Novel ultra-fine hollow needles formed on Silicon membranes

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ABSTRACT

We report a self-defined method for the formation of hollow needles and micro-cylindrical structures on silicon substrates using a high precision deep reactive ion etching. The fabrication process exploits a combination of high aspect ratio vertical etching and small angle vacuum deposition techniques to allow hollow needle formation. Using this method, features with aspect ratios of the order of 50 have been realized. In addition, the formation of hollow cylindrical structures with an inner diameter of less than one micrometer and a height of 7µm are feasible. Hollow structures with a diameter of 15µm have been employed to make a liquid-based capacitive sensor. The presence of a cavity under the needle parts, allows insertion of liquid in the hollow structure. The change in the capacitance depends on the angle of silicon membrane inclination and can be 0.6 pF per degree.

Keywords: hollow needles, reactive ion etching, silicon membrane, liquid-base device, capacitance

1 INTRODUCTION

Smart drug delivery lends its success to the evolution of hollow micro-needles [1-2]. The transfer of drug through little holes inside such structures allows a safe replacement for regular injection needles at macroscopic scale, which could cause pain as well as non-programmable injection. The evolution of micro-needles allows the transfer of drug in a programmable fashion and without pain [3-4]. Apart from drug delivery, micro-needles have been proposed as possible electrodes for biological and medical applications [5]. In addition, in electro-cardiograph units the use of microneedles has been investigated as a replacement for applying external gel and skin preparation [6]. Apart from biological applications, the cup-like structures can be used as gas transfer media for mass spectroscopy and as an ionization source [7].

Deep reactive ion etching (DRIE) of silicon has drawn significant attention, as a goal in recent MEMS fabrication, which allows the evolution of vertical structures on silicon and glass substrates [8]. Robert Bosch introduced for the first time the process with consecutive passivation and etching sub-cycles of the silicon surface to achieve high aspect ratio features [9]. Generally, Bosch process uses a polymeric coating like C_4F_8 during the passivation cycle whereas this layer is removed in the subsequent steps using an inductively coupled RF-plasma. In another process, called as cryogenic etching, intensive cooling of the silicon substrate to cryogenic temperatures by means of liquid nitrogen is practiced [10]. Recently we have developed a hydrogen assisted deep reactive ion etching (HDRIE) technique which replaces the polymeric passivation in Bosch process by a combination of hydrogen/oxygen and SF_6 gases to obtain high aspect ratio features with no need to high density plasmas [11].

In this paper, we use our high-resolution vertical etching process, to realize needles and vertical features at deep micrometer and nanometer scale. Depending on the process, the formation of hollow needles or cup-like structures is possible using a self-defined slant angle deposition and with no need to a three-dimensional lithography. The physical characteristics of the fabricated structures has been studied using Hitachi SE4160 filed emission scanning electron microscope operating at 15-30kV and with secondary electron spectroscopy.

2 EXPERIMENT

Single-side polished p-type <100>-oriented Si substrates with a thickness of 550µm are used. The cleaned samples are placed in an e-beam evaporation unit to deposit a 40 nm chromium layer as the mask for the subsequent processing steps. The masking layer is patterned using precision projection lithography to achieve features of the order of 1 to 20µm and with a width well below 1µm that can be further reduced to values of the order of 100nm with an extra step of oxygen plasma ashing. If the formation of hollow needles on silicon membrane is desired, the fabrication process starts on micro-machined samples. For this step a 30% molar solution of KOH in water is used at a temperature of 60^{o}C. Fig. 1 demonstrates the procedure for the formation of hollow needles or cup-like structures on Si membranes. After proper patterns are obtained (Figure 1.a), a sequential hydrogen-assisted deep etching is used to realize ultra fine features. The process consists of two subcycles of passivation and etching, where a mixture of H_2, O_2 and SF_6 gases with typical flow rates of 100, 85 and 3 sccm at a plasma power of 150W is used during the passivation sub-cycle. The etching step is carried out in mere SF_6 with a flow 40 sccm and in the presence of RF plasma with a power of 130 W. These passivation/etching subcycles should be repeated as many times to achieve desired depths. Details about this technique can be found elsewhere [11]. Since lithography is not possible with high aspect ratio features, we used a rotating small angle deposition method to coat the outer walls as well as outer surfaces of the substrate selectively, while leaving the inner bottom of the little cylindrical features uncoated (Figure 1.c). The vertical etching of silicon can proceed and at this stage only the inner side is etched away (Figure 1.d). The overall depth of the needles depends on the original thickness of the Si-based membrane.

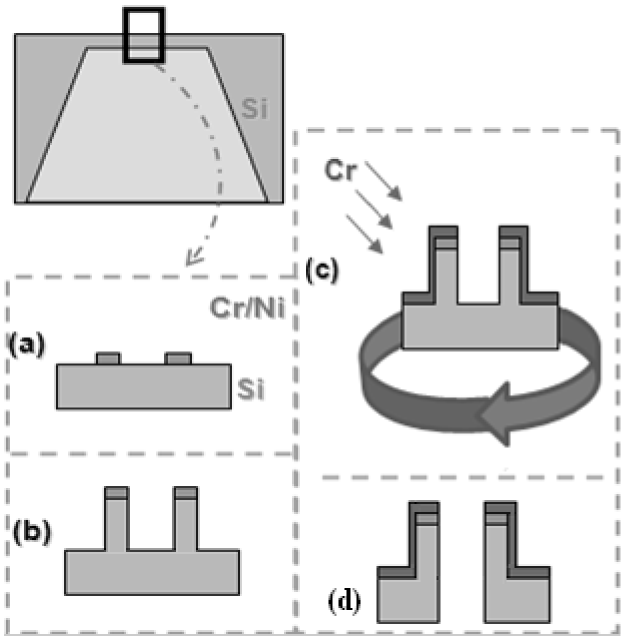


Figure 1: Cross sectional illustration of hollow needle fabrication (a) formation of rings, (b) vertical etching of Si and (c) deposition of Cr using a rotating small angle deposition method to coat the outer sides of the recessed craters while inner parts and especially the inner bottom remains uncoated. (d) The evolution of hollow structures by continuing the etching process.

3 RESULTS AND DISCUSSIONS

The evolution of high precision rings is achieved by projection lithography as seen in Figure 2. The width of the rings can be as small as 500nm which can be further reduced by plasma ashing and over-developing.

Fig. 3 collects the results of deep etching of silicon created by a high precision vertical removal. Part (a) depicts an array of small cylindrical structures whereas in part (b) one can see a magnified view of the features. A high aspect ratio feature with a height of 7μm and a wall width of 109nm is observed in part (c). The fabrication process has continued to form fully hollow structures on silicon membranes. As stated before, this etching procedure can be applied to structures of the order of 1 to 20μm in diameter.

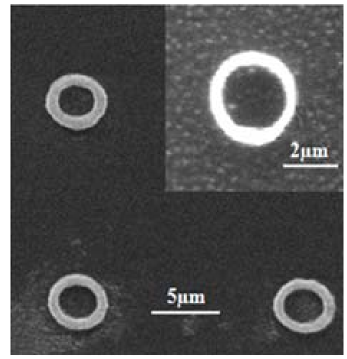
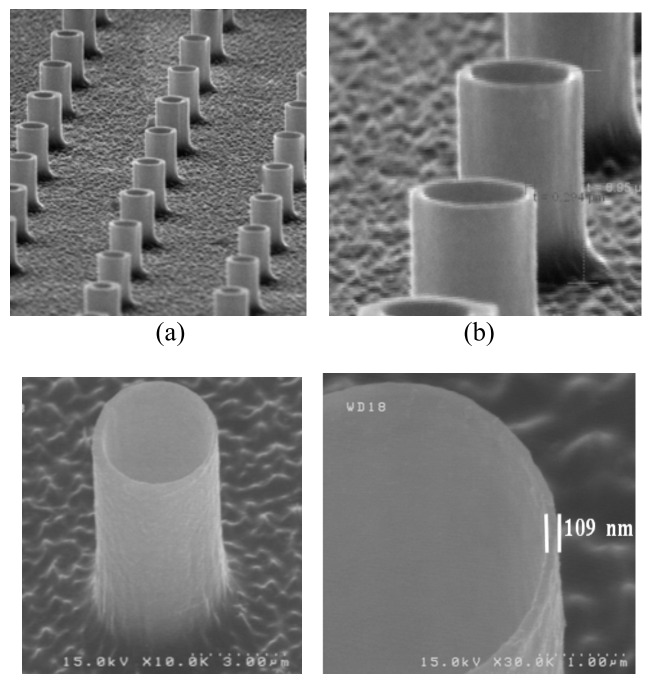


Figure 2: The SEM top image of the rings realized on silicon substrate just prior to deep etching. An oxygen plasma ashing combined with over-developing can be used to further reduce the width of the rings.



(a) (b)

(c) (d)

Figure 3: Collection of SEM images of some of the cylindrical features obtained for this work. Part (a) shows the image of an array of silicon micro-needles. (b) Magnified image showing a wall thickness of the order of 300nm and a height of 7μm height. (c) The SEM image of a silicon needle with wall thickness of 109nm, and (d) a closer view of the wall edge of silicon needle.

Fig. 4 displays the SEM images taken from the backside of a membrane, which contains 20μm diameter microneedles on its front-side. In part (a) one can observe an image of the membrane from backside to better observe the micromachined membranes which carries holes on the central part. Part (b) shows an optical image of the fully processed membrane where holes are obtained. The bright spots in this image correspond to the light passing through the holes once exposed from the other side, further indicating the hollow structure of the needles.

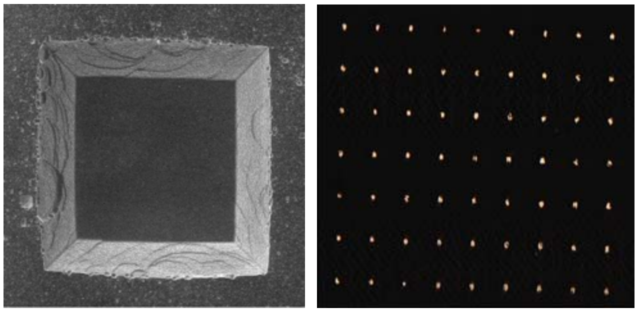


Figure 4: (a) The SEM image of the backside of the Si membrane where the micro-needles are placed on its front side. (b) The optical image from the backside with typical diameter around 15µm which shows the light transmission, further corroborating the evolution of hollow needles.

Since the silicon membrane is part of a cavity, it can be filled with a liquid to form a capacitor. By first oxidizing the needle-containing silicon sample followed by depositing a metal layer (Cr) on the backside of the membrane, one can form a capacitor between the silicon membrane and an opposite plate located just on top of the silicon substrate (see Fig. 5).

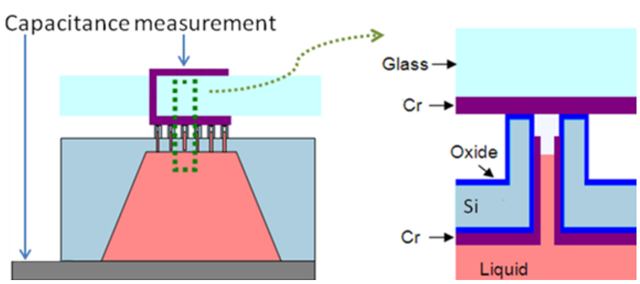


Figure 5: Schematic presentation of liquid-stimulated capacitance measurement. Inclusion of a water droplet into the backside cavity of the sample would yield in the penetration of liquid into the little holes, increasing the effective permittivity (ε) which in turn leads to an increase in the capacitance value.

The value of the capacitor depends on the thickness of the membrane and the height of the cylindrical needles. By inserting a water droplet onto the cavity, part of the water would penetrate through the hole and as a result, the total value of the capacitance would rise. This is mainly because the relative permittivity of water (ε), which has been inserted into the hole, is more than Si and air. Fig 6 collects the results of capacitance voltage characteristics of the samples after water inclusion. The capacitance value remains around 8 pF for the dry sample whereas the wetted sample shows a rise to 10 pF because of raising water through the little holes. By applying an inclination of 5 degrees, a significant rise to 13pF is measured. Such devices can be used to study the liquid penetration through little holes and to fabricate low frequency, high sensitivity inclination sensors.

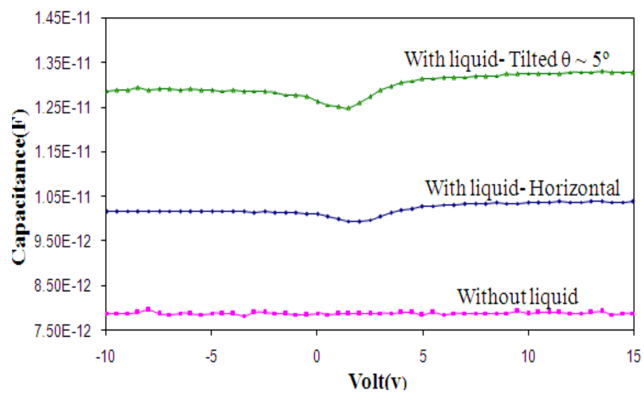


Figure 6: Capacitance voltage characteristics of the liquid-stimulated capacitor. Bottom curve relates to the dry sample capacitance measurement. A considerable rise in the capacitance from 10 to 13 pF is observed upon slanting the specimen. The C-V results show a small valley, which could be due to the creation of a depletion region in the silicon surface similar to a MOS structure.

As an important parameter in ultra small needles is the capillary force which could be quite high in such a tiny features. The wetting angle is an important parameter affecting the capillary force. In Fig. 7 we have presented an optical image of a water droplet placed on a chromium-coated silicon sample. The silicon surface has been oxidized and coated with Cr to simulate the conditions in the inner walls of the tiny needles. As observed in this figure, the wetting angle is 90 degree which minimizes the capillary force.

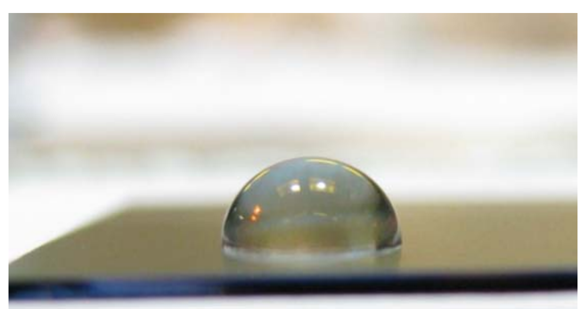


Figure 7: The optical image of the wetting of a water droplet on a Cr-coated oxidized silicon sample, indicating a 90 degrees angle.

4 SUMMARY AND CONCLUSION

In this paper, we reported the realization of hollow needles directly on silicon with micrometer diameters and nanometer wall features. The formation of such structures was possible using a precision lithography combined with high aspect ratio vertical etching of silicon membranes. By means of a small angle deposition method, we have been able to open up the bottom side of the craters and to achieve hollow needle structures at a record small size of 2-3 µm directly on silicon substrates. The thickness of wall can be as small as 100nm. We believe this process can be tailored for holes with diameters of the order of 200-500nm as well. By proper metallization, we have been able to realize liquid-based capacitive sensors, which can eventually be used as inclination (angle) sensing devices. This work and its applications in low frequency sensor fabrication are currently being pursued.

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