Polarity-indicative two-dimensional periodic relief gratings of tethered poly(methyl methacrylate) on silicon surfaces for visualization in volatile organic compound sensing

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We grafted poly(methyl methacrylate) (PMMA) from a 200 nm-resolution hole array of photoresist on a silicon substrate as a pillar array of two-dimensional periodic relief grating (2DPRG). The resulting 2DPRGs have been used as detectors of organic solvents in surrounding media, based upon structure change of the 2DPRG as a consequence of the solvent induced reversible swelling-deswelling of PMMA chains, through effective refractive index. Dramatic colors change, purple, green, yellow, and red, was observed by naked eyes along an incident angle of 60°–70° as the surrounding media of PMMA-modified 2DPRG was acetone, tetrahydrofuran, dioxane, and chloroform, respectively. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4802022]

Volatile organic compounds (VOCs) constantly risk our wellbeing as well as the environment around us. We can be exposed to VOCs through ambient environment, soil, groundwater, atmosphere, and workplaces including research labs and industries.1 Sources that contribute to production of VOCs include agricultural, energy, food processing, and manufacturing industries as well as items with daily usage such as solvents and perfumes.2 Many of VOCs are carcinogens that can incur diversiform cancers such as lymphatic and haematopoietic types. VOCs are also known to cause other chronic health threats to human beings. They can cause serious harm to liver and kidney as well as the immune, nervous, and reproductive systems.2,3 Therefore, VOC detection techniques have been in high demand for many applications such as environment monitoring and homeland security.4 Up to date, metal oxide semiconductors,5 conjugated polymer conductors,6,7 and conductive particle-polymer hybrids8 are well-known as promising VOC-sensing materials. These materials are all highly responsive to various VOCs, and some of them are now used in commercial chemical sensors.

Nano-fabrication technologies are of paramount importance in fabrication of SWS surfaces with applications ranging from microelectronics,10 pH-sensor,11 biomimic actuator,12 and micro-optical components.13 When the gratings interact specifically or nonspecifically with target molecules, the geometrical parameters of the gratings and/or the refractive index contrast typically change.14 In this paper, we describe a simple method to pattern poly(methyl methacrylate) (PMMA) brush as a two-dimensional periodic relief gratings (2DPRGs) by lithography and oxygen plasma treatment (OPT).12 On the basis of this idea, polarity-indicative 2DPRG of tethered PMMA was prepared as a type of VOC-sensing layer, based on the swelling behavior of PMMA under these VOC environments. We tested the 2DPRGs of tethered PMMA layer for their use as transition media for VOC detection. This versatile process is particularly amenable to the creation of large-area uniform coatings on essentially any surface with precise control over thickness and optical properties.15 Specifically, a VOC-induced reformation mechanism in the tethered PMMA grating system was shown to enable a large-scale morphological reorganization.

The basic strategy for the fabrication of the patterned polymer brushes using the very-large-scale integration (VLSI) process was developed in previous reports;16 the process is depicted in Figure 1. (a) The Si wafer was treated with hexamethyldisilazane (HMDS) in a thermal evaporator to transform the hydroxyl groups on the surface of wafer into an inert film of Si(CH3)3 groups. The photoresist was spun onto the HMDS-treated Si wafer to pattern 200 nm-resolution contact hole array by lithography process. (b) The sample was then subjected to OPT to form hydroxyl groups from the HMDS-treated surface. OPT caused the bottom surface to become chemically modified (strongly hydrophilic or polar) only in the areas not covered by the photoresist.17 (c) Atom-transfer radical-polymerization (ATRP) initiator units assembled selectively onto the bare regions of the bottom Si surface after...
carried out according to a previously reported method. ATRP of MMA was performed in a sequential process: (a) Si wafer treated with HMDS in a thermal evaporator; (b) OPT used to chemically modify the exposed regions presenting Si(CH₃)₃ groups and to convert the topographic photoresist pattern into a chemical surface pattern; (c) Initiator selectively assembled onto bare regions of the Si surface. Sample grafting via surface-initiated ATRP of MMA from the functionalized areas of the patterned SAM as pillar arrays of PMMA brushes. (d) Finally, photoresist removed from the substrate. The 2DPRG of tethered PMMA layer on the surface exhibited VOC-dependent morphology and optical properties according to solvent species.

FIG. 1. Schematic representation of the process used to fabricate 2DPRG of tethered PMMA layer. (a) Si wafer treated with HMDS in a thermal evaporator, photoresist spin-coated onto the Si surface presenting Si(CH₃)₃ groups, and lithography process used to pattern the photoresist as a hole array. (b) OPT used to chemically modify the exposed regions presenting Si(CH₃)₃ groups and to convert the topographic photoresist pattern into a chemical surface pattern. (c) Initiator selectively assembled onto bare regions of the Si surface. Sample grafting via surface-initiated ATRP of MMA from the functionalized areas of the patterned SAM as pillar arrays of PMMA brushes. (d) Finally, photoresist removed from the surface. The 2DPRG of tethered PMMA layer on the surface exhibited VOC-dependent morphology and optical properties according to solvent species.

OPT, where it reacted with Si–O and Si–O–O species. This procedure resulted in a surface patterned with regions of the initiator for ATRP and regions of photoresist. ATRP of MMA was carried out according to a previously reported method. Polymerization of the monomer was allowed to proceed inside the square hole array of photoresist to generate pillars as the basic structure of 2DPRG surface. Afterward, the wafers were taken out of the polymerization solution and rinsed thoroughly with toluene. (D) Finally, the remaining photoresist was removed from the PMMA-grafted silicon surface by rinsing with slight basic aqueous solution, leaving behind the chemically nanopatterned PMMA brush surface.

The VOC analyses tested in this work are divided into several types of organic solvents as follows: cyclohexane, toluene, chloroform, 1,2-dichloroethane (DCE), tetrahydrofuran (THF), dioxane, and acetone. Detection of these VOCs was carried out in a cylindrical glass chamber, fitted with a gas inlet and a 301 min⁻¹ two-stage rotary pump attached to a liquid nitrogen cold trap. Next, the subjects were introduced gradually into the chamber to evaporate by a vacuum environment until their pressures at 20 Torr. Sequentially, air was introduced into the chamber upon 1 atm as detection environments for 5 h; 20 Torr of partial pressures was below their saturated vapor pressures of VOCs. After VOC exposing, the subjects were treated under –40 °C for 10 min to remain the surface structure in vacuum freeze dryer (BENCHTOP 2 K, VIRTIS, America). The PMMA-grafted surfaces were analyzed using ellipsometry (SOPRA SE-5, France) and X-ray photoelectron spectroscopy (XPS, Scientific Theta Probe, UK). The morphologies of varied 2DPRG of tethered PMMA were analyzed using an atomic force microscope (AFM, Veeco Dimension 5000 scanning probe microscope).

The chemical compositions of the pristine Si surface and the Si surfaces at various stages during the surface modification process and the presence of grafted PMMA brushes were determined using XPS in previous reports. In the following, properties of thin PMMA brush films in the dry state are reported. PMMA brush films were characterized in the dry state by AFM and ellipsometry to determine brush parameters such as roughness, thickness, grafting density, and surface coverage of the dry film (Table I). The typical structural brush parameters grafting density σ, distance between grafting sites d₁, and the surface coverage Sc were determined based on the ellipsometric dry layer thickness h.

The PMMA brush was grafted from the bottom surface of these square hole arrays by ATRP as a pillar array. After removing the photoresist from the surface, atomic force microscopy (AFM) was used to visualize the morphology of the 2DPRG of tethered PS layers. 2D (left), 3D (right), and line cross-section (bottom) analysis AFM topographic images of the 200 nm-resolution 2DPRG of PMMA brush surface are depicted in Figure 2(a), revealing that the

![Table I. Dry layer parameters (molecular weight Mn and Mw, surface conversion Sc, grafting distance dg, grafting density σ, and the roughness), the refractive indices, and static water contact angle (SWCA) of typical PMMA brush layer on silicon surface.](table.png)

<table>
<thead>
<tr>
<th>Grafting Time (h)</th>
<th>Thickness (nm)</th>
<th>Mn (kg/mol)</th>
<th>Mw (kg/mol)</th>
<th>PDI (Mw/Mn)</th>
<th>Sc (kg/m²)</th>
<th>dg (nm)</th>
<th>σ (nm³)</th>
<th>Refractive Index</th>
<th>Roughness (nm)</th>
<th>SWCA (deg)</th>
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<tr>
<td>4</td>
<td>161.3</td>
<td>48.1</td>
<td>34.1</td>
<td>1.41</td>
<td>191.9</td>
<td>0.54</td>
<td>3.39</td>
<td>1.487</td>
<td>6.1</td>
<td>57.2 ± 3</td>
</tr>
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<td>8</td>
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<td>76.9</td>
<td>57.4</td>
<td>1.34</td>
<td>293.6</td>
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<td>3.08</td>
<td>1.491</td>
<td>4.7</td>
<td>58.3 ± 3</td>
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<td>64.9</td>
<td>1.36</td>
<td>354.7</td>
<td>0.55</td>
<td>3.29</td>
<td>1.488</td>
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<td>59.1 ± 3</td>
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<td>97.6</td>
<td>76.9</td>
<td>1.27</td>
<td>380.3</td>
<td>0.58</td>
<td>2.98</td>
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<td>56.8 ± 3</td>
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<td>3.12</td>
<td>1.488</td>
<td>2.1</td>
<td>56.6 ± 3</td>
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*a A bulk density of PMMA of 1.19 g/cm³ was used for the calculations.
*b Sc = ρh
*c dg = d₁²
*d σ = d₁²
*e Measured by ellipsometry at 633 nm.
tethered PMMA layers on the Si surface existed as a dense distinctive overlayer, with square hole scale of ca. 200 nm, within a scanning area of 10 \times 10 \mu m. From line cross-section (bottom) analysis, the surface texture with the same depth (ca. 341.5 nm) was clearly shown. As a result, the scale of each pillar of tethered PMMA extends from ca. 200 nm to 313 nm under VOC exposing of toluene at 20 Torr for 5 h, as a result of the slight swelling transition (Figure 2(b)). Moreover, scale of each pillar of tethered PMMA extends significantly under VOC exposing of chloroform (Figure 2(c)). Scale of each pillar alternates substantially from ca. 200 nm to 648 nm. VOC gas exhausting for 12 h and subsequent lyophilizing results in deswelling of the PMMA brush and shrinking of the layer to the original deswelling (dry) state. Scale of the pillar array turned from ca. 200 nm to ca. 648 nm under VOC exposing of chloroform; it returned to ca. 200 nm after VOC exhausting, verifying the reversibly VOC-responsive 2DPRG. This behavior was reversible over 5 cycles (Figure 2(d)). Scale extending increases gradually with the VOC species in the order of chloroform, DCE, dioxane, toluene, THF, cyclohexane, and acetone. The results reveal that swelling behavior of tethered PMMA is related to the VOC species, but not polarity index, consistent with the pervious reports.17,18

We measure the refractive index of PMMA thin film at 633 nm, reported to be 1.4914, as a standard value to measure the refractive index of 2DPRG of tethered PMMA layer by ellipsometry. Figure 4 records the $n_{\text{eff}}$ changes, measured by ellipsometry, under VOC exposing in the order of chloroform, dioxane, toluene, THF, cyclohexane, and acetone. The results reveal that swelling behavior of tethered PMMA is related to the VOC species, but not polarity index, consistent with the pervious reports.17,18

FIG. 2. 3D (left), 2D (right), and line cross-section (bottom) analysis AFM topographic images of 200 nm-resolution 2DPRG of tethered PMMA surface (a) in dry state, under VOC exposing of (b) toluene and (c) chloroform at 20 Torr of partial pressure for 5 h. (d) Variation in the scale of the pillar array of 2DPRG after five cycles of VOC exposing and exhausting of chloroform.

FIG. 3. Swelling ratios of tethered PS layer under VOC exposing with their polarity indices of solvent species.
DCE, dioxane, toluene, THF, cyclohexane, and acetone. The 2DPRG of tethered PMMA layer in the initial state reveals a 1.15 of $n_{eff}$ less than that of tethered PMMA layer without 2DPRG structure. The $n_{eff}$ changes with swelling degree of PMMA for VOC exposing of various species, because swelling PMMA brush leads to change of filling space of the pillar array. The results indicate that the tethered PMMA layer possessing 2DPRG structure could also recognize the VOC species through their $n_{eff}$ changes. The resultant 2DPRG is also capable of undergoing a reversible, VOC-responsive $n_{eff}$ change, driven by changes in the degree of PMMA deswelling and a concomitant change in the collapse degree of a polymer brush. Photographic images of the 2DPRG of tethered PMMA layer under VOC exposing, obtained at angle ca. 60°, are inserted in Figure 4. The 2DPRG of tethered PMMA layer was prepared into a die using etching process with a 1 cm contact mask. The light impinging the sample at an incident angle is linearly polarized, with the electric-field vibration parallel $p$ or perpendicular $s$ to the plane of incidence. The reflected light will also be $p$- or $s$-polarized. In this work, we observe the reflection of the 2DPRG of tethered PS by naked eyes under an invariable incident angle. At an incident angle closed to 60°–70°, the 2DPRG of the tethered PMMA displays purple, green, yellow, and red color under VOC exposing of acetone, THF, dioxane, and chloroform, respectively. The color of these samples return to purple color after VOC exhausting.

Moreover, the index in the direction normal to the grating vectors of a 2D subwavelength grating is given in effective-medium theory by

$$n_{eff} = \left[1 - f_x f_y \right] n_1^2 + f_x f_y n_2^2 \right]^{1/2},$$  \hspace{1cm} (1)

where $f_x$ and $f_y$ are the fill factors of medium 2 in the x and y directions, respectively. The fill factors in the x directions ($f_x$) is set to equal to that in y direction ($f_y$) for description of the pillar structure for convenience. Equation (1) could be rewritten as Eq. (2) in the following, respectively. In this case, air fills into the pillar array, suggesting that the $n_1$ and $n_2$ represent the refractive index of air and PMMA respectively.

We calculated filling factors of the 2DPRG from the $n_{eff}$ using Eq. (2). Figure 4 also presents the VOC-dependence of the calculated filling factors of the 2DPRG. The results suggest that the 2DPRG featured decreasing the filling volume of air inside the PMMA film, consistent with the results of morphology change under VOC exposing. These filling factors exhibited VOC-dependence over the range of the VOC species, verifying that the major conformational change of the 2DPRG of tethered PMMA layer occurred under VOC exposing.

We have used the “grafting from” system with ATRP to prepare dense grafted PMMA brushes on the surface to generate a 200-nm-scale pillar array on Si wafers as a 2DPRG by lithography and plasma processes. By selecting a suitably functional polymer and optimizing the patterning process, profile of the nanostructures could be readily altered under VOC exposures. The light impinging the 2DPRG of tethered PMMA layer at an incident angle of 60°–70° displays various colors, purple, green, yellow, and red, observed by naked eye according to VOC exposing species. The 2DPRG of tethered PMMA could be fabricated substantially on a large area with capable of VOC detection. Such controllable and reversible gratings with tunable films are ideal materials for optical technologies.

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