Patterning Wrinkle Architectures in Nanocomposite Glasses with Self-Inscribing Optical Waves

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ABSTRACT

We describe ways in which light induced self inscribed (LISI) waveguides can impose constraints on wrinkle patterns when nanocomposite hybrid sol-gel glass films become unstable to perturbations of a certain wavelength, which reflects some length scale in the microscopic system. Periodicity of wavy structures from nano- to micro- length scales can be generated reproducibly in the presence of microlithographic features created by inscribing guided waves in the photosensitive nanocomposite. Partial wet-etching of network glass films stimulates buckling of the surface whose wave length, orientation and patterning are controlled over large areas by self-inscribed waveguide relief structures.

Keywords: wrinkling, pattern formation, nanocomposite patterns, microrelief, nanoscale patterns, self inscription

1 BACKGROUND

Pattern formation and spatiotemporal complexity have emerged as important problems in the study of materials where collective self-organization effects and chaotic behavior are commonly linked to the nonlinear response of the medium [1]. We have been exploring pattern formation and the optical responses of a class of nanoscale network gel phase composites derived from “alloys” of photopolymerizable organic monomers covalently attached to a silica network structure [2]. There is widespread interest in the micro- and nano-patterning of matter and in the dynamic control of patterning by recruiting spontaneous processes to achieve desirable effects [3]. We can harness instabilities caused by differences in mechanical properties between network glass films, their substrates and microstructures created in the films by an unusual guided wave self-inscription technique. These instabilities manifest themselves in ordered patterns that spontaneously appear over several length scales when the films are exposed to solvent. We direct the latent instabilities to give hierarchies of patterns over nano-, meso- and micro-length scales without the use of photomasks, embossed relief structures or metal or oxide overlayers [3,4,5].

2 EXPERIMENTAL

2.1 Sol Formation

5 molar equivalents of 3-methacryloxypropyltri-methoxysilane (MAPTMS) were combined with 3.75 eq of acidified water. The phase-separated mixture cleared rapidly after hydrolysis This solution was then added to 2 eq of 1:1 methacrylic acid:zirconium-*n*-propoxide, prehydrolzyed with 10.5 eq 0.05 M HCl. An additional 6.75 eq of water was added to the solution. **XXX** g of titanocene dichloride photoinitiator was then added to the sol.

2.2 Film Formation, Self-Inscription and Patterning

The sol was filtered through a 0.2 μm PTFE membrane directly onto a 500 μm thick silicon wafer equipped with a 2 μm thermal silica overlayer. Films were then spin coated at 5000 rpm to a thickness of approximately 1 μm. The entire structure was the baked on a regulated hotplate at temperatures and times depending on film thickness. Prism coupling was used to launch the TE_0 (fundamental) mode of the 488 nm line of a cw Ar ion laser into the asymmetric slab waveguide. The guided wave appears as a yellow fluorescent streak growing at a rate of ~2.5 cm/min through the film slab. With our prism coupling setup we can counter-propagate guided waves and generate complex surface patterns based on primitive device constructs like y-junctions, splitters, crosses and 2D square, rectangular and diamond grids. Partial or complete etching was conducted by immersing coated substrates in isopropanol.

3 RESULTS AND DISCUSSION

3.1 Guided Wave Self-Inscription with Periodic Patterning

In the guided wave self-inscription event, a transverse electric ($TE_{m=0}$) wave having no nodes in the electric field intensity (m=0) causes a permanent refractive index change by crosslinking the photosensitized hybrid glass. The progress of the guided wave through the slab is retarded by absorption by the photoinitiator. Its decomposition (photobleaching) causes radical initiated polymerization of the methacrylate moieties in the film. The formation of C-C single bond crosslinks densifies the matrix in the path of the optical beam. Accordingly, the local refractive index, $\boldsymbol{n}_{loc}$, increases. The propagating wave senses $\boldsymbol{n}_{loc}$ and effectively “writes” a positive lens for itself while it bleaches the initiator. This leads to self-focusing (narrowing) of the guided wave and inscription of a hybrid glass optical waveguide (Figure 1).

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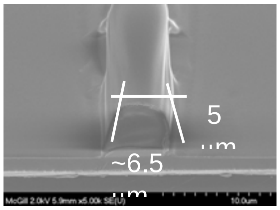

Figure 1: Self-inscribed waveguide attached to a silica-on-silicon wafer substrate. The "fiber-on-a-chip" was revealed by wet-etching the surrounding hybrid glass matrix with isopropanol. Waveguides have been fabricated up to 6 cm in length.

In an "optical read" experiment [6], we have used real time polarized Raman waveguide scattering during self-inscription to follow the decrease in intensity of vibrational modes associated with in-plane methylene C-H deformation (1408 cm^{-1}) and C=C stretching (1638 cm^{-1}) as the olefin groups are consumed in the process. The Raman experiment also shows that densification proceeds with additional Si-O-Si network bond formation. For films supporting a limited number of modes and having a sufficiently high threshold for photosensitivity, an unusual effect is observed. After 90 min of writing, a periodic pattern appears which is visible as light and dark bands on the waveguide as shown in Fig 2a. Complete etching liberated a standing waveguide about 60 mm long which has uniformly narrowed by a factor of ~20 in the transverse direction to about 11± 1μm. An 8 μm period corrugation in Fig 2b was imaged by atomic force microscopy. The amplitude of these features is ~ 0.3 μm. As anticipated by the theory of Snyder et al. [7], the increased refractive index in the mature self-written waveguide means that it can support additional modes, where the even order species can optically beat to modulate the density and stress in the waveguide. This is the first physical evidence of recording periodic patterning in a self-written waveguide.

3.2 Patterning Wrinkle Architectures by Self-Inscription

Patterning can be observed over several other length scales in our hybrid glass films. Spin-coating, syneresis and drying, place our films under equi-biaxial uniform compressive stress. They can therefore become unstable with respect to perturbations of a certain wavelength. These instabilities manifest themselves as wrinkle patterns in our films. Our interest is in controlling how these patterns evolve by self-inscribing dense features in the films. Figure3 shows the pattern that emerges when a waveguide is written and then partially wet-etched. Note that the writing process exhibits the phenomenon of filamentation (cf. Figure 2a): self-inscription is a thresholded event in which the guided wave can break up into rays that propagate parallel to the main structure. Most striking is the

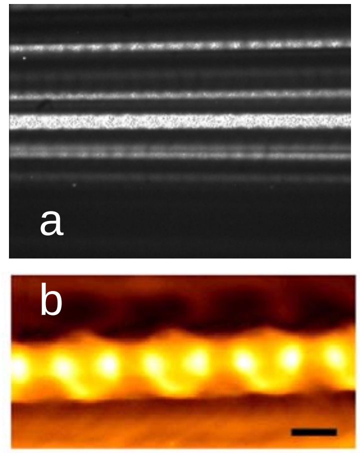

Figure 2: a) Filamentation observed during self-inscription (before wet etching) when the input power at the coupling prism exceeds 50 μW. The brightest band is the central waveguide, whereas the nearby bands result from filamentation. b) AFM image of physical corrugation in the central waveguide. The calibration bar is 8 μm.

orientation of the wrinkle pattern along the waveguide filament long axes, ie, in the direction of these rays. Some wrinkles are oriented orthogonal to the long axis rays. Visible also is some evidence of more nanoscale wrinkle

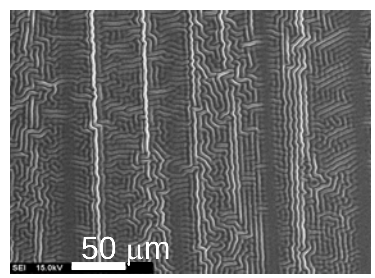

Figure 3**:** Nanoscale texture in photo-inscribed film that has been partially wet etched. Relief features are ~ 200 nm wide.

in some regions of the network glass. We also observe (not shown) wrinkle patterns along rays scattered at various angles away from the walls of the guide. We suggest that photo-inscription in the hybrid glass establishes anisotropic strain fields that manifest themselves as orientated patterns that evolve during etching. The wrinkles at this scale of observation have a characteristic wavelength of 200 nm.

Figure 4 shows the outcome of linking self-inscription to wrinkle formation at other length scales. Wrinkles are oriented perpendicular to the waveguides which are evident as the two thin horizontal lines. The wrinkles collide to form a chain-stitch pattern that shows a preference for

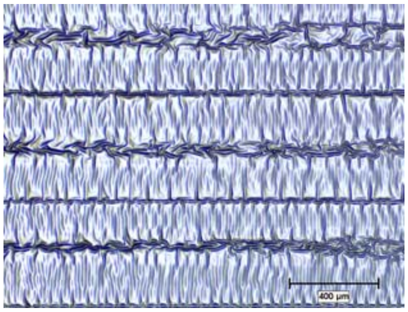

Figure 4: The waveguide tracks are the two thinnest horizontal lines that exhibit a slight chain-like texture. These thin lines are set between the wider chain-like horizontal texture. Wrinkles propagate vertically away from the sidewalls of the waveguides. They collide to produce the cable-stitched texture of the three wider horizontal lines. Bar is 400 μm.

roughly. uniaxial orientation. In Fig 5 a and b, we have selected from optical cross (diamond) and rectangular grids. These were created by writing waveguides in one direction and then in the other. They are also created by counter-propagating two beams simultaneously in the film. In 5a there is a periodic texture running the length of each waveguide. The wavelength is 15 μm. In the region of intersection we observe a tilting and distortion of the wave front of the wrinkles. Outside the waveguide, the network consists of larger cells (see 5b) with interconnected skeletal features. These patterns probably arise due to spontaneous contraction of the underlying gel phase network structure as internal stresses due to solvent evaporation and drying process are relieved. Cracking is avoided by wrinkling. In an equi-biaxial state of stress, there is no preferred orientation for the waves; nor is there a reason for the waves to form systematic patterns. This corresponds to the regions outside the x-crossed waveguides in Figure 5a. It is similar to the isotropic wavy morphology observed by Kwon for wrinkled sol-gel derived ZnO films [8].

The presence of the waveguide features interrupts this uniform state giving a strong orientation to the stress in the vicinity of the waveguide. In Figures 4 and 5b the waves are aligned perpendicular to the waveguide in the direction of the greater stress. The blank regions on both sides of the waveguides in Figure 5b are artifacts of the microscope optics. Close examination of these areas reveals that the period corrugation extends through them to the boundaries visible as the darker texture.

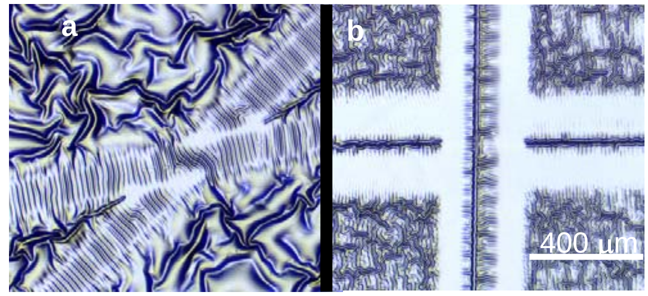

Figure 5: Wrinkle patterns after partial etching a) in the region of a self-inscribed optical cross and b) in a portion of a grid of orthogonal self-written waveguides.

The mechanical instabilities that lead to patterning that we observe are thought to be induced by a combination of effects. Before photoinscription and wet etching, the film is already in a state of internal (syneresis) stress, σ_z, with a z orientation imposed by the substrate [9]. Internal stresses that arise during the syneresis stage are sufficient to bend the film; however, prior to solvent exposure, the films have an rms roughness on the order of 2 nm. The coating film and Si substrate have different Young's moduli, coefficients of thermal expansion and swelling response to solvent. The mismatch between these properties can strain the film when immersed in a solvent. When immersed, the film can expand freely out of the plane of the film, but remains confined laterally. Iinstability in the surface can then propagate with a characteristic wavelength. Exposure of the film surface to the alcohol solvent leads to spontaneous uniform patterning, resembling that observed when organic polymer gel films are immersed in solvents [10].

The non-uniform patterning we observe around the waveguides probably involves significant anisotropy in the in-plane stress tensors σ_x and σ_y. The waveguide can be viewed as a rigid member to which the remaining film is attached as a flexible unit. If we assume y oriented along the long axis of the waveguide then a simple model [5] reveals that for $\sigma_y > \sigma_x$ the wave pattern should show maximum amplitude aligned parallel to the y-axis, as observed in Figure 4.

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