Polymer based chemical sensor array fabricated with conventional microelectronic processes

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A polymer array fabricated on the same substrate with conventional microelectronic processes is introduced for gas sensing applications. The process is based on photolithographic processes and takes advantage of the balance between UV exposure dose, material tone and developers used. The sensing properties of the lithographically defined films in the array were characterized for various analytes through in situ monitoring of films swelling by white light reflectance spectroscopy. The sensing responses are post processed by Principal Component Analysis and the discrimination between analytes with similar and totally different analytes is presented.

1. Introduction

One of the most important problems in chemical sensor fabrication is the controlled deposition of the chemically sensitive layer on the transducer [1]. This problem becomes more critical in the case of sensor arrays where different sensing materials should be deposited on the same substrate [2].

A typical approach for the realization of a gas sensor array is through the use of sensors coated with polymers e.g. conductive polymers [3] with different response in the presence of various analytes. In these sensors, the resistance of each conductive polymer stripe changes in accordance to the volatile compound concentration in their ambient [4, 5]. In addition in the capacitive chemical sensors, polymer films should be selectively placed between the electrodes [6, 7].

Polymeric materials are usually applied onto sensor devices through solution-based methods such as spin coating, spray coating, dip coating or drop casting [8]. Alternatively, chemical responsive films can be applied by ink-jet printing [9]. Furthermore, electrochemical deposition is used mainly for the formation of conducting polymer films [10] while Langmuir-Blodgett (LB) film deposition method leads to sensing layers made of lipids, polymers or lipid-polymer blends [11]. However, ink jet printing lacks in pattern precision and repeatability, and the problems become more severe as the demand for smaller, more complex sensors increases, Films fabricated by electrochemical deposition are severely limited as regards the selection of deposited materials. In addition, self-assembled monolayers (SAMs) of various types have been investigated as sensing layers [12]. In general, SAMs influence the adsorption of vapors on the surface, and cannot provide the same sorptive capacity as a thin film

providing bulk absorption. Vacuum deposition techniques are also possible methods of obtaining thin polymer films including mostly sputtering [13], plasma polymerization [14].

In the present work a series of photosensitive polymeric materials is defined on the same substrate using conventional lithographic techniques only. The suggested approach is based on careful tuning of selected processing parameters such as: the material application sequence, the exposure dose for each exposure step, the material tone (negative/positive) and the developers used. The use of lithographic processes allows for the definition of polymeric films at the desired layout and for a wide film thickness range. In addition the deposition of multiple polymer areas provides with two important advantages a) a parallel process allowing the fabrication of multiple arrays (dies) on the same substrate (e.g. silicon wafer), b) microelectronic processing compatibility that allows the integration of sensors with electronics on the same die.

The polymers to be deposited with the proposed methodology should fulfil three criteria: a) patterning capability, b) complementary solubility parameters in order to form a polymer array covering a wide solubility parameter range and c) patterning compatibility i.e. the deposition of a polymeric area does not affect the already defined polymer areas.

In the present work, as a first step, the response of the deposited polymer array in the presence of selected analytes (methanol, ethanol, toluene vapors and humidity) is characterized through polymer swelling measurements by White Light Reflectance spectroscopy (WLRS) [15]. In addition the potential application of the proposed sensor array for the discrimination of the analytes by using a Principal Component Analysis (PCA) algorithm is demonstrated.

2. Experimental

2.1 Measurement Set-up

For the measurement of polymeric film thickness changes due to absorption and desorption of analytes, a dedicated set-up (Fig. 1) combining a white light reflectance spectroscopy module, a delivering subsystem for controlled concentrations of analytes and the measuring chamber was used. In the analyte-delivering unit initially dry nitrogen flux is split in a carrier and a diluting part with the help of two mass flow controllers (Brooks). The carrier is bubbled through the analyte of interest, and thus is saturated, and subsequently mixed with the diluting part to achieve the desired concentration level in the measuring chamber. The set-up offers four bubblers operated through four values controlled via the PC. The sensor's chamber volume is ~150ml and the gas flow is 1000ml/min; thus saturation within the chamber is reached quickly. The temperature in the gas delivering subsystem and in the measuring chamber is kept constant at 30 ± 0.5^{o}C via a PID controller.
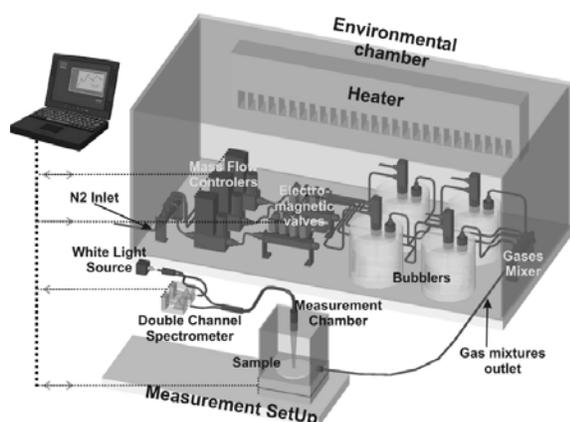

Fig. 1. Schematic representation of the measurement set-up.

In the WLRS subsystem, a 50%-50% splitter optical fiber is connected to a VIS-NIR light source (AvaLight-HAL). The one beam is directed to the slave channel of a PC driven double VIS-NIR spectrometer (Ocean Optics USB SD2000) and the other is connected to a bifurcated optical fiber. The bifurcated optical fiber guides then the white light onto an appropriate reflective substrate spin coated with a thin polymer layer to be studied. At the same time the optical fiber collects the reflected beam, directing it to the master channel of the spectrometer.

In the WLRS methodology, the substrate should be highly reflective at the spectrum used. Therefore standard silicon wafers constitute a reasonable choice. The Si wafers were thermally oxidized at 1100 ^{0}C for 200 min (wet oxidation) forming a SiO_2 film with 1060nm thickness. This dielectric film provides with an adequate number of fringes within the reflectance spectrum which is necessary in order to monitor minute film thickness changes of the polymer layers on the top [16, 17].

By fitting the reflectance spectra with the interference equation it is possible to calculate the layer thicknesses for a given film stack, considering the refractive indices of the layers employed are known e.g. [18]. Under certain conditions WLRS methodology could be also extended and further applied for the measurement of the refractive index of a particular layer. However the refractive index changes due to absorption / desorption of analytes at the concentration range studied here are expected to be very small and at a range that does not affect significantly the calculated film thickness. Furthermore it should be stressed that since we are interested on real time monitoring of swelling behavior, the refractive index of the polymeric film is considered constant throughout the measurement. The refractive indices of the polymeric films, for the spectrum of interest, are calculated only once at the beginning of the experiment and these values are used for all absorption/desorption steps. Application of this method for every measured spectrum yields the temporal evolution of film thickness. At the same time the spectrum of the light source recorded at the slave channel of the spectrometer, is used as a reference (multiplier in the interference equation) to adapt the theoretical approximation to the experimental data.

2.2 Materials

For the fabrication of the polymer array several materials, either homopolymers or photosensitive resists, were examined. The polymers evaluated were: poly(methyl methacrylate) (PMMA), poly(hydroxy ethyl methacrylate) (PHEMA), poly(hydroxyl propyl methacrylate) (PHPMA), poly(butyl methacrylate) (PBMA), and poly(n-propyl methacrylate) (PPMA). These polymers are methacrylates and are expected to present positive lithographic behaviour when irradiated with light of suitable wavelength that causes chain scission. More over this assumption was based on the fact that for two of these methacrylate polymers, PMMA and PHEMA, the lithographic behaviours have been proved in several cases so far, [19, 20] for example.

On the other hand, the resists studied are epoxy based experimental resist (EPR), poly(dimethyl siloxane) copolymer (PDMS) with chemical composition 94.5% PDMS, copolymer 5% diphenyl siloxane, copolymer 0.5% methyl-vinyl-siloxane and M_w = 990K from UCT, poly(hydroxy ethyl methacrylate) negative experimental resist.

For the polymeric solutions the following solvents and photoacid generators (PAG) were used: ethyl-(S)-lactate from Sigma-Aldrich, Methyl Iso Butyl Ketone (MIBK) from Merck, Propylene Glycol Methyl Ether Acetate (PGMEA) from Sigma-Aldrich, UVI6974 from Union Carbide, TPS-SbF$_6$ from General Electric. The analytes used in the present study were methanol, ethanol, toluene from Sigma-Aldrich (analytical grade) and distilled water.

For the patterning needs of the present work, the conventional wavelength of 365nm where most exposure

tools are operating, is not adequate because irradiation at this wavelength doesn't initiate the chemical reactions for lithographic behavior of the resists while at this wavelength chain scission of the methacrylate chains is not possible. In order to fulfill the lithographic needs of the selected polymers and resists exposure in DUV are necessary and a broadband Hg-Xe lamp (Oriel) was used.

3. Results and discussion

Prior to the fabrication of the polymeric array the swelling response of the selected materials over certain analytes and their patterning properties needed to be studied in order to select the most promising materials that could fulfil the previously mentioned three criteria. The analytes selected for the swelling response were methanol, ethanol, water and toluene. Furthermore material properties were selectively examined and mainly the molecular weight effect in the fabrication of the polymeric array and the swelling results.

3.1 Swelling response of the studied polymers

From a previous study [15] it is known that polymeric films with a film thickness above 100nm present swelling equal to bulk polymer. For that reason the polymer solutions and spin coating conditions were carefully tuned in order to achieve film thickness in the 110 – 150nm range that allows fast response and bulk properties. If film thickness is very high, then the time to equilibrium is very long because the analyte molecules should travel long distances. In fig. 2 the dynamic response of a PHEMA film in a wide range of water vapors (1000ppm - 20000ppm) is illustrated. Swelling starts immediately after the supply of the water molecules and the equilibrium between the concentrations at the gas phase and in the polymeric film is reached very fast.
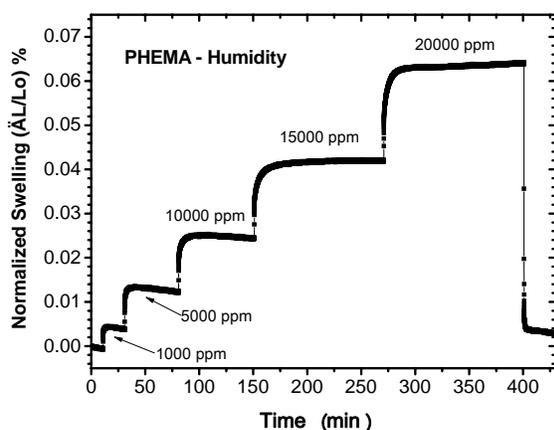

Fig. 2. Dynamic response of PHEMA film in a wide range of water vapors.

In Fig. 3 the normalized swelling response ($\Delta L/L_o$) at equilibrium of selected polymeric materials over methanol, ethanol, humidity and toluene, all at 5000ppm concentration, are plotted. It is clear that the swelling response depends strongly on the polymer – analyte combination. The maximum swelling response for methanol, ethanol, water vapors is obtained for the PHPMA, most probably due to large number of hydroxyl groups in the monomer, while the maximum response for toluene is monitored for the PPMA film.
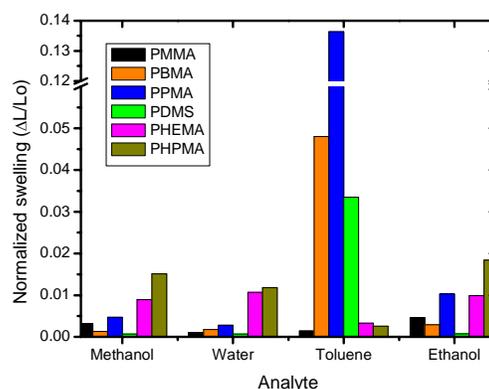

Fig. 3. Normalized swelling responses of selected polymeric films at equilibrium. The normalization is over the initial film thickness (nitrogen atmosphere).

Certainly the employment of multiple materials in an array would increase the discrimination capabilities, however not all polymers/resists studied here, fulfil the three criteria described above. In particular, several of the studied materials either do not present patterning capability (e.g. PBMA, PHPMA) or their processing affects drastically the already deposited polymers. From the above studied materials those fulfilling the three criteria are:

a) EPR [21] (8% w/w in ethyl-(S)-lactate) and 1% UVI6974 as PAG,

b) PDMS copolymer with code PS 264 [22] (3% w/w in, MIBK),

c) PMMA [23] (5% w/w in PGMEA),

d) PHEMA negative tone [24], (4% w/w in ethyl-(S)-lactate) and 2% TPS-SbF$_6$ as PAG.

3.2 Molecular weight effect on swelling properties

In the case of PMMA we studied four molecular weights (Mw=15K, Mw=120K, Mw=350K, Mw=996K). However from previous studies [23] it is known that the lithographic performance of the low molecular weight PMMA is moderate but most importantly significant thickness losses are observed even in the unpatterned areas. For that reason even though the response of this molecular weight is higher than the ones of the higher

molecular weights (fig. 4a) it is excluded for the fabrication of the polymer array.
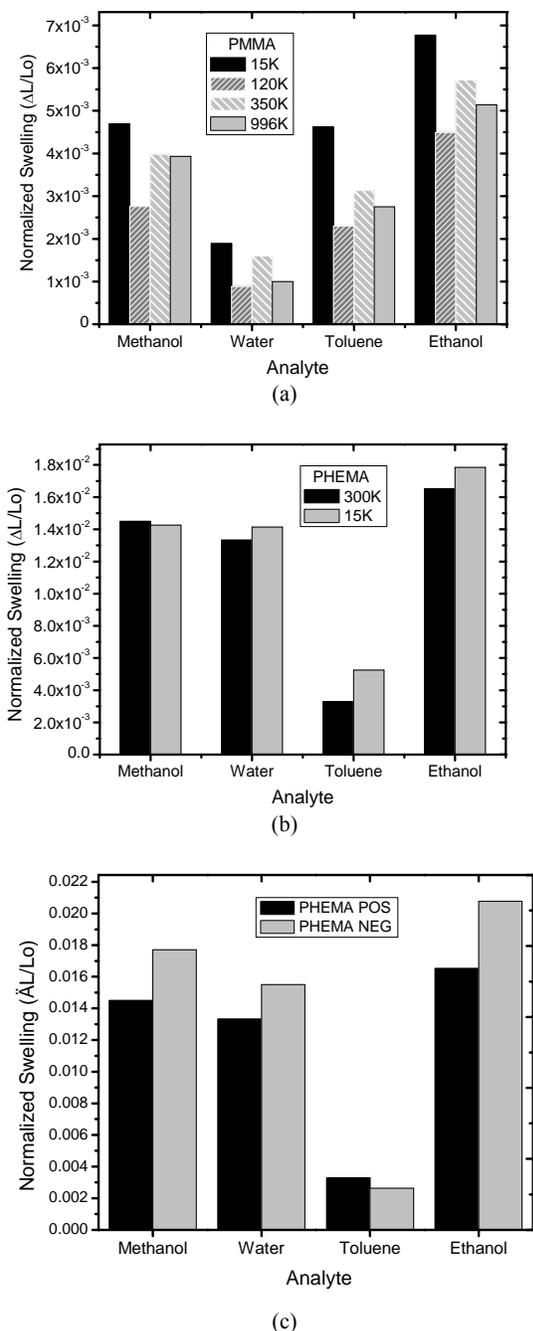

(a)

(b)

(c)

Fig. 4. Normalized swelling responses in various analytes. a) evaluation of the swelling responses in case of various PMMA molecular weights b) evaluation of the swelling responses in case of two PHEMA molecular weights c) comparison of the swelling values for positive and negative tone PHEMA.

In Fig. 4b the swelling response for two molecular weights of PHEMA are plotted. The response of these two molecular weights is almost the same. Given the lithographic performance of the higher molecular weight and the tolerance to post processing (i.e. processing of additional resist layers spin coated above) are better it was decided to use this molecular weight for the fabrication of the array. In fig. 4c, the swelling response for positive tone PHEMA (pure PHEMA) and negative tone PHEMA are plotted. The response is the same and because PHEMA negative is more resistant in post lithographic processing due to the crosslinking formation it was used in the fabrication of the polymer array. The lithographic steps of PHEMA negative involves spin coating, baking, exposure, baking again and development in organic solvent contrary to pure PHEMA.

3.3 Fabrication of the Polymeric Array

The polymer deposition process on the same substrate (1060nm SiO_2/Si), consists of the following sequence of steps:

(a) EPR is spin coated on the substrate, followed by a Post Apply Bake step (PAB) for the evaporation of spin casting solvent, DUV exposure with the desired layout and post exposure bake (PEB) for cross-linking of the exposed areas and development in PGMEA to remove the unexposed and thus uncrosslinked regions. (b) PDMS spin coating, PAB, DUV exposure after alignment (exposure areas are different from the EPR ones) and PEB for cross-linking of the exposed areas and removal of the unexposed regions through development in MIBK. (c) PMMA spin coating, PAB followed by DUV exposure through a properly aligned mask and development in MIBK-IPA 2:3 solution. (d) PHEMA negative spin coating, PAB, DUV exposure after alignment, PEB and development in methanol.

At the end of the processing the final structure consists of four regions with the sensitive films on the same wafer. The above process is based on photolithographic processes and takes advantage of the balance between UV exposure dose, material tone and developers used. The presented patterning sequence is the only one allowing the deposition of these materials. If any of the above steps is carried out earlier or later it will cause several problems (materials mixing and / or removal of already deposited polymeric areas). The layout of each polymer could be of any size, however due to the size of the reflectance probe used in the WLRS setup, each polymeric area is a rectangular area with dimensions 6x10mm.

During the realization of the polymeric film array, each polymer undergoes the lithographic processing (spin coating, PAB, exposure, development) of the subsequent layers. From those steps, spin coating and development appear to be the most critical since, the solutions used for spin coating use organic solvents and also in several cases the developer is also an organic solvent.

3.4 Swelling response over various analytes

The four polymers selected to be deposited on the same substrate present considerable different solubility parameter values, Table 1, allowing for the sensing of a wide range of analytes and their potential discrimination.

In Fig. 5 the response of the polymer array over a variety of analytes is illustrated. The analytes selected for the present study were DIPE, Toluene, Chloroform, MEK, THF, Ethanol, Methanol, Water. These analytes have a wide range of characteristics and solubility parameters.

Table 1. Solubility parameter values of polymeric materials.

Polymeric materials	δ_H	δ_P	δ_D	δ_{total}
PMMA	5.1	4.5	6.6	9.5
EPR	5.4	4.5	8.9	11.4
PHEMA	7.2	6.4	6.9	11.8

DIPE, Toluene, Chloroform and THF are absorbed more efficiently by PDMS and the responses are clearly different. The response in MEK vapors is rather moderate for all polymers in the array. On the other hand, the response in methanol, ethanol and water is high in the PHEMA area most probably due to the hydrophilic nature of both the polymer and the analytes. Overall, PDMS presents the higher responses for the organic solvents and PHEMA the higher responses for the alcohols and water and the discrimination of analytes would be impossible with only those two polymers. PMMA presents clearly a higher relative response for chloroform, which is actually one of the well-known solvents for this polymer. On the other hand, EPR presents a good ratio of ethanol over methanol response and allows for the discrimination of those two analytes.

Further quantification of the above findings should be done through application of suitable algorithms, such as Principal Component Analysis (PCA) [e.g. 25, 26]. Principal Component Analysis (PCA) is a well-known statistical method for reducing the dimensionality of numerical data sets and is widely used for analyzing gas-sensing data [e.g. PCA1, PCA2]. In the present study, the experimental data (swelling response) for all analytes in fig. 5 were examined with PCA in order to visualize response patterns in the feature space of principal components.
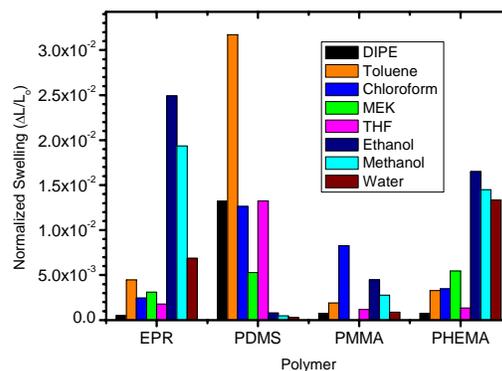

Fig. 5. Normalized swelling response at equilibrium of the four-polymer array to eight analytes at 5000ppm.
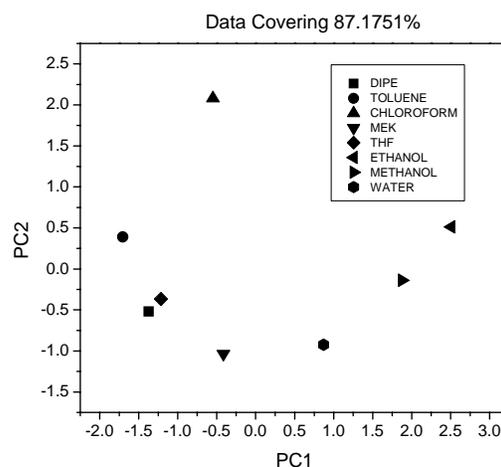

Fig. 6. PCA results of the four polymer array.

The first two principal components were kept because they accounted for ~87% of the variance in the data set. Fig. 6 shows the PCA results of all eight analytes examined in the present study. It is evident that each analyte's signature is considerably different from the others.

4. Conclusions

The successful definition of four polymeric areas with different sensing properties on the same substrate has been successfully demonstrated. The definition was performed by conventional photolithographic processing and the sensor array was optimized in terms of processing conditions and material properties. The polymer array was evaluated for gas sensing application through swelling measurements and it was revealed that good discrimination can be achieved through the application of suitable PCA software.

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