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Three-dimensional micromachining for microsystems by confined etchant layer technique

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Abstract

The micromachining of GaAs with three different truly three-dimensional (3D) molds were performed by the confined etchant layer technique (CELT). The etched patterns were found, approximately, to be the negative copy of the 3D molds. The general comparison of CELT with the existing micromachining techniques, such as two-dimensional (2D) projection lithography and electro-discharge machining, was made. The replication of the complex microstructures down to micrometer scale has been done by CELT in a single step. The photoresist layer, together with the procedures of exposure, developing and removal of resist, could be eliminated. The advantages of CELT over the existing lithography techniques and its potential applications are discussed briefly. It has been shown that CELT could be developed as a complementary technique to the existing micromachining techniques in fabricating microdevices for microsystems. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrochemical micromachining; Confined etchant layer technique (CELT); Microsystem; Microelectromechanical systems (MEMS); GaAs

1. Introduction

The micromachining of materials is considered to be a key technology in microsystems or microelectromechanical systems (MEMS). So far the surface micromachining technology by lithography has been successfully used for the fabrication of microelectronic devices in batch process. The information of the two-dimensional (2D) patterns in the masks can be transferred onto the workpiece as 2D thin film structures, which meet the requirements of the microelectronic device, in the IC technology and in MEMS fabrication at an early stage very well [1]. However, more requirements should be met in microsystems because of the combined functions of microelectronics with micromechanics and/or micro-optics, etc. For example, thicker structure with high aspect ratio or a truly 3D structure could be more useful for the performance of microsystem and could provide more flexibility on designing microsystems. Therefore, advanced micromachining technologies should be further developed.

LIGA (an abbreviation of the German words for lithography, electroplating, and molding) is a combined technique of lithography and electrochemistry which has become a powerful tool for making integrated micromechanical devices with high aspect ratios, even though they are limited to pseudo-3D microstructures with shapes similar to the extrusions from the 2D mask. All the cross-sections of different depths of these structures perpendicular to the light beam are similar to the 2D mask [2–4]. Since the amount of information contained in a 2D pattern in the mask is much smaller than that contained in truly 3D mold (e.g. geomorphologic map), new techniques for quick replication (transference of the information) of truly 3D micro-mold to the

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workpiece is highly desirable for batch production of microsystems. Examples of micromechanical devices are miniaturized springs, screws, and universal joints, motors and engines, turbines, gearboxes, chain drives, clutches, propellers and solenoids. Other examples of micro-electrical or optical devices are on-chip microwave transmission lines and high-Q inductors, switches or lens array for optical communications.

EFAB (an abbreviation for Electrochemical Fabrication) technique was proposed by Cohen et al. in 1999 [5]. A truly 3D mold (e.g. geomorphologic map) was resolved into contour map (a series of contour lines) automatically with the help of a computer and the workpiece was automatically fabricated layer by layer according to contour lines one by one. The process for production of many 2D masks and the alignment for each mask are thus simplified. However, a great number of steps should be taken if a truly 3D structure is desired.

All the above-mentioned techniques are based on the 2D mask and the direction sensitive characteristic of the incident beams (UV light, X-ray etc.). Along with the avenue of electrochemical etching method, using microelectrodes as the tool [6–9], two methods of a totally new class based on the 3D mold and the distance sensitive characteristic (vide infra) has been proposed, allowing the fabrication of real complex 3D microstructures in a single step.

CELT (an abbreviation for Confined Etchant Layer Technique) as a new approach of electrochemical 3D micromachining was proposed by Tian et al. in 1992 [10]. The active etchant is electrochemically generated at the surface of a stable mold with 3D micro-pattern, and is rapidly consumed during its diffusion away from the surface into the solution. Therefore, the etchant is confined within an extra thin diffusion layer around the surface. As a result, a 3D pattern of the mold can be replicated on the etched substrate on approaching to the mold. Since then studies on semiconductor etching have been going on in our group [11–16]. For example, we have used a microelectrode as simple tip mold for silicon etching and the agreement between the size of the etching spot and that of the tip mold is satisfactory [15].

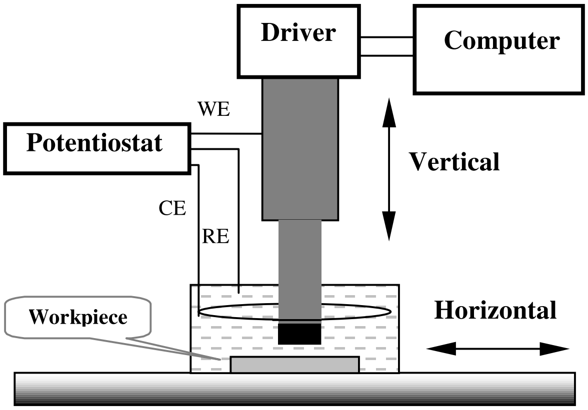

Fig. 1. The schematic representation of the experimental setup for CELT.

Very recently another important approach of electrochemical 3D micromachining was reported by Schuster et al. [17]. The principle of this method is based on the time constant for local double layer charging, which varies linearly with the local distance between a tool electrode and a conductive workpiece in an electrochemical environment. On applying ultrashort voltage pulses with several tens of nanoseconds, significant charging of the double layer of workpiece only occurs at electrode separations in the nano- to micrometer range. Because the rates of electrochemical reactions are exponentially dependent on the potential drop in the double layer, the anodic dissolution is strongly confined to these polarized electrode regions in very close proximity [17].

In this paper, we will present the work of electrochemical micromachining of GaAs surfaces using CELT. Three different types of 3D molds including two with regular patterns and one with arbitrary pattern have been used. These results will prove the feasibility of CELT in fabricating complex 3D microstructures. Finally, the advantages of the CELT over the existing lithography techniques and its potential applications will be discussed briefly.

2. Experimental

The scheme of the equipment setup of the CELT is illustrated in Fig. 1. The movement of the mold is driven by computer controlled step motor and PZT with a precision of 0.01 μm along the vertical direction. The horizontal movement of the workpiece in the $X-Y$ direction is adjusted by two step motors with precisions of 0.5 μm. The workpiece to be etched is chemically polished GaAs (111) doped with Si ($n = 7.0 \times 10^{17}$ cm^{-3}). The size of the workpiece was ca. 10 mm^2 diced from a 2 in. chip. It was first washed with acetone in ultrasonic bath, then with deionized water, and finally with ultra pure water (Nanopure, Barnstead, USA) prior to use. During the experiment the 3D mold generating the etchant is set as the working electrode in a three-electrode system. The counter electrode is a Pt wire ring surrounding the working electrode, and the reference electrode is an Ag/AgCl electrode. The patterns of the mold and the etched workpiece are characterized by atomic force microscopy (Nanoscope IIIa, Digital Instruments), scanning electron microscopy (S-520, HITACHI), and a microscope with a head of a CCTV camera (WV-Cp230/G, Panasonic) connected to a computer.

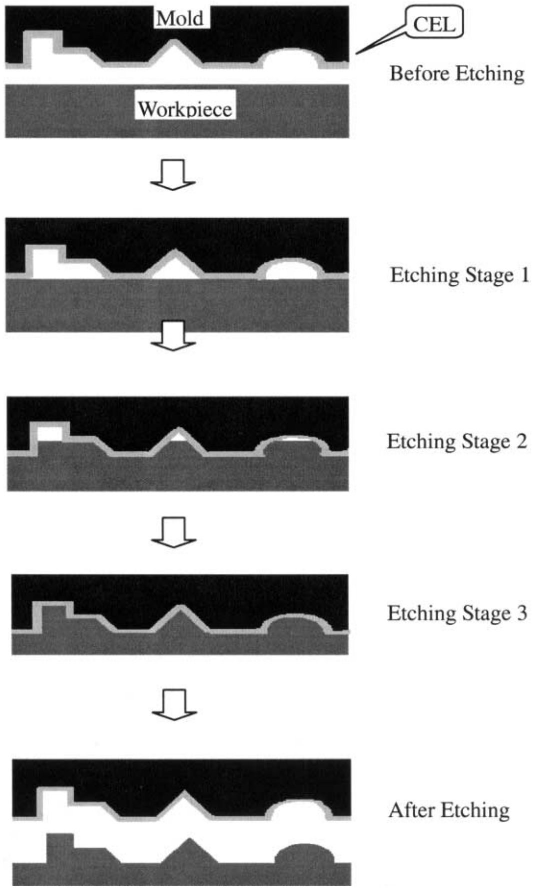

Fig. 2. The schematic illustration of the etching process by CELT.

In the present study two molds with regular microstructures were fabricated by bulk silicon etching technique on silicon wafer [18]. One of them has a gear-like pattern and the other is of micro-cone array shape. This fabricated silicon wafer was cut into 1 mm^2. As the mold for electrochemical micromachining must have excellent conductance, a Pt film with thickness of several hundreds nanometers was deposited by RF magnetron sputtering (Keyou Vacuum Company, Shenyang, China) on the mold surface after a Cr film with thickness of several nanometers was sputtered on as adhesion layer. The conductive connector between the mold surface and the current lead is also formed by sputtering a Pt film; see Fig. 1.

The third mold having an arbitrary microstructure was a spherical platinum electrode with rough surface. It was prepared simply by melting the tip of a platinum wire (100 μm in diameter) with a hydrogen–oxygen flame to form a sphere. The wire was then sealed into a capillary with the sphere head remaining out. The electrode surface with micron scale roughness was prepared by polishing it with 0.3 μm alumina powders. All chemicals used in the experiment were of analytical reagent grade and diluted with ultra-pure water.

3. Results and discussion

3.1. Schematic illustration of the etching process by CELT

The schematic illustration of the etching process by CELT is shown in Fig. 2. The active etchant is generated electrochemically by applying proper electrode potential on the mold having the 3D micro-pattern. When the etchant is diffused away from the mold surface, it is rapidly consumed (destroyed) by a specially designed chemical reaction in the solution, causing a thin confined etched layer (CEL) to be formed around the mold surface. As the mold approaches the workpiece, only the part of the workpiece touching the CEL is etched (see etching steps 1 and 2). As the mold is controlled precisely to move forward, a whole negative pattern of the mold can be transferred into the workpiece (etching step 3). As a result, a 3D pattern of the mold can be replicated on the workpiece.

Fig. 2 clearly demonstrates the key feature of the CELT to be distance sensitive. This feature is essential for 3D microlithography with one step. The electrochemical 3D micromachining proposed by Schuster et al. [17] also possesses the characteristic of being distance sensitive. The workpiece used by Schuster was the working electrode, hence it must be an electrically conductive material. From this point of view, the CELT is a more flexible method, as the workpiece can be either conductive or non-conductive.

It may be necessary to point out that electro-discharge machining (EDM) is totally different from CELT in principle, even though they apparently have some similarities. They both are conducted in liquid medium and are equipped with a tool electrode (or the so-called mold in CELT) against the workpiece. The machining to a metal workpiece by EDM is mainly through the melting and evaporating of the spot on the workpiece in a critical circumstance produced by the electro-discharge between the tool and the workpiece when applying a high voltage pulse between them [19,20]. While for CELT, the machining of the materials is the chemical reaction process in a mild condition (normally at room temperature and with the voltage applied less than 10 V). More importantly, the voltage applied is not between the tool electrode and the workpiece, but rather an additional counter electrode, as shown in Fig. 1.

3.2. Etching of GaAs with a gear-like patterned mold

A top view of the mold with a gear-like pattern is shown in Fig. 3a. The patterned area is measured to be 55 μm in width and 110 μm in length. It has nine protruding lines and eight slots. Its cross-sectional analysis (Fig. 3b and c) shows that they are periodically

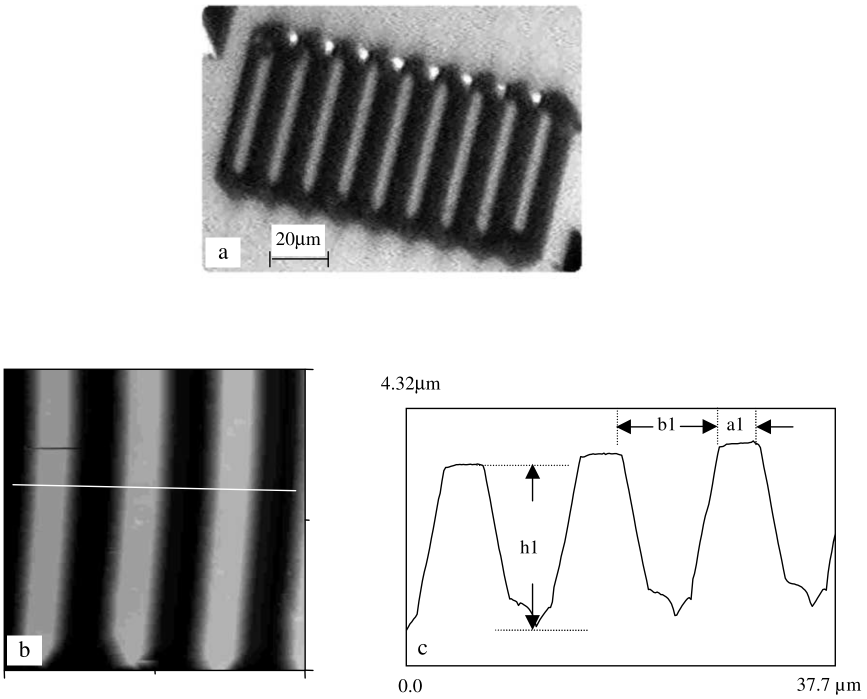

Fig. 3. A photograph of a mold with regular pattern (a) and its AFM image (b) with the cross-sectional analysis (c). Parameters: $h1 = 2.86$ μm, $a1 = 3.44$ μm, $b1 = 8.90$ μm.

arranged with a trapezium profile. The height of the trapezium is ca. 3 μm. Fig. 4 illustrates the etched pattern on GaAs with the above mold. The etching process was performed in 10 mM HBr + 100 mM HCl + 50 mM H_3AsO_3 with a constant current $i = 4.1 \times 10^{-3}$ A/cm^2 for time $t = 8$ min. The etched pattern has nine slots and eight protruding lines, being the negative copy of the mold.

The electrochemical and chemical reactions that take place during the etching are expressed as follows:

$$2Br^- \rightarrow Br_2 + 2e \qquad (1)$$

$$Br_2 + AsO_3^{3-} + H_2O \rightarrow 2Br^- + AsO_4^{3-} + 2H^+ \qquad (2)$$

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

When the etchant Br_2 was electrochemically generated at the mold surface (reaction (1)), it diffused into the solution. At the same time, AsO_3^{3-} as the scavenger in the solution reacts quickly with the etchant (reaction (2)). As a consequence, the etchant Br_2 is confined in a very thin layer surrounding the mold surface. When the mold approaches the GaAs substrate as the workpiece, GaAs is then etched according to the pattern of the mold.

From the differences of the structure parameters (as shown in Figs. 3 and 4) between the mold and the etched pattern, Δa, Δb and Δh, one can estimate the

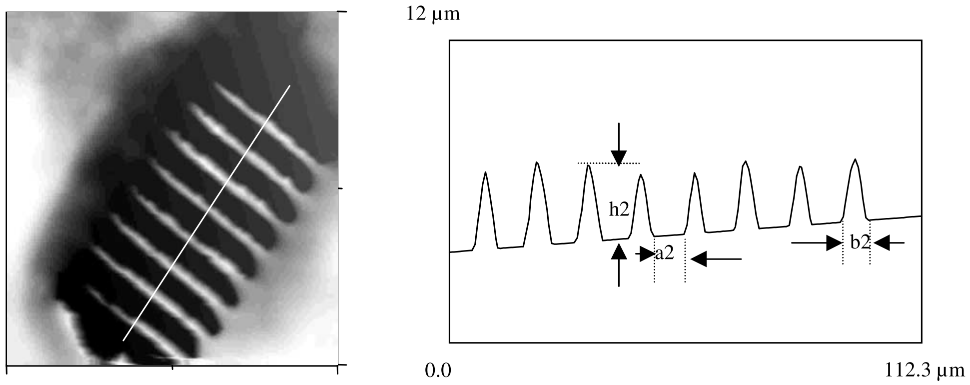

Fig. 4. The cross-section of the etched patterns of GaAs substrate with CELT in 10 mM HBr + 50 mM HCl + 100 mM H_3AsO_3 at a constant current $i = 4.1 \times 10^{-3}$A/cm^2, $t = 8$ min. Parameters: $h2 = 2.82$ μm, $a2 = 7.07$ μm, $b2 = 5.68$ μm.

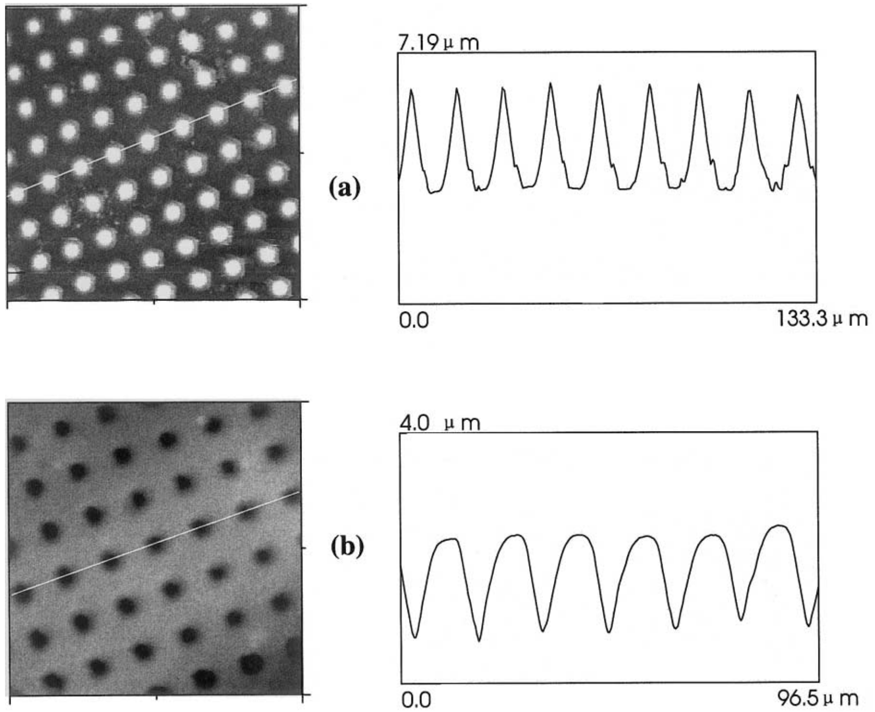

Fig. 5. The cross-section of the mold with 2D pyramid array (upper) and that of the etched patterns (down). The etching condition is the same as in Fig. 4.

precision of the micromachining. Their values can be calculated as follows: $\Delta a = (a2 - a1)/2 = 1.82$ μm, $\Delta b = (b1 - b2)/2 = 1.61$ μm and $\Delta h = h1 - h2 = 0.06$ μm. The reason of the first two formulae to be divided by 2 is that each tooth of the gear-like mold has two sides. Because the AFM tip has a conical shape, when it scanned on such deep slot, the little distortion of the AFM image in the z-direction must be considered. Therefore, the value of $h1$ (2.82 μm) is not the real height. We took an SEM image of the mold's side view; the real value of the height was measured to be ca. 3.30 μm. Thus the value of Δh is 0.48 μm and the precision of the etching in this experiment was ca. 1 μm.

The precision is determined by the thickness of the CEL. If the concentration of the scavenger is much greater than that of the etchant generated at the mold, it can be assumed that the scavenger concentration remains constant during the whole process and the homogeneous reaction (2) is of pseudo-first-order with rate constant k_s. The thickness of the CEL can be estimated by the specific thickness of the diffusion layer (μ), which is given by [10]

$$\mu = (D/k_s)^{1/2} \tag{4}$$

where D is the diffusion coefficient of the etchant in the solution. Since the order of magnitude of D is 10^{-5} cm^2/s, the value of μ is ca. 1 μm, 30 nm and 1 nm corresponding to that of k_s, 10^3 s^{-1}, 10^6 s^{-1} and 10^9 s^{-1}, respectively.

3.3. Etching of GaAs with a pyramid-like patterned mold

Another regular mold has many small pyramid-like microstructures periodically laid on the base, as shown in Fig. 5a. Every pyramid has a square bottom with a width of ca. 10.1 μm. The height of the pyramid is 2.86 μm. The average distance between the bottom lines of the two nearest pyramids is ca. 5.30 μm. The corresponding etched pattern on GaAs shown in Fig. 5b was obtained under the same etching condition as in Fig. 4. The depth of the holes varies from 1.4 to 1.6 μm. The distance between the bottom points of the two nearest holes is ca. 14.9 μm, which is in agreement with that between the highest points of the two adjacent pyramids 15.4 μm.

It should be noticed from Fig. 5 that the shape is transformed from pyramid for the mold to cone for the workpiece. The reason for this shape change is that the thickness of the CEL was not absolutely uniform especially in the case that the radius of curvature of the mold surface is not much greater than the thickness of CEL. In these cases, spherical diffusion should be considered instead of the planar diffusion. CEL becomes thinner on the convex site of the mold and thicker on the concave site of the mold. Since the radius of curvature of the mold surface at the sharp edge parts of the pyramid is very small, the pattern was smoothened to round shape. However, this result should not be too disappointing as it has a potential application. The microholes with conical shape meet the demand in many cases for microdevices and microsystems because these are difficult to be fabricated through conventional lithography on semiconductors. For example, the head of the bubble jet printer can be fabricated by silicon technology and the shape of its spray mouth is square instead of round. With the need of higher quality of printing, round spray mouth could be better.

3.4. Etching of GaAs with an arbitrary microstructure mold

The above two CELT experiments using the mold with regular microstructure just demonstrate the feasibility of CELT in fabricating complex 3D microstructures. The fabrication of more complex microstructures than pyramids is also not difficult for CELT according to its working principle. However, these molds with complex 3D microstructures are rather difficult to make. Unfortunately, so far we have not yet found a partner to fabricate such kind of mold for CELT. Thus we have to use a small spherical platinum electrode having arbitrary microstructure as the mold for the preliminary test. Fig. 6 shows two etched patterns duplicated by using the same sphere electrode with a rough surface that has an arbitrary 3D pattern. The solution was 20 mM $KBr + 0.1$ M $HCl + 0.1$ M $CH_2CHCH_2NH_2$ (used as the scavenger of Br_2). The operation mode is constant potential and the applied potential to the mold was 1.1 V, and the etching time was 10 min. As can be seen from Fig. 6, these two patterns are very similar to each other even in the very fine structure with scale down to micrometer, such as the 'valleys' and the 'mountains' on geomorphologic map. Although this arbitrary 3D microstructure cannot be used for the purpose of microsystem, this preliminary result may provide evidence that CELT is a potential method for 3D replication of very complex micro-patterns.

4. Remarks and conclusions

It has been shown that CELT could be a potential technique for replication of 3D structures in the micrometer scale. This technique can be further developed to replicate the structure down to nanometer scale based on its working principle. However, two technical problems should be solved. First, the mold having nanostructure has to be fabricated by some beam techniques, such as ion, electron or photon beams, or SPM techniques. Although the fabrication process is rather time consuming, the fabricated mold can be used in CELT many times. Secondly, the etching system should be properly chosen in order to reach the nanometer precision of etching. For example, when the value of the scavenging reaction rate constant k_s is set to be 10^{-7} s^{-1}, the thickness of the CEL became ca. 10 nm from Eq. (4).

For complex 3D micromachining and possibly nanomachining for the batch production, CELT has some advantages over the existing lithography techniques. Firstly, since the etchant is confined within an ultra-thin layer around the patternized surface, the etching process exhibits distance sensitive character. This is different from the direction sensitive character of the existing projection lithography techniques, in which the patterns replicated are generally 2D or psuedo-3D patterns for each replication process. Secondly, most of the existing lithography techniques require a photoresist layer. On the contrary, CELT can design a specific chemical system so that the etchant can directly etch the specified coating of the wafer in a single step. Therefore, the photoresist layer, together with the procedures of exposure, developing and re-

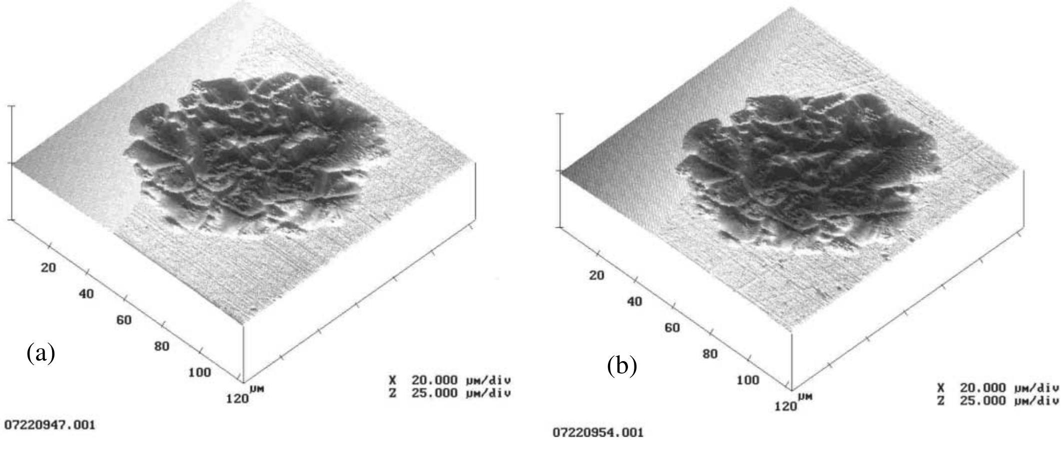

Fig. 6. The AFM images of complicated micro-patterns at the GaAs (111) surface replicated by using the same mold with arbitrary 3D structure (see text).

moval of resist, could be eliminated. The 3D replication of integrated micro-devices, such as micro-lenses and micro-actuators, can be realized more easily. Thirdly, as the etchant can be designed to possess chemical selectivity of etching to the workpiece, the risk of attacking the underlayer can be avoided. For the lithography techniques, the high energy radiation in physical etching processes may penetrate into the underlayer and cause various types of damage, e.g. modification of the structural, chemical and electrical properties due to intrinsic bonding damage, permeation of impurities, etc.

It should also be pointed out that the realization of CELT as a technique of the electrochemical microsystem technology certainly requires many surrounding technologies from different aspects. Many technological problems have to be solved in the course of its realization. We have mentioned the difficulty to fabricate the 3D patternized mold. The aspect ratio of the etched microstructure is limited as the etching rate is not usually very high. For making a structure with high aspect ratio, a special experiment is required to design to avoid the dominant ohmic drop. Improvements of CELT are under investigation in our laboratory.

In conclusion, the CELT developed in our laboratory as a wet indirect etching technique exhibits the character of being distance sensitive and the potentiality of complex 3D pattern replication. It is feasible for the machining of various materials such as metals, semiconductors, ceramic, glass, etc. by using different etchants and etching conditions. It could be further developed as a potential technique for nanolithography. As a complementary tool of the existing fabricating techniques, such as photolithography and LIGA, CELT will make a contribution to the development of microsystems (or MEMS).

Acknowledgements

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