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Concept for laser-assisted nano removal beyond the diffraction limit using photocatalyst nanoparticles

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ABSTRACT

A new concept for the laser-assisted removal of material is proposed for achieving nanoscale correction in next-generation functional microstructures such as nanostructured photoresist surfaces and micro 3-D objects fabricated using microstereolithography. This proposed method is characterized by the entrapment of TiO_2 photocatalyst nanoparticles by a remotely controlled radiation force, which allows not only for remote processing using the inherent properties of light, but also a fine process resolution that goes beyond the limits of diffraction focusing. Both theoretical and experimental analyses are used to verify the basic feasibility of this proposed concept.

1. Introduction

In the world of micro manufacturing, microstructure formation processes such as photolithography and microstereolithography [1] play an important role in ensuring the functionality of semiconductors and micro-3D functional devices, as their overall performance is greatly dependent on the fine microstructure of photosensitive materials. This has led to a rapid increase in both the micronization and complexity of the functional structures created as a way of increasing device performance [2–5]; however, the more micronized and complex the microstructure becomes [6,7], the more important it is to minimize the formation of the various imperfections that can be generated. For instance, as process resolutions approach an order of several tens of nm [6], surplus curing that extends beyond the intended structure has become a major problem (Fig. 1). Thus, in order to improve the structure quality in next-generation micro manufacturing processes, there is a need for a material removal process that can be used to remove surplus curing defects from complex micro-3D structures with a 10-nm process resolution.

Many material-removal methods already exist for soft substances such as photosensitive resin [5,8], and these can be mainly classified as either mechanical-probe-based (Fig. 2(a)) or laser-assisted methods (Fig. 2(b)) based on the physical principle employed. The former type has a considerable advantage in that the process resolution is determined by the physical contact size of the mechanical-probe, thus allowing for a high resolution. Indeed, if an atomic force microscope (AFM) cantilever is used, then a resolution of less than 10 nm can be easily achieved [8]. However, the practical application of this technique is not reliable, as the process resolution gradually deteriorates due to the low wear resistance of the fine AFM tip. Furthermore, this method can only be applied to the removal of surplus curing on surfaces that are nearly perfectly flat, and therefore cannot be used on 3D-structures with a high degree of flexibility. The second option is characterized

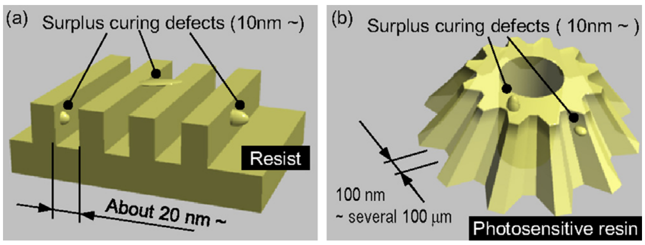

Fig. 1. Typical imperfections (surplus curing defects) present in: (a) micro periodic structures produced by photolithography, (b) micro mechanical structures created by microstereolithography.

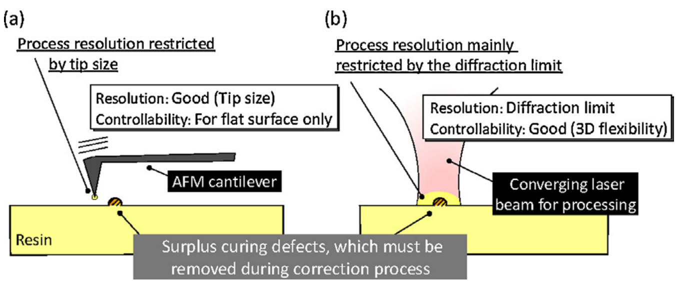

Fig. 2. (a) Mechanical-probe-based and (b) laser-assisted micro/nano material-removal.

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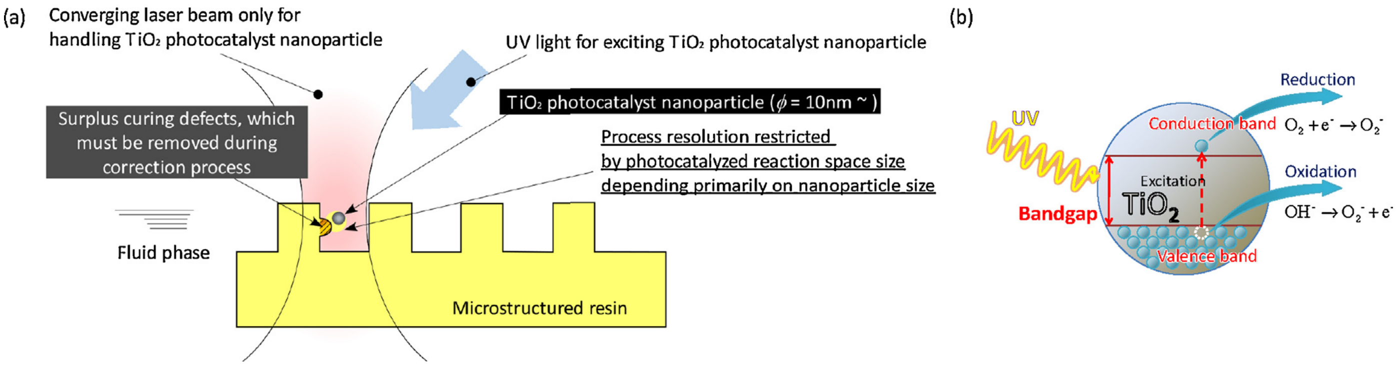

Fig. 3. Proposed laser-assisted removal process using photocatalyst nanoparticles: (a) conceptual diagram, (b) oxidation-reduction of TiO_2 photocatalyst.

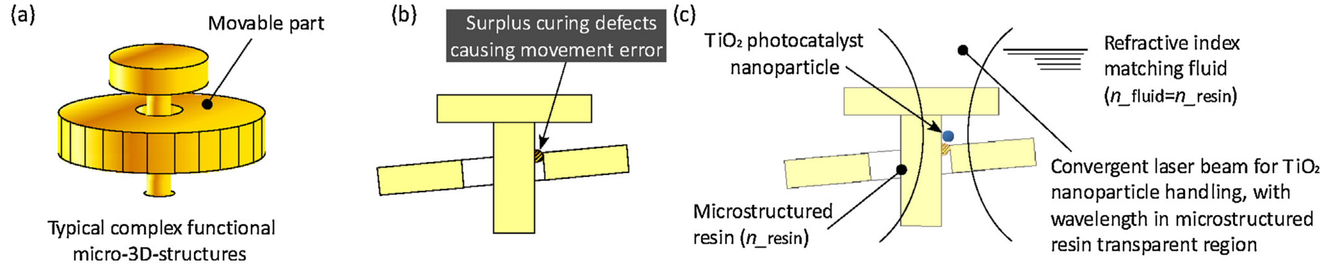

Fig. 4. Applicability to surplus curing defects in a complex micro-3D-structure: (a) functional microstructure with a movable part; (b) surplus curing defects under the overhang, causing movement error; and (c) nano correction process for defects under such an overhang using a refractive index matching fluid. Other energy-beam-based correction techniques cannot be used with such a complex target.

by the use of laser ablation; and by taking advantage of remote processing using the inherent properties of propagating light energy, can be applied to both flat surfaces and complex, highly flexible 3D-structures. There is, however, a critical problem regarding the process resolution, which is largely determined by the diffraction limit of the light source [5].

Given the problems associated with using conventional micro material-removal methods for the nanoscale correction of surplus curing defects in complex micro 3D structures, this study aims to develop an approach that is not only suitable for highly flexible structures like a laser-assisted process, but also offers the high process resolution of a mechanical-probe based method.

2. Laser-assisted removal using photocatalyst nanoparticles

Fig. 3 shows a schematic diagram for a new material-removal concept based on using photocatalyst nanoparticles. This method is applicable to complex micro 3D structures with a high degree of flexibility, and has a fine process resolution that goes beyond the diffraction limit. This is made possible by using laser-trapping technology [9] as a nano processing tool to manipulate photocatalyst TiO_2 nanoparticles. When this TiO_2 absorbs photons with an energy corresponding to its energy gap an electron is excited from the valence to conduction band, thereby generating an electron-hole pair [10]. The resulting oxidation-reduction reaction, which is shown in Fig. 3(b), is capable of decomposing polymer materials in contact with the TiO_2 [11–13]. Thus, by illuminating and exciting the TiO_2 nanoparticles with UV light, they can function as a nano removal tool for microstructured resin objects fabricated by photolithography, microstereolithography, etc., such as those shown in Fig. 3(a). Furthermore, the process resolution of this proposed method is not restricted by the diffraction limit of the laser-trapping beam or the UV light, but rather by the size of the TiO_2 nanoparticles. Being based on the inherent properties of propagating light gives the process a similar degree of target flexibility to the laser-assisted process, while the near-contact of the TiO_2 nanoparticles gives a resolution similar to that of the mechanical-probe-based method. More importantly though, as its physical principle is based on catalytic reaction, there is no problem of tip wear.

Similar micro processing methods based on using both laser ablation and laser-trapping technology have been reported [14–16], but as their physical principles were still based on laser energy, their processing direction is directly dependent on the direction of laser beam propagation. As such, it is difficult to apply such methods to the correction of surplus curing in complex micro 3D structures. The proposed new method, on the other hand, does not use laser energy directly, and so omnidirectional processing is independent of the laser propagation direction. This should allow for the nano removal of surplus curing defects even if they are on side walls.

Furthermore, by using a fluid with a refractive index matched to that of the resin object being processed (Fig. 4), the converging laser beam used for trapping can illuminate the target particle without optical disturbance. This allows for the correction of surplus curing defects underneath the overhanging parts of complex micro-3D-structures [7,17], and is most significant features of this approach. That is, accessing such particles is not something that is possible with other energy-beam-based correction techniques, including electron-beam-machining.

As a step toward the practical realization of this proposed concept, we herein present theoretical analyses of the TiO_2 nanoparticle handling characteristics using laser-trapping. The development of a basic nano removal processing system is also presented along with the core principle of the proposed concept, i.e., that the process resolution does not depend on the laser spot size, but on the TiO_2 tool size.

3. Theoretical analyses of TiO_2 nanotool handling characteristics

A number of theoretical analyses have been conducted on the laser-trapping characteristics of dielectric micro particles such as SiO_2, which has refractive index of around 1.46 [18], but few reports exist regarding TiO_2 micro/nanoparticles that have a much higher refractive index of 2.97. Thus, in order to confirm the feasibility of the proposed concept, it is important to understand how the handling characteristics of TiO_2 micro/nanoparticles differ from that of SiO_2 particles. Figs. 6 and 7 show the numerically calculated radiation forces for a SiO_2 and TiO_2