Superhydrophobic Polytetrafluoroethylene Coated Micro-fluidic Chip for Bio-applications Integrated With THz Spectroscopy Technology

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Abstract — The hydrophobic properties were achieved for RF-sputtered ultra-thin polytetrafluoroethylene (PTFE) films deposited on silicon surfaces. In our investigation, super-hydrophobic surfaces with water contact angles higher than 90° were achieved on RF-sputtered ultra-thin PTFE films of less than 100 nm coated on silicon surfaces prepared for electrowetting on dielectric (EWOD) applications. The plasma deposition mechanism is discussed in this letter. We analyze here the EWOD principles applied to microfluidic devices which have double hydrophobic layer materials, ZnO and PTFE. We also compared sputter coated polymer with ZnO and InP films using atomic force microscope (AFM). AFM images were measured to correlate the data with surface shapes.

Index Terms — (Polytetrafluoroethylene) PTTE, terahertz (THz) spectroscopy, bio-materials.

I. INTRODUCTION

Both polytetrafluoroethylene and ZnO films find extremely diverse applications because of their unique electrical, chemical and surface properties. Polytetrafluoroethylene consist from group fluoropolymers and have been an important family of polymers for the packaging of microelectronics because of their proprieties of thermal stability up to few hundred degrease, dielectric constant that is applicable for GHz and THz frequencies range and good hydrophobic proprieties for electrowetting on dielectric (EWOD) applications. The highly transparent self-cleaning surfaces of zinc oxide were reported [1,2] and the hydrophobicity improving of the ZnO film by PTFE incorporation is discussed in ref [3]. Electrowetting is the electrically induced modification of wetting properties of a conductive liquid on a surface. By applying an external electric field on EWOD chip contacts, it becomes possible to actuate or manipulate small volumes of liquid by altering its interfacial tension and hence the macroscopic contact angle or by inducing bulk liquid motion through an interfacial electric stress.

There are many application for EWOD devices, like manipulating droplets by chemical [4], thermal [4], acoustic [5], and electrical [6] means.

II. EWOD STRUCTURE

In this paper we present the EWOD chip transparent for THz radiation that allows scanning easily any biofluid slipping through microchannel. The structure is obtained by thermal oxidation of a (100) Si wafer. The grown ${\rm SiO_2}$ on top is 500 μm thick. A positive photoresist (PMMA) was used to configure Cr-Au pads, obtained by liftoff method. ZnO and PTFE were deposited by RF magnetron sputtering.

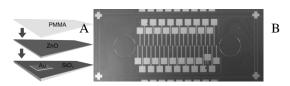


Fig. 1. Technological processes (A), and EWOD device photo (B)

In order to have qualitatively improved structure with hydrophobic surface we added the new layer on top of ZnO [7] and cover the EWOD chip with PTFE on the surface. As the undoped ZnO is considered dielectric one, $R\!=\!10^5~\Omega_\square$, we remove it from external pads for contacting with microcontroller circuit.

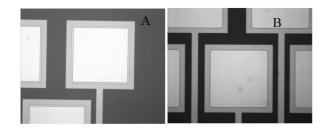


Fig. 2. ZnO removing from pads (A) before removing PMMA, and after (B)

When a voltage (V) is applied between the embedded electrode and the liquid droplet on the dielectric layer, the solid-liquid interfacial tension decreases and it reduces the contact angle from θ_0 to θ_V . Here θ_0 represents the angle between contact surface area and lateral surface of droplet at applied 0 volts, and θ_V after applied voltage (V), respectively (Fig. 3a). If an array of embedded electrodes is patterned, the droplet can move to the activated area when a partial area of the droplet base is activated by controlling a part of the embedded electrode array (Fig. 3b and 3c). Then the EWOD device can be used to manipulate droplets for dispensing, transporting, splitting, merging, and mixing. For our designed EWOD we chosen a method to manipulate liquid droplets in digital (discrete droplet-based) microfluidics, however, the required voltage for driving a droplet has been several tens to hundreds of volts. We made various attempts to reduce the applied voltage by changing the zinc oxide thickness [8]. At the same time, it can serve as an optical window for most of frequencies especially for IR and THz that we are interested in.

Lippmann-Young equation gives the relationship between the contact angle change and the applied voltage through the dielectric layer, depending on the liquid-vapor interfacial tension and dielectric properties, as follows:

$$\cos\theta_V = \theta_0 + \frac{\varepsilon_0 \varepsilon_r}{2\gamma_b d} V^2 \tag{1}$$

Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the dielectric, γ_{lv} is the liquid-vapor interfacial tension, and d is the thickness of the dielectric layer. According to this equation, a thinner dielectric layer with a high permittivity is desired to lower the driving voltage. This paper presents the fabrication and the driving characteristics of a low-voltage EWOD which was realized by using magnetron sputtering deposition of zinc oxide (ZnO).

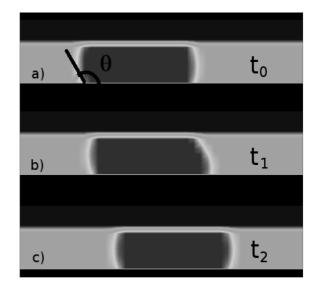


Fig. 3. Moving of microdroplet inside of microchannel. a, b, c) position of the microdroplet for moments of time t₀, t₁ and t₂, respectively

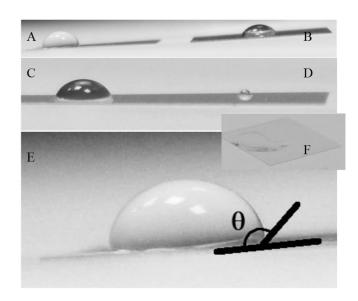


Fig. 4. Image of droplet on the PTFE film (A, E), InP film (B), ZnO film (C, D).

Figures 3a, b and c represent the moving process inside of microchannel at different moments of time t_0 , t_1 and t_2 respectively.

In Figs. 4A and B is represented the image of microroplet on the PTFE and InP films. Fig. 4C and D show the comparison between different size of microdroplets. In Fig. 4E the θ angle for the PTFE is estimated to be about ~150° as compared to ~60° and ~80° for InP and ZnO, respectively.

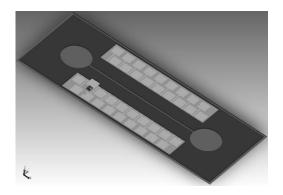


Fig. 5. Coventor and CleWin mask design

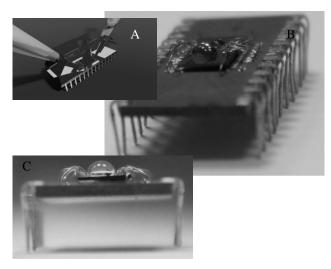


Fig. 6. An example of EWOD device (A) 3D representation, (B, C) the image of encapsulated EWOD chip on DIP24 package

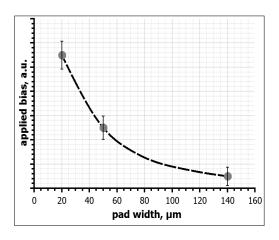


Fig. 7. Applied bias on pads estimated in Coventor software

The pad form has been optimized in order to have a smooth moving of bio sample through microchannel. The applied bias depends also on width of pads and of the interdistance between them, which was estimated in Coventor software by using BabbleDrop module.

In order to have a THz signal from the bio sample, we need to use preconfigured pads (Fig. 7 and 8 from ref [7]), similar to metamaterials [9]. In connection with EWOD we can scan each microdroplet in real time mode by THz-TDS and identify the biomaterial that at the moment of

time t_0 is situated on EWOD THz-pad resonator (Fig. 4 from ref [7]).

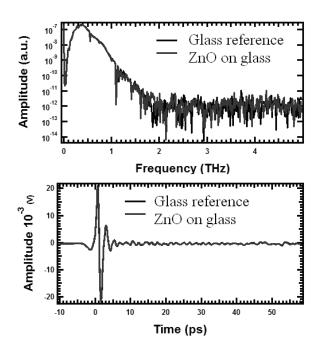


Fig. 8. THz spectra from glass and ZnO deposited on glass

The deposited ZnO film on the chip has a 400 nm thickness, and it is of around 100nm in the experimental glass. In order to estimate the quality of deposited ZnO we studied the Raman scattering [10] and AFM. The roughness has been studied and it was found to be around 220 nm on the chip and 5nm for the experimental glass, respectively. That means that we have a variation of 400±220nm. We believe that these variations are due to applied potential on the surface (see Fig. 11 from ref [7]). In order to understand this effect we suppose that surface acoustic waves (SAW) propagate in the film.

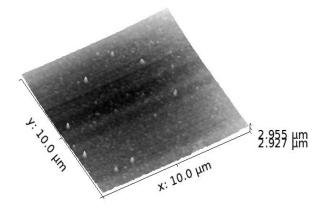


Fig. 9. 3D AFM image of PTFE deposited layer

The roughness parameters have mean values of ~10nm for ZnO, 0.4nm for glass, 1nm for InP and 2nm for PTFE films. All surfaces are more or less hydrophobic except the glass (we haven't seen any droplets formation on glass surface, Fig. 4F).

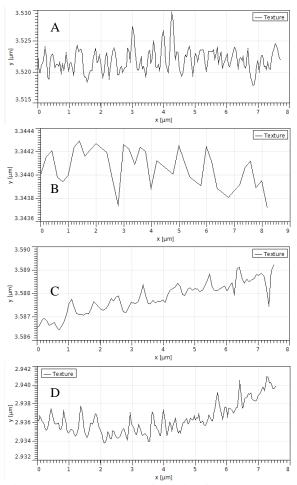


Fig 10. AFM topography of one line from the measured surface of (A) ZnO (B) glass (C) InP and (D) PTFE polymer

Since ZnO films are promising for fabrication of THz devices, we tried to implement them into EWOD device. Recently THz birefringence has been reported [11].

The glass has been taken as reference material in studding the THz emission and it has been compared with the ZnO film deposited on the same glass (Fig. 12 from ref. [7]). One can see from the THz spectrum that significant changes do not occur. We suppose that the weak absorption is due to small thickness of the deposited film.

III. CONCLUSIONS

The surfaces coated with different materials showed in this study that the roughness parameter with hydrophobic proprieties don't have any correlation between them. Nevertheless the surfaces coated with PTFE polymer showed the best result. We demonstrate the possibility to fabricate a device that is able to handle with liquids. The SAW piezoelectric effect may give us additional

information about the bio sample, like mass loading, membrane characterisation, etc.

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REFERENCES

- [1] Javier Rubio-Garcia et all Transfer of hydrophobic ZnO nanocrystals to water: an investigation of the transfer mechanism and luminescent properties, J. Mater. Chem., 2012,22, 14538-14545
- [2] S Patra et al Hydrophobic self-cleaning surfaces of ZnO thin films synthesized by sol-gel technique, Journal of Physics D: Applied Physics Volume 42 Number 7 075301 2009
- [3] Meenu Srivastava, Bharathi Bai J. Basu, and K. S. Rajam, Improving the Hydrophobicity of ZnO by PTFE Incorporation, Journal of Nanotechnology
- [4] F. Brochard, Motions of droplets on solid surfaces induced by chemical or thermal gradients, Langmuir 5 (1989) 432–438.
- [5] A. Wixforth, C. Strobl, C. Gauer, A. Toegl, J. Scriba, Z.V. Guttenberg, Acoustic manipulation of small droplets, Analytical and Bioanalytical Chemistry 379 (2004) 289–991.
- [6] M. Washizu, Electrostatic actuation of liquid droplets for microreactor applications, IEEE Transactions on Industry Applications 34 (4) (1998) 732–737.
- [7] Lilian Sirbu, Lidia Ghimpu, Raluca Müller, Irina Vodă, Ion Tiginyanu, Veaceslav Ursaki, Traian Dascalu Hydrophobic ZnO used in EWOD technology and SAW devices for better bio-fluid slip at microchannel walls controlled by DC pulses, CAS2012, Proceedings, Vol.I, 15-17 oct 2012, Sinaia, Romania, p. 231-234.
- [8] Li-Yin Chen, Chun-Han Lai, et al "Electrowetting of Superhydrophobic ZnO Inverse Opals" The Electrochemical Society
- [9] Hou-Tong Chen, Willie J. Padilla, Richard D. Averitt, et al "Electromagnetic Metamaterials for Terahertz Applications" Terahertz Science and Technology, Vol.1, No.1, March 2008
- [10] Zalamai V.V, Ursaki V.V., Rusu E., Arabadji P., Tiginyanu I.M., Sirbu L.. Photoluminescence and resonant Raman scattering in highly conductive ZnO layers. Applied Physics Letters, Vol. 84, Nr. 25, 2004, p. 5168-5170.
- [11] Youngchan Kim, Jaewook Ahn, Bog G. Kim, and Dae-Su Yee, Terahertz Birefringence in Zinc Oxide, Japanese Journal of Applied Physics 50 (2011) 030203