In-Process Measurement of Resin’s Curing Degree in Micro-Stereolithography Using Internal Reflection at Critical angle

D Kong¹, M Michihata²#, K Takamasu³ and S Takahashi²
¹ Department of Advanced Interdisciplinary Studies, the Univ. of Tokyo, Japan
² Research Center for Advanced Science and Technology, the Univ. of Tokyo, Japan
³ Department of Precision Engineering, the Univ. of Tokyo, Japan

# E-mail: michihata@nanolab.t.u-tokyo.ac.jp

Abstract. Micro-stereolithography has been proposed to fabricate resin in arbitrary structures using optical energy. This technique is essentially based on the polymerization feature of photosensitive resin. Once original resin is cured by light in a specific wavelength range, polymerization reaction will start and resin’s state will turn from liquid to solid. The curing degree of resin determines the solidification degree of products and also largely impacts final fabrication qualities. Therefore, an in-process measurement that monitors states of resin and provides the possibility of feedback in a fabrication system shows a great significance. However, so far there are seldom investigations on curing degree in micro-stereolithography. In our research, we raised a measurement method that utilizes the variation of resin’s refractive index in polymerization and the high refractive-index sensitivity of internal reflection at the critical angle. The feasibility of this method has been confirmed by using simulations based on the rigorous coupled-wave analysis (RCWA) method. In our experiment work, curing process of resin has been successfully monitored and recorded. The formation and variation of cured resin has been directly observed. The distribution of refractive index was calculated according to the grey value of reflection distribution. Our research will be a start point of in-process measurement in micro-stereolithography. Fabrication systems with in-process measurement functions will be wildly investigated in the future.

1. Introduction
Micro-stereolithography, using luminous energy to polymerize photosensitive resin, is one of the most powerful ways to fabricate complex polymeric-based micro structures layer-by-layer [1 2]. Since resin cured by light turns its state from liquid to solid, each layer of resin will be solidified in same pattern with projection. Three dimensional structures can be obtained by stacking each layer together. One of the inevitable problem of micro-stereolithography is that the curing (polymerization) process of resin is extremely sensitive and influenced by many environment factors [3]. Since excessive, inadequate or uneven curing of resin directly leads to fabrication failures, an in-process measurement on curing degree that grasps the real-time states of resin can make remarkable benefits to fabrication. Besides, for further understanding the formation process of cured resin, in-process measurement as a power tools to study curing of resin shows great significance and value. However, so far there are seldom investigations related with in-process measurement in micro-stereolithography. Although there are some research in organic chemistry field utilized FTIR (Fourier transform infrared spectroscopy), differential scanning calorimetry (DSC) and Raman spectroscopy [4] to dynamically monitor the
curing degree of resin. These methods are hard to obtain spatial information of cured resin and therefore, cannot meet the demands of measurement on distributions of curing degree. In our investigations, considering the requirements of spatial resolution, sampling speed and required operation space, a suitable measurement method has been proposed to meet the requirements of in-process measurement in micro-stereolithography.

2. Theoretical background
During curing process, not only the states but also the optical characteristic (refractive index) of resin change. Our measurement method just utilizes this variation on refractive index. In organic chemistry field, conversion degree of double carbon bond (C=C) in monomers has been used to evaluate the curing degree of polymer. In this research, since we directly measured the variation of refractive index of resin, the curing degree is based on the change value of resin’s refractive index. A larger variation of refractive index means a higher curing degree. The relationship between refractive index and conversion degree of has been proved in linear relation [5].

A schematic diagram of our measurement method is shown in Fig. 1 (a). Besides the exposure light for fabrication, another beam of light in a larger wavelength used as the measurement light was launched from the bottom of the resin. It is worth mentioning that photosensitive resin can only be cured by light in a certain wavelength range. Influence of the measurement light on curing process can be minimized by properly selecting the measurement light with a specific wavelength. In order to utilize the high sensitivity of total internal reflection in critical condition, the incident angle of the measurement beam is fixed at the critical angle of substrate and uncured resin. The mechanism of measurement method can be explained by model of internal reflection, as shown in the insert figure in Fig. 1 (a). It shows that light is launched from the bottom side through the high-refractive-index prism to the resin with a relatively low refractive index. Due to the variation of resin’s refractive index during curing process, light reflected from cured resin in various curing degree has different critical angle and reflectivity according to Fresnel’s equations:

\[
\theta_{\text{Critical}} = \arcsin\left(\frac{n_{\text{Resin}}}{n_{\text{Prism}}}\right) \quad (1)
\]

\[
R_p = \frac{n_{\text{Prism}} \cos \theta_R - n_{\text{Resin}} \cos \theta_R}{n_{\text{Prism}} \cos \theta_R + n_{\text{Resin}} \cos \theta_R} \quad (2)
\]

where \(\theta_R\) is the refractive angle and defined as \(\theta_R = \arcsin\left(\frac{n_R \sin \theta}{n_p}\right)\). Fig. 3 (b) shows the reflectivity as a function of the incident angle calculated from Eq. 2 when \(n_p = 1.78\) and \(n_R = 1.47\) and 1.51 representing uncured and cured resin, respectively. It is shown that the angular spectrum of reflectivity positively shifts after resin is cured. At the critical angle of the uncured resin, the reflectivity between the uncured and the cured resin differs greatly. Fig. 3 (b) shows the reflectivity drop in various incident angle when resin’s refractive index keeps increasing. As expected, reflectivity simultaneously decreases with the increase of refractive index. In addition, for a specific refractive range, exist optimal measure angles for different refractive range. In consideration of the experimental difficulty to change the incident angle during curing process (extremely fast reaction), the incident light should be fixed and 55.7 degree was used in our investigation.

![Fig 1](image-url)

Fig 1. Theoretical explanations. (a) Diagram of measurement method; (b) Reflectivity as a function of incident angle; (c) Reflectivity in an increasing refractive index.
3. Simulation

In order to acknowledge the near-field response when reflection is at the critical and confirm the reflectivity drop in the existence of lithography structure, a simulation has been done using the rigorous coupled-wave analysis (RCWA) method. Simulation diagram is shown in Fig. 2 (a). Calculation field was in a width of 200 μm and in a thickness of 50 μm. The width of cured resin was fixed at 50 μm. The refractive index of resin and prism was same with the theory value mentioned in above section. P-polarized light in a wavelength of 632.8 nm was launched from bottom in an incident angle of 55.7 degree. Fig. 2 (b) shows the intensity of field distribution (E-field). It can be seen that total internal reflection below cured resin was destroyed and an obviously low intensity field of reflection appeared. This proves our speculations that cured resin with a higher refractive index breaks total internal reflection at the critical angle and results in a reflection drop. In addition, a monitor of power flow was set below the interface to detect the reflection from resin. Reflection drops as an increasing refractive index of cured resin was plotted with theoretical value in Fig. 2 (c). It is noticeable that the tendency of the reflection drop was same with the theoretical reflectivity drop. However, there are some periodic oscillations in simulation results. These oscillations might be caused by the scattering at the two vertical boundaries of cured resin and it should be greatly weaken in experiment since there will be no such perfect boundary in real production. Moreover an imaging system in experiment will limit this influence at the boundary. In a word, according to simulation results, we proved that even in the existence of structure, the reflection will drop with the increasing of resin’s refractive index in the same tendency with their theoretical relation. It is feasible to calculate the refractive index distribution using reflection distribution.

![Fig 2. Simulation Verification. (a) Diagram of simulation model; (b) Intensity distribution of E-field; (c) Reflection drop in simulation and theoretical reflectivity drop as a function of refractive index of cured resin](image)

4. Experiment

Fig. 3 (a) depicts the optical configuration of verification experiment. The whole experiment system consists of two sections including fabrication and measurement. Two light sources in different wavelengths were used and light used for measurement does not lead resin to be cured. Fabrication light in wavelength of 405.8 nm was used. It was transmitted through an aperture and then narrowed to small beam width by lens system. A micro-sized light spot was projected into resin. In the measurement section, the polarized laser light in the wavelength of 638 nm was launched into the bottom of resin at an incident angle of 55.7 degree.

The curing process was monitored from the beginning of curing irradiation. The distribution of reflection was recorded at 0.00, 0.125, 0.50 and 2.00 s of exposure, as shown in Fig. 3(b). Since the cured resin shows a lower reflectivity than the uncured resin, the formation of polymerization was clearly shown in this figure. It is noteworthy that resin started polymerizing from a small point and gradually increased to a larger size. This is because the center of spot had largest intensity and resin in this region was at a higher reaction speed. The shape of cured resin approximated to be elliptical rather than perfect round. This is because the measurement light was oblique incidence (55.7 degree), and inclined projection results in the distortion of image. Fig. 3 (c) shows the gray value of cross-section...
Fig 3 Experimental Verification. (a) Experiment setup; (b) Measurement results of reflection distribution in various exposure time; (c) Cross-section of grey value; (d) Distribution of refractive index

marked by black dash line in Fig. 3 (b). It is obvious that not only the range of cured resin increased with exposure time but also the gray value in the exposure region kept dropping. This well agrees with the fact that the curing degree continually increases during exposure and higher curing degree shows higher refractive index and results in a lower reflectivity in our measurement system. The reflectivity drops were obtained by calculating their gray values in contrast with uncured resin (0.00 s exposure). The distribution of refractive index can be numerically obtained using their theoretical relation with the reflectivity drop. The final results of the refractive index distribution were shown in Fig. 3 (d). By applying image subtraction, uneven distribution of measurement light was deducted. However, the slight oscillation of system during experiment and the scattering generated by cured resin will still to some extent results in the unavoidable noise which directly causes the formation of small glitch on distribution. Since a higher refractive index of resin represents a higher curing degree, the distribution of curing degree can be clearly depicted in this figure. In the future, more detailed research will be done, including the relation between curing degree and refractive index and the in-process measurement of evanescent-wave based micro-stereolithography.

5. Conclusion
In summary, the reflectivity detection at the critical angle has been applied to achieve an in-process measurement on the cured resin in micro-stereolithography. The feasibility of our measurement method has been confirmed by simulation based on RCWA method. In verification experiment, the formation of cured resin has been in-process measured and the distribution of refractive index has been calculated according to the intensity of reflection. Our research will be a start point of in-process measurement in micro-stereolithography.

6. Reference
[1] Melchels F P, Feijen J, and Grijpma D W, 2010, Biomaterials, 31 24.
[2] Suzuki Y, Michihata M, Takamasu K. and Takahashi S, 2016 Procedia CIRP 42.
[3] Kaur M and Srivastava A K, 2002, Polymer Reviews 42 2.
[4] Chiou B S and Khan S A, 1997, Macromolecules, 30 23.
[5] Howard B, Wilson N D, Newman S M and Stansbury J W, 2010, biomaterialia, 6 6.