on n-GaAs and p-Si [9, 10].

The mechanism of the etching process for the Si and GaAs can be expressed as follows:

Generation reaction at tip:

$10Br^- \rightarrow 5Br_2 + 10e$ (8)

Homogeneous scavenging reaction:

$5Br_2 + RSSR + 6H_2O \rightarrow 2RSO_3H + 10H^+ + 10Br^-$ (R = $CH_2CH(NH_2)COOH$) (9)

Heterogeneous surface etching reaction:

$Br_2 + Si + 6HF + 4e^-_{CB} \rightarrow 2\,Br^- + SiF_6^{2-} + 3H_2$ (10)

$6Br_2 + 2GaAs + 6H_2O \rightarrow 2Ga^{3+} + 2AsO_3^{3-} + 12Br^- + 12H^+$ (11)

Fig.4 (b) is the microstructures fabricated on p-Si with the Pt-Ir mold bearing the logo of "XMU". In order to achieve 1 μm resolution, the etching experiment was performed in 1×10^{-3} M HBr + 5×10^{-2} M L-cystine + 2×10^{-4} M CTACl (cetyltrimethylammonium chloride) + 0.5 M H_2SO_4 + 0.5 M HF. During the etching process, the potential applied to the mold was kept at 1.0 V vs. SCE and the distance between the mold and the Si was kept constant. The confocal microscope image shown in Figure 4(b) shows that the etched structure is a fine, negative etched copy of the mold. The sizes of the protruding ridge and the three hemispherical convex features were approximately those of a negative copy of the mold. The resolution of the micromachining is deduced to be around 1 μm from the difference between the diameter of the convex feature (diameter = 105.0 μm) in Fig.4 (b) and that of the concave feature (diameter = 107.2 μm) in Figure 4(a).

In the process of micromachining on p-Si, CTACL is added to remove the evolved hydrogen owing to the chemical mechanism illustrated in Eq. (10). The concentration of hydrogen is increasing during the etching process, which influences the subsequent etching process since the hydrogen bubbles mask the mold surface from the electrolyte. Therefore, surfactant such as CTACL is added, the wettability of Si is enhanced and the surface tension at the Si–solution interface is dramatically reduced. The H_2 bubbles can escape easily and the influence of hydrogen evolution can be almost neglected.

Although the etching solutions for these two semiconductors contain both Br^- and L-cystine, the mechanism of micromachining on p-Si is completely different with that of n-GaAs. The different heterogeneous reaction between the etchant and the substrate takes an important role in the etching precision. As shown in Eq. (11), the etching of n-GaAs is a fast process with a direct chemical decomposition.

However, in the etching of Si shown in Eq. (10), the initial step is a chemical process of attack on a Si–Si back bond and formation of silicon hydride products as surface state intermediates. The rate-determining step is where the intermediates react with HF to give rise to hydrogen evolution and SiF_6^{2-}.This difference in mechanism explains why the micromachining of GaAs can easily attain high resolution, unlike Si micromachining.

A Pt mold with a hexagonal array of hemispherical cavities was employed. The composition of the etching solution was 0.5 M H_2SO_4 + 8.3 × 10^{-3} M L-cystine + 2.77 × 10^{-3} M KBr. The diameter of the hemispherical cavities on the Pt mold was 104.7 μm as shown in Fig.5 (a). A hexagonal pattern of convex features with an average diameter of 103.0 μm was fabricated on the surface of the n-GaAs, and the resolution of the micromachining in Fig.5 (b) was measured to be in the region of submicrometer.

Furthermore, it is very necessary to mention in all the images shown in Fig. 2-5 that the depth of the microfabricated holes is not equal to the thickness of CEL. Actually, the depth of fabricated microstructure by CELT is closely related with several factors including the total amount of the etchant in the very thin CEL, the distance between the substrate and the mold, the reaction rate between the etchant and the substrate. The AFM characterization revealed the height of the well-replicated microstructures by CELT as shown in Fig. 5 (b) is mostly less than one micrometer without approaching of the mold to the workpiece. To fabricate completely negative microstructures, it is mandatory to renew the electrolyte beneath the mold and the bulk solution. Since this process is also easily influenced by a lot of unpredictable factors, a larger etching precision is expected to achieve after feeding the mold for several times.

In conclusion, CELT has been developed well in our lab to fabricate complex 3D microstructures on the bulk metals and semiconductors. Thus, it is desirable that CELT will make an important contribution to the development of micro(nano) machining as a new technology complementary to the existing fabrication techniques.

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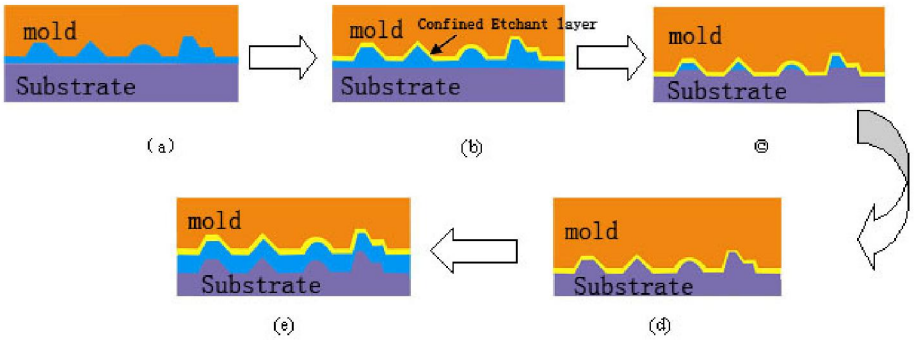

Fig.1 Schematic illustration of principle of confined etchant layer technique (CELT). Reproduced from Ref.[10].

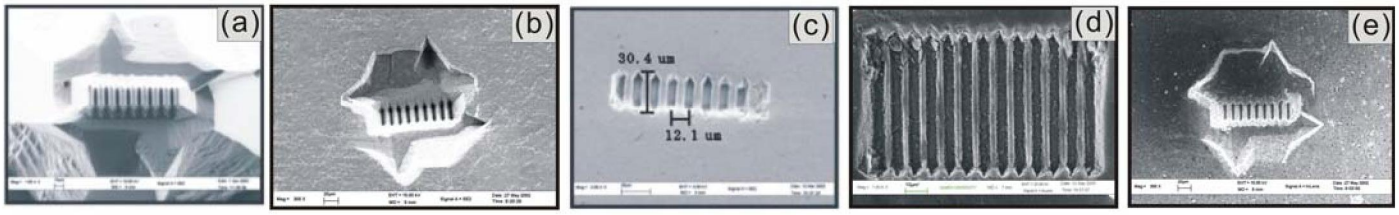

Fig. 2 Microstructures were fabricated by CELT on the metal of Cu (b), Ni (c), Ti (d), Al(e). (a) is the complex 3D mold. Reproduced from Ref. [8]

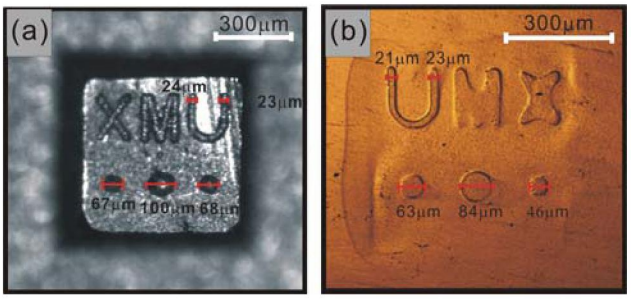

Fig. 3 Electrochemical micromachining on the alloy of nitinol. (a) is the complex 3D mold made of Pt-Ir.

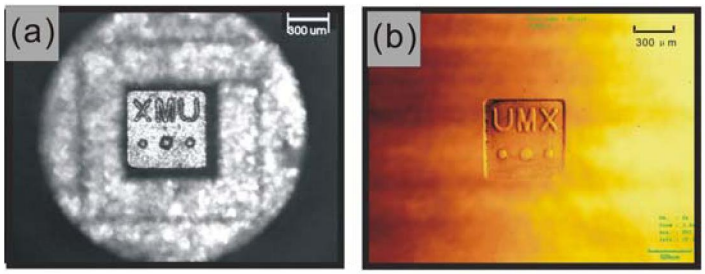

Fig.4 Electrochemical micromachining on the semiconductor of p-Si. (a) is the complex 3D mold made of Pt-Ir. Reproduced from Ref. [10].

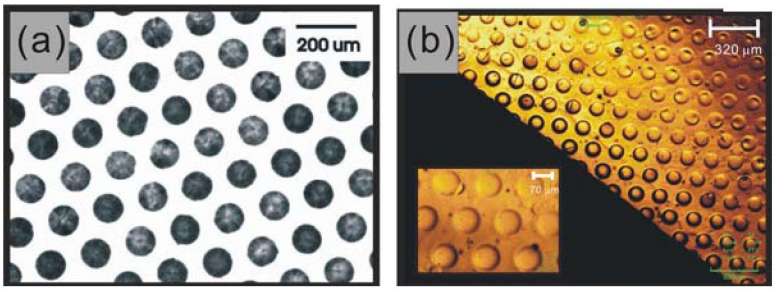

Fig. 5 Electrochemical micromachining on n-GaAs. (a) is the mold fabricated by a through-mask electrochemical micromachining technique. Reproduced from Ref. [10].