

## NANOSTRUCTURED SURFACE AS EWOD COUNTER ELECTRODE FOR MATRIX-FREE MASS SPECTROMETRY ANALYSIS

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Current digital microfluidic systems are often based on the electrowetting on dielectric (EWOD), which allows fundamental droplet handling operations [1]. To date, the best EWOD results obtained for MALDI analysis concern a set up consisting of two parallel plates, a base and a cover preventing from evaporation, between which microdroplets of biological liquid are sandwiched [2]. Classically the base is made of an electrode array coated with a bilayer composed of a dielectric and an amorphous fluoropolymer plane layer. The cover, working as a counter electrode, is made of a conductive substrate (ie silicon) coated with the same amorphous fluoropolymer layer.

This paper reports on the preparation of a superhydrophobic nanostructured surface consisting of chemically modified silicon nanowires for the realisation of EWOD counter electrode and matrix-free mass spectrometry analysis. The main advantages associated with such a substrate are: (i) flow resistance of droplets is dramatically reduced, (ii) simple realisation of hydrophilic and functionalized pads in the superhydrophobic surface allowing analytes trapping and enhancement of the liquid / surface interaction, (iii) subsequent analysis by matrix-free desorption/ionization MS-DIOS on these pads.

The bottom plates were fabricated using standard microfabrication techniques. The bottom glass plate consists of an array of independently addressable control electrodes (1 mm<sup>2</sup>) patterned in a 10 nm thin layer of nickel, which is further coated with a SU-8 layer (2µm) as a dielectric. A hydrophobic layer of Teflon AF 1600 (20 nm) is then deposited (Fig.1, contact angle = 115°). Silicon nanowires are synthesized on silicon substrate (counter electrode) using the well-known Vapor-Liquid-Solid (VLS) technique (Fig.2-3) [3]. The formation of a superhydrophobic layer on the silicon nanowires surface was achieved by chemical derivatization with octadecyltrichlorosilane (OTS) (Fig 4, contact angle = 149°) while the DIOS pads are prepared by a simple exposure of the octadecyl-terminated silicon nanowires surface to UV-ozone through a physical mask containing 20\*50 µm apertures. Thus, we can control locally the wetting properties of a macroscopic hydrophobic surface.

The gap between two plates is 300µm so that a 1µL droplet of biological liquid (Substance P amide, 5.10<sup>-5</sup>Mol/L) can be moved under 68 V compared to 100 V required to displace the same droplet with a classical cover (silicon wafer coated with Teflon).

Finally, mass spectrometry analysis of the targets in the hydrophilic DIOS pads is carried out using MALDI TOF-TOF without addition of an organic matrix. We have found that silicon nanowires can successfully be used as a substrate for MS analysis without any organic matrix (Fig 5) [3].

[1] S.K. Cho, H. Moon and C.J. Kim, *J. Microelectromech. Syst.*, 2003, 12, pp. 70-80

[2] A.R.Wheeler, H. Moon, C.A. Bird, R.R. O. Loo, C.J. Kim, J.A. Loo, R. L. Garrell, *Anal. Chem.* 2005, 77, pp. 534-540

[3] R. Boukherroub et al. (to be published)

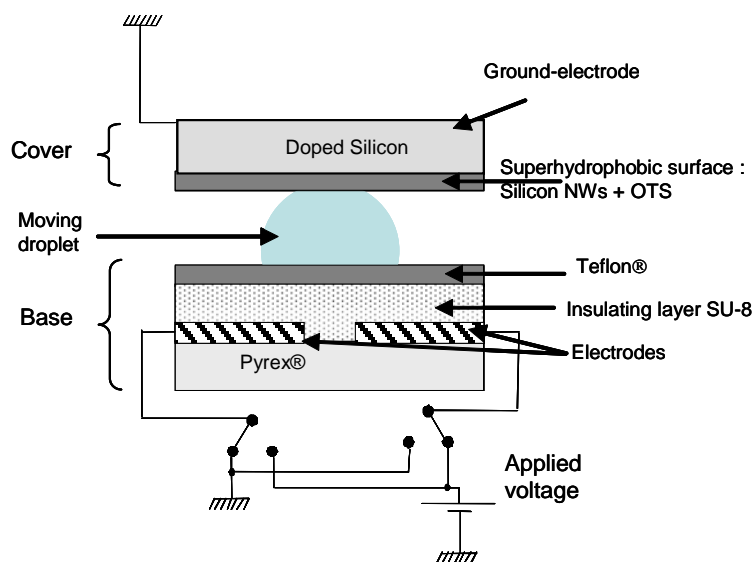


Figure 1: Setup of the EWOD platform

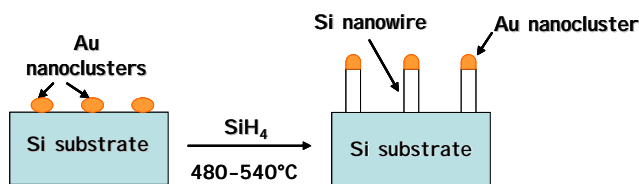


Figure 2 : Silion nanowires growth using VLS technique

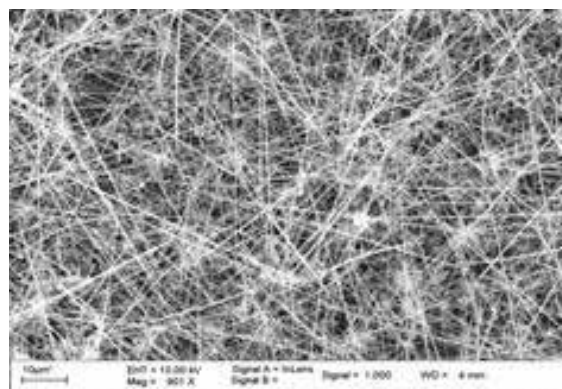


Figure 3: SEM view of silicon nanowires

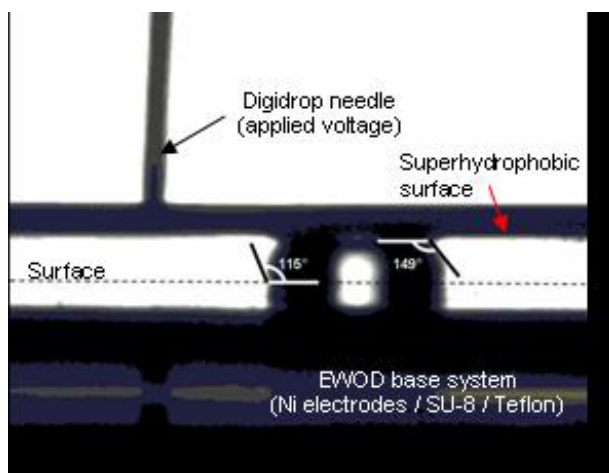


Figure 4: Droplet sandwiched between two plates system (base coated with Teflon, cover with NW / OTS)

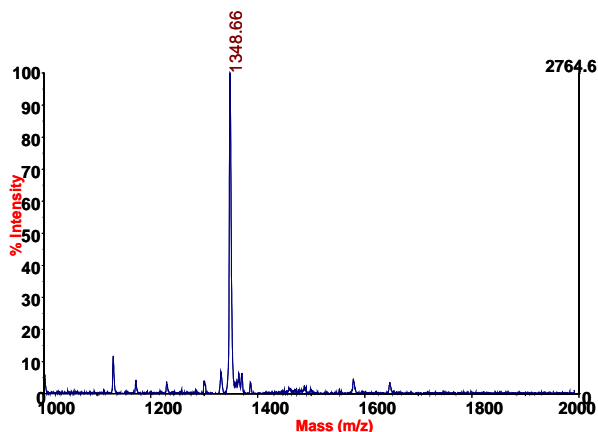


Figure 5: Mass spectrum of Substance P amide on VLS hydrophilic pads