Summary

Functionalized monolayers of alkylsilanes on silicon oxide have been employed as well-defined platforms for surface patterning and sensing. Host monolayers of β-cyclodextrins (β-CDs) were prepared and characterized in detail. These host monolayers have been utilized as molecular printboards by patterning them with suitable guest molecules using lithographic techniques. Fluorescent guest molecules that could bind to the β-CD monolayer via two host-guest interactions created stable, yet reversible fluorescent patterns. The patterns were visualized using confocal fluorescence microscopy. Employing dendrimers that bind via multiple interactions resulted in very stable patterns on the molecular printboard. The immobilized dendrimers function as 'molecular boxes' for anionic dye molecules. Vertical amplification of the patterns was accomplished by electroless deposition of metals on dendrimer-stabilized colloids, generating metal lines of less than 100 nm high on an insulating surface. In addition, monolayers have been applied in microfluidics networks for sensing purposes. Monolayers carrying fluorescent groups were immobilized inside microchannels, where they could sense the acidity of fluids by their fluorescent properties.

A literature overview of self-assembled monolayers (SAMs) on silicon oxide is presented in Chapter 2, which covers the aspects of monolayer formation and subsequent derivatization. The last part of this chapter focuses on the application of SAMs on silicon oxide in nanotechnology. Lithographic techniques that may utilize SAMs, such as photolithography, soft lithography, and dip-pen nanolithography are included.

Chapter 3 describes the preparation of β-CD host monolayers on silicon oxide. An ordered and stable cyano-terminated monolayer was modified in three consecutive surface reactions. Detailed characterization of all monolayers by contact angle measurements, ellipsometric thickness measurements, Brewster-angle infrared spectroscopy, X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry indicated the formation of a densely-packed cyclodextrin surface.

The β-CD monolayer binds suitable guest molecules in a reversible manner as was shown by adsorption and subsequent desorption of a divalent fluorescent guest molecule. From the desorption data a binding constant was obtained, which corresponds well to previously obtained results with a divalent guest molecule on β-CD monolayers on gold, reflecting the similarity between β-CD monolayers on gold and on glass.

Chapter 4 deals with the use of β-CD monolayers on silicon oxide as molecular printboard. Several fluorescent guest molecules, effectively binding through a divalent interaction, have been used for patterning the molecular printboard via lithographic techniques such as microcontact printing and dip-pen nanolithography. Patterns of (sub-)micrometer dimensions were produced, and the stability of the patterns toward rinsing with aqueous solutions was investigated by monitoring with laser-scanning confocal microscopy (LSCM). In addition, fluorescence microscopy was employed to assess the long-term stability of the patterns, and to quantify the relative amount of molecules that was transferred to the surface upon microcontact printing.

Chapter 5 describes how the molecular printboard is patterned with 5th generation poly(propylene imine) (PPI) dendrimers, which bind in a quasi-irreversible fashion from aqueous solutions. Like in solution, the immobilized dendrimers can be used as a 'molecular box' for the encapsulation of anionic dye molecules such as Fluorescein and Bengal Rose. The encapsulation process is reversible, which was demonstrated by emptying the dendrimers and subsequently filling them with a different dye molecule. In addition, immobilized individual dendrimers, filled with fluorescent molecules, were studied by LSCM. Preliminary single-molecule experiments were performed by extracting Oregon Green 514 (OG514) dyes into the dendrimers in solution, after which they were spin-coated on a glass surface. LSCM images of single OG514 dyes are clearly different from dendrimer images, suggesting that single dendrimer molecules filled with OG514 dyes were observed.

Chapter 6 describes the use of immobilized dendrimers as templates for the electroless deposition of metals. Two procedures to generate less than 100 nm high metal wires on an insulating surface are presented. The first employs electrostatic interactions between the protonated PPI-dendrimer core and aurate anions to prepare dendrimer-stabilized gold colloids in solution. Patterning the molecular printboard with these dendrimer-stabilized colloids, followed by electroless deposition of copper

resulted in the selective growth of copper on the patterned areas. In the second procedure poly(amido amine) (PAMAM) dendrimers are immobilized on the β-CD monolayer and subsequently Pd-containing ions are coordinated to the amino and amido groups of the dendrimers. Selective electroless deposition of cobalt yielded cobalt lines of ca 60 nm in height.

SAMs can be implemented in microfluidics devices. Chapter 7 describes the use of monolayers bearing fluorescent groups for optical sensing of acidity in microfluidics devices. SAMs carrying a Rhodamine derivative were prepared inside glass microchannels. It is shown that the fluorescence from the monolayer can be switched 'off' or 'on' by flowing basic or acidic organic solutions through the microfluidics network, respectively. When acidic and basic solutions were introduced simultaneously, the mixing of the two solutions could be monitored by LSCM. In addition, a different fluorescent group was attached to a monolayer to monitor the pH of *aqueous* solutions in microfluidics devices. In this case, a hybrid system consisting of glass and PDMS was employed.

The results presented in this thesis demonstrate the ability of SAMs to create functional surfaces that can be employed as molecular platforms. Employing non-covalent interactions between guest molecules and a host monolayer allows the formation of stable, yet reversible patterns depending on the number of interactions. These immobilized guest molecules may act as templates for further functionalization, providing new strategies for nanofabrication. Combining SAMs with microfluidics devices exploits the high surface to volume ratio to create robust functional interfaces that may find application in fields like sensing or catalysis.