

報告番号	※	第	号
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## 主論文の要旨

論文題目  
**STUDY ON THE PHOTOINDUCED MORPHOLOGICAL CHANGES IN AZOBENZENE-CONTAINING LIQUID CRYSTALLINE THIN FILMS**  
 (アゾベンゼンを含む液晶薄膜における光誘起形態変化に関する研究)

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### 論文内容の要旨

This research is focusing on the photoinduced mass migration of thin films made from azobenzene derivatives.

#### Chapter 1. General introduction

Chapter 1 of my thesis is a general introduction on surface relief gratings (SRG). As a mass migration of polymer chains over micro-meter scale, interference laser induced SRG of azobenzene materials (**Figure 1**) has drew many attentions from researchers ever since 1995.

In this respect, our research, the use of soft liquid crystalline azobenzene polymers allowed remarkable enhancements in the SRG formation upon pattern irradiation. Typically, based on the increase of sensitivity, we were able to use a Xe-Hg lamp to replace the laser lamp for the inscription of SRG.

In experiment, we used photo mask patterned UV or visible beam to inscribe SRG on azobenzene containing liquid crystalline films. The process is named as highly sensitive SRG inscription.

However, as a disadvantage, due to the high sensitivity, the inscribed SRG are relatively easy to be erased. Either to anneal the film above  $T_i$ , or to expose the whole film to homogeneous UV light can simply wipe off the inscribed SRG pattern.

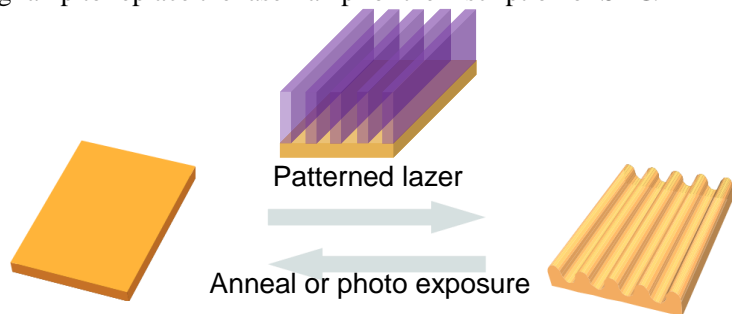


Figure 1. SRG inscription by patterned lazer

#### Chapter 2. Fixation of SRG pattern

Hence, in Chapter 2, two methods to fix the SRG pattern for long term storage and high temperature stability were compared. These two methods are chemical-crosslinking and photo-crosslinking method.

In handling, the chemical fixation is a wet process, which requires for a steam environment of reactants. In addition, it also needs 6 hours' reacting time.

In contrast, by involving cinnamate unit into the polymer as another sidechain, the photo-crosslinking method was carried out (**Figure 2**), which turned out to be a simple dry procedure. And it worked efficiently in 15 minutes.

In operation, the experiment went through a UV-Vis.-UV process. First UV was a homogenous 365 nm UV, to prearrange the azobenzene mesogens for a cis-rich state. Later, this isomerized cis-rich film was irradiated to pattern beam of 436 nm for the formation of SRG patterns. When the SRG were inscribed, it was exposed to homogenous UV of 313 nm for 15 minutes for photo-crosslinking. As a result, the fixed SRG became insoluble in THF and showed a strong stability to high temperature.

### Chapter 3. Photoinduced dewetting

When used dendritic azobenzene derivative D6 as the material, some extraordinary SRG patterns were observed accidentally. To discover the secret behind that phenomenon, more experiments were carried out, which actually first lead to the research in Chapter 3, photoinduced dewetting for D6 (Figure 3).

If the D6 film is no more than 100 nm thick, it would possibly dewet when exposed to homogenous UV. The mechanism is explained below.

At room temperature, Cis-isomerized dendrimer is easy to slide and flow, which leads the packing density of azobenzene group different from that of trans-isomerized dendrimer. With UV irradiation, the initial flat film ruptures either spontaneously or under the influence of extrinsic defects, such as air borne particles, resulting in the formation of holes and bumps at random sites. The holes and bumps then grow laterally and coalesce resulting in polymer ridges which disintegrate to spherical droplets. Dewetting therefore tends to minimize the interface between the film and its substrate (domain area).

In addition, it was studied that the influence of photon dose and film thickness on this morphological change caused by dewetting. The results will be shown clearly by AFM pictures and data plots.

### Chapter 4. Formation of hierarchical SRG

Based on the research in photoinduced dewetting of D6, this research moved forward to Chapter 4, a hybrid of mass migration and surface dewetting, which leads to a new method for the formation of hierarchical SRG patterns (Figure 4).

The AFM pictures showed that there are mainly 3 types of such hierarchical morphologies. One is a single column domain structure, like the back of a crocodile. Another one is a double column domain. The other one is a multi-needle shaped brush structure. All of them can be obtained under the same photon dose and same photo mask pattern. The only difference lied in the thickness of their initial film. In experiment, all of the films are just irradiated to the same stripe pattern UV beam at room temperature, displayed by a plot on the relationship between film thickness and domain numbers in the SRG pattern. The result perfectly reflected the hybrid of photoinduced SRG and photoinduced dewetting mechanism.

### Chapter 5 Conclusion

In summary, this whole work concentrated on the change of the mobility of SRG patterns. By applying photo-crosslink, the mobility was decreased and the pattern could be fixed. By involving photoinduced dewetting, the mobility was increased and many unusual hierarchical SRG patterns were formed.

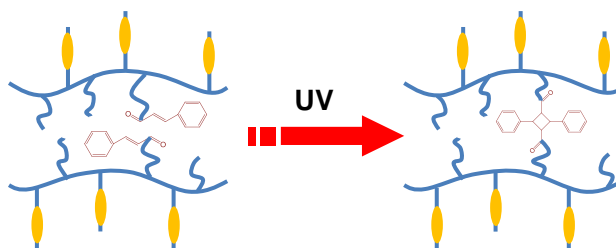


Figure 2. Photo-crosslinking of a cinnamate contained azobenzene derivative.

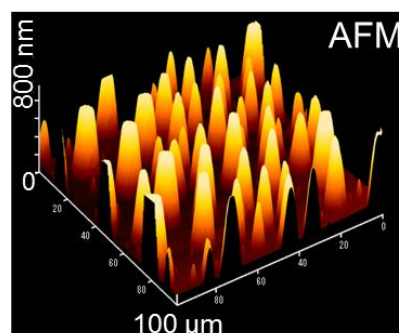


Figure 3. A typical photoinduced dewetting morphology of D6

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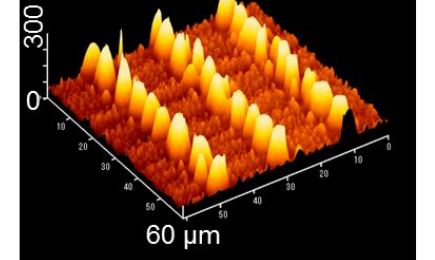


Figure 4. A typical hierarchical SRG pattern