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Novel microlens array fabrication utilizing UV-photodecomposition of polysilane

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An array of 10 μm sized microlenses was fabricated from the adhesion of a silicasol on a polysilane film patterned by UV-light irradiation. This was achieved by increase in wettability to the aqueous sol–gel solution induced by the UV-photodecomposition of polysilane. By simply soaking the UV-patterned polysilane film into the sol–gel solution, a convex xerogel layer adhered only to the UV-exposed polysilane, and then was cured to form a 'glass'. The protuberant xerogel functioned as a condensing lens.

1 Introduction

Microlens arrays are required in many optical applications and in digital optical imaging systems. The typical uses of refractive microlens arrays are to condense light (as for laser arrays, fibres, charge-coupled devices, photosensors, and interconnects), to illuminate (as for light-emitting diode arrays, displays, and projectors), and to process images (for integrated photography, facsimile and photocopying machines, surface characterization, and beam diagnostics). A number of techniques for fabricating microlens arrays have been developed using glass or other materials. One approach involves the patterning of circular mesas from photoresist layers that are subsequently melted.[1] The melted photoresist assumes a spherical lens shape because of surface tension. If glass or semiconductor lenses are desired, then the photoresist pattern can be transferred into the substrate using reactive ion etching.[2]

To be useful, the microlens array must possess excellent uniformity in focal length and *f*-number, and must exhibit low aberration. Methods employing photolithography can satisfy such uniformity requirements. In this work, we intended to fabricate a microlens array by using polysilanes as photoresist materials.

Polysilanes have been recognized as being a new class of functional polymers, characterized by a σ-conjugated Si backbone and an ultraviolet (UV) photodecomposition due to the photochemical nature of the Si–Si bonds.[3–16]

Recently, several novel applications have been proposed that focus on the UV-modification of polysilanes. The formation of Si–O–Si and Si–OH bonds due to UV photodecomposition in air induces changes in the nature of polysilane films, such as their wettability or swelling with water. These changes occur only in the UV-exposed area. As a further development of our previous results showing that UV-exposed polysilane film could be selectively dyed by simply soaking it in an aqueous dye solution,[17] coloration based on pigments, instead of dyes, was successfully demonstrated by applying the micelle electrochemical deposition method[18] and the sol–gel method.[19] The latter method showed a high potential for practical use in the manufacturing of colour filters for TFT liquid crystal displays. As an alternative application of the UV-induced swelling effect, the electrochemical polymerization of thiophene in a polysilane film has also been investigated.[20] The conducting polymer pattern formed in the polysilane film showed a high electrical conductivity, as well as clear electrochromic behaviour, depending on the doping and de-doping states. Moreover, a novel printing system that utilizes the water wettability change of a polysilane film surface induced by UV-exposure showed that the development process was not necessary in alkaline solution.[21]

In this paper, from the viewpoint of exploiting the further application of polysilanes, we have tried to fabricate a convex microlens array of xerogel to a desired size on polysilane films patterned by UV-light irradiation. By modifying the polymer composition to enlarge the water wettability difference between the UV-exposed and unexposed areas, and the silicasol solution to enhance the adhesion of the silicasol, we have successfully demonstrated an array of microlenses of 10 μm in size.

2 Experimental

2.1 Materials

2.1.1 Synthesis of polysilane. Poly[methyl(phenyl)silane] [PMPS, Fig. 1(a)] was prepared by the Wurtz-type coupling reaction of dichloro(methyl)(phenyl)silane with a highly dispersed molten sodium powder in dry toluene at 110 °C. The fluorine-containing polysilane poly[(methyl)(phenyl)silane-*co*-methyl(3,3,3-trifluoropropyl)silane] [CF_3PMPS, Fig. 1(b)] was prepared using a similar procedure from a mixture of dichloro(methyl)(phenyl)silane and dichloro(methyl)(3,3,3-trifluoropropyl)silane monomers with a molar ratio of 10 : 1. The elementary analysis of CF_3PMPS gave

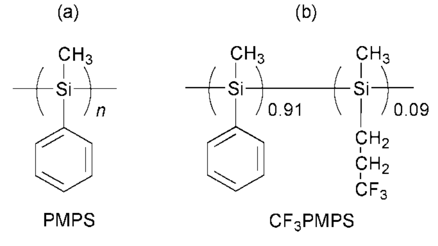

Fig. 1 Chemical structures of the polysilanes used in this study: (a) poly[methyl(phenyl)silane] (PMPS), and (b) poly[methyl(phenyl)silane-*co*-methyl(3,3,3-trifluoropropyl)silane] (CF_3PMPS).

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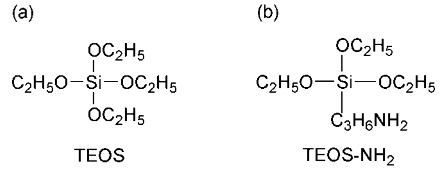

Fig. 2 Chemical structures of the silicasol reagent used in this study: (a) TEOS (tetraethoxysilane) and (b) 3-aminopropyltriethoxysilane (TEOS-NH$_2$).

(element, wt%) C, 66.35; H, 6.63; F, 4.38; Si, 22.64. So the theoretical data of CF$_3$PMPS is (element, wt%) C, 66.27; H, 6.55; F, 4.25; Si, 22.93, it was considered that the resulting polymer possessed an identical composition to that of the monomer feed (10 : 1). The molecular weights of both PMPS and CF$_3$PMPS were determined to be 15 000 by gel-permeation chromatography using polystyrene as the standard.

2.1.2 Sol–gel process. The silicasol was prepared according to the literature.[22] A mixture of 25 g of tetraethoxysilane [Si(OC$_2$H$_5$)$_4$, TEOS, Fig. 2(a)], 38 g of acetonitrile, 24 g of water, and 0.5 ml of concentrated hydrochloric acid was stirred for 2 h. A sample of 5 g of the resulting sol was mixed with 17.5 g of aqueous acetonitrile solution (acetonitrile–water = 1 : 8), and then stirred for 4 h. We also prepared the silicasol from 3-aminopropyltriethoxysilane [Si(OC$_2$H$_5$)$_3$(C$_3$H$_6$NH$_2$), TEOS-NH$_2$, Fig. 2 (b)] using the above procedure. Hereafter, to avoid confusion, the silicasol obtained from 3-aminopropyltriethoxysilane will be abbreviated as "aminated silicasol".

2.2 Adhesion of silicasol to the PMPS film

The sample, consisting of a PMPS or CF$_3$PMPS film, typically 0.8 μm thick, laminated on a common glass plate, was prepared by spin coating from a toluene solution of PMPS or CF$_3$PMPS, respectively. The fabrication of the microlens on the polysilane film was accomplished using the following procedure (see Fig. 3). Image exposure was carried out using UV light (10 mW cm^{-2} for 310–400 nm) from an Hg lamp (TOSCURE, Toshiba, 400 W) through a photomask, usually for an exposure of 5 min. The UV-exposed polysilane film was then soaked in the silicasol solution for 1 min. After soaking, the unexposed xerogel on the polysilane film was dried. Only the xerogel exposed to UV light adhered to the polysilane. The xerogel was then cured at 80 °C for 1 h, and allowed to 'glass'.

2.3 Characterization of the surface topology

The images for the surface topology of the PMPS films were obtained using a Seiko Instruments Inc., Nanopics 1000.

2.4 Characterization of xerogel microlens

The refractive index of the microlens prepared by the sol–gel glass was measured by using a Mizojiri, Auto Elipsometer DXA-XAIR/S3. The geometric optical focal length was evaluated from the displacement of the image positions between the lens surface and the focused light spot using an optical microscope (Nikon, ECLIPSE ME600).

3 Results and discussion

3.1 PMPS films as lens forming plates

The PMPS films were first examined as plates to fabricate a microlens array, because of their good film-forming ability, and their large absorption in the UV region makes them suitable for UV-exposure from the Hg lamp. When the microlens fabrication was carried out using the usual, widely used, silicasol solution, the adhesion of the silicasol solution spread over the whole surface area, and was not confined to the UV-exposed area. This may have been caused by the low wettability difference between the UV-exposed and unexposed areas. The PMPS surface seemed not to be sufficiently hydrophobic enough to reject the silicasol solution. Although the PMPS films showed a relatively large change in the water contact angle on UV-exposure, from about 90° to 60°, such a change in the degree of wettability seems to be insufficient for our purpose.

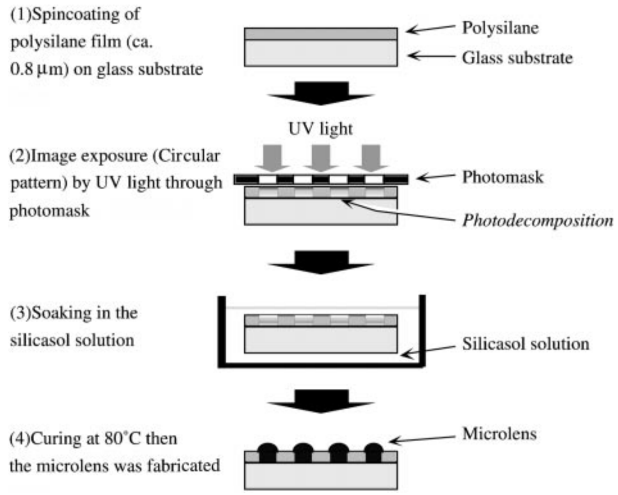

Fig. 3 Schematic illustration of the procedure for fabrication of the microlens array.

3.2 Enhancement of wettability difference

To enhance the wettability difference induced by UV-exposure, the following material modification and process improvements were carried out.

At first, instead of PMPS, a fluorine-containing polysilane (CF$_3$PMPS) was used to increase the water rejection in the UV-unexposed surface. The synthesized CF$_3$PMPS exhibited a larger water contact angle of 108°, and showed almost the same absorption spectra, and a similar UV photodecomposition behaviour, to that of PMPS, as has been previously observed.[21] Secondly, the silicasol was also modified to increase the adhesion between the silicasol and the UV-exposed polysilane. Instead of tetraethoxysilane, 3-aminopropyltriethoxysilane (APTES) was used as the starting material for the silicasol. Owing to the Si–OH groups formed on exposure to UV, the polysilane surface possesses a weak acidic nature. Indeed, it has been suggested that there exists a specific interaction between basic dyes and the Si–OH moieties formed by the UV photodecomposition of polysilane in the selective dying of basic dyes on polysilane films.[16]

Using this property, we tried to induce a specific interaction between the amino group in aminated silicasol and the Si–OH moieties formed by UV irradiation of polysilane. However, as the aminated silicasol solution formed from 3-aminopropyltriethoxysilanes had a pH value of 12, the specific adhesion to the UV-exposed PMPS was not much improved when the aminated silicasol solution was used. Therefore, the pH of the aminated silicasol solution was changed to a value of 9–10 by adding concentrated hydrochloric acid. The addition of the hydrochloric acid had a twofold purpose: (1) to control the dehydrogenation of the –SiO$^-$H$^+$ moiety in the PMPS, and (2) to control the hydrogenation of the –N$^+$H$_3$ moiety in the aminated silicasol. Thus, the –N$^+$H$_3$ moiety can exchange a hydrogen ion with the –SiO$^-$H$^+$ moiety, and thereby enhance the hydrophilicity due to an increase in the number of hydroxy groups. So, by controlling the pH in general, a dramatic effect on the course of sol–gel coupling reactions may be predicted compared to the conventional method (where the concentration

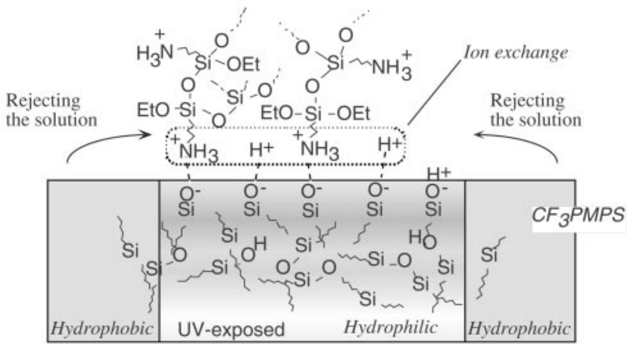

Fig. 4 Speculative model for the adsorption of the aminated silicasol onto the UV-exposed CF_3PMPS film.

of silicasol is generally high). However, as the concentration of the sol–gel material used here was much lower than that used in the conventional sol–gel method, so we speculate that the change of pH 12 to pH 9–10 had a small effect on the course of the sol–gel coupling reactions in the case of APTES. Although we know that the CF_3PMPS film has a larger water contact angle than that of PMPS by about 20°,[21] the incorporated fluorine groups may, however, effectively weaken the interaction between the hydroxy groups formed on the surface of the CF_3PMPS film and the $-N^+H_3$ moiety of the aminated silicasol. The CF_3PMPS, however, showed almost the same degree of difference in the water contact angle between the UV-exposed and unexposed films as did PMPS. In virtue of this ion exchange, adhesion between the silicasol and the UV-exposed polysilane succeeded, as is shown in Fig. 4. These results clearly indicate that an enhancement of the wettability difference between the UV-exposed and unexposed surfaces was accomplished by employing both by using CF_3PMPS to assure water repulsion, and by adding hydrochloric acid to the silicasol solution to control the hydrophilicity of the UV-exposed surface. As a result, the xerogel adhered protuberantly above the exposed part of the polysilane film. In contrast, in the gels with a low pH of 2–3, adhesion between the silicasol and the UV-exposed polysilane was unsuccessful as the silicasol adhered to the unexposed polysilane film, because the dehydrogenation of the $-SiO^-H^+$ moiety in PMPS did not occur with the hydrochloric acid.

In this process being protuberant above the part of unexposed polysilane film, it is claimed that the difference in water repellent properties plays an important role. Moreover, the enhancement in the surface tension of the aminated silicasol, as a result of water repulsion, may be considered to be a contributory factor toward the microlens fabrication process.

Using a CF_3PMPS-coated plate and aminated silicasol, we have succeeded in obtaining the microlens array shown in Fig. 5. Optical microscopic observation revealed that the true circle pattern, 10 μm in diameter, was completely reproducible. In addition to the observations using optical microscopy, each of the arrays was characterized using a scanning probe microscope (SPM). Fig. 6(a) shows a three-dimensional SPM image of the array, and Fig. 6(b) shows a typical lens profile (grey) fitted to the arc of a circle (dotted line), respectively. There were an estimated 25 microlenses in this array. The radius of the best-fit circle was taken as the radius of curvature of a lens. It should be noted, however, that a difference between the typical lens profile (grey) and the arc of a circle (dotted line) was observed in most lenses, and that this difference in most lenses was approximately the same magnitude. In the envisaged application of our microlens array, as an optical component, this difference may not be considered to be a technical limitation.

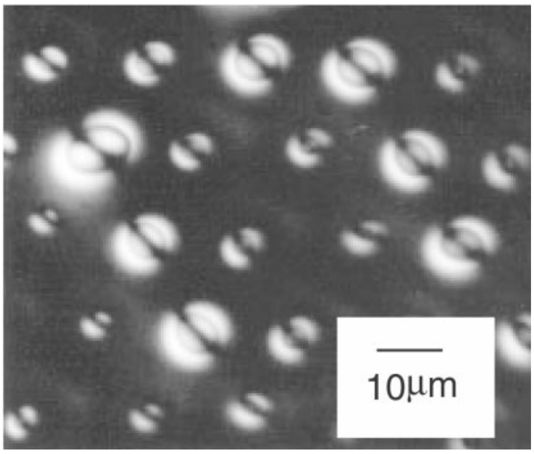

Fig. 5 Optical microscope image of the microlens array fabricated from the aminated silicasol and the CF_3PMPS film.

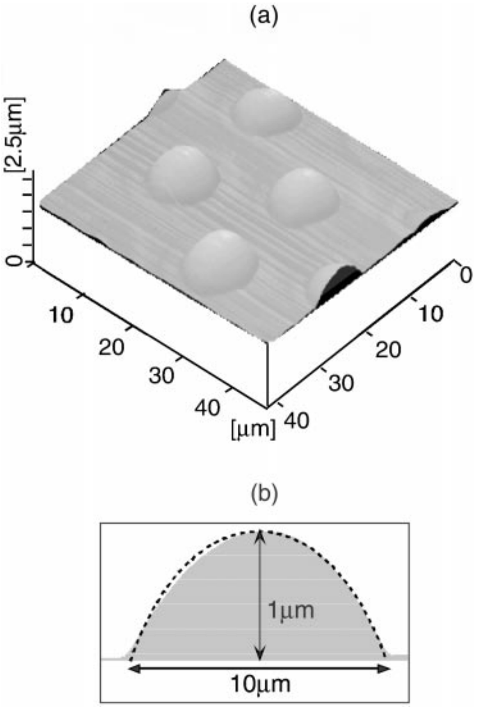

Fig. 6 (a) Scanning probe microscope image of the microlens array with lens diameter = 10 μm obtained from the aminated silicasol and the CF_3PMPS film. (b) Surface cross section of a microlens in the fabricated array with lens diameter = 10 μm (grey) and the best spherical fit (dots) obtained using the scanning probe microscope.

3.3 Optical characterization

In measuring the properties of microlens arrays, it is not always possible (or appropriate) to employ techniques used with larger lenses. The small size of the lenses makes it difficult to measure properties such as wave front aberrations. The only optical property we estimated was the focal length: both the *f*-number and aberration were not characterized. The geometric optical focal length was first measured by imaging the lens surface and then repositioning the microlenses to image a focused spot using a microscope at high magnification. The geometric optical focal length of the lens measured in this manner was approximately 28 μm (see Fig. 7). We calculated the paraxial focal length, f, as follows. We assumed that the lens was spherical. The paraxial focal length of a lens consisting of a single spherical surface as shown in Fig. 8 is given by eqn. (1)

$$f = \frac{R}{n-1} \tag{1}$$

where n is the refractive index, and the radius of curvature, R, is given by eqn. (2)

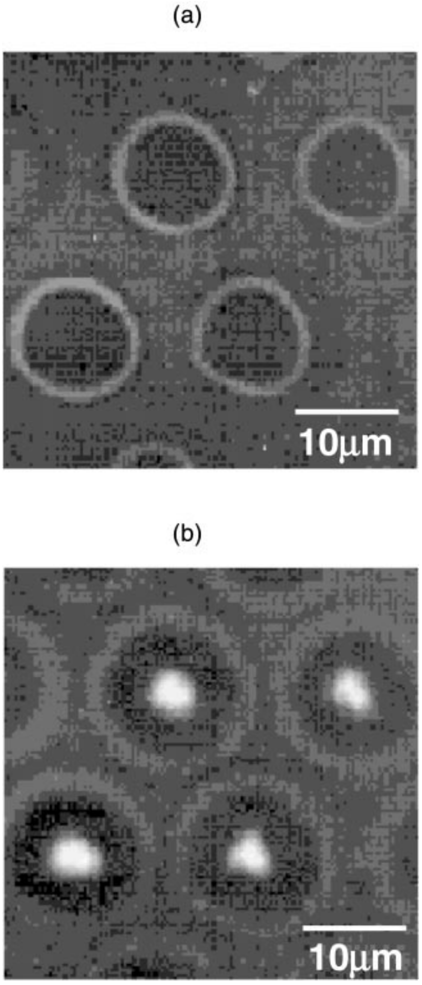

Fig. 7 (a) The white light transmission image of a surface using an array of microlenses. (b) An image plane using the same array illuminated from the back by a white light. The bright areas in the middle of the features demonstrate light focused due to the microlens, while the ring structures demonstrate light diffracted as a result of the photoinduced index variations that surround each lens.

$$R=\frac{h^2+r^2}{2h} \tag{2}$$

where h is the height of the surface undulation of a lens of radius, r.

The refractive index of the microlens prepared by the aminated silicasol was $n=1.49$. Consequently, R was calculated using the diameter of microlens $r=5$ μm, and the height of microlens $h=1$ μm to give $R=13$ μm [see eqn. (2)]. Therefore the geometric optical focal length $f=26.5$ μm. There was a small difference in the optical focal length between the microscopic measurement value (*ca.* 28 μm) and the theoretically calculated value (26.5 μm).

The total number of lenses in which the size and the focal length was characterized was 25. In these 25 lenses, the magnitude of the focal length was the same.

We are convinced that these microlenses obtained from the swollen xerogel prepared by 3-aminopropyltriethoxysilane can function as collimating lenses for critical optical elements in applications such as laser diode to fibre couplings, beam formation devices, free-space focusing optical back planes, free-space to waveguide fibre array couplers, and beam formation devices for free-space optoelectronic cross-connect switches.

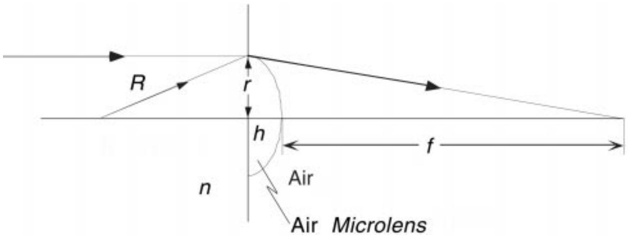

Fig. 8 The parameters describing a single surface microlens.

4 Conclusion

An extremely simple, low-cost technique for the fabrication of microlens arrays has been presented. The lenses are formed by the chemical property of polysilane and the sol–gel process without a conventional microlens fabrication process such as in the semiconductor manufacture process. This was achieved utilizing wettability enhancement induced by UV-exposure in polysilane. Future work will focus on further elucidation of the formation of microlenses with polysilanes and silicasol and on the fabrication of microlenses with an enlarged refractive index.

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