Self-Organization Effects in Photopolymerizable Nanocomposite

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The main problem of photolithography is to overcome the diffraction limit. A possibility of overcoming this limit by the application of self-writing effects is discussed. Some of these effects are studied in the present work: the self-focusing of light in a photopolymer with a positive change of the refractive index, photo-induced transportation of nanoparticles, and the threshold of oxygen-based polymerization. The results of applications of these effects to the lithography process are shown.

Introduction

The primary obstacle for a continued increase in the integrated circuit density is the limitation on the resolution and the focus depth in the photolithography stage. The smallest feature size $X_{\min}$ that can be projected by a coherent imaging system is $X_{\min} = \lambda/2NA$, and the depth of a focus (DOF) is $DOF = \lambda/[2NA^2]$, where λ is the illumination wavelength and NA is the numerical aperture. The most direct route to attain smaller feature sizes is to reduce the wavelength from the modern *i*-line standard of 365 nm to excimer laser wavelengths (248 or 193 nm). The NA is equal typically to 0.5, so the feature size is of the order of the exposure wavelength. At the present time, semiconductor fabrication facilities are forecasted to use a 32-nm process, at which the constraints on resolution and focus depth in optical lithography become severe.

Figure 1 plots the resolution against the film stack's minimum refractive index *n* for a number of *k*-factors. Note that the calculation includes 0.90 as the practical optics limit for $\sin\theta$. This requires that the refractive index of immersion fluids be at least by 10% higher than the theoretical minimum value. It is also assumed that all other refractive indices in the stack are higher than the fluid's refractive index.

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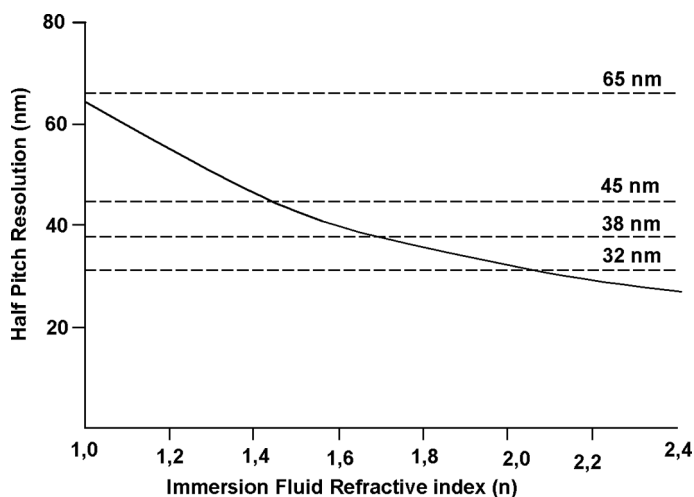
Figure 1. Half-pitch resolution plotted vs. the immersion fluid refractive index [1].

To overcome the pitch size of 32 nm, it is necessary to use a fluid with the refractive index of higher than 2.0, which is impossible.

Therefore, techniques to enhance the performance of optical lithography are of particular technological and economic significance. As the fundamental limits of optical lithography are approached, the nonlinear optical properties of a photoresist become increasingly important. This nonlinearity arises from a change in the complex index of refraction of a photoresist at the UV exposure. A common nonlinear optical phenomenon is the light-induced change in the imaginary part of the index of refraction, i.e., a change in the absorption at the exposure. For instance, contrast enhancement layers (CEL) composed of a photobleachable dye are often overcoated on a photoresist [2,3] to introduce the exposure thresholding. For the same reason, a special UV-curable nanocomposite with strong non-linear and self-writing effects which is overcoated on a photoresist to improve a light distribution in the spot can be used.

If a nanocomposite system with self-writing effects is fabricated and is placed as a topcoat, we will obtain a self-writing subwavelength artificial waveguide that will guide light to a small subwavelength spot in the photoresist. To realize it, a special material with self-writing effects should be developed.

Experimental Conditions

The UV-curable composition was made according to the results of our previous investigation on this matter described in our works [4]. As acrylic monomers, we used the 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 of 5:2:1:2, respectively) from Aldrich and the solid composition of 2-carboxyethyl acrylate and RSX 51027 (from USB) (in the ratio of 1:3, respectively). As an initiator, we took 2,2-dimethoxy-2-phenylacetophenone. The initiator type was chosen according to the light source with $\lambda = 365$ nm. The initiator concentration allows the light penetration into a monomer material down to 5 mm.

Nanocomposites used in our work are based on nanoparticles dispersed in monomers. We used ZnS, ZnO, and SiO$_2$ nanoparticles. The concentration of nanocrystals in the composite is about $10-20\%$ by volume, and their size ($1.5-20$ nm) will ensure a low light scattering by the nanocomposite. ZnS nanocrystals were synthesized by the original method, and ZnO and SiO$_2$ (Aldrich No. 066K0110) nanocrystals were purchased from Aldrich. In our experiments, we used aromatic carboxylic acids (5-phenylvaleric acid) as a shell, because carboxylic acids are not toxic, and we wanted to develop a synthesis method which would be suitable for the factory-scale production. 5-Phenylvaleric acid was used as a shell.

Prepared nanoparticles covered by the shell were mixed with a mixture of UV curable monomers: 2-carboxyethyl acrylate (CEA); 2-phenoxyethyl acrylate (PEA); and bisphenol A glycerolate (Bis) from Aldrich.

All experiments were accomplished at room temperature in air without special inert atmosphere (argon). The UV curing was made with a mercury lamp (100 W) with maximum emission at the mercury line 365 nm.

The size of nanoparticles was determined by the exciton absorption maximum shift. Our results are consistent with the earlier report on ZnS nanoparticle sizes [5].

The preparation of nanocomposites is described in our work [6] in detail.

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

For the preparation of submicronic 3D microelements, we used the holographic method based on an interferometer with a 320-nm He-Cd laser source. In the current experiment, the angle between two laser beams is 10 degrees, and the writing lattice period is 2 μm.

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

Experimental Results

Some self-writing effects occurred in our materials will be discussed in what follows. The application of these effects to the photolithography process will result in a possibility to overcome the diffraction limit due to a nonlinearity of photopolymerization.

Self-Focusing of Light in the Material with Positive Refractive Index Change at Photopolymerization

When a negative photopolymer is illuminated with low-intensity UV radiation, the exposed regions crosslink to form a solid with a real index of refraction typically by from 0.01 to 0.1 larger than that of a liquid. This change of the index leads to
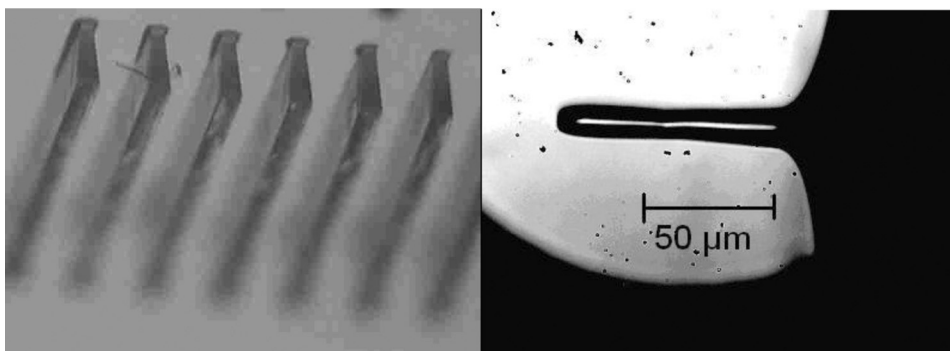
Figure 2. Small structures obtained by self-focusing light under a photo mask. On the left – a decrease of the structure width; on the right – the light self-focusing on the optical fiber top.

the self-focusing, in which light induces a lens, and the self-trapping, in which light induces an optical waveguide [7].

The light self-focusing effect in optical materials having properties of a positive change of the refractive index (RI) at the light action is widely investigated now. For example, work [8] summarizes the results on the light self focusing and the preparation of a self written waveguide obtained on a glass light-sensitive material.

Self-written waveguides can evolve 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 the intensity, the initially diffracting beam causes the refractive index to build up along the propagation axis, which results in the narrowing and the increasing peak intensity of the outcoming beam. On 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 called the self-written waveguides, as the same light that induced the waveguide is also guided by it [9].

This effect takes place not only at coming up the 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 a UV-curable composition layer at passing the light beam formed by a photomask or a lens system through it (Fig. 2).

According to our results of the previous work, the angle of structure narrowing depends on the light absorption in the structure. So, it is possible to tune this process by addition of a dye [10]. In the present work, this effect is used to obtain vertical structures even at the light dispersion in a material.

Oxygen Inhibition Action

Our experiments show the main influence of the oxygen inhibition action on the reinforcement of self-focusing light in a photopolymer. We have realized the UV photopolymerization of the structure under different conditions, in air and in argon, as we suspect the oxygen-induced inhibition there [11].
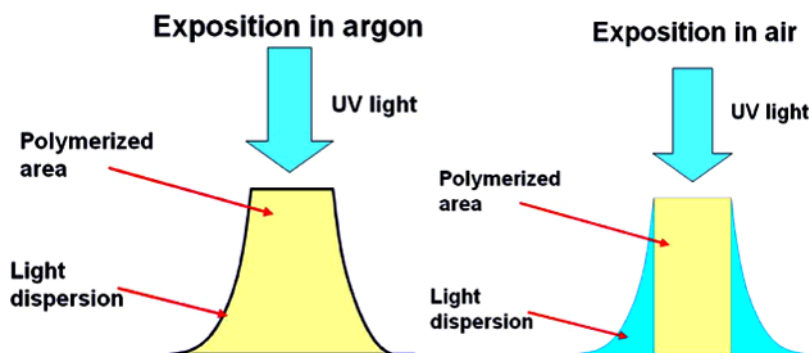
Figure 3. On the left – UV-curing of a composition of monomers in argon. On the right – the same in air.

Photopolymer irradiation was made over a photomask. Due to the light diffusion, the light field behind the photomask was widen (Fig. 3).

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 exposition in air, a vertical element is formed without a base spreading as a result of the light diffraction in the strip. In argon, we observe a widening of the element base related to the light diffraction. The bridges between the strips are easily formed. We think that this effect is connected to the action of oxygen.

During the photopolymerization, oxygen disappears in a polymer firstly due to the production of active photoradicals and their reaction with oxygen. While dissolved oxygen presents in the composition of a monomer, its photopolymerization do not begin. As a result, the exact border between polymerized and nonpolymerized areas is formed. At the self focusing, this will result in the formation of a vertical structure. On the contrary, in the absence of oxygen, the photopolymerization happens in the usual way, and a wide element is formed (Fig. 3).

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

Short-Distance Transportation of Nanoparticles

The light-induced redistribution of nanoparticles in a nanocomposite is a new effect found recently. It takes place at the irradiation of a photopolymeric nanocomposite under a periodic light distribution, for example, by a lattice made by the interference of two laser beams.

For the first time, these processes were studied by Tomita and co-workers on organic–inorganic nanocomposite photopolymer systems, in which inorganic nanoparticles with a refractive index larger than that of photopolymerized monomers
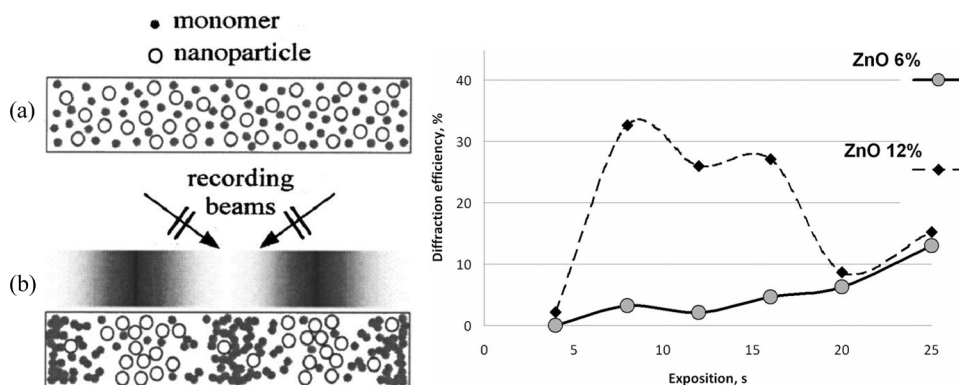
Figure 4. On the left – the transportation of nanoparticles in a photopolymer according to work [14], on the right – our experimental diffraction efficiency versus the exposition at various concentrations of nanoparticles.

were dispersed in unreacted monomers [12]. Inorganic materials possess a wide variety of refractive indices, which gives us the opportunity to obtain much higher changes of the refractive index, Δn, than those in conventional photopolymers [13].

The explanation of the effects was made in work [14]. For monomers with radical photopolymerization, the spatially nonuniform light illumination produces free radicals by the dissociation of initiators. Then the subsequent reaction of free radicals with monomers leads to the chain polymerization of individual monomers in the illuminated regions.

This process of polymerization lowers the chemical potential of monomers in the illuminated regions, by leading to the diffusion (short-distance transportation) of monomers from the dark to the bright regions. On the other hand, photoinsensitive inorganic nanoparticles experience the counterdiffusion from the bright to the dark regions, as illustrated in Figure 4 on the left, since the particles are not consumed, and their chemical potential increases in the bright regions as a result of the consumption of monomers. Such a mutual diffusion process essentially continues until the monomers are consumed completely by the monomolecular and bimolecular termination processes and until the high viscosity of a surrounding medium consisting of polymerized monomers makes monomers and nanoparticles immobile. As a result, the spatial distribution of nanoparticles is also fixed, and a refractive-index grating is created as a result of the compositional and density differences between the bright and the dark regions. The possibility of the diffusion of nanoparticles of the order of 10 nm in diameter in a liquid monomer is supported by the following numerical estimation: assuming a spherical nanoparticle with diameter d in a liquid with viscosity ν, the diffusion constant D of the nanoparticle is given by the Stokes–Einstein relation $D = kT/3\pi\nu d$. Substituting $d = 10$ nm and $\nu = 50$ cP (a typical value of photopolymerizable monomers for holographic recording) into this formula, we obtain $D < 1 \cdot 10^{-8}$ cm^2/s at room temperature. This value is comparable with that of monomers (10^{-9}–10^{-7} cm^2/s), by suggesting that the mutual diffusion is possible [14].

Figure 4 shows the dependence of the diffraction efficiency of a photopolymerizable nanocomposite material on the exposition time and the concentration of
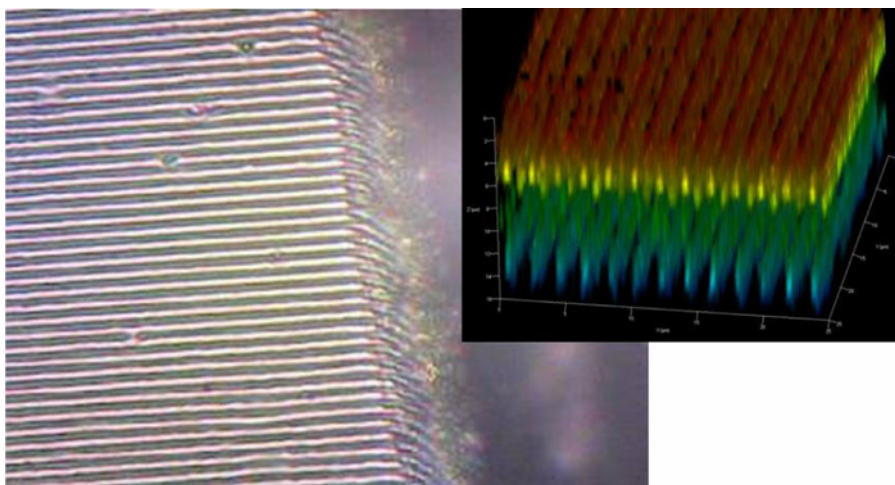
Figure 5. Photo of a microsection of the 3D structure (objective 160x, aperture 1.4) and a confocal microscope photo of the same structure (insert).

nanoparticles. Unlike the classical holographic photopolymer, the unpolymerized material in our studies was dissolved by alcohol after the exposition. According to the scheme (Fig. 4, on the left), the unpolymerized monomer in dark areas was removed by dissolution. The multiple augmentation of the diffraction efficiency at the 12% concentration of nanoparticles shows the main role of the redistribution of nanoparticles in this process.

As a result, we obtain 3D parallel plates of the polymerized material with nanoparticles. Our measurement was made by transmission optical microscopy on a microsection of the structure, and the same results obtained by confocal microscopy are shown in Figure 5. According to Figure 4 (right), there occurs the short-distance transportation of nanoparticles to the bright regions with a change of the solubility of a material and the intensification of the formation of a polymerized 3D lattice.

The above results show the intensification of the 3D plate writing process as a result of the short-distance transportation of nanoparticles. So, displacement of nanoparticles is a self-writing process or the enhancement of the self-focusing process discussed above.

Application of These Effects for the Improvement of Polymerized Areas in Photolithography

The self-writing and self-focusing effects discussed above are applicable to improve polymerized areas initially corresponding to the light distribution area in an objective spot. The main effect is the light self-focusing effect that will be enhanced by the oxygen inhibition and the redistribution of nanoparticles in a photopolymer. Figure 6 shows an application of self-writing processes in projection photolithography.

The objective forms a conical UV light beam with the formation of asmall spot on the photopolymer surface. Behind the surface, the light beam will be widened. In
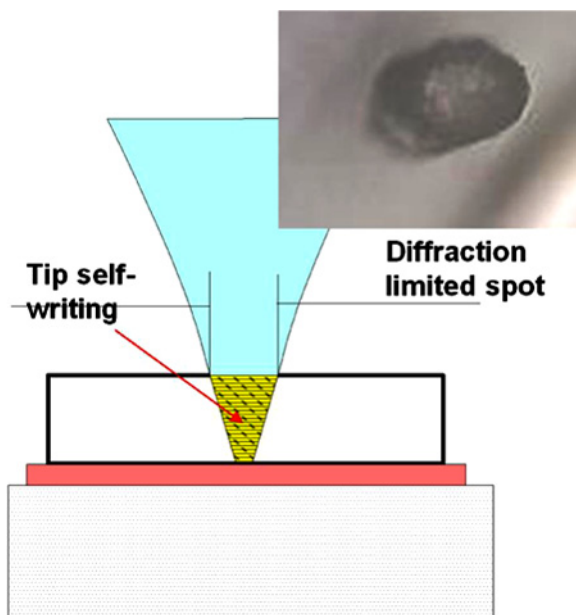
Figure 6. Model of light redistribution behind of a lens spot as a result of self-writing processes. 1 – UV light beam, 2 – nanocomposite, 3 – tip self-writing, 4 – photoresist. The polymerized cylinder with vertical borders is produced by this process (insert).

spite of the light beam widening, the self-focusing processes in a photopolymer will result in a gripping of the polymerized area with the formation of a self-written tip with the possible subwavelength spot.

The first experiments on gripping the photopolymerized area at the irradiation of a polymerizable nanocomposite with a 0.4-aperture lens revealed the formation of a cylinder (but not a 20-degree cone) with vertical borders $30\,\mu m$ in height and $6\,\mu m$ in diameter (Fig. 6, insert).

In the future, we would like to obtain the same cylinder with a diffraction-limited size of $0.5\,\mu m$ and next to diminish the size by using a high-aperture immersion lens (1.4) to obtain a nanoelement about $100–120\,nm$ in size.

Conclusion

The nanocomposite photopolymerizable material show a number of self-writing effects due to the light beam redistribution by the light self-focusing in a nonlinear photopolymer with a positive change of the refractive index at the photopolymerization. The effects of the inhibition of photopolymerization by oxygen and the short-distance displacement of nanoparticles will result in the enhancement of light self-focusing and the grasping of a polymerized area.

The process is applicable to photolithography. Experiments made with the use of a 0.4-aperture lens show the possibility of a transformation of the initial conical light distribution to the cylindrical one due to the processes under study in a nanocomposite UV-curable material.

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