

A combinative technique to fabricate hot embossing master for PMMA tunneling sensors

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Abstract A combinative approach of anisotropic bulk etching and modified plasma etching has been successfully employed in a single wafer to fabricate silicon masters for the hot embossing process. The masters hold both pyramid pits and positive profile sidewalls with smooth surfaces and steep angles. The SiO₂ layer is utilized as a etching mask with the aid of photoresist in three steps of photolithography patterning. The first polymethyl-methacrylate (PMMA)-based tunneling transducer with polymer membrane structures is fabricated by hot embossing replication with the silicon master. Consequently, the exponential relations between tunneling currents and applied deflection voltages are also reported.

1 Introduction

With the research and development on LIGA process [1, 2, 3] – X-ray Lithography, Electroforming (Galvanoformung), and molding (Abformung), three micromachining ways (electroforming, moulding, and embossing) to fabricate high-aspect-ratio microstructures have been attracting more and more attention in microelectromechanical system (MEMS). As one of the most attractive micromachining techniques, hot embossing for replicating microstructures at a high performance-to-cost ratio has such advantages as good uniformity, the surface roughness of only 3.9 nm at a large substrate area [4], simple processing, one step instead of multiple steps, and high lateral resolution of only a few nanometers [5]. Moreover, for the inexpensive thermoplastic materials such as polymethyl-methacrylate (PMMA) or polycarbonate (PC), the cost of fabrication can be further reduced in addition that hot embossing itself consumes less chemical, runs out of less time, and needs less instruments than the conventional microfabrication. Therefore hot embossing has been selected as one of the most potential tools for mass production.

In recent years, hot embossing has been widely used in many applications by exploiting the characteristics of

PMMA, one of the thermoplastic materials. Due to such characteristics as insulating, biocompatible, and transparent, PMMA has been chosen to build microstructures like microfluidic channels [6], biotechnology patterns [7], and optical gratings [8, 9]. The direct usage of silicon which has been micromachined with various technologies as a tool material for hot embossing of polymers has represented a significant reduction in cost and fabrication time for an embossing master in comparison to the previous tools as well as allowing access to high-aspect-ratio structures without the need of complex technologies like LIGA. [10, 11]

In this paper, PMMA is specifically used to fabricate tunneling transducers because it is relatively softer than silicon, which produces a potentiality in higher sensitivity. When using hot embossing for replication, a polymer plate is laid on the bottom heating plate of the hot embossing machine, and the surrounding vacuum chamber is closed. Next, under vacuum the heated mold insert is pressed into the softened polymer. After subsequent cooling, demolding takes place by removing the plastic part from the cavities. The demolding process is more important because all the parameters should be well controlled so that the microstructures are not destroyed by either the crack of the mold or by the friction of the side wall. Currently there are mainly three methods to build hot embossing masters. The first approach is wet anisotropic etching for silicon master, which is simple but has low aspect ratio. The second one is deep reactive ion etching for silicon master, which has high aspect ratio, but the process needs to be controlled with more complicated conditions so that the side walls are smooth, which is necessary to avoid cracking at demolding. The last one is electroplating of Nickel with the aid of photolithography mold and seed layer, the most complicated and slow method in addition to the tricky conditions for profile control. As shown in Fig. 1, the sensor includes mechanical components and three electrodes. The mechanical components are compromised of a top membrane part with proof mass and a tunneling tip, standing oppositely to the film on the bottom. The electrodes include a tip electrode, a counter electrode opposite to the metallic film covered PMMA tip, and a deflection electrode. The structure of tunneling sensor needs different areas such as tunneling pyramid, which has a sharp tip to warrant producing tunneling current, and some grant blocks, which should have steeper and higher sidewalls. In the meantime, the height of proof mass needs to be changed from chip to chip so that the parameters of transducers can be adjusted promptly.

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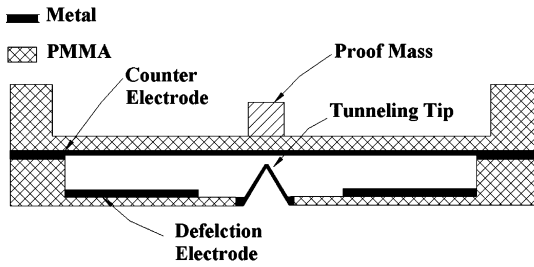


Fig. 1. Cross section of a membrane-type PMMA-based tunneling sensor

Consequently, it is hard to obtain a single hot embossing master only by the conventional processes. In this paper, the combination of KOH (potassium hydroxide) etching and deep reactive ion etching is used to construct the silicon masters so that the needs for different parts can be met. The first generation of all-PMMA tunneling transducers made by hot embossing has been fabricated and exhibited exponential relationship between the tunneling current and the displacement.

2 Experiments

2.1

Master choice

There are two types of masters that can meet the requirements of the tunneling sensor's fabrication. One is the metal master based on the electroplating of Nickel or other metals, and the other is silicon master with the fabricated microstructures on the silicon wafer. With a metal master, Nickel electroplating is always necessary to fabricate the microstructures. However, the electroplating process is rather slow, and it is almost impossible to obtain sharp edges and pyramid-like profile, which makes it the only choice of the silicon master. When using KOH wet etching, a layer of SiO_2 is often used as the etching mask. Since the etch ratio between SiO_2 and Si is about 1/100, the thickness of SiO_2 is chosen as 2 μm . In addition, the hot embossing process requires that the masters bonded onto a holder, which requires the wafer have a smooth surface at its backside. Altogether, double-side polished silicon (100) wafers coated with 2 μm thermal oxide are selected for the masters.

2.2

Structure synthesis for PMMA-based tunneling sensors

The intended z -direction sensitive tunneling sensors have membrane-based microstructures. The narrow gap between the tunneling tip and the counter electrode is about 10 \AA when the device is functional. The small distance is hard to be realized without the aid of deflection electrode acting as a capacitive actuator, which not only pull down the counter electrode membrane at proper position, but also produce feed-back static forces to keep these distance constant [12–14]. Therefore, the membrane thickness, the original gap between the counter electrode and the tunneling tip, and the static force distribution between the counter electrode and the deflection electrode are synthesized with ANSYS, a Finite Element Analysis tool.

Because the Young's modulus of PMMA is about 3.9 GPa, about 2/9 of the silicon's value of 17.9 GPa [15], the PMMA is rather soft compared with silicon. The membrane could be thicker than silicon membrane, which is another reason why all-PMMA structures are chosen. The structure of a well synthesized PMMA tunneling sensor includes a membrane of 30 μm in thickness and 2 mm \times 2 mm in square, a pyramid tunneling tip of 50 μm in height and 70 μm in base line, and a proof mass of 100 μm \times 100 μm in square and flexible in height. The detailed description will be reported elsewhere [16].

2.3

Fabrication process

The preparation of silicon masters for hot embossing begins with KOH wet etching. Because KOH solution is a typical development liquid for positive photoresist, photoresist can not be used as the etching mask even if it has not been exposed. Most chemical etchant selectively etch either Si or SiO_2 without etching the other. This selectivity has been extensively used for Si-based technology. Silicon dioxide is extensively selected as the etching mask because KOH has negligible effect on it. A well-known system is the thermal oxide coated silicon selectively etched by the buffered HF (hydrofluoric acid) to pattern SiO_2 , and then selective etchant KOH for Si patterning. As shown in Fig. 2a, the SiO_2 is patterned by positive photoresist (PR1813), and etched by the diluted BOE, so that the etching rate can be well controlled at a relative slow rate of 800 $\text{\AA}/\text{min}$. After that, the photoresist is removed by acetone, and the whole wafer is soaked into 45 wt % KOH etchant. The etchant is kept at 85 $^\circ\text{C}$ with a stirrer rotating at 200 rpm. The etching time is about 60 min with a rate of 1 μm per min (Fig. 2b). Following that, another buffered HF etching is performed after the second photolithography (Fig. 2c). The deep pyramid pits are then protected thoroughly with the photoresist because a plasma etching is followed. The usually used high density plasma, SF_6 and O_2 , will result in an isotropic undercut profile, which is unsuitable for hot embossing. When demolding, there

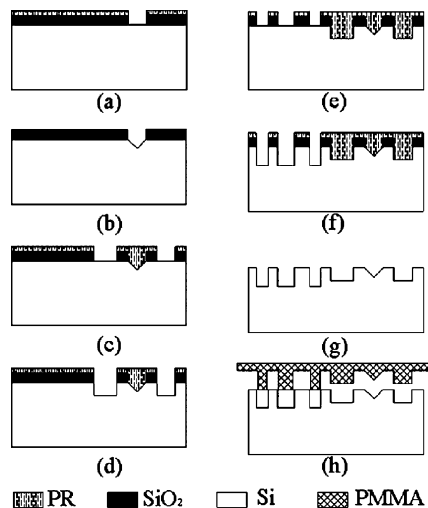


Fig. 2a-h. The combinative technique to fabricate a silicon master for hot embossing

occurs either the cracking of silicon master or the broken of PMMA structures. Traditional etching by Bosch recipe, in which the gases switches between SF_6/O_2 and C_4F_8 , does not work either, though it can achieve a vertical or positive taper profile, but a rather rough surface (“grass”) is observed in the large etched areas [17]. We used a modified process, SF_6 , O_2 , and C_4F_8 used simultaneously, to acquire a vertical or positive sidewall profile and a smooth surface. As synthesized above, there is a small distance between the tunneling tip and the counter electrode, about $5\ \mu\text{m}$ to be controllable. The depth of the groove is about $55\ \mu\text{m}$ (Fig. 2d). After the first ICP (Inductive Coupling Plasma Etching), the wafer is cleaned, and another photolithography is carried out (Fig. 2e). This time, the photoresist is much thicker since the second plasma etched groove will be about 80 to $100\ \mu\text{m}$, changeable due to the sensor performance (Fig. 2f). Subsequently, the thermal oxide is removed, and the silicon master is well cleaned (Fig. 2g), which thereby is bonded to the Pyrex glass by the anodic bonding. The hot embossing is executed at a force of $20\ \text{kN}$ with the temperatures of $165\ ^\circ\text{C}$ for molding and $80\ ^\circ\text{C}$ for demolding (Fig. 2h). The PMMA is then sliced into two parts, patterned with electrodes separately and assembled together by conductive epoxy glue.

3 Results and discussions

3.1 Optimum conditions for silicon masters

The most important part of a tunneling sensor is the tunneling tip since the tunneling current requires that the tip should be sharp enough to hold several atoms in a single layer. Therefore, the formation of the tip point in a silicon master is crucial. Next, the wet etching time is of importance because a non-well etched platform will result in no tunneling effect. Fortunately, the wet etching can continue after an inspection under microscope. The best etching time should be controlled within one minute. A SEM picture is shown in Fig. 3, in which the sidewall of pyramid is smooth and the four edges are sharp.

As described above, three types of chemicals, SF_6 , O_2 and C_4F_8 , can realize both isotropic chemical etching and

anisotropic physical etching in the plasma etching. The positive and smooth sidewall, as shown in Fig. 4, is obtained by optimizing the conditions as $200\ \text{sccm}\ \text{SF}_6$, $20\ \text{sccm}\ \text{O}_2$ at $100\ \text{W}$ (ICP), $20\ \text{W}$ (bias), a working pressure of $60\ \text{mT}$, and a temperature of $10\ ^\circ\text{C}$. The $4\ \text{inch}$ silicon wafer with micromachined structures are then attached on the holder of hot embossing system. The hot embossing machine is produced by Jenoptik Microtechnik GmbH and the model is HEX 01/LT.

3.2 Hot embossing with a combinative etched master

According to the data in reference [18], the glass transition temperature of PMMA is about 100 – $105\ ^\circ\text{C}$, and the melting temperature is about 112 – $130\ ^\circ\text{C}$. The molding temperature is set at $165\ ^\circ\text{C}$, a little bit higher than the melting temperature in case of uncertainty. When molding, the chamber top is compressed down, with the master’s maximum contact force of $20\ \text{kN}$. The background pressure is about $1.5\ \text{mbar}$. The master has been kept under these working conditions for about $60\ \text{s}$, and the temperature is cooling down. The demolding system is designed to overcome the holding forces between the tool and the PMMA sheet with the aid of compressive air, which is applied from the top of master holder. In our case, the demolding temperature is set at $80\ ^\circ\text{C}$. The speed of master movement is $1\ \text{mm}/\text{min}$. The fabricated PMMA pyramids (shown in Fig. 5) have smooth surfaces, sharp tip points, and steep edges, which compete with other tunneling tips acquired by micromachining on silicon.

3.3 PMMA-based tunneling transducer

Similar to the traditional electrodes for a silicon-based tunneling sensor, two layers of Ti/Au metal films are sputtered on a PMMA sheet and patterned by I_2/KI solution (weight ratio: $\text{I}_2:\text{KI}:\text{H}_2\text{O}=1:5:50$) and BOE (Buffered Oxide Etchant) etching. Different from the silicon baking at high temperatures, the PMMA substrates are dehydrated under vacuum after the nitrogen dry blowing at high pressure. The photograph of a tunneling tip with a patterned electrode is shown in Fig. 6. Conductive Silver Epoxy Kit is used for both wire bonding and adhesive. As

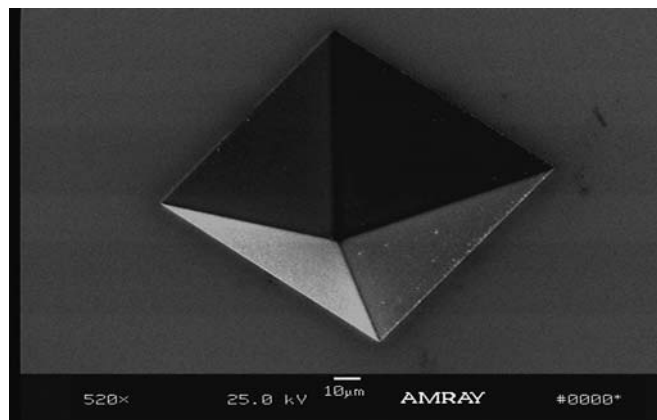


Fig. 3. Pyramid structure with a sharp pit in a silicon master at optimized conditions

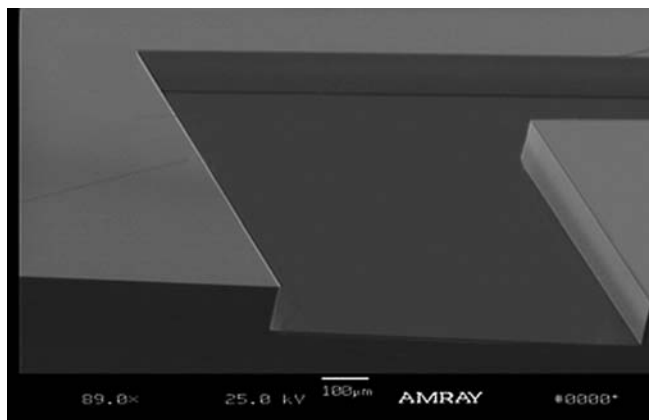


Fig. 4. Positive and smooth sidewalls in a silicon master by optimized deep reactive ion etching

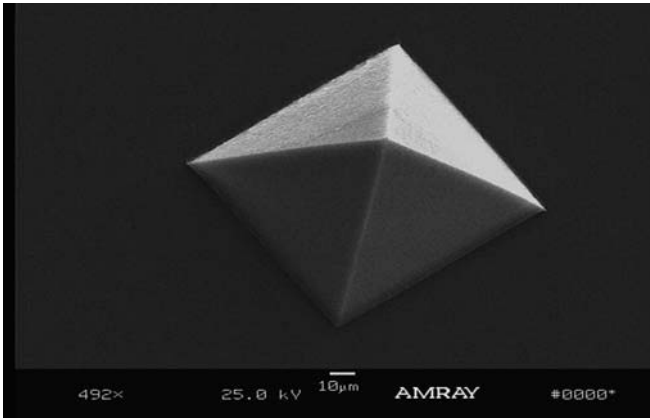


Fig. 5. Smooth surfaces, sharp edges, and square basement of a pyramid PMMA tunneling tip embossed by the combinative etched silicon master

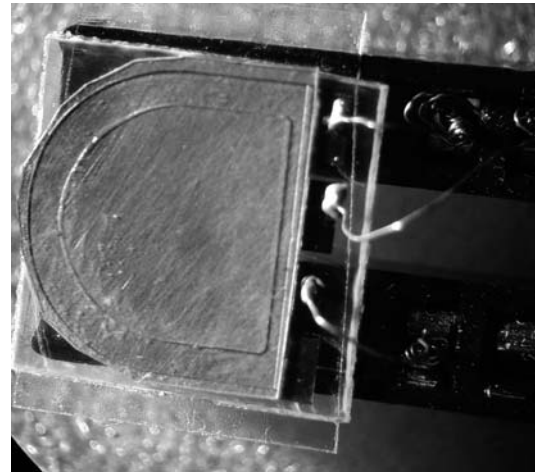


Fig. 7. Packaged PMMA-based membrane tunneling sensors. The three electrodes are connected with measuring wires by epoxy

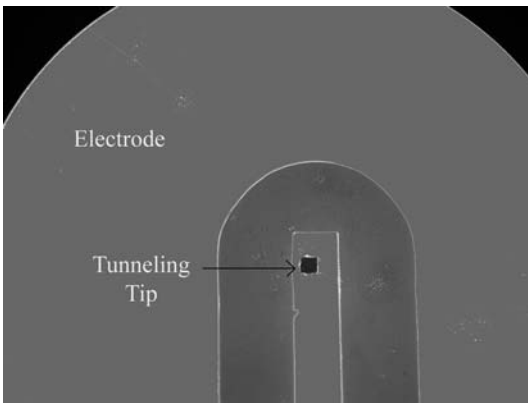


Fig. 6. Hot embossed tunneling tip with gold electrode patterns, the electrodes of Pt/Au metallic films, tunneling tip at the center covered with metallic film

shown in Fig. 7, the proof mass part and the tunneling tip part are glued together, and fixed onto the IC multiple-pin socket. The tunneling currents are measured when the feedback voltages are applied onto the deflection electrode. The exponential relationship between the tip tunneling currents and the applied deflection voltages is plotted in Fig. 8. Because the displacement is linearly proportional to the applied voltage on the capacitive actuator [12], the tip current is proved to be the tunneling current. The tunneling barrier height derived from the plot is about 0.168 eV, which is almost the same as the values of other groups [19].

4 Conclusions

The KOH wet anisotropic bulk etching and the improved deep reactive ion etching (ICP) using chemicals of SF₆, O₂, and C₄F₈ have been successfully mixed together for a combinative etching technique in the preparation of silicon masters for the hot embossing process. There should be a small gap of less than 5 μm between the tunneling tip and the counter electrode. That is why the wet etching time needs to be well controlled. As the sizes of proof mass need to be changeable and the heights of blocks are different,

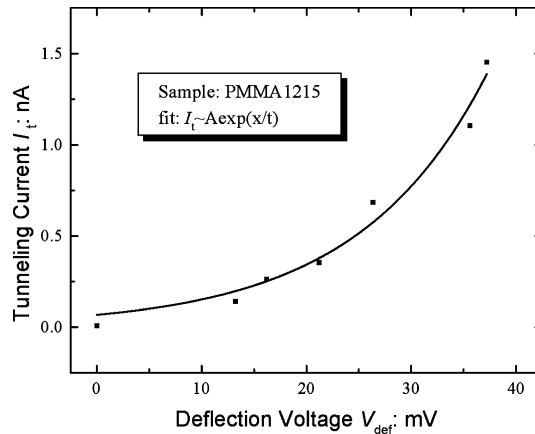


Fig. 8. The exponential relationship between tunneling currents and applied deflection voltages

two other deep reactive ion etchings are required. Under the optimum conditions of ICP, the fabricated masters keep pyramid pits with the base angles of 54.73° and the sharp edges. The sidewalls of blocks have smooth surfaces and positive profiles, which are critical for the demolding of hot embossing. The first generation of vertical PMMA-based tunneling sensors with membrane structures have been replicated by hot embossing with molding and demolding temperature of 165 °C and 80 °C, respectively. The relationship between the tip currents and the deflection voltages shows that the tunneling current is exponentially dependent on the displacement changes.

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