Two types of integrated heaters for synthesis of TiO_2 nanoparticles in microreactors

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Abstract — In this paper it is shown how we fabricated two types of heaters for microreactors which are used in synthesis of TiO_2 nanoparticles. We used standard photolithographic processes to design gold and p-type heaters diffused in n-type silicon substrate. Heaters are designed to be integrated part of microreactors. The temperature necessary for synthesis of TiO_2 nanoparticles is achieved with both types of heaters. P-type diffused heaters are shown better in terms of power consumption.

***Keywords*—microreactors, gold, p – type diffusion, heaters**

I. Introduction

Microreactors are devices in which physical and chemical processes occur in cells or channels of micrometer dimensions. A typical microreactor consists of a channel system whose width and depth ranges from tens to hundreds of micrometers. Microreactors provide for better control of the size, distribution and the shape of the produced nanoparticles due to the improved control of the conditions under which the reaction takes place. In addition, they are very suitable for use in cases where there is an inevitable use of toxic substances, because the hazard is reduced to a minimum with use of microliter quantities, as well as for the synthesis of expensive materials [1]. The microreactor must allow rapid heating and cooling of the channels to facilitate synthesis of TiO_2 nanoparticles.

Silicon and Pyrex glass are used as the main materials for the production of microreactors [2]. Microreactors are mostly fabricated using process of anodic bonding of micromachined Pyrex glass and silicon. Silicon has excellent mechanical and electrical properties due to its crystalline structure. In addition, it has good thermal conductivity and low coefficient of expansion. The thermal expansion coefficient of the Pyrex glass is approximately the same as the thermal expansion coefficient of Si. Pyrex glass has good biocompatibility, chemical stability and it is transparent for a wide range of wavelengths.

Temperature is one of the most important parameters of the reaction in the nanoparticle synthesis. The synthesis of TiO_2 takes place at high temperatures, so microreactors, in which these reactions occur, are called high temperature microreactors. Several types of these microreactors have been reported in the literature so far. One of the first examples of a high-temperature microreactor was presented by Chal and co-authors [3]. Microreactor from these authors was glass microreactor with a constant-flow and it was used for the synthesis of CdSe nanoparticles at elevated temperatures. Another example is a microreactor with capillary tubes. In this type of reactor capillary tubes are immersed in a heated oil bath [5-11]. Microreactors made of silicon and Pyrex glass were also tested [11-12]. Compared to capillary microreactors, these reactors had higher flexibility in terms of the possibility of making different forms of microchannels. Yen and co-authors designed a microreactor with a droplets flow for the synthesis of CdSe nanoparticles [11]. This microreactor had heating zone and cooling zone, both isolated from one another, using two phases (gas and liquid) that flow through the microchannel. Winterton and coauthors [10] first introduced the concept of a silica-based microreactor with isolated thermal zones where nucleation and nanoparticle growth occur. Erdem and coauthors have designed a silicon microreactor with Pyrex glass as a cover of microchannels for the synthesis of TiO_2 with different zones that are heated at different temperatures [12]. All of the mentioned examples of high temperature microreactors use external heaters. Our plan is to create a microreactor for the synthesis of TiO_2 nanoparticles with integrated heaters. Materials of choice for the heaters are gold layer and process of p-type diffusion in silicon for fabrication of integrated heaters. Heaters will have meandering shape and will be integrated into the

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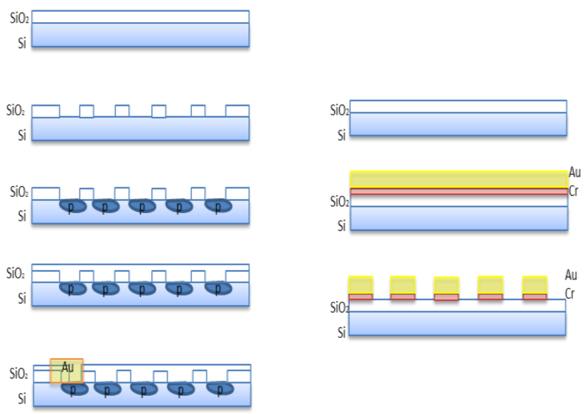
microchannels (depth and width are 75µm and 200µm, respectively) etched in Pyrex glass. This way chemical reaction will use as much heat as possible. Required temperatures for synthesis of TiO_2 nanoparticles in microreactors are from 60°C to 100°C depending of wanted size of nanoparticles. At higher temperatures smaller particles are obtained. Our goal is to use as low a current value as possible to get higher temperature on two types of heaters with same design and shape.

II. Experiment

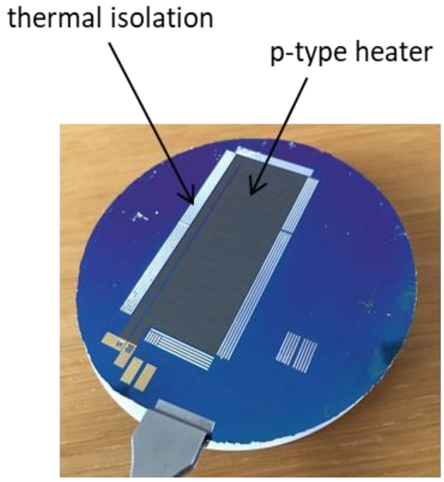
We used double side polished, 3 inch in diameter, n - type Si wafers as a platform for integrated heaters. On the first Si wafer we grew a layer of SiO_2 in oxidation furnace as a masking layer. The thermal oxide was obtained at temperature of 1100 °C. The thickness of masking oxide was 0.6 µm. After that we performed photolithographic process to pattern the heater. Second step was p-type diffusion to obtain the heater. Diffusion of boron dopants was performed at the temperature of 1025°C for 1 hour and obtained depth was 1µm. Fig. 1a) shows steps for fabrication of p-type Si heater. Another layer of thermal oxide, above diffusion layer, was grown, at temperature of 1100 °C for 25 min. Thickness of the layer was about 0.3 µm. This thin thermal oxide was used as masking layer for etching in TMAH water solution. We etched holes in Si which are used as thermal isolation for the rest of the microreactor from the heaters, as shown in Fig 2a). As a metal contact we sputtered thin layer of gold with sublayer of chromium. Sublayer was used to obtain better adhesion between gold and silicon. Thicknesses of Cr and Au were 10nm and 100nm, respectively.



a) b)

Figure 1. Schematic view of fabrication: a) p-type diffused heater b) gold heater.

On the second Si wafer we also fabricated thermal oxide of 0.6 µm thickness, as a masking layer for wet chemical etching of Si in TMAH water solution. After that we sputtered thin layer of gold with sublayer of chromium. Thicknesses of Cr and Au were 10nm and 100nm, respectively. We used Cr for better adhesion between gold and SiO_2. Standard photolithography processes were used to obtain same pattern of heater and thermal isolation like on the first p-type diffused heater. Fig. 1b) shows steps of fabrication for gold heater. Fig. 2b) shows fabricated gold heater with thermal isolations. Both fabricated heaters, Fig.2, had 296 squares. Measured resistance of gold and p – type heaters were 289Ω and 1KΩ, respectively.



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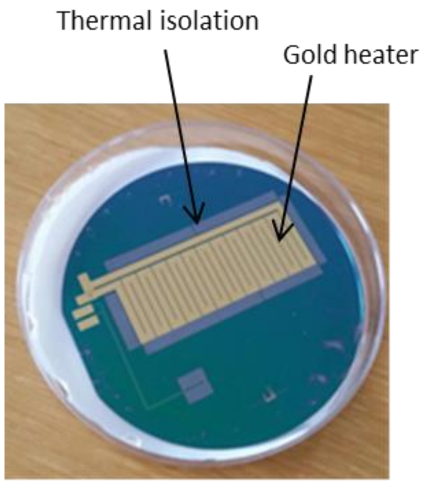

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Figure 2. a) p-type diffused and b) gold heaters on Si platform with thermal isolations.

III. MAIN RESULTS

After the fabrication, both heaters were connected to the current source to obtain temperature which is required for synthesis of TiO_2 nanoparticles.

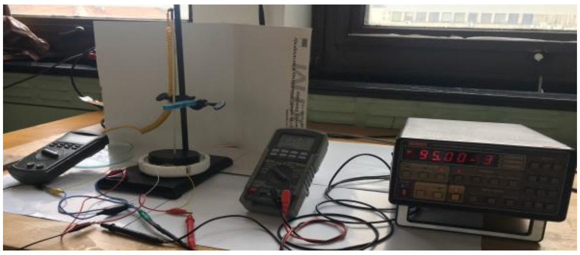
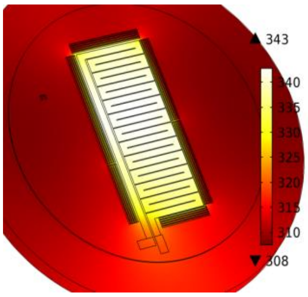


Figure 3. Experimental setting for temperature measurements

For temperature measurements, before anodic bonding, we used K-type thermocouple to measure temperature on the surface of the heaters. Temperatures on both heaters were measured with dark cover. We used source of current with limit of 100mA (Keithley, programmable current source). Fig 3. shows experimental setting for temperature measurements.



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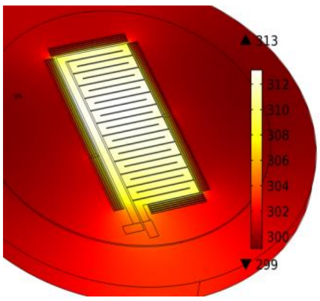

b)

Figure 4. Temperature profile for both heaters in stationary state for current of 50mA: a) p-type diffused heater b) gold heater.

Before experimental measurements we did simulations for both heaters. The simulations were made in the Comsol Multiphysics commercial package. We simulated temperature change of heaters in stationary state. Fig. 4. shows temperature profile for both heaters in stationary state for current of 50mA. Simulations have shown that gold heater obtained 39°C and p-type heater obtained 67°C as maximum of temperature, with applied current of 50mA, which was confirmed in the following experiment.

In experiment, we first measured temperature using gold heater. First we applied current of 50 mA. Temperature was measured at consecutive moments of time: 5 min, 10 min, 15 min, 20 min, 25 min, 30 min and temperatures measured at these moments were 39 °C, 39 °C, 39.1 °C, 39.4 °C, 39.2 °C, 39.3 °C, respectively. Also, we measured temperatures with applied currents of 75 mA and 95 mA for the same time intervals. A temperature dependency of gold heater with the applied current is shown in Fig. 5. On Fig. 5 we can see that the temperature increases with current and the highest temperature was measured at 95 mA current after 30 min, and it was 69.5 °C.

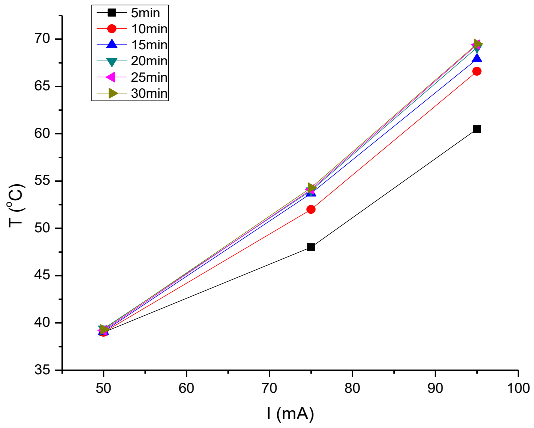

Figure 5. Diagram of the temperature dependence of gold heater for the applied current at 5 min, 10 min, 15 min, 20 min, 25 min and 30 min.

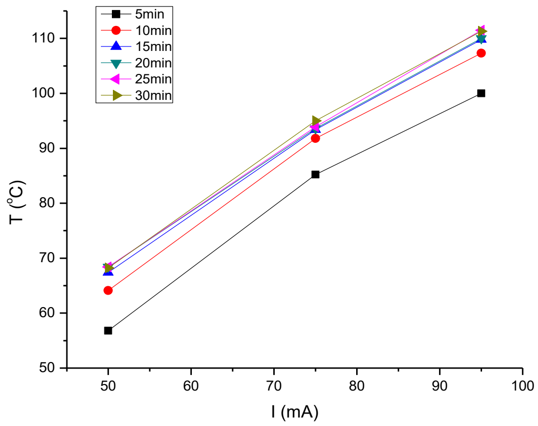

Figure 6. Diagram of the temperature dependence of the current at 5min, 10min, 15min, 20min, 25min and 30min for p – type heater

Temperature measurement for the p-type heater started with 50 mA, as for the gold heater. Again, temperature was measured at consecutive moments of time 5 min, 10 min, 15 min, 20 min, 25 min, 30 min and measured temperatures were 56.8 °C, 64.1 °C, 67.4 °C, 68.4 °C, 68.4 °C, 68.2 °C, respectively. Temperature was also measured at 75 mA and 95 mA current value for the same periods of time. Fig. 6. shows dependence of p-type heater temperature, for the applied currents. We can see that temperature increase with a current. At a current of 95 mA temperature reached 111.3 °C after 30 min, which is more than enough for our application. We can conclude that the p-type heater is more advantageous than the gold heater for our desired application as it reaches temperatures of interest for much smaller currents. Also, designed p – type heater will not influence the anodic bonding of Pyrex glass wafer with Si wafer, which is not the case for the gold heater.

IV. Conclusion

In this paper we have shown the fabrication of two types of heaters for microreactors, which will be used for synthesis of TiO_2. First one was gold heater and the second one was heater fabricated by process of p-type diffusion in n-type Si. After applying various currents and measuring temperature after different periods of time we can conclude that the temperature to current ratio is better for p-type heater as it reached higher temperature for lower current values. Another benefit of p – type heater is that it will not influence anodic bonding of Pyrex glass with fabricated microchannels and Si wafer. In our future work we will measure the temperature of various integrated p-type heaters in Pyrex glass microchannels in order to obtain better power consumption.

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