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# Surface holograms for sensing application

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**Abstract.** Surface gratings with periodicity of 2  $\mu\text{m}$  and amplitude in the range of 175 and 240 nm were fabricated in a plasticized polyvinylchloride doped with a metalloporphyrin (ZnTPP), via a single laser pulse holographic ablation process. The effect of the laser pulse energy on the profiles of the fabricated surface structure was investigated. The sensing capabilities of the fabricated diffractive structures towards amines (triethylamine, diethylamine) and pyridine vapours were then explored; the holographic structures were exposed to the analyte vapours and changes in the intensity of the diffracted light were monitored in real time at 473 nm. It was demonstrated that surface structures, fabricated in a polymer doped with a metalloporphyrin which acts as analyte receptor, have a potential in sensing application.

## 1. Introduction

Two research problems are being addressed in the herein paper. First concerns fabrication of surface holographic gratings, while the second focuses on exploring the sensing potential of such structures.

Surface holograms can be fabricated using various approaches. Surface relief structures can be formed upon exposure of a photoresist to a patterned light (holographically or with a mask), which process is followed by wet processing needed to develop the surface profile. In mass production, the photoresist structures are copied to create a master which is used in embossing.[1] Surface relief structures can also be created by direct inscription in self-processing photopolymers, but this technique is limited to low spatial frequencies.[2] Post-recording thermal treatment [3] can produce surface profiles at higher spatial frequencies, but this process is time and energy consuming and thus more difficult to implement on a large production scale. Another method of surface hologram fabrication consists of holographic patterning of a material using high power laser which ablates locally material from the surface. This technique is a flexible one-step patterning method that can be applied to a range of materials.[4] The herein paper utilises this technique in patterning of dye doped polymer material. The potential applications of surface structures created in dye doped polymers range from holographic sensors, security devices [5] to distributed feedback lasers (DFB) [6] and DFB lasers based sensors [7].

The herein paper explores the sensing capabilities of the produced structures. The dye used to dope the polymer in which the holographic structure is inscribed belongs to a metalloporphyrin class of dyes which are known to exhibit good binding properties towards various analytes including volatile organic compounds. The sensing capabilities of metalloporphyrins were widely explored in various types of sensors [8], yet to our knowledge they have not been investigated in surface holographic sensors before. The sensing principle of such sensors relies on the change in the refractive index of the sensing material and/or swelling of the grating, which induce changes in optical characteristics of the



light diffracted by the surface structure. The operation of the herein sensor is based on detecting changes in diffraction efficiency of the holographic grating, occurring upon its exposure to amines (diethylamine and triethylamine) and pyridine vapours.

## 2. Experimental details

### 2.1. Materials

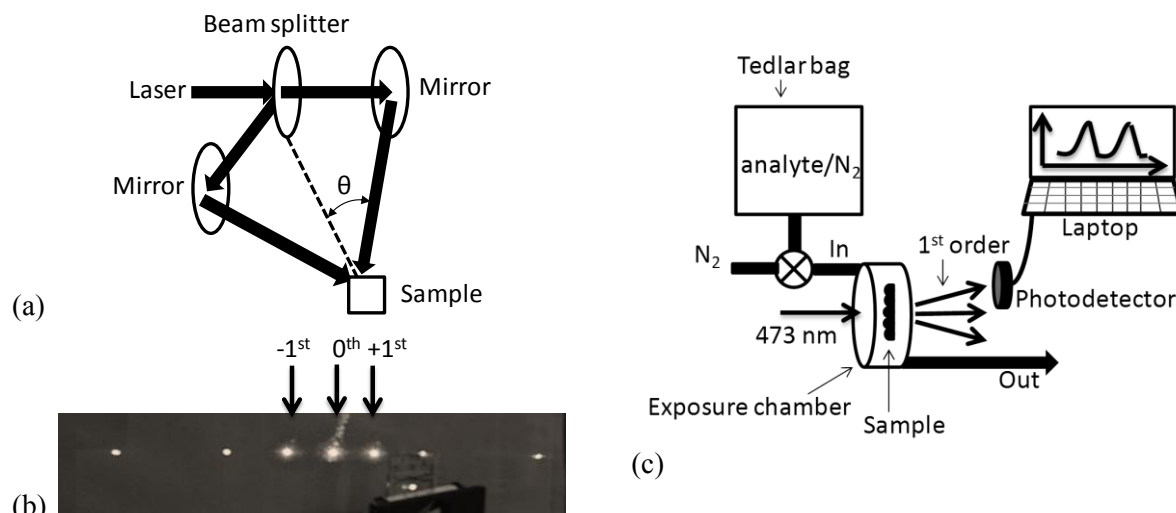
High molecular weight polyvinylchloride (PVC), dioctyl terephthalate (DOTP),  $\text{Zn}(\text{acac})_2$  and 5,10,15,20-tetraphenylporphyrin (TPP) were obtained from Sigma-Aldrich. Diethylamine (DEA) and pyridine (Pyr) were purchased from Fisher Scientific, while THF, DCM and triethylamine (TEA) were supplied by Roth. All chemicals were used as received. 5,10,15,20-tetraphenylporphyrin zinc(II) (ZnTPP) was synthesized by metallation of TPP with  $\text{Zn}(\text{acac})_2$  in DMC under reflux using a procedure adapted from literature.[9]

### 2.2. Fabrication and characterisation of plasticized PVC films doped with ZnTPP

Plasticized PVC films doped with ZnTPP were fabricated by spin coating 100  $\mu\text{l}$  of polymer solution on half of a microscopic glass slide (3000 rpm, 30 s). The polymer solution was prepared by mixing together 75 mg of PVC, 15 mg of DOTP and 6.6 mg of ZnTPP in 3 ml of THF. The thickness of the film was measured with Asylum Research MFP Bio AFM to be  $174 \pm 20$  nm. UV-vis spectra of the films were recorded with Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer.

### 2.3. Fabrication of surface gratings via holographic ablation and their characterisation

Surface gratings were fabricated in PVC films doped with ZnTPP using holographic set-up presented in figure 1(a). Ns pulsed Nd:YAG laser (Continuum Surelite) operating at 532 nm was used in this studies. The ablation was carried out with a single laser pulse. The energy of the laser pulse is an average laser pulse energy measured with a pyroelectric detector (Newport, 919E) over 30 s exposure at the laser repetition rate of 10 Hz. The surface profiles of the fabricated structures were investigated with Nanosurf AFM. To determine diffraction efficiency of the 1<sup>st</sup> order (figure 1(b)), the structures were illuminated with a diode laser operating at 473 nm and the intensity of the diffracted 1<sup>st</sup> order beam  $I_1$  was measured with a photodetector (Newport, 818-SL/DB); diffraction efficiency  $\eta$  was calculated from  $\eta = I_1/I_0$  where  $I_0$  is the intensity of the incident beam.



**Figure 1.** (a) Set-up used to holographically pattern the material ( $\theta = 7.6^\circ$ ) (b) photograph of the light pattern obtained upon illumination of the fabricated structure with 473 nm laser with indicated  $\pm 1^{\text{st}}$  and  $0^{\text{th}}$  orders (c) set-up used to investigate response of the holographic structures to analyte vapours.

#### 2.4. Experimental set-up used to examine the response of the holographic structure to analytes vapours

The scheme of the set-up used to investigate the sensing response of the holographic structures to TEA, DEA and Pyr vapours is illustrated in figure 1(c). The sample was placed in a 100 ml chamber connected to a gas inlet switchable between pure N<sub>2</sub> and mixture of the analyte vapours and N<sub>2</sub>. The outlet of the chamber was connected to the pump. The mixtures of the analytes and N<sub>2</sub> at the analyte concentration of 10 000 ppm were prepared by injecting the appropriate volume of the liquid analyte into a 10 L Tedlar bag, which was then followed by filling the bag with N<sub>2</sub>.

The general procedure for the investigation of the response of the holographic structure to analyte was as follow. First, the sample was exposed to N<sub>2</sub> flow (1 L/min); once the signal stabilized the inlet gas was switched to the analyte mixture; then after the response saturated, N<sub>2</sub> flow was turned on again in order to study the recovery of the initial signal and check the reversibility of the sensor's response. The signal, being the intensity of the diffracted 1<sup>st</sup> order at probing wavelength of 473 nm, was monitored in real time with a photodetector connected to the computer interfaced with software for data acquisition.

### 3. Results and discussion

#### 3.1. Surface holographic gratings fabricated through single pulse ablation

Ablation, in general, depends simultaneously on the properties of the laser and these of the material. The decomposition of the material can go through various pathways depending on the nature of the interaction of the light with the material. For ns pulsed lasers, ablation is often driven by thermal processes and it is wavelength dependent.[10] In our studies, the ablating laser wavelength of 532 nm coincides with edge of the absorption peak corresponding to the Q-band of ZnTPP (figure 2(a)). The absorbance of the polymer film at 532 nm was found to be 0.0177.

Employment of ablation in holographic patterning combines the advantages of a one-step fabrication process with the flexibility of the experimental set-up which can be easily adjusted to obtain structures with the desired periodicity. Since periodicity of the grating often limits the achievable thickness of the grating  $d$ , and diffraction efficiency  $\eta$  depends on  $d$  as per equation (1) (thin grating regime), the periodicity of the grating must be adjusted to obtain structures of the desired  $d$  and thus  $\eta$ .

$$\eta = J_1^2(\Phi) \quad (1)$$

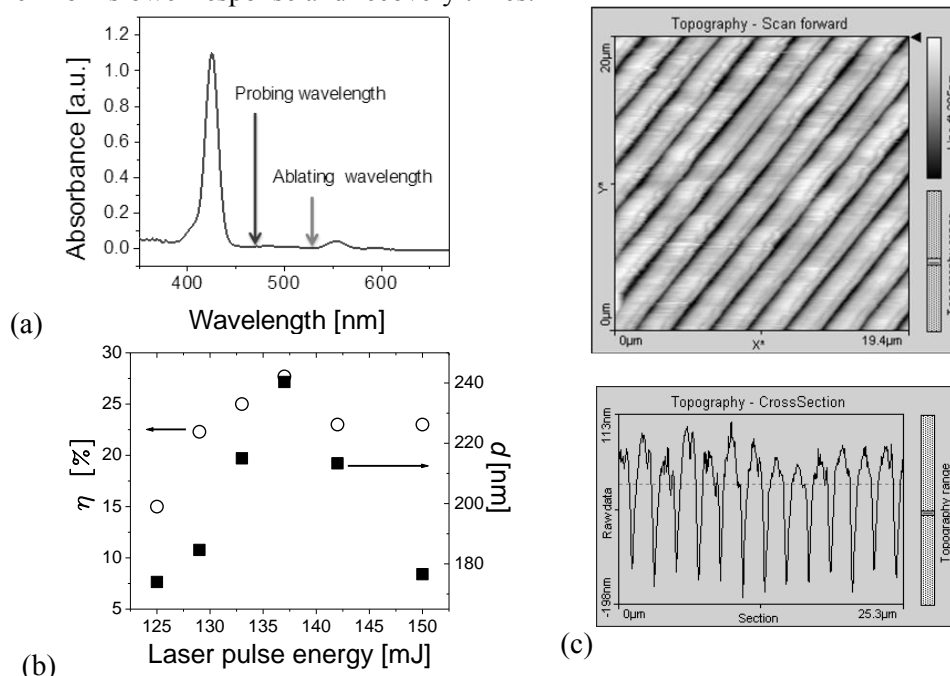
$$\Phi = 2\pi\Delta n d / \lambda \quad (2)$$

where  $J_1$  is the Bessel function of the first kind,  $\Phi$  is phase,  $\Delta n$  is refractive index modulation of the grating and  $\Delta n = n_g - n_m$  with  $n_g$  being the refractive index of the grating material and  $n_m$  - refractive index of the medium surrounding the grating, and  $\lambda$  is wavelength of the interrogating laser.

For the periodicity of 1  $\mu\text{m}$ , the achievable  $d$  was on the order of 100 nm. Increasing periodicity to 2  $\mu\text{m}$  allowed formation of structured with  $d = 240$  nm. The maximal  $d$  was obtained upon optimisation of the energy of the ablating laser pulse. The results of such optimisation for structures with the periodicity of 2  $\mu\text{m}$  (being of main interest in the herein studies), are illustrated in figure 2(b). It can be seen from figure 2(b) that  $d$  and  $\eta$  follow similar trend, in accordance with equation (1). It should be mentioned that formation of the surface structure became already visible at the laser pulse energy  $\sim 10$  mJ, yet structures with highest  $\eta = 28\%$  were obtained with laser pulse energy reaching 133 mJ.  $\eta = 28\%$  is close to the theoretical maximum (33.5%) for thin holographic surface grating and was obtained for the structures with  $d = 240$  nm. An example of data on surface studies obtained with AFM is illustrated in figure 2(c).

Apart from studies discussed above, optimisation of the structures was also carried out through adjustment of the composition of the material. The starting composition was based on the formulation often used in fabrication of sensors, with 1:2 weight ratio between PVC and plasticizer, respectively.[11] Such highly plasticized composition was reported to result in quick response time of a sensor. Although, it was possible to fabricate holographic structures in materials with such high

plasticizer content, the structures were unstable over the time ( $\eta$  was noted to decrease over the time). Using composition with 5:1 (PVC:DOTP) ratio allowed fabrication of stable structures which thought might suffer from slower response and recovery times.



**Figure 2.** (a) UV-vis spectrum of the polymer film (b) diffraction efficiency  $\eta$  and thickness of the grating  $d$  plotted versus energy of the laser pulse used to fabricate surface holograms through ablation (c) AFM data showing surface map (upper) and cross-section of the grating (lower).

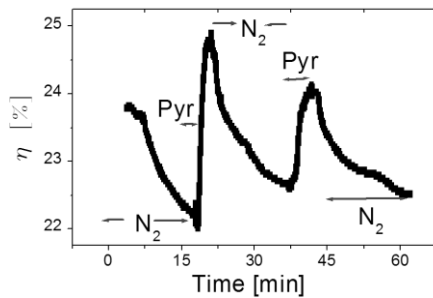
As illustrated above, holographic patterning based on ablation offers quick fabrication of efficient surface structures. The limitation of the technique is the size of the structures, which is determined by a need for high power laser irradiation necessary for the ablation process. The diameter of the structures fabricated in the herein studies was  $\sim 6$  nm.

### 3.2. Sensing capabilities of the produced structures towards TEA, DEA and Pyr vapours

Metalloporphyrins are good receptors of many volatile organic compounds, which capability was broadly employed in colorimetric sensors.[12] The question of the herein studies was whether their binding capabilities can be used in surface holographic structures to produce effective sensors. The working principle of such sensors is based on the change in the refractive index which arises in the material in presence of the analyte and/or swelling of the structure (equation (1)).

The changes in  $\eta$  occurring upon exposure of the structures to analytes was monitored at  $\lambda = 473$  nm. This  $\lambda$  is in the spectral window of both ZnTPP and ZnTPP coordinated by the analytes.[13] (Alternatively, interrogation could be carried out at  $\lambda > 650$  nm, but for the same grating thickness a lower diffraction efficiencies will be detected, as seen from equation (2)).

Table 1 summarises the responses of the holographic structures to the three analytes. No changes in  $\eta$  were observed upon exposure to DEA, while an increase by 1 and 3% in  $\eta$  was noted for TEA and Pyr, respectively. The response to vapours was immediate, yet saturation of the signal occurred in 10 min for TEA and 5 min for Pyr. No full recovery of the baseline could be achieved upon subsequent exposure of the holographic structure to pure  $N_2$  in the following step (up to 30 min) for TEA or Pyr; it could be seen that the colour of the samples outside holographic structures differed from that of the fresh sample. This indicated that the analytes were not affectively removed from the layer, which problem could potentially be solved by incorporation of a heater to the sensor's architecture. Subsequent exposure of the grating to the analyte vapours resulted again in an increase of the signal (figure 3).



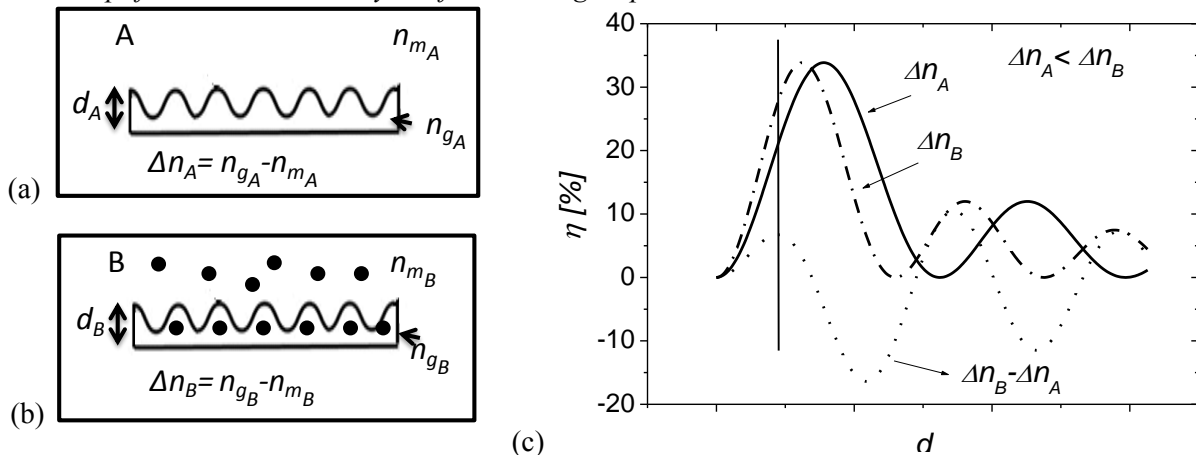
**Figure 3.** Changes in  $\eta$  monitored over the time upon exposure of the holographic structure to the flow of  $N_2$  followed by flow of Pyr/ $N_2$  mixture (two cycles of exposure).

It should be mentioned that structures with  $\eta = 24\%$  (and not with max  $\eta$ ) were used in sensing studies; this should provide larger dynamic range for sensor operation, which will be illustrated in the following part (figure 4).

**Table 1.** Summary of the responses of the surface structures to analytes.

Analyte	$\Delta\eta$ [%]	Time of max $\Delta\eta$ [min]
Pyr	3	5
TEA	1	10
DEA	0	-

### 3.3. Simplified theoretical analysis of the sensing response



**Figure 4.** (a) and (b) illustrate grating before and after exposure to analyte. Graph (c) illustrates  $\eta$  plotted versus  $d$  (equation (1)) (similar graph could be obtained for  $\eta = f(\Delta n)$ ). It is assumed that changes in  $d$  are negligible in comparison to changes in  $\Delta n$ . For a given thickness  $d$  indicated with a vertical line in the plot,  $\eta$  will increase if  $\Delta n$  increases provided that  $\Delta n_B - \Delta n_A > 0$ . Optimal operation regime is where  $\Delta n_B - \Delta n_A$  reaches max or min. (The figure is just for illustration purpose and it is highly simplified; other interpretations including variation in surface amplitude are also possible.)

To fully understand the sensing response and the observed trend for the three analytes, further studies on refractive index of the whole system under investigation are needed and the part below only speculates about possible processes responsible for the observed responses. The response of the herein grating is governed by equation (1). As can be seen from equation (2) the change in the diffraction efficiency  $\eta$  can be caused by either a change in the thickness of the grating  $d$  or a change in the refractive index modulation  $\Delta n$ . Exposure of the polymer films to analytes can induce swelling thus the thickness of the grating  $d$  can potentially increase. As far as changes in the refractive index modulation  $\Delta n$  arising due to exposure of the film to the analyte are concerned, there are two contributors  $n_g$  and  $n_m$ . Introduction of analytes vapours to the medium surrounding the grating ( $N_2$ ) will result in an increase of  $n_m$ . Changes in  $n_g$  are more difficult to predict; introduction of the analyte into polymer matrix should lead to increase of  $n_g$  while material swelling will have the opposite effect. Taking into account experimental data from table 1 and comparing them against the refractive index of the analyte, it can be seen that trend in  $\eta$  observed experimentally for the three analytes  $\Delta\eta(\text{Pyr}) > \Delta\eta(\text{TEA}) > \Delta\eta(\text{DEA}) = 0$  is correlated to refractive index of the analytes ( $n(\text{Pyr}) = 1.509 > n(\text{TEA})$

=1.401 >  $n(\text{DEA})$  =1.385). Based on this, it can be speculated that this is an increase in  $\Delta n$  which governs the response with the main contribution coming from  $n_g$ . Figure 4(c) depicts the predicted operation regime of the sensor. Further experimental and modelling studies are yet needed to confirm and to fully understand the response. Measurements of the refractive index of the unpattern layer under exposure to the analyte will help understanding the observed phenomena.

#### 4. Summary and future perspectives

It was demonstrated that holographic ablation is a quick and flexible fabrication technique of surface holographic gratings in functionalized polymer materials. The sensing capabilities of the fabricated structures to volatile organic compounds such as amines and pyridine were explored and presented. Although further studies and improvements on the characteristics of the holographic structures' responses to analytes are needed to obtain competitive sensors, the results reveal still unexplored application potential of surface holograms in sensing. Other potential and important applications of surface holograms fabricated in functionalized materials could include stimuli responsive security devices and actuators.

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