Deposition of micropatterned coating using an ink-jet technique

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Abstract

Microlenses made of hybrid organic-inorganic materials have been fabricated on glass substrates using a commercial drop-on-demand ink-jet printing system using a 50 μm diameter nozzle driven by a piezoelectric device. After deposition and evaporation of the solvent, the drops have been polymerized by UV light irradiation. Viscosity, solvent evaporation, drop-substrate wetting condition and drop and substrate temperatures are the main parameters which govern the obtention of reproducible lens shapes. The shape and surface roughness of the lenses have been characterized by atomic force microscopy and profilometry. Their optical properties have been determined by light microscopy and spectrophotometric techniques. The printing technique allows to obtain single and arrays of plano- convex spherical microlenses with diameters varying from 50–300 μm, focal length from 70 μm to 3 mm and *f*-number as low as 0.6. The doping with organic dyes allows to produce colored lenses with similar shapes.

Keywords: Ink-jet; Printing; Hybrid organic-inorganic; Microlens

1. Introduction

Microoptics technology is becoming increasingly important in the development of optical systems. Optical components such as diffractive and refractive microlenses are now incorporated in many systems and commercial products. They are used, for example to focus light on detector array, optical fibers and sensors, for illumination in flat panel displays, computers and for imaging in photocopiers and lithography [1–3]. Transparent microspacer arrays are also used in touch-screen panels. Refractive microlenses provide an attractive low cost alternative to diffractive components and for devices using short wavelength (< 1 μm) requiring low *f*-number ($F < 4$) they are still the only available components. Refractive microlenses have been fabricated in various ways using e.g. a photolithographic process [4–6] or by filling a negative form with a polymer, which after heating, transforms into small plano- convex lenses [1,7,8] or by reactive ion etching and ion milling [3]. Cylindrical shape lenses made by graded refractive technology also allows the preparation of micro optical systems [1].

The ink-jet process is of common use in computer controlled printing [9–11]. To our knowledge sol-gel based inks have been only recently proposed to decorate ceramic tiles using a continuous process [12]. In this paper we describe the use of such a technology to manufacture single or array of transparent and colored microlenses on glass substrates using sols prepared from hybrid organic-inorganic materials.

2. Experimental

The equipment used is a drop-on-demand printer (Microdrop, SP-K 130), composed of a piezoelectric ceramic nozzle (50 μm diameter), connected to a reservoir by a capillary tube (Fig. 1). The shape of the drops is visualized by a CCD camera coupled to a stroboscope. After travelling a few millimeters at a speed of about 10 m/s, the drops become spherical, typically 50 μm in diameter. The rate can be varied from one to 2000 drops/s. Single and array of droplets have been deposited on *x,y* driven clean glass substrates and glass substrates coated with a thin layer of a low surface energy perfluorated polymer (FTS/TEOS/MPTS/2-Propanol Irgacure 184) [13] in order to vary the drop/substrate wetting conditions.

Hybrid-organic inorganic sols have been prepared first by hydrolyzing methacryloxypropyltrimethoxysilane (MPTS, Fig. 2) and then mixing the solution with an ethanolic solution of tetraethyleneglycoldimetacrylate (TEGDMA, Fig. 2) and a 1–10 wt.% UV photoinitiator (Irgacure 184). The sol was then diluted with ethanol to achieve a low enough viscosity to not block the 50 μm nozzle.

After deposition, the drops have been polymerized either by UV light irradiation (Kombistrahler Beltron) or by heat-

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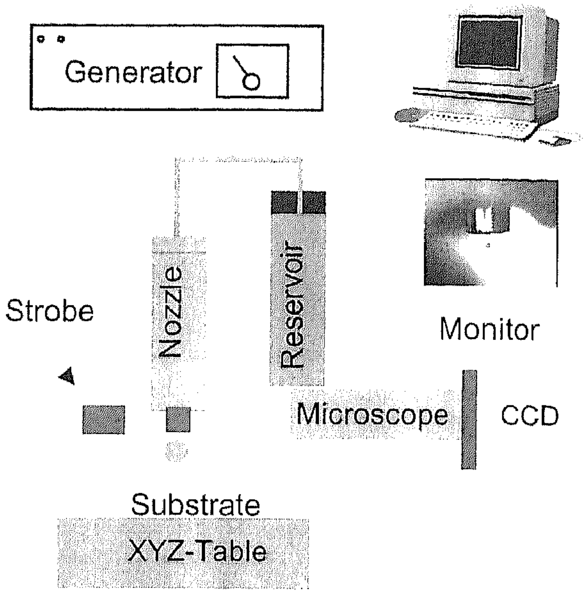

Fig. 1. Scheme of the drop-on demand ink-jet printing equipment.

ing at temperature as high as 200°C for different length of time. The visible and near infrared optical transmission of the sol and the polymerized material has been measured using a Varian Cary 5E spectrophotometer.

The shape and surface roughness of the lenses have been measured by atomic force microscopy (Topometrics Explorer 2000 AFM) and a Tencor PIO profilometer. The focal length of the plano convex lenses has been determined at $\lambda = 632.8$ nm using an optical microscope equipped with a scanning knife-edge device [14] and a silicon photodiode. The intensity image profiles of a parallel beam at the focus plane have been also recorded with a 3D Spiricon laser beam analyzer. The lens *f*-numbers have been calculated using the thick lens formula

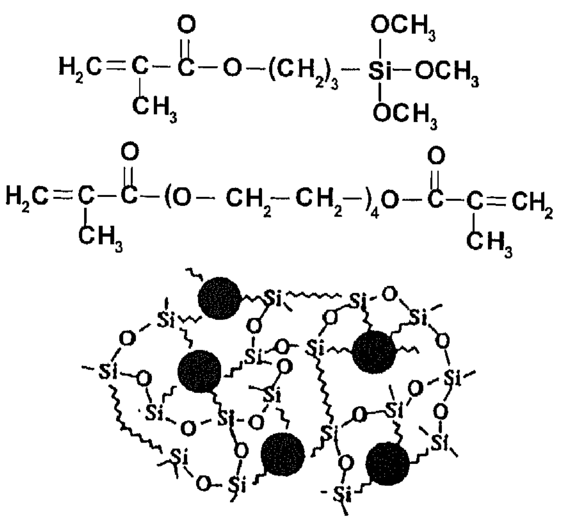

Fig. 2. Structure of the MPTS- molecule (top), TEGDMA (middle) and of the resulting organic- inorganic network due the polymerization.

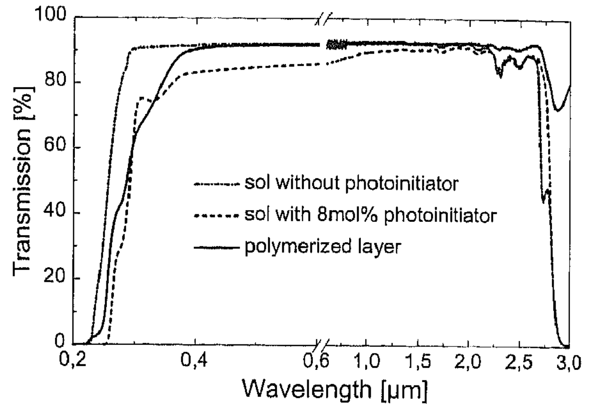

Fig. 3. Optical transmission spectra of (---) polymerized layer, (- - -) sol with 8 mol.% photoinitiator, (-·-·-) sol without photoinitiator.

$$F = \frac{1}{2z}\left\{n\left(1 - z^2\right) - \left[\left(1 - (nz)^2\right)\right]\right\}$$

where n is the refractive index (assumed $n = 1.5$) and $z = a/r$ with a the lens radius and r the radius of curvature.

3. Requirements

The sols used in ink-jet printing must satisfy particular requirements. As the flow velocity in the nozzle is very high (10 m/s) and the aperture very small (50 μm) the shear rates are very high (500 s^{-1}) and this places constraints on the rheological properties of the sols. For the preparation presently used, the kinematic viscosity of the ink at room temperature cannot exceed 3 mm^2/s. Conventional sols, which gel through hydrolysation and polycondensation processes cannot be used as they rapidly block the fine nozzle. After arriving on the substrate, the final shape of the deposit depends on the equilibrium between the van der Waals forces which act at the border of the drop/substrate interface (surface tension of the liquid, α) and attractive forces between liquid and solid (interfacial tension, α_{12}) These vary rapidly as the solvent evaporates and depend on the substrate temperature and the composition of both the drop and the substrate.

4. Results and discussion

A typical sol prepared with 18 mol.% MPTS, prehydrolized with a mol ratio MPTS : H_2O = 1 : 2, 18 mol.% TEGDMA, 64 mol.% ethanol and 0.1 mol.% Irgacure 184, has a room temperature kinematic viscosity $\eta = 3$ mm^2/s. Its value decreases slightly with increasing temperature. The effect of the UV irradiation (17.5 J/cm^2 total energy in the wavelength range 280–320 nm) on the networks building (polymerization) was analyzed by studying the evolution of the infrared absorption band at 1636 cm^{-1} of the C=C bonds of MPTS and TEGDMA as a

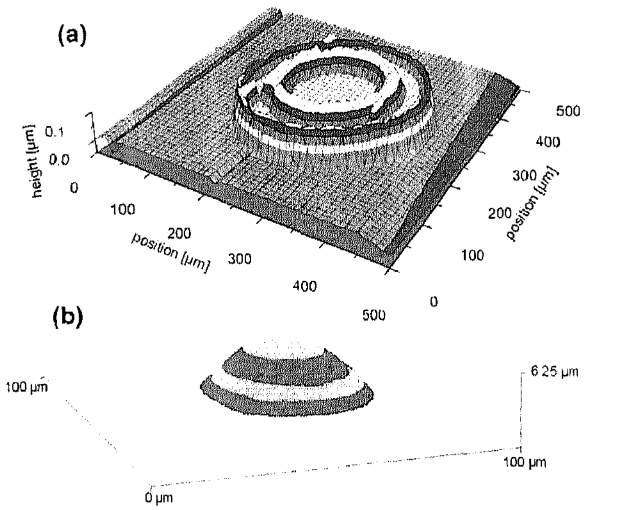

Fig. 4. a)Ring shape of a lens obtained on a borosilicate glass substrate measured by profilometry. The sol has a high ethanol content (40 wt.%) b) AFM micrograph of a lens obtained on a glass substrate with optimized ethanol content (30 wt.%).

function of the irradiation time using a 0.1 μm thick film deposited by spin coating on a Si-wafer. For a 10 wt.% photoinitiator, the polymerization is completed after 200 s. Fig. 3 shows the visible/near IR optical transmission of precursor sols with and without photoinitiator and of the UV polymerized layer. The UV absorption bands of the Irgacure 184 at 244 nm and at 285 nm are clearly visible for the sol. After polymerization the bands practically disappear and the final material is highly transparent in the region 375 nm $< \lambda <$ 2.7 μm. Its optical properties are therefore adequate for the preparation of lenses.

Typical shapes of single lens deposited on borosilikate glass with two different sols are illustrated in Fig. 4. A sol with a too high ethanol amount ($>$ 40 wt.%), wets well the glass substrate and spreads on it. The inorganic-organic material is transported to the border of the drop and creates a ring shape lens due capillary effect (Fig. 4a).Sols containing an ethanol fraction smaller than 30 wt.% have a higher kinematic viscosity, $\eta > 5$ mm^2/s, and tend to block the piezoelectric nozzle. A spherical lens formation was obtained with 30 wt.% ethanol fraction with a mixture of 50 mol.% MPTS and 50 mol.% TEGDMA (Fig. 4b), with the following properties: radius $a = 25$ μm, height $h = 6.25$ μm, radius of curvature $r = 53.1$ μm, focal length (at 632.8 nm) $f = 100$ μm, lens power $F = 0.62$ and a surface roughness $Ra = 40$ nm. The effect of the spreading of the sol having a high ethanol content can be reduced by depositing lenses on a substrate coated with a 100 nm layer of a low surface energy polymer [13]. Spherical lens with the following properties have been obtained: radius $a = 37.5$ μm, height $h = 9$ μm, radius of curvature $r = 82.6$ μm, focal length at 632.8 nm $f = 125$ μm, lens power $F = 0.72$, surface roughness $Ra = 40$ nm. Fig. 5 shows a vertical cross section of a lens measured by the profilometer passing through the center of the lens and a fit by a semi circle. The agreement is good.

Two-dimensional intensity profiles of the light spot created at the focal plane by a collimated 632.8 nm laser beam travelling on the substrate side of the above lenses are

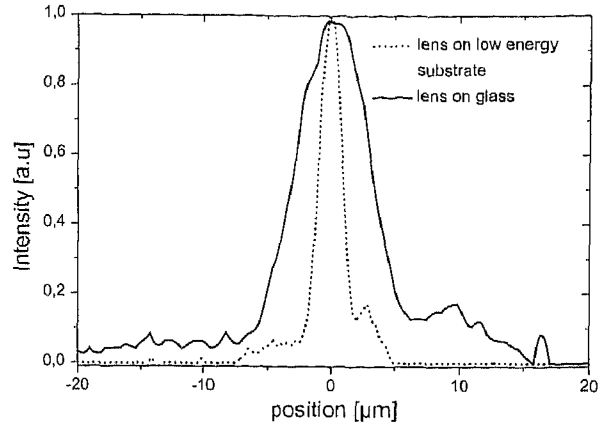

Fig. 6. 2-dimensional intensity profile of the focused light spot measured by knife- edge method for two lenses.

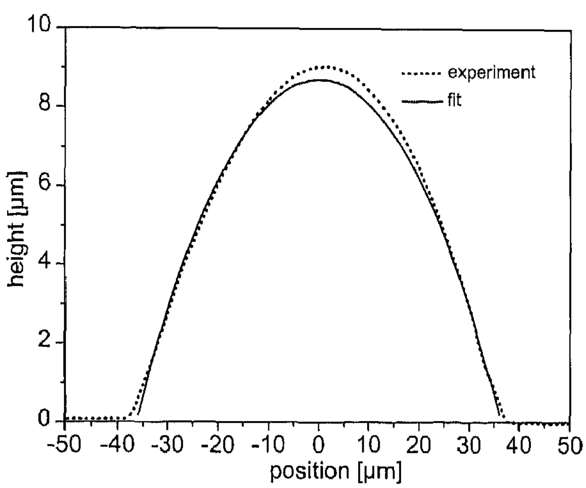

Fig. 5. Cross-section and fit by a semi circle of a lens deposited on low surface energy glass substrate.

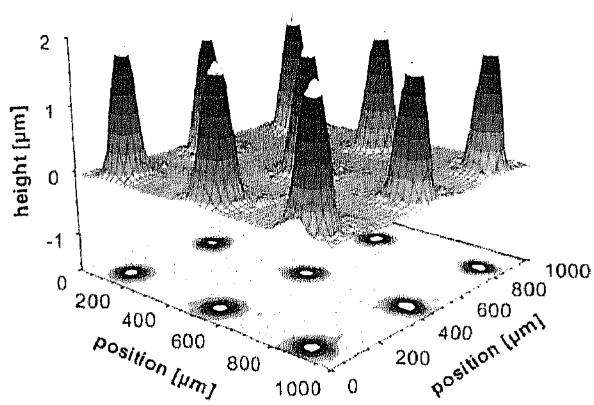

Fig. 7. 3D-plot and a 2D projection of a 3 × 3 array of ink-jet printed microlenses.

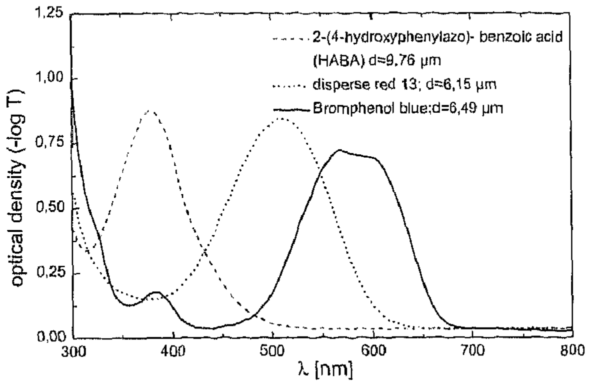

Fig. 8. Optical density of coatings made with MPTS doped with 3 wt.% of different dyes.

shown in Fig. 6. Their shapes are practically Gaussian with a full width at half maximum (FWHM) equal to 1.8 and 6.2 μm, respectively. These values are small and close to the values calculated for a perfect diffraction limited lens (FWHM ~ 0.7 μm).

Another way to reduce the effect of the spreading of the sol is to modify the prehydrolyzation of MPTS using a smaller amount of water (Mole ratio MPTS: $H_2O = 1 : 1.5$). The MPTS and the final sol have both a smaller viscosity, so that the ethanol fraction in the final sol system can be reduced to 20 wt.%. The polymerization time extends accordingly to 1 h. Fig. 7 shows a 3D-profilometer plot of a 3 × 3 array of microlenses produced with such a modified sol. These lenses are also spherical and have the following properties: radius $a = 60$ μm, height $h = 2$ μm, radius of curvature $r = 0.9$ μm, focal length (at 632.8 nm) $f = 1.2$ mm, lens power $F = 3.8$.

The system MPTS/TEGDMA/EtOH can be doped with dyes such as Rhodamin B, Bromphenole blue, Malachite-green, disperse red and HABA. The solubility of these organic dyes is high, up to 10 wt.%. Fig. 8 shows the optical density of red, blue and yellow coatings polymerized at 130°C during 4 h and having a thickness similar to the height of lenses.

The shape and physical parameters of the printed spherical lenses are nearly identical to the lenses made without dye.

5. Conclusion

A drop-on-demand ink-jet process has been successfully used to fabricate single, 1 and 2 dimensional arrays of refractive transparent microlenses on glass substrates using organic-inorganic sols containing MPTS, TEGDMA and a photoinitiator. These components have been polymerized by UV- irradiation at room temperature or by heating to 130–200°C. They are transparent between 375 and 2700 nm and have a refractive index $n = 1.5$. The lenses are plano convex and spherical with a diameter and *f*-number as small as 50 μm and 0.62, respectively, and a typical surface roughness $Ra = 40$ nm. The doping of the sol with dyes is possible. Arrays of spherical fluorescent and colored lenses of similar shape have been obtained.

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