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Unraveling the nucleation and growth of spontaneous surface relief gratings

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ABSTRACT

Nucleation and growth of spontaneous surface relief gratings (SSRGs) on a Disperse Red 1 (DR1) glass-forming derivative were investigated. No interference pattern is applied and surface patterning is induced using single-beam irradiation: the gratings are self-organized. Grating growth is assumed to initiate from an interference pattern formed between the incident light beam and waves scattered at grazing angle by surface defects. However, the mechanism is not yet fully understood and there is not a comprehensive explanation of the structure formation process. Herein, the grating formation procedure is studied by monitoring the surface topology of thin films exposed to one writing beam for various periods of time, under both linear and circular polarizations, using AFM. Even in the absence of surface defects on the initial film, irradiation produces light-induced surface defects due to the reorientation and mass movement of the azo molecules. These defects act as seeds for SSRG around which gratings gradually emerge and propagate throughout the sample. To consolidate this hypothesis, the formation of gratings was studied on samples with controlled surface roughness. Pore-shaped defects do not diffract light on top of the sample, and thus have no impact on SSRG growth, while for hill-shaped defects, growth rate decreases sharply with defect sizes larger than the writing beam wavelength. Two other analogous glass-forming azobenzene derivatives were studied, and in all cases, SSRG formation was correlated with the induction of birefringence in the early stages of the irradiation.

1. Introduction

All-optical surface patterning of azobenzene derivatives has attracted a lot of attention in the literature in the past decade, both at the fundamental and applied levels. Materials containing azobenzene chromophores exhibit a range of photoresponsive properties, which all originate from their reversible photochemical *cis-trans* isomerization [1]. While the photo-reorientation of azobenzene moieties induces birefringence, repeated *cis-trans* isomerization cycles caused by extended exposure to light results in mass movement in the material, eventually leading to macroscopic surface deformations. For example, irradiating a thin film of azobenzene-containing material with two laser beams forming an interference pattern induces a surface deformation where parallel grooves with well-defined depth and width form on the surface. While these surface relief gratings (SRG) have been widely studied, the fundamentals of their formation are not yet completely understood. It is well-known that SRG formation strongly depends on both intensity and polarization gradient [2], and more recently it has been shown that the surface deformation also depends on the phase and wavefront of the inscribing beams [3]. Photo-fluidity due

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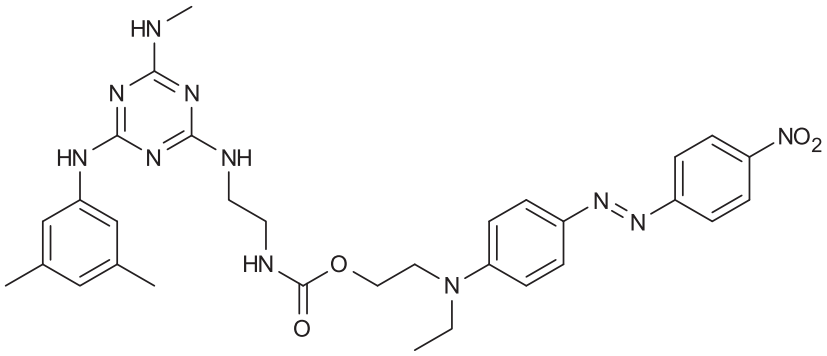
to isomerization [4] and π-shift of SRG relative to the interference pattern [5] under moderate power irradiation (a few hundred mW/cm^2) are some of the main observed features underlying light-driven mass transfer. Several models have been proposed to explain the driving force responsible for the macroscopic mass transport of azo moieties on the micrometer scale at temperatures well below the glass transition temperature. For example, the pressure model [6], one of the first proposed models, attributes SRG formation to the change in volume occupied with azo isomers during isomerization. The mean field theory [7] model proposes that SRG formation is due to the anisotropy of molecular interactions. The field gradient force model [8] postulates that SRG originate from a dependence towards the polarization and intensity gradients, in a fashion similar to optical tweezers. The diffusion model [9] attributes SRGs to an inchworm-like motion of the azo moieties during *cis-trans* isomerization and reorientation. The random walk model [10], which is strictly equivalent to the latter model, confirmed the perspective of anisotropic light-driven molecular diffusion. Each model explains distinct aspects of SRG formation, but owing to the particular nature of the materials involved, none of them could provide a fully comprehensive explanation of all observed aspects of SRG formation.

More recently, it was demonstrated that SRG can be inscribed under uniform single-beam irradiation [11,12]. No external interference pattern is applied, and thus the structures form spontaneously. A common proposed approach to these spontaneous surface relief gratings (SSRG) formation is the stimulated Wood anomaly model [13], in which a diffraction order is coupled into the sample. The incident beam is then scattered by tiny surface defects, leading to interferences between the scattered beams at the grazing angle and the incident beam. This self-organized interference pattern then initiates SSRG formation. As the grating grows, more light is trapped into the sample and couples into counter-propagating guided modes, which interfere with the incident beam, thereby causing the SSRGs to grow over the irradiated area [14].

Molecular architecture has a predominant impact on reorientation and mass movement of an azo compound. Typically, SSRG growth is reported on azo polymers in which chain length and the nature of binding would determine the shape and the growth rate of SSRG [15–17]. To mitigate the impact of the rheological effects of polymers, small molecules are an appealing alternative [18]. Furthermore, small molecules yield a more homogeneous behavior, not only between different samples, but also within a given sample because all molecules are identical [19]. While most azobenzene derivatives readily crystallize, thereby limiting their usefulness for thin film applications, a glass-forming material incorporating the Disperse Red 1 chromophore (thereafter referred to as DR1-glass)[1] previously synthesized in our group has been shown to form high-quality amorphous thin films [19].



DR1-glass

In an earlier study, growth and erasure of SSRGs on DR1-glass were investigated [20]. It was proven that SSRG formation in azo-materials is exclusively an optical process and light polarization was the main factor determining the orientation of the structures. Under linear polarization, SSRGs form along two directions over a patchwork of domains, while circular polarization yields a circular crossed grating. SSRG formation follows hole burning saturation effect. The rate of grating growth increases as a function of laser intensity, but the gratings saturate at the same modulation amplitude independently of the laser intensity. Entanglement of light coupling in the SSRG growth process was confirmed by observing directional back-scattered light. It has been evidenced that SSRG grow due to interferences between the incident light and beams scattered by the sample. Nevertheless, our comprehension of how SSRG originate from surface defects, grow, and organize into well-defined domains remains inadequate.

SSRG formation takes place in three time-periods: nucleation, growth and saturation. Growth and saturation periods were previously modeled comprehensively using diffusion and coupled wave theory [14]. Herein, the nucleation and growth of SSRG on films of DR1-glass is studied using Atomic Force Microscopy (AFM). Samples with controlled surface roughness were prepared either using electric field corona poling on smooth thin films or during film deposition using various solvents, with the expectation that SSRG would grow at an even greater rate in these cases, because of the light scattering caused by the already present defects [21]. Birefringence was monitored in DR1-glass and two analogues with similar chromophores to establish a correlation between SSRG nucleation and the induction of birefringence in the early stages of irradiation. Our findings have allowed to clarify the mechanism by which SSRG nucleate and grow from irradiation with a single beam.

2. Experimental

2.1. Thin film deposition

Smooth thin films of DR1-glass were prepared on glass

[1] Marvin was used for drawing, displaying and characterizing chemical structures, substructures and reactions, Marvin 15.1.12, 2015, ChemAxon (www.chemaxon.com).