

# Modification Of Polymer Swelling By UV Irradiation For Use In Chemical Sensing

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## Abstract

The effect of UV irradiation on the swelling properties of polymer layers as a function of the chain scission degree is studied, using white light interferometry. The use of patternable polymeric films and their subsequent UV irradiation treatment as a means to engineer individual sensor sensitivities in chemical sensor arrays is proposed. First results with the polyhydroxy-ethyl-methacrylate (PHEMA) before and after deep UV irradiation, for three different exposure doses are presented. The relative expansion of the layer was clearly found to depend on the irradiation conditions.

## Keywords

Polymer modification, chemical sensors, swelling properties

## INTRODUCTION

The swelling properties of polymers are of particular interest in bimorph chemical sensors where the polymeric film expansion, upon exposure to analyte vapors, is used to inflict a chemical induced stress on the underlying micromechanical silicon structures. In the case of silicon microcantilever structures this results in bending which is then monitored with optical methods [1], resonance frequency shift [2], capacitance change between the structure and the substrate [3-4] or in the case of piezoresistive detection a change in resistance [5]. Single cantilever sensors have shown to be able to detect quantities below the detection limit of classical methods [6].

For the detection of complex odors, larger arrays of differently functionalized microcantilever sensors are needed. In such cases, each microcantilever is coated with a specific sensing layer to transduce a physical process or chemical reaction into a nanomechanical response. Polymer layers are obvious candidates as sensing layers, but the selective deposition or patterning of more than one polymer is not compatible with batch fabrication. Irradiation of few or even one polymeric film to engineer its sensing properties is technologically much more attractive, while application of other treatments like ion implantation [7] or plasma [8] are less straightforward.

In our work the effect of UV irradiation on the swelling properties of appropriate polymer layers as a function of the chain scission degree is studied, using white light interferometry. The use of patternable polymeric films and their

subsequent UV irradiation treatment as a means to engineer individual sensor sensitivities in chemical sensor arrays is proposed. The study focuses on polyhydroxy-ethyl-methacrylate (PHEMA). PHEMA is well known for its hydrophilic properties, deep-UV irradiation patterning potential and visible spectrum insensitivity [9]. It presents negligible absorption for wavelengths above 240nm, thus is insensitive to ambient light, and exhibits lithographic positive tone behavior if exposed with radiation wavelength below 230nm. Therefore, it was a suitable candidate for the present study.

## EXPERIMENTAL

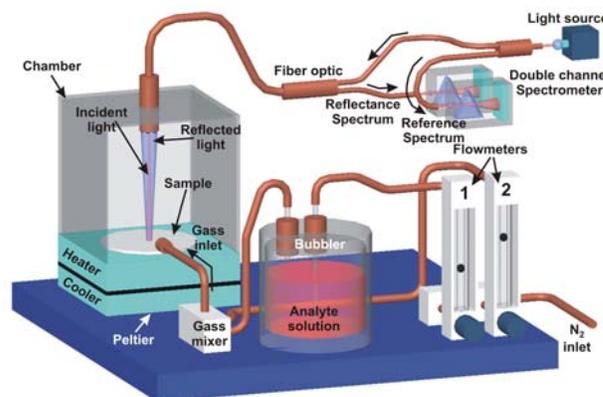


Figure 1. Measurement Setup.

Experimental measurement of the expansion of PHEMA films due to absorption/desorption of analyte molecules, was performed in a specialized measurement setup, which is described in detail elsewhere [10]. The experimental apparatus (Fig. 1) combines a white light interferometry setup, a gas delivering subsystem for introducing controlled analyte concentrations and a measuring chamber. In the gas delivering subsystem a dry nitrogen flux is splitted in a carrier and a diluting part with the help of two mass flow controllers [11]. The carrier is bubbled through the volatile of interest and subsequently mixed with the diluting part to achieve the desired concentration level in the chamber. The chamber volume is ~150ml and the gas flow is 1000ml/min, thus the saturation within the chamber is reached in a very short time.

In the white light interferometry setup, a splitter optical fiber is connected to a VIS-NIR light source through SMA connectors. The delivered optical power is equally divided

into two beams: one directed to the slave channel of a PC driven double spectrophotometer, with a resolution of approximately 0.4nm (Ocean Optics USB SD2000), and another connected to a bifurcated optical fiber. The outer part of the bifurcated optical fiber guides the light vertically onto an appropriate reflective substrate spin coated with the polymer of interest (in this case PHEMA). The reflected beam is collected from the central part of the bifurcated optical fiber and is directed to the master channel of the spectrophotometer. The temperature of the whole system is controlled to within 0.5°C and the whole apparatus is controlled through a software developed with LabView.

At each wavelength interference takes place, due to the light traveling through the polymer film, and the final spectrum is recorded to the PC every 2 seconds. Film expansion, as analyte molecules are absorbed in the polymer layer, is monitored as a change in the recorded interference spectrum. In order to increase the number of interference fringes in the recorded spectrum, a SiO<sub>2</sub> layer is thermally grown on the Si substrate prior to spin coating [10]. By applying the interference equation [12] for all wavelengths in the 470-740nm spectrum range, the film thickness is calculated for each recorded spectrum. The refractive index dependence on the wavelength is taken into account and is considered as constant during the absorption/desorption of the analyte.

## RESULTS

Samples of oxidized silicon wafers (1080nm SiO<sub>2</sub>) covered with thin PHEMA films (140 nm thick) were prepared by spin coating an ethyl-actate PHEMA solution (4%, 1500rpm). The samples were subsequently post apply baked at 120°C for 30min in an oven to insure solvent evaporation.

Three different experiments involving two analytes (methanol and ethanol) and humidity were used to assess the effect of three exposure conditions of UV irradiation on the swelling of the polymer film, and compared to unexposed sample behavior. For methanol and ethanol vapors, four concentrations (0, 5.000, 10.000, and 20.000ppm) were used. For humidity testing, relative humidity levels of 10, 30, 50 and 70 % were used. Deep UV irradiation dose was regulated by exposing the sample for 360, 1080 and 1680 seconds at a broadband Hg-Xe lamp from Oriel. The three exposure times correspond to three different points in the contrast curve for the polymer film used.

The contrast curve measures the normalized remaining thickness of the film as a function of exposure time for a specific development step (here 1:5 AZ726:H<sub>2</sub>O from Hoechst, for 60 seconds), and is actually a measure of the chain scission in the polymer bulk [13]. For our film this curve is depicted in figure 2. For low exposure times (<500 seconds) chain scission is limited, while at higher exposure times (>600 seconds) the percentage of broken chains is increasing. According to figure 2, for the first 360 second exposure time chain scission remains low, for the

1080 second exposure, very few polymer chains have been left intact, while for 1680 seconds we are well in the low plateau of the curve and the polymer chains are completely broken.

A typical measurement consists of stepping through the different gas concentrations over time, as shown in figure 3 for the case of methanol. All samples were exposed at the prescribed doses and have not gone through any development phase before the measurements. A heating cycle of 30-100-30 °C precedes each measurement, and then the temperature remains stable at 30 °C for the whole measurement duration. In figure 4, 5 and 6 the expansion of the 140nm PHEMA film as a function of methanol, ethanol concentrations and humidity are presented. From these data, it is seen that film swelling is increasing for all three analyte mixtures for the samples with low exposure. For mid exposure (1080 sec), the behavior of the film changes returning to its original swelling rate, while for the high exposure time of 1680 the film swelling capability actually decreases compared with its unexposed state.

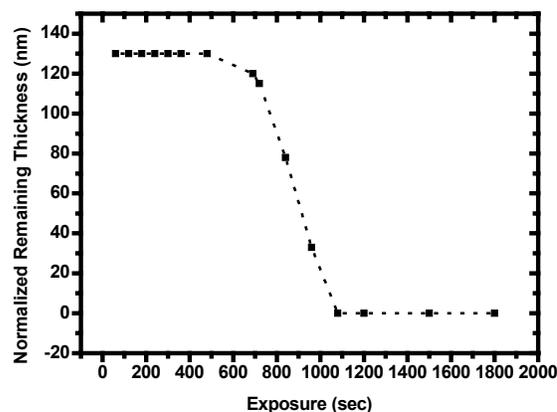


Figure 2. PHEMA contrast curve as a function exposure time.

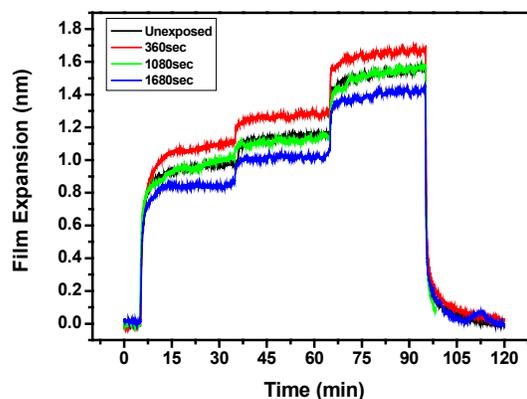


Figure 3. A PHEMA film (140nm) is exposed to 0, 5000, 10000 and 20000ppm concentration of methanol.

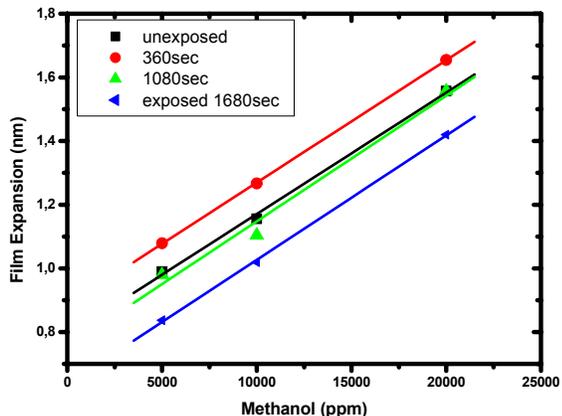


Figure 4. Expansion of PHEMA films as function of methanol concentration

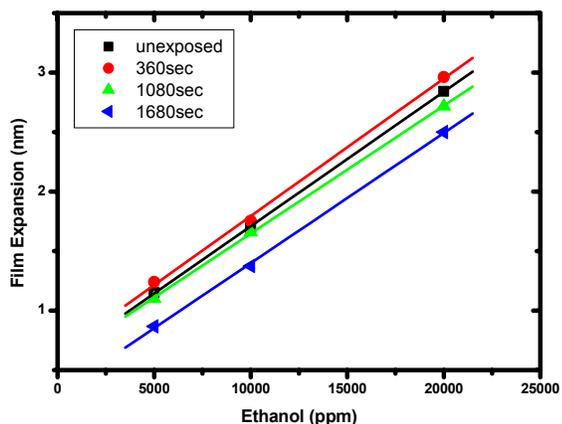


Figure 5. Expansion of PHEMA films as function of ethanol concentration.

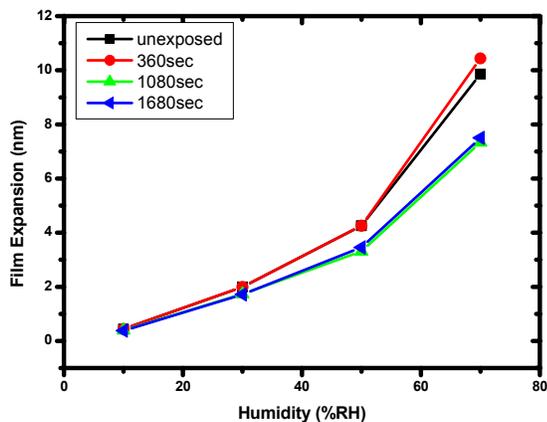


Figure 6. Expansion of PHEMA films as function of relative humidity.

In order to understand the mechanism related with the swelling behaviour of exposed PHEMA films, contact angle measurements are performed using a Digidrop DGW-EWS. These results, summarized in Table 1, show little influence of the UV irradiation treatment on the hydrophilicity of the surface.

Table 1. Contact Angle of UV treated films

Exposure Time (sec)	0	360	1080	1680
Contact angle (°)	48	49	50	53

In a first attempt to explain the modification of the behavior of PHEMA swelling as a function of UV exposure dose the chemical structure of the hydroxy-ethyl-methacrylate (HEMA) monomer, depicted in figure 7, has to be taken into account. From previous study [9] it is suggested that UV irradiation causes chain scission and small molecule formation. As seen from the contrast curve (fig 2), a small percentage of the polymer chains begin to break into smaller molecules, with increasing UV dose. This initially may provide additional paths for analyte molecules to diffuse into the polymer layer and increase swelling as seen for the 360 second exposure time.

For higher exposure doses, the percentage of the broken chains increases further, releasing HEMA monomers and volatiles through the breakage of the  $-\text{COOCH}_2\text{CH}_2\text{OH}$  group from the main chain, resulting in PHEMA of lower molecular weight and higher packing density in the polymer bulk. These phenomena could be the reason for the slight increase in surface hydrophobicity and the reduction of the swelling capability of the polymer.

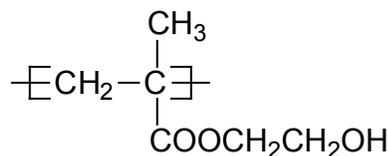


Figure 7. Chemical structure of PHEMA.

## CONCLUSIONS

The effect of UV irradiation on the swelling properties of polyhydroxy-ethyl-methacrylate (PHEMA) layers as a function of the chain scission degree using white light interferometry has been investigated. The swelling properties of the polymer have shown dependence on the UV irradiation dose. For low doses, polymer swelling is enhanced, while for higher doses, where the chain scission is dominant, it decreases again, and degrades further for even higher doses. In a first attempt to explain this behavior we suggest that the high chain scission observed for high UV exposures results into higher packing density hindering polymer swelling.

## ACKNOWLEDGEMENTS

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