論 文 の 内 容 の 要 旨

論文題目　In-process Measurement in Micro/nano-Stereolithography Using Optical Response from Near-Substrate Resin with Refractive Index Variation
（光近接場領域における樹脂屈折率変化応答に基づくナノ光造形のインプロセス計測）

氏　　名　　孔　徳卿

In this research, in-process measurement of curing process of resin in the micro/nano-stereolithography has been proposed to be achieved by detecting the optical response from resin near substrate. Micro/nano- stereolithography is one of the most powerful ways to fabricate complex three-dimensional polymeric-based structures layer-by-layer using optical power. Photosensitive resin are used as the ingredient to generate polymer by the photo-polymerization (curing) process. In order to ensure quality and improve accuracy of products, the in-process measurement of the resin in the fabrication process shows great importance to the micro/nano-stereolithography.

The curing process of the resin is an essentially photo-polymerization process. After the initiators absorb optical energy and active the monomers in the resin, the curing degree of the resin continually increase with monomers breaking their carbon double bond and connecting with each other to develop polymer network. When the conversion degree of carbon double bond increase from zero to the maximal value, the physical state of resin gradually changes from liquid to gel and solid. The conversion degree of carbon double bond can provide an intuitive evaluation of the polymerization level of the resin; however, it is difficult to directly measure the conversion degree in the micro/nano-stereolithography. It is notable that the refractive index of the resin increases with the conversion degree in a linear relationship. Therefore it is possible to in-process measure the curing process by detecting the variation of refractive index of the resin using optical method. Based on this point, the strategy in this research is to measure optical response from the bottom of the resin.

In order to achieve the in-process measurement in micro/nano-stereolithography using the variation of refractive index and optical response, we proposed a measurement method based on measuring the optical response from near-substrate resin when measurement beam is incident at the critical angle of total internal reflection. By this way, in the curing process of resin, the increase of refractive index destroys the total reflection and results in the reflection drop. When cured layer is thin enough and near wavelength scale, the optical response is also largely affected by the thickness of cured resin as the reflection from top and bottom surface of cured resin develops the reflection-phase-contrast interference that is sensitive to the thickness of cured layer. Based on this principle, proposed method of in-process measurement is firstly applied in evanescent-wave-based nano-stereolithography (EWNSL) to measure the thickness of each cured layer. When cured layer is in a large thickness, measurement light in cured resin propagates away from the sides of cured resin because of the large refraction angle. In this case, the optical response is mainly determined by the refractive index of resin near substrate. Therefore, in conventional projection micro-stereolithography (MSL) this measurement method is applied to measure the refractive index distribution of resin near substrate and infer the distribution of curing degree. In the following paragraphs, the detailed investigation procedure of in-process measurement in EWNSL and conventional MSL is explained respectively.

In MSL, the near layer is directly fabricated on already-cured layer and therefore it is impossible to measure the thickness of each layer. In the other hand, due to exposure propagate deeply into resin, the scattering, diffraction and multi-reflection of exposure beam make lateral pattern distorted easily, therefore the conversion degree distribution of resin that provides not only the potential pattern but also the curing state of resin is an important parameters to be in-process measured. As a result, in MSL we used same method based on internal reflection at critical to in-process measure the conversion degree distribution of near-substrate resin. We did a verification experiment of this topic. In this experiment, the reflectivity from resin in exposure area dropped obviously. It is notable that in MSL the reflection is mainly determined by the reflectivity of the interface between high-refractive-index substrate and resin near the substrate. According to the Fresnel equation, the distribution of refractive index of resin near substrate can be calculated from the variation of reflection distribution. Furthermore, it is possible to further infer the conversion degree in curing process. In order to obtain the exact relation between refractive index and conversion degree, a measurement experiment was done. In this experiment, Raman spectroscopy was used to measure conversion degree by detecting the variation of absorption peak of carbon double bond; in the same time, the refractometer based on critical angle shift was applied to detect the refractive index. Same point of resin in an increasing exposure duration condition was measured by both methods. It is notable that, Raman spectroscopy as well as Fourier Transform Infrared Spectroscopy (FTIR) are two technique widely used on the measurement of conversion degree; however, both require long measure time or high intensity irradiation that will damage or burn the cured resin. That is why we take the strategy that uses refractive as an indirect parameter. By the usage of experimental relationship with refractive index, the conversion degree was in-process measured. The results show that the range of cured resin enlarged and the maximum conversion degree in the center of exposure area increased from 0 to around 3%, 22% and 53%, in 0.125, 0.50 and 2.00 second exposure, respectively. This proves that our method can directly obtain the dynamical shape of the bottom of cured resin and further gain the curing condition of whole resin layer by calculating the distribution of conversion degree.

In EWNSL, in order to confirm the feasibility of proposed method, the verification experiment has been done at first. In this experiment, measurement light in wavelength of 632.8 nm was incident into resin from high refractive-index substrate in the critical angle, the reflection distribution from bottom of resin is detected by an optical system with CMOS camera. Another beam of light in a wavelength of 405 nm was incident in an angle much larger than the critical angle to provide exposure energy in a form of evanescent wave. Experiment results showed that there is an obvious intensity drop of the reflection from the corresponding area exposed by fabrication beam. In order to achieve the in-process measurement of thickness of cured resin, the relation between the reflectivity and the thickness must be known; however, it is hard to get a theoretical relationship, as the thickness of cured resin is not only determined by the curing process but also the etching process that removes the uncured and a part of half-cured resin in a low conversion degree. The in-process measurement is before the etching process, which means our in-process measurement work is actually to predict the potential thickness of cured resin. Based on above fact, we did an experiment to measure this relationship rather than make mathematical derivation. In this experiment, reflectivity in various exposure durations has been measured, and corresponding thicknesses of the resin were measured by AFM after the washing and drying process. We found that, when the thickness of cured resin increase from 0 to 400 nm, the reflectivity drop 54 percent in an approximate linear relationship with thickness. In order to confirm the repeatability of proposed method, the in-process measurement was applied to study the curing process when resin were continuously and discontinuously exposed. Results showed that, even in same total exposure time, resin had a larger potential thickness when it was cured by continues exposure time. The potential thicknesses were calculated from the reflectivity using experimental linear relationship. By comparing potential thickness in in-process measurement and the absolute thickness measured by AFM, we found that potential thicknesses were well agree with the absolute thicknesses. Even though some detail part was lost in the in-process measurement results, the feasibility and repeatability of proposed method was confirmed.

Above in-process measurement method is on the basis of the optical response in the condition of internal reflection at the critical angle. There is another method that can detect the slight change of refractive index based on the Surface Plasmon Resonance (SPR). SPR occurs when propagating light strikes on and resonantly induces the free electrons of the metal to oscillate the metal/dielectric interface. Thin metal coating (50 nm for gold film) on high refractive index substrate is required for applying SPR in the in-process measurement. SPR has higher sensitivity of refractive index and provides better resolution than critical-angle-reflection method. In addition, SPR has the advantage that the reflection drop is caused by the absorption in resonance condition rather than increase the transmittance, which means even in low reflection condition, there will be no light propagating deep into cured resin and generate scatting or reflection that become the noise of optical response. We have done the theoretical investigation of SPR and proposed an effective refractive index theory in SPR to transverse the variation of thickness to change of the effective refractive index when thickness of cured resin is in submicron scale. This theory has been confirmed by optical simulation using Rigorous Coupled Wave Analysis (RCWA) method. In addition, we proved that a 1 nm resolution of thickness measurement can be achieved by applying phase-detection based SPR, however, the measure range is extremely narrow due to the sensitivity drop largely when refractive or thickness of cured resin vary with the resonance condition. The measurement range can be simply control by slightly changing the incident angle, but it is not suitable for in-process measurement. Therefore, we also proposed a novel multi-layer SPR substrate using PLZT (one of the electro-optic ceramic material, whose refractive index is changes by applied voltage, $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$, x/y=9/65). The high sensitive measurement range can be therefore changed by applied violated on PLZT layer. Until now, most of theoretical work has been done and a suitable measurement system that can integrated into micro/nano-stereolithography system has been designed.

In conclusion, to meet the strong requirement of in-process measurement in micro/nano-stereolithography techniques, this research started from the investigation of the essential photo-polymerization in curing process of resin. Based on the fact that the refractive index increase in the curing process, an optical method measurement method has been proposed to detect optical response from near-substrate resin using total internal reflection at the critical angle. We experimentally proved that proposed measurement method can be applied into conventional EWNSL and MSL system. The thickness of submicron-thin resin layer and the distribution of conversion degree of thick resin layer was in-process measured in EWNSL and MSL respectively. At last, we made theoretical and innovative investigation of in-process measurement using SPR measurement.