Optica Applicata, Vol. XXIV, No. 1–2, 1994

Porous glass as a storage medium

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The possibility of porous glass usage as a base of light-sensitive capillary composites for holography is discussed. The principles of hologram formation in such a heterogeneous medium are examined. Predicted formation mechanisms of the holographic structure are realized experimentally. It is shown that porous glass not only determine the composites structure, but can be used as one of the components of light-sensitive system.

1. Introduction

Information storage and treatment is one of the promising branches of modern optics. Among other means of solution to this problem, 3-D holography is very attractive due to unique information capacity of the hologram [1] and capability to secure parallel access. A set of holograms may be recorded sequentially in the same region of volume material by using high angular selectivity (angular multiplexing) or spectral selectivity (wavelength multiplexing) of 3-D holograms. In both cases any particular page of information may be extracted independently from such a memory by using Bragg-match wave for reconstruction of an appropriate partial hologram. Besides, it is possible to restore the whole recorded image using only its fragment for 3-D hologram reconstruction which enables us to create an associative optical memory. It was experimentally confirmed that recording density $\sim 9 \times 10^4$ bits/mm^2 is quite attainable with use of volume material [2], [3]; this is nearly an order of magnitude higher than the recording density in traditional hologram memories with a 2-D information carrier.

Another attractive feature of 3-D holograms is the possibility of carrying out narrow-band spectral selection of radiation. Holographic selectors can be based on either reflection holograms or transmission ones. Selectors of the first type were developed to isolate a narrow spectral radiation band in laser radar [4]. For a band half-width of 0.1 nm and reflectance of 0.9 at the maximum of the band, they are characterized by a low level of spectral background.

Selectors based on transmission holograms have been developed for use as the elements of demultiplexor of fiber-optics communication lines [5]. The possibility of making elements of multichannel IR demultiplexor with 2 nm spectral channel separation has been confirmed experimentally.

It should be mentioned that the more the recording material thickness, the more the hologram selectivity and the less the noise level. Therefore, the so-called deep holograms with physical thickness of 10^3 μm have very good perspectives for practical application in information technology. Just this type of volume hologram is the subject of the present paper.

Practical realization of deep hologram promising application directly depends on advances in the elaboration of light-sensitive materials which are used for hologram registration. The recording of holograms of physical thickness of the order of 10^3 μm imposes a number of specific requirements on the photosensitive material. In addition to high resolution and transparency, it is necessary to achieve structural stability of the recorded hologram with changes in environmental temperature and humidity and also under various mechanical stresses. Unavoidably, this makes it necessary to utilize a rigid matrix. This circumstance together with extremely large hologram thickness substantially complicates or makes impossible the post-exposure treatment and fixation of recorded hologram. The choice of thick light-sensitive materials is not wide: electrooptic crystals, photochromic media, few types of photopolymers. Most of them do not allow us to fix a recorded hologram and are useful mainly for model experiments but are not quite suitable for technical application.

The purpose of our investigation was to search for the ways to overcome these contradictions and to work out thick light-sensitive materials which secure hologram fixing and long-time exploitation.

2. Principles of microheterogeneous media creation with use of porous glasses

To meet some of the practical needs, it is necessary to enhance the physical-mechanical parameters of volume recording materials and their thermal stability up to the level of the parameters of silicate glass. On the other hand, the use of homogeneous glass matrices excludes the possibility of post-exposure treatment because of their extremely low penetration even for low-molecular reagents.

To resolve this contradiction, which is fundamental to homogeneous media, an approach to fabrication of microheterogeneous light-sensitive materials with capillary structure has been proposed [6]–[8]. The essence of the approach is in the following. In the bulk of stiff matrix with interconnected microcavities, a photosensitive composite is formed being rigidly bounded to the microcavities walls (Fig. 1).

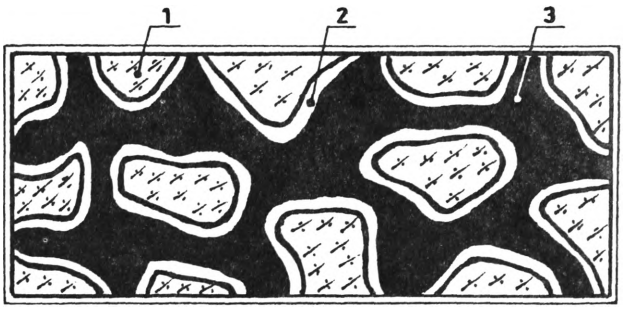

Fig. 1. Schematic diagram of the capillary composite structure. 1 – rigid porous frame, 2 – light-sensitive substratum coating, 3 – through capillary grid

The composite fills only the path of microcavities volume, but the remaining free volume forms a continuous capillary network that permits the reagents to penetrate into the bulk of the sample during post-exposure hologram processing. With "wet" processing the penetration of these reagents is simplified due to the presence of capillary pressure that reaches 10–35 atm when capillary diameter is 220 nm. Therefore, the possibility appears not only to amplify the latent image greatly, but to eliminate the absorption of light-sensitive substrate necessary at the recording stage, *i.e.*, to realize a record of a pure phase hologram with diffraction efficiency close to a theoretical limit without any loss of light-sensitivity level. The capillary structure of microheterogeneous media is responsible for the presence of light scattering. But if the characteristic size of inner cavities is less that the light wavelength, the level of scattering can be diminished to an acceptable level (less than 1%) by introducing an immerse compound even in the case of relatively high difference in the refractive indices of the frame ($n_m = 1.44-1.46$) and immerse compound ($n_f = 1.33-1.54$).

Finally, such media are practically shrinkproof. And, in fact, as light-sensitive substrate in this case is stiffly connected with the rigid frame and characteristic size of cavities, in which it is distributed, it is less than the light wavelength, its deformation during post-exposure processing is purely local and does not distort the hologram structure. The coral-like frame of the capillary composites must be made of a rigid material which is transparent over the entire visible spectrum range and has a relatively large free volume of interconnected inner cavities with a highly developed surface.

The porous glass completely meets these requirements [9], [10]. Porous glass is a material with a capillary structure, its composition being from 90 to 99 per cent of silica dioxide which is completely transparent over the wavelength range of 300–1500 nm. The process of porous glass production is as follows. The initial alkali borosilicate glass of a particular chemical composition being isothermally treated over the range of 500–700° C becomes completely separated into two interpenetrating phases of substantially different chemical properties. When subsequently treated by acids one of these phases containing mainly non-silica components passes into solution. The other phase contains mainly SiO_2 and is resistant toward acids. Therefore, it retains the structure of a porous high-silica frame thus practically completely preserving geometrical sizes of an initial sample.

By the processes of polycondensation and coagulation the SiO_2 of the soluble phase remains in the channels of the main silica frame as amorphous gel having a branched pore system. This silica is called a secondary silica as opposed to the vitreous silica of the chemically resistant phase which does not change its structure. Porous glasses containing secondary silica are conventionally called microporous ones. The characteristic properties of the structure of these glasses depend upon the initial glass composition and conditions of its thermal and acid treatment. The typical pore radii of these glasses can range from 1 do 10 nm, specific total pore volume varies between 0.15 and 0.30 cm^3/g, while their specific surface is variable up to 100 m^2/g.

An additional treatment of porous glasses by alkali solutions results in pre-

ferential removal of secondary silica from the channels of the main frame which gives rise to macroporous glasses with pore sizes determined basically by phase separation of initial glass. Pore volumes in macroporous glasses reach 0.4–065 m^3/g, pore radii can range from 10 to 200 nm and specific surface can vary between 10 and 70 m^2/g. Thus, the advantage of porous glass as a frame of heterogeneous light-sensitive systems are determined by its transparency and possibility to change its structure over a wide range with variations in controlled technological factors (glass composition). In terms of introducing light-sensitive compositions into such a frame the unimodal nature of pore distribution in sizes is of great importance. Immobilization of a stiff-phase coating of light-sensitive substance is promoted by high surface concentration of polar silonolyc groups (in the order of 10^{18} unit/m^2) on the frame walls. This provides efficient chemisorption and offers possibilities of their more rigid chemical attachment to pore surfaces.

An advantageous characteristic of porous glass as a matrix for hologram recording media is the fact that such glass compares favourably with optical polymers in its physical-chemical properties. The first attempts of hologram recording in composites based on porous glass [11], [12] were made by a local change in the refractive index of an immerse light-sensitive composite introduced into it. It is essential that such microheterogeneous disperse systems are superior in their physical-mechanical properties to the polymers introduced in them. The thermal expansion coefficient of a porous glass–polymethylmethacrylate composition is an order of magnitude less than that of block polymer sample (2.5×10^{-5} deg^{-1} and 2×10^{-4} deg^{-1}, respectively). However, the entire filling of inner glass cavities, similar to the case of homogeneous media, practically excludes the possibility of two-stage processes application for hologram production with post-exposure processing. On the contrary, light-sensitive composites with capillary structure permit accomplishing such a processing very easily.

3. Calculation of hologram parameters in capillary composites

To calculate hologram parameters in capillary composites, it is necessary to determine the effective refractive index of the medium whose real part determines the phase shift of the light wave, and whose imaginary part determines the decrease in amplitude due to scattering. In analyzing this complex refractive index we utilize a model in which it is assumed that the cavities of the principle silica matrix, like the micropores of the secondary silica, are nonintersecting spheres of radius $A = L/2$ and $a = l/2$, respectively.

Let us further assume that it is possible to characterize the contents of the micropores by the effective refractive index n_a. In this heterogeneous system, the effective sizes of all phase inhomogeneities will be much shorter than the wavelength of light.

Taking into account the assumption mentioned and the approach developed in [13], [14], we obtain the expression for refractive index n_s of heterogeneous composite

$$n_s = n_m \left[\frac{(1+2F)n_a^2 + 2(1-F)n_m^2}{(1-F)n_a^2 + (2+F)n_m^2} \right]^{1/2} \tag{1}$$

where: n_m is porous matrix refractive index, $F = f_A f_a$ is the relative micropore volume in the porous glass (f_A and f_a – relative volume of the cavities in the primary matrix and secondary silica, respectively).

So far, in analyzing the optical properties of the capillary composite we have abstracted from the nature of the distribution of the photosensitive material in the micropore volume. Let us now analyze three of the most characteristic cases of location of the photosensitive phase in the micropore volume:

1. Photosenstive phase is concentrated on the surface of the micropore and covers the micropore walls almost uniformly.
2. Photosensitive material forms a compact particle.
3. Photosensitive substratum forms a crumbly structure with consideralbe free volume.

Let us suppose that free volume of composite, which is not filled by photosensitive substratum with the refractive index n_p, contains a filler with the refractive index n_f. To estimate n_a for three cases mentioned above, we shall use the following models:

1. Spherical shell with the refractive index n_p and the curl with the refractive index n_f.
2. Spherical shell with the refractive index n_f and the curl with the refractive index n_p.
3. Homogeneous mixture of photosensitive molecules and molecules of the filler.

Henceforth, we refer to these models as the shell, the curl and the homogeneous mixture, respectively.

To determine n_a for the shell and curl models, the polarizability of a spherical shell particle should be equalled to that of a homogeneous spherical particle with the refractive index n_a (the equations for the polarizabilities of spherical homogeneous particles and shell particles are presented in [15]). For the homogeneous mixture model the Clausiuss–Mosotti equation can be applied. On this basis, n_a for these models is determined by following equations, respectively:

$$\begin{aligned}
n_a &= n_p \left[\frac{n_f^2 + 2n_p^2 + 2(1-f_p)(n_f^2 - n_p^2)}{n_f^2 + 2n_p^2 - (1-f_p)(n_f^2 - n_p^2)} \right], \\
n_a &= n_p \left[\frac{n_f^2 + 2n_p^2 + 2f_p(n_p^2 - n_f^2)}{n_f^2 + 2n_p^2 - (1-f_p)(n_f^2 - n_p^2)} \right]^{1/2}, \\
n_a &= \left[\frac{2b+1}{1-b} \right]^{1/2}, \quad b = f_p \frac{n_p^2 - 1}{n_p^2 + 2} + (1-f_p)\frac{n_f^2 - 1}{n_f^2 + 2}
\end{aligned} \tag{2}$$

where f_p is volume fraction of photosensitive substratum in the micropores.

Note that the differences between the values calculated within the framework of different models achieve their maxima for $n_f = 1$ and decrease when the difference

$n_p - n_f$ decreases. At the same time even for $n_f = 1$ and practical values of n_p ($n_p < 2$) such a difference does not exceed 3×10^{-2}.

After determining the effective refractive index of capillary composites, let us calculate the parameters of the recorded holograms.

As follows from Equations (1) and (2), spatial modulation of n_s can be created both by local modification of the parameters n_p and f_p describing the optical properties and the relative volume of the photosensitive phase in the micropores, as well as by varying f_A and f_a, *i.e.*, spatial modulation of the porous glass structure. Moreover, the volume fraction of photosensitive substratum in micropores can be expressed as

$$f_p = \frac{V_p C_p}{F} \tag{3}$$

where C_p is the concentration of photosensitive molecules and V_p is their molecular volume. Therefore, without affecting the structure of the porous glass, a hologram can be recorded by modifying the refraction of the photosensitive material n_p initiated by changes in its polarizability; by modifying the molecular volume V_p as a result of photoinduced structural transformations and, finally, by spatial modulation of the molecular concentration C_p of the photosensitive material in the composite bulk. Moreover, the hologram can be formed by spatial modulation of the relative pore volume (f_a) in the secondary silica or by modulation of cavity size in the primary matrix.

As a result of hologram processing all the parameters of capillary composite (n_p, V_p, C_p, f_A and f_a) may appear to be spatially modulated. We denote the amplitude of the first harmonic of the spatial distribution of these parameters by Δn_p, ΔV_p, ΔC_p, Δf_A, Δf_a, respectively, and by $n_1^{(q)}$ the partial hologram components attributable to spatial modulation of corresponding parameter $q \in (n_p, V_p, C_p, f_A, f_a)$. Let us assume that Δn_p, ΔV_p, ΔC_p, Δf_A, Δf_a are small. In this case with use of Eqs. (1), (2) and (3) partial hologram components $n_1^{(q)}$ can be represented as

$$n_1^{(n_p)} = \Phi^{(n_p)}[F_p \Delta n_p], \tag{4}$$

$$n_1^{(V_p)} = \Phi^{(F_p)}\left[F_p(n_p - n_f)\frac{\Delta V_p}{V_p}\right] - \Phi^{(n_p)}\left[F_p \frac{(n_p-1)(n_p+2)}{6n_p}\frac{\Delta V_p}{V_p}\right], \tag{5}$$

$$n_1^{(C_p)} = \Phi^{(F_p)}\left[F_p(n_p - n_f)\frac{\Delta C_p}{C_p}\right], \tag{6}$$

$$n_1^{(F_m)} = \Phi^{(F_m)}[(n_m - n_f)\Delta F_m] \tag{7}$$

where $F_p = Ff_p$ is the volume fraction of photosensitive substratum in the volume of a composite, and $F_m = 1 - F$ is the relative volume of silica. The first term in Eq. (5) describes the contribution due to a variation of the molecular volume of photosensitive substratum, while the second one describes the contribution to the grating amplitude resulting from the change in the refractive index of the photosensitive phase caused by change in its molecular volume. A contribution of the latter is

estimated by means of the Clausiuss–Mosotti equation. It should be underlined that Eq. (4) describes the contribution due to a modulation of the photosensitive molecule polarizability only. The multipliers in square bracket in Eqs. (4)–(7) describe the partial amplitudes calculated by the use of the additive equation of the effective refractive index of a composite, *i.e.*, $n_s = F_m n_m + F_p n_p + F_f n_f$, where F_f is the volume fraction of filler in the volume of a composite. Factors $\Phi^{(q)}$ describe local field effects and are dependent on structure parameters and the selected distribution model for the photosensitive material inside the micropores [14]. Note, however, that the functions $\Phi^{(q)}$ are near unity with small differences $(n_m - n_f)$ and $(n_p - n_f)$.

Let us estimate the maximum hologram modulation amplitudes that can be achieved for different mechanisms of hologram formation. The recording by means of spatial variation of photosensitive molecules polarizability (see Eq. (4)) can be realized by a broad range of photophysical processes: photopolymerization and photostructuration [16]–[19], photooxidation reactions [20], [21], photochromic transformation [12], and so on. The characteristic values of Δn_p for such systems vary within the range of $10^{-1}-10^{-4}$.

The most suitable processes to realize the recording by means of modulation of the photosensitive substratum molecular volume (see Eq. (5)) are photopolimerization and photostructuration. Changing in the molecular volume due to these processes may reach 10^{-3} [16]. It should be mentioned that changes in V_p as a rule are accompanied by changes in the molecular polarizability. Consequently, recording of grating of amplitude $n_1^{(V_p)}$ will always be accompanied by corresponding grating with the partial amplitude $n_1^{(n_p)}$.

Formation of the hologram by spatial modulation of the photosensitive molecules concentration can be realized using the photostructured systems with subsequent removal of an original or transformed form of a photosensitive substratum from the composite volume [22], [23]. The maximum value $\Delta C_p/C_p = 0.5$ can be achieved by complete removal of photosensitive molecules from the vicinity of minima or maxima of the interference pattern.

The recording by means of a structuration of porous glass can be realized by a selective removal of secondary silica from the main silica frame in accordance with the intensity of the recorded interference pattern [14]. The values of ΔF_m cannot exceed 0.15.

Note that in accordance with Equations (5)–(7) $n_1^{(V_p)}$, $n_1^{(C_p)}$ and $n_1^{(F_m)}$ depend on difference $(n_p - n_f)$ or $(n_m - n_f)$. In most important practical cases these differences lie within the ranges: $0.5 \geqslant n_p - n_f \geqslant -0.2$, $0.5 \geqslant n_p - n_f \geqslant -0.2$. The largest values $|n_1^{(C_p)}|$ and $|n_1^{(F_m)}|$ will be achieved at the upper bound of ranges mentioned, but $|n_1^{(V_p)}|_{\max}$ – at the lower one.

Finally, the typical value of F_p for capillary composites does not exceed 0.15.

Taking into account parameters determined the maximum attainable hologram modulation amplitudes for different mechanisms of hologram formation were calculated with use of Eqs. (4)–(7). These values are listed in the Table.

From the analysis of the data in the Table it follows that the greatest grating amplitudes are achieved with recording mechanisms that one way or another

modulate the free volume of the capillary composite (*i.e.*, spatial variation in the molecular volume V_p, volumetric concentration C_p of the photosensitive component as well as the relative volume of the glass cavities F). At the same time, hologram formed in capillary composites by spatial modulation of free volume will be characterized by a dependence of their amplitude on the refractive index n_f of the filler (see Eqs. (5)–(7)) introduced to reduce hologram scattering level during use.

Table. Peak parameters of capillary holograms

Modulated parameter	Δn_p	$\Delta V_p/V_p$	$\Delta C_p/C_p$	ΔF_m
Suitable photosensitive system and process	Photopolymers Photochromic Photorefractive media Photostructured system	Photopolymers Photostructured composites	Photoresists: organic and inorganic	Photolithographic process in porous glass bulk
Maximum value of modulated parameter	10^{-2}	3×10^{-2}	0.5	0.15
Maximum attainable grating amplitude	1.5×10^{-3}	3.5×10^{-3}	3.7×10^{-2}	7.5×10^{-2}

Therefore, in real experimental cases a reasonable compromise is necessary between the light scattering level and the attainable diffraction efficiencies.

4. Experimental results

The first step in the experimental study was to synthesize a composite in which each of the mechanisms considered above is realizable. Moreover, under proper choice of recording conditions and post-exposure processing only one of these mechanisms must be predominant. In synthesizing such a composite, it was also necessary to solve the problem of the compatibility of all components of the photosensitive phase with the porous glass and the problem of grating parameters uniformity over the depth of a sample.

The composite we have synthesized consists of microporous glass with $2A = 25$ nm, $2a = 7$ nm and specially prepared organic photoresist with $n_p = 1.5$ and $f_p = 0.1$. Photoresist can be photostructured, its polarizabilty and molecular volume being changed, and it is not destroyed by diluted alkali which is used to remove the secondary silica from a porous glasses.

Let us consider each stage of the hologram structure formation.

1. The light exposure of a composite containing the special immersion ($n_f = 1.38$) in free capillary volume causes the structurization of the photoresist and leads to the spatial modulation of the polarizability and molecular volume of photosensitive phase.

2. During the post-exposure treatment, the molecules of the photoresist, which have not been structurized, partially remove from the volume of porous glass together with the non-photolyzed sensitizer. As a result of this process, the photoresist molecule concentration C_p appears to be spatially modulated in accordance with the recorded interference pattern.

3. During further treatment of the recorded hologram with use of diluted alkali, the structured photoresist molecules linking with the micropores walls will inhibit dissolution of the silica. As a result, the secondary silica appears to be removed preferably from the region with the lower concentration of photostructured photoresist molecules. After a removal of the organic products from the porous glass volume, the concentration of the secondary silica and, as consequence, the free volume of the capillary composite appears to be spatially modulated. The products of interaction of sensitizer with silica structure make a minor addition to the sum grating amplitude.

Each of the stages listed was accompanied by hologram diffraction efficiency η measurements with fillers of different refractive indices introduced in hologram capillary volume. Using the results obtained hologram modulation amplitudes n_1 were calculated with use of the relation

$$n_1 = \frac{\lambda \cos\Theta}{\pi d} \arcsin\sqrt{n} \tag{8}$$

where: Θ – incidence angle of interfering beams on hologram surface, d – hologram thickness.

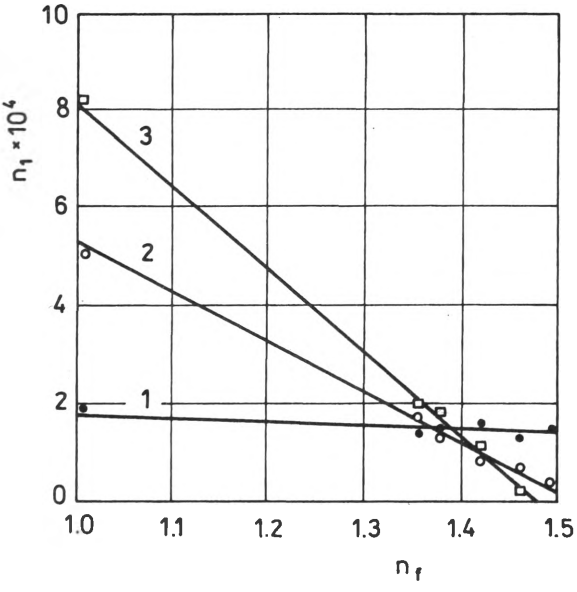

Fig. 2. Dependence of grating amplitude n_1 on refractive index n_f of the filler. (For recording on a composite with a photoresist as the light-sensitive phase). 1 – in the recording process itself, 2 – developed hologram, 3 – glass hologram

It is advisable to represent the experimental data as a plot of n_1 dependencies on refractive index n_f for each stage of hologram structure formation (Fig. 2).

Let us now analyze the experimental data together with Equations (4)–(7). This analysis is simplified greatly when $n_f = n_p$. Here and henceforth we assume that the quantities $\Phi^{(q)}$ are unity, while their derivatives $\partial\Phi^{(q)}/\partial n_f$ are near zero.

Let us first analyze the amplitude of partial hologram component obtained directly during exposure of the medium. In this case only n_p and V_p are spatially modulated in the capillary composite bulk, *i.e.*

$$n_1 = n_1^{(n_p)} + n_1^{(V_p)} \tag{9}$$

where $n_1^{(n_p)}$ and $n_1^{(V_p)}$ are defined by Eqs. (4), (5). On a level with experimental value n_1 we can also use the slope of the dependence of the grating amplitude on n_f to calculate both Δn_p and ΔV_p

$$\frac{\partial n_1}{\partial n_f} = \frac{\partial n_1^{(n_p)}}{\partial n_f} + \frac{\partial n_1^{(V_p)}}{\partial n_f}. \tag{10}$$

In accordance with Equations (9), (10), (4) and (5) for $n_f = n_p$ we can write:

$$F_p \Delta n_p = n_1 + F_p \frac{\Delta V_p}{V_p} \frac{(n_p^2 - 1)(n_p^2 + 2)}{6n_p}, \tag{11}$$

$$F_p \frac{\Delta V_p}{V_p} = -\frac{\partial n_1}{\partial n_f}. \tag{12}$$

Using the experimental values n_1 and $\dfrac{\partial n_1}{\partial n_f}$ and Equations (11) and (12), we have $F_p \dfrac{\Delta V_p}{V_p} = 4.8 \times 10^{-5}$ and $F_p \Delta n_p = 1.76 \times 10^{-4}$. Therefore, the amplitudes of partial hologram components at $n_f = n_p = 1.5$ are equal, respectively:

$$n_1^{(n_p)} = 1.76 \times 10^{-4},$$
$$n_1^{(V_p)} = 2.8 \times 10^{-5},$$

i.e., contribution of the component attributable to the photoinduced change in polarizability is predominant at first stage of hologram formation.

Let us now analyze hologram structure after development. Accounting for the process that occurs in development it is logical to assume that the dominant contribution to the sum amplitude in this stage will derive from spatial modulation of the volumetric concentration C_p of the photosensitive phase and its refractive index n_p. In accordance with Eqs. (4), (6), using the procedure described above, we can write for $n_f = n_p$:

$$F_p' \frac{\Delta C_p}{C_p} = -\frac{\partial n_1}{\partial n_f}, \tag{13}$$

$$F_p' \Delta n_p = n_1 \tag{14}$$

where F_p' is volume fraction of the photosensitive phase in the composite bulk following development of the hologram, while $\Delta n_p'$ is the modulation depth of refractive index, which in general case will deviate from Δn_p, determined by Eq. (11) due to partial elimination of components of photosensitive phase from the composite bulk. Substituting the experimental values (curve 2 in Fig. 2) into Eqs. (13), (14), we obtain: $F_p \cdot \Delta C_p/C_p = 9.6 \times 10^{-4}$, $F_p \Delta n_p = 3.6 \times 10^{-5}$.

Note that the partial grating $n_1^{(C_p)}$ is antiphase to the partial component $n_1^{(n_p)}$ for $n_f < n_p$. But if the difference between n_p and n_f is sufficiently large ($n_p - n_f = 0.5$, for example), the ratio $n_1^{(n_p)}/n_1^{(C_p)}$ reaches value 7.5×10^{-2}, and it is possible to neglect the contribution of component attributable to the spatial modulation of the refractive index.

Finally, let us analyze a glass hologram (Fig. 2, curve 3), in whose bulk the distribution of light field intensity is recorded as a corresponding distribution of the volumetric silica concentration F_m. Consistent with Eq. (7), for $n_f = n_m$, we write

$$\Delta F_m = \frac{\partial n_1}{\partial n_f}. \tag{15}$$

Substituting the experimental values for curve 3 in Figure 2, we obtain $\Delta F_m = 1.6 \times 10^{-3}$ for $n_m - n_f = 0.5 n_1^{(F_m)} = 8 \times 10^{-4}$.

Hence, all previously predicted formation mechanisms of phase hologram were realized experimentally for a capillary composite based on porous glass and photoresist as a light-sensitive phase. Especially note that not only photoresist, but a variety of systems ranging from silver halide to photostructured polymers may be used as a photosensitive phase [8]. Porous glass is used in the capillary composite not only as the rigid support matrix, but to a considerable extent defines photophysical processes taking place in the composite bulk. Moreover, porous glass frame itself may be used as information carrier. One example of hologram recording by means of porous glass structuration during post-exposure treatment of capillary composite is described above. But to some extent this way is artificial, because an additional light-sensitive face is used to structure porous glass chemically. On the other hand, porous glass contains a lot of chemically active centres, therefore there is hope to use them for direct photophysical structurization of porous glass, *i.e.*, to use a porous glass as one of the components of light-sensitive system.

To verify this hypothesis, the experiments were performed with a system in which the chromic acid salts have been introduced in the bulk of porous glass without any additional organic components. After exposing such a system the hologram was washed out from the dichromate and dried. The dependence of hologram amplitude on the filler refractive index was measured (see Fig. 3, curve 1) and analyzed. As a result, it was established that such a hologram consists of two partial components with amplitudes $n_1^{(n_m)} = 7 \times 10^{-5}$ and $n_1^{(F_m)} = 0.35 \times 10^{-3}$ when $n_m - n_f = 0.5$. The first is caused by Cr^{3+} compounds that are bound to the porous glass frame. Therefore, the process described leads to structurization of porous glass being accompanied by spatial modulation of its free volume and refractive index. The attempts of hologram amplification were undertaken by means of their additional

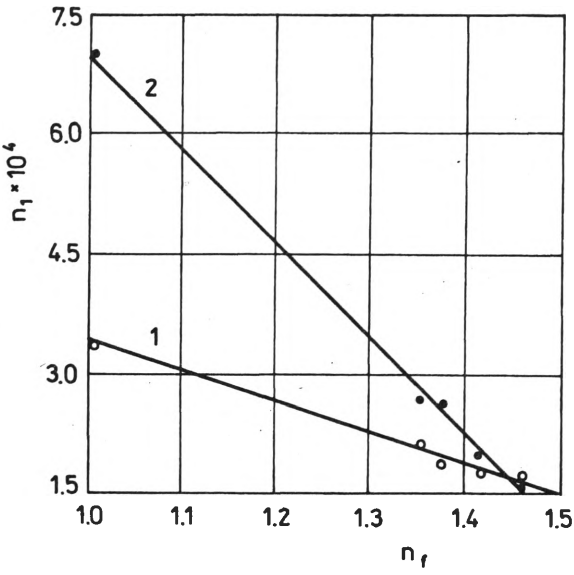

Fig. 3. Dependence of grating amplitude n_1 on refractive index n_f of the filler. (For recording by means of direct photophysical structurization of porous glass). 1 — developed hologram, 2 — after additional treatment

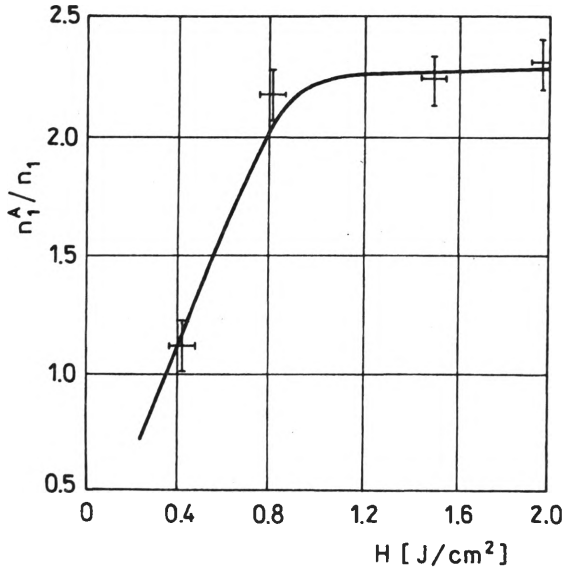

Fig. 4. Grating amplitude enhancement *vs.* absorbed energy H during hologram recording (n_1 — grating amplitude before additional hologram treatment, n_1^A — grating amplitude after chemical treatment)

treatment with use of dilute alkalis. These attempts were successful only when exposure during hologram registration is relatively high (see Fig. 4), *i.e.*, when deep primary photophysical structurization of porous glass takes place. As follows from the analysis of the hologram amplitude dependence on the filler refractive index

(see Fig. 3, curve 2), it consists of only one component attributable to spatial modulation of porous glass free volume. Note that attainable value of hologram amplitude in this case ($n_1 \sim 10^{-3}$) is comparable with the same parameter of hologram produced by etching of porous glass through the photoresist mask.

Therefore, the results of experiments performed show that porous glass itself can be used as light-sensitive medium with promising characteristics.

5. Conclusions

The primary results of the research performd can be formulated as follows.

The possibility of high-efficient hologram recording in composites based on porous glass is demonstrated. It is shown that capillary composites make possible not only hologram fixing, but also amplification of hologram as a result of post-exposure processing. It is confirmed both theoretically and experimentally that hologram recording can be performed by means of spatial modulation of different composite parameters, including direct photophysical structurization of porous glass. The combination of useful properties of capillary composites (high resolution, sensitivity to visible light, very good physical-chemical parameters, absence of shrinkage, high stability of hologram parameters during exploitation) makes it possible to use them for information storage and holographic optical elements making.

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Received June 6, 1994