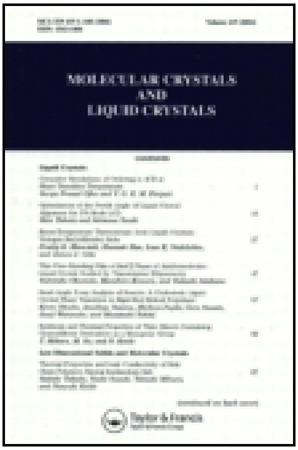

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The results of deep lithography based on the long-wavelength UV photopolymerization with a light self-focusing effect are presented. The effect of the formation of "bridges" between the nearest photopolymerization areas is revealed. Its sources such as the inhibition of photopolymerization by oxygen due to its diffusion to the exposed area are discussed. The conditions for a high aspect ratio of microelements (up to 100) are determined.

Keywords: deep lithography; microelements with high aspect ratio; photopolymerization

INTRODUCTION

At present time, there is an increasing demand for 3D micromachined components, and it is expected that this demand will continue to grow exponentially. In the last several years, the miniaturization of actuators, sensors, etc., has continued apace. Micromechanical components are also increasingly integrated with electronic devices in the so-called MEMS (microelectro mechanical systems).

There are many lithographic techniques [1], but only a limited number of techniques are able to produce the high aspect ratio, very small microstructures. The LIGA process (German abbreviation for Lithographie, Galvanoformung and Abformung) is one of the processes

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currently used to produce microstructures with high aspect ratio. According to the irradiation type of the exposure, the element form profile can be varied (Fig. 1). There is the need to take the possible diffraction of light over a photomask into account. As the light wavelength decreases, the diffraction decrease also, this is a reason for the use of X-ray radiation for the production of structures with high aspect ratios. In X-LIGA, synchrotron X-ray radiation is used to irradiate high aspect ratio masks. Today, the X-LIGA technology, while offering extremely accurate patterning capabilities, has a limited potential for industrial applications because of the high cost related to the exposure procedure and the manufacturing of masks. Furthermore, the depth of irradiation, i.e., the thickness of structures cannot be controlled. The UV-LIGA which uses UV light is much cheaper but has a minimum feature size larger than 1 μm. Electron beams can be highly focused and can produce very fine structures, well below 100 nm. However, electrons are very light and therefore scatter easily in a material, which results in a loss of resolution in depth. Therefore, only 2D structures can be made in well-known photoresist layers.

The example of a typical microstructure with high aspect ratio produced by LIGA is shown in Figure 2 according to work [2].

The aim of the present work was to develop a method of formation of high aspect ratio elements by using long-wavelength UV light and the effects of light self-focusing resulting in a decrease of the element width at the light propagation into a material. This process was investigated in our works on the self-recording of microstructures at the fiber top at photopolymerization by UV light outgoing from it [3–5].

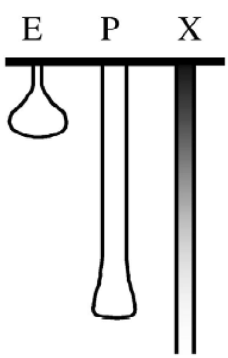

FIGURE 1 Beam profile of the mostly used radiation when traversing a matter: E – electron beam; P – high-energy proton beam; X – X-ray radiation.

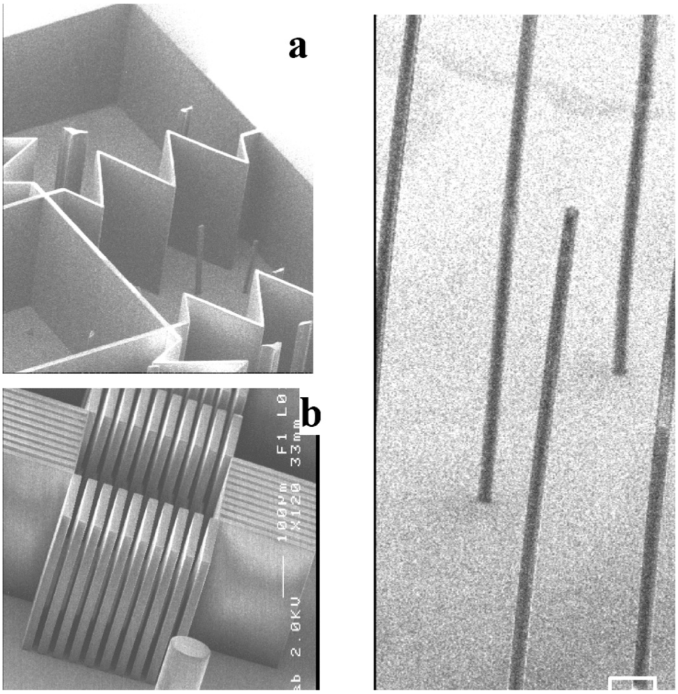

FIGURE 2 Typical structure with a high aspect ratio made by the LIGA process.

In the present work, the same process is studied in case of UV light coming over a photomask to the UV-curable monomer volume.

EXPERIMENTAL CONDITIONS

An UV-curable composition was made according to our previous investigation [6]. As acrylic monomers, we took a liquid composition of 2-carboxyethyl acrylate, bisphenol A glycerolate, 1,6-hexanediol diacrylate, and trimethylopropane ethoxylate (1 EO/OH) methyl ether diacrylate (in the ratio 5:2:1:2, respectively) from Aldrich and a solid composition of 2-carboxyethyl acrylate and RSX 51027 (from USB) (in the ratio 1:3, respectively). As an initiator, we used 2,2-dimethoxy-2-phenylacetophenone. The initiator type was chosen according to the light source with $\lambda = 365\,\text{nm}$. A concentration of the initiator allowed the penetration of light in the monomer material at 5 mm.

The process of formation of microstructural elements was as follows: we used a photomask with thin layer of siloxane deposited on it and the active substrate (glass in our case) having a chemical interaction with acid groups of the composition. A drop of the composition was placed on the substrate and covered by a photomask. The composition layer thickness was determined by spacers. UV-curing takes place at UV irradiation of the composition through a photomask. After curing, the photomask is removed, and the substrate is washed by isopropyl alcohol to remove the non-cured composition. For UV-curing, we used a 365-nm mercury lamp or a 400-nm LED lamp with a suitable photoinitiator.

For the experiments on photopolymerization in air and in argon, we used a vacuum camera with UV source.

DISCUSSION

The effect of the self-focusing of light in an optical material with a positive change of the refractive index (RI) under the light action is now widely investigated: see, for example, [7], where the results on the light self-focusing and the self-recording process realized on a light sensitive material are summarized.

The self-written waveguides arise if a Gaussian laser beam is focused onto and allowed to propagate through a photosensitive material that shows a positive change of the refractive index in response to the laser exposure. Since the refractive index increases with intensity, the initially diffracting beam causes the refractive index to build up along the propagation axis, which is reflected in the narrowing of the outcoming beam and an increase in the peak intensity. In the early stages, an adiabatic taper is formed, and, in the course of time, a channel waveguide can be created throughout the sample. These are the so-called self-written waveguides, because the same light that induces the waveguide is also guided by it [8,9].

This effect takes place not only at the coming up of light from the fiber end, but in all cases of the directed passage of light through a suitable mixture of UV-curable monomers. In our experiments, similar structures are generated in the UV-curable composition layer under the passage of the light beam formed by a photomask or a lens system through it (Fig. 3).

According to our results of the previous work, the structure narrowing angle depends on light absorption in the structure, so it is possible to tune this process by the addition of a dye [4]. In the present work, this effect is used to obtain vertical structures even at the light

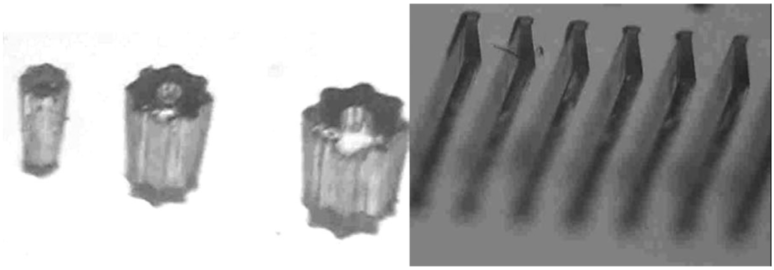

FIGURE 3 Small structures obtained by self-focusing light under a photomask. On the left, the decrease of the structure width is clearly visible.

dispersion in a material that is shown in the scheme in Figure 4. Our structures are shown in Figure 3.

At the preparation of complex structures with few elements close to one another, we have revealed a new effect of the formation of bridges between these structures (see Fig. 5).

While approaching two holes in a photomask, the photopolymerization of the liquid composition takes place not only under holes,

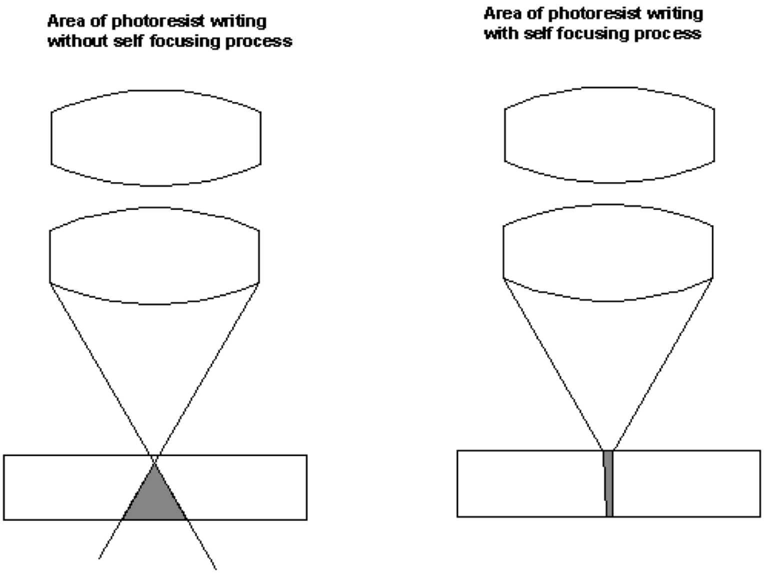

FIGURE 4 Diminution of the written point as a result of the light self-focusing (on the right). The maximal aspect ratio obtained in our experiments (height/width ratio) was 100.

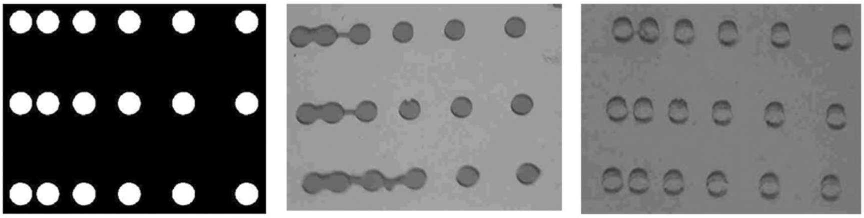

FIGURE 5 (a) – photomask, (b) – structure obtained at UV-curing of the liquid composition over a photomask, (c) – structure obtained at the use of the solid composition.

but also between them with the formation of some bridges. At the use of a composition of solid monomers in the experiment (see Section "Experimental conditions"), this effect slackens (Fig. 5b). This effect is very bad for the preparation of complex structures, and we made experiment to clear up its source. We carried out the UV photopolymerization of these structures under different conditions: in air and in argon, because we suspect the inhibiting effect of oxygen there [10].

EXPLANATION OF THE RESULTS

It is well known that oxygen inhibits the UV-curing process in acrylate. We made two similar experiments with the same UV-curable material in air and in argon over a strip photomask under the same conditions. At the exposure in air, a vertical element with the absence of a base spreading is formed. In argon, we observe the widening of the element base, which is as a result of the light diffraction. Bridges between the strips are formed easily.

We think that the former observation is related to the action of oxygen. During the photopolymerization, oxygen disappears in a polymer due to its reaction with oxygen and the production of active photoradicals. If dissolved oxygen is present in a composition of monomers, its photopolymerization do not begin. As a result, the exact border between polymerized and nonpolymerized areas is formed, which together with the self-focusing will result in the formation of a vertical structure (Fig. 6). On the contrary, in the absence of oxygen, the photopolymerization occurs in the usual way, and a wide base of the element is formed (Fig. 7).

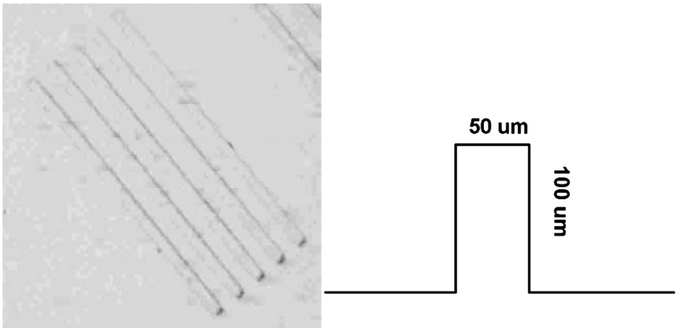

FIGURE 6 Formation of strips by the UV-curing of a composition of monomers in air. On the right – the strip profile.

From this point of view, the formation of the bridges between near elements is a result of the burn of oxygen between elements (that occurs certainly), and the photopolymerization of a liquid composition happens in dissolved oxygen even at low expositions with the formation of bridges (Fig. 5). At the use of a solid composition, the diffusion rate of oxygen in the exposed zone is small, and the formation of bridges is also slow.

So, the presence of oxygen and its inhibition of the photopolymerization process play a main role in the effect of the formation of vertical polymeric structures. Their formation would be impossible if the inhibition would not stop the photopolymerization process in low-exposure areas.

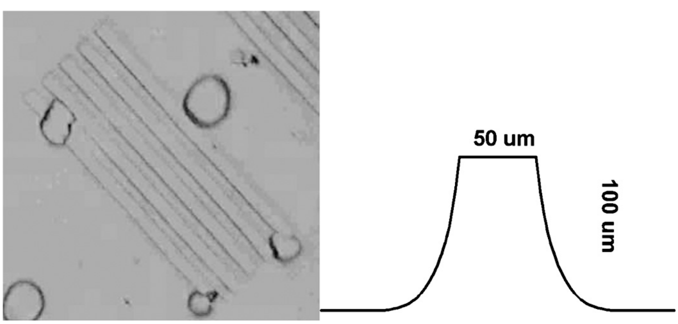

FIGURE 7 Formation of strips by the UV-curing of a composition of monomers in argon. On the right – the strip profile.

CONCLUSION

The process of self-focusing of light in UV-curable optical materials with a positive change of the refractive index under the light action is an interesting way to diminish the size of microelements in photolithography and to produce the structures with high height/width ratio.

The formation of vertical structures by this process is determined by the interrelation between the inhibition by oxygen, the self-focusing of light, and the distribution of light behind a photomask, so that it is possible to obtain the structures with high aspect ratios (up to 100) within the developed method.

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