A Sensing Device Using Liquid Crystal in a Micropillar Array Supporting Structure

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Abstract—We present the design of a micropillar array that leads to the formation of stable and uniform liquid crystal (LC) thin films for sensing applications. Photolithography and electroplating methods were employed to fabricate the micropillar array. By using this microfabricated structure, thin films of LC (5CB: 4'-pentyl-4-cyanobiphenyl) were formed and stabilized against gravitational forces and mechanical shock. The geometric profile of the supported LC thin film was simulated by using finite element methods. Orientational ordering transitions of nematic LCs in the supported thin films were used to detect liquid- and vapor-phase analytes via changes in the intensity of light transmitted through the LCs. The LC thin films supported by these microfabricated structures were tested and found to respond to dimethyl methylphosphonate gas. [2009-0051]

Index Terms—Dimethyl methylphosphonate (DMMP), liquid crystal (LC), microfluidics, micropillar, microsensor.

I. INTRODUCTION

DETECTION of chemical and biological analytes with high sensitivity is an important technological challenge. Devices that are capable of performing such analyses may find application in chemical and biological warfare detection [1], [2], point-of-care diagnostics [3], or lab-on-a-chip systems [4]. To enable chemical/biological analyses outside of a laboratory, these devices need to be portable and have fast response times,

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in addition to being cost effective, so that many such devices can be deployed at strategic points to form a sensor network [5]. Other detection schemes that have been studied include methods based on fluorescence [6], chromatography [7], spectroscopy [8], and mass spectrometry [9]. These schemes provide possible means to detect a chemical and biological analyte in the range from hundreds of parts per billion (ppb) to parts per million (ppm) in 1–20 min [10]. However, most of these methods require fairly complex and expensive instrumentation, which limits the utility and potential portability of the system.

Recently, nematic liquid crystals (LCs) [11] have been used to detect molecular events taking place at interfaces [11]–[13]. The interfacial molecular events cause transitions in the orientational ordering of molecules within the LC, which are detected by monitoring the changes in the intensity of light transmitted through the LC. LCs have been demonstrated to permit detection of vapor-phase analytes that are present in the ppb concentration range [12], [14], [15] with shorter response times (about 20 s) compared to other detection schemes [10]. The LC-based sensing schemes do not require power supplies, thus leading to the possibility of passive sensing devices that are suitable for fielded applications. The realization of robust and inexpensive LC-based sensors requires the development of methods to support thin LC films with thicknesses in the micrometer range. Here, we note that the control of the thickness of the LC device is important because the physical dimensions of the LC film impact the performance of the sensor. A dominant force that acts at the microscale is the capillary force. In the study that we report in this paper, we sought to create a microstructure that would generate sufficient capillary force to stabilize a thin film of LC on a substrate. In past studies, discrete metal grids and polyurethane wells have been used for this purpose [11], [13]–[15]. Those approaches require manual manipulation, can be difficult to fill, and possess constraints in terms of design flexibility and robustness. Here, we address these issues by using a nickel (Ni) micropillar array to stabilize the LC (5CB: 4'-pentyl-4-cyanobiphenyl) through the use of capillary forces. Previously, similar pillar structures were used to form stable thin films of liquids for realizing multiphase reactions [16], liquid chromatography [17], and air-to-liquid sampling [18]. With micropillar structures, the capillary forces generated by the micropillars facilitate the wetting and spreading of the LC into the structure. As a result, the LC thin film assumes a uniform thickness across the sensing area. Once filled, the capillary forces acting between the LC and the micropillar array stabilize the LC film within the microfabricated device, making it insensitive to gravity and mechanical shock.

We previously presented preliminary results using a micropillar array to stabilize thin LC films for vapor-phase sensing [19], [20]. The fabrication process combined photolithography and Ni electroplating to form the micropillar arrays. The planar geometry of the micropillar array was defined by a photo mask, and the height of the micropillars was controlled by the electroplating process. In this study, a device with micropillars having diameters of 200 μ m and heights of 20–30 μ m, each separated by 200 μ m, was fabricated. The LC thin film within such a device exhibited a fast orientational response in the context of liquid- and vapor-phase sensing. The orientational response was detected by a change in the intensity of polarized light transmitted through the LC film. Dimethyl methylphosphonate (DMMP; a simulant of sarin gas) was used to demonstrate the vapor-phase sensing with the micropillar array supporting the LC thin film.

II. PRINCIPLE OF OPERATION

LC-based sensing exploits the following four properties of LCs [11], [13].

- 1) The approach exploits the long-range ordering of mesogens (molecules that form the LC phase) within LCs; changes in the orientational ordering of mesogens at the interfaces of LCs can propagate deep into the bulk of an LC (up to 100 μ m from the interface); this permits amplification of signals generated when analytes bind to chemically functionalized surfaces.
- 2) Because mesogens possess liquidlike mobility, information about the binding of analytes can propagate rapidly through thin LC films (within seconds or subseconds).
- The birefringence of a thin LC film provides a means to transduce binding events on surfaces into an optical signal that can easily be visualized by the naked eye.
- 4) Because the orientation of a thin LC film near a surface is influenced by the molecular-level structure of the surface, it is possible to functionalize the surface such that the orientational transitions of LCs can selectively be triggered by the exposure and subsequent binding of targeted molecules [21], [22].

To obtain a thin film of LC supported on a functionalized surface [23], [24], here, we describe the use of the microfabricated pillars. As shown in Fig. 1, the micropillar array is surrounded by a Ni ring having the same height as the micropillars. The pillars and the ring are fabricated by electroplating Ni on top of the glass substrates. When the space between the pillars is filled with LC, capillary forces can dominate over gravity as well as other external forces, such as those generated by mechanical shock, to hold the LC between the pillars under commonly encountered conditions. A detailed analysis of this balance of forces is presented in the later sections. The thin LC layer is stable within this device even when the device is inverted or mechanically vibrated.

In these devices, the 5CB molecules of the LC assume an orientation that is perpendicular to the substrate (homeotropic orientation) because the nitrile groups of 5CB bind to the surface-immobilized aluminum ions within an aluminum perchlorate $[Al(ClO_4)_3]$ layer [the latter is deposited onto a



Fig. 1. Schematic illustration of the micropillar array. (a) Ni pillars and ring are electroplated on the glass substrate. The bottom surface between the micropillars is coated with a semitransparent 20-nm-thick Au layer and functionalized with a SAM of 11-mercaptoundecanoic acid (MUA) and aluminum perchlorate [Al(CIO_4)₃] for the purpose of anchoring the LC. (b) LC is filled in the space within the ring and between the micropillars. The LC thin film is stabilized by the micropillar array.

self-assembled monolayer (SAM) with a carboxylic-acidterminated thiol, 11-mercaptoundecanoic acid (MUA)]. The SAM is formed on a gold film that was deposited by physical vapor deposition onto the substrate. The ordering of the LC within the device changes upon exposure to different phases or analytes. Upon contact with air or N2, the LC assumes a homeotropic orientation at the upper interface. The LC also assumes a homeotropic anchoring at the bottom surface, as shown in Fig. 2(a). This alignment profile of the LC does not change the polarization of light that is transmitted through the LC film. Hence, when the LC is sandwiched between crossedpolarizing filters and illuminated by white light, the intensity of transmitted light is low. LC thin films that do not possess homeotropic alignment at the upper interface lead to a change in the polarization of the transmitted light, resulting in a bright image when viewed between crossed polarizers. For example, when the LC thin film makes contact with deionized (DI) H_2O at the top surface, the mesogens at the H_2O/LC interface assume a planar alignment, which results in a hybrid alignment profile (homeotropic at the bottom and planar at the top) across the thickness of the LC thin film as shown in Fig. 2(b). Under these conditions, the LC appears bright when viewed with crossed polars. The orientational profile of the LC thin film can also change in the presence of vapor-phase analytes [19]. As shown in Fig. 2(c), in the presence of the gas DMMP, the molecules of the gas diffuse through the thin film of LC and reach the interface between the LC and the $Al(ClO_4)_3$ layer. DMMP competitively displaces the LC from its complex formed with $Al(ClO_4)_3$, and this causes the LC mesogens to lose the homeotropic orientation at the bottom of the thin film, resulting in an ordering transition within the film of LC and change in the polarization of the transmitted light. In this study, such devices based on the micropillar arrays are designed and fabricated, and vapor-phase DMMP is used as a model to test some sensing characteristics.



Fig. 2. Ordering of the LC through the thickness of the LC layer can be manipulated and observed optically. (a) When in contact with air or N_2 stream, the LC assumes a homeotropic alignment through the thickness of the LC layer, thus appearing dark between crossed polars. (b) Upon contact with DI H₂O, the LC at the aqueous/LC interface assumes a planar orientation. This LC layer appears bright under crossed polars. (c) Vapor-phase DMMP defuses into the LC layer. The LC loses its homeotropic orientation and appears bright between crossed polars. The drawings are not to scale. Experimental images are shown in the following sections.

III. FABRICATION

For the study reported in this paper, we transduce the ordering transitions of the LC films using light. Therefore, we chose a transparent glass as the substrate on which to fabricate the device. There are several methods that are available for fabricating micropillar array structures with a thickness of 20–30 μ m. In our experiments, we chose to fabricate the



Fig. 3. Microfabrication process flow. (a) PR mold for electroplating the micropillar array is patterned on a glass substrate having Ti/Cu/Ti metal layers. (b) Ni is electroplated using Cu as the seed layer, after removing the top Ti. (c) Layer of Au is evaporated after removing the PR mold and the seed layers. A SAM of carboxylic-acid-terminated thiol is formed on the Au. Al(ClO₄)₃ is deposited on the SAM. (d) LC is introduced into the micropillar array.

micropillar arrays by electroplating Ni [25], [26] because it is an established process and is readily available to us. A photoresist (PR) patterned by photolithography was used as the plating mold. Each micropillar was separated from its neighboring micropillars by a spacing s that is equal to the pillar diameter d, forming an equilateral triangle. This pattern was replicated throughout a circular area on the substrate within a ring with an inner diameter of 10 mm and an outer diameter of 11 mm.

The fabrication with the Ni electroplating process is illustrated in Fig. 3. Seed layers of titanium/copper/titanium (Ti/Cu/Ti, 225/300/450 Å) were coated using a CVC 601 dc sputterer on microscope glass slides (Fisher Scientific, Pittsburgh, PA, USA). A PR mold was patterned on the Ti/Cu/Ti-coated glass slide to define the Ni-plated micropillar array. Two layers of PR (AZ P4620, Clariant Corporation, Somerville, NJ, USA) were spin-coated on top of the seed layers so that a 40- μ m-thick PR mold could be formed. Each PR spin-coating process was followed by a soft bake on a hot plate at 110 °C for 80 s.

To pattern the PR, a film mask was printed with a resolution of 3000 dpi by Imagesetter, Inc. (Madison, WI, USA). An ultraviolet lamp (OmniCure Series 2000, EXFO Photonic Solutions Inc., Mississauga, ON, Canada) was used to expose the PR at an intensity of 25 mW/cm² for 80 s. After patterning of the PR, as shown in Fig. 3(a), a Ti etch [1:100 hydrofluoric (HF) solution] was used to remove the top Ti layer that was not covered by the PR, thus leaving Cu exposed. The Ni electroplating bath, agitated at a constant 200 r/min, consisted of 1:0.01 Microfab NI 100 makeup solution and Microfab NI 100 wetting agent (Enthone-OMI, West Haven, CT, USA). The bath temperature, maintained at a temperature of 50 ± 1 °C, was continuously monitored by a type-K thermocouple probe. High-purity Ni gauze (#39704, Alfa Aesar, Ward Hill, MA, USA) was used as the Ni source (anode) for electroplating. Ni was electroplated



Fig. 4. SEM images of the fabricated micropillar array.

onto the active sites on the glass slide (cathode; where Cu was exposed) at a rate of approximately 0.60–1.00 μ m/min using a current density of 5×10^{-4} A/mm². Depending on the desired Ni thickness, electroplating sessions lasted 20 to 30 min. The PR mold was removed by rinsing with acetone. The Ti/Cu/Ti seed layers were removed by the Ti/Cu etch [acetic acid (HAC) : H₂O₂ : H₂O = 1 : 1 : 10], leaving the Ni pillar and the ring structures supported on the clear glass substrates. A device with 200- μ m-diameter pillars and 200- μ m spacing was fabricated. Fig. 4 shows the scanning electron microscopy (SEM) images of the electroplated Ni micropillar array. The SEM images were taken with a LEO DSM 1530 field emission scanning electron microscope (Carl Zeiss SMT Inc., Peabody, MA, USA).

In order to functionalize the glass substrate in the area between the pillars so that 5CB assumed a homeotropic orientation, a thin film (thickness of ~20 nm) of Au was deposited using a CHA-600 e-beam evaporator, as shown in Fig. 3(c), followed by the formation of a carboxylic-acid-terminated thiol monolayer by the immersion of the device into a 2-mM ethanolic solution of 11-mercaptoundecanoic acid for 90 min. Aluminum perchlorate $[Al(CIO_4)_3]$ was deposited onto the monolayer by spin coating with a 5-mM ethanolic solution of $Al(CIO_4)_3$ at 3000 r/min for 60 s. A capillary tube was used to deliver the LC into the structure. Excess LC was removed by using a second capillary tube to achieve a flat surface with a height that is equal to the micropillars.

IV. EXPERIMENTAL RESULTS

A. Surface Energy and Contact Angles of LC

The apparent surface energy per unit area $\gamma_{\rm LC}$ of 5CB at room temperature was measured using a pendant drop method (OCA20, Dataphysics Instruments GmbH, Filderstadt, Germany) [27]. Knowledge on the density of 5CB (1008 kg/m³) permitted the evaluation of $\gamma_{\rm LC}$ as 37.5 \pm 0.1 mN/m (or equivalently mJ/m²). Here, we note that the apparent surface

 TABLE
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 Contact Angles of 5CB on Various Solid Surfaces

	$\mathrm{Al}(\mathrm{ClO}_4)_3{}^a$	Au	Ni	Glass
5CB	$2.1^\circ \pm 0.3^\circ$	$6.3^\circ\pm0.6^\circ$	$17.4^\circ \pm 1^\circ$	$5.9^{\circ} \pm 0.7^{\circ}$

 ${}^{a}Al(ClO_{4})_{3}$ is deposited on the SAM of 11-mercaptoundecanoic acid on top of a Au layer.



Fig. 5. Illustration of the simplified geometry used to calculate the capillary and gravitational forces. (a) Top view. (b) Cross-sectional view (drawing not to scale). The LC is slightly underfilled and is pinned at the edge of the sidewalls of the Ni pillars by surface tension.

energy of 5CB depends on the orientation of 5CB at the interface of the droplet. When using the pendant drop method, the 5CB molecules assume a homeotropic alignment at the LC/air interface. Therefore, the surface tension measured in our experiments likely corresponds to the homeotropic condition. During the sensing process, the LC molecules may assume either homeotropic or planar alignments. However, the difference between the LC surface energy in the homeotropic and planar alignment is small ($\sim 10^{-3}$ mN/m) [28]. This difference is neglected in the following calculations.

The static contact angles of 5CB on relevant materials were measured with a goniometer. The results are shown in Table I.

B. Dominance of Capillary Force

To estimate the mechanical stability provided by the micropillar array, the capillary and gravitational forces acting on the LC in the structure were calculated and compared using the results described previously. In the calculation, the micropillar structures were assumed to be cylindrical, whereas the actual shape of the fabricated micropillars is more complex with a tapered sidewall. The structure of the actual micropillars is shown in Fig. 4.

As shown in Fig. 5, the structure consists of an array of cylindrical micropillars, each with diameter d and height h. This array is surrounded by a ring of inner diameter D. In the experiments, the shapes of the LC menisci formed between the pillars depend on the amount of LC deposited into the pillar array structure. To obtain a robust LC thin film, the capillary force should be dominating over gravity and other external mechanical forces. Two scenarios satisfy that requirement: 1) The pillar structure is underfilled with LC. The top surface of the LC layer is slightly lower than the top of the micropillars, and the menisci depend on the contact angle of the LC on the sidewalls of the Ni pillars; 2) LC is filled to the top level of the Ni pillars, and the angle between the tangent of the LC meniscus

and the Ni pillar, θ as in Fig. 5, can vary in a certain range as long as the capillary force is dominating.

We performed a simplified calculation to compare the capillary force with gravity. The capillary force generated by the micropillar array depends on the total length of the line of contact (L_C) between the LC and the micropillar array

$$L_C = n(\pi d)$$
(1)
$$F_C = L_C \gamma_{\rm LC} \cos(\theta) = n\pi d\gamma_{\rm LC} \cos(\theta)$$
(2)

where F_C is the capillary force, n is the total number of micropillars, d is the diameter of each micropillar, $\gamma_{\rm LC}$ is the surface tension of LC, and θ is the angle between the tangent of the LC meniscus and the Ni pillar, as shown in Fig. 5. Because, in the fabrication process, the Ni pillar is coated with Au and the Au surface is treated with the carboxylic-acid-terminated thiol monolayer and $Al(ClO_4)_3$, the contact angle of LC on top of Al(ClO₄)₃ was used for this calculation. The difference between the static, advancing, and retrieving contact angles should be noted here. In our experiment, however, the contact angle of 5CB on the Al(ClO₄)₃-coated Au surface was so small that the difference was difficult to measure. It is safe to state, however, that the difference between the contact angles is less than 10° , and the influence on the calculation of F_C is thus less than 2%. To find the number of pillars within the ring, as shown in Fig. 5, the ring area is divided into triangular areas. In each triangular area, the portion of the area occupied by the Ni pillar R_p can be determined as follows:

$$R_p = \frac{\frac{3}{6}\pi \left(\frac{d}{2}\right)^2}{\frac{1}{2} \times 2d \times \sqrt{3}d} = 22.67\%.$$
 (3)

Therefore, 22.7% of the area within the ring is occupied by the Ni pillars. The number of Ni pillars within the ring area can be determined

$$n = \frac{22.67\% \times \pi \left(\frac{D}{2}\right)^2}{\pi \left(\frac{d}{2}\right)^2} = 0.2267 \left(\frac{D}{d}\right)^2.$$
 (4)

The gravitational force acting on this volume of LC can be calculated as

$$F_G = \rho_{\rm LC} g V_{\rm LC} = \rho_{\rm LC} g h A_{\rm LC} = \rho_{\rm LC} g h (1 - R_p) \pi \left(\frac{D}{2}\right)^2$$
(5)

where $\rho_{\rm LC}$ is the density of 5CB [see (5)], $g = 9.8 \text{ m/s}^2$ is the gravity, h is the thickness of the LC film, which is equal to the height of the Ni pillars, and $A_{\rm LC}$ is the area covered by 5CB. To compare the gravitational and capillary forces, we take the ratio of these two forces and define the resulting dimensionless number to be N_C

$$N_C = \frac{F_C}{F_G} = \frac{4n\gamma_{\rm LC}\cos(\theta)}{\rho_{\rm LC}g(1-R_p)} \cdot \frac{d}{hD^2}.$$
 (6)

The device we fabricated has a micropillar array with 200- μ m pillar diameters and spacing. Hence, the geometric parameters are given as D = 10 mm, $d = 200 \ \mu$ m, $h = 20 \ \mu$ m (for instance), n = 567, and the length of the line of contact $L_C = 0.3561$ m. Referring to Table I, $\theta = 2.1^{\circ} \pm 0.3^{\circ}$; thus,

Fig. 6. Plot of (6) (ratio of capillary force to gravitational force) as a function of micropillar diameter d. In this study, the space between the pillars s is set to be equal to d.



Fig. 7. Representative structure with an array of four micropillars is simulated with Surface Evolver. The typical LC-filling scenario in the experiment, i.e., the underfilled micropillar array with LC, was simulated. Due to the surface tension of the LC, a curved interface is formed between the pillars.

we find the capillary force $F_C = 1.31 \times 10^{-2}$ N, $F_G = 1.20 \times 10^{-5}$ N, and $N_C = 1117$. Therefore, the capillary force, which holds the LC within the Ni pillar structure, dominates over the gravitational force. From (6), N_C is a function of d and h, given that D is constant and the space between adjacent pillars s is equal to d. Fig. 6 plots N_C as a function of d, while s is set to be equal to d. As shown in Fig. 6, $N_C \gg$ 100 if $d < 250 \ \mu$ m. Furthermore, as indicated in Fig. 6, N_C decreases as the diameter of the micropillars increases, and a lower height of the micropillars h results in a higher N_C . Therefore, theoretically, the micropillars with smaller diameters should lead to more robustly supported LC structures. However, the geometry of these pillar structures also appears to influence the aspects of the dynamics of the LC reorientation process; this is currently being investigated.

The surface roughness on the Ni pillar sidewall, which would affect the angle θ , has not been considered in this calculation. Therefore, the calculated result is an approximation. It should also be noted that the elastic energy of the LC was not taken into account. For a slab of LC with thickness h, the elastic energy in the bulk of the LC per unit area of the thin film can be estimated as K/h, where K is the elastic constant of the LC, while the surface energy per unit area can be estimated as γ_{LC} . Comparing the elastic energy with the surface energy, the ratio is $K/(h \cdot \gamma_{\rm LC})$. K is on the order of magnitude of 10^{-11} N, and $\gamma_{\rm LC}$ is around 10^{-2} N/m [28]. For a micrometer-scale system, the ratio of the elastic energy to the surface energy is thus on the order of 10^{-3} . The bulk elastic effects thus appear to be small compared to the capillary effects. The structure was tested with LC films and found to be resistant to gravity and shock during our handling in the experiments.





Fig. 8. Micropillar array with functionalized surfaces that cause LC to assume a homeotropic alignment. [(a) and (b)] In contact with air at the top surface of the LC film, the LC assumes a homeotropic alignment through the thickness, resulting in a dark image with bright rings when viewed using crossed polars. The bright rings around the micropillars result from the perpendicular anchoring of 5CB on the micropillar sidewalls. (c) Interference pattern consisting of two crossed isogyres in the conoscopic image indicates the homeotropic alignment of the LC in the thin film.



Fig. 9. [(a) and (b)] LC film in contact with DI H_2O at the top surface. The LC assumes an orientation at the interface with water that is close to parallel to the interface. (c) Conoscopic image confirms the nonhomeotropic alignment of the LC in the thin film.



Fig. 10. Area of LC in the micropillar array covered by DI H_2O appears bright and colored under crossed polars, indicating a nonhomeotropic orientation of 5CB, while the area exposed to air appears dark, indicating homeotropic alignment. A capillary tube is used to pull water away from the 5CB thin film. Image (a) is taken at 0 s when the removal of water starts, (b) 0.5 s, (c) 1 s, and (d) 2 s. 5CB supported by this micropillar array demonstrates a fast response to the change of interfacial conditions. As soon as 5CB is exposed to air, the molecules regain homeotropic position, and the image returns dark again.

The profile of the meniscus of the LC thin film supported in the micropillar array was difficult to observe with optical microscopy. Therefore, to predict the surface profile, simulations of the LC thin film supported by the micropillar array structure were carried out using Surface Evolver software, a public-domain finite-element package on a computer with a Core 2 Quad processor and 2-GB RAM. Surface Evolver calculates minimal energy surfaces by a gradient descent method [29], [30]. It has been employed in studies of droplets and multiphase interfaces [31], [32]. We simulated the "underfilled" scenario, where the surface of the LC was slightly lower than the top of the Ni pillars, and the meniscus of the LC depended on the contact angle of the LC on the sidewall of the Ni pillars. Fig. 7 shows the simulated LC profile between the micropillars. The initial state of the LC bulk consists of six flat surfaces surrounding each micropillar structure. The meshes used in the simulation were refined three times, and 600 iterations were used to evolve the shape of each surface. For clearer illustration, the structures are not depicted isometrically. In the simulation process, the surface energy, contact angles, and other physical properties of 5CB, as well as the properties of the device materials, were taken into consideration.

C. Performance of the Micropillar Array on LC Alignment

The micropillar device was subject to surface functionalization as described previously. LC was then filled into the chemically functionalized support structure. Once the microstructure was filled with LC, the capillary force firmly held the LC within the microstructure.

The orientation of 5CB was determined by using planepolarized light with a stereomicroscope (Nikon SMZ1500, Nikon Instruments Inc., Melville, NY, USA) with crossed polarizers (transmission mode). The micropillar array was placed on a rotating stage located between the polarizers. All images were captured using a charge-coupled device (CCD) camera (Imperx Camera, Imperx Inc., Boca Raton, FL, USA) mounted on the microscope. All images were obtained using a CCD integration time of 0.032 s. The images in the same experiment set were obtained using the same incident light intensity. The alignment profile through the thickness of the LC thin film results in an optical retardance, which is a function of the angle between the LC and the film normal. The homeotropic alignment of LC mesogens throughout the film thickness results in zero or low retardance, corresponding to a dark image under crossed-polar observation [33]. The homeotropic alignment was confirmed by observing the absence of transmitted light during a 360° rotation of the LC layer supported by the micropillar array. When the retardance increases, the color of the film changes in a manner described by a Michel-Levy chart, which presents the relationship between the optical retardance, birefringence, and film color [33]. As shown in Fig. 8(a) and (b), the LC thin film supported by the micropillar array appeared dark in the area between the micropillars. Bright rings with widths of micrometers were observed around the micropillars. This is because the LC was aligned perpendicular to the sidewalls of the micropillar, i.e., parallel with the substrate, as schematically illustrated in Fig. 2(a). The alignment profile around the micropillars resulted in an in-plane birefringence of 5CB in the proximity of the micropillar sidewall, hence the bright rings at crossed-polar observation. It should be noted that dewetting of the LC from the micropillar array will also lead to a dark image under crossed-polar observation when the observation is made under air or water. Therefore, to confirm the homeotropic alignment of the LC (and the absence of dewetting), we used the insertion of a condenser below the stage, and a Bertrand lens above the stage allowed conoscopic examination of the device. An interference pattern consisting of two crossed isogyres, as shown in Fig. 8(c), confirmed the homeotropic alignment [34], [35]. For this situation, the LC alignment profile in the micropillar array device is schematically shown in Fig. 2(a).

The in-plane orientation of the 5CB layer is indicated by a bright colored appearance when the sample was viewed between crossed polarizers. This was achieved by introducing distilled water on top of the LC layer supported by the micropillar array device. As indicated in Fig. 2(b), 5CB at the aqueous–LC interface assumes a planar orientation. This device appeared bright when viewed between crossed polarizers, as shown in Fig. 9.

The orientational response of 5CB was confirmed to be reversible. The 5CB supported by the micropillar array was initially aligned with a homeotropic orientation, and the LC layer appeared dark. When water was introduced on top of the LC layer, a bright colorful image was observed where water covered the LC layer. Subsequently, water was removed from one side with a capillary tube. When the LC layer was exposed to the air again, the molecules regained their homeotropic alignment. As shown in Fig. 10, the area of 5CB covered by water



Fig. 11. *Test apparatus*. The sensor was placed in a flow cell with tubes for gas entry and exit. The flow cell was fed by the diluted DMMP. The gas flow rate was \sim 500 sccm. The sensor was placed between crossed-polarizing films illuminated by a white light source. Images of the sensor were captured periodically by a digital camera and monitored on a computer (not shown).

possessed a tilted or planar orientation and appeared bright under crossed-polar observation. When water was removed by a capillary tube, the LC resumed the homeotropic alignment and returned to a dark image. We observed several repeating cycles of these responses in the experiment. The response time of the LC film was as short as 1 s.

D. Vapor-Phase Sensing Using Micropillar Array

The LC device fabricated using the micropillar array was tested for sensing of DMMP from a vapor sample. Fig. 11 shows the test apparatus. The sensor was placed in a flow cell having inlet and outlet ports for gas entry and exit. The top and bottom surfaces of the flow cell possessed glass windows to allow optical transduction of the ordering transitions. The sensor was sandwiched between a pair of crossed polars. This assembly was illuminated by a white light source. A 10-ppm source of DMMP was fed to the sensor. The DMMP vapor was mixed with air at a ratio of 1:1 before reaching the sensor. The concentration of DMMP reaching the sensor was 5 ppm. The relative humidity (RH) of the chamber in which the sensor maintained was 30%. The status of the sensor was monitored by a digital camera connected to a computer.

Fig. 12 shows the response of the sensor to 5-ppm DMMP gas. In Fig. 12(a), the LC was aligned perpendicular to the interface. Since the polarizing films on the top and bottom of the sensor were crossed, the intensity of light transmitted through the system was low and resulted in a dark image at the digital camera. In Fig. 12(b) and (c), the regions where the concentration of DMMP at the surface was sufficient to cause an orientational transition in the LC appear bright. As reported previously [19], DMMP diffused through the LC film and caused the LC to depart from its initial homeotropic orientation. The change in orientation of the LC was evident within 30 s of introduction of the DMMP vapor into the test device, and the LC reached a new steady state at 60 s [Fig. 12(d)], resulting in a completely bright image. This rate of response of the 5CB thin film was consistent with the results reported in [14]. In our previous report using micropillars [19], the response time was



Fig. 12. *Time sequence images of the sensor's response to DMMP gas* (5 *ppm*). At t = 0 s, the initial state of the system corresponds to the homeotropic orientation of the LC. At t = 15 s, after introducing DMMP, the response of the sensor is evidenced by an increase in the transmitted polarized light intensity in certain regions. In 60 s, the orientational transition of the LC completes, and the LC in the micropillar array demonstrated the maximum brightness.

much slower (range of 30 min). The difference between the previous and current results is likely due to differences in the fabrication and the test processes. First, the micropillar array was electroplated using a poly-isobornyl acrylate mold in [19], whereas, in this study, a PR was used as the electroplating mold. The difference in the fabrication process may have impacted the quality of the micropillar structure. Second, in the previous study, the micropillar array supporting the 5CB thin film was tested with dry DMMP vapor, whereas, in this study, the humidity of the test vapor was controlled to be 30% RH. Differences in humidity may impact the rate of response of the LC sensors. The possible role of humidity on the dynamics of the sensors remains to be determined.

V. CONCLUSION

We have presented the design and fabrication of a micropillar array that supports LC thin films for sensing applications. The molecules in the supported LC thin film undergo orientational ordering transitions upon contact with liquid- or vapor-phase analytes. These transitions in orientation change the polarization of light passing through the LC and thus modulate the intensity of light transmitted through crossed polars. The micropillar array generates capillary forces that, at the micrometer scale, can stabilize the LC film. The LC thin film supported in this device was found to be robust and resistant to gravitational forces and mechanical shock. The sensing device with an LC thin film was tested. DMMP was used to demonstrate the vapor-phase sensing using the micropillar-supported LC thin film. DMMP vapor at a concentration of 5 ppm was detected with a response time of 30–60 s.

In future studies, we aim to quantify the relationships between analyte concentration, LC film color/brightness, film thickness, effective birefringence, optical retardance, etc., so that sensing devices with optimized quantitative analyzing capabilities are realized. Alternative fabrication methods to create microfabricated structures, such as deep reactive ion etching on glass, will be explored to achieve potentially higher quality and better uniformity structures. The micropillar arrays will also be integrated into microfluidic devices, where controlled microfluidic interfaces will be formed in an automated fashion [36]. We envisage that several functional microfluidic components can be integrated into this sensing device. For example, a sample filtration or preparation component might be used to reduce impurity and address sample contamination issue. A microtemperature control component integrated into the device might also be useful. In future studies, we will also investigate sensing devices with different LCs, such as E7, to establish broad operating temperatures and also investigate approaches that will enable the detection of other analytes, such as virus and enzymes.

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