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We have investigated a new dry route for etching ZnO films at low temperatures (i.e., <200 °C). Using gaseous hfacH, thin films of ZnO were etched at temperatures as low as 130 °C and with rates as high as 317 nm/min at 350 °C. The overall qualitative behavior of the etch process was characterized by an Arrhenius plot, which indicated that at temperatures below 325 °C the etching was surface reaction rate limited, while at temperatures above 425 °C decomposition of the hfacH, adsorbed hfac*, or the metal-organic product Zn(hfac)₂ began to occur.

Experimental

Experiments were conducted using a hot-wall reactor system consisting of a flask containing hfacH, a 30 inch long (1 inch \approx 2.54 cm) 1 inch outer diameter quartz reactor tube, 1 inch inner diameter tube furnace, a liquid nitrogen trap, and pumping system (Fig. 4). The ZnO film was placed in the furnace tube while the leak valve on the hfacH reservoir was closed. The ZnO film was then heated to the desired temperature in vacuo (10⁻³ torr). The leak valve for the hfacH was then opened and the pressure of the reaction was maintained using a throttling valve on the pump and the leak valve on the hfacH flask. Reactions were run for 3 min at film temperatures from 130 °C to 500 °C and the total pressure was held constant at 20 torr. Sputtered thin films of ZnO (1 µm thick), obtained from Thin Film Technologies were characterized before and after etching by scanning electron microscopy (Hitachi S-800), X-ray diffraction (Siemens D5000; CuKα radiation source ($\lambda = 1.5406$)), and Auger electron spectroscopy. Thickness changes for the films were determined by weighing the wafer sections on a microbalance before and after etching.



Fig. 4. Hot-wall etching reactor.

AES data were collected with a cylindrical mirror analyzer (PHI 10-155), with an electron beam energy of 3 keV, at a base pressure of 10⁻⁹ torr. The Auger peaks of C (KLL) at 271 eV, O (KLL) at 510 eV, and Zn (LMM) at 994 eV were used for estimation of the composition and stoichiometry of the samples. An Ar⁺ ion gun with ion beam current intensity of 10 μ A/cm² at 1 keV beam energy and 4 × 10⁻⁵ torr base Ar⁺ pressure was applied for etching the surface impurities and for depth profiling the films.

Estimation of the elemental composition by AES was based on the experimental sensitivity factors. Experimental sensitivity factors were obtained from Auger spectra of standard stoichiometric samples of ZnO (i.e., thin films of ZnO deposited by sputtering and ZnO powder (Aldrich)). At a fixed sensitivity factor of oxygen $S_{\rm O} = 0.5$ the stoichiometric samples yielded the following sensitivity factors for the above mentioned peaks; $S_{\rm C} = 0.2$, $S_{\rm Zn} = 0.53$. This approach proved more accurate compared to application of handbook-derived sensitivity factors.

Since etching of thin films did not generate sufficient material for elemental analysis, ZnO powder was also reacted with hfacH. The solid reaction products that condensed on the cooler section of the furnace tube were collected and determined via elemental analysis to be $Zn(hfac)_2$.

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Photoinscription of Surface Relief Gratings on Azo-Hybrid Gels

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It is now well known that a high birefringence (>0.01) can be created in materials containing azo dyes via the photo-excitation of azobenzene groups by polarized light. The mechanism involves successive *trans–cis* photoisomerization and thermal *cis–trans* relaxation, leading to the alignment of azo groups in a direction perpendicular to the polarization of the incident light. The birefringence resulting from this alignment has been used in organic polymeric materials^[1,2] as well as in hybrid sol-gel^[3] matrices for the inscription of birefringence phase gratings and for other applications that need photoinduced motions of molecules. Moreover, an irreversible *trans–cis* isomerization has been

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photoinduced in rigid silica gels and the resulting large and stable refractive index change (0.1) allowed the inscription of refractive index gratings.^[3] However, volume phase gratings thus inscribed in films a few micrometers thick exhibited weak diffraction efficiencies (<5 %).

In such thin films and in Raman–Nath diffraction regimes, surface relief gratings show much higher theoretical diffraction efficiencies (30–40 %) for modulations of a few hundred nanometers. Such surface gratings could then be considered for many applications, such as holographic storage, optical filters, and resonant couplers.^[4] In fact, these high diffraction efficiencies have recently been reported by several groups, who used the photoisomerization mechanism of azo dyes to write surface gratings in acrylate and epoxy polymers.^[5–7] This required the employment of low molecular weight polymers (<30 000), allowing mass transport and surface deformation induced by the photoisomerization process.

No surface grating has been observed so far in silica gels prepared by the hydrolysis–condensation of alkoxide precursors. This is probably owing to the usual high rigidity of the sol-gel matrix caused by the partial or entire achievement of inorganic polymerization.

This paper reports the way to writing stable surface relief gratings having high modulation depth ($\geq 0.7 \mu m$) on a 1.3 μm thick hybrid film containing azo side groups. Thin films were prepared by the sol-gel technique using modified alkylalkoxysilane-type precursors. The gratings were obtained immediately after the gel film was spin-coated onto the glass substrate. In this state, the condensation degree is low enough to have a weakly crosslinked network, allowing volume and surface deformations in the film to be photoinduced by the photoisomerization of azobenzene molecules. This contrasts with the rigid condensed state obtained after heating the sample for 24 h at 100 °C on which no surface relief grating could be photoinscribed.

Hybrid films containing azo side groups were synthesized from silane-modified monomers previously developed for the preparation of photorefractive materials.^[8] Coating solutions were obtained from copolymerization of modified silane monomers with tetraethoxysilane (TEOS), leading to the silica-based backbone presented in Figure 1. Films of about 1 µm in thickness were fabricated by spin-coating onto glass substrates for laser irradiation and on single crystalline silicon substrates for Fourier transform infrared (FTIR) measurements. Concerning recording IR spectra, we used p-polarized IR light at oblique incidence (Brewsters angle = 60°) to avoid interference fringes on the transmission spectra of the films due to multiple reflections in the hybrid film.^[9] The spectral consequences of the condensation of silanols Si-OH into siloxane Si-O-Si groups (Fig. 2) are revealed through the decrease of the Si-O(H) and (Si)O-H stretching modes at 920 and 3340 cm⁻¹, respectively, and the increase of the Si-O-Si asymmetric stretching modes between 1030 and 1150 cm⁻¹. The degree of condensation of the thin film could easily be controlled



Fig. 1. Schematic representation of the hybrid network containing azo side groups (R = $-(CH_2)_3$ -NH-CO-, R' = $-(CH_2)_2$ -O-CO-NH- $(CH_2)_3$ -). The presence of the large carbazole units reduces the degree of crosslinking of the gel network.



Fig. 2. IR spectra of hybrid thin films deposited on a Si substrate, illustrating the condensation of silanol into siloxane groups during the drying-heating process. "t = 0" refers to the spectrum recorded just after the film was spin-coated The inset shows the progressive decrease of the intensity for the silanol IR band at 920 cm⁻¹.

by the drying-heating process, as shown by the temperature dependence of the IR band intensity at 920 cm^{-1} .

The surface gratings were written with an interference pattern created from coherent laser light at a wavelength located inside the absorption band of the material. The laser beam issued from a continuous wave Ar⁺ laser (514 nm) was divided into two p-polarized beams of equal intensity (6.5 mW), which were superposed onto the sample on the same spot (2 mm in diameter). The angle between the two beams was equal to 16°, leading to a grating period of 1.85 µm. The energy density of the incident writing beams was low enough to avoid the photobleaching process that was previously reported in silica gels.^[3,10] The evolution of the optically induced grating was probed by an unpolarized 670 nm laser diode. At this wavelength, the absorption of the film was sufficiently low so that the probe beam did not disturb the formation of the grating.

The efficiency of the *n*th diffracted order was measured by dividing the intensity of the *n*th diffracted order by the intensity of the incident probe beam. In this experimental configuration, three different diffracted orders were observed. Figure 3a shows the evolution of the first diffracted order as a function of time. The diffraction efficiency reaches a maximum value of about 33 % after 350 s, corresponding to a recording energy density of 1.4 J/mm². Such a high diffraction efficiency cannot be obtained with a birefringent volume grating and has been found to be due to a modulation of the thickness of the film.



Fig. 3. a) Evolution of the diffraction efficiency of the first diffracted order as a function of the time. b) Inscription of stable gratings with different diffraction efficiencies. The recording beams were switched off at different times (40, 80, and 100 s from bottom to top).

Figure 4a presents the surface profile observed by scanning electron microscopy (SEM), revealing a regular surface relief grating similar to the light intensity pattern. The modulation depth was estimated to be about 0.7 μ m. The shape of the profile is not perfectly sinusoidal. This result had not been explained yet, but we believe that the photo-induced thickness deformation response is not linear versus the recording energy. For a lower recording energy density of 0.6 J/mm², the thickness profile was found to be perfectly sinusoidal, as illustrated in Figure 4b.

If the writing beams at t = 40, 80, or 100 s were switched off, we could observe stable gratings, showing different diffraction efficiencies in the first order (see Fig. 3b) and thus different modulation depths varying between 0.1 and 0.7 µm. Actually, whenever we switched off the writing beams, the gratings remained definitely stable. Thus, we can easily control the depth of the profile by controlling the incident energy of the writing beams. Moreover, the gratings can be erased if the sample is heated above 100 °C. However, the gratings cannot be written again after the heating treatment. This is explained by an achievement of the sol-gel condensation, which drastically increases the rigidity of the matrix.

For different intensities of the writing beams, in the range between 7 and 26 mW, we note that the diffraction efficiency was found to be only dependent on the energy. Such a result can be accounted for by the proportionality of the photoisomerization rate to the recording intensity and it also excludes thermal effects.^[11]

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Fig. 4. SEM images of the surface profile of sol-gel films after grating inscription: a) with a recording energy density of 1.4 J/mm², b) with a recording energy density of 0.6 J/mm², c) surface profile of two gratings inscribed after a sample rotation of 90° .

We also analyzed the response of the film with different polarizations of the writing beams. In these experiments, we found that the highest diffraction efficiency (40 %) was observed when the film was exposed to p-polarized writing beams. This result has been previously reported by Barret et al.^[12] and Kim et al.^[11] in organic polymers. These authors claimed that intensity and polarization gradients are necessary to inscribe significant surface gratings. In this case of p-polarization recording, the simultaneous presence of an intensity gradient and a non-zero component of the p-polarization along this gradient, i.e., perpendicular to the grating grooves, leads to higher modulation relief.

When writing beams are both s-polarized or perpendicularly polarized (polarization recording), we only observed a weak diffraction efficiency (≈ 0.4 %). In the case of two parallel polarizations of writing beams (s-polarization) a high intensity gradient is inefficient for writing a surface grating



because the electric field is parallel to the grating grooves. However, a birefringence volume grating can be induced with a weak diffraction efficiency expressed as $\eta = (\pi \Delta n h_0 / \lambda)^2$. Assuming $h_0 = 1.3 \,\mu\text{m}$, we have $\Delta n \approx 0.01$, which is consistent with previous experiments on azo-silica thin films.^[3] In the case of polarization recording, no intensity gradient exists but the polarization gradient can also create a birefringence grating.

This polarization dependence of the surface grating definitely excludes thermal effects and clearly suggests that a translation motion of the dye molecules is the main step of the surface deformation (mass transport). This translation probably occurs via the photoisomerization process: the trans-cis photoconversion increases the free volume of the dyes, allowing their motion along the polarization direction during the cis-trans back-conversion. This process is repeated until the dyes are oriented perpendicularly to the p-polarization of the excited light. This molecular translation mechanism had been proposed in organic polymer systems containing azo dyes.^[13] Moreover, the crucial role played by the photoisomerization in the thickness deformation process was further confirmed by experiments realized on thin gel films in which dyes that did not exhibit photoisomerization were incorporated. In these samples no surface grating could be inscribed.

Finally, the possibility of producing multiple grating azogel films is illustrated in Figure 4c. Two perpendicular gratings were inscribed on the same spot by rotating the sample 90° between two successive inscriptions. This double grating exhibited the same behavior as single gratings: no relaxation under uniform illumination and erasure by heating the sample above $100 \,^{\circ}$ C. This result led us to believe that other kind of motifs, such as blazed gratings, could be inscribed on azo-gel films.

In conclusion, very stable surface gratings can be inscribed in azo-hybrid thin films prepared by the sol-gel method in appropriate optical and material configurations. This firstly requires a weakly crosslinked network in the gel whose degree of condensation can easily be controlled by heat treatment and also by the functionality of the sol-gel precursor. Concerning this latter point, further improvements of the thin film are expected by using bifunctional precursors. The second requirement to obtain high modulation depths is the simultaneous presence of an intensity gradient and a non-zero component of the resultant optical field along this gradient.

Under these conditions, high diffraction efficiencies in three different orders can be obtained, depending on the illumination time. Explanations for the mass transport mechanism have been proposed that consider the photoisomerization process. Complementary experiments are in progress in order to understand the nonlinear behavior of the growth of the thickness profile versus recording energies. [1] T. Todorov, L. Nikolova, N. Tomova, Appl. Opt. 1984, 23, 4309.

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Solid-State Amplified Spontaneous Emission in Some Spiro-Type Molecules: A New Concept for the Design of Solid-State Lasing Molecules**

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The technological prospects of being able to construct electrically pumped lasers based on molecular or polymeric solids as the gain media has recently generated considerable interest in the stimulated emission and lasing properties of these materials. Recently, it was shown that the photoluminescence (PL) of various conjugated polymers, prepared by spin-coating on glass substrates, exhibits spectral narrowing upon irradiating with pulsed radiation of appropriate wavelength and of sufficient energy.^[1-8] These polymer materials are suitable as the gain media in solid-

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