TiO_2 THIN FILMS USED IN FABRICATION AND FUNCTIONALIZATION OF MICROFLUIDIC CHANNELS

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This paper is focused on titanium oxide (TiO_2) preparation by selective electrochemical anodization inside the pre-fabricated microfluidic channels. The microchannels have been configured by deep reactive etching (DRIE) of silicon substrate. Our approach includes a simple lift-off process for obtaining the titanium oxide inside the microchannels by using standard lithography and thin-film deposition exclusively and employing the same mask for all the technological steps.

The TiO_2 configuration into microchannels was analyzed by contact angle in order to design a capillary flow microfluidic device and to control the flow. By UV irradiation, a very hydrophilic surface can be obtained, even for a small contact angle of 10 degree, while the exposure to nitrogen tends to change the surface properties to hydrophobic ones. We have manufactured a microfluidic device with TiO_2 thin film in microchannels and the flow velocity of a fluid composed from deionized water and red alimentary dye was measured.

Keywords: TiO_2; microchannels; electrochemical anodization

1. Introduction

Microfluidic structures have various applications in drug delivery, diagnostics, biosensors, chemical synthesis, due to the use of very small volumes of liquids in the process [1].

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Transport of liquids in a microfluidic system is often controlled by external pumps such as syringe pumps, pneumatic pumps or peristaltic pumps. These pumps usually require peripheral equipment, resulting in low portability of the device. Also, electroosmatic flow is a successful implementation, but portability is reduced due to the requirement of a high voltage source. Another option would be to incorporate the micropumps into microfluidic system, but they are not cheap enough for a disposable device and easy to use.

The control of capillary flow in microfluidics provides an attractive mechanism for fluid transport limited resources. Using capillary flow devices eliminates the requirement for external or incorporated pumps, thus reducing the manufacturing costs and limiting the user error.

A number of studies have investigated the possibility of immobilizing titanium dioxide (TiO_2) used in microsystems. Mayer et. al. [2] used anodic spark deposition to create a TiO_2 film. Lindstrom [3] investigated the sol-gel method in order to deposit porous TiO_2 inside of a microreactor.

Titanium dioxide is a semiconductor intensely studied for various applications: electrodes used in photoelectrochemical cells [4,5], capacitors[6,7], solar cells [8-10], sensors [11-15], in medicine for the inactivation of cancerous cells [16,17], photodegradation of organic compounds in water or air treatment [18-22], control flow and velocity in microfluidics [23].

Titanium oxide is one of the most studied material because of its properties and utilization in different applications including microfluidic devices due to the capacity of changing properties [24]. TiO_2 being a photosensitive semiconductor, regarding the exposure to ultraviolet radiation (UV) and N_2 [25], it has the capacity to modify the wettability of surface giving a conversion hydrophilic – hydrophobic.

An important factor for obtaining a capillary flow is the wettability of the material. A microfluidic device based on TiO_2 layer has the advantage of softening agreement between super hydrophobic surface and a super hydrophilic one. The fabrication procedure is very simple. Titanium dioxide layer can be used inside the microfluidic channel as valve function [26]. Some devices use passive microfluidic valves that are based on surface tension of hydrophobic material of the valve or valve geometric blocking the flow of liquids.

In our research, the titanium oxide was configured by using the UV lithography inside the microfluidic channel and by electrochemical anodizing of the titanium thin film. A simplified method has been elaborated in order to allow the TiO_2 patterning inside the microfluidic channels using standard photolithographic techniques with integrated lift-off process.

2. Experimental

Due to the configuration difficulties of the TiO_2 [27], obtained by anodization, through wet etching or reactive ion etching (RIE) the lift-off procedure was used for patterning. In Fig.1 it is shown the technological steps.

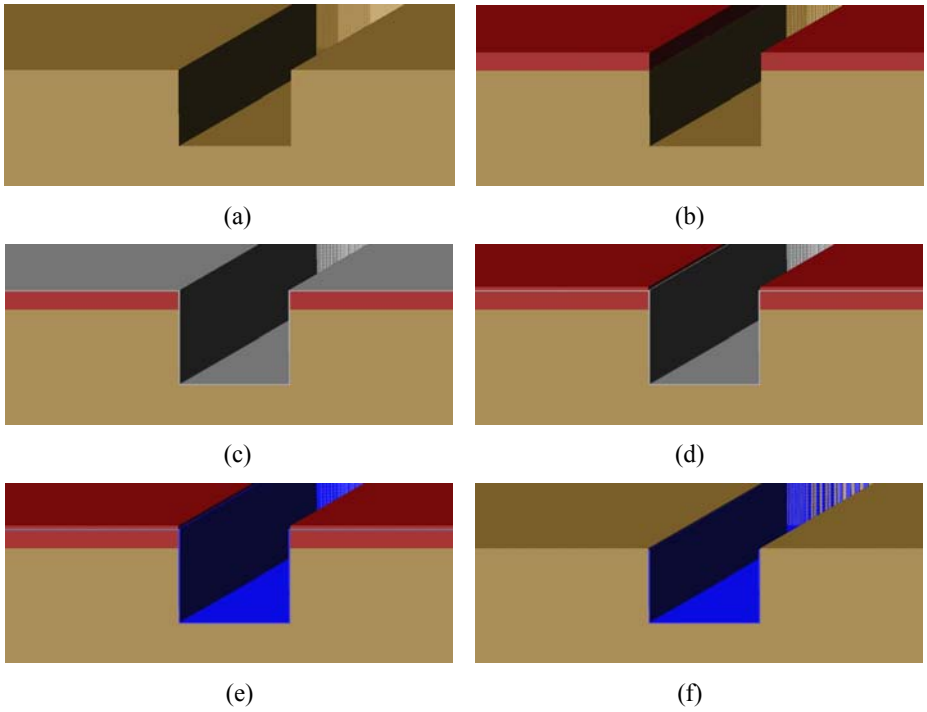


Fig. 1: Fabrication process of titanium oxide thin film configuration in microchannels: (a) Substrate with microchannels; (b) Spin-coating a sacrificial photoresist layer and micropatterning by UV-lithography; (c) Deposition of a titanium layer (90 nm); (d) Spin-coating a sacrificial photoresist layer and micropatterning by UV-lithography through the same mask; (e) Electrochemical anodization of titanium; (f) Lift-off and annealing

i. The employed silicon wafers are cleaned using RCA standard cleaning process and then microchannels are patterned by photolithography using the positive resist as mask for DRIE etching. The depth of microchannels in silicon is approximately 60 μm, Fig.1.a.

ii. A sacrificial positive resist layer (HPR 504 – Fujifilm) was spin-coated and micropatterned by UV-lithography through the same mask used for the microchannels configuration. This sacrificial layer is intended for the final lift-off process performed after the titanium anodization developing the TiO_2 Fig.1.b.

iii. The 90 nm thick titanium sputtering deposition was conducted in argon flow of 2,5 sccm and the 100W sputtering power was selected, Fig.1.c.

iv. Spin-coating a sacrificial positive resist layer (HPR 504 – Fujifilm) and micropatterning by UV-lithography employing the mask used for the microchannels' fabrication. The secondary photoresist layer has the role to define the area in which the electrochemical anodization will take place in order to obtain the titanium oxide, Fig.1.d.

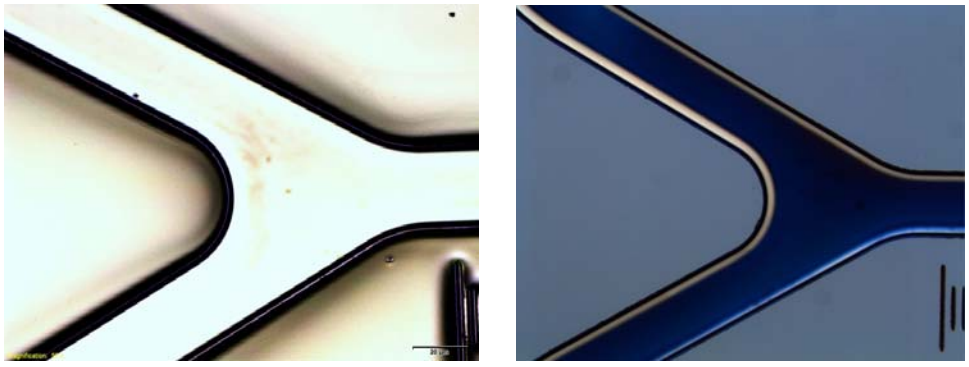
v. The TiO_2 was obtained by electrochemical anodizing of the metallic Ti thin film using 10% NH_4F: MEG: H_2O_2 (1: 199: 36) with, pH=6.8 as electrolyte. Applied voltage was 5V for 30 sec. [6], Fig.1.e.

vi. The lift-off process will remove the two photoresist layers along with the titanium thin deposition separating them by immersion in acetone.

TiO_2 was annealed at 450°C for 30 min in forming gas (3%H_2 in N_2), Fig.1.f.

3. Results and Discussion

TiO_2 thin layer obtained through electrochemical anodizing of the titanium thin film and its configuration by UV lithography inside the microchannels was investigated by optical (Fig. 2) and SEM techniques (Fig. 3).

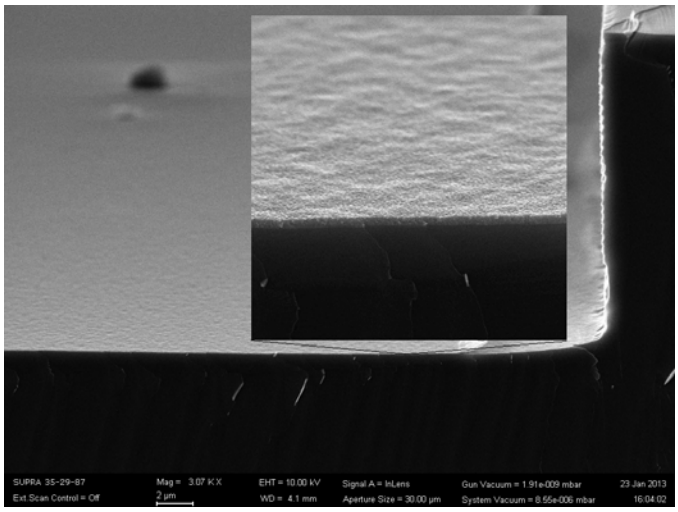


(a) (b)

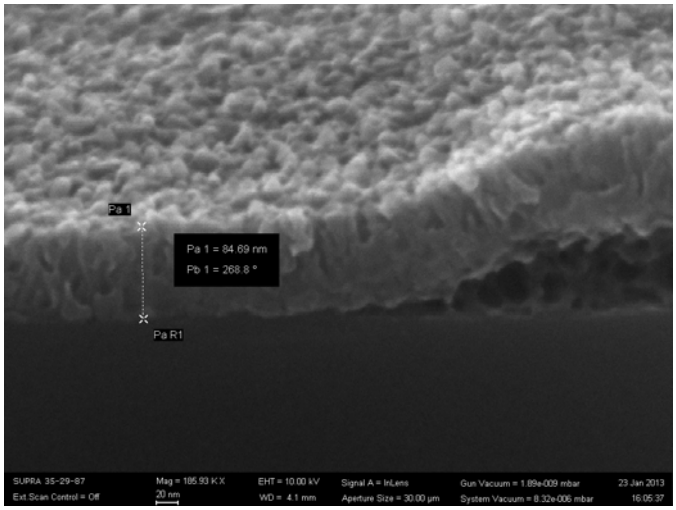
Fig. 2. (a) Optical microscope images of structures before anodization of titanium, (b) Optical microscope images of structures after anodization and immersion in acetone

In Fig. 2(a) and Fig. 2(b) optical images of structures after anodization of titanium and immersion in acetone. Nanoporous titanium oxide films were formed by anodization of titanium thin films and annealing at 450°C in N_2, for 30 minutes proves improving the crystallisation of the anodic thin film (from amorphous to anatase phase) and increases its transparency.

FEI Nova NanoSEM 630 has been employed for the high-resolution SEM morphological examination of the nanostructures, thickness of TiO_2 layer (84,5nm) and pores geometry associated to the parameters of anodizing process.



(a)



(b)

Fig. 3. SEM examination of TiO_2 microstructures obtained by anodization of titanium deposition inside the microchannels: (a) SEM micrograph of TiO_2 deposition in microchannel; (b) Morphological configuration of TiO_2 layer

Fig. 3(a) and (b) shows the nanostructure titanium oxides thin film microstructures obtained by anodization of titanium deposited inside the microchannels, after heat treatments at 450°C in nitrogen, for 30 minutes. The formation process of the porous structure and the change in surface morphology induced by heat treatments is evident.

The wettability surface analysis at different exposures in ambient air room temperature was performed using the contact angle measurements with the KSV Theta Optical Tensiometer equipment.

Wettability conversion of the TiO_2 surface depending of the exposure at UV irradiation (λ=365 nm) and N_2 is illustrated in Fig. 4. The exposure at UV radiation for 5 min. or 20 min. leads to a hydrophilic surface and a treatment with N_2 treatment tends to a hydrophobic surface.

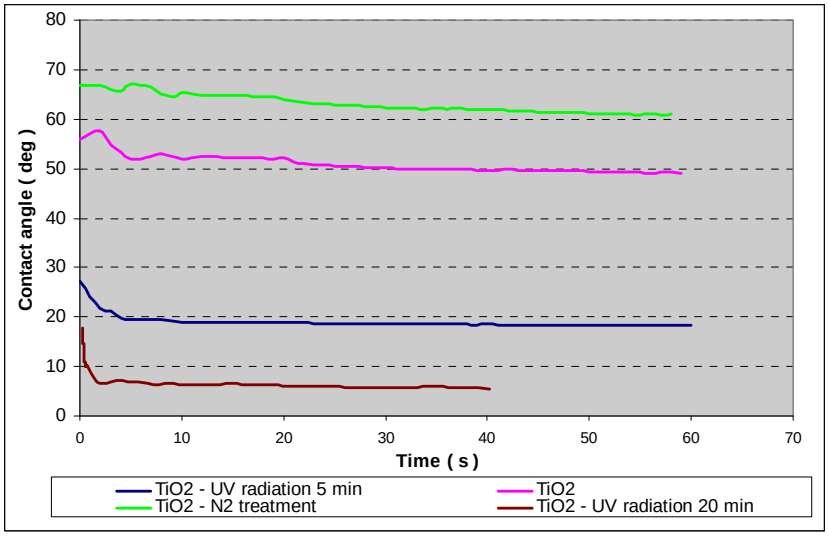
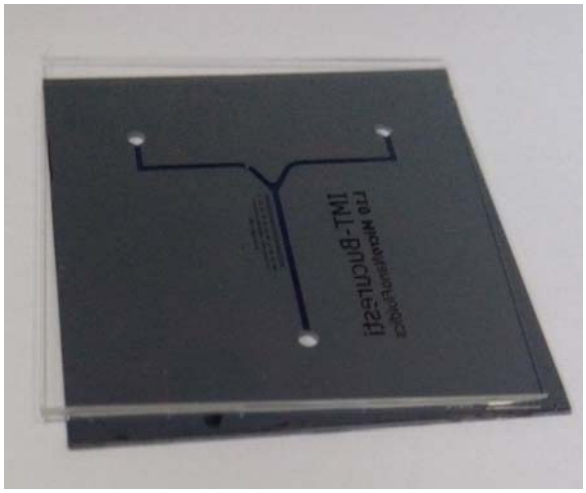


Fig. 4: Graphical representation of the contact angle measurements

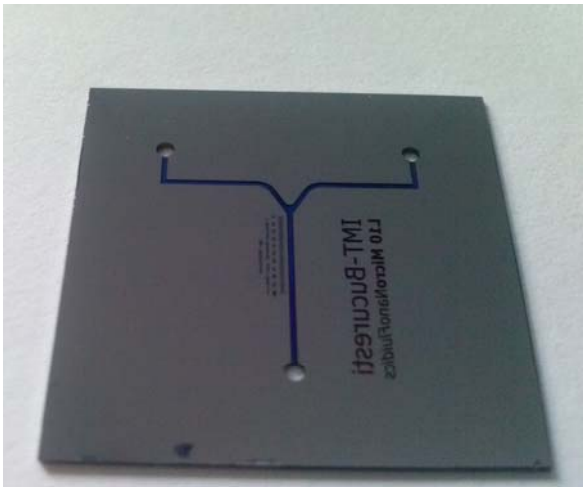
The manufactured microfluidic device was covered with a polydimethylsiloxane (PDMS) plate, as seen in Fig. 5, in order to be tested. PDMS elastomer and curing agent are mixed with a weight of 10:1. Air bubbles are removed by relaxing the mixture between PDMS elastomer and curing agent for 30 minutes. Pour the PDMS mixted on a petri dish and cured for 90°C for one hour in oven and carefully cut through holes in the PDMS film for the inlet and outlet.

A mixture of deionized water and red alimentary dye was used for testing and characterization of the devices presented in Fig.5 a. A large drop is placed at the inlet of microfluidic device using a pipette. For microfluidic device without TiO_2 layer, no liquid flowing inside the silicon channels was noticed. For microfluidic device with TiO_2 layer configured on the bottom of microchannels and UV irradiated for 20 minutes was observed a very high flow rate through the channel, resulting in flow velocity of 66 μm/seconds, for UV irradiation of 5 minutes, respectively 25 μm/seconds and for exposure to N_2, filling the channel

with flow velocity of 3,87 μm/seconds. Measurements were made using an optical microscope equipped with an accurate video camera and a stopwatch in milliseconds.



(a)



(b)

Fig. 5. (a) microfluidic device covered with a PDMS plate, (b) microfluidic device without PDMS.

6. Conclusions

TiO2 thin films for microfluidic devices application have been prepared and selective micropatterned.

This selective micropattering of TiO_2 demonstrates the possibility of integration in different microfluidic devices. The electrochemical anodization, UV lithography and lift-off procedure were used for titanium oxide implementation in microfluidics.

The TiO_2 thin film fabricated by this method revealed no structural defects and the SEM morphological characterization displayed a resulting edge much higher than the ones reported for other methods, such as sol-gel.

From flow velocity measurements, we demonstrated the capability of flow velocity regulation depending on the application of UV radiation during fluid flow through silicon etched microchannels.

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