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Investigation of Ion Concentration Polarization in original Micro-Nanofluidic devices

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Abstract

Ion perm-selectivity is one of the major proprieties of nanofluidic devices. Within the influence of an electric field through an ion-selective nanochannel, a phenomenon called ICP "Ion Concentration Polarization" appears and creates near the micro-nanojunction an ion depletion/concentration zone at the anodic/cathodic side, respectively. Recent works have shown that the anodic depletion can be used as a powerfull preconcentration tool for detection of molecules (DNA, proteins…). Here, we present an original micro-nanofluidic device realized by standard silicon technology which exhibits circular micro-nanojuction. The ICP phenomenon was demonstrated on fluorescent molecules (fluorescein). The radial configuration of the nanochannels may bring different advantages compared to the classical "Bypass" device mostly reported in literature.

Stabilization, nanochannels, nanofluidic, concentration polarization, nanojunction

1. Introduction

Ion perm-selectivity can be seen as one of the major promising propreties of nanofluidic devices [1-2]. Because the Debye layer thickness (λ_D) is non-negligible compared to the nanochannel thickness, the electrical double layer can overlap inside the nanochannels under certain conditions (appropriate buffer, ionic strength...). Within the influence of an electric field through the nanochannels, a phenomenon directly dependent on the double layer overlap, called ICP "Ion Concentration Polarization" appears. Near the micro-nanojunction, an ion depletion zone and an ion concentration at the anodic and cathodic side

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are created, respectively. The first investigation of this phenomenon in a micro-nanofluidic device has been done by Pu et al [3] on molecules such as Rhodamine and fluorescein. Also, the commonly used micro-nanofluidic device, called the "Bypass" device [4-5], consist on two (or more) microchannels bridged by a nanojunction which can consist in an array of nanochannel(s) or nanopores [6-7]. The Bypass device is suitable for experimental studies but can be limited, due to its configuration which needs at least 4 outlet holes, considering its integration into MicroTotal Analysis Systems. In this paper, we propose a new generation of micro-nanofluidic device, called ring like devices. With there original architecture, they can be an alternative to classical Bypass devices. A Simple and Double Ring like device, which exhibit either one or two circular nanojunctions composed of 4 radial nanochannels, were tested to perform the ICP phenomenon.

2. Experimental section

2.1. Chip Fabrication

A single and double ring like devices composed of one and two circular micro-nanojunctions, respectively, were fabricated by the same standard silicon fabrication steps. Figure 1 shows the fabrication steps of the single device and the top view of the circular micro-nanojunction. The radial nanofluidic channels (100nm in height), the microchannels (15µm in depth) and through-holes (600µm in diameter) were defined and etched into a 100 mm silicon wafer using photolithography and reactive-ion etching technique. A profilometer was used to carefully measure the channel height (at step c) which is the only critical dimension of our chip. A good uniformity of 100+/-5nm was measured on the overall 100mm wafer (figure 1-B).

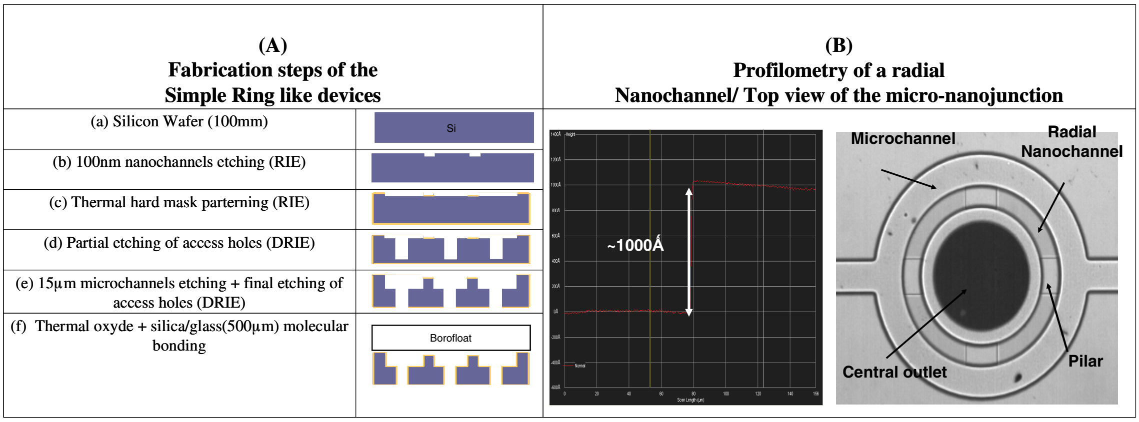

Figure 1: (A) Schematic description of the simple Ring like device fabrication on a silicon substrate. (B) Profilometry of a nanochannel and top view of the circular micro-nanojunction. Silicon pillars, between each radial nanochannel, were etched and sealed with the glass cover in order to avoid its deflexion under pressure and to keep the nanochannel height constant.

3. Results

3.1. Investigation of ICP phenomenon in the Simple and Double Ring like devices

In figure 2-A, anodic depletion was induced in the simple ring like device. At t=0, no electric field was applied across the nanochannels and the fluorescence of fluorescein (diluted in deionized water in order to satisfy the conditions of double layer overlap) was homogenous in the entire sample microchannel. Ten seconds after a 50V potential drop was applied, we observed four depletion zones induced by the four radial nanochannels. The depletion zones are represented by a strong decrease of fluorescence. A characteristic “depletion shock” [8], represented by a local enrichment located at the boundaries of the depletion zone was observed. The depletion zone has extended in the entire device only one minute after ignition of the depletion process. Instead, the double device allowed the cohabitation of both anodic depletion and cathodic concentration by connecting one circular nanojuction to the positive voltage (+50V) and the other one to the negative voltage (-50V) (figure 2-B). Then, a stable enrichment in a specific region of the device over 20min was observed and up to 100 concentration fold was obtained.

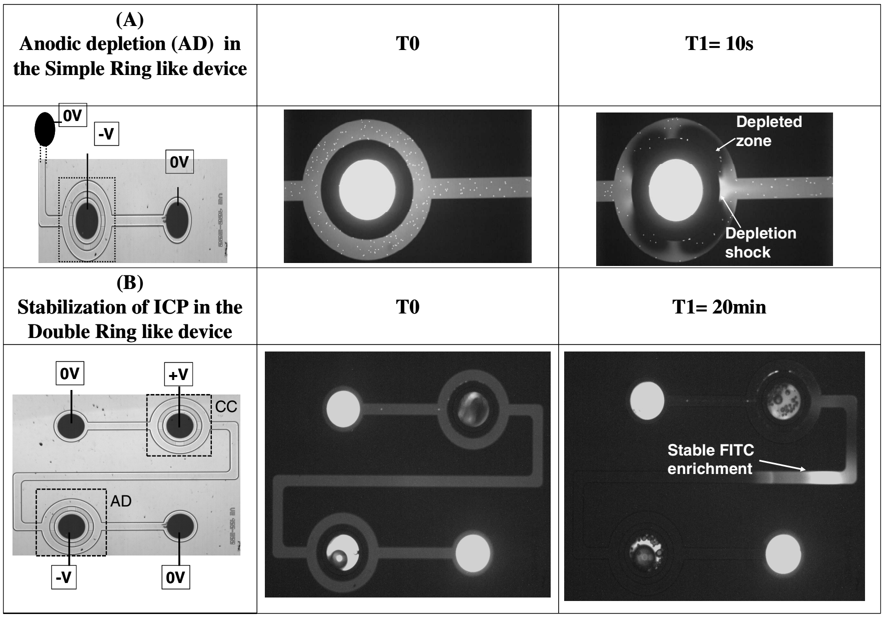

Figure 2 :(A) Anodic depletion induced in the simple ring like device. After 1 min, the depletion zone has extended in the whole device. (B) Stabilization of the ICP phenomenon with the double ring like device. Stable enrichment (~100 fold) was obtained over 20min. Air bublles are observed in the center holes but our interest only focuses in the microchannel.

4. Discussions

While most studies use nanochannels with a height around 50nm [3-4], it is interesting to notice that ICP phenomenon can be initiate with relatively deep nanochannels (100nm). With the simple ring like device, we performed a strong and fast anodic depletion. As demonstrated by Wang et al [4], nanofluidic devices can be use as powerfull tools to accumulate species against the depletion zone which act as an electrostatic barrier to any charged particle. However, we observed that this depletion zone quickly extends toward the outlets leading to unstable concentration process. This phenomenon has already been reported in literature [9], and, in the case of the Bypass device, one solution demonstrated by Kim et al [9] was to prevent the extension of the depletion zone when using an heterogeneous nano-junction to allows for the cohabitation of the ion-depletion and concentration zone. In comparison, with our double device, no complicated heterojunction is needed since only adequate potentials have to be connected to the circular micro-nanojuctions to create a stable ion depletion-concentration junction in a specific region of the device. Also, as mentioned by Kim et al [9], such a device might be used to achieve a stable ion concentration gradient or ionic conductance. Our different results show that the ICP is a robust and promising phenomenon for sample preparation. The circular configuration could be easier to integrate into Micro Total Analysis Systems because of the reduction of the number of outlet holes and its simplicity of use. This could provide other advantages, and further studies will focus on the possible advantages of the natural axi-symmetrical shape such as a symmetrical electrical distribution for better stability compared to the classical Bypass device.

5. Conclusion

To the best of our knowledge, it is the first demonstration of the Ion Concentration Polarization phenomenon with a circular micro-nanojunction. A simple and double Ring like device composed of a single and a series of two circular micro-nanojunctions respectively were tested. While the simple device shows the expected extension of the depletion zone, the double device allows for the stabilization of the ICP phenomenon and lead to a stable concentration of fluorescent molecules thanks to a simple electrical configuration that could not be possible with the classical bypass device. Further studies will focus on the role of the axi-symmetrical shape in stabilization processes. The investigation of such original configurations may open the door to a next generation of micro-nanofluidic devices more suitable to the integration into Micro Total Analysis Systems.

Acknowledgments

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