Design and fabrication of a multiple-thickness electrochemical cantilever sensor

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Abstract

This paper presents a new design and fabrication process of a multiple-thickness electrochemical cantilever sensor, in order to assess the role of the cantilever's thickness on the chemically-induced mechanical effects. Each cantilever can act not only as a functionalized cantilever, but also as an independent working electrode (WE) for electrochemical measurement. The different thicknesses of the silicon nitride layer are achieved by successive masking and reactive ion etching of partially overlapping openings at a low etch rate (10.8 nm/min, 15.8 nm/min, 20.1 nm/min, or 26.5 nm/min). A small-scale thickness difference (<30 nm) is successfully obtained. One advantage of this fabrication process is that the thickness distribution of cantilevers can be altered and broadened by combination of different RIE recipes or modification of the etching time. In addition, the integration of the cantilever chip with a fluidic cell, a printed circuit board (PCB) and a temperature-controlled plate to form a hybrid system is also addressed.

1. Introduction

In the last decades, the ability of cantilever sensors to detect a wide range of molecular interactions has been demonstrated [1]. Cantilever sensors are usually operated in either dynamic or static mode [2]. In dynamic mode, absorption or adsorption of analyte molecules leads to a shift of the resonance frequency. In static mode, the cantilever bends as a result of preferential adsorption of analyte molecules on one side of the cantilever. The dynamic mode is sensitive to mass variations whereas the static mode is sensitive to surface effects.

For cantilever sensors in the static mode, the cantilever's curvature change is assumed to be homogeneous [3] and is used as an indicator that the thought reaction occurred. In order to increase the sensor's specificity, various groups have focused on improving the performance of cantilever-based sensing by introducing an electrochemical actuation [4-7]. However, it is questionable to interpret the cantilever deformation through Stoney's equation when dealing with chemically-induced effects. To address this issue, alternative mechanical frameworks have been proposed [8-9], featuring different relationships between the cantilever's thickness and the shape of the displacement field. These models differ by the way the thickness of the cantilever is involved. Therefore, testing for the validity range of these models requires to experimentally access chemically-induced displacement fields [8-9] obtained for cantilevers of different thicknesses. In order to achieve that with cantilevers featuring the same material properties, our goal is to fabricate multiple-thickness cantilever beams in a single chip. The values of material parameters driving the dependence on thickness however remain unknown, and the achievable thickness distribution in turn define the range of accessible material parameters. This first attempt is thus intended to explore the achievable thickness range. The fabricated chip is to be placed in a fluidic cell in order to monitor the cantilevers' displacement field when they are subjected to a surface (electro-) chemical modification.

It is extremely challenging to achieve micro-fabrication of multiple-thickness cantilever beams on a single chip, simultaneously ensuring their combined electrochemical and mechanical capabilities as well as the necessary accessibility for optical readout, electrical connection, and fluid access for real-time deflection measurements. In this work, we focus on the design and fabrication of a multiple-thickness cantilever sensor platform. In addition, the assembly of the hybrid system featuring the obtained cantilever chip, a fluidic cell, a homemade printed circuit board (PCB), and a temperature-controlled plate is also presented.

2. Materials and methods

2.1 Configuration of the hybrid system

The proposed hybrid system is depicted in Figure 1, integrating a fluidic cell, the cantilever chip, a printed circuit board (PCB), and a temperature-controlled plate. The fluidic cell is designed to hold liquid and to set an electrochemical cell. It provides fluidic inlet and outlet, and includes two channels for inserting a reference electrode (RE) and a counter electrode (CE). The cantilever chip includes four identical cantilever arrays. Each cantilever array houses 20 cantilever beams featuring different thicknesses. Each cantilever is used as the independent working electrode (WE) and also as the functionalized platform. In order to contact the cantilevers, a home-made PCB is designed to electrically connect the cantilever chip by wire bonding. A small square hole (12.8 mm × 12.8 mm) in the middle of the PCB allows the backside of the cantilever chip to directly contact with a temperature-controlled plate. The positioning reference is used to achieve a reproducible positioning of the chip with respect to the temperature-controlled plate.

4 rods through the corresponding holes provide an alignment reference when the fluidic cell is bonded to the front side of the cantilever chip (which is firstly glued on the PCB). The entire assembly is pressed together via 4 screws through the other 4 holes and 4 spring clips mounted on the temperature-controlled plate.

2.2 Fluidic cell

The fluidic cell is designed by using the SolidWorks 2011 software and fabricated by a 3D printer (3D Systems ProJet™ SD 3500). The obtained poly (methyl methacrylate) (PMMA) fluidic cell is shown in Figure 1. It is 3.8 mm thick, 22 mm wide, and 22 mm long. A 0.5 mm-thick hexagon step of the cavity is designed to glue a pyrex slice (10 mm diameter, 0.17 mm thick, not shown in Figure 1). The whole fluidic chamber volume is 37 µL with the cover glass. 8 holes are used to insert 4 rods for positioning the fluidic cell with respect to the front side of the cantilever chip, and 4 screws for fixing the full assembly.

2.3 Cantilever chip

The proposed chip features: a) a positioning reference on the backside, b) multiple cantilever thickness on the front side, c) an electrode layer, d) an electrical connection layer, and e) an insulation layer. In the following, the fabrication process is described by using two cross sections and by focusing on cantilever No. 9, shown in Figure 2.

1) In Figure 2.b, low-stress silicon nitride is first deposited on both sides of a four-inch silicon (100) wafer with 500 µm thick by Low Pressure Chemical Vapor Deposition (LPCVD) (NH_3/SiH_2Cl_{l2}:18/60 sccm, temperature: 820°C, Pressure: 200 mTorr, time: 180 min). The silicon nitride thickness is measured to be about 805 nm. After baking the wafer for 10 min at 120°C, the wafer is spin-coated with a 2.4 µm thick layer of SPR 220-3.0 positive photoresist. Then, the photoresist is exposed to UV irradiation (365 nm, 300 mJ cm^{-2}) through a mask with the designed alignment reference pattern. After developing the photoresist with the MF 26A developer for 75 s, the exposed silicon nitride is reactive ion etched at a 26 nm/min etch

rate (Pressure: 60 μbar, CHF_3/C_2F_6: 10/5 sccm, DC bias: 245 V; RIE PLASSYS). Afterwards, the photoresist is stripped.
2) The cantilever beams (15 μm wide and 80 μm long) are patterned on the front side of the wafer by using double-side EVG 620 alignment system. Then, the pattern of cantilever beams is achieved by reactive ion etching (RIE) of the exposed silicon nitride layer (shown in Figure 2.c). The whole RIE time (40 min) is divided into two 20 min etching times, with 30 s oxygen surface cleaning process (20 sccm, 60 μbar, 95 W, 410 V) inbetween. Then, the photoresist is stripped.
3) To achieve different cantilever thicknesses, a single mask is specially designed and successively used with different alignment marks. Using this mask referring to mark 1 (shown in Figure 2.d), some of the cantilever beams are firstly covered by photoresist (SPR 220-3.0, 2.4 μm thick). The photoresist pattern is used as an etching mask in the RIE etching process with a low etch rate (10.8 nm/min, 15.8 nm/min, 20.1 nm/min, or 26.5 nm/min) for 1 min. Shifting the mask by referring to mark 2 (shown in Figure 2.e), partially overlapping openings are photo-patterned and etched by another 1 min RIE. In Figure 2.f, this step is repeated twice by shifting the mask referring to mark 3 and mark 4, respectively. By successive photo-patterning and etching of partially overlapping openings, different thicknesses are thus achieved.
4) Corresponding to Figure 2.g, a Cr/Au (10 nm / 30 nm) electrode layer is deposited by electron beam evaporation (EVA 450, Alliance Concept), and then lift-off in selected areas by dissolving the underlying photoresist. In order to independently bridge the electrode layer to electrode pads on borders of the chip, one electrical connection layer is added. This connection layer (Cr/Au: 20 nm / 250 nm) is sputtered (MP 500, PLASSYS) and shaped by lift-off process. A potassium hydroxide (KOH) solution (28%, 1 hour at 80°C) is used to etch 60 μm of silicon on both sides of the wafer, thus releasing the cantilevers and defining the alignment reference. Finally, the electrical connections are insulated by spray coating (AltaSpray 8) a 7 μm thick SU-8 layer.

3. Experimental results

3.1 The repeatability and stability of RIE

The repeatability and stability of RIE is critical to obtain a well-defined thickness difference. By using RIE PLASSYS machine, we have developed four recipes (shown in Table 1). Keeping the same pressure and the same gas flow rates, we can obtain four different etch rates by changing the DC bias voltage. As shown in this table, recipe No.2 has the best stability with a 0.68 nm/min standard deviation.

3.2 The produced cantilever chip

As seen in Figure 3.a, a produced chip (12.55 mm × 12.55 mm) includes four identical cantilever arrays. Each cantilever array houses 20 cantilever beams serving as both a functional cantilever and also an independent WE. These cantilevers are divided into 4 groups. Each group contains cantilevers featuring five different thicknesses. In addition, there is a large opening on the backside, which is the alignment reference for achieving a reproducible positioning of the chip with respect to the temperature-controlled plate. Figure 3.b shows a SEM picture of one group of cantilevers featuring 5 different thicknesses of silicon nitride (t_1, t_2, t_3, t_4, or t_5). Figure 3.c is a SEM picture of one cantilever. The cantilever is 14.7 μm wide and 80.7 μm long. These values are very close to our design (15 μm wide and 80 μm long). Figure 3.d is a cross-section of a 780 nm thick cantilever. One can observe that a thin layer of Cr/Au is above the silicon nitride layer.
To observe the resulting diversity of silicon nitride thicknesses, focused ion beam (FIB) is used to cut the free end of the cantilever. A Cr layer is firstly deposited to protect the top layer

(~120 nm, Figure 4.a). After using FIB tool (Helios NanoLab 600i), SEM pictures of the cross-section can be obtained for each cantilever. Figure 4.b shows an example of the thickness distribution obtained by using different RIE recipes. The thickness t_5 is defined by the LPCVD deposition process. RIE recipe No.4 is used for 1 min to get a 26 nm difference between t_4 and t_5 and thus achieve t_4. We similarly use Recipe No.3 and No.2 to realize t_3, t_2 and t_1. The results are close to the target values. It should be highlighted that it is also possible to realize different thickness distributions by using the same RIE recipe with different etching times.

3.3 Assembly of the hybrid system

The hybrid system assembly is depicted in Figure 5. First, the cantilever chip is glued to the PCB. The electrical interconnection between gold contact pads on the chip and copper connections on the PCB is established by wire bonding (ball-wedge bonder) with an Au wire (50-60 µm thick, 25 µm diameter). Then, four rods are used to mount the fluidic cell onto the PCB, and the fluidic cell is bonded to the front face of the chip with SU-8 photoresist applied on its backside. The PMMA fluidic cell holds two Teflon tubings, one platinum wire and one silver-silver chloride wire, used for pouring solutions and for setting an electrochemical cell. Finally, the full assembly is mounted on the temperature-controlled plate with screws (not shown in this picture).

4. Conclusion

In this work, a hybrid system is proposed to experimentally assess the role of the cantilever's thickness on the chemically-induced mechanical effects. To achieve the cantilever chip featuring different thicknesses, a single mask is specially designed and successively used at different locations. By successive photo-patterning and etching of the exposed silicon nitride layer with optimized low etching rate recipes, a small-scale thickness difference (26 nm, 23.2 nm, 16.3 nm and 16.9 nm) is achieved. By using this fabrication process, different thickness distributions can be achieved. A PMMA fluidic cell, in which the fabricated chip is integrated, is designed to pour solutions and set an electrochemical cell. It also allows for in-situ displacement fields measurements. Further work is underway to achieve a broader thickness distribution. Another perspective is to integrate other functions in order to access in-situ information on the material's mechanical behavior.

5. Acknowledgement

This work is carried out within the ANR funded CheMeCo project (ANR-11-JS09-0019), and is partially supported by the French RENATECH network and its FEMTO-ST and LAAS facilities. The authors would like to thank Roland SALUT for SEM pictures acquisition by using FIB tool; Laurent ROBERT and Gwenn ULLIAC for helpful discussions of the fabrication processing, and also Sébastien THIBAUD for assistance in fabricating the fluidic cell.

References

[1] A. Boisen, S. Dohn, S. S. Keller, S. Schmid and M. Tenje, *Rep. Prog. Phys.*; **74**(2011) 036101 (30pp).
[2] C. Ziegler, *Anal Bioanal Chem*, **379**(2004) , 946–959.
[3] G. Stoney, *Proc. Poy. Soc. London Ser A*, **82**(1909), 172.
[4] R. Raiteri, M. Grattarola, H.-J. Butt, and P. Skládal, *Sensors and Actuators B*, **79**(2001) 115-126.
[5] V.Tabard-Cossa, M. Godin, L.Y. Beaulieu, and P. Grütter, *Sensors and Actuators B* **107**(2005) 233-241.
[6] F.Amiot, F. Hild, F. Kanoufi, and J. P. Roger, *J. Phys. D: Appl. Phys.*, **40**(2007), 3314-3325.
[7] L. M. Fischer, C. Pedersen, K. Elkjær, N.N. Noeth, S. Dohn, A. Boisen, and M. Tenje, *Sensors and Actuators B*, **157**(2011) 321-327.
[8] F.Amiot, *Journal Mech. Mat. Struct.2*, **9**(2007), 1787-1803.
[9] F. Amiot, *Phil Mag Letters*, (2013), doi:10.1080/09500839.2012.759294.

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Figure Caption

Figure 1. Configuration of the deflection measurement hybrid system: a) Fluidic cell, b) Cantilever chip, c) Printed circuit board (PCB), and d) Temperature-controlled plate.

Figure 2. A fabrication diagram: a) a schematic depicting two cross sections, b) creating the positioning reference layer on back side, c) forming the pattern of cantilever beams, d-f) realizing different cantilever thicknesses, g) depositing electrode and electrical connection layer, releasing cantilevers, and spray coating an insulation layer, and h) a profile diagram depicting the layers of the cantilever chip.

Figure 3. a) A photograph of a produced chip, b) A SEM image of a cantilever group, c) A SEM image of a cantilever, and d) A cross-section SEM image of a 780 nm thick cantilever.

Figure 4. a) A side view depicting the layers of a cantilever covered by a Cr protection layer, and b) SEM images showing a thickness distribution.

Figure 5. A flow chart of the hybrid system assembly.

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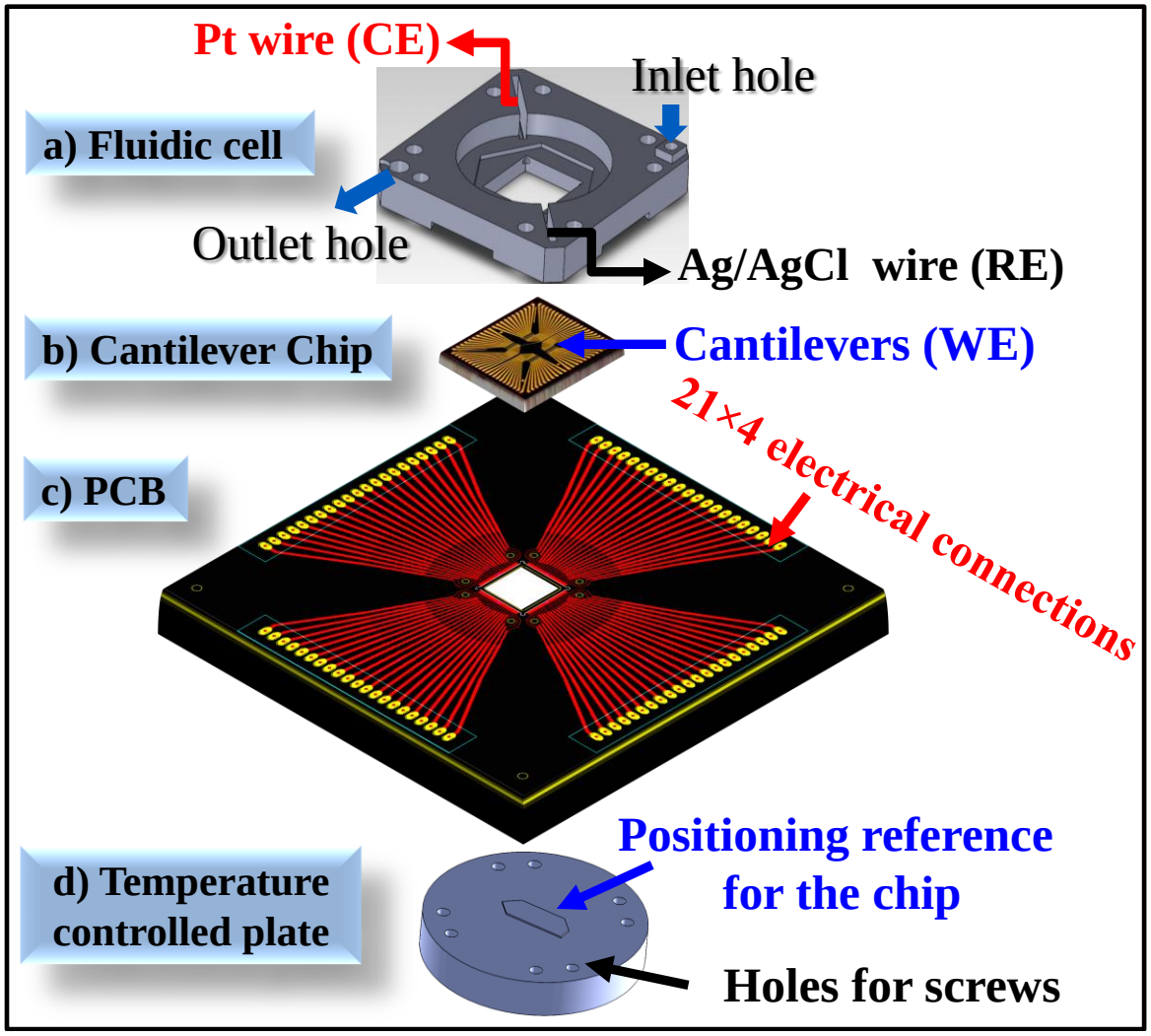

Figure 1.

Design and fabrication of a multiple-thickness electrochemical cantilever sensor

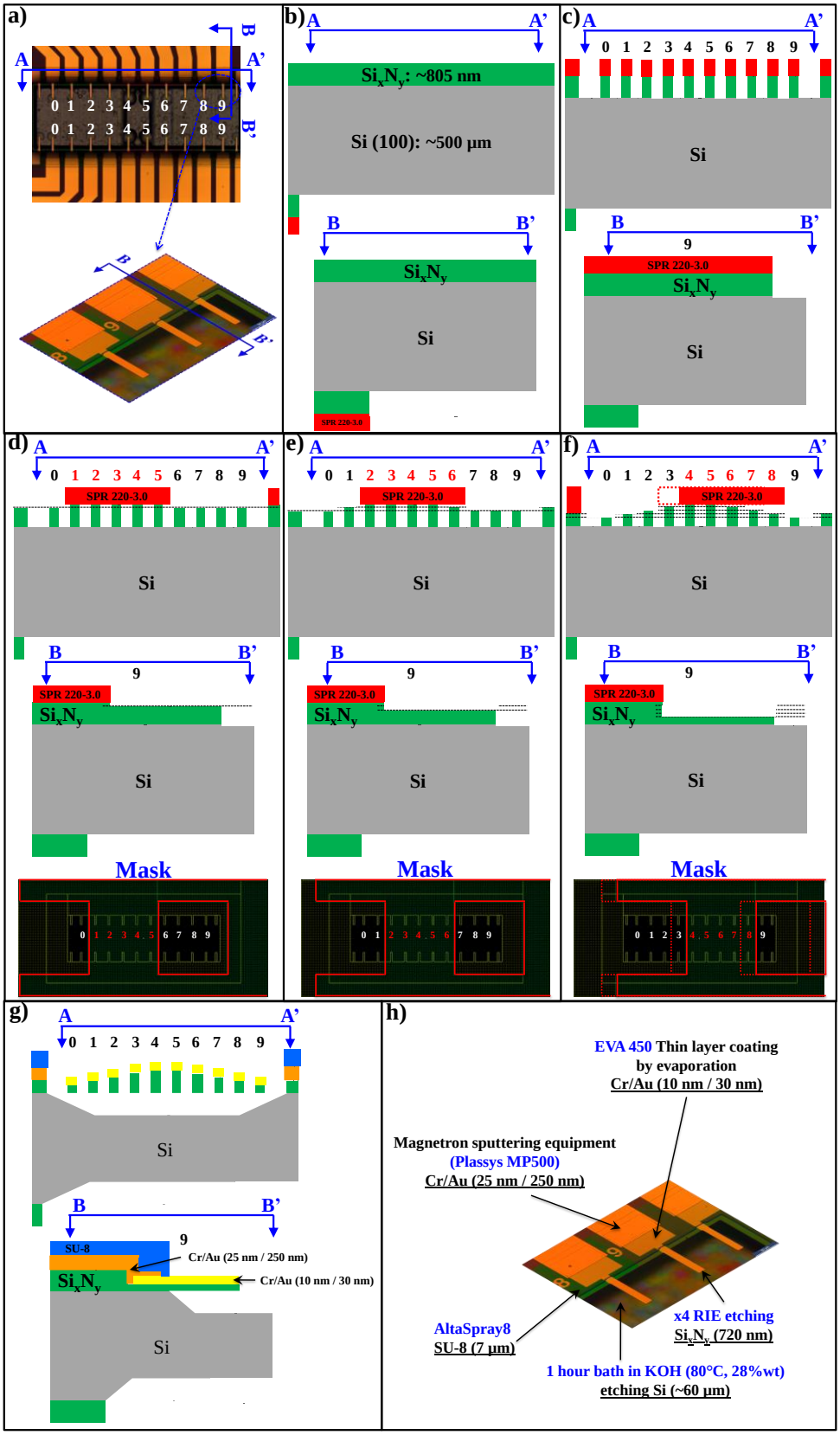

Figure 2.

Design and fabrication of a multiple-thickness electrochemical cantilever sensor

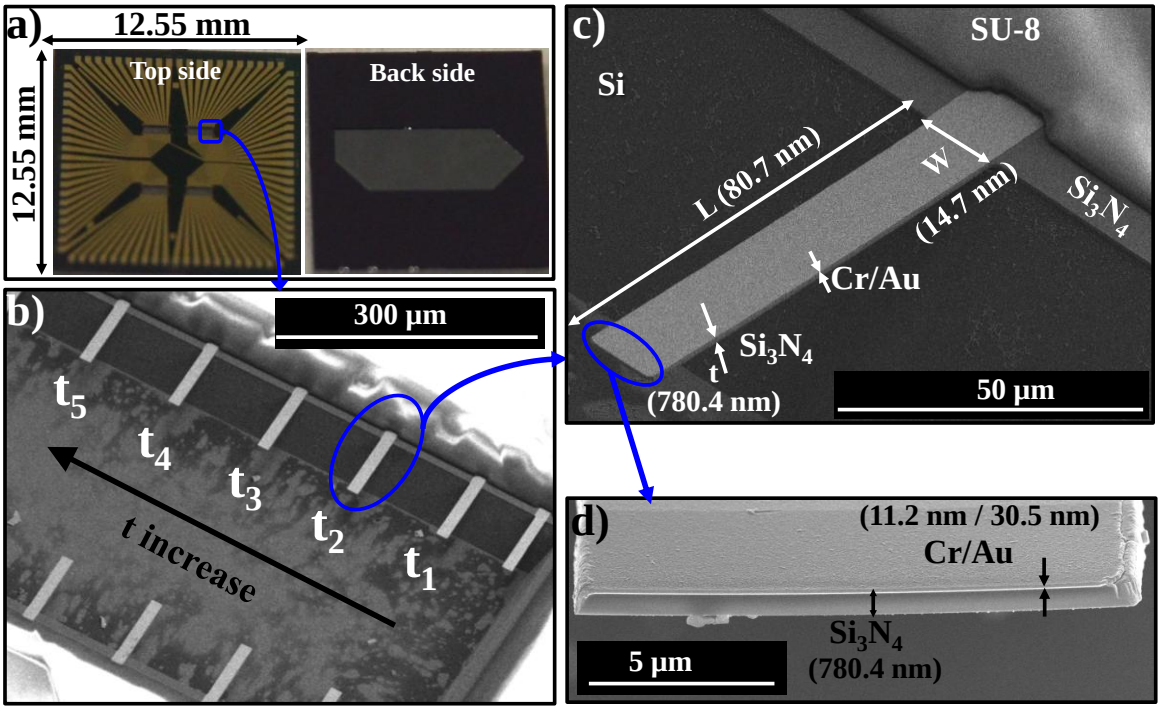

Figure 3.

Design and fabrication of a multiple-thickness electrochemical cantilever sensor

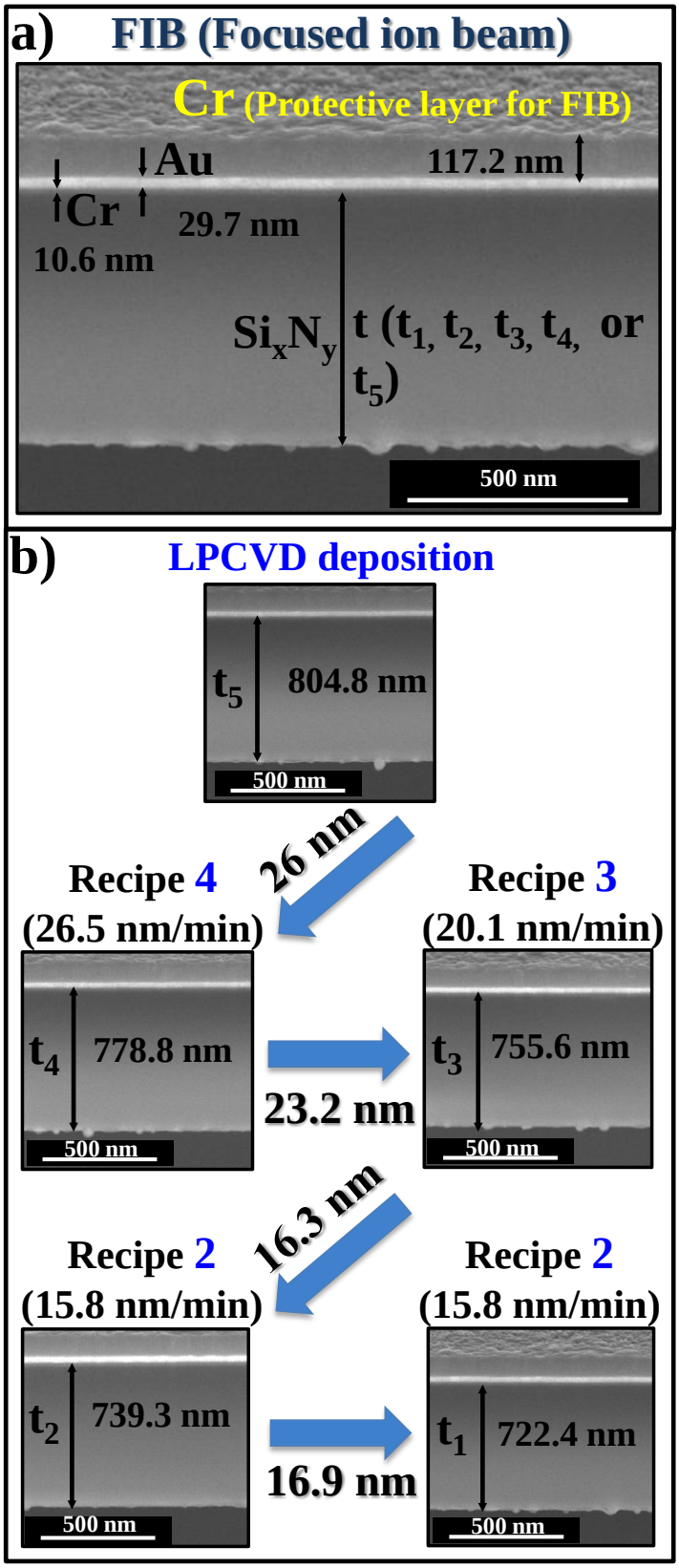

Figure 4.

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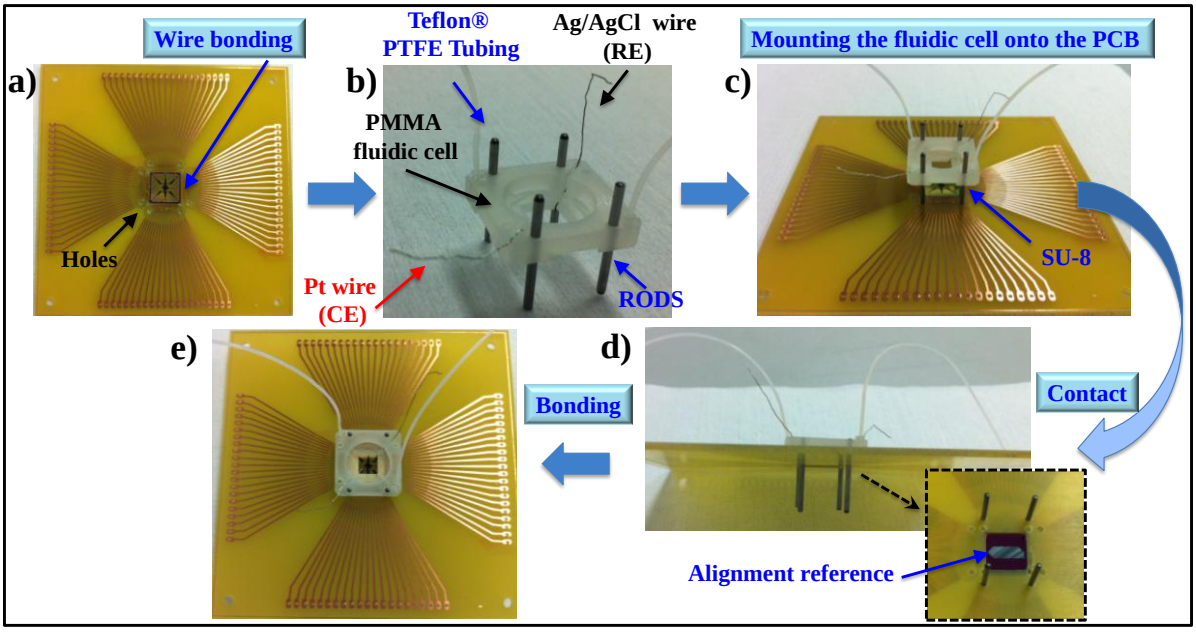

Figure 5.