I. INTRODUCTION

Fast and selective sensing of drugs or other solutes is a challenge for on-line analytics and control. Molecular imprinted hydrogels offer a selective solute recognition in water even on trace level [1] and can be combined with a microresonator as transducer. The solute sensitive hydrogel shall be immobilized on a mass sensitive resonator [2,3]. The mass sensor consists of a bridge, whose torsional vibration mode is excited via electromagnetic Lorentz forces. Solely the integrated sensing plate (Ø=5 μm) is wetted by the solution, thus reducing damping. The adsorption of mass on the surface of the plate respectively in the immobilized hydrogel is monitored by the detection of the declining resonator frequency.

To our knowledge there are different ways mentioned in the literature for microstructuring of hydrogels [4-7], from which only dry-etching of thin hydrogel layers using a metal or photoresist masks [4] seemed suitable for this approach. While it is suitable for a wide range of hydrogels and can be integrated into the MEMS fabrication process easily, the achievable aspect ratio strongly depends on the nature (mostly isotropic) of this etching process. Feature sizes down to 2.5 μm have been reported for hydrogel layers of only 1-2 μm thickness.

Here we report on the synthesis of macro-initiator based hydrogels for thin layer deposition through spin coating. In addition, high resolution structuring, integration into MEMS and their behavior in saline solutions will be shown.

II. EXPERIMENTAL

Spin coatable hydrogels. Hydrogel precursor solutions usually contain very polar and low viscosity monomers due to their water solubility, resulting in low wetting and droplet formation when spin coated. To counteract these issues, a macronitiator based hydrogel was developed and a solvent screening was done. Macronitiators are linear polymer strands with initiator groups along their backbone. Due to their high molar mass, they increase viscosity drastically, even with low viscosity monomers in solution. In addition, their lower vapor pressure of the mixture result in more consistent results. Two different protocols were developed for macronitiator synthesis.

For ion strength dependend hydrogel precursor synthesis, an in situ synthesis of a macronitiator was done [8,9]. During synthesis, sodium chloride is formed, which can not be washed out after photopolymerisation
due to high crosslinking.

As alternative to this, a benzophenone based macroinitiator was developed additionally. These macroinitiators can easily be optimized for multiple different purposes in regards to viscosity, amount of initiator groups, and functional monomers along their backbone. A typical procedure was conducted as followed: Under nitrogen atmosphere and light exclusion, 2-hydroxyethylmethacrylate (HEMA) (1530 mg, 1430 μl, 11.8 mmol) and 2-hydroxy-4-methoxybenzophenone (560 mg, 2 mmol; HEMA/2HMBP=6/1) were dissolved in 8 ml dimethylsulfoxide (DMSO). Azobis(isobutyronitril) (AIBN) in 20 ml ethanol (138 μmol, 23 mg) was stirred vigorously at 80°C for 24h. The resulting polymer was precipitated in diethyl ether and redissolved in small amounts of methanol and acetone for three times. After drying in vacuo, the solid product was crushed. The main benefits of this protocol lie in the precision tailoring of the viscosity via chain length distribution and the amount of macroinitiator. For the primer solution of pH sensitive hydrogels, macroinitiator (200 mg), tetraethyleneglycole dimethacrylate (350 μl), HEMA (400 μl), acetone (1ml) and methanol (0.2 ml), DMSO (500 μl), cyclopentanone (1000 μl) and methacrylic acid (MAA) (50 μl) were mixed and filtrated. The carboxyl group of MAA is a weak acid, thus, after polymerization, the hydrogel swells in high pH solutions.

**Structuring of hydrogels.** As described in a previous publication [8,9], the hydrogel was spin coated on adhesion promoter functionalized silicon or silicon nitride surfaces and sputtered with 200 nm titian. After structuring of the metal layer with common photolithographic methods, the uncovered parts of the hydrogel were etched via Reactive-Ion Etching (RIE) with a mixture of Ar/O2 = 3/2 and a self-bias of 200 V. This way, a highly anisotropic etching could be achieved, especially for the ion strength sensitive gels.

**Integration of hydrogels into microsensors.** In previous works, the hydrogels were integrated into a cantilever structure, where swelling processes were read out via beam deflection method. As was shown, lateral resolution for the structuring was very high and smooth surfaces could be produced. Also, measurements in different saline solutions proofed the concept of the ion strength dependency, even at high osmolarities.

Since the results of the cantilevers showed a high resolution when structured in RIE, experiments on the previously fabricated microresonator were conducted. Therefore, the adjustment crosshairs on the resonator chips were covered with tape before spin coating to allow for a precise adjustment. The primer solution for pH sensitive hydrogels was spin coated onto the chip at 2000 rpm, resulting in a layer thickness at around 1 μm. The hydrogel was structured as described before.

![Figure 1](image)

**Figure 1** left: microresonator with structured hydrogel; right: bent sensory plate with hydrogel.

As can be seen from Fig.1, the hydrogel is structured on top of the resonator with sharp borders. Due to the use of a photomask with shorter holes, there are free standing hydrogel structures, that are etched from the backside. In addition, some of the primer solution gets under the sensory plate, bending it during drying (Fig. 1, right). Current investigations aim to bypass this problem by structuring the gel together with the column of the sensory plate. It is clearly visible, that the protocol gives high resolution and an almost vertical etch profile for very thin layers of hydrogel polymers. It was even possible to optimize the primer solutions to achieve layers as thin as 500 to 700 nm through spin coating.

**III. SUMMARY**

A general protocol for spin coatable, multifunctional hydrogels was developed. Its applicability was tested through swelling experiments on cantilevers. In addition, the integration into more sensitive structures was tested on microresonators. It was demonstrated, that a resolution similar to photoresists could be achieved. In addition,
the protocol allows for a facile optimization of the hydrogel and its primer solution for different applications and layer thicknesses.

IV. REFERENCES


