

# **SUMMER STUDENT REPORT**

## **DESY HAMBURG 2011**



### **In Situ microfluidic GISAXS experiments**

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06.09.2011

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## **I. Introduction**

The purpose of the experiments with a microfluidic cell is to develop methods of producing surface structures from metal nanoparticles deposited in an ordered pattern with high spatial density and controllable size.

The ordered patterning of metal nanoparticles on solid surfaces is important for possible applications in nanocatalysts, nanoelectronics, bioelectronics, magnetic recording devices, and gas sensors. The advantage of the influenceable self assembly and easy processability of polymers have enabled the low-cost fabrications of integrated micro-and nanosystems with a high degree of complexity and functionality. Especially block copolymers have attracted immense interest for nanotechnology applications because of the selective affinity of the nanoparticles for a particular block of the block copolymer film, which will provide a controllable localization of nanoparticles.

As one possible process is considered creation of nanowires in a two-step process:

1. Produce parallel channels by rubbing polymer-coated sample with velvet
2. Fill channels with gold by microfluidic treatment

## **II. Preparation part**

I have used a microfluidic cell, shown in Figure 1. The top window of the cell was kept thin and transparent to visible light in order to allow for optical characterization. The whole channel is brought in contact with the surface of a variable flat substrate (e.g., a glass surface or silicon wafer). The complete assembly (top surface with channel system and substrate) is then attached on the x-ray goniometer via a rigid metal clamp. In order to prevent contamination of the investigated substrate surface via diffusion of adhesive, no glue is used to seal the channel. This channel was machined in a TOPAS foil (length of 75 mm, width of 25 mm, and thickness of 1 mm) which was then bonded to a 200 m thick TOPAS

window. The channel has a Y shape (see Fig. 1) in such a way that mixing of solutions can be realized.

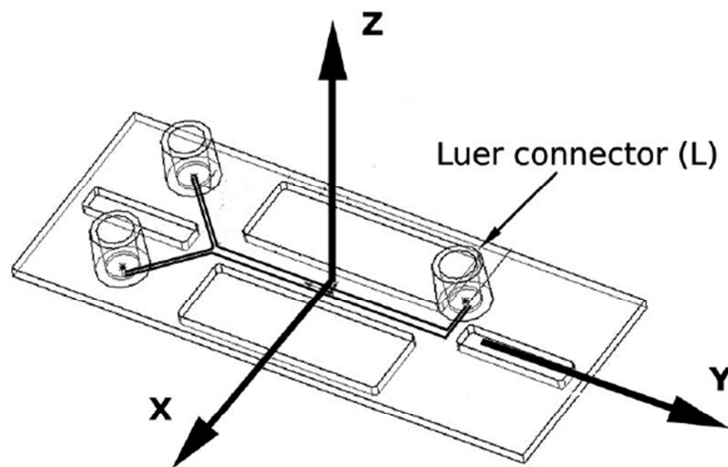


Fig 1. Design layout of the TOPAS part of the fluidic cell. The asymmetric design with two inlets and one outlet or vice versa enables mixing of fluids. The channel system itself is shown in dark gray. Included is a real space coordinate system.

The thin channel walls are quite fragile and can easily be twisted during sample preparation. We thus reinforced the structure by leaving two bridges that can be easily cut away once the setup is locked in the clamp (see Fig. 2).

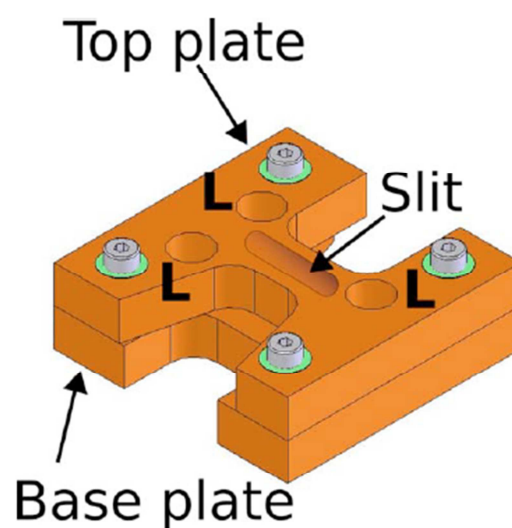


Fig 2. Design layout of the metal clamp which allows for a sealing of the cell body to various substrates without using glue. The openings for the Luer connectors are shown (L) as well as the slit for optical observation.

Sample (for the preliminary experiments, I used a glass slide 1 mm thick) is placed in the cavity on the surface of the base plate of metal clamp, then the sample is installed on top of a microfluidic cell with attached connectors to terminals. After that, the whole structure is covered by top plate and fixed with 4 screws in the corners of the structure.

Injection of the filtered solutions was performed using a syringe pump model PHD 2000 infuse/withdraw from Harvard Apparatus. The syringes were connected to the cell via 1.8 mm inner diameter silicone tubes and Luer adapters.

One of the problems immediately arose in the first experiments is the problem of leakage of fluid between the microfluidic cell and the sample. Such drops of liquid hinder the passage of X-ray beam in GISAXS experiments and distort the information. Using a special dynamometric key I changed the torque applied to each of the screws, thereby affecting the pressure microfluidic cell and in particular the channel on the sample.

To prevent leakage, we can change two parameters:

- The rate of flow through the channel, thus changing the fluid pressure in the channel wall due to viscosity of the medium-pressure syringe and injecting device
- Torque attached to each screw, thereby changing the force that must be overcome in the fluid channel to form a leak. Also do not forget about the fact that when a large stress can strain the channel cells to form new leaks.

I changed the torque applied to each screw using a measuring key, and used values of - 2.5, 5, 7.5, 10, 12.5 and 15 N m. Using the latest torque I accidentally smashed a glass slide and it formed cracks. Also conducted some estimations I changed the velocity of the fluid in the channel of a microfluidic cell with 0.005 to 0.1 ml / min. Also, as I said before, I improved the connection pipes having wrap them with rubber of gloves from the laboratory) and had a few experiences, turning the iron construction (metal clamp) of 180 degrees, so that tube stuck down. This should minimize the pressure of the liquid in them. The most optimal from the standpoint of lack of fluid between the sample and microfluidic cell experiment - torque - 5 N m flow rate - 0.05 ml / min. Although still a small amount of liquid remains between the two planes.

Therefore we want the liquid to flow across the sample - one has to check if this is the case if the sample is used upside down - and we do not want any leakage on the sample.

We have another idea how leakage might be prevented: To use the pump in refill mode instead of infuse mode. This means a tube will lead from a bottle with liquid to one connector of the microfluidic cell, on the other side of the microfluidic cell a tube will lead to an empty syringe in the pump. By using refill mode, the liquid will be sucked across the sample towards the syringe. The third connector will either be closed by a tube with a knot or it will also be connected to the bottle with liquid.

Thus, we remove the excess pressure in the pipe caused by friction of the fluid channel wall.

Research has shown that for laminar flow in a circular tube maximum speed is on the tube axis. At the pipe wall the velocity is zero, since fluid particles coated with a thin inner surface of the pipe fixed bed. From the tube walls to the axis of the velocity increases smoothly. The graph of the velocity distribution over the cross section the flow is a paraboloid of rotation, and cross axial plane of a paraboloid - a quadratic parabola.

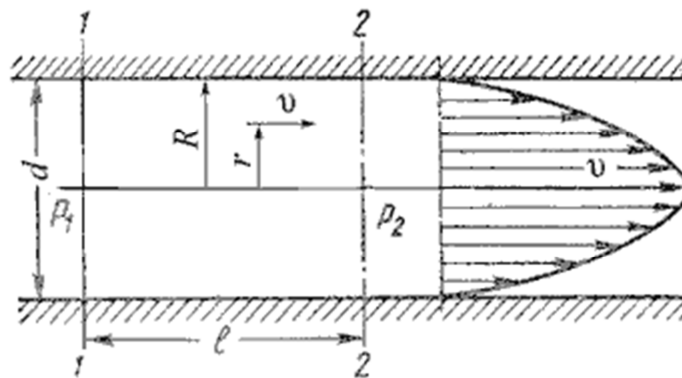


Fig. 3. Diagram for consideration of the laminar flow

The equation relating the variables  $u$  and  $r$ , is as follows:

$$u = \frac{P_1 - P_2}{4\mu l} (R^2 - r^2)$$

Where  $P_1$  and  $P_2$  - pressure, respectively, in sections 1 and 2, and  $\mu$  is a liquid viscosity.

Thus aligning the pressure ( $P_1 - P_2$ ) can reduce the load exerted by the fluid on the entire structure and to avoid leaks.

### III. Experimental Part

#### A. Substrate Cleaning and Polymer Coating.

Glass substrates ( $2.5 \times 7.5 \text{ cm}^2$ ) were cleaned as follows: sonication in dichloromethane at  $35^\circ\text{C}$  for 15 min, water rinsing for 5 min, and then soaking in the cleaning bath at  $80^\circ\text{C}$  for 15 min. The cleaning solution was composed of 100mL of 96%  $\text{H}_2\text{SO}_4$ , 35mL of 35%  $\text{H}_2\text{O}_2$ , and 65 mL of deionized water. The cleaned substrates were further rinsed in deionized water for 10 min and finally spin dried. A diblock copolymer polystyrene-*block*-polyethyleneoxide, denoted P(S-*b*-EO), with a total number-average molecular weight of  $M_n = 26.5 \text{ kg/mol}$ , a weight ratio of 75:25 (PS/PEO), and a polydispersity index ( $M_w/M_n$ ) of 1.05 was purchased from Polymer Source Inc. The polymer was dissolved in benzene at different concentrations and used for the coating step. The precleaned silicon substrates were coated using the spincoating method (2500 rpm, 30 s). The polymer films (65 nm) were solvent annealed inside an inverted beaker that fit a Petri dish containing 20 mL of benzene. The annealing setup was finally moved to an unsealed chamber that was placed in a hood with a controlled humidity of 30% at room temperature for 48 h.

#### B. Control of mixing of the fluid as a function of flow rate.

For the experiment of mixing, I used ordinary pure water and the same, but tinted in blue ink. After that, changing the velocity of fluid flow, the observations of channel were made with an optical microscope. I have plot a graphs intensity of the blue channel of the image to the sum of the three channels (red, green, and blue). This makes it possible to estimate the concentration of water tinted with blue paint at each of our channels. At high flow rates the flow of the mixing of two liquids happens slowly, we can also see a clear border between liquids (Fig 4a). At low flow rates the point of fluids mixing move closer to the input of the channel as the boundary between the liquid flows spreads out, which allows to determine the concentration of blue ink as a function of distance from the channel. (Fig 4c)

Optical observations and calculations of Reynolds numbers for certain parameters of the system make it possible to say exactly that the flow is in the lamellar regime, and the influence of surface roughness of the polymer and channel bends are negligible.

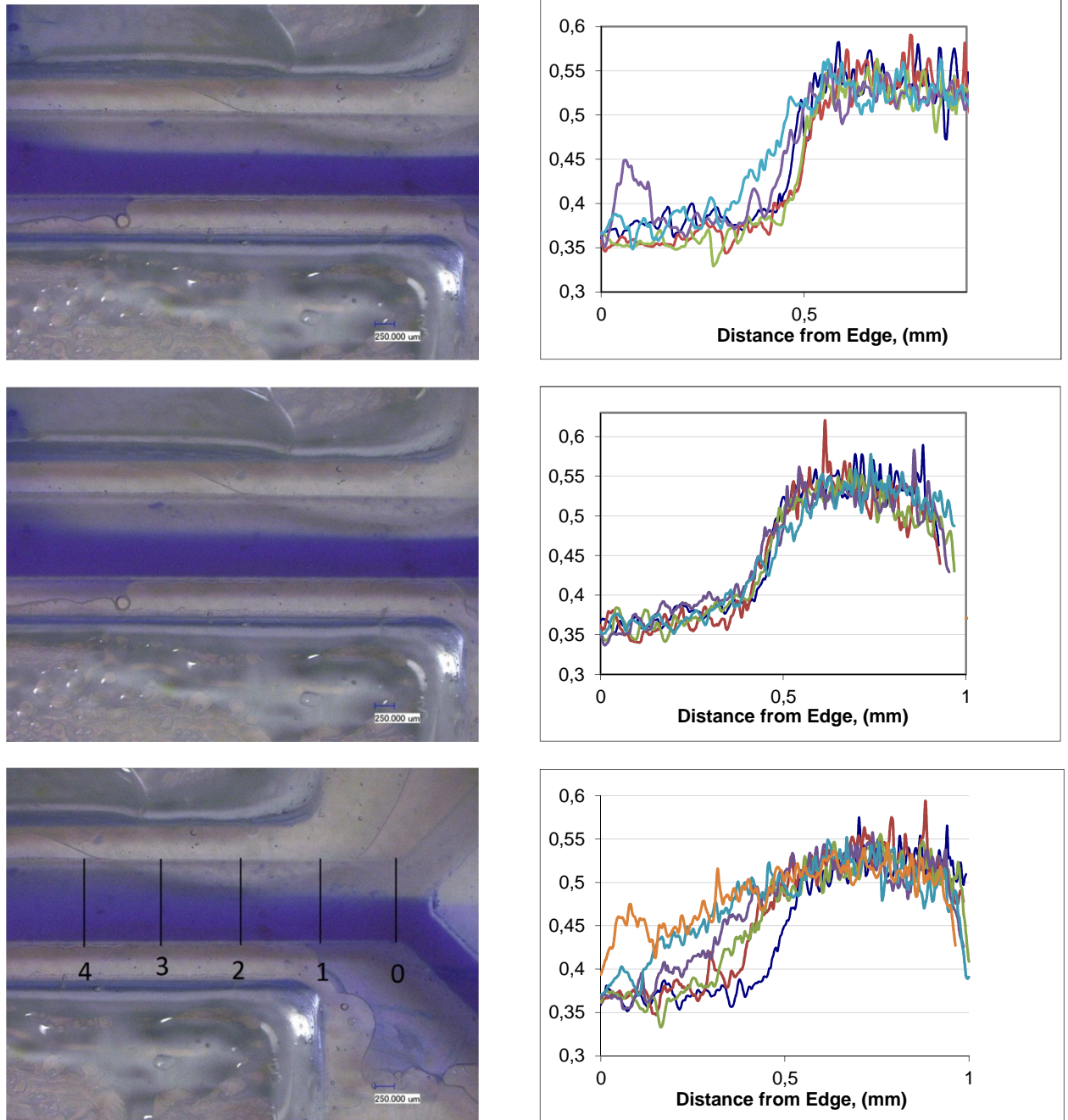


Fig 4. Optical investigation of a mixing experiment. The left column of images shows optical micrograph scale bar is 1 mm. The right column of images shows the profile analysis in terms of relative color intensity blue/ (red+green+blue) from the RGB CCD channels at various cutting positions shown as overlay to the optical image (left). From the bottom to the top the flow rate increases (0.015, 0.15 and 1.35  $\mu\text{m/s}$ ).



### C. Optical observation

In preliminary experiments revealed several problems, such as:

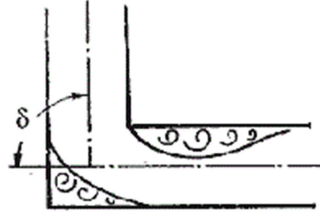
- Polymer holding on a glass substrate is not stable, and at high rates the flow possible detach the polymer along the length of the channel.
- Deposition of gold occurs only at borders channel and, occasionally, large dislocations in it.

Optical observations are not given the opportunity to obtain the dependence of the ability of the polymer absorbing ability from diameter of the gold nanoparticles.

Sample	Polymer type	Flow Rate ml/min	The presence of polymer	annealing
GHAC1-A1	PPs0,05	0,005	no	no
GHAC1-A2	PPs0,05	0,001	no	no
GHAC2-A1	PPs0,05	0,005	no	no
GHAC6-A1	PPs0,05	0,001	yes	no
GHAC6-A2	PPs0,05	0,001	no	no
GHAC5-1	PPs0,1	0,001	yes	yes
GHAC5-2	PPs0,1	0,005	yes	yes
GHAC4-1	PPs0,05	0,01	yes	yes
GHAC4-2	PPs0,05	0,005	yes	yes

It may be noted that the maximum flow rate attained values reach values of 0,01 ml / min. This suggests that the experiments take place in the laminar regime. From this it can be assumed that the fluid in the channel interacts with the polymer only by its lower layer, and deposition of gold on the surface involved not all the gold nanoparticles. Perhaps setting the stage for a turbulent flow rates will be raised in this process. Raising the rate of flow there is the threat of obliteration of the polymer substrate, while creating bumps and obstacles in the channel can cause flow separation and vortex formation.

Perhaps that such processes occur in the bend of the pipe, the supply fluid from the connector to the input of channel. However, with such low flow speeds the influence of this phenomenon is negligible.



I make the measurement, in which were found positive effect pre-annealing sample at the connection force the polymer with substrate material. (Fig 5)

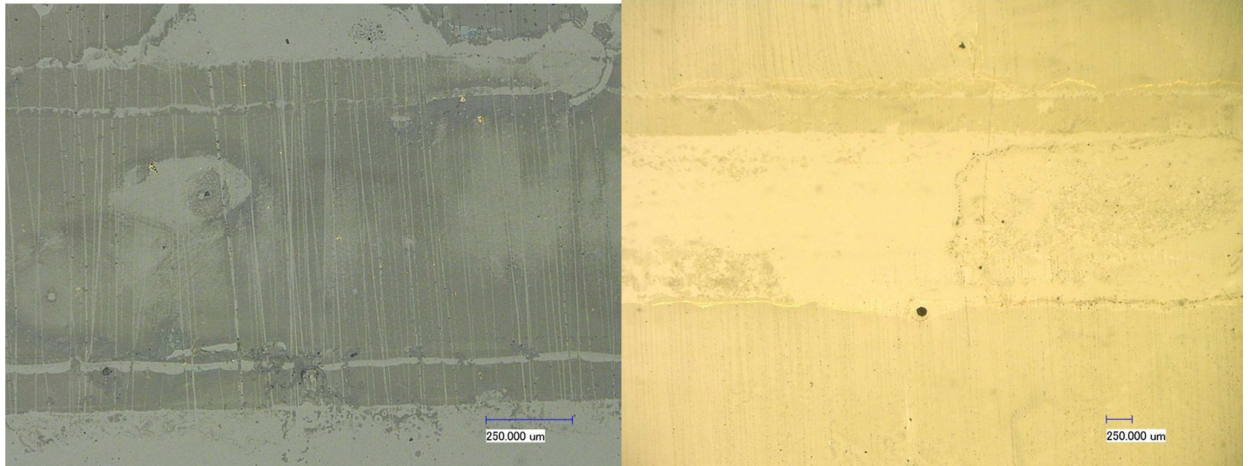


Fig 5. Optical images of the sample with the polymer, after the experiment. Left sample affected by annealing at a temperature of 150 degrees C. for one hour, the right sample do not. Polymer inside the right sample channel is absent.

#### D. GISAXS measurements

Microbeam grazing incidence small angle x-ray scattering ( $\mu$ GISAXS) testing of the cell was performed at beamline P03 at HASYLAB DESY in Hamburg. The wavelength was 0.138 nm and moderate microbeam focusing was achieved using beryllium compound refractive lenses beam size of  $40 \times 20 \mu\text{m}^2$ . The two dimensional 2D detector, a PILATUS 300k pixel detector (readout time  $< 3$  ms and pixel size  $172 \mu\text{m}$ ), was placed at 1.9 m from the sample. The incident angle was set above the critical angle for total external reflection from the glass substrate  $\alpha_i = 0.5^\circ$ .

We define our coordinate system as follows: The X axis is oriented parallel to the incoming direct beam and oriented in the beam direction. The Z axis is chosen vertical and points upwards (normal to the sample surface) and, as a result, the Y axis is lying in the plane of the sample, normal to the direct beam. The incident angle is noted  $\alpha_i$ , and a given exit beam is defined by the angle  $\alpha_f$  it

forms with the XY plane and the angle  $\psi$  between its projection in the XY and the X direction, see Fig. 6. In order to identify the characteristic features introduced by each component of the setup, the diffuse scattering was measured in (GISAXS configuration for the bare substrate glass) and a sheet of TOPAS. The signal measured for a complete empty fluidic cell was then measured and compared to these references.

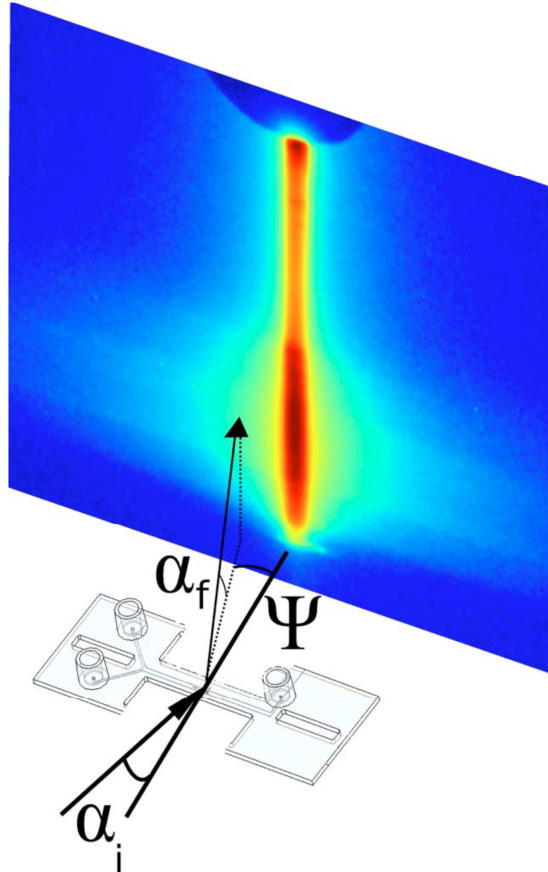


FIG. 6. Sketch of the GISAXS geometry.

Figure 7 shows the 2D images recorded in each case. In the upper central part of each image, at a position corresponding to  $\alpha_i = \alpha_f$  and  $\psi = 0$ , the shadow of a beamstop is visible. Such a setup is required to prevent saturation or even damage of the 2D detector due to the high intensity of the specular reflected intensity. At lower exit angles  $\alpha_f$  one can observe the increased diffuse scattering, presenting a maximum intensity at the position of the so-called Yoneda peak.[6] This peak is located at an exit angle equal to the critical angle of the surface and is thus material dependent.

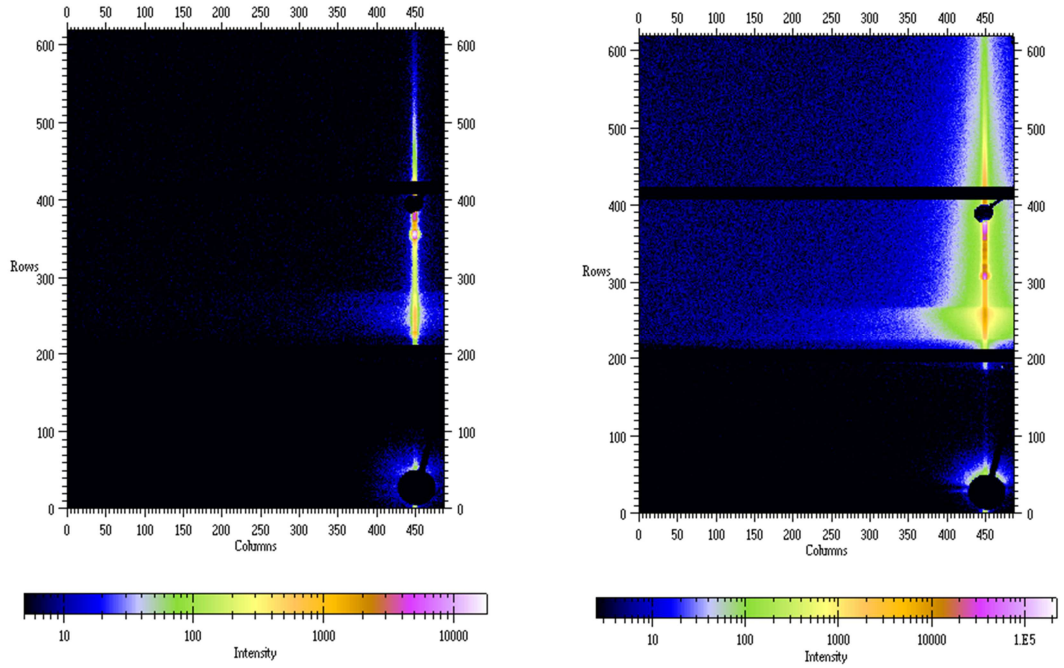


FIG. 7. Typical  $\mu$ GISAXS patterns (intensity as a function of the exit angle  $\alpha_f$  and the out-of plane angle  $\psi$ ) recorded with a two dimensional detector for the empty fluidic cell (left), and the fluidic cell filled with a flowing gold nanoparticle suspension (right).

Using vertical cuts of obtained graphs we can find the peaks corresponding to gold and materials of microfluidic cell and the substrate, we can also assess the availability of settled gold on the polymer. (FIG 8)

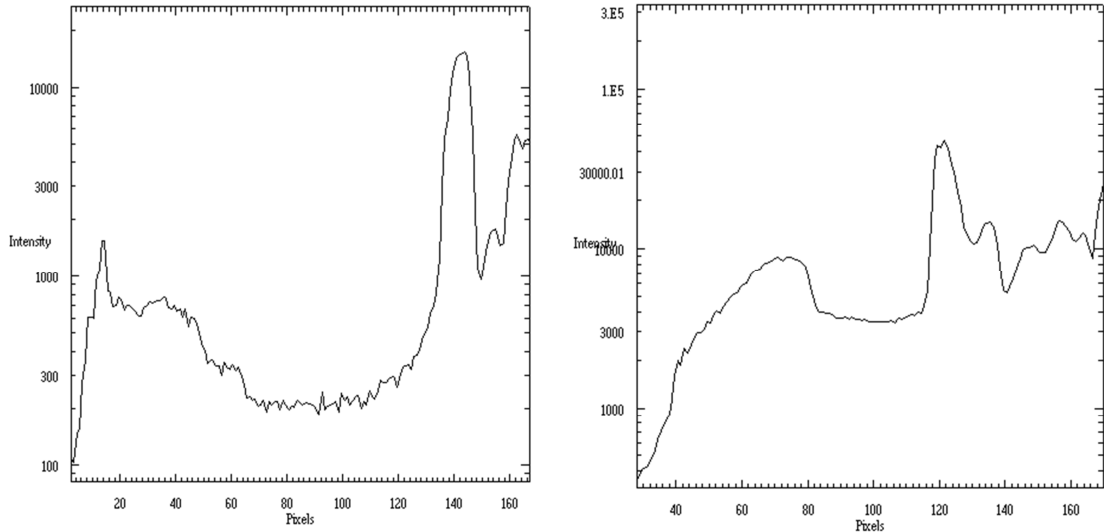


FIG. 8. Vertical cuts from the 2D GISAXS pattern shown as a function of the detector angle ( $\alpha_i + \alpha_f$ ) for the empty fluidic cell (left) and the fluidic cell filled with a flowing gold nanoparticle suspension (right)..

## **IV. Conclusion**

I showed the possibility of conducting experiments with a microfluidic cell, which optimized for GISAXS characterization of surface structures liquid - substrate. I have developed a model of experiment and computed the necessary parameters. According to the results in situ experiments were found gold nanoparticles in water flow, as well as on the surface of the polymer. This setting allows the future to open new prospects for the study of nanotechnology and microfluidics devices. Extending this work likely required in the selection of appropriate materials, as well as changing the channel geometry.

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## **Acknowledgements**

I would like to thank all people who made this trip possible for me, all people of Desy for their kindness to all summer students, all of the members of FS-PE group for their willingness to help us and the good cooperation with summer students and especially my supervisor, Stephan Roth and Gerd Herzog for their support, for his help and his willingness to answer all my questions.