In-process Measurement of Gradient Boundary of Resin in Evanescent-wave-based Nano-stereolithography using Reflection Interference near Critical Angle

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Evanescent-wave-based nano-stereolithography, which uses the ultra-thin field distribution of evanescent wave to solidify photosensitive resin, provides a sub-micrometer vertical resolution of each layer. In fabrication process, cured resin (solid state) is submerged in uncured resin (liquid state). The interfaces between the cured and the uncured resin are made up of half-cured resin in a state of the uncompleted polymerization. Due to the gradient boundary directly determines the thickness of each fabrication layer and greatly influences the quality of products, it is of great significance to study the gradient boundary in the fabrication process. We proposed in-process measurement of gradient boundary using the reflection interference technique to monitor the formation of cured resin and investigate the gradient boundary. In this method, the variation of refractive index of resin in curing process has been utilized in the measurement. Measurement light was deduced near the critical angle to obtain a susceptible total internal reflection condition. In the verification experiment, a compact experiment system including fabrication and measurement sections has been developed. Two beams of light in the different wavelength have been delivered into the system as fabrication and measurement light, respectively. Resin exposed by increasing time has been measured by our proposed method at various incident angles near the critical angle. The refractive index distribution and the depth gradient boundary have been successfully measured. The results prove that the refractive index of cured resin is different in the position; the span of gradient is not constant as well. The maximum span of gradient boundary in center was measured in around 250 nm. This work that helps us clearly understand the curing process and the formation of the cured layer in EWNSL provides a research basis for further and detailed research in the nanoscale stereolithography.

Keywords: Photosensitive resin, Curing process, Nano-stereolithography, In-process measurement, Gradient boundary

1. Introduction

Micro-stereolithography, as one of the most powerful techniques of micro manufacturing, has been developed to produce micro-sized three-dimensional polymer structures layer-by-layer [1,2]. Evanescent-wave-based nano-stereolithography (EWNSL) utilizes evanescent wave instead of propagating light to provide optical energy [3,4]. It can produce each layer of resin in a sub-micrometer vertical resolution. Figure 1 illustrates the basic mechanism of EWNSL. In order to generate evanescent wave, base resin needs to be placed on a high-refractive-index substrate, and a beam of exposure light needs to be incident at an angle larger

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than the critical angle of total international reflection (TIR). Evanescent wave occurs at the interface of TIR. The intensity of optical field of evanescent wave exponentially decays with the distance to the interface between resin and substrate. Only resin closed to the substrate is exposed by sufficient optical energy. Therefore, by providing appropriate exposure time, it is possible to fabricate cured resin in a thickness of sub-micrometer. One of the biggest problems of EWNSL is the gradient boundary between the cured and uncured resin made by the half-cured resin. This is caused by the exponential intensity decay of evanescent wave. Resin exposed by light in different intensity has different curing speed. The gradient boundary is made by the half-cured resin in a state of uncompleted polymerization and nonuniform curing degree; its physical characteristic is a medium between liquid and solid like gel; it can be removed by solvent or further cured in the exposure condition [5,6]. The existence of half-cured resin largely influences the shape and quality of cured resin. In order to improve the fabrication accuracy and further study of the curing process in EWNSL, the investigation of the gradient boundary shows great significance. To date we only theoretically know the existence of gradient boundary; however, the gradient boundary in EWNSL has never been measured. The difficulties on this work are mainly on, first of all the spans of gradient boundary in EWNSL is in sub-micro scale. In addition, the gradient boundary has the gradient physical and chemical characteristic. The gradient boundary is not totally in the solid state and therefore, it can be easily disturbed by contacting measurement. Based on above demands and difficulties we proposed a measurement method utilizing the reflection interference at the critical angle of total internal reflection to measure the span of gradient boundary. In the following contents, principle and proposed method will be briefly explained. The feasibility of proposed method will be proved by experiments.

2. Theoretical background

2.1. Curing process of resin

Essentially, the curing process of photosensitive resin is one of the photo-polymerization reactions. The mechanism and the synthetic process are shown in Fig. 2. The uncured resin contains photosensitive initiators and monomers. The curing process starts from initiators break into reactive species when resin is exposed by light in a particular wavelength. The reactive species may be a free radical, cation or anion, determined by the type of initiator. In following reactions, the reactive species add to monomer molecules to form the excited monomer as new radical, cation or anion centers, as the case may be. The process is repeated as the monomer molecules are successfully connected to the continuously propagating reactive centers, which finally results in the generation of the high-molecular-weight polymers [5]. It is known that polymerization is a continual chemical reaction experience a certain duration time. Therefore, resin has intermediate states in curing process. The gradient boundary is made up of cured resin in such intermediate states.

2.2. Principle of measurement method

A schematic diagram of our measurement method is shown in Fig. 3 (a). Besides the exposure light for fabrication, another beam of light in a larger wavelength was launched from the bottom of the resin used as the measurement light. It is notable that photosensitive resin is cured by light in a certain wavelength range. Effects of the measurement light on curing process can be minimized by properly selecting a wavelength of the measurement light. The exposure light for fabrication is set around 65° (larger than the critical angle) which guarantees the formation condition of the total internal reflection and the evanescent field. The measurement beam is launched near the critical angle of the total internal reflection. Intensity distribution of the reflection is used to calculate the effective refractive index and the depth of the cured resin.

The in-process measurement on cured resin is based on three significant principles; increase of resin’s refractive index in the curing process, abrupt reflectivity change at the critical angle, and interference of reflection from bottom and top of the
cured resin. The increase of refractive index is an accompanying phenomenon in the curing process caused by a decrease of intermolecular distances. Increments of refractive index vary from types of resin and is normally in a range from 0.01 to 0.05 refractive index units (RIU). As the cured resin has larger refractive index than the uncured resin, when light incident from a high-refractive-index prism to resin, as shown in the insert figure of Fig 3(b), the critical angle defined by Eq. 1 becomes larger with refractive index increasing.

\[ \theta_c = \arcsin\left(\frac{n_R}{n_P}\right) \]  

(1)

where \( n_R \) and \( n_P \) is the refractive index of resin and prism, respectively. If measurement light is incident exactly at the critical angle of uncured resin, then the increase of refractive index in curing process will destroy the total internal reflection and results in a reflectivity drop, as shown in Fig. 3(b). Eq. 2 calculates the reflectivity in various incident angle.

\[ r_p = \frac{n_p \cos \theta_I - n_R \cos \theta_c}{n_p \cos \theta_c + n_R \cos \theta_I} \]  

(2)

When the total internal reflection does occur, light will be transmitted into the cured resin. Due to the measurement light is transmitted from the substrate to the uncured resin at the critical angle of these two mediums, the total internal reflection occurs when the light transmits to the uncured resin. Therefore, all the light that transmitted into cured resin will be reflected from the top end of the gradient boundary, as shown in Fig. 3(c). The reflection from the bottom side (\( R_1 \)) and the top side (\( R_2 \)) of resin generate the reflection interference. The reflection depth of \( R_2 \), that directly determines the length difference of optical path, largely influences the interference conditions and the reflection intensity. Therefore, is possible to obtain the reflection depth boundary by detecting the intensity of reflection. However, not only the depth of gradient boundary, but also the refractive index of the cured resin determines the length of optical path and therefore, the refractive index should be introduced into the calculation. It is known that the refractive index of resin increases with its curing degree, and resin’s curing degree decreases with its distance to the substrate due to the special field distribution of evanescent wave. It can be reasonably inferred that resin’s refractive index decreases with its distance to the substrate. However, the profile of refractive index is unknown and cannot be easily measured in fabrication process. In our investigations, based on the facts that the spans of gradient boundary are in sub-micrometer, we used the effective refractive index as an averaged refractive index of the cured resin. By this way, the prism, cured resin with gradient boundary, and uncured resin were treated as a three-layer-reflection model.

The effective refractive index of cured resin was
measured by changing the incident angle of measurement light and finding the critical angle of cured resin. The relationship between refractive index and critical angle is shown in Fig. 3 (d). Once the effective refractive index of cured resin is measured, the reflectivity from the bottom side of cured resin ($R_1$) can be calculated according to Eq. 2. The intensity of reflection contrast is calculated by Eq. 3.

$$I_{RII} = R_1^2 + (1 - R_1^2)R_2^2 + 2\sqrt{(1 - R_1^2)R_2^2}\cos(2\pi\Delta\phi + \frac{\pi}{2})$$ (3)

where $\Delta\phi$ is the phase difference generated by two different optical paths of $R_1$ and $R_2$. It can be expressed by the following equation,

$$\Delta\phi = \frac{d_s n_{eff}}{\lambda \cos(\theta_s)} - \frac{d_s \sin(\theta_i) \tan(\theta_i) n_r}{\lambda}$$ (4)

where $\theta_i$ is the incident angle and $\theta_r$ is the refractive angle calculated by Fresnel equations. Equations (3) and (4) show the relation between the reflection depth and the reflection intensity, which means it possible to obtain the value of reflection depth by measuring the reflection intensity in fabrication process. Figure 3 (c) shows the reflection intensity of interference as a function of reflection depth in various effective refractive index of cured resin. It is notable that only the first order reflection was counted in our calculation. This is because the refractive angle is very large and the top side of gradient boundary is not perfect flat in experiment, which results in the high order reflections propagate long distance in horizontal direction and be scattered easily.

3. Experimental

The whole experiment system is shown in Fig. 4. It includes fabrication and measurement two sections. Light in the wavelength of 405 and 638 nm were used as curing light and measurement light, respectively. As we mentioned above, resin can be cured by light in a particularly wavelength range. In this experiment, the operation of measurement does not impact on the fabrication as the wavelength of measurement light was out of the range of curing wavelength. In the fabrication section, exposure light was transmitted through the collimator and the polarizer. A shutter was used to control the exposure time. In order to fabricate cured resin in a smaller width seeking the real size of production in micro/nano-stereolithography, the beam width of curing light was focused by a lens before launching to prism. In the measurement section, the polarized laser light in a wavelength of 638 nm was delivered by the left arm of and reflected from the interface between resin and substrate. The reflected light propagated into the imaging section and was collected by the CMOS camera. In the experiments, two arms were respectively fixed on two rotation stages centered on the prism. The incident angle of fabrication light was fixed at 65 degree while the measurement light changing with the rotation stage is in various incident angles near the critical angle. Urethane-acrylate-based resin was used in the experiments. Its refractive index is 1.478 before curing. The prism was in the refractive index of 1.78. In order to avoid the damage on the prism, resin was put on the substrate that in the same refractive index with the prism.

4. Results and discussion

After exposure of light in intensity of 1 mW for one second, resin in the exposure filed was cured. Figure 5 shows the experiment and calculation results. The intensity distributions of reflection were measured when a beam of measurement light was incident at 55.10°, 56.19°, 56.24°, and 56.13°, as shown in Fig. 5 (a) to (d). The refractive index of cured resin that corresponds to the critical angle in these degrees are 1.478, 1.479, 1.480, and 1.481, respectively.

In Fig. 5 (a), incident angle of the measurement light is equal to the critical angle of uncured resin. In this case, the total internal reflection occurred at the boundary between the uncured resin and the substrate, which leads the highest intensity of reflected light from uncured resin; while cured resin in a relatively higher refractive index destroyed the condition total internal reflection; and therefore, cured resin with a relatively lower reflectivity was clearly distinguished with the uncured resin.

In Fig. 5 (b), the incident angle was increased to
The corresponding maximum refractive index of resin that meets the requirement of total internal reflection also increase from 1.478 to 1.479. In this case, cured resin whose effective refractive index smaller than 1.479 generates the total internal reflection. Therefore, in Fig. 5 (b), the bright area in cured resin means where resin’s effective refractive index smaller 1.479. The dashed line that marks the range of the total internal reflection in cured resin is the contour line of effective index 1.479.

By slightly changing the incident angle step-by-step, distribution of effective refractive index was measured. In this verification experiment, due to the oblique observation influence the quality of imaging (this problem can be solved by applying immersing objective lens to control incident and observation angle), the distribution of effective refractive index was only roughly measured. Figure 5 (e) shows the cross-section of effective refractive index marked by red line in Fig. 5 (a) measured various incident angles.

Figure 6 (f) shows the image of cured resin after washing and drying process measured by optical microscopy. It is notable that Fig. 5 (a) to (d) was measured in fabrication process when cured resin was still submerged in liquid resin and gradient boundary still existing; while Fig. 5 (f) was obtained after removing the liquid resin and the gradient boundary was destroyed before measurement.

The reflection depth, which calculated by using the effective refractive index and reflection distribution was plotted in Fig. 5 (g). The red point is the raw date. The dark solid line is the processed results. In order to know the span of gradient boundary, the thickness of cured resin after washing and drying process was measured AFM as shown by the blue line in Fig. 5 (g). In the proposed method, the measurement light was oblique incidence and inclined projection results in the distortion of image, while Fig. 5 (f) and AFM do not have this problem. In order to make subtraction to calculate the span of gradient boundary, the transverse span of AFM results was scaled down. In Fig. 5 (f), we can see the gradient boundary is slightly larger than the thickness of cured resin. The span of gradient boundary different with the position, and is a maximum value around 250 nm in the center of cured resin. In addition, comparing the shape and the tendency of reflection depth thickness of cured resin, we found that these two curves have better similarity in the left side. This is because the measurement light was only incident from one side (from the left, and from the top side in Fig. 5 (a) to (d)). The reflection distribution in another side might be influenced by the scattering and multi-reflection. This problem can also be solved by applying immersion objective lens in to experiment system, which can provide measurement at particular incident angle from various directions. According to above results, the gradient boundary of resin in EWNSL has been successfully measured. The problem is that it is hard to examine rightness.
and accuracy of our measurement method. In our future work, experiment setup will be improved by applying an immersion objective lens and a higher resolution imaging system in experiments, and some calibration works might be done.

5. Conclusion

In conclusion, we proposed a measurement method based on the reflection interference at the critical angle in EWSL to measure the gradient boundary. The variation of refractive index of resin in curing process was utilized in measurement. The distribution of effective refractive index of cured resin was measured by changing the incident angle of measurement light near the critical angle. This distribution was used to calculate the reflection depth, which represent the top surface of gradient boundary. After deducing the thickness of cured resin after washing process from the reflection depth, the span of gradient boundary was successfully calculated.

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