Self-organization of planar microlenses by periodic precipitation

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(Received 9 December 2004; accepted 10 March 2005; published online 20 June 2005)

Arrays of planar, Fresnel-like microlenses are prepared by a spontaneous chemical process of periodic precipitation (PP) occurring in a thin layer of a dry gel, and initiated by wet stamping. The PP lenses focus white light more efficiently than the conventional Fresnel zone plates of similar dimensions. Nanoscale topographies of the micropatterned gels can be replicated into transparent elastomers, and used for focusing based on optical path differences. Experimental observations for both types of structures are in agreement with the Fresnel diffraction calculations. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1899757]

Fresnel zone plates and lenses[1]—that is, optical elements that focus light by diffraction—have important technological applications in x-ray[2] and neutron optics,[3] microwave focusing,[4] and imaging systems.[5] Although current manufacturing methods[6–9] are capable of high-resolution fabrication of lens arrays, they are limited to binary topographies and/or require expensive and elaborate manufacturing processes. We have previously suggested that self-organization based on reaction-diffusion[10] (RD) can provide a facile and general route to the fabrication of microstructures and microdevices,[11] including optical elements.[10,12] In particular, using the wet stamping technique (WETS) we developed, we were able to control RD processes in small, complex geometries to prepare microfluidic circuits,[11] diffraction gratings,[10,12] and arrays of curved lenses.[13] Here, we use WETS to guide self-organization of arrays of planar microlenses whose optical characteristics are comparable to or better than those of the Fresnel zone plates (FZPs) of similar dimensions. In our system, lenses are created by periodic precipitation[14] induced from ring-shaped sources of silver nitrate on thin layers of dry gels doped with potassium dichromate. The precipitation zones (Liesegang rings) form optically opaque concentric rings whose spacing and dimensions can be controlled by the concentrations of the chemicals used. In addition, periodic precipitation causes buckling of the patterned substrates—these surface topographies can be replicated into optically transparent elastomers[15] to give quasi-three-dimensional focusing elements with potential applications in microfluidics[16] and waveguides.[17]

Figure 1(a) illustrates the experimental procedure. A 10% w/w high-strength agarose (OmniPur high gel strength agarose, EM Sciences, Darnstead, Germany) stamp patterned with outlines of lenses (diameter, $D=500$—1000 μm) was soaked in an aqueous solution of silver nitrate ($AgNO_3$, 5%–15% w/w) for 12 h. Gelatin (20% w/w) doped with potassium dichromate ($K_2Cr_2O_7$, 0.2% w/w) was first spin-coated on a glass slide at 320 rpm and then dried for 12 h to give a $\sim$10-μm-thick film. The stamp was blotted and blown dry with nitrogen, and then gently applied onto the gelatin. Silver nitrate was transported into the dry film by diffusion enhanced by a gradient of osmotic pressure,[18] and reacted with $K_2Cr_2O_7$ contained therein. Directly under the stamp, this reaction produced a uniform layer of $Ag_2Cr_2O_7$; inside the circles, the inwardly diffusing $AgNO_3$ precipitated periodi-

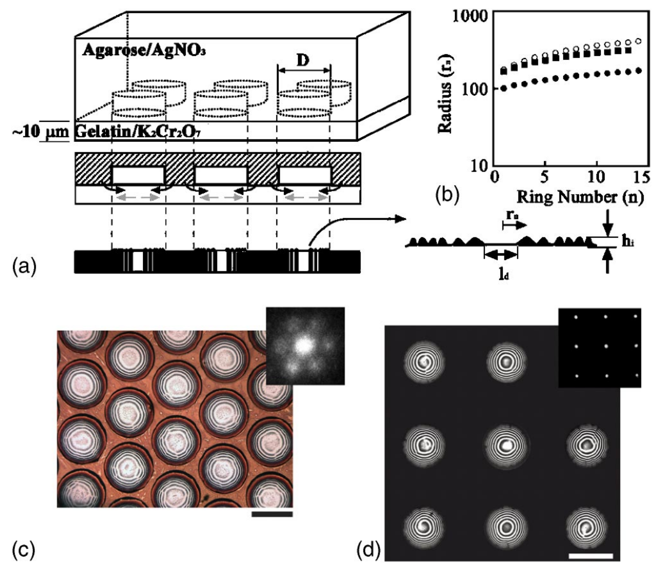

FIG. 1. (Color online) (a) The experimental scheme showing a stamp with outlines of the lenses ($D=500$–1000 μm) applied onto a 10-μm gelatin layer doped with $K_2Cr_2O_7$. The arrows indicate the directions of the diffusion of Ag^+ cations (black arrows) towards the centers of the circles and of chromate ions (gray arrows) in the opposite direction. Reaction between Ag^+ and $Cr_2O_7^{2-}$ gives rise to discrete bands of periodic precipitation (bottom graph). The thickness of the bands decreases with the distance r_n from the middle of the stamped circles (from $\sim$50 μm near the center down to several micrometers near the edge). At the locations of the bands, gelatin buckles up to heights $h_i\sim300$–1000 nm (insert). (b) The semilogarithmic plot of the position r_n of the nth precipitation band. (● $-D=500$ μm, ■ $-D=750$ μm, and ○ $-D=1000$ μm). The data is compiled from periodic precipitation (PP) lenses stamped from 10% w/w $AgNO_3$. The standard deviations of the ring positions were less than 5% for $D=500$ μm, less than 3% for $D=750$ μm, and less than 1% for $D=1000$ μm. The optical micrographs of the (c) hexagonal ($D=600$ μm) and (d) square ($D=500$ μm) arrays of lenses with the experimental images of the corresponding focal planes shown in the inserts. The pattern in C is before and that in D is after blackening with formaldehyde. All scale bars are 500 μm.

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cally in the form of concentric circles[14] that served as the basis of the planar lenses. After the reactions were complete, the regions containing $Ag_2Cr_2O_7$ were further blackened by the exposure to the vapors of formaldehyde, which reduced the silver salts to black colloidal silver. Buckled topographies of the patterned surfaces were replicated into a transparent elastomer, poly(dimethyl siloxane) (PDMS), by casting its prepolymer against the patterned gelatin and curing overnight at 30 °C.

The radii, r_n, of the periodic precipitation (PP) bands within each circle were well approximated[19] by the so-called Jablczynski-like law,[20] $\ln(R\text{-}r_n) \propto (N-n)$, where R is the lens radius, N is the total number of resolved bands, r_n is measured from the circle's center and n is the ring number counted from the center outwards [Fig. 1(b)]. In addition, the location of the first distinct band that was resolved near the edge of the circle (i.e., $n=N$) depended on the concentration of $AgNO_3$: for low concentrations, it was close to the edge of the stamped circle, for high concentrations, it was located further inwards, and the region near the edge was covered by a uniform precipitate (transient precipitation zone).[21] In all cases, the number of the resolved bands depended on both $[AgNO_3]$ and the dimensions of the stamped circle, and could be controlled by the amount of time that the stamp was in contact with the gel (the longer the time, the more bands were resolved). The maximum number of bands we obtained was 18 for a 1-mm circle.

The developed PP patterns focused visible light efficiently. This is illustrated in Fig. 1(d), which shows a square array of PP lenses ($D=500$ μm) and the corresponding image of the focal plane located ~4 mm away from the plane of the patterned film, and with the focal points ~15 μm in diameter.

To determine the focusing ability of our microlenses, we calculated the Fresnel complex-amplitude distribution,[1] $U(x_i)=\int_{-\infty}^{\infty}\tau(x_o)\exp[-i2\pi(x_o-x_i)^2/z\lambda]dx_o$, in the plane parallel to that of the patterned film, and located at a distance z away from it (a "screen"). In the expression above, x_o designates the coordinate in the plane of the lens, x_i is the coordinate along the screen, and λ is the wavelength of light. The transmission function $\tau(x_o)$ was taken as binary from a digitized optical micrograph of the PP pattern: $\tau(x_o)=1$ for dark precipitation bands and zero otherwise. The intensity of light at the screen was then evaluated by numerical integration as $I(x_i)=|U(x_i)|^2$, and the focal distance for a given lens was found by varying z and finding the minimal value of the width at half height (WHH) of the main intensity peak (zeroth order).[22] These calculations, performed for a wavelength of light $\lambda=532$ nm, predicted the value of WHH ~10 μm, in good agreement with the experiment.

Interestingly, modeling indicates that PP lenses have better focusing properties than Fresnel zone plates of similar number of bands. The graphs in Figs. 2(b) and 3(c) compare the intensity profiles in the focal plane of various PP lenses consisting of 17 bands with those of FZPs "designed" to have the same focal distances. In all cases, FZPs must have significantly larger number of bands (40–70) to achieve the same half height width at the focal point. In other words, the FZPs must be larger than PP lenses of identical focusing properties.

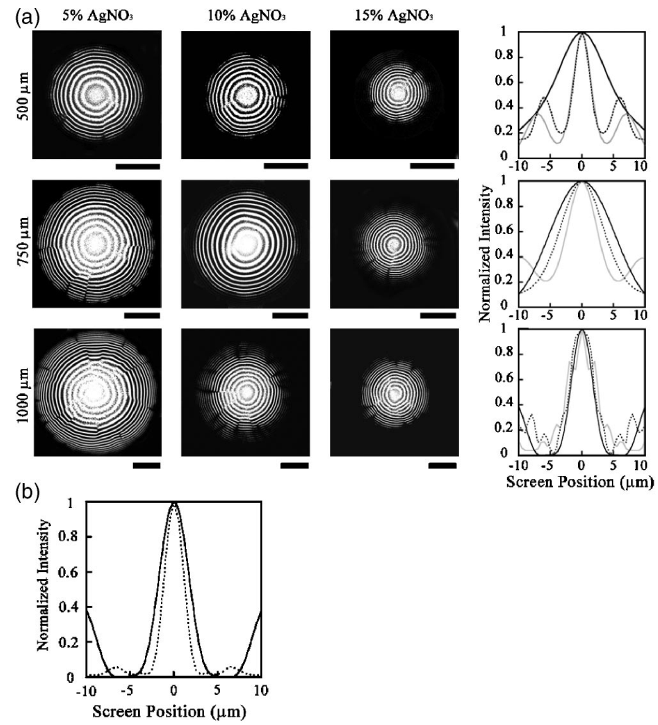

FIG. 2. (a) Optical micrographs of the periodic precipitation (PP) lenses obtained from circles of different diameters, and with different concentrations of $AgNO_3$. All scale bars are 250 μm. The graphs in the rightmost column have the calculated distributions of the light intensity at the focal planes of the corresponding lenses (solid lines 5% $AgNO_3$, dashed lines 10% $AgNO_3$, and gray lines 15% $AgNO_3$). (b) Calculated light intensities at the focal plane for a PP lens ($D=1000$ μm) composed of 10 bands (solid line) and a Fresnel zone plate designed for the same focal length and having 40 bands (~7 mm in diameter, dashed line).

In addition to providing an optical contrast between the opaque precipitation zones and the remaining portions of the patterned gel, PP led to the formation of regular arrays of surface microbuckles in the regions corresponding to the precipitation bands. We have previously shown that this effect is due to the $Ag_2Cr_2O_7$ collected in the PP bands causing surface deformation that is proportional to its amount at a given location.[14,23] In the context of the present work, we were interested in replicating the PP surface buckles into optically transparent polymers and investigating the diffractive properties of such materials. Unlike micropatterned elastomers of binary topographies that have been previously used in wave front engineering,[15,24] our microbuckled surfaces had grooves not only of varying periodicity but also of varying depths (Fig. 3).

The PDMS replicas of the PP patterns proved to be efficient lensing elements focusing light to spots of ~30–50 μm in diameter. We note that focusing was not due to the overall residual curvature of the patterns (most notable in those obtained using 5% $AgNO_3$ solutions). This curvature alone would give a focal point $z \sim 0.15$ m away from the lens, based on $n_{PDMS}=1.43$.[15] In contrast, focal points produced by diffraction were located at $z \sim 1$–2 mm. We also briefly mention that the fact that the grooves in the PDMS lenses differed in height improved their focusing

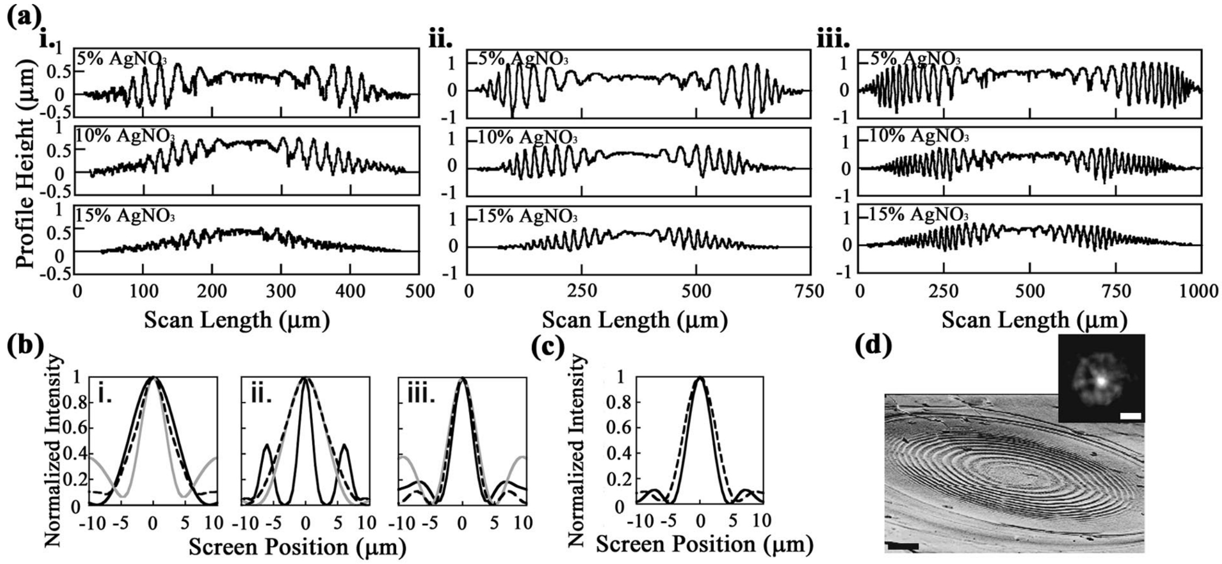

FIG. 3. (a) Experimental profilograms of PDMS lenses taken from the gelatin molds; $D=500$ μm in (i), 750 μm in (ii), and 1000 μm in (iii). As the concentration of $AgNO_3$, increases, the buckles appear closer to the center of the lens [cf. Fig. 2(a)], and their heights decrease. This is because the amounts of the inner electrolyte ($K_2Cr_2O_7$) and the total amount of precipitate are kept constant. Since the increase in the amount of the outer electrolyte ($AgNO_3$) delivered decreases the amount of precipitate in each band, the heights of the bands also decrease. (b) Light intensities calculated along focal planes at calculated focal distances (i) 500 μm, (ii) 750 μm, and (iii) 1000 μm lenses; solid lines correspond to 5% $AgNO_3$, dashed lines to 10% $AgNO_3$, and gray lines to 15% $AgNO_3$. (c) Focusing (at equal focal distances) by a PDMS Fresnel zone plate with 70 bands (dark line), and having a binary topography with grooves 1-μm-deep, compared to a PDMS lens made by molding against a periodic precipitation pattern (15% $AgNO_3$, 1000 μm, gray line). (d) A SEM image of an elastomeric lens made from a gelatin mold (scale bar is 200 μm), the insert is an optical micrograph of the focal point of the lens (scale bar is 100 μm).

characteristics–a hypothetical PDMS structure in which the ridges would be located at the same locations, but would have uniform depths would give a much worse focusing. Finally, the PDMS replicas of the PP patterns focused better than PDMS FZPs having the same number of uniform-depth grooves [Fig. 3(c)].

To model light focusing by the PDMS lenses, we accounted for the dependence of the phase function on the optical path through the elastomer,[15] $\tau(x_o)=\exp i\varphi(x_o)$, where $\varphi(x_o)=2\pi(n_{\mathrm{PDMS}}-n_{\mathrm{air}})h(x_o)/\lambda$ is the phase shift due to the elevation $h(x_o)$ of the buckled surface at location x_o, n_{air} is the index of refraction in air ($n_{\mathrm{air}}=1.0$), and n_{PDMS} is the index of refraction in PDMS ($n_{\mathrm{PDMS}}=1.43$). The intensities of light at various screen locations were calculated as for the planar PP lenses [Fig. 3(b)], and the results of these calculations were in agreement with what was obtained experimentally [Fig. 3(d)].[25]

In summary, we have described an experimental system in which a spontaneous chemical process initiated from well-defined geometries can produce high-quality optical microlenses. The periodic precipitation phenomena we used here can provide a general basis for the fabrication of microstructures and microcomponents of arbitrary shapes. The degree of control over the vertical surface buckling (to within ~50 nm) makes this approach an interesting route to nanostructured surfaces of nonbinary topographies.

One of the authors (B.G.) gratefully acknowledges the financial support from the Northwestern University start-up funds and from the Camille and Henry Dreyfus New Faculty Awards Program. One of the authors (C.C.) was supported in part by the NSF-IGERT program "Dynamics of Complex Systems in Science and Engineering" Grant No. (DGE-9987577).

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