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The method of integration of silicon – micromachined sensors and actuators to microreactor made of Foturan® glass

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In this article results of unique low temperature anodic bonding silicon and Foturan® glass are presented. The new method of anodic bonding can be useful in designing and fabrication of intelligent microreactors equipped with microsensors and other microdevices suitable both to control and to steer chemical process. Direct assembling onto microreactors allows to think about integrated microreactors equipped with set of sensors, *i.e.*, pressure sensors and other devices, *i.e.*, valves, flow meters, *etc*. The demand for integration microreactor with measuring/steering setup, following the technology of low temperature anodic bonding and application of this technique are described.

Keywords: microreaction technology, sensors integration, low temperature anodic bonding, Foturan® glass and silicon anodic bonding.

1. Introduction

Microreaction technology is developed over the past several years. Unique reactions behavior in microscale and technical properties of microreactor cause that the microeraction technology is readily applicable in laboratories and chemical industry. Some examples of microreactors made of different materials are presented in Fig. 1.

Accepted constructions of microreactors for dangerous reactions using harsh reagents are made of Foturan® glass (Fig. 2). Such microreactors, made of Foturan® glass, are key components of microplant for nitration process being currently realized under NEPUMUC FP6 project [1].

Foturan® is photosensible glass. Such unique feature allows to build intricate, 3D constructions of microreactors. Microreactors made of this glass can handle dangerous

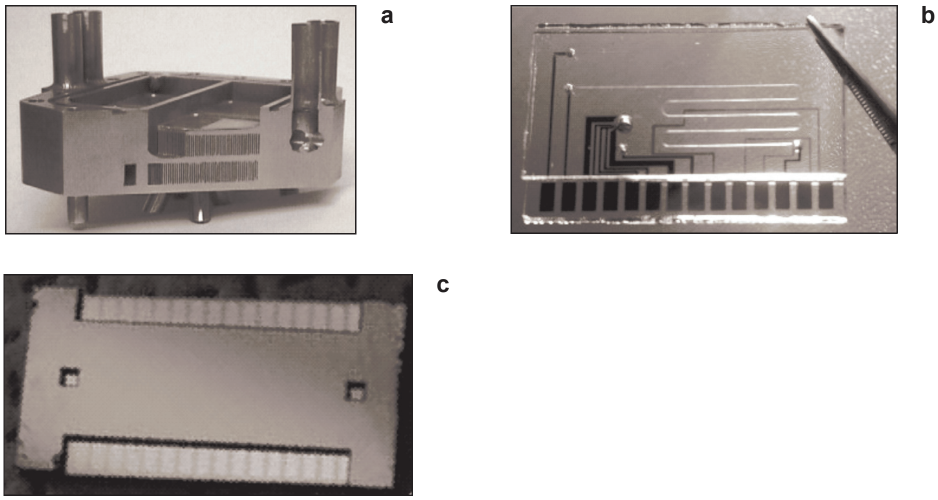


Fig. 1. Examples of microreactors: metal microreactor for catalytic processes, Pacific Northwest National Laboratory (**a**), lab-on-chip made of glass and polymer for DNA amplification and detection, Rutherford Appleton Laboratory (**b**), palladium-based micromembrane for Hydrogen Purification, M.I.T (**c**).

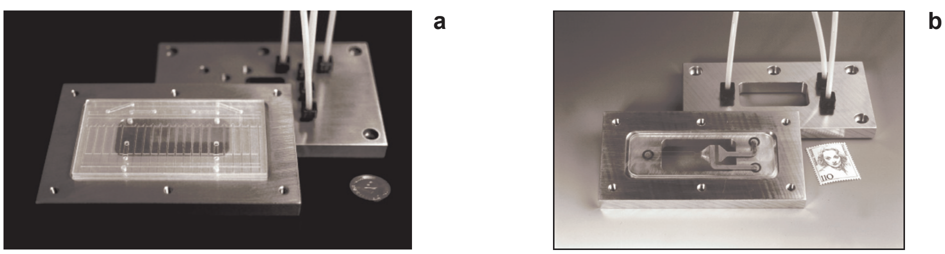


Fig. 2. Examples of microreactors made of Foturan® glass, Mikroglas Chemtech GmbH (Mainz, Germany): enables to mix two liquids and to remove or add the process heat 20 channels in parallel (**a**), enables to mix two liquids 30 channels in parallel (**b**).

chemical reactions (use of aggressive agents, explosion risk, *etc*.), allow to visual monitoring of reaction course, within a wide range of work temperature [2].

Despite the features described above the crucial problem is to measure essential parameters of chemical reaction inside the microreactor (pressure, temperature, flow). Standard sensors, taken from the "macro" world, can not be applied, because dead (inner) volume of such sensors is several times bigger then total volume handled inside microreactor. For precise controlling of the chemical reactions course directly inside the microreactor it is necessary to select and/or fabricate proper sensors. Consequently, the integration methods of sensors and microreactors are required to be worked out.

In this work the new method of integration of micromachined pressure sensors to Foturan® glass is presented for the first time. Low temperature anodic bonding as the method allowing to assemble micromachined sensors to Foturan® glass is described.

2. Silicon and silicon/glass structures of sensors

The extremely low dead-volume and flow factors are characteristic for microreactors, so the *in-situ* measuring/controlling of the microreactions by use of "macro" sensors, commonly applied in chemical industry, is not possible [3, 4]. Moreover, some measuring/controlling devices must be resistant against hard working conditions (temperature, aggressive chemicals). The scale factor problem can be solve by small, directly integrated onto the microreactor, microfluidical devices (sensors, flow control elements). Silicon and silicon/glass micromachined microdevices are suited to this requirements. In addition, commonly used materials (silicon, glass) are highly resistive against chemicals and able to work in wide temperature range. Those microdevices can be assembled onto microreactors in several ways. It is proved that gluing (photo-hardened glue, epoxy glue) or adhesive bonding through thin foil (Kapton®, Teflon) can not be applied. The test done in 1:1 mixture of concentrated sulphuric and nitric acids shows, that only anodic bonding allows to achieve strong, tight and long-time stable sealing of sensors and microreactors.

Anodic bonding is a technological procedure sealing permanently solid-state materials with smooth and flat surfaces, by chemical reactions. This method of materials sealing is commonly used in microsystem technology for bonding of unprocessed flat wafers, deeply micromachined wafers, wafers with movable micromechanical structures, whole wafers or particular chips or small details. Bonding is not only simple packaging method of microsystem technology, as the most often is classified, this is the integral procedure of microsystems fabrication playing a role of the front-end

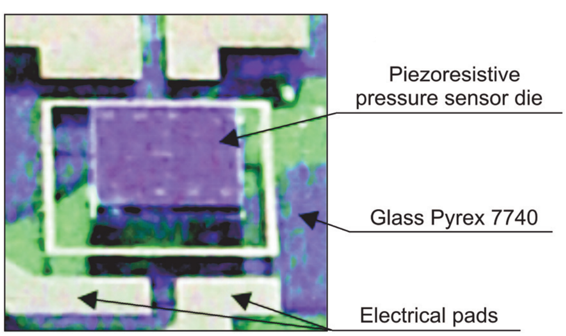


Fig. 3. Piezoresistive pressure sensor die anodically bonded onto microreactor made of silicon and Pyrex glass.

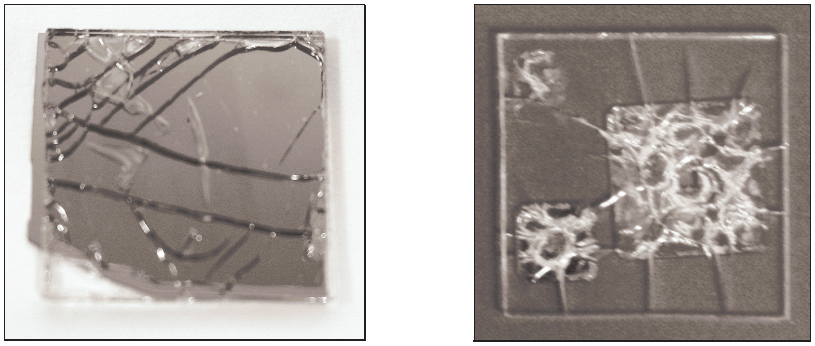


Fig. 4. Result of not optimal anodic bonding procedure of silicon and Foturan® – cracks after cooling down indicated by thermal stress.

as well as back-end technological procedures. The widest application in microsystem technology has found bonding of two silicon wafers and bonding of silicon wafer to glass substrate, as well as bonding of chips and components made of these materials [5].

Usefulness of anodic bonding procedure in microreactor technology is proved. The silicon micromachined, piezoresistive pressure sensor is anodically bonded under standard conditions ($T = 450$ °C, $U = 1500$ V) onto microreactor made of silicon and Pyrex-like glass (Fig. 3) [6]. Unfortunately silicon can not be easily bonded to Foturan® glass. The fundamental difference is temperature expansion coefficient ($\alpha_{\mathrm{Foturan}} = 8.6\times10^{-6}\ \mathrm{K}^{-1}$, $\alpha_{\mathrm{Si}} = 3.2\times10^{-6}\ \mathrm{K}^{-1}$). First results of anodic bonding Foturan® glass and silicon are shown in Fig. 4.

Work out of the low temperature anodic bonding procedure, as a integration method of silicon and silicon/glass micromachined microdevices, is absolutely required.

3. Low temperature anodic bonding

Tests have been done for raw and structured Foturan® glass pieces and pieces of silicon substrate are used. The raw Foturan® glass pieces are 1 mm thick and 20×20 mm^2 large; structured Foturan® glass pieces with two holes of 1 mm in diameter are 1 mm thick and 10×10 mm^2 large; silicon substrate is $\langle 100 \rangle$ crystallographically oriented, 380 μm thick and 10×10 mm^2 large.

Anodic bonding process demands clean and hydrophilic surfaces of combined elements. Standard procedure of silicon washing (removing grease in organic solver, hydrophilling in hot 30% H_2O_2 in water, cleaning in DI water) has been used. Foturan® glass pieces have been prepared using several procedures, known from [5]. The temperature of anodic bonding process has been changed from 200 °C up to 300 °C, the voltage has been changed from 250 V up to 2000 V. Two configurations of electrodes are tested: 1st – with electrode (cathode) sticks directly to Foturan® glass, 2nd – with additional intermediate electrode.

4. Results

The goal of the following works is to select the appropriate anodic bonding conditions and to obtain strong, tight connection of Foturan® glass and silicon. The first tests were done in standard configuration of electrodes. For voltage above 400 V and temperature 300 °C the electricity leakage of Foturan® glass was observed. This behavior seams to be explained by Foturan® glass composition. The glass composition includes photosensitive compounds, which are mostly silver and lithium compounds. In this materials under relative low temperature and supplied voltage, the ion channels were formed. The same problem of electricity leakage of Foturan® glass has been observed by BRIAND *et al.* [7] – see Fig. 5.

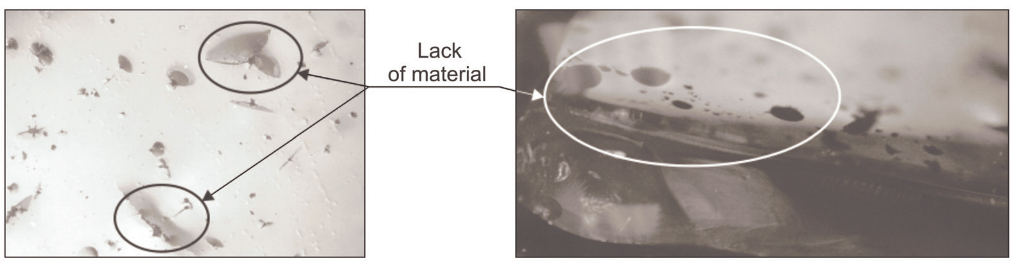


Fig. 5. Destroyed Foturan® glass – an effect of not optimal electrode configuration.

In the following, the intermediate electrode, described in [8], has been added for better electric field distribution and, consequently eliminating of electricity leakages of Foturan® glass.

For the temperature range from 450 °C (suitable for standard anodic bonding of Pyrex-like glass and silicon) to 300 °C the cracks of Foturan® glass were observed (Fig. 2). In the case, of the temperature lower than 230 °C, the connection was not stable. The explanation of this effect is that ions which take part in anodic bonding process have too low mobility. The optimal temperature for low temperature anodic bonding was about 250 °C.

Over fixed temperature the optimum voltage of anodic bonding is found. For supplied voltage less than 750 V bonding is not observed. The range from 750 V up to 1500 V the anodic bonding gives no long time stable connection. The best results are achieved for supplied voltage of about 2 kV.

Several cleaning and hydrophilic methods were tested. It was found that procedures which use acids are totally useless. The acids can penetrate into Foturan® structure

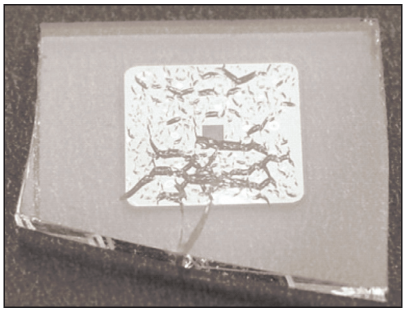


Fig. 6. An effect of not optimal cleaning procedure – microcracks coming into existence during anodic bonding process are visible.

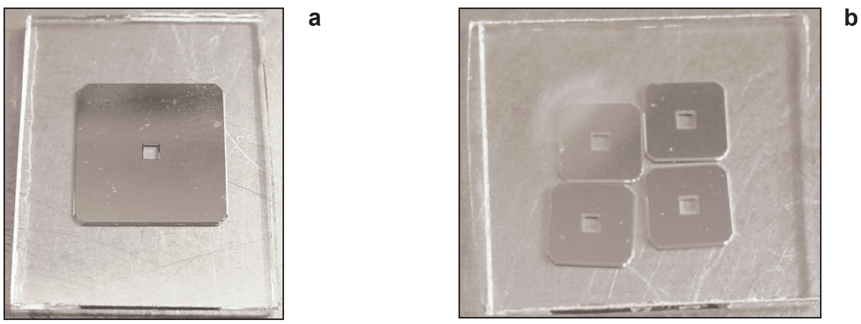


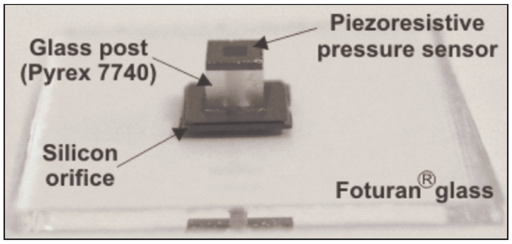
Fig. 7. Optimal procedure of low temperature anodic bonding: raw Foturan® glass and silicon orifice 10×10 mm^2 (**a**), raw Foturan® glass and four silicon orifices 5×5 mm^2 (**b**).

and they are surfaced during anodic bonding process (Fig. 6). In optimal conditions of low temperature anodic bonding the raw Foturan® glass pieces and silicon orifices, as well processed Foturan® glass pieces and silicon orifices were successfully bonded (Fig. 7).

The connection quality was tested. Anodically bonded structures were heated up to 150 °C and left in free air to cool down. After the test no changes were observed. In another test the Foturan®-silicon structures were bathed in mixture of concentrated nitric and sulfuric acids for 24 hours. The total resistance against highly corrosive substances was proved.

5. Applications

The worked out procedure of low temperature anodic bonding has been used to integrate micromachined sensors to Foturan® glass. At first the piezoresistive pressure sensor die on 2 mm high glass post (Borofloat 3.3) was anodically bonded to 5×5 mm^2 silicon orifice, micromachined in previous step. After that sensor structure with silicon orifice was anodically bonded to the Foturan® glass (Fig. 8**a**). Such construction of



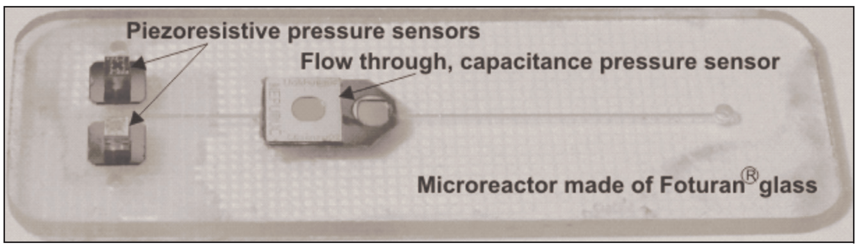


Fig. 8. Silicon and silicon/glass pressure sensors anodically bonded onto: raw Foturan® glass piece (**a**), microreactor made of Foturan® glass (**b**).

the sensors module eliminates temperature induced stresses and, in consequence, temperature induced error.

Successfully done work of piezoresistive pressure sensors integration to Foturan® glass piece allowed us to make next step and build a microreactor made of Foturan® glass equipped with piezoresistive pressure sensors and flow through capacitance pressure sensor. The piezoresistive pressure sensors structures were prepared and assembled to microreactor as described above. The flow through capacitance pressure sensor structure bonded directly onto microreactor surface is shown in Fig. 8**b**.

6. Summary

In this work the microreactor made of Foturan® glass with integrated pressure sensors is described as a results of investigations of low temperature anodic bonding of Foturan® glass and silicon. The successfully done work of the low temperature anodic bonding Foturan® glass and silicon, as well the usability of the worked out method for integration micromachined sensors to Foturan® glass has been shown. The optimal process conditions (temperature 250 °C, supplied voltage 2 kV), proper cleaning and hydrophilic procedure (removing grease in organic solver, cleaning in acid-free solver, hydrophilling in hot 30% H_2O_2 in water, cleaning in DI water), as well as the best electrodes configuration (additional intermediate electrode) are worked out.

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