Fabrication of electron transparent membranes and nanostructures in fluidic devices by nanoimprint lithography and *"Flow-Through"* gas phase deposition

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Abstract

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) allow the visualization and analysis of samples at nanometer resolution. The integration of liquid cells into these microscopy techniques has further extended their capabilities by enabling dynamic imaging and real-time analysis of samples under controlled flow conditions [1,2]. However, the use of liquid cells in SEM and TEM comes with limitations, such as their high cost, limited geometries and reliance on slit-like chambers formed by connecting two membranes with spacers in between.

In this work, we present a fabrication method to produce polymeric foils (<10 µm) which contains micro-, and nanofluidic structures selectively coated from the inside with Al_2O_3 by gas-phase deposition. These inorganic structures can be suspended by removing the polymer material from above and below. This allows the samples to be used as liquid cells for the investigation of the dynamic behavior of molecules in confined spaces, for example, with a TEM.

The fluidic devices are fabricated by direct UV nanoimprint lithography (NIL) [3]. Briefly, this uses photolithography and reactive ion etching (RIE) to first create a pattern on a silicon stamp which is then copied to a softer PDMS stamp. This PDMS stamp is used to imprint the fluidic devices. The design of the stamp is variable and versatile, and can be adapted to geometry of interest for the specific liquid cell. The method has the unique advantage of allowing the fabrication of liquid cells with reduced lateral dimensions (even down to nanochannels), and with complex 3D structures, with graded depths and widths. In the example shown in Fig. 1 (a), the fluidic device contains two microchannels which connect the inlet and outlet holes. These microchannels are interconnected by several nanochannels, as shown in Fig. 1 (b). To create the fluidic devices, the stamp is placed and aligned onto a polycarbonate plate which has been covered with a UV curable polymer (such as Ormostamp or mrNIL210 from micro resist technology GmbH) containing pre-patterned holes. The assembly is then cured with UV light, and the substrate and stamp are separated manually (Fig. 1 (a) step 2). Next, a polymer coverslip is used to seal the channel system of the fluidic device (Fig. 1 (a) step 3). To ensure a conformal coating of the inner walls with Al_2O_3, a specialized atomic layer deposition (ALD) reactor has been constructed which can be used in a "*Flow-Through"* mode [4]. The reactor's gas and vacuum ports match with the holes in the polycarbonate plate, allowing for connection to the imprinted fluidic circuit. By flowing the precursor gases with optimized conditions from one side of the microchannel to the other, a controllable pressure gradient is created. Using this method, we are able to achieve conformal Al_2O_3 coating of a variety of structures, including slits, chambers, and micro-, and nanochannels, with coating layer thickness possible from just a few nanometers to tens of micrometers. The precise control over the deposited Al_2O_3 thickness in the ALD process allows fine tuning of the wall thickness for applications requiring mechanical stability and electron transparency. This approach allows us to overcome the current limitations on liquid cell geometries to only slit-like chambers. In subsequent fabrication steps, the nanochannels or membranes can be selectively suspended by masking and reactive ion etching (RIE). Fig. 2 (c) and (d) show an example of a suspended, hollow Al_2O_3 membrane nanochannel with a cross-section of 500 x 500 nm and a suspended length of 20 µm.

To demonstrate the electron transparency of the Al_2O_3 membrane, we fabricated a TEM grid sample with an Al_2O_3 membrane deposited in our self-developed ALD reactor. We then deposited polystyrene beads above and below the Al_2O_3 membrane and imaged them with a SEM and with a TEM (Fig. 3 (a) and (b), respectively). Fig. 3 (a) shows two SEM images of the same area, obtained with two different detectors. The polystyrene beads below the membrane can only be detected using the secondary electron secondary ion (SESI) detector. Fig. 3 (b) shows the same sample

at a different location imaged in transmission mode with a TEM. These results show that it is possible to image the beads through the Al_2O_3 membrane, and thus demonstrates its electron transparency. To use this system as liquid cells in a TEM specimen holder, it is necessary to detach the structured and coated polymer foil from the substrate (shown in Fig. 1 (a) step 5) and cut it to 3 mm total diameter. Further results on the use of the samples inside a SEM and TEM will be shown at the conference.

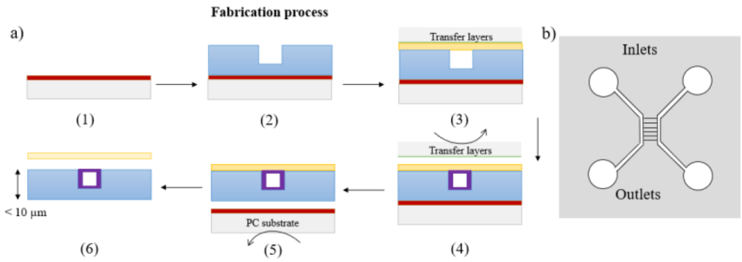

Figure 1. (a) Sketch of the sample fabrication process. A polycarbonate (PC) substrate is treated with perfluorooctyltrichlorosilane (1). The devices are made by casting a UV-curable polymer (2) on a substrate with holes. Then, using a soft stamp, the channels are patterned by UV nanoimprinting (2). A coverslip is used to seal the fluidic system (3). The sample is put in our self-built ALD reactor, and a Al_2O_3 layer is deposited on the inside of the enclosed channels (4). The transfer layer of the coverslip is removed. After coating the inner walls of the system, the PC substrate is removed (5). A structured and coated polymer foil (<10 µm) remains. Here the coverslip is etched by RIE (6). (b) shows a sketch of the fluidic structure on the substrate with inlets and outlets. The microchannels are connected via nanochannels.

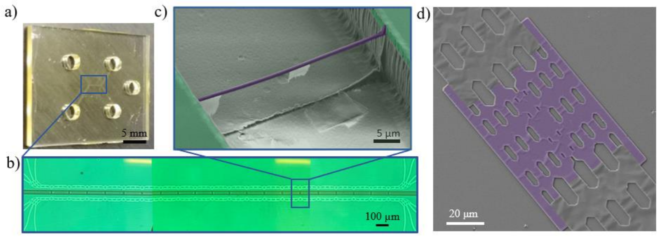

Figure 2. (a) These images show a close up of the fluidic structure on the PC substrate. To suspend the nanochannel, a trench is etched into the polymer by RIE (b). (c) shows the suspended nanochannel with a cross section of 500 x 500 nm and a suspended length of 20 µm. (d) shows a suspended Al_2O_3 membrane in a liquid cell.

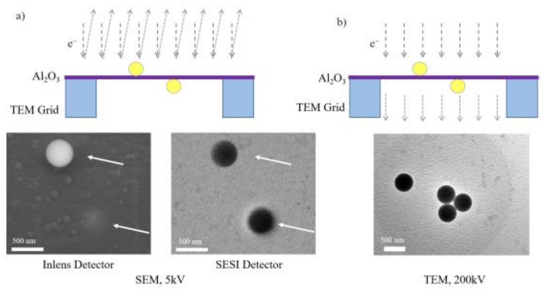

Figure 3. Electron microscope images of polystyrene beads placed on top and underneath an Al_2O_3 coated TEM grid. The sketches show the schematic structure of the TEM grid and the placed beads. Furthermore, it is illustrated how the electrons are scattered from the sample (a) or pass the membrane (b). The SEM images using a SESI detector in (a, right) show one polystyrene bead sitting on top of the Al_2O_3 layer and one underneath. With the Inlens detector (a, left) only the bead on top can be seen. (b) With the TEM all polystyrene beads can be observed, showing that the Al_2O_3 membrane is electron transparent.

Acknowledgements

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