NanoSystemsEngineering: NanoNose
Final Status, March 2011

The Nanonose project is based on four research projects (VCSELs, 3D nanolithography, coatings and system integration). Below, the major achievements in the four research projects are described.

VCSEL based light source and detector (project 1)

Self-mixing interferometry in VCSELs has been used to measure displacements of TOPAS-cantilevers (made in project 2) in the set-up shown in Figure 1. A detection limit of 0.2 nm was reached, which is on the same order as the thermal movement of the cantilever. The set-up was also used to characterise the influence of the driving current of the VCSEL (Figure 2b), and the average distance between VCSEL and cantilever. Concerning the driving current a zero sensitivity spot was found and simulations were undertaken to investigate this zero sensitivity. Simulations of an optimised VCSEL design has also been undertaken and resulted in a publication. A VCSEL design optimised for self-mixing sensing can increase the sensitivity with ~80 % . The experimental investigations also showed that the voltage over the laser diode responds to the cantilever movements and gives a signal that is good enough to be used for detection of the cantilever movement (Figure 2 a and b).

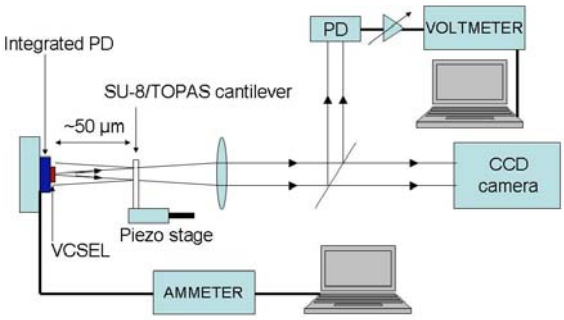

Figure 1: Schematic drawing of optical set-up.

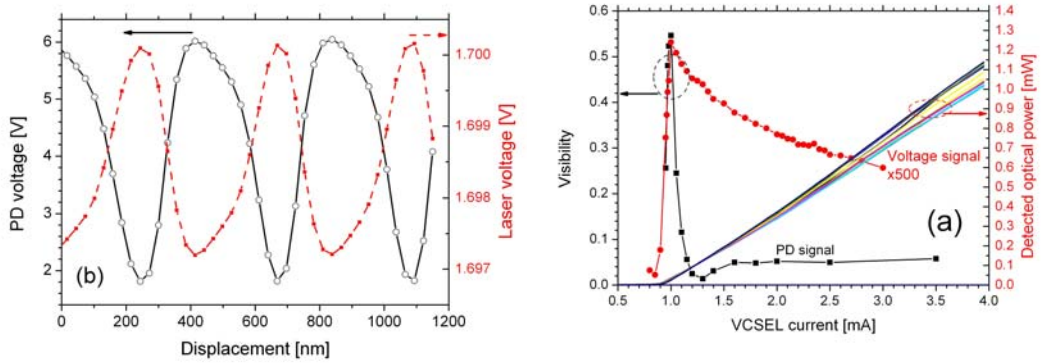

Figure 2: Signal from external photodetector during feed-back from Topas cantilever at a distance of 35 micrometer from laser. The sensitivity is ~45 mV/nm at the steepest part, which gives a minimum detectable deflection below 0.2 nm.

VCSEL-arrays (2x9) with emission windows in 2 directions and glass substrates (through which the bottom emission can escape) with metal pads have been fabricated at DTU-Danchip in order to facilitate the integration with both cantilever and an external detector. By collaboration with ULM Photonics we also got hold of VCSEL-arrays with integrated photodetector (Fig 3) that were diced, bonded and mounted to fit with the experimental set-up in project 4.

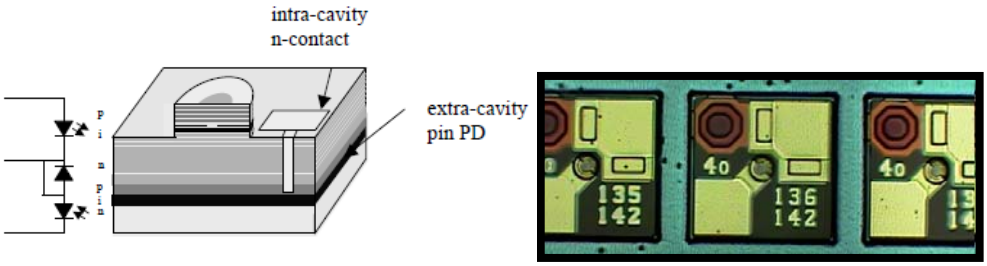

Figure 3: Sketch of ULM-VCSEL with integrated PD and photo of part of array.

A master student has been supervised in order to investigate the possibility of using self-mixing in VCSELs to detect the resonance frequency of silicon cantilevers. A set-up was built for this purpose and the resonance frequency was detected.Finally, we have also investigated (both theoretically and experimentally) the possibility of coating the VCSEL itself with a coating from project 3 and using it as a sensor (Figure 4). This was possible but the measured sensitivity was not very good. The reason for the low sensitivity was not identified. The patenting possibilities were investigated but seemed small.

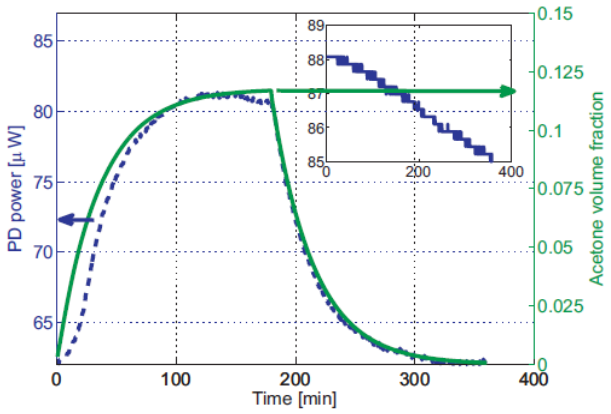

Figure 4: Coated VCSEL's response to acetone. Inset shows reference VCSEL with no coating.

3D nanolithography for self-aligned nano- and microstructures (Project 2)

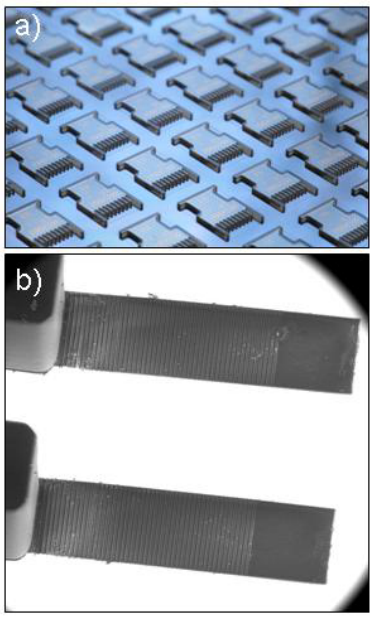

Figure 5: Optical microscope image (a) and scanning electron image (b) of imprinted TOPAS cantilevers. In (a) the cantilever chips are placed on a carrier wafer – ready for functionalization.

A process sequence for fabrication of cantilever sensors using nano imprint lithography (NIL) has been developed. The process builds on our previous experience with fabrication of cantilevers in the negative epoxy-based photoresist called 'SU-8' by UV-lithography. The thin polymer cantilevers are now defined by NIL instead of UV lithography. First, a silicon carrier wafer is coated with an optimised Teflon coating. Next, a layer of imprintable polymer is spin coated on top of the Teflon layer. A silicon stamp with the cantilever structures is then used to imprint the cantilever layer. Subsequently, a thick layer of SU-8 is structured on top of the thin cantilever layer (this will be the support structure). Finally, the complete device is lifted off from the Teflon layer by the use of tweezers.

Best results are obtained when only the outline of the cantilever is imprinted. Hereby a minimum of material needs to be displaced. Figure 5 shows micrometer sized cantilevers made in the thermoplast Topas, which is known to be stable over time and which is biocompatible. It is therefore a perfect material for cantilever-sensors. SU-8 has some limitations in terms of long time stability and drift due to continuous cross linking of the material. These issues are avoided when using Topas. Figure 5b, demonstrates that it is possible to

nanostructure the cantilever surface in the same imprinting step. The ripples in the cantilever surface are made by structuring the silicon stamp in the areas of the cantilever.

A wafer scale functionalisation scheme has been developed in collaboration with project 3. The principle is illustrated in figure 6. Before the cantilever chips are released from a carrier wafer a shadow mask (fabricated in silicon) is clicked on top of the carrier wafer. The shadow mask has openings above the cantilevers and can therefore ensure that only specific cantilevers are functionalised. The shadow mask concept has been developed to facilitate complete wafer scale functionalization and cantielvers have been functionalized using plasma polymerization. Even closely spaced cantilevers (500 µm pitch) have been coated individually by using two different shadow masks with different openings. For example, coatings specific to water and acetone vapour have been deposited and used for sensing in collaboration with project 4.

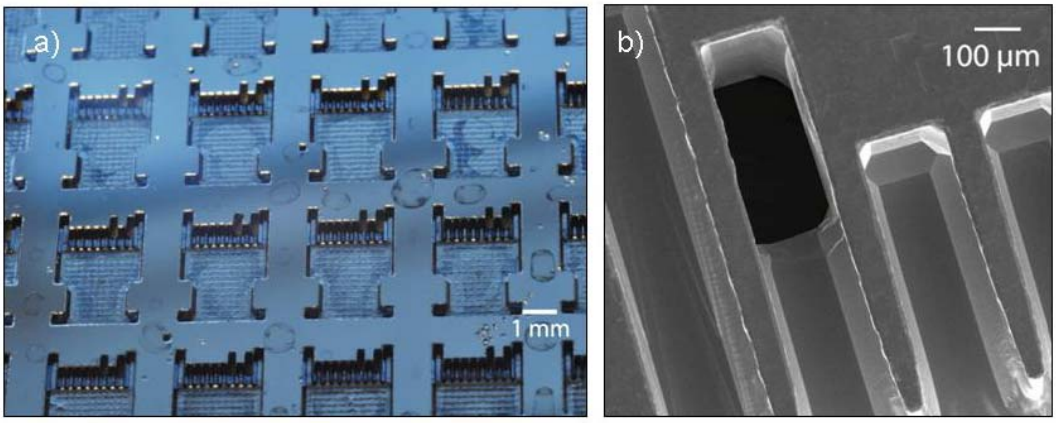

Figure 6: Optical microscope image (a) and scanning electron image (b) of silicon shadow mask for wafer-scale functionalization. The shadow mask is an 'inverse' of the cantilever chip geometry and openings in the mask define which cantilevers to be functionalized.

Patterning of Ultrathin Sensor Coatings (project 3)

This part of the NanoNose project has focused on functionalization of sensor surfaces and characterization of these surfaces to evaluate their performance as gas sensors. Surfaces have been functionalized by plasma polymerization. Quartz Crystal Microbalances (QCMs) are used for gas sorption/desorption characterization of the polymer thin films. A flow system in which four QCMs can be exposed to varying concentrations of analyte gas (Figure 7), and a system for data acquisition and flow control has built.

Figure 7: Flow system with temperature and flow control. Four QCMs can be characterized simultaneously.

The sensor coatings are not designed for specific response towards a particular compound but rather as having partial and differing responses to many compounds. By applying Principal Component Analysis (PCA) on response data of 8 different coatings ranging in polarity from highly polar (maleic anhydride) to highly unpolar (perfluorodecene) it was demonstrated that these coatings are capable of discriminating between 6 solvents of variable polarity: water, ethanol, benzodioxol, acetone, 1-pentanol and heptane. Different mathematical approaches to obtain optimum predictive quality were explored in a published collaboration with DTU Informatics (Figure 8).

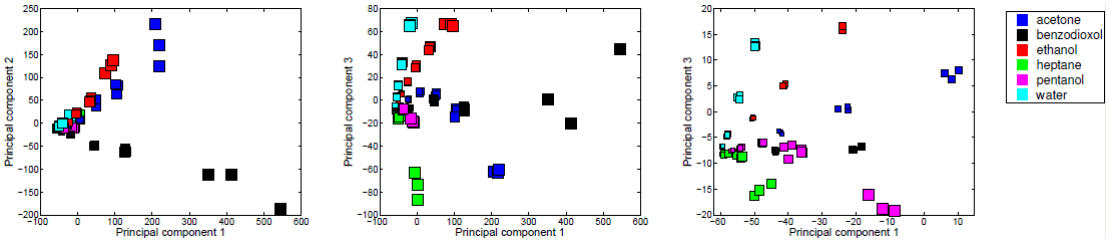

Figure 8. Principal component analysis of the sensor coating responses to six different solvents. The area of each symbol is proportional to the solvent concentration. Clear separations of all solvents are seen for combinations of the first three principal components.

The use of plasma polymer coatings on other sensor devices than cantilevers was also demonstrated. Deposition of ppPS on a photonic crystal dye laser allowed for the detection of ethanol at a detection limit of 100 ppm, while the latter sensor device was insensitive to humidity changes from 35%RH to 80%RH.

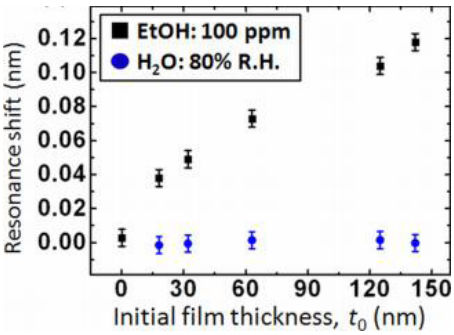

Figure 9. Sensor response on plasma polymerized polystyrene on a photonic crystal dye laser. The coating responds to ethanol vapor but not to water vapor.

As an alternative to the plasma polymerization, a molecularly imprinted polymer (MIP) was tested. A MIP is created to detect a specific compound. This specificity is obtained by having a template present during polymerization. After polymerization the template is desorbed from the polymer and leaves a small cavity. If the targeted molecule is present in the surroundings it will easier adsorb into the MIP than into another polymer with the same composition, since it fits perfectly in the cavity. As a target molecule 1,3-benzodioxole, that has a similar structure to the drug precursor safrole, was chosen. Several different polymer compositions were tested. For each MIP, a blank, non-imprinted, polymer with the same composition was made as a reference. The monomer solutions were sprayed onto a QCM-crystal and then UV-cured. Two of the MIPs showed promising results in the QCM tests, both in sensitivity and selectivity. Initial test on commercial Si-cantilevers were made with these polymers. They were deposited on the cantilevers with a µ-spot system to ensure that the same amount of polymer was present on all of the cantilevers. The cantilever deflection is significantly increased when using the MIP coating (see Figure 10).

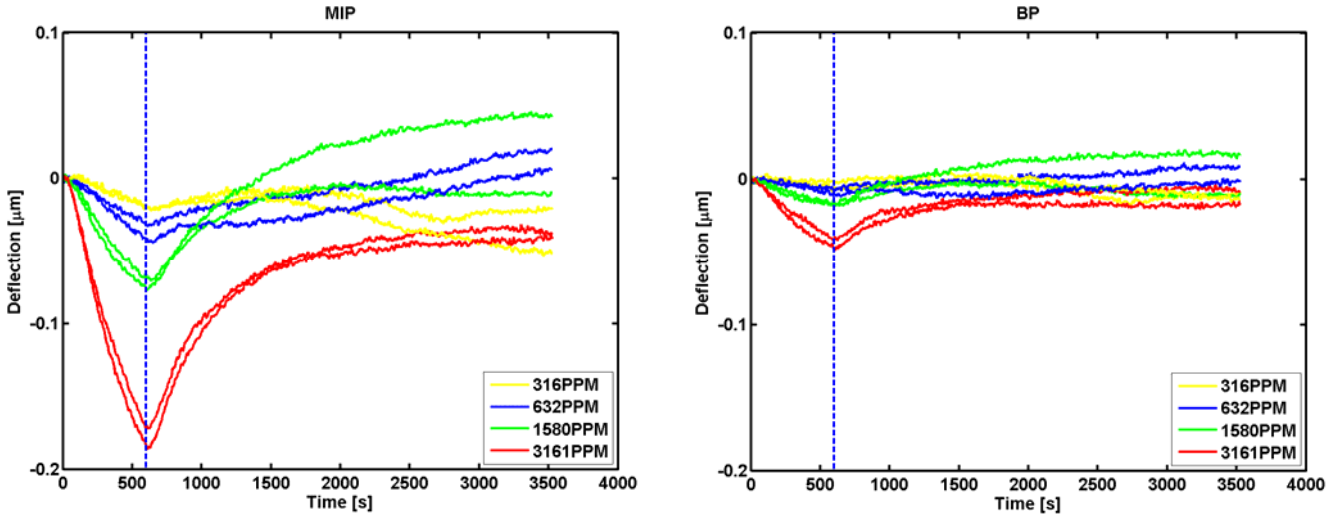

Figure 10: MIP (left graph) and blank polymer (right graph) on Si-cantilever tested at different concentrations of benzodioxole.

Mass measurements and system integration (project 4):

To enable complete control of the gaseous environment during measurements an environmental chamber was designed and built during the first phase of the project. The chamber comprises a lid with a quartz glass opening for visual inspection and optical measurements, several flanges for electrical connection to the Nanonose device, and inlets/outlet for gasses. A double laser-optical system for external readout of the cantilever bending has been designed and fabricated. This chamber has facilitated many initial tests of our cantilever structures. In the second stage (measurements of the deflection of the cantilevers using VCSELs) a miniature setup has been designed and fabricated. The miniature setup is shown in Figure 11. The setup ensures that VCSEL and cantilever chip are fixed and positioned to read individual cantilevers. The miniature setup features complete positioning control in all dimensions while being able to fit into the environmental chamber. This setup has been used to obtain VCSEl based read-out from TOPAS cantilevers functionalised for water vapour (5 parts pr thousand) detection (PVP coated). See Figure 12. The measurements are simple to implement since only 2-D alignment is needed. This has been found to be a great advantage of the VCEL system compared to the normally used optical leverage system. Also, the sensitivity is in the sub-nanometer range and the readout electronics required for this is only a voltmeter and a current source. Thus we see the presented read-out as a very promising candidate for simple, compact and highly sensitive deflection detection.

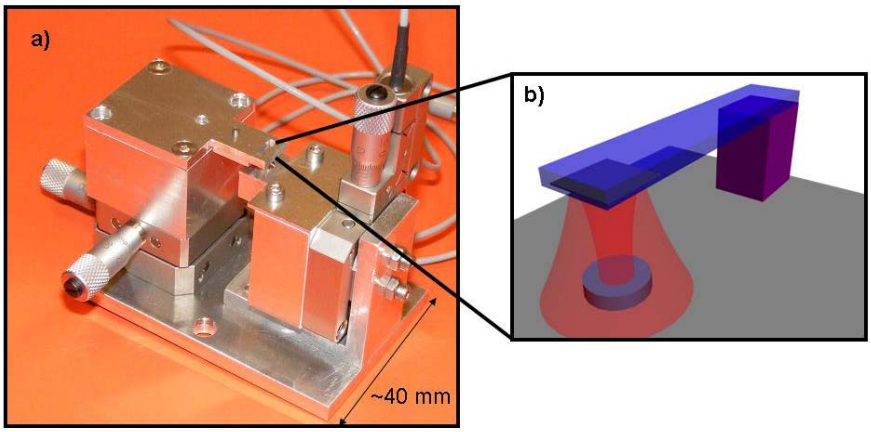

Figure 11: Photograph of setup for holding and aligning VCELS and cantilevers (a). The inset shows the position of the placement of the cantilever and VCEL unit.

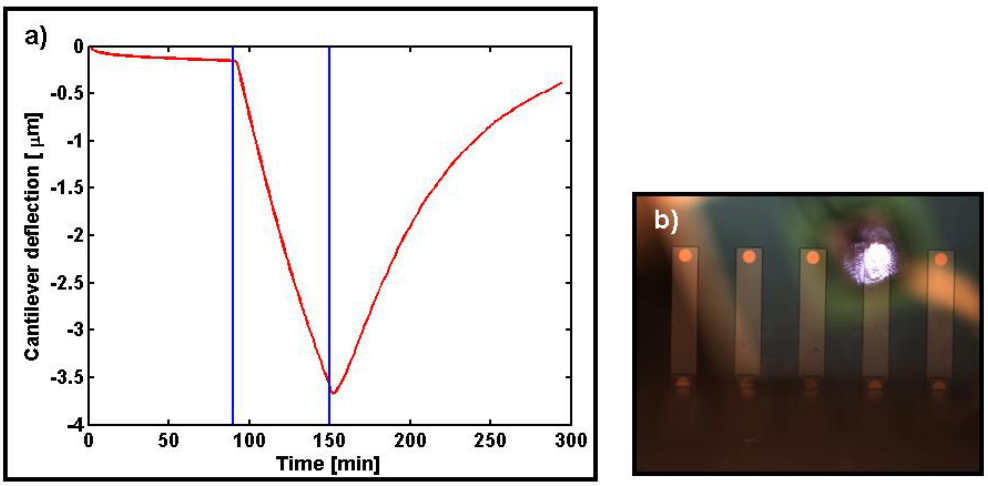

Figure 12: Cantilever deflection as a function of time read-out by VCSEL (a). The PVP coated cantilever is exposed to water vapor in the region confined by the blue lines. The laser spot is clearly focused on the cantilever (b).