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A photopolymerizable glass with diffraction efficiency near 100% for holographic storage

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Permanent holographic storage has been demonstrated in a photopolymerizable organically modified silica glass. The glass was prepared by dispersing a titanocene photoinitiator and a high refractive index acrylic monomer in a porous silica matrix. This glass exhibits unprecedented sensitivity and refractive index change upon a moderate exposure to green light and can be fabricated in thickness up to several millimeters. A photopolymerizable storage medium of such a thickness with good holographic properties is needed for practical holographic storage devices. Lack of such medium has been considered the main obstacle in development of write-once holographic memories. In our glass, we have stored permanent volume holograms of diffraction efficiency approaching 100% and refractive index modulation up to 4.5×10^{-3} , making this photopolymerizable material suitable for use in holographic data storage. © 2001 American Institute of Physics. [DOI: 10.1063/1.1354665]

Photopolymerizable materials are of considerable interest for development of holographic data storage devices.¹ Exposure of these materials to optical patterns of light and dark fringes such as that produced in holographic recording initiates a photoreaction that occurs preferentially in regions of high illumination. The photoreaction typically involves polymerization of an acrylic monomer dispersed together with a photoinitiating species in a polymeric film. After exposure, the material contains a record of the fringe pattern as a spatial variation of its chemical composition and corresponding variation of refractive index. A number of photopolymerizable materials for holographic applications have been developed^{2,3} since the first holographic photopolymer was reported in 1969.⁴ However, their application to data storage is severely limited due to their limited thickness, high shrinkage during holographic exposure and need for solvent processing.⁵ A recording medium of millimeter thickness or more and exhibiting high photoinduced refractive index change is required to achieve high storage density by recording multiple volume holograms, separated from each other by the Bragg effect, in the same spatial location.^{6,7} Our glass provides both excellent holographic properties and fabricability into thick films or monoliths, as required for holographic storage applications.

In our photosensitive glass, the characteristics required for volume holographic recording, including photosensitivity, high refractive index modulation, desired material thickness, high optical quality, and dimensional stability, are achieved by a combination of organic photoinitiating and monomeric species with silica in a hybrid organic-inorganic glass. The glass is prepared by the sol-gel technique, which has been widely used in the preparation of oxide glasses by hydrolysis and condensation of metal alkoxides⁸ since the

first synthesis of silica from silicon alkoxide was reported by Ebelmen in 1844.⁹ Given that the sol-gel process can take place at room temperature, organic molecules with modest thermal stability can be incorporated into an inorganic glassy host. The organic dopants can be dispersed in the host over domains of several nanometers, which results in materials exhibiting very low optical scattering, even if the refractive indices of the dopants differ from that of the host matrix.¹⁰

The host matrix is a crucial component affecting physical properties of the composite glass, such as its rigidity, environmental stability, dimensional changes upon holographic exposure, and maximum achievable thickness. It also affects optical properties of the composite, including bulk refractive index, optical homogeneity and photoinduced refractive index change. In holographic photopolymers, the photoinitiating and monomeric species are typically dispersed in a film-forming polymeric host also called "binder."¹¹ For holographic storage, the most important limitations imposed by organic polymeric binders are the limited thickness of the medium, usually less than 200 μm , and temperature- and light-induced dimensional changes that can distort the holograms and degrade the fidelity with which the stored images can be retrieved. An approach to prepare thicker photopolymers is to use resins consisting of two independent photopolymerizable systems,^{12,13} in which matrix-forming oligomers are first precured to a gel state and then the hologram is recorded by photoinduced polymerization of monomers dissolved in the resin. However, this approach does not simultaneously achieve high dimensional stability and maximum photoinduced refractive index change. To increase the rigidity of the material, higher levels of precuring are required, which decreases diffusional mobility of the monomer in the resin¹⁴ and degrades holographic properties of the photopolymer.¹⁵ In addition, some monomeric species are inevitably consumed (polymerized) during the precuring step, which in turn reduces dynamic range of the holographic

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recording¹² and, ultimately, limits the data storage capacity of the material.

In our material, the disadvantages outlined above are overcome by replacing the organic polymeric binder with an inorganic glassy host. The photosensitivity in blue and green parts of the visible spectrum is achieved by a free radical generating titanocene photoinitiator bis(μ^5 -2,4-cyclopentadien-1-yl)-bis-[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium. We chose a low concentration of the photoinitiator in the glass, typically 0.4–0.8 wt % depending on the glass thickness, to assure a uniform light absorption through the entire volume of the glass. This also helps eliminate spurious gratings produced by diffusion of photoinitiator molecules, resulting from its own concentration gradients induced by holographic exposure. Crucial for the holographic performance of a photopolymerizable material is the monomer. To obtain an efficient image formation, the latter should be capable of polymerization at high propagation and low termination rates¹⁶ and should be highly soluble in silica sol without degrading the optical and mechanical properties of the composite. Furthermore, as will be explained below, a high refractive index of the monomer is preferred. We chose an ethylenic unsaturated monomer ethylene glycol phenyl ether acrylate, which satisfies these requirements. The monomer concentration in the glass was 40 wt %. Both photoinitiator and monomer were added into silica sol prior to the gelation point. After stirring the solution for 20 min at 40 °C, a homogeneous solution was obtained. It was then cast into Teflon vials and allowed to gel and dry for ten days at 60 °C. Dry monoliths were polished to optical-grade slabs of thickness ~ 1 mm. We also prepared films of ~ 260 μm thickness by casting 0.1 ml of the solution onto a borosilicate glass plate. The films were dried for five days at 60 °C.

To characterize holographic performance of our glass, plane gratings were recorded in the glass by two mutually coherent plane-wave writing beams 1 and 2 (Fig. 1). The writing beams (wavelength 514.5 nm, beam diameter 1.5 cm, and intensity of each beam 50 mW/cm²) were from an Ar-ion laser operating in a single longitudinal and transversal mode. The grating growth was studied during and after the holographic exposure by diffraction of read-out beam 3. The angle of incidence β of the read-out beam was set to satisfy the first-order Bragg condition at which the intensity of the first-order diffracted beam (beam 4) and thus, diffraction efficiency η , is maximized. To minimize a possible photochemical influence of the read-out beam, we used a low-intensity (0.8 mW/cm²) beam of 632.8 nm wavelength (from a He-Ne laser) at which the absorption of the photoinitiator is low. In all experiments, polarization of the writing and read-out beams was perpendicular (“s” polarization) to the plane defined by the sample normal and wave vectors of the writing beams. After the holographic exposure, the sample was kept in the dark for 15 min to allow any dark reactions to subside. The photoreaction was then completed by uniformly exposing the sample 5 min to UV light (wavelength 254 nm and intensity 1350 $\mu\text{W}/\text{cm}^2$) from a low-pressure mercury vapor lamp. The diffraction efficiency dependence on the angle of incidence was measured by detuning β from the Bragg condition. This measurement yields the grating

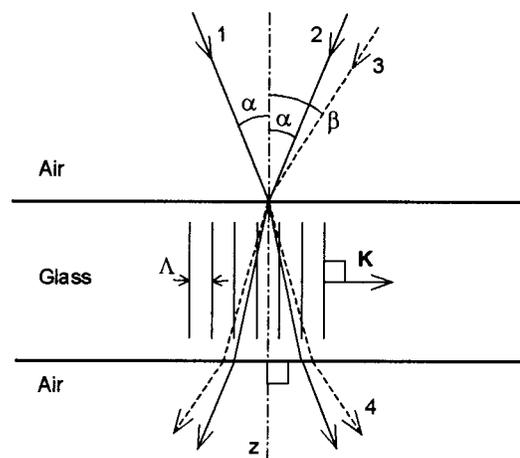


FIG. 1. Geometry used for the gratings recording in photosensitive glass. Collimated writing beams 1 and 2 of wavelength λ_1 (514.5 nm) inside on the glass symmetrically with respect to the sample normal. The angle between the writing beams is $2\alpha = 3^\circ$ and 34° for gratings of a period $\Lambda = 9.8$ and 0.9 μm , respectively. The glass refractive index was measured as $n = 1.47$ by a prism-coupling technique. The grating is probed by diffraction of the read-out beam 3 of wavelength λ_2 (632.8 nm) into the beam 4 (first Bragg order). The angle of incidence of the beam 3 is $\beta = 1.8^\circ$ and 20.6° for $\Lambda = 9.8$ and 0.9 μm , respectively. At this angle, the first-order Bragg condition $\mathbf{k}_3 + \mathbf{K} = \mathbf{k}_4$ is satisfied; \mathbf{K} is the grating vector and \mathbf{k}_3 and \mathbf{k}_4 are the wave vectors of the beams 3 and 4, respectively.

angular selectivity θ defined as full width at half maximum of the angular selectivity curve. The refractive index modulation amplitude Δn and effective thickness of the grating were calculated from the diffraction efficiency and angular selectivity data using Kogelnik's coupled-wave theory.¹⁷

Figure 2 shows dependence of the diffraction efficiency η and refractive index modulation Δn (Fig. 2 inset) on exposure when a holographic grating of a period $\Lambda = 9.8$ μm is recorded in a glass monolith of 950 μm thickness with photoinitiator content of 0.4 wt %. A short induction period of virtually no growth of η can be observed at the beginning of the exposure. This is due to rapid destruction of the thermal inhibitors and consumption of dissolved molecular oxygen by the photogenerated free radicals.¹⁸ Once the inhibiting species have been consumed, polymerization of the monomer starts. η increases with the exposure and reaches a maximum of 98% at $E = 0.23$ J/cm², yielding a refractive index modulation $\Delta n = 3 \times 10^{-4}$. Further increase of the exposure leads to an oscillatory evolution of η , typical for volume gratings.^{17,19} Steady-state diffraction efficiency and $\Delta n = 1.3 \times 10^{-3}$ are achieved at the exposure $E \sim 1.5$ J/cm², which corresponds to a sensitivity $S = \Delta n/E = 8.6 \times 10^{-4}$ cm²/J. A dynamic sensitivity $S^* = d(\Delta n)/dE = 1.8 \times 10^{-3}$ cm²/J was achieved in the region of exposure 0.1–0.35 J/cm². To our knowledge, these values of Δn , S , and S^* are the highest reported to date in a photopolymerizable material of similar thickness.^{3,20–22} In the angular selectivity experiment $\theta = 10$ mrad was measured, yielding an effective grating thickness of 941 μm . This shows that the grating was recorded practically in entire depth of the monolith. We also recorded gratings in films of 260 μm thickness with photoinitiator content of 0.8 wt %. We achieved $\Delta n = 4.5 \times 10^{-3}$ for $E = 0.72$ J/cm² and thus, a sensitivity $S = 6.2 \times 10^{-3}$ cm²/J, for gratings of a period $\Lambda = 0.9$ μm . These values by far exceed both the refractive index modulation

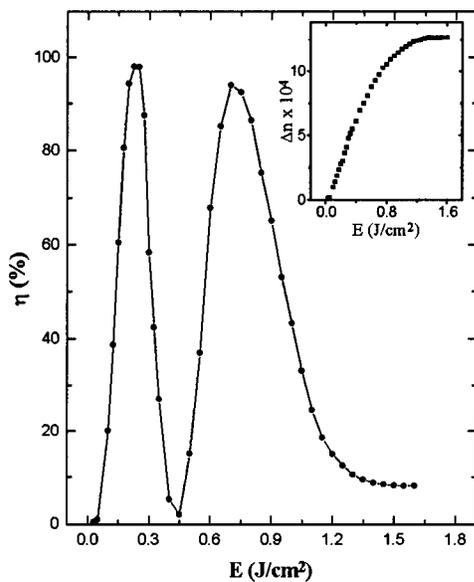


FIG. 2. Grating growth measurement in photosensitive glass. Writing beams: wavelength 514.5 nm, intensity of each beam 50 mW/cm²; read-out beam: wavelength 632.8 nm, intensity 0.8 mW/cm². All beams are “s” polarized. Main Figure, exposure dependence of the diffraction efficiency η (circles). η was calculated as the intensity ratio of the light diffracted into the first Bragg order (beam 4) to the intensity of the read-out beam 3, the latter being measured at its exit from the sample prior to the holographic exposure. The solid lines are guides to the eye. Inset, exposure dependence of the refractive index grating amplitude Δn (squares) obtained from the coupled-wave theory for volume transmission gratings (Ref. 17).

and sensitivity reported to date in photopolymers developed for applications in holographic data storage.^{3,12}

The mechanism of grating formation in our glass can be elucidated by the models developed for holographic photopolymers.^{23,24} The monomer polymerization starts and proceeds preferentially in the light regions of the illumination pattern. The depletion of the monomer in the light regions sets up a spatial concentration gradient resulting in a diffusional flux of monomer molecules from the dark to the light regions, along the grating vector. In addition, it is well known that acrylic monomers shrink on polymerization. As the monomer molecules separated at van der Waals distances are converted to covalently bonded polymer, voids are created in the light regions, and the resulting capillary forces draw the fresh monomer from the dark to the light regions.¹¹ This process continues until either there is no more unreacted monomer in the dark regions or transport of monomer is hindered by increased rigidity of the polymer in the polymerized regions. Ultimately, permanent compositional and density changes and associated refractive index modulation are induced in the material. The diffusion of monomer is a critical mechanism in the formation of holographic gratings in photopolymerizable materials.²⁵ A porous host, such as our silica glass, facilitates efficient liquid monomer transport. Moreover, the resulting low effective refractive index of our host matrix contributes to the high refractive index modulation. It is known that the refractive index modulation increases with difference in refractive indices between the host and the monomer,¹¹ and that high refractive index of the monomer is required to maximize the refractive index change per one diffusing monomer molecule.²⁶ These requirements are satisfied in our glass by combination of the

aromatic monomer of refractive index $n = 1.52$ with the porous silica host of refractive index $n = 1.44$.

Our results offer a significant advance in the field of research on holographic recording materials. We demonstrated unprecedented sensitivity and refractive index modulation capability for a thick photopolymerizable material. The holograms stored in our glass are permanent and stable, which was confirmed by the constancy of Δn over a period of 6 months at room temperature. This excellent performance was achieved by substitution of the polymeric binder used to date in holographic photopolymers with a porous inorganic host and dispersing a titanocene photoinitiator and a high refractive index acrylic monomer in the latter. An additional advantage of our glass compared to holographic photopolymers is that it can be easily fabricated into samples of high optical quality and thickness of several millimeters. The failure to make photopolymers of such a thickness with good holographic properties has been the main obstacle in development of holographic write-once memories.² We consider that prospects are excellent for practical holographic storage devices using similar organically modified sol-gel glasses.

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