Characterization of polymer films for use in bimorph chemical sensors

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Abstract. In the present work white light interferometry is applied for the characterization of polymer films commonly used in bimorph chemical sensors. The study focuses on methacrylate polymers with positive tone patterning capabilities. The behavior upon exposure to controlled concentrations volatile organic compound and water vapors of thin poly (hydroxy ethyl methacrylate) (PHEMA) and poly (methyl methacrylate) (PMMA) layers was evaluated. The normalized film expansion for PHEMA, compared to PMMA, is higher in the case of water and methanol vapors, almost equal for ethanol and significantly lower in the case of acetone. This behavior could be attributed to the combination of polarity and hydrogen bonding capability of the analytes. A wide polymer film thickness range was examined and it was revealed that the normalized film expansion in both PHEMA and PMMA is nearly constant for films thicker than 100nm and increases for thinner films.

1. Introduction
Polymeric layers [1] are commonly used for the fabrication of bimorph micro/nano cantilever chemical sensors [2, 3] operating in resonance or bending mode. In these sensors, one side of the cantilever is covered with a chemically selective polymer layer whose expansion upon exposure to volatile organic compounds (VOC) inflicts a differential stress between the upper and lower surfaces of the cantilever. An alternative approach is based on the capacitance changes of silicon membranes covered with polymer films [4]. The study, therefore, of the swelling properties of the various polymer materials used in this kind of structures is of great importance.

In the present work, polymer layers used in the fabrication of bimorph chemical sensors are characterized by means of an optical method based on white light interferometry. The present study focuses on poly (hydroxy ethyl methacrylate) (PHEMA) and poly (methyl methacrylate) (PMMA), which are methacrylate polymers with positive tone patterning capabilities at radiation wavelength below 230nm. Therefore, selective coating of areas of the microstructures is possible allowing for the optimization of device design. The behavior of these polymeric layers upon exposure to VOC is examined in terms of film expansion. The film thickness is calculated from the fitting of the reflectance spectrum with the interference equation. The study covers a wide range of polymer film thicknesses exposed to methanol, ethanol, acetone and humidity.
2. Measurement setup

For the measurement of polymeric film thickness change due to absorption and desorption of VOC an experimental apparatus (Figure 1) combining a white light interferometry setup, a delivering subsystem for controlled concentrations of VOC and the measuring chamber was used. In the VOC delivering subsystem initially a dry nitrogen flux is split in a carrier and a diluting part with the help of two mass flow controllers [5]. The carrier is bubbled through the volatile and subsequently mixed with the diluting part to achieve the desired concentration level in the chamber.

In the white light interferometry setup, a splitter optical fiber is connected to a VIS-NIR light source through SMA connectors. Light is then 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 layer. The reflected beam is collected from the central part of the bifurcated optical fiber and 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 with LabView.

At each wavelength interference takes place, due to the light traveling through the polymeric 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. By applying the interference equation [6] for all wavelengths in the 470-740nm spectrum range, the film thickness may be calculated in situ time for each recorded spectrum.

3. Results and discussion

The two methacrylate polymers (PHEMA, PMMA) selected for the study present negligible absorption for wavelengths above 240nm, thus are insensitive to the ambient light. In addition, DUV treatment may be used to alter the swelling behavior of these polymers as described in [7]. Furthermore, the polymers are expected to exhibit different swelling behavior upon exposure to analytes due to their differing hydrophilicity (42° contact angle for PHEMA and 68° for PMMA) owing to the presence of a hydroxyl group in PHEMA. For this series of experiments, PHEMA solutions in ethyl-lactate (4-8% concentration) and PMMA solutions (2-11% concentration) in propylene glycol mether ether acetate (PGMEA) were prepared after 72h stirring. After spin coating on oxidized silicon wafer samples, the films were post apply baked at 120°C for 30min in an oven to insure solvent evaporation. The resulting polymeric film thicknesses are in the 50-600nm range. Use of oxidized Si samples increases the number of interference fringes in the recorded spectrum enhancing the overall accuracy.

For this experiment, PHEMA and PMMA coated samples were exposed at concentrations of 1000, 5000, 10000 and 20000ppm water and VOC vapors. Typical results for 53nm thick PHEMA and
42nm thick PMMA films for the case of methanol are shown in figure 2. In this graph, the relative film expansion, defined as the difference between the film thickness at each concentration level and the initial value at dry nitrogen atmosphere, is depicted. Film expansion for both films increases linearly with methanol concentration and with a different slope.

![Graphs showing film expansion](image)

**Figure 3.** PHEMA and PMMA relative film expansion plots in the case of various analytes at 10,000 ppm: (a) Humidity, (b) Methanol, (c) Ethanol, (d) Acetone. Film thickness is 53nm for PHEMA and 42nm PMMA.

A comparative film expansion study for the case of methanol, ethanol, acetone and water vapors was performed for both polymers. In figure 3 the normalized film expansion is plotted for 30% relative humidity (a), 10,000 ppm methanol (b), 10,000 ppm ethanol (c) and 1000 ppm acetone (d). As it can be seen from these figures, the final film expansion depends on the polymer type while the time to reach the saturation level depends on both polymer type and analyte. In the methanol and humidity cases, both films reach the saturation level in a short time while in the case of ethanol and acetone the absorption time to reach saturation is considerably longer. In the case of methanol and humidity, PHEMA films expand with higher rate than in PMMA films. On the other hand, in the case of ethanol, both polymers expand almost equally while for acetone the situation is reversed and the PMMA film rate of expansion is higher. This behavior could be attributed to the different hydrogen bonding capability and polarity properties of the two polymers. PHEMA presents, due to the presence of the hydroxyl group, higher hydrogen bonding and polar parameters compared to PMMA. Thus, polar molecules such as water and methanol are able to diffuse more easily in the PHEMA film causing higher film expansion values. On the other hand, acetone presents higher chemical affinity with PMMA and therefore the expansion is higher for this polymer film.

In figure 4, both relative film expansion and normalized film expansion vs. initial film thickness are depicted in the case of 10,000 ppm methanol and ethanol for both polymers. The relative film expansion increases linearly with the film thickness but with different slope for each polymer. On the
The other hand, the normalized film expansion is almost constant for films thicker than 100nm for both polymers while for thinner films the normalized film expansion is higher. This kind of behavior has also been reported in other studies employing very thin films (< 1µm), as for example in the case of moisture absorption in polyelectrolyte films in the 3-200nm range [8], and has been attributed to thin film confinement effects.

![Figure 4](image)

**Figure 4.** Relative and normalized film expansion of PHEMA and PMMA as a function of film thickness (a) 10000ppm methanol, (b) 10000ppm ethanol.

### 4. Conclusions

White light interferometry has been applied in the study of film swelling of two methacrylate based materials: PMMA and PHEMA. The relative expansion slope increase was found to depend on both the polymer film and the analyte. The normalized film expansion, on the other hand, was found to be almost constant for films thicker than 100nm for both polymers and higher for thinner films. This behavior can be attributed to thin film confinement effects. The normalized film expansion vs. analyte for both polymers reveals a correlation between the type of polymer material and the analyte. Analytes with high polar and hydrogen bonding properties such as methanol and humidity cause higher expansion in PHEMA films due to the presence of hydroxyl group in its chemical structure. In the case of acetone the expansion is higher for the PMMA film while for ethanol both polymers present almost equal expansion. Further research effort is underway on the diffusion kinetics during absorption/desorption of the analytes in these polymers and other patternable materials.

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