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Photo-Pens: A Simple and Versatile Tool for Maskless Photolithography

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Abstract

We demonstrate conical pores etched in tracked glass chips for fabricating patterns at micron-scale. Highly fluorescent patterns based on photopolymerization of diacetylene films were formed by irradiating UV light through conical pores called “*photo-pens*”. The properties of photo-pens were investigated through experiments, Finite-difference-time-domain (FDTD) simulations and numerical calculations based on Fresnel equations. We show that the pattern dimensions are easily controlled by adjusting the exposure time. Thus, patterns with a range of dimensions can be fabricated without any need of changes in the pore diameter. Parallel patterning was also demonstrated by simultaneously exposing the films to photons through multiple pores in the chip. Our method provides an inexpensive, versatile, and efficient way for patterning without the use of sophisticated masks.

Introduction

Photolithography is a microfabrication technology widely used to selectively remove parts of a thin film or a bulk substrate [1–4]. It uses light to transfer a geometric shape present in a mask onto an optically sensitive resist on the substrate. The pattern on the photoresist is then generated on the substrate with a series of chemical or physical development processes[3]. To date, photolithography is the most commonly employed form of lithography[4]. Therefore, it has been extensively used in the fabrication of electronic integrated circuits (IC)[1,2], optical circuits[5], micro electro-mechanical systems (MEMS)[6], microfluidic devices[7] and biochips[8]. Compared with other lithographic methods such as dip-pen lithography[9], nanopipette-based[10] and nano-fountain lithography[11], and electrified jet printing,[12] photolithography is a massively-parallel, cost effective, and high output process. Its resolution is, however, limited due to diffraction limit. Unless special and expensive methods are employed, photolithography renders a poorer resolution than probe-based lithography techniques. This is because diffraction imposes physical limitations on the photons irradiating the photoresist through the masks where the resolution is limited to $\sim\lambda/2$ (λ is the wavelength of the irradiation light).[1] An important consideration in photolithography is the cost of the photomasks fabrication with features <2 microns which is usually a costly and time consuming process, and often it relies on expensive instrumentations[7,8]. Furthermore, the features in the masks can not be altered once they are engraved on the mask, making this process less versatile and efficient. Therefore, there is a great demand for inexpensive and fast “*maskless lithography*” where patterning can be performed without the use of masks.

Here, we investigate pattern fabrication using conical pores fabricated in glass. Our Finite-difference-time-domain (FDTD) simulation results showed that the light transmission was

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much higher for a conical pore than for a cylindrical pore whose pore diameter was equal to the smaller pore diameter of the conical pore. We fabricated the conical pores in tracked glass by using a mature chemical etching technique¹³ which is routinely performed under ordinary laboratory conditions and does not require clean room facilities. The instrumentation involved in our fabrication method is inexpensive, and all elements of the fabrication process can be performed in a wet laboratory. In principle, any given pattern in photo-active films on a variety of surfaces can be prepared using this method with patterns resolution of ~400 nm.

For the proof-of-concept experiments, we deposited electrostatically negatively-charged self-assembled diacetylene liposomes as our photoresist on positively charged glass substrates. Following exposure to UV photons at 254 nm through pores and washing and heating of the resist, we obtained stable and highly fluorescent patterns which were easily observable under a microscope. A low power UV source of intensity $15 \mu\text{W}/\text{cm}^2$ was sufficient to perform the desired lithography with an exposure time of < 1 minute. We also investigated experimentally and through simulations and numerical methods, the dependence of the pattern size on the pore diameter and the exposure time. We found that the pattern dimensions can be easily modulated through the use of exposure time without any need to change pore size. Computer-controlled parallel patterning was also accomplished by exposing the resist through multiple conical pores fabricated in a chip without any down time in the lithographic process. Since the controlling the exposure time is relatively straight forward and inexpensive to accomplish, our method would provide an efficient, inexpensive and versatile way of photo-patterning and will find potential applications in materials and life sciences.

Experimental Section

Fabrication of pores in the glass chips

We adopted a chemical etching method to prepare the pores in the glass chips. The glass chips were tracked with an ion flux of 10^2 – 10^5 ions/ cm^2 at GSI (Darmstadt, Germany). The tracked glass chip was adhered to a microscope glass slide with a polydimethylsiloxane (PDMS) film (~0.2–0.5 mm in thickness). PDMS also acted as a stress absorber cushion during mechanical handling and related processes such as etching and patterning. Before adhering the two glasses, a hole (5 ± 0.5 mm in diameter) was drilled through the microscope glass slide. The uncured PDMS was applied to the surface of the altered microscope glass slide. During the curing process, the tracked glass was then adhered to the microscope slide which left naked an area through which the chemical etching was performed.

Briefly, the fabrication of conical pores is as follows. We used anisotropic etching to create conical pores in the glass chips. Our etching apparatus consists of two half-U tubes in between the tracked glass chips were placed. The conical pores were formed due to anisotropic etching of the chip of which one side was exposed to HF (24.5%) solution in NaCl (0.5 M, etching solution) while the other side of the glass chip was in contact with a saturated $\text{Ca}(\text{NO}_3)_2$ (blocking solution). NaCl in HF solution was used to enhance the ionic conductivity of HF solution. The etching process was monitored by measuring ionic current; a spike in the ionic current across the glass chip indicated through-pore formation in the glass. At this time, the etching was stopped. The etching time for our chips was ~700–900 sec. This corresponded to an etching rate of ~75–100 nm/s along the tracks, which is much faster than etching along the lateral direction.¹⁴ The characterization of the pores in glass chips was carried out by FEI Quanta 600 FEG (equipped with a Bruker EDX detector) and Hitachi 570 scanning electron microscopes (SEM) (Figure 1A) and an optical microscope

(Lieca DMIRB) equipped with a QImage (Cooled Mono 12-bit) CCD camera. The topology of liposome on surfaces was measured using AFM (Topometrix TMX1010).

Synthesis and characterization of liposomes.[15,16]

The procedure to make the liposome solution is described as the following: 10,12-pentacosadiynoic acid (from GFS Chemicals) was dissolved in chloroform. The large aggregates from the solution were filtered through nylon membranes with 450 nm pores. The solvent was then evaporated to form thin dry film on the surface of a round bottom flask. Then 50 mL of deionized water was added into the flask coated with the dry film to make monomer concentration of 1 mM. The solution was sonicated (Branson 2510) until the film was suspended. The suspension was further sonicated using a tip probe sonicator (Model CV33, Sonics Vibracell) for 30 minutes to reduce the size of the liposomes (50–400 nm)[15,16]. To promote the self-assembling of monomers, the solution was kept at 4° C overnight.

Deposition of unpolymerized self-assembled diacetylene liposomes on aminosilane functionalized glass

The resist for patterning was composed of self-assembled diacetylene liposomes deposited on 3-aminopropyltriethoxysilane (APTS) treated glass slides. Figure 1C shows the 1,4 addition polymerization reaction of self-assembled diacetylene molecules. The photopolymerization of diacetylene is well-known and many excellent reviews and books are available on this topic.¹⁷ Prior to APTS reaction, the glass slides were washed thoroughly with soap and rinsed with ethanol and deionized (DI) water. They were then soaked in fresh piranha solution for 30 minutes followed by a thorough rinse in copious ethanol and DI water. *Caution: Piranha solution is a strong oxidizer, and all the safety precautions must be taken when working with this.* The functionalization of glass with amino-silane was performed by immersing the glass slides in 10% v/v APTS in 95% ethanol containing solution for one hour. The slides were rinsed with sequentially ethanol and DI water and were cured at 90° C for 5 hours. The amino-functionalized slides were kept at 4° C until further use.

The negatively charged liposomes were electrostatically adhered to positively-charged glass substrates by immersing the silanized glass slides in the self-assembled unpolymerized diacetylene liposome solution at 25° C for 4 hours resulting in a single layer of liposomes on the surface. Figure 1B shows an AFM image of diacetylene liposome deposited from a diluted solution on a glass slide. The self-assembled liposomes had 3-D structures with dimensions of 100–300 nm which matches with our previous studies.¹⁵

Lithography using conical pores in glass chips

We used a home-assembled xyz piezoelectric stage to accurately control the exposure of the pattern positions. A schematic of the lithographic apparatus is shown in Figure 1D. *A*, *B* and *C* are the *X*, *Y* and *Z* piezoelectric stages respectively. *X*, *Y*, and *Z* stages can be moved independent of one another with a step-size of 50 nm. *D* was an “L” shaped holder mounted on *C* which supported the UV lamp system (*E* and *F*), and the photomask system (*G* and *H*). *E* and *F* are the UV lamp and UV-light blocker respectively. The UV-light blocker protected the operator from harmful UV exposure. *G* was a stress absorbing cushion made of rubber or sponge for the purpose of mechanical passive compliance and for protecting the glass chip *H* from excessive stress. *I* was a microscope slide for providing mechanical support for pores-containing chip. We adopted the contact mode for the monomer coating UV exposure portion of the experiment. The exposure position was accurately manipulated by the piezoelectric stages driven by controller software. The liposome coated glass slide was placed on the *X* and *Y* piezoelectric stages. The stages were then moved in a desired pattern

by a computer program. The UV exposure along the programmed path produced the desired pattern after washing-off the unpolymerized liposomes from the surface.

As-photopolymerized diacetylene (PDA) films were in '*blue*' form (Figure 1C). Because the quantum yield (Q_y) of blue-PDA is extremely small ($<10^{-4}$) [15–18], the emission of patterns were not observable. Heating the patterns to 70–90° C or exposed to ethanol (in vapor or liquid form) for a few minutes (1–5 minutes) to convert it into '*red*' form [18]. Q_y of red-PDA is known to increase many orders of magnitude [15–18] and was easily observed as an intense red emission when excited with a 41004 Texas Red filter using a CCD camera (exciting and emitting band widths of the filter used were 527–567 nm and 605–682 nm respectively).

Results and Discussion

Using conical pores, we investigate and demonstrate an inexpensive, fast, and easy to implement lithographic technique. Its versatility is further demonstrated by the fact that we were able to fabricate patterns with feature sizes ranging from 1.5 to 50 μm under wet laboratory conditions without any clean room facilities.

Conical pore characterization

Figure 1A shows SEM images of cross-section (left) and top view (right) of typical pores etched in a glass chip. The pore has a conical structure with the smaller (d_s) and larger pore (d_l) diameters $\sim 10\ \mu\text{m}$ and $63\ \mu\text{m}$ respectively, and the length of the pores $\sim 70\ \mu\text{m}$. The pore diameter and number of pores in a given chip were easily controlled by choosing the appropriate etching conditions for a desired result, such as concentration, temperature of etching solution, etching time and pore-tracking density. In our experiments, we have prepared chips with smaller (d_s) pore diameters ranging from $1\ \mu\text{m}$ to $20\ \mu\text{m}$, and larger (d_l) pore diameters from $15\ \mu\text{m}$ to $50\ \mu\text{m}$ [14]. A typical optical micrograph of a conical pore fabricated in glass chip is shown in Figure 2A. The dark rings with the bright center indicate the positions of pores, the dark rings corresponding to the conical side walls of the pores. They looked dark because light was refracted away from these regions, and the transmission of the light to the detector was drastically reduced. The bright centers, on the other hand, corresponded to the small openings of pores through which the transmitted light reached the detector [14]. The absorption spectrum of the glass in 200–800 nm region shows that the photons with wavelength $<300\ \text{nm}$ were almost completely absorbed by the glass (Figure 2B). For a wavelength 254 nm where liposome polymerization was performed, the transmission efficiency through glass chip was $<1\%$. This corresponded to a transmission intensity $<15\ \text{nW}/\text{cm}^2$ that passed through glass matrix and was insufficient for photopolymerization of self-assembled diacetylene monomers for shorter exposure times of $<5\ \text{s}$ (see below). Our glass chips are, thus, an excellent choice for pattern fabrication on photoresists that utilize UV photons for development.

FDTD simulations

We used FDTD simulations to gain a better understanding of light propagation through the pores. FDTD simulations were based on solving Maxwell's electrodynamic equations (Eqs. 1 and 2).¹⁹ A home-written code was used for all the simulations.

$$\nabla \times E = -\partial B / \partial t \quad \text{Eq. 1}$$

$$\nabla \times H = \epsilon \partial E / \partial t \quad \text{Eq. 2}$$

where $\nabla \times = (i\partial/\partial x + j\partial/\partial y + k\partial/\partial z) \times$ is curl operator, i, j and k are orientation unit vectors; E and H are electric and magnetic field of the light respectively; and $B = \mu H$. μ and ϵ are permeability and permittivity respectively of the media (air in our case). A two-dimensional FDTD method was adopted to simulate the propagation of light. We assume a transverse magnetic (TM) polarized light ($\lambda = 254$ nm) is normally incident on the larger opening side of the glass chip, and a CCD detector was located at the smaller side of the chip. The refractive index and absorption index coefficient of the glass chip were 1.54 and 65.8 mm^{-1} respectively. The transmission through the conical pore can be classified into three groups (Figure 3): the first portion propagated directly out of the smaller pore of the cone (labeled as A'); the second part impinged on the side of pore, was reflected and then transmitted out of the pore (labeled as B'); and the third part impinged on the side of pore and was refracted into the glass chip after a significant attenuation then penetrated into free space (denoted as C'). The transmission through the cylindrical pore is highly nonuniform because few light modes are coupled out. These modes interfere with one another to generate a nonuniform intensity distribution.

The ratio of the integrated intensity for conical and cylindrical pores was obtained with FDTD simulations 1.47. Higher transmission output for conical pores can be attributed to a larger photon coupling efficiency for conical structures that significantly enhances the transmission output. Therefore, the use of conical pores over cylindrical pores is preferred for photolithographic applications. Furthermore, the measured photon transmission out of the smaller pore diameter of conical pores ($d_s \sim 12 \mu\text{m}$ and $d_l \sim 42 \mu\text{m}$) was found to be $\sim 20\%$ higher than that of incident light intensity. The reason why the light transmission for conical pores was higher than the incident intensity can be explained by the intensity overlap at the smaller opening of the pore (transmission A' and reflection B' overlap at the small opening of the conical pore in Figure 3A).¹⁴

Fluorescent Patterning

A bright fluorescent 6×5 dot array of PDA films fabricated on a glass substrate is shown in Figure 4A. For each dot, UV exposure time through a conical pore ($d_l = 21 \mu\text{m}$ and $d_s = 2.8 \mu\text{m}$) was 15 sec. An SEM image of the small opening of the pore used for patterning is shown in the inset of Figure 4A. The diameter of the dot patterns was $3.85 \pm 0.4 \mu\text{m}$. The pattern dimensions and emission intensities between different spots were $\sim 8.4\%$ and $\sim 9\%$. These variations are attributed primarily to small differences in the liposomal coating thickness and photon exposure intensity over the pattern areas. Although the pore was in contact with the PDA coated substrate, the patterns were slightly larger than the pore size. This is discussed in detail in the following paragraphs. To evaluate the pattern quality, we adopted the Michelson contrast which is defined as $(I_{\text{max}} - I_{\text{min}}) / (I_{\text{max}} + I_{\text{min}})$, where I_{max} and I_{min} represent the maximum and minimum emission intensity of the patterning and the background respectively [20]. For Figure 4A, a contrast value between dots and background was ~ 0.81 (maximum contrast value is 1), suggesting an insignificant background emission after washing off the unpolymerized liposomes at non-irradiated areas.

After polymerization of the liposomes, the patterns were chemically stable for a long duration (> 7 days). We immersed the patterns into methanol for 2 hours but did not find any obvious changes in the emission or dimensions. We also investigated the contrast values for the patterns after 1 month and found insignificant changes in the contrast values ($< 5\%$). These studies clearly suggested that the adhesion of the polymerized patterns on amine-functionalized glass was strong which contributed to their resistant to washing with organic

solvents whereas the non-polymerized liposomal coating adhered poorly on positively-charged glass substrates. Although it is not fully clear why the adhesion of polymerized liposomes was much stronger than those of unpolymerized liposomes, we believe that this could be attributed to cooperative effect of multi-dentate electrostatic interactions between multiple negatively charged groups present on polymerized liposomes with abundant positively charged amine-groups on the substrate surface. On the other hand, for unpolymerized-surface cases, the interaction between positively charged amine- and negatively-charged diacetylene carboxylic acid is probably much weaker, and the self-assembly was easily destroyed by washing in ethanol or water solutions.

Exposure time-dependent patterning

A given pattern was also easily programmed by controlling the piezoelectric stage movements using a commercial software. The logos of the “NSF” and “NIH” were fabricated by controlling the stage movements while simultaneously irradiating the liposomal films with 254 nm photons (Figure 4B). These logos were constructed by exposing the film with different exposure times. For example, letters ‘N’, ‘S and I’; and ‘F and H’ were exposed for 10 s; 20 s and 30s respectively through a conical pore with $d_s = 11.2 \mu\text{m}$ and $d_l = 47.3 \mu\text{m}$. Surprisingly, the diameter of ‘N’; ‘S and I’; and ‘F and H’ patterns were $(13.5 \pm 0.4) \mu\text{m}$, $(17.5 \pm 0.6) \mu\text{m}$, and $(19.5 \pm 0.5) \mu\text{m}$ respectively. The resolution of our instrument is $\sim 0.33 \mu\text{m}$, and the dimensions of patterns were significantly larger than the instrumental resolution. Thus, the measured dimensions of patterns represented the true pattern dimensions. These experiments clearly indicated that pattern size was dependent on exposure time and that it can be easily modulated without changing the pore size. This will be extremely useful in photolithography and can significantly reduce the cost and down time for photopatterning.

To further investigate the exposure time-pattern size dependence, we synthesized a dot array with different exposure times (t) (inset in Figure 5A). The dots in the same column had the same exposure duration, and each subsequent column had an exposure time incremented by 5 s. Initially, the intensity and the dimensions of the patterns increased with exposure time until a saturation was reached (Figure 5A and 5B respectively). x-axis in Figure 5B is natural logarithmic.

Now the question is why does pattern size increase with exposure time? More insight about this was obtained by performing FDTD simulations that indicated two distinct photon transmission intensity levels for a conical pore (with d_s and d_l of $11.8 \mu\text{m}$ and $47 \mu\text{m}$ respectively, Figure 5C): (1) the central high intensity region with width d_{in} of $\sim 9 \mu\text{m}$; and (2) the exponential decayed sidelobe with full-width-at-half-maxima (FWHM) of d_{max} of $\sim 25 \mu\text{m}$ (Figure 5C). The appearance of the fast decaying portion of the light transmission out of the smaller pore is due to leakage of the light out of the small pore. Because of the conical shape of the pore, the glass matrix is very thin near the smaller pore diameter that resulted in incomplete absorption of light and so a small fraction of light leaked out of it. The dimensions of patterns formed at short (~ 5 s) and very long exposure (180 s) times were in agreement with the values of d_{in} and d_{max} respectively. For example, the feature sizes of the fluorescent patterns for short and long exposures were $(9.2 \pm 1) \mu\text{m}$ and $(25 \pm 2) \mu\text{m}$ respectively which matched well with our simulation data. At shorter exposure times, the large intensity of the central transmission region (d_{in}) was large enough to photopolymerize self-assembled diacetylene molecules. This produced pattern dimensions corresponding to d_{in} (Figure 5B). On the other hand, the number of excitation photons in the exponent decayed curves is ~ 40 – 60% less than that of the central intense region. Therefore, a longer time was needed for photopolymerized patterns to occur with leaked photons having dimensions corresponding to d_{max} . Our simulations also predicted that the transmission intensity in the fast decayed transmission profile is an exponential function of distance from

the center (Figure 5C). This also explains an exponential increase (which is a mirror-image of the exponential decayed profile in the Figure 5C) in the pattern dimensions with time (Figure 5B). The limiting pattern dimensions (d_{max}) will also depend upon the cone angle of the pore. For example, the larger cone angles will provide larger limiting pattern dimensions (d_{max}). Thus, the shape and size of the conical pores provides unique opportunities for photolithography where a range of patterns can be synthesized without changing pore size in the chips.

We have also developed a quantitative model that explains the increase in the dimension size of the patterns (d) with exposure time. This model is based on the ray diagram shown in Figure 5D. Since the photo-polymerization rate of the central region is much faster than that corresponding to side-lobed area, we assume the pattern size (d) consists of a constant central region specified with radius r_1 and time-dependent side regions specified with r_2 . i.e., $d=2(r_1+r_2)$. In the side regions, the emission intensity I_e can be written as (see supporting materials for the derivation of Eq. 3):

$$I_e(r)=I_{es}\left(1-e^{-aI_p(r)t}\right) \quad \text{Eq. 3}$$

where I_{es} is the saturated emission intensity for exposure time (t) > 120 s, a is a polymerization coefficient that depends upon the interaction of photons with diacetylene monomers, and $I_p(r)$ is the exposure intensity as a function of the position (r) at the smaller pore diameter to which photoresist was exposed to. We defined r_2 as the distance whose intensity decayed to half of the saturated intensity (Figure 5D), i.e. $I_e(r_2)=0.5I_{es}$, and solving Eq. 3 provided:

$$I_p(r_2)=\frac{\ln(2)}{at} \quad \text{Eq. 4}$$

The exposure intensity ($I_p(r)$) at the smaller pore was calculated as follows: The intensity of the incident light was I_{inc} (15 $\mu\text{W}/\text{cm}^2$) and the refractive index of glass was n (=1.54) (Figure 5D). The light is refracted by the side-wall of the pore and penetrates into the glass 2. After a significant absorption across the glass, the light impinges on the bottom of the glass and transmits into free space 3. The intensity transmittivity from 1 to 2 and from 2 to 3 are T_{12} and T_{23} , respectively; and the absorption coefficient is ϵ . The refractive intensity I_p can be expressed by, [21]

$$I_p(r)=T_{23}T_{12}I_{inc}e^{(-\epsilon L)}, \quad \text{Eq. 5}$$

With

$$L=\frac{\sin(\theta_1)}{\sqrt{1-\left(\frac{\sin(\theta_1)}{n}\right)^2}}r_2 \quad \text{Eq. 6}$$

and T_{ij} ($i=1,2; j=2,3$) satisfies Fresnel's transmission formula:

$$T_{ij}=\frac{\sin(2\theta_i)\sin(2\theta_j)}{\sin^2(\theta_i+\theta_j)\cos^2(\theta_i-\theta_j)}, \quad \text{Eq. 7}$$

where θ_i and θ_j are incident and refractive angles respectively, and satisfy Snell's law, [21]

$$n_i \sin(\theta_i) = n_j \sin(\theta_j) \quad \text{Eq. 8}$$

n_i and n_j are refractive index of the i th and the j th spaces. The refractive indices of air and our chip were 1 and 1.54 respectively; the measured absorption coefficient (ϵ) of the glass at 254 nm was 65.8 mm^{-1} and thickness $w=70 \mu\text{m}$. The pore etched in the glass chip has a large opening $d_l=47 \mu\text{m}$ and a small opening $d_s=12 \mu\text{m}$, so the incident angel $\theta_1=76^\circ$. By combining Eqs. 5 through 8, we obtained by $I_p(r)$:

$$I_p(r_2) = 0.86 I_{inc} e^{(-0.3569 r_2)} \quad \text{Eq. 9}$$

where I_{inc} is the intensity of the incident light at the larger pore.

Combining Eqs. 4 and 9 and solving for r_2 , we obtained:

$$r_2 = 2.78 \ln(1.24 a I_{inc} t) \quad \text{Eq. 10}$$

Using $a I_{inc} = 0.09 \text{ s}^{-1}$ (obtained from fitting of the experimental data in Figure 5A), the diameter of the patterns (d) is:

$$d = 2r_1 + 2r_2 \sim 5.6 \ln(t) \quad \text{Eq. 11}$$

The experimental data in Figure 5B fits well with the theoretical model (Eq. 11). Excellent fit between experimental and theoretical data will be a major advantage of this method over existing photolithographic techniques because in the present case the dimensions of the patterns can be empirically predicted before hand using a simple equation. This will save time and will reduce cost of patterning.

We have also fabricated more complex patterns at higher throughput rates by using multiple conical pores in the glass chips. Figure 6A shows the programmed parallel patterns (a 2×6 dot array and the 'SIU' logos) using a chip with two pores $2.3 \mu\text{m}$, and $4.5 \mu\text{m}$ by controlling the movements of the x-y stages. The exposure time for each dot was 10 seconds. A typical line pattern was also fabricated by scanning a pore over a liposomal film (Figure 6B). Thus with this method, any discrete, continuous and parallel patterns with the multiple pores can be fabricated with almost zero down time.

Emission intensity-exposure time dependence

Surprising, we also observed that the pattern emission intensity was dependent upon exposure time. To further investigate the impacts of exposure time on the emission intensity of the patterns, we synthesized a dot array pattern with different exposure times (inset in Figure 5A). The dots in the same column had the same exposure time, and there was a 5 second increment in the exposure time for dots in the subsequent column. Initially, the intensity of patterns increased quickly with the exposure time, but reached saturation at longer exposure times (Figure 3A). The emission intensity-exposure time curve resembles a Langmuir-isotherm plot.

In general, for radical photopolymerization process, the degree of polymerization depends upon many factors including the presence of initiators, quenchers and photon intensity of

polymerizing beam. In the present case, the presence of the oxygen molecules in the films is believed to play a crucial role in the pattern emission intensity dependence on the exposure time. Oxygen is a known powerful free-radical quencher,[22,23] and can react with the growing chains; terminating them through coupling or disproportion reactions.[23] Oxygen molecules are hydrophobic in nature and are known to present in hydrophobic molecules and bilayers. Our bilayer liposomes contained both hydrophilic and hydrophobic parts. The hydrophobic part of the bilayer (the emissive functionality, the backbone of PDA is also hydrophobic) contained a higher oxygen concentration than in/near hydrophilic portion of the liposomes.[24] The degree of polymerization was lower for shorter exposure time due to the presence of oxygen which can readily quench growing PDA (both biradical and bicarbene) chains. A lower polymerization degree of PDA resulted in a lower emission intensity. However, with longer irradiation time an higher PDA content in the patterns was formed that provided a higher emission intensity (Figure 5A).

Resolution of the patterning

We now comment achieving a lower resolution using this technique. In principle, our patterning method can be used for making nanoscale patterns through the use of nanoscale conical pores fabricated in the chips. The transmission intensity through nanoscale pores however will be significantly attenuated. This can be compensated either by longer exposure time or use of very intense light sources. Another option is coupling of the photons with surface plasmons where the photon transmission output from nanoscale pores can be significantly increased.[25] Photon-surface Plasmon coupling along with exposure time and intensity can be used for pattern development at nanoscale. Furthermore, one can also improve the pattern resolution and intensity by optimizing the shape and size of pores.

In summary, we demonstrate a “maskless” photolithographic method for patterning at the micron scale by using conical pores etched in tracked glass chips. The functionality of the mask was provided by movable stages. We found that the dimensions of the patterns can be easily modulated by controlling the exposure time without changing the size of pores in the chips which will significantly reduce the cost and downtime of patterning. We also show that different patterns can be developed simultaneously by exposing photoactive polymer through multiple pores present in the same chip. This method can potentially provide an inexpensive, versatile and efficient way for patterning molecules and films for applications in microelectronics, photonics, materials and life sciences.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1A

Figure 1B

Figure 1C

Figure 1D

Figure 1E

Figure 1.

(A) SEM images of cross-section (left) and top view (right) of typical pores synthesized in a glass chip; (B) An AFM image of the fluorescence diacetylene (DA) liposome monomers on a silanized glass slide; (C) Scheme showing 1,4 addition polymerization of self-assembled diacetylenic acid in liposomes. Blue square represents color of the film after polymerization whose quantum yield (Q_y) is extremely small, whereas red color denotes “red”-PDA form whose Q_y increased many orders of magnitude and was easily detected with fluorescence microcopy. The effective conjugation length is believed to be lower in the red-PDA form than that in the blue-PDA form. (D) Schematic diagram of the UV photolithographic process using conical pores; (E) Schematic of the exposure apparatus we used, where A, B and C are the X, Y and Z piezoelectric stages, respectively; D is the holder mounted on the Z-stage, supporting the UV lamp system and the glass chip mask system; E and F are the UV lamp

and the glass lampshade, respectively; G and H are the cushion sponge and glass mask; I is the substrate slide on which the patterning is recorded.

Figure 2.

(A) The optical micrograph of conical pores in the glass. Bright dots at the center of circles represents small pore whereas dark concentric circles represent walls of the conical pores.

(B) A typical UV-vis absorption spectrum of an unetched glass chip.

Figure 3.

FDTD simulations of the light passing through a conical and a cylindrical pore. The intensity distributions of the UV light passing through (A) a conical pore, and (B) a cylinder pore in a glass chip. The integrated photon intensity for conical pores ($d_s=12\mu\text{m}$, and $d_l=47\mu\text{m}$) was ~47% larger than that of cylindrical pores (diameter of the pore = $12\mu\text{m}$).

Figure 4A

Figure 4B

Figure 4.

(A) A 6×5 dot array PDA fluorescence pattern fabricated using a pore ($d_s = 21 \mu\text{m}$ and $d_l = 2.8 \mu\text{m}$) in a tracked glass chip. Each dot has the same exposure time of 20s. The Michelson contrast for the patterns was 0.81. The inset in Figure 4A shows an SEM image of the small diameter of a pore used for lithography, $d_s \sim 3.85 \mu\text{m}$; (B) Fluorescent patterns of “NSF” and “NIH” logos. The exposure times for 'N'; 'S and T'; and 'F and H' are 10s, 20s and 30s, respectively. The corresponding averaged contrast value was 0.85.

Figure 5.

(A) Fluorescence intensity vs. exposure time for an array of dots fabricated using a pore with (d_s and d_l of 11.8 μm and 47 μm respectively). The red line is a fit for experimental dots array which is shown in the inset of the figure. The exposure time for the left most and right most columns are 5s to 45s respectively with a 5s increment for successive columns. (B) The feature size of the patterns vs. log (exposure time) for an array of dots fabricated using a pore with (d_s and d_l of 11.8 μm and 47 μm respectively). The red line is a fit for the experimental data. (C) The calculated FDTD transmission intensity profile at the small opening of a conical pore ($d_s = 11.8$ μm and $d_l = 47$ μm), where d_{in} and d_{max} depict the sizes of the patterns that can be fabricated at short and long exposure times respectively using this pore; (D) The light ray tracing diagram showing the leakage of the light that led to increased pattern size with longer exposure time.

Figure 6.

(A) A fluorescence micrograph showing the results of parallel patterning (dot pattern and SIU logos) made using two pores in the chip. (B) Fabrication of line patterns by scanning the pores over photo-resists. Exposure time was 25 sec.