Self-Processing of Surface-Relief Gratings in Photosensitive Hybrid Sol-Gel Glasses

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In 1978 it was reported[1] that laser light counterpropagating in a glass optical fiber could inscribe a Bragg diffraction grating, ostensibly by altering the local refractive index of the glass in a periodic manner through an optical damage mechanism. Now, 20 years later, this discovery underscores a global multi-million-dollar activity in the manufacture of Bragg fiber gratings for the emerging photonics industry. Indeed, fiber optic gratings have asserted themselves as key elements in Mach–Zehnder interferometers for dense wavelength division multiplexing (DWDM) systems that enable fibers to carry more channels (wavelengths) of information. DWDM, in turn, has blossomed into a multi-billion-dollar optical bandwidth solution to fiber saturation created by burgeoning Internet traffic. In a broader context, Bragg gratings find widespread use in integrated optics devices such as distributed feedback lasers, filters, compensators, and mirrors for optical interconnects. Of course, this simple optical element can also find application across the entire field of spectroscopy, but the present trend toward miniaturization has created a new impetus for developing materials and methods to implement Bragg gratings in semiconductor and dielectric micro-optoelectronic benches for chemical sensing (biochips). Optical methods are among the preferred techniques for fabricating Bragg gratings. Ironically, there is as yet a rather incomplete understanding of the mechanisms used to create physical or refractive index gratings by photoinscription into glasses.[2] In this communication, we describe the preparation of acrylate-modified silica–titania sol-gel glass thin films and their use in direct optical "self-processing" of micro-optical diffractive elements.

For some time, we have been exploring the chemistry and photoprocessing of hybrid organic–inorganic sol-gel glasses for integrated optics device fabrication.[3,4] In this context, we were motivated to examine the potential of these materials for optical data storage and grating fabrica-

tion. Hybrid glass media would be particularly attractive for these purposes if a single-step photoprocess were involved. While investigating a variety of multinary hybrid glasses, we discovered that the incorporation of simple titanium alkoxide precursors yielded a particularly responsive glass for grating fabrication. We have shown previously that photoresponsive hybrid glasses can be used to record microscopic volume (refractive index) gratings in ridge waveguides by irradiation with an ArF+ laser (193 nm) through a phase mask.[5] To create surface-relief gratings (SRGs) from hybrid glasses, a different procedure is required. Earlier research by our group[6] showed that volume compaction occurs during photoinduced acrylate monomer polymerization in families of hybrid glasses. Densification occurs by carbon–carbon bond formation during polymer chain growth, which induces collateral structural relaxation and condensation reactions in the metastable silica network. Since spatially resolved gradients in composition can be produced in this manner, we reasoned that constrained densification might be used to make a surface-relief grating. Because the desired physical change would be completed without any form of etching post-treatment, the hybrid glass formation could then be described as "self-processing". To date, only a few reports have appeared in which SRGs in hybrid glasses have been detailed; however, these procedures introduce a wet-etching step to reveal the surface structure.[7–9] We were encouraged that direct optical "self-processing" could be realized in a hybrid glass by evidence that periodic surface corrugations can be created either by polymerization (thick-film acrylate photopolymers[10–12]) or resonant excitation of trans–cis–trans bond isomerizations (azo polymers[13–15]). The development of photorelief in our hybrid glass differs fundamentally from the grating formation in these latter media.

Material Preparation: A hybrid organosilicate glass was prepared from combinations of a) methacryloxypropyltrimethoxysilane, b) titanium(IV) isopropoxide, and c) methacrylic acid. Various ratios of these three compounds (a:b:c) were studied over the range from 10:4:4 to 10:0.5:0.5 to vary the optical response of the material. As a result, we found that the 10:1:1 composition yielded films suitable for contact mask alignment and grating contrast. Partial hydrolysis and polycondensation of methacryloxypropyltrimethoxysilane was initiated with 0.75 equivalents of acidified water (0.01 M HCl). In a second step, titanium(IV) isopropoxide was dissolved in isopropanol and complexed with methacrylic acid before being dispersed into the prehydrolyzed organosiloxane medium. Hydrolysis and condensation of the remaining silicon alkoxide functional groups and titanium propoxide were resumed with additional water (total H_2O/Si and H_2O/Ti molar ratio = 1.5). A photoinitiator in the form of 3 wt.-% bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819, CIBA Geigy) was added to the solution. This was filtered and allowed to age for 48 h before use. The free-flowing sol was passed through a 0.2 μm filter before deposition. Films were spin-coated on

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glass or SiO_2 substrates at speeds ranging from 2000 to 5000 rpm for 60 s. The refractive index of the films at $\lambda = 0.6328$ µm was 1.505. This increased to 1.515 after irradiation with a mercury lamp (10 mW/cm² for 30 min).

Spectroscopic Characterization: Photoinduced structural changes in the hybrid glass thin films were monitored by UV-vis and Fourier transform infrared (FTIR) spectroscopy. The electronic absorption spectra of a non-irradiated sample and one irradiated for 30 min with UV light (10 mW/cm²) are compared in Figure 1 (top). Photoinitiated polymerization is signified by the depletion of the 240 nm band, assigned to the $\pi \rightarrow \pi^*$ transition of the unsaturated methacrylate group.[16] We attribute the growth of a broad low-energy band at longer wavelengths to polymerized methacrylate products.
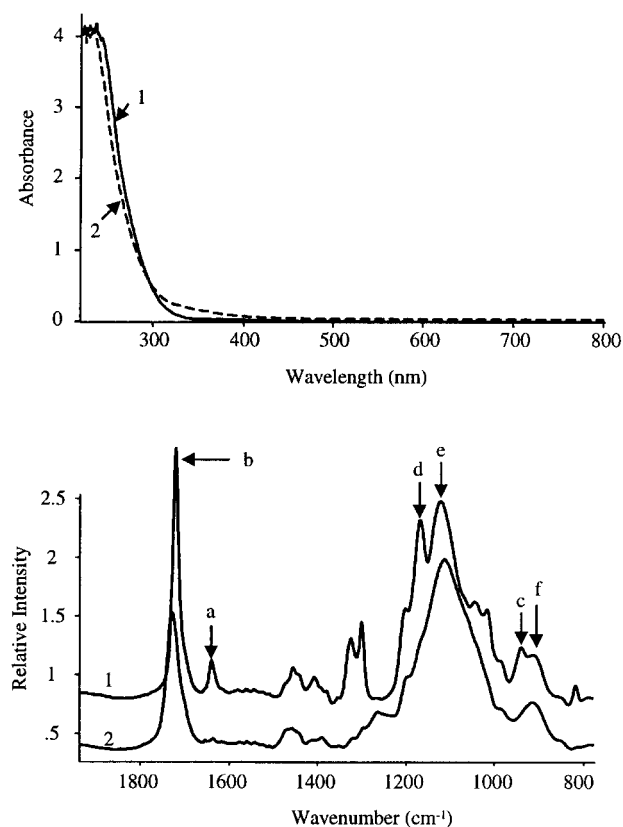

Fig. 1. Absorption spectra of an organically modified silica–titania sol-gel thin film before (1) and after (2) UV irradiation (10 mW/cm² for 30 min). UV-vis spectrum (top) and FTIR spectrum (bottom).

Polymerization is clearly evidenced in the mid-IR absorption spectra (Fig. 1, bottom) by the loss of intensity of the vinyl group v(C=C) mode (a) at 1638 cm⁻¹ [spectra 1 (non-irradiated) and 2 are offset for clarity]. This is accompanied by a characteristic shift of the carbonyl v(C=O) stretching mode (b) from 1717 to 1728 cm⁻¹ on irradiation. A concurrent condensation reaction between silanol and the alkoxy (and probably water) in the metastable siloxane network is indicated by the diminishing intensities of v[Si–O(H)] at 944 cm⁻¹ (c) and the –CH₃ rock at 1166 cm⁻¹ (d). An increase in the distribution of the siloxane bond an-

gles and an overall decrease in the average Si–O–Si bond angle are indicated by the significant broadening of the v_{as}(Si–O–Si) band (e) and by its shift to lower wavenumbers (1120–1110 cm⁻¹),[17] respectively. This spectroscopic evidence reinforces our view[6] that, in these hybrid glass systems, polymerization of the organic moieties promotes the growth and densification of the inorganic host. We attribute the band at 920 cm⁻¹ (f) in the IR spectrum to the presence of Si–O–Ti bonds.[18]

Grating Fabrication and Characterization: After spin-coating, films were briefly irradiated with UV light to cross-link the surface and near-subsurface region of the glass. This step was introduced to create a hardened layer that would not adhere to the photomask. An exposure time of 5 min and power density of 3 mW/cm² were used for this purpose. Diffraction gratings with periods ranging from 1.4 to 4 µm were recorded by illuminating the sample at a quasinormal incidence, with a non-collimated 100 W UV-mercury lamp, through a chromium amplitude mask. No further steps (wet etching, thermal curing, or UV fixing) were necessary to reveal and stabilize the surface relief. The results presented below were obtained after irradiation for 30 min on 5 µm thick samples. Surface corrugation was investigated with an atomic force microscope (AFM). Figure 2 (top) shows a three-dimensional view of a 4 µm period grating with an amplitude of 785 nm. The profile is sinusoidal, which offers the advantage of reducing the intensity diffracted into the higher orders. The diffraction efficiency (η_i) of the grating is demonstrated in Figure 2 (center) by the high light intensity diffracted into the plus/minus first order. Gratings with a smaller period were recorded in the same way. Figure 2 (bottom) shows an AFM profile of a 1.4 µm period grating with an amplitude of 230 nm. η_i was measured using the intensity of a 632.8 nm He–Ne laser light transmitted in the ith order, normalized to the total diffracted intensity. Table 1 compares the experimental η_i values to the theoretical ones computed from a source method.[19] Small discrepancies between the two sets of data can be accounted for by the imperfect sinusoidal shape of the corrugated surface.

Table 1. Typical experimental and theoretical values of diffraction efficiencies transmitted in the various orders (wavelength = 0.6328 µm). All gratings were UV-imprinted in silica–titania sol-gel films with a mercury lamp through an amplitude chromium mask. The amplitude of the surface corrugation measured by AFM is represented by h.

	Experimental [%]	Theoretical [%]
Grating 1: $\Lambda = 4$ µm ($h = 790$ nm)	$\eta_0 = 3.30$	$\eta_0 = 6.10$
	$\eta_{\pm1} = 34.60$	$\eta_{\pm1} = 34.80$
	$\eta_{\pm2} = 11.60$	$\eta_{\pm2} = 12.10$
	$\eta_{\pm3} = 2.00$	$\eta_{\pm3} = 0.05$
Grating 2: $\Lambda = 1.4$ µm ($h = 230$ nm)	$\eta_0 = 85.70$	$\eta_0 = 82.30$
	$\eta_{\pm1} = 7.10$	$\eta_{\pm1} = 8.80$

The roughness intrinsic to the film surface on the relief was evaluated as a parameter that might decrease the performance of the grating through scattering. The root mean
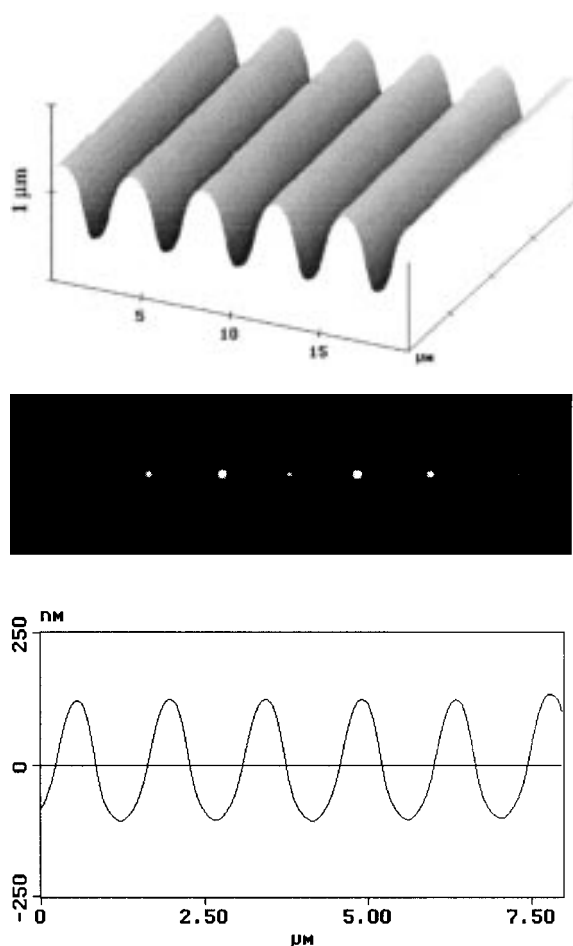
Fig. 2. AFM three-dimensional view of a 4 μm period grating (top) and photograph of the Fraunhofer diffraction pattern from a 4 μm period grating (center) recorded in an organically modified silica–titania sol-gel thin film. AFM profile of a 1.4 μm period grating imprinted in an organically modified silica–titania sol-gel thin film (bottom).

square roughness values (R_q) measured with AFM on random 100 nm × 100 nm areas of the grating averaged 0.2 nm, indicating that the grating walls were very flat. These values are as low as those measured on the surface of BK7 glass substrates and are well below the 1 nm limit for high-quality optical surfaces.[7]

The robustness of the gratings was also tested under adverse conditions. No change in η_i was measured when the gratings were submitted to a second UV exposure (10 mW/cm² for 30 min). Similarly, dipping the gratings in a bath of isopropanol or water for 30 min did not affect their performance. Gratings were baked for 1 h at different temperatures ranging from 110 to 240 °C. The η_i value for the first diffracted order (η_1) was monitored after each heating and remained unchanged up to 220 °C.

Mechanism of Corrugation: There are several theories in existence that explain photoinduced grating-relief formation. Lavielle and Lougnot[10] reason that growth of SRGs in photopolymers is caused by competition between the chemical reaction, diffusion, and gradients in surface free energy. Photopolymers consist of light-sensitive molecular

components dissolved in a solid (plasticized) polymer matrix. When illuminated, these materials swell because of monomer diffusion, creating ridges in the regions exposed to light. Lavielle and Lougnot[10] rationalize that gradients in surface free energy create a strain that is relieved by the flow of monomer from dark to illuminated zones. However, this cannot explain the effect in our glasses. In the hybrid glasses, diffusion of the monomer is strongly suppressed because the acrylate moieties are either chelated to titania or covalently bound through silicon to the silica network. We have demonstrated elsewhere[20] that the polymerization event is highly spatially confined and, in fact, is considerably more so than that occurring in some photopolymers where monomer diffusion degrades resolution.[11,21] In any case, corrugation in our hybrid glasses in the light regions of the mask corresponds not to ridge formation, but to trough formation (i.e., to a region of volume shrinkage, as evidenced by an AFM view of the edge of a grating; see Fig. 3). "Self-processed" SRGs are also formed in polymers of azo dyes. The most recent explanation[22] for the response of the azo systems suggests an optomechanical effect in which the chromophore threads itself via trans–cis–
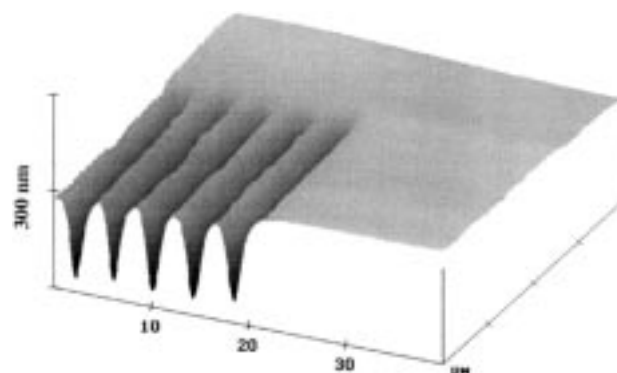

Fig. 3. AFM three-dimensional view showing the absence of swelling at the edge of a grating and shrinkage of the irradiated zones, as recorded in an organically modified silica–titania sol-gel thin film.

trans bond isomerization to give a worm-like motion of dye through the polymer. Surface relief arises because of a photoassisted build-up of a concentration grating, with an amplitude proportional to the increase in the number of dye molecules in the dark regions. This effect apparently leads to a viscoelastic flow, as discussed by Barrett et al.[23] It is consistent with the results of Darracq et al.,[24] who observed SRG in azo-dye-containing hybrid sol-gel glasses. Because we have discounted diffusion of the monomer in a concentration gradient, and because there is no resonant excitation/bond isomerization mechanism available to our monomer, we offer an explanation based on stress and strain fields for SRGs in hybrid glasses containing monomer undergoing free-radical polymerization.

Photoinduced pressure gradients can be created from the internal strain caused by constrained densification.[25] For this, a continuum elastic model can be used to give the density response of the glass to the imposed strain. Suppose a

slab of glass is uniformly irradiated beneath an opening in the mask. Coincident with polymerization of the organic phase, the glass will begin to contract. If a roughly rectangular region of glass below the mask opening were completely free to contract in the x, y, and z dimensions, its new volume would shrink by ΔV. However, the irradiated volume is not free to contract, and so the new volume is determined by the surrounding volume of non-irradiated glass (Fig. 4). In this instance, the actual densification must be non-uniform (constrained), so that the shrinkage $\Delta V'$ must be less than that for the free volume element. The final density must be greatest near the sample surface, where
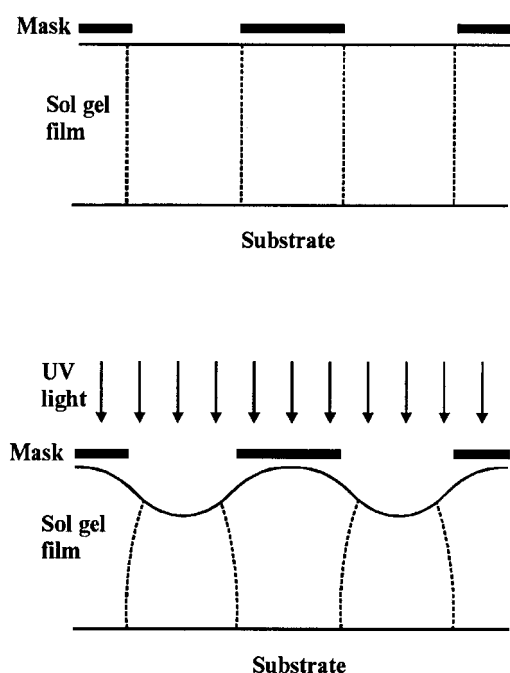

Fig. 4. Cross-sectional view showing the mechanism of the formation of surface corrugation in an acrylate-containing sol-gel glass before (top) and after (bottom) UV irradiation.

constraints from the surrounding glass are the least. This non-uniformity in compaction near the surface is increased by the exponential attenuation of the light in the subsurface regions. At the surface, the densified region will develop tensile stress surrounded by compressive stress in the undensified region, whereas the whole volume of the material will develop tensile stress. We argue that it is this effect that gives rise to the surface-relief features we observe in our films. This mechanism is comparable to the one observed in some photocurable materials operating by cross-polymerization. We believe, however, that photoinduced shrinkage has not been used to record patterns in such materials. On the contrary, efforts have been made to suppress this effect for imaging applications.[26]

SRGs have been created in photosensitive hybrid sol-gel glass derived from an acrylate-modified silica–titania compound. Constrained densification of the glass occurs in illuminated areas when UV light is admitted through a contact amplitude mask. Self-optical processing is defined for this class of hybrid glass in the sense that the creation of the grating does not require any resist, etching, or development step. No thermal post-treatments or UV fixing are necessary to stabilize the surface corrugation. "Self-processing" of the surface relief produces smooth sinusoidal profiles with a very low value of wall roughness. The use of photomasks for imprinting microdiffraction features is simpler and substantially less capital-intensive than direct e-beam writing. The hybrid glasses described in this paper offer the advantages of transparency and resistance to temperature (up to 220 °C), water, and simple alcohol solvents. Furthermore, because SRG formation does not rely on a large-scale diffusion mechanism, the polymerization/densification event is highly spatially confined. In the same glass, we have recently recorded surface gratings with feature sizes as small as 0.26 μm, using a phase mask and a 193 nm wavelength. This process, therefore, appears promising for the production of micro-optical elements with applications in the fields of telecommunications, data communications, and sensing.

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