Atomic Force Lithography of Nano/Microfluidic Channels for Verification and Monitoring of Aqueous Solutions

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Abstract
The growing interest in the physics of fluidic flow in nanoscale channels, as well as the possibility for high sensitive detection of ions and single molecules is driving the development of nanofluidic channels. The enrichment of charged analytes due to electric field-controlled flow and surface charge/dipole interactions along the channel can lead to enhancement of sensitivity and limits-of-detection in sensor instruments. Nuclear material processing, waste remediation, and nuclear non-proliferation applications can greatly benefit from this capability. Atomic force microscopy (AFM) provides a low-cost alternative for the machining of disposable nanochannels. The small AFM tip diameter (< 10 nm) can provide for features at scales restricted in conventional optical and electron-beam lithography. This work presents preliminary results on the fabrication of nano/microfluidic channels on polymer films deposited on quartz substrates by AFM lithography.

Introduction

A continuing challenge to the analytical community is the quantification of the concentrations of compounds, elements, and isotopes at ultra-trace levels in the presence of huge quantities of competing species. Nuclear material processing, waste remediation, and nuclear non-proliferation applications all need this capability. Recent progress in nano- and micro-fluidics have provided the underlying technical foundations for developing a high fidelity nanoscale detection technology for radionuclides at a low cost. The technology would provide for ultrahigh sensitivity, selectivity and fast response times in portable and field deployable devices. Savannah River National Laboratory (SRNL) in collaboration with the University of South Carolina (USC) has initiated a program for the development of fluidic sensors with the following technical objectives: (i) apply novel concepts based on electrokinetics and electrophoresis principles to develop a high sensitive detection system based on nanofluidics, (ii) fabricate prototypic components using micro and nano fabrication technology, (iii) measure flow velocities in the prototype devices using laser photobleaching technique (USC), (iv) visualization and measurement of analyte concentrations using an inverted fluorescence microscope, and (v) use state-of-the-art multiphysics numerical simulations for computational prototyping to optimize key process parameters when fabricating sensors.

Technical Basis

Electrokinetics plays a critical role for analyte separation as well as the manipulation and control of the fluid flow in micro/nanofluidic devices. When a polar liquid comes in contact with a solid surface, the latter spontaneously acquires an electric charge. Ions in the liquid are then attracted toward the charged surface, building a very thin layer called

Stern layer, in which the ions in the liquid are paired with the charges on the surface. The Stern layer then affects the ion charge distribution in the liquid away from the surface, creating a thicker layer of excess charges of the same sign as those in the Stern layer. This layer is known as the diffuse or Gouy-Chapman layer. Consequently both of these layers form an electric double layer (EDL) [1]. The EDL strongly influences the migration of charged analyte within the liquid near the solid surface. Since the EDL has a net charge, there is an electric potential within it, called zeta potential (ζ).

The thickness of the EDL can range from 1 nm to a theoretical maximum of ~ 1 μm for typical aqueous electrolytes. This thickness can usually be neglected in a microchannel. However, in nanochannels, the EDL can be on the same order as the channel size. Thus, the effect of the negative electric field generated by the EDL in the transverse direction on negatively charged ions and molecules within the fluid can not be neglected. This effect can be employed for sample preconcentration and million-fold preconcentration of proteins and peptides has been achieved [2]. Such a preconcentration enables detection of extremely small analyte concentration in the sample, and is very important for non-proliferation policy verification. In negatively charged channels, the interactions between a negatively charged analyte and the channel walls can pinch the analyte in the transverse center region of the nanochannel. This effect gives rise to higher velocities for the negatively charged analyte due to a parabolic velocity distribution in the nanochannel, and may be exploited for new applications such as chiral separations and accelerated analyte preconcentration. Since the nanochannel itself can exert a physical constraint on single molecules and ions, the technique could prove viable for fast radionuclide detection at a low cost.

Experimental Approach

Atomic force microscopy (AFM) has been applied to nanoscale lithography as a suitable alternative to conventional optical and electron beam lithography (EBL) for the fabrication of nanostructures and nanodevices on soft substrates [3-4]. While electron beam lithography has been extensively used for the fabrication of masks for optical lithography, the fabrication of patterns at resolutions below 30 nm is difficult because of proximity effects. The main merit of the AFM-based technique is that the machining scale of the structure is primarily determined by the geometry and size of the AFM probe, potentially allowing for resolutions superior to EBL [3, 5]. The close proximity of the AFM tip to the substrate allows for surface modifications at resolutions below 50 nm.

AFM nanolithography can be grouped into two larger categories: electrical methods, where modifications of the surface are obtained by imposing an electric field between the AFM tip and the sample, and mechanical methods [6]. One of the most extensively studied electric-field variants involves the local anodic oxidation of the surface by applying a bias with respect to the AFM tip in a high humidity atmosphere. A second method applies a positive voltage between the tip and the surface, inducing localized electrical breakdown of the polymer. The electrical current results in a localized temperature increase, creating holes or raising the scanned area. In mechanical techniques, a trench is cut by rastering the tip across the surface with enough force to penetrate the sample. The preliminary results of this work are based on the use of the AFM mechanical scribing approach for the fabrication of nanochannels on low-hardness samples.

Results

Preliminary experiments were conducted utilizing standard Si cantilevers for scribing furrows in soft polymer slides to investigate the influence of working parameters on the furrow depth. Poly(methyl methacrylate) (PMMA) was used as a model material due to its optical and mechanical properties. Figure 1 shows the UV-Vis transmision spectra of a spin-coated PMMA film on a glass substrate. The minimal absorption at the far-UV and visible region should allows for easy characterization of fluorescent ions and molecules.

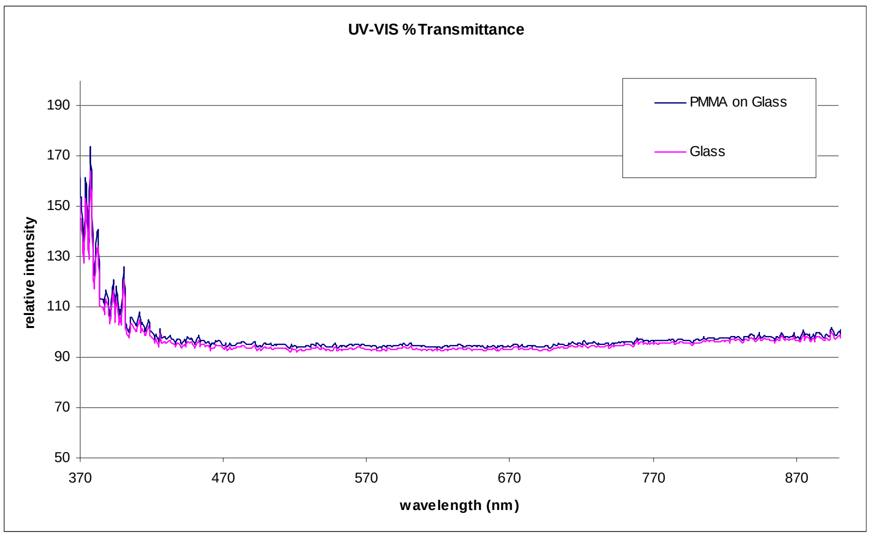

Figure 1. Transmission spectra of poly(methyl methacrylate) on glass.

PMMA slides were imaged using on tapping mode using a Digital Instruments (Bruker) Multimode II AFM and high spring constant cantilevers (k_c=40 N/m, 8nm diameter, Veeco RTESP). Figure 2 shows a PMMA slide prior to scribing and the resulting 200nm wide nanochannel from mechanically forcing the AFM tip on the sample. The channel was formed by 32 line rasters, each raster being repeated 19 times. The tapping-mode images verified the shallow trench. Current experiments are focused on enhancing the contrast of the channel with smoother samples prepared by spin coating (RMS roughness < 2nm).

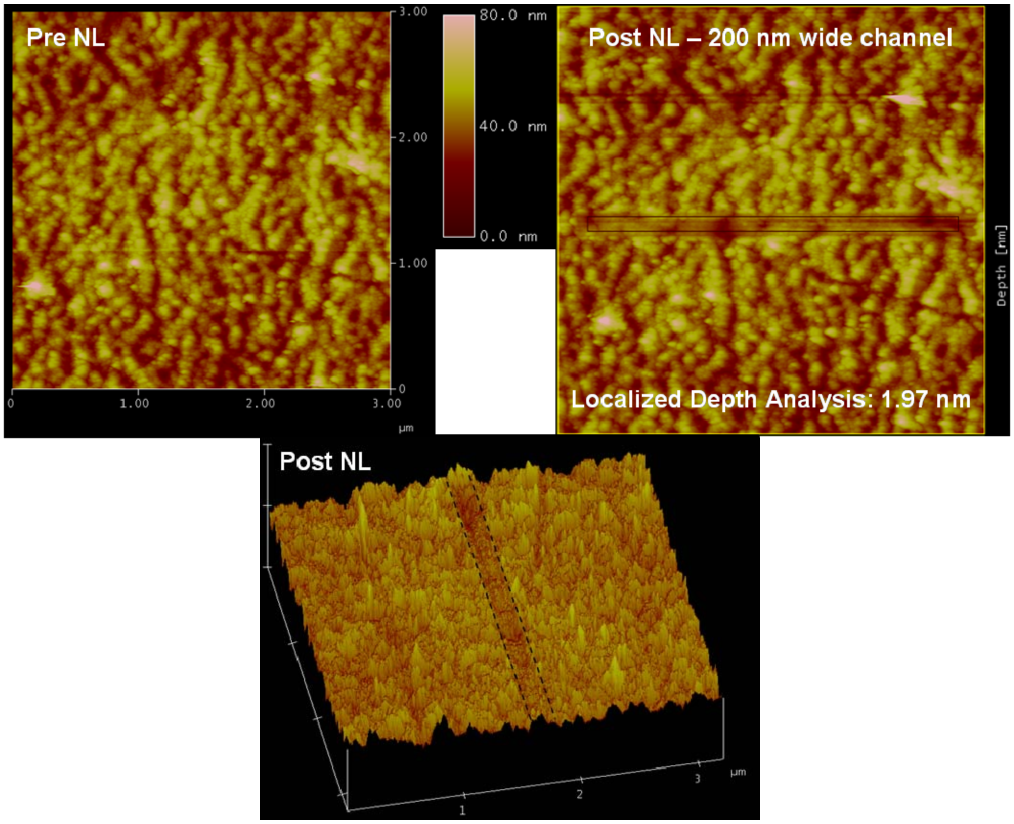

Figure 2. AFM non-contact mode images of PMMA surface prior to and following mechanical scribing.

Conclusions and Future Work

Preliminary AFM nanolithography experiments have been conducted to demonstrate the ability to mechanically scribe nanochannels on soft polymer samples. Current experiments are focused on understanding the processing conditions to optimize channel depth. The working parameters being considered include the applied load by the cantilever, the number of scribing cycles, the scribing speed and the scribing feed, and their effects upon surface roughness, surface depth and material removal rate. The discussed fabrication process could potentially be scaled up by integration of a cantilever line-array on a modified AFM driving head. Electric-field and solvent-assisted variations of the technique can also be employed to improve feature resolution. Nanofluidic devices offer a means of integrating electrochemical and optical sensing on the same device platform, for verification and monitoring of aqueous solutions containing SNM. These devices would allow rapid detection of SNM in nuclear waste streams or water supplies without the need of expensive and environmentally harmful chemicals.

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