Key Engineering Materials Vols. 523-524 (2012) pp 610-614
© (2012) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/KEM.523-524.610

Fundamental study on nanoremoval processing method for microplastic structures using photocatalyzed oxidation

Takahiro SEKINO [1, a], Satoru TAKAHASHI [1,b], Kiyoshi TAKAMASU [1,c]

[1] Department of Precision Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

[a]sekino@nanolab.t.u-tokyo.ac.jp, [b]takahashi@nanolab.t.u-tokyo.ac.jp,
[c]takamasu@nanolab.t.u-tokyo.ac.jp

Keywords: micromachining, nanoprocessing, removal processing, photocatalyst

Abstract. Microplastic structures, typified by photoresists for semiconductor devices or various MEMS devices, photosensitive resins of microstereolithography, and so on, play one of the most important roles in microdevice manufacturing. In order to process finer plastic structures with higher reliability for more complexly modulated microdevices in the next-generation micromanufacturing field, it is necessary to develop a nanoremoval processing method that can be applied to a corrective machining process with a removal resolution of less than 10 nm in both the lateral and vertical directions. In this paper, we propose a novel nanoremoval processing method for microplastic structures using photocatalyzed oxidation. Here, we use photocatalyst microparticles as an effective, specially designed material removal tool tip. Since light energy is not directly used for processing the material, the material removal resolution does not depend on the diffraction limit. Further, using photocatalysts eliminates microtool wear problems. In order to verify the fundamental feasibility of the proposed method focusing on the vertical resolution, we carried out basic experiments using TiO_2 microparticles with a diameter of 500 nm on a cured photosensitive resin surface. AFM observation of the processed surface showed that a vertical removal resolution of 8 nm was achieved.

1. Introduction

The processing of microplastic structures, such as photoresist polymers for lithography and resins for stereolithography, plays one of the most important roles in microdevice manufacturing today. In particular, the increasing demand in the microdevice industry, which manufactures devices such as microelectromechanical systems, micro-optomechanical systems, and microfluidic systems, has made it necessary to develop a nanoremoval processing method that can be applied to a corrective machining process with a removal resolution of less than 10 nm in both the lateral and vertical directions. Thus, next-generation 3D micromanufacturing requires a removal processing method for microplastic structures with the highest degree of flexibility and a process resolution of less than 10 nm.

There are many microprocessing techniques, which can be classified into two main types on the basis of the principle employed: processing using light or mechanical processing. The former type, which uses light energy, is well known as one of the most effective methods of achieving a high degree of flexibility in 3D microfabrication. However, in this method, it is impossible to process with a spatial process resolution beyond the diffraction limit of freely propagating light. Thus, this type does not meet the next-generation requirements, which calls for a process resolution of less than 10 nm. The latter type of microprocessing technique, which uses a mechanical tool, is one of the most common methods. Generally, an AFM (atomic force microscope), which is one of the highest resolution profilometers, can be also used as a microfabrication tool. Using an AFM mechanical probe tip, it is possible to scratch off the surface of soft materials with high process resolution in both the lateral and vertical directions. However this method does not afford a high degree of flexibility in 3D microfabrication. Moreover, the process resolution gradually deteriorates because an AFM mechanical probe tip easily wears while scratching surfaces.

Consequently, it is difficult to use typical conventional processing methods in next-generation microprocessing. To overcome these difficulties, we propose a nanoremoval processing method for microplastic structures such as photoresist polymers and resins for stereolithography using photocatalyzed oxidation. In our method, photocatalyzed microparticles are used as an effective, specially designed tooltip. This paper is organized as follows. Section 2 describes the proposed method and how it overcomes the above difficulties. Section 3 presents results of an experimental verification of the proposed method using TiO_2 particles. Section 4 concludes the paper.

2. Nanoremoval processing method for microplastic structures using photocatalyzed oxidation

We propose a nano removal processing method for micro plastic structure such as photoresist polymers and resins for stereolithography with photocatalyzed oxidation. Fig. 1 shows the basic concept of our proposed method, in which a photocatalyst nano particle applied as a specially designed material removal tool tip. We project UV light on the photocatalyst and excite it. The excited photocatalyst causes oxidation and removes the nearby solid plastic. This is why a submicrometer spatial resolution can be expected. For containing and handling nanoparticles, we assume that some techniques can be applied to this method, such as optical trapping by a single-beam gradient force [1-3].

In our study, we used titanium dioxide (TiO_2) microparticles as photocatcatalysts. Not only is TiO_2 a stable material and safe for use on the human body but it also reacts readily with relatively weak light [4]. When TiO_2 absorbs a photon that has energy corresponding to the energy gap of TiO_2, an electron is excited from the valence band to the conduction band, and then an electron-hole pair is generated. This results in the oxidation-reduction reaction as depicted in Fig. 2. In this reaction, three active oxygen species, O^-, O_2^-, and O_3^-, are formed. They have a strong enough oxidation effect to decompose organic matter. Some studies have been published on using this reaction for photocatalyzed oxidative decomposition of solid plastics [5-8]. However, these studies mainly sought to address issues in the environmental field, such as developing photodegradable plastics, and few investigations have been conducted on applying photocatalyzed oxidative decomposition to micromanufacturing.

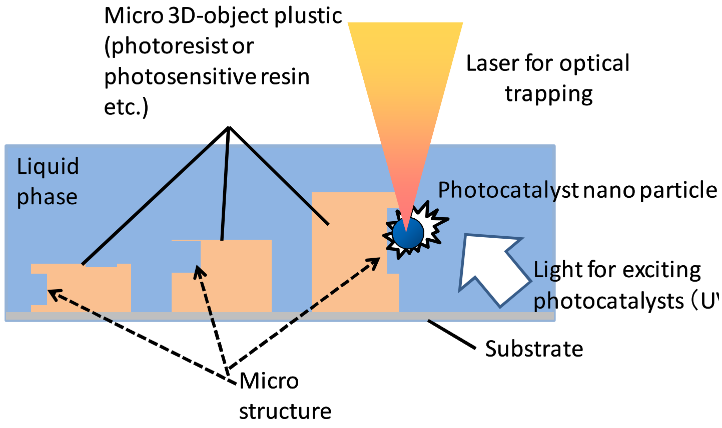

Fig. 1. Concept of nanoremoval processing method for microplastic structures using photocatalyzed oxidation.

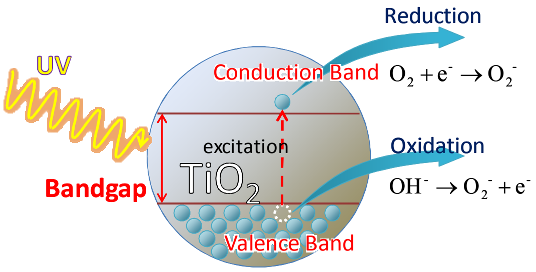

Fig. 2. Oxidation-reduction reaction of TiO_2.

Here, we aim to achieve submicrometer processing spatial resolution by controlling photocatalyzed oxidation. The characteristics of our proposed method can be summarized as follows. (1) The spatial resolution of this method depends on the size of the photocatalyst particles. We expect high spatial resolution improvement beyond the diffraction limit of light, in spite of using freely propagating light energy for processing. (2) We assume that we can apply optical trapping to handling the photocatalyst particles in order to take advantage of the high degree of flexibility of light in 3D space. (3) Using photocatalyst nanoparticles as a process tool tip eliminates the microtool wear problem, which is inevitable for mechanical processing. We can expect high durability of the micromanufacturing tool and stability of the processing resolution even if processing continues for a longer time.

3. Nanoremoval verification experiment

We carried out a basic experiment for verifying vertical removal resolution on the order of 10 nm, which is one of the most important process characteristics in order to realize the proposed method. As the first step in this experiment, in order to focus on essential process resolution characteristics, photocatalyst nanoparticles of diameter 500 nm, which is a relatively large size, were employed. It is reasonable to assume that the diameter of the particle would dominate all the other factors, including UV power and temperature, in determining the lateral decomposed size. The amount of vertical decomposition involves considerable uncertainty, and controlling the vertical decomposition is very important for the proposed method to be practical Therefore, our experiment and analysis focused on the vertical process resolution.

3.1. Experimental methodology

Fig. 3 shows the apparatus developed for this verification experiment. The left side of Fig. 3 shows how to make a target sample for removal processing of cured resin. We employed a free-radical-type photosensitive resin (JSR Corp., KC1162) as a target sample because we suppose that this method can be applied to modify the 3D microstructure fabricated with stereolithography.

As shown in Fig. 3 (a), we placed about 5 cc of liquid resin on a thin glass substrate and projected light on the resin from beneath for 90 s. For projecting light, we used Koehler illumination from the 100-mW halogen lamp of a microscope (Olympus BX51). The light exposure caused the resin to cure. As shown in Fig. 3 (b), after the resin cured, the resin was peeled off the glass substrate and turned over. The resin's flat side, which originally faced the glass, was then subjected to the processing and the measurements and analysis that we describe below.

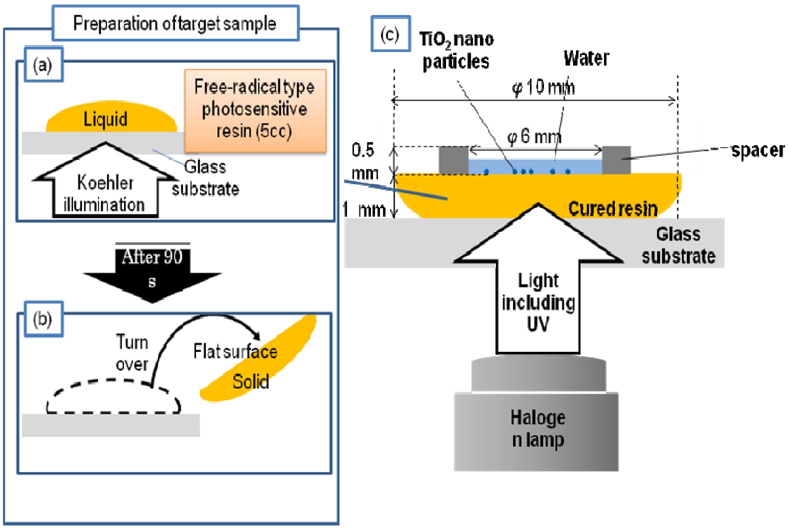

Fig. 3. (a) and (b) Preparation procedure for target sample. (c) Basic experimental apparatus for nanoremoval verification experiment.

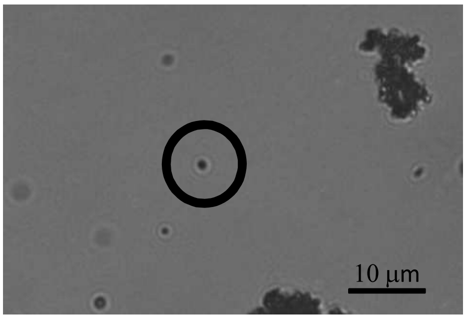

Fig. 4. Optical microscope image of the TiO_2 nanoparticle solution we employed.

Fig. 4 shows the photocatalyst nanoparticles used in this experiment. We employed a TiO_2 nanoparticle solution (Showa Titanium Co., Ltd., crystal architecture: Rutile (95 %), φ: 500 nm). Fig. 5 shows the procedure for the nanoremoval verification experiment. TiO_2 nanoparticles were located on the sample resin (Fig. 5 (a) and (b)). We exposed them to UV light for 10 minutes in the liquid phase (Fig. 5 (c)). In order to achieve in-process monitoring during the experiment, we used the UV included in the output of the halogen illumination light source of a microscope to excite the TiO_2. After the TiO_2 was exposed, we evaluated the samples with an AFM (Fig. 5 (d)).

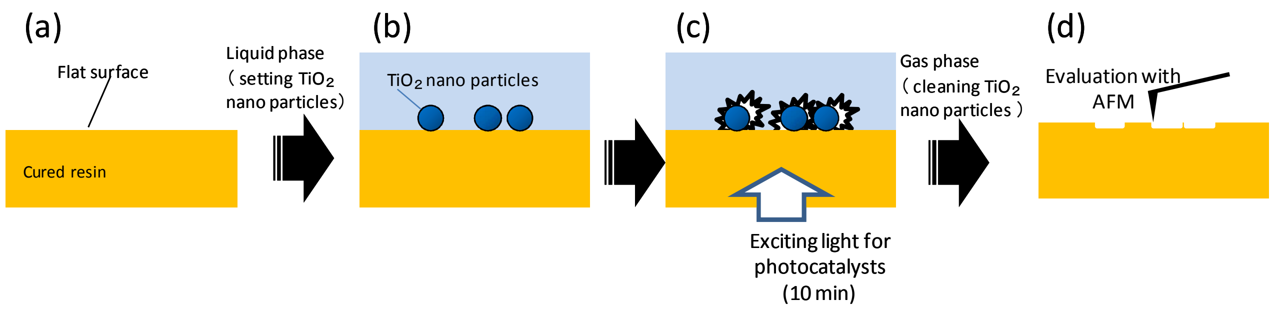

Fig. 5. Procedure for nanoremoval verification experiment.

3.2. Experimental result

Fig. 6 (b) shows the result of the AFM analysis of the target after processing. For comparison, Fig. 6 (a) shows the AFM image of the sample surface without processing. There are some small projections but no dents. Also, we can see that, with the exception of the projections, the surface is smooth enough to evaluate nanoprocessing on it. In contrast, in Fig. 6 (b), we can see that there are several dents, whose distribution almost corresponds with the density of TiO_2 particles in the solution as observed with the microscope. Their sizes are about 300–500 nm in diameter and almost correspond with the diameter of the TiO_2 particles. The dents are about 8 nm in depth. For evaluation, as a control experiment, we made two more samples. One was the resin exposed to UV for 10 minutes without TiO_2. The other was the resin with TiO_2 but not exposed to UV. We found no dents on either of their surfaces. These results suggest the possibility that TiO_2 photocatalyzed oxidation allows nanoremoval processing with a process resolution of less than 10 nm.

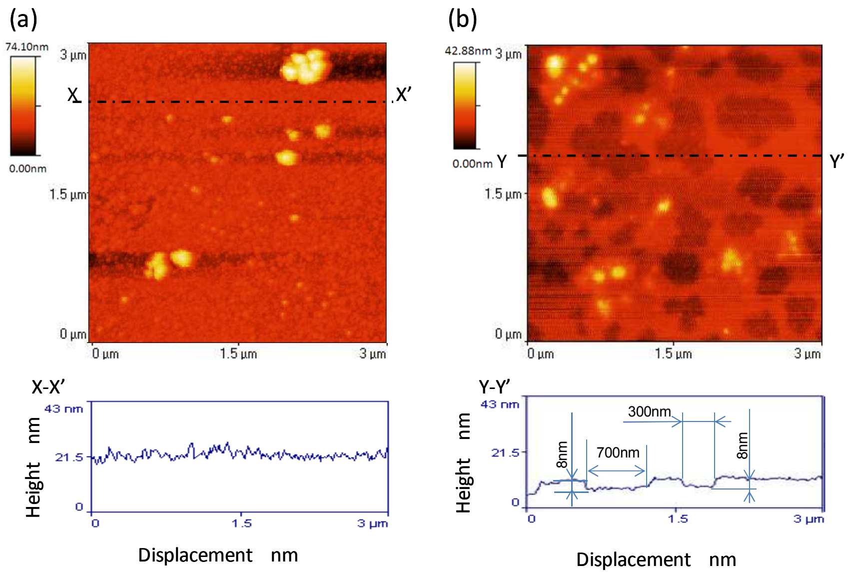

Fig. 6 AFM images of the target surface. (a) Without processing. (b) After processing.

4. Conclusion

In this paper, we proposed a nanoremoval method for microplastic structures based on photocatalyzed oxidation and used photocatalyst particles as a micromanufacturing tool to achieve submicrometer spatial resolution. The experimental analyses, which focused on the vertical fabrication characteristics, show that the assumed TiO_2 photocatalyzed oxidation is effective for nanoremoval processing with a resolution of 10 nm. These results suggest that the proposed method is a practical solution for achieving a submicrometer process resolution. In the future, we will carry out further experiments to analyze the photocatalyzed oxidation mechanism in further detail especially for the lateral resolution and the controllability of decomposition by changing the UV power.

Acknowledgement

This work was supported by JSPS under a Grant-in-Aid for Scientific Research (A) (23246028). The photosensitive resin was provided by JSR Corporation.

References

[1] A. Ashkin, Acceleration and trapping of particles by radiation pressure, Phys. Rev. Lett. 25 (1970) 156-159

[2] A. Suzuki, et al., Nano-structures fabrication using local electrophoretic deposition associated with laser trap, Proc. JSPE (2008, spring), 12p-G-21

[3] H. Shimizu, et al., Study on micro-machining using a small particle controlled by optical pressure, Proc. JSPE (1996, autumn), 483

[4] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37-38

[5] S. Horikoshi, et al., Photocatalyzed degradation of polymers in aqueous semiconductor suspensions. 1., Environ. Sci. Technol. 32 (1998) 4010-4016

[6] H. Hidaka, et al., Photocatalyzed degradation of polymers in aqueous semiconductor suspensions. 1., J. Polym. Sci.: Part A Polym. Chem. 34 (1996) 1311-1316

[7] J. Shang, et al., Photocatalystic degradation of polystyrene plastic under fluorescent light, Environ. Sci. Technol. 37 (2003) 4494-4499

[8] X. Zhao, et al., Enhancement of photocatalystic degradation of polyethylene plastic with CuPc modified TiO_2 photocatalyst under solar light irradiation, Appl. Surf. Sci. 254 (2008) 1825-1829