

**Research  
Report****Nano-Fabrication on the Surface of an Azopolymer Using the Optical Near-Field**Osamu Watanabe, Taiji Ikawa, Masaaki Tsuchimori, Hideki Takagi

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**Abstract**

We demonstrate a photoinduced nanofabrication method using azobenzene-containing polymers that is applicable to dimensions beyond the diffraction limit. We present an example of nanometer-scaled patterning induced by the optical near-field around arrayed polystyrene microspheres, and present a method of high-speed

optical recording by means of an optical fiber probe with a small aperture. We also discuss the mechanisms of deformation on the azopolymer surface. Azopolymers are expected to become attractive materials for near-field application due to their sensitive deformation characteristics.

**Keywords**

Nano-fabrication, Optical near-field, Optical recording, Azopolymer, Photoisomerization, Surface deformation, Fiber probe aperture

## 1. Introduction

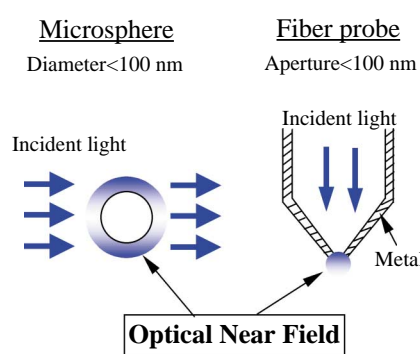
Optical recording and photofabrication techniques that exploit changes in material properties have grown in popularity as useful industrial technologies, where there is a requirement for the dimensions of recording and processing to decrease year by year. Resolution of recording or fabrication processes is determined by how tightly irradiating light can be focused, and in practice this equates to about half the wavelength of the irradiating light due to diffraction limits. Use of the optical near-field can overcome diffraction limits in order to reach nanometer-scale dimensions. Recently, use of the optical near-field has been expected to become a powerful tool for attaining nanometer-scale manufacturing capability.<sup>1, 2)</sup> If a microsphere is irradiated with light, an optical near-field is induced around the microsphere, as shown in **Fig. 1**(left). In the case of a fiber probe with a small aperture, an optical near-field is also induced around the aperture, as shown in **Fig. 1**(right). Therefore, a light source with dimensions smaller than 100 nm would be available if we used an aperture or microspheres smaller than 100 nm.

Various optical recording techniques using the optical near-field, such as the solid immersion lens,<sup>3, 4)</sup> and the super-resolution technique,<sup>5)</sup> have been proposed as a realistic solution to this problem, and may be used in the near future. On the other hand, near-field magneto-optical recording using a fiber probe with a small aperture has been reported for the first time.<sup>6)</sup> Likewise, optical recording with a fiber probe has been demonstrated using Ge-Sb-Te alloy

film as a recording layer.<sup>7)</sup> Recently, a near-field recording and reading technique using an apertured silicon contact slider probe that allows us to attain high-speed performance has been reported.<sup>8)</sup> In these trials, 50-100 nm spot sizes were recorded. However, a smaller spot size (below 25 nm) is required in order to realize extremely high-density recording of over 1 Tbits/in<sup>2</sup>. Since the optical power around the aperture decreases exponentially with decreasing aperture size, the development of an aperture probe with a structure that promotes the effective utilization of light is a problem that needs to be resolved. Furthermore, a material that is highly sensitive to photo-irradiation is also required for near-field optical recording in order to achieve a density of 1 Tbits/in<sup>2</sup>.

Photolithography is a useful nanofabrication technique due to the ease with which this technique can be reproduced and its applicability to fabrication of large areas. Optical near-field lithography is also anticipated as a new technology, and many research groups have demonstrated the patterning of surfaces at resolutions below the diffraction limit using either evanescent near-field optical lithography<sup>9, 10)</sup> or an embedded-amplitude mask.<sup>11)</sup> Highly sensitive materials are required for optical near-field lithography, just as they are for optical near-field recording.

In this report, we demonstrate the nanometer-scale deformation phenomena induced by the optical near-field using polymers that contain azobenzene. We focus our attention on one such polymer (azopolymer) that exhibits a unique photo response, and we demonstrate the potential of this azopolymer for application to a new near-field technology.



**Fig. 1** Schematic representation of the optical near-field induced around microsphere (left side) and a probe aperture (right side).

## 2. Photonic response of azopolymers

Over the past decade, polymeric systems containing azobenzene moieties have attracted a great deal of attention because of their potential uses in various photonic applications.<sup>12-24)</sup> It is well known that azobenzene derivatives can exist in two configurations. The first of these is the *cis*-form, which has a bent formation, and the other is the more stable *trans*-form, which is rod-like in shape, as shown in **Fig. 2**. When exposed to light of a certain wavelength, the *trans*-form can be

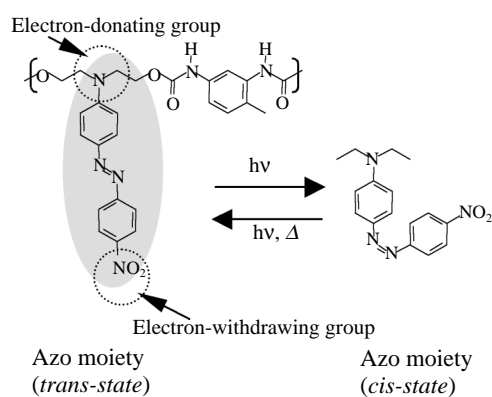
photoisomerized to the *cis*-form. *Cis-trans* back-isomerization can take place thermally and/or photochemically. This property of azobenzene derivatives leads to a drastic change in physical and optical properties of the polymer matrix, which has aroused the interest of many research groups.

In particular, intramolecular charge-transfer azobenzene, which contains a donor-acceptor substituent with a large dipole moment and has a high absorption coefficient, exhibits not only a high degree of hyperpolarizability, but also shows interesting deformation behaviour under photo-irradiation. The *cis*-form of charge-transfer azobenzene back-isomerizes thermally very quickly to *trans*-form. A typical azopolymer with a donor-acceptor substituent is shown in Fig. 2. Two research groups<sup>25, 26)</sup> have reported a surface relief grating produced in an azopolymer by a light interference pattern, as shown in Fig. 3, and a great deal of related research has been reported up to now.<sup>27-29)</sup> This surface deformation is thought to be caused by photoinduced plasticization that takes place due to fast *trans-cis-trans* cycles induced by photo-irradiation.

We report a photoinduced surface deformation that exhibits an optical near-field, and show that nanometer-scale fabrication is now possible.

### 3. Nanometer-scale patterning induced by the optical near-field<sup>30-33)</sup>

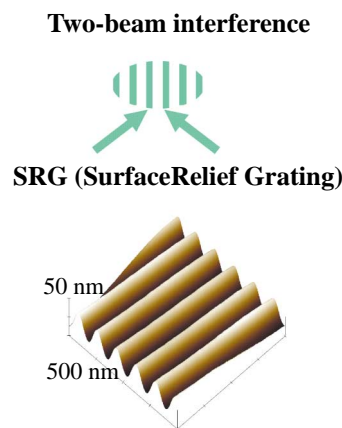
We can easily obtain various sized microspheres, from tens of nanometers to several micrometers,



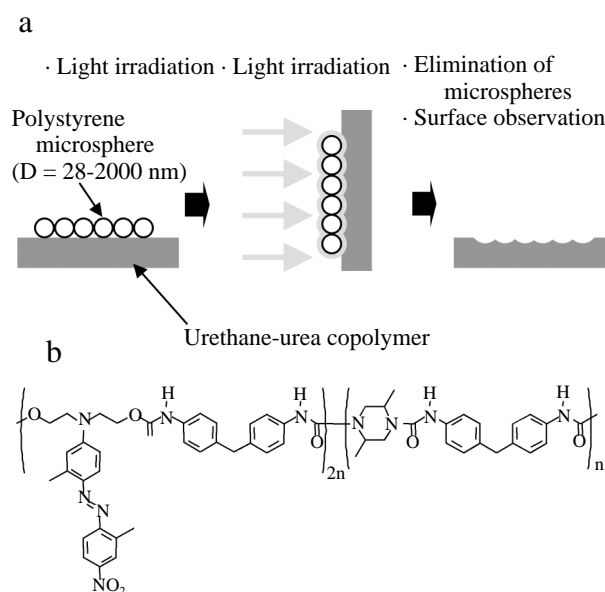
**Fig. 2** Chemical structure of typical azobenzene-containing polymer. The azo moiety changes the structure through isomerization to allow two configurations, *trans*- and *cis*- states.

made from various materials such as polystyrene or silica. It is possible to place these into an ordered arrangement due to the uniformity of their diameter. We selected microspheres such as these for the near-field light source, and demonstrated a topographical nanostructure patterning technique on the surface of the azopolymer.

Nanostructured patterning was carried out as shown in Fig. 4a schematically. A urethane-urea copolymer containing azobenzene moieties was



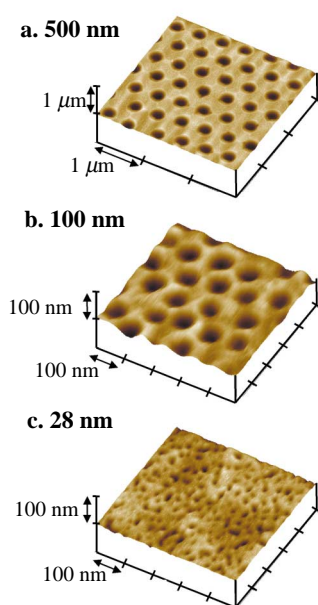
**Fig. 3** Formation of surface relief grating on the azopolymer, generated by two-beam interference irradiation.



**Fig. 4** Schematic representation of a nano-patterning process (above) formed by using microspheres as the near-field source, showing the alignment of the microspheres and light irradiation and the elimination of the microspheres. Chemical structure of the urethane-urea copolymer used (below).

used, as shown in Fig. 4b, with a glass transition temperature of 145 °C and absorption maximum of 475 nm. A film of azopolymer was spin-coated onto glass substrate from a pyridine solution. Microspheres with preselected diameters of between 2000 nm and 28 nm were arranged on the azopolymer. The microspheres self-assembled into a hexagonal structure that was one monolayer thick. The sample film was irradiated from the side by 488 nm Ar<sup>+</sup> laser with an intensity of tens of mW/cm<sup>2</sup>, in order to eliminate the influence of gravity as shown in Fig. 4. After irradiation, the sample was washed with water and benzene to remove the microspheres. After drying the sample, surface structure of the polymer film was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

**Figure 5** shows AFM images of the resulting polymer surface. The surface of the films prior to irradiation by Ar<sup>+</sup> laser showed no regular structural periodicity. Hexagonal structure was directly transcribed onto the polymer surface as a series of indentations in the cases of the 500 nm and 100 nm microspheres. In the case of 28 nm microspheres, an indented structure following the pattern of the microspheres was also formed, although the arrayed structure was distorted. We can confirm that these

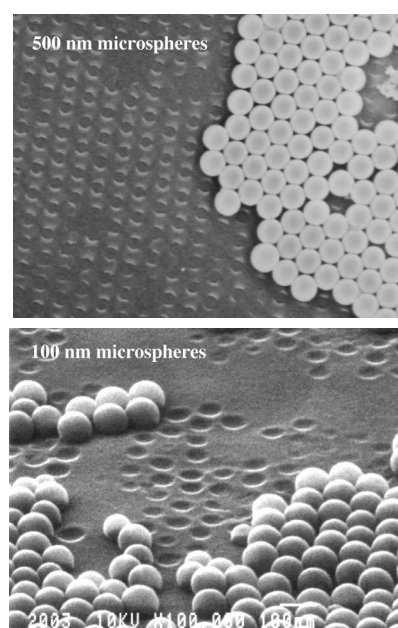


**Fig. 5** AFM images of nano-patterned structures formed on the azopolymer. a: 500 nm microspheres b: 100 nm microspheres c: 28 nm microspheres

structures were induced by the optical near-field around the polystyrene microspheres, because the dimensions of the 100 nm and 28 nm diameter spheres are beyond the diffraction limit.

**Figure 6** shows SEM images of the polymer surface, including both the indented structure and the remaining microspheres. It is confirmed that the indentations are formed directly below the microspheres.

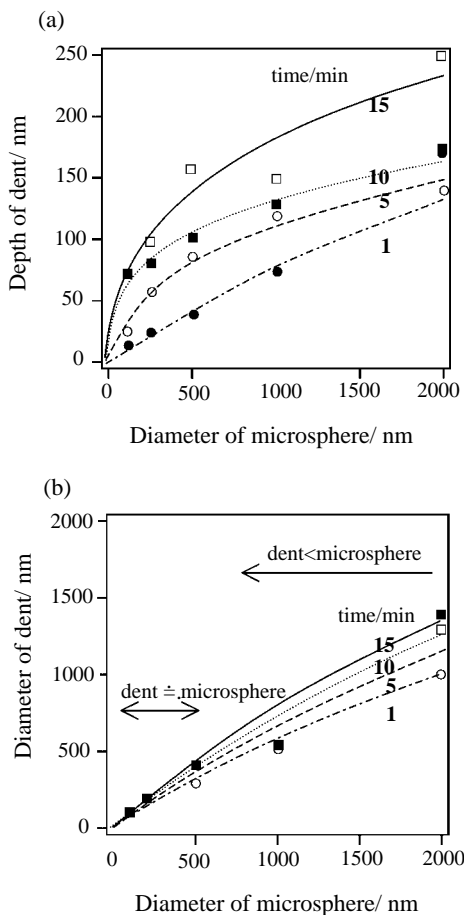
We explored size effects on the dents formed. **Figures 7** (a) and (b) show changes in the dent depth (a) and the dent diameter (b), respectively. Both depth and diameter increased as we increased the size of the microspheres. For microspheres smaller than 250 nm, the diameter of the dents formed was nearly equal to that of the microspheres used. For microspheres larger than 250 nm, on the other hand, the diameter of the dents formed was smaller than that of the microspheres. In the case of larger microspheres, relatively small dents would be formed due to the collection of light beneath the microsphere, and in the case of smaller microspheres beyond the diffraction limit, dents of the same size as the microsphere would be formed due to the near field around the microsphere. Figures 7(a) and (b) indicate that for every size of microsphere, dent depth increased with increasing irradiation time, but



**Fig. 6** SEM images of the nano-patterned structures formed on the azopolymer. The microspheres partially remain.

that dent diameter changed very little with time. In other words, the depth of the dents that were formed increased with increasing irradiation time while maintaining the same diameter. Therefore, since the deformation process did not spread laterally along the plane of the microspheres, we can rule out surface tension or down-welling as factors causing the deformation.

Deformation changed depending on the wavelength of irradiating light used. Deeper dents were obtained by irradiation close to the absorption maximum, while depth decreased at longer wavelengths with decreasing absorption coefficient. No noticeable deformation was caused by prolonged irradiation at 647 nm, where the absorption coefficient is practically zero. This demonstrates that deformation is induced by photo-isomerization resulting from photo-irradiation. We could also



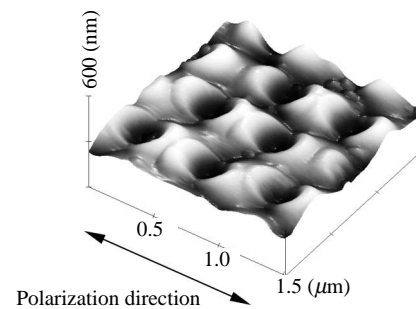
**Fig. 7** Change in the dent depth (a) and the dent diameter (b) as a function of the diameter of the microspheres. Open square, solid square, open circle and solid circle show the results of the nano-patterning experiment for 15 min, 10 min, 5 min and 1 min irradiation, respectively.

compare the dependence of the degree of deformation on optical power density, provided that the light irradiation produced some minimal increase in temperature (below about  $1\text{W}/\text{cm}^2$ ). Although the amount of deformation tended to increase with increasing optical power, the incremental increase was only slight. Use of the same optical energy, which means that light irradiation under a low power density for a long time is the same as using a high power density for a short time, caused the same amount of deformation. This demonstrates that significant photoinduced plasticization takes place, even at low power densities (below a few  $\text{mW}/\text{cm}^2$ ), and that heating effects cause no significant deformation.

We studied the dependence of deformation on polarization of the irradiating light. **Figure 8** shows an AFM image observed after irradiation with linearly polarized light. The periphery of the dent formed a large hump in the direction of the irradiated light. In the case of irradiation with circularly polarized light, the deformation yielded an isotropic structure without any directional dependence. This suggests that the deformation induced by the optical near-field is dependent on the polarization of the irradiated light.

#### 4. Mechanisms of deformation<sup>34, 35)</sup>

Intensity of the electric field around the polystyrene microspheres was calculated using Mie theory, under the assumption that the microspheres were irradiated with a linearly polarized plane wave. Calculated results are shown in **Fig. 9**. A relatively strong intensity was calculated in the direction of the traveling wave at the microsphere end-tip in the case



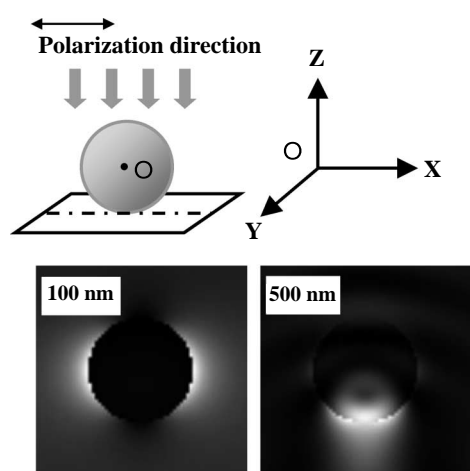
**Fig. 8** AFM image of the nano-patterning structure formed on the azopolymer, exhibiting polarization dependency.

of a 500 nm microsphere, while a relatively strong intensity was calculated at the lateral part of the microsphere in the case of a 100 nm microsphere. As described above, Fig. 6 shows that dents are formed directly below 500 nm and 100 nm microspheres. Comparing experimental results with the calculation, dent formation does not follow the intensity distribution of the electric field around the 100 nm microspheres, but it does for the 500 nm microspheres. In the cases of SRG formation<sup>36)</sup> and direct beam irradiation,<sup>37)</sup> deformation follows the intensity distribution of the electric field in the surface plane, as in the case of the 500 nm microspheres. Therefore, we need to investigate a new mechanical force to explain deformation of the polymer surface with 100 nm microspheres. With regard to azopolymer surface deformation in the experiment with the microspheres, we have proposed that the mechanism originates from the radiation force, including three-dimensional near-field gradient force and scattering force.

Dielectric materials in a vacuum are affected by the optical electromagnetic field. We can obtain an equation relating to dynamic force,

$$\mathbf{F} = -\epsilon_0 \chi' \left( -\nabla \left( \frac{1}{2} E^2 \right) \right) + 2\pi f \chi'' \mathbf{p}_e$$

where  $\mathbf{F}$  is the force working on the dielectric materials,  $\epsilon_0$  is the electrical permittivity,  $\chi'$  and  $\chi''$  are the real part and the imaginary parts,

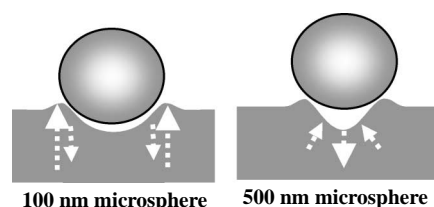


**Fig. 9** Calculated distribution of the optical intensity on the X-Z plane of the polystyrene microspheres, 100 nm (left) and 500 nm (right). The bright region indicates a relatively strong intensity.

respectively, of the electrical susceptibility of the material,  $\mathbf{E}$  is the electric field,  $f$  is the frequency, and  $\mathbf{p}_e$  is the momentum of light. The first term in the equation indicates the gradient force that attracts polymer from the region with weaker electric field towards the stronger field, while the second term indicates the scattering force that acts parallel to the momentum of the photon by absorption. We estimated gradient and scattering forces around the microspheres from the equation, with the resultant forces shown schematically in **Fig. 10**. Deformation induced by the near-field around the polystyrene microspheres can therefore be explained successfully.

As described above, photoinduced plasticization caused by fast trans-cis-trans isomerization softens irradiated parts of the azopolymer in spite of its high glass transition temperature ( $T_g$ ). Furthermore, decrease in  $T_g$  near the surface has also been reported.<sup>38, 39)</sup> Therefore, the softened surface of the azopolymer makes it possible to form an indentation, even though the radiation force is very weak.

The direction of polymer migration was confirmed by tapping mode AFM (TMAFM). The phase image of the TMAFM provides a map of stiffness variations across the surface, where a positive relative phase shift implies a stiffer region.<sup>40)</sup> Images of the phase shift reveal that the periphery of the dent becomes harder than the interior in the case of 100 nm microspheres, and that the interior of the dent becomes harder in the case of 500 nm microspheres. If the material becomes hardened in the direction of polymer migration, results of the phase image support a deformation mechanism as



**Fig. 10** Schematic representation of the direction of the forces acting on the azopolymer. The up-arrow shows the gradient force and the down-arrow shows the scattering force.

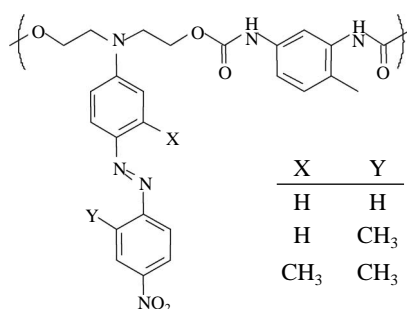
explained by radiation force.

## 5. Various azo derivatives<sup>32, 41-43)</sup>

We have examined the deformation phenomena induced by the optical near-field using various kinds of azo derivatives. We prepared three different kinds of polyurethane, each containing a slightly different azobenzene moiety, as shown in **Fig. 11**, and performed nanostructure patterning using polystyrene microspheres. Although these polymers all had virtually the same molecular weight, T<sub>g</sub>, and absorptivity at the wavelength of the irradiated light, the modified depth of the dent observed for each of the films was very different. The polyurethane containing no methyl-substituted azobenzene moiety showed effective deformation. No noticeable change in quantum yield was reported with regard to the methyl-substituted azobenzene moiety. Therefore, the different deformation characteristics could be ascribed to the efficiency of the trans-cis isomerization cycle.

We compared the deformation efficiency of various urethane copolymers, each consisting of a different main chain and containing the same azobenzene moiety and the same content. We synthesized various urethane azopolymers having different T<sub>g</sub>, as shown in **Table 1**. The nanostructure patterning was performed in the same way as before. The deformation efficiency of these polymers increased with increasing T<sub>g</sub>. We presume that this phenomenon involves elastic recovery.

We also explored an organic-inorganic hybrid, where we prepared an azobenzene moiety containing a glass (silica) matrix. We synthesized various

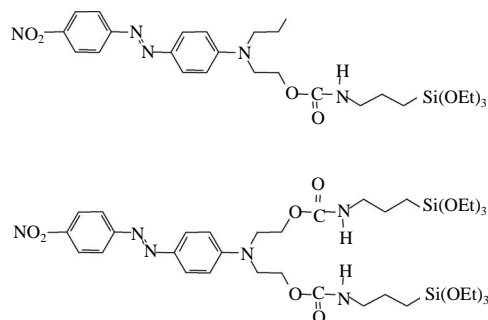


**Fig. 11** Chemical structure of the azobenzene-containing polyurethane. Three kinds of polyurethane were prepared, each containing a slightly different azobenzene moiety.

azobenzene-containing monomers, as shown in **Fig. 12**, and prepared the film with the monomer and triethoxysilane using a sol-gel technique. Nanostructure patterning was again performed in the same way. An indented structure was formed on the glass surface, in spite of the surface being hard. On one hand, the indented nanostructures obtained from

**Table 1** Copolymerization of diol and diisocyanate.

Diol	Diisocyanate	T <sub>g</sub> /°C
		143
		126
		118
		114
		99
		72
		46



**Fig. 12** Chemical structures of the azobenzene-containing monomers for the sol-gel process.



the azopolymer could be erased by heating the films above  $T_g$ , but on the other hand, the structure obtained from the azobenzene-containing organic-inorganic hybrid maintained the same structure up to a relatively high temperature.

We also succeeded in carrying out an enhanced fabrication technique on azopolymer films using Au nanoislands, which show a local surface plasmon resonance. The depth and diameter of the dents induced by the near-field around the polystyrene microspheres changed depending on the mass thickness of the Au nanoislands. We also observed an enhancement of the UV-vis spectrum of the azopolymer due to the Au nanoislands.

In this way, we can use materials incorporating azobenzene moiety creatively because the deformation behavior can be controlled by changing the molecular structure.

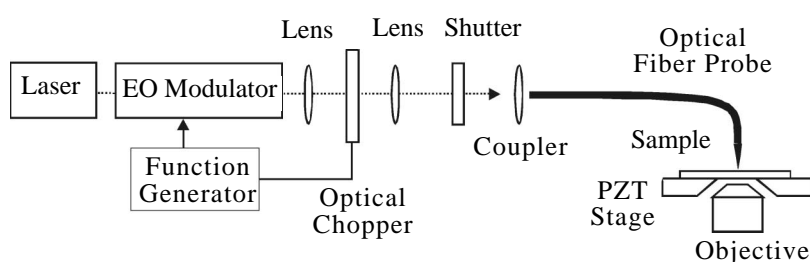
## 6. Optical recording with an optical fiber probe<sup>44, 45)</sup>

Thus far, we have described a nanostructure patterning method induced by the optical near-field, which requires a relatively long fabrication time. In order to apply the modification of azopolymers to optical recording using the optical near-field, we need to achieve a fast-recording speed of less than 100 ns. We also need to perform an experiment in

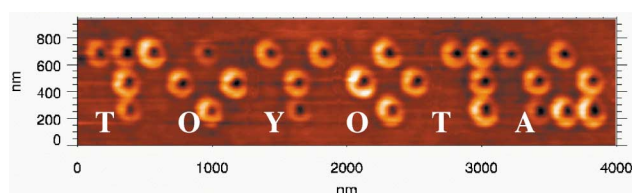
which we make a recording while maintaining the recording layer within several tens of nm from the generation part of the near-field.

We examined optical near-field recording on an azopolymer surface using an optical fiber probe. The experimental set up for the recording is shown schematically in **Fig. 13**. An optical fiber probe within 100 nm in diameter (JASCO: throughput of optical power = 0.0019) was attached to a scanning near-field optical microscope (SNOM) manufactured by Omicron. The fiber probe was brought into proximity with the azopolymer surface by controlling the distance between the tip of the probe and the surface using the shear-force method. A short single laser pulse was coupled into the counter side of the probe to generate a near-field around the aperture. The resulting polymer surface was observed with AFM and SNOM. **Figure 14** shows a two-dimensional topographic image of the azopolymer surface recorded in sequence with the near-field of a 125 ns pulse. Indentations with diameters of around 200 nm were recorded on the surface, and the shape and size of the dents were almost identical. This indicates that the tip around the aperture was not damaged during the irradiation. We also succeeded in recording indentations on the azopolymer with a 50 ns single pulse.

The depth of the indentations decreased with increasing distance between the probe and the surface. Furthermore, their depth changed depending on the wavelength of the irradiated light, i.e. the depth decreased with decreasing absorption coefficient. These results denote that the deformation was caused by the absorption of light as well as the nanostructured patterning with the microspheres. However, the power density at the aperture was estimated at several  $\text{kW}/\text{cm}^2$ , which produces an increase in temperature. In fact, the diameter of the dents decreased with decreasing pulse duration. This suggests a heating effect during fast recording. We therefore consider that the fast recording was achieved by a thermal effect as well by a photoinduced effect.



**Fig. 13** Experimental setup for the optical near-field recording.

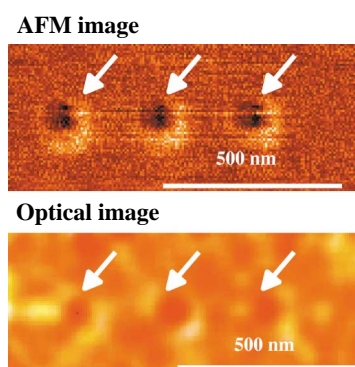


**Fig. 14** AFM image of the deformed azopolymer surface recorded with the fiber probe with 125 ns laser pulse.

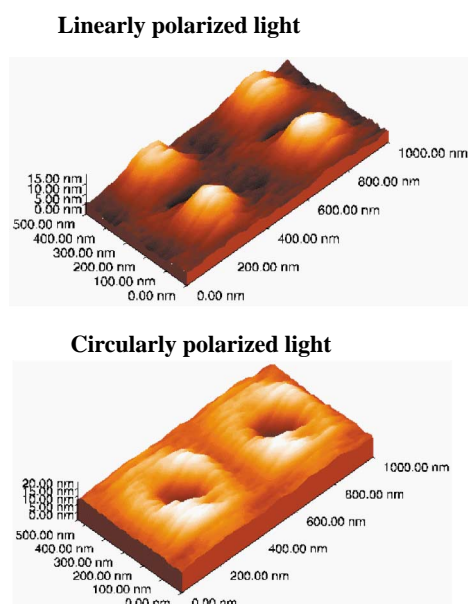


Near-field optical images of the deformed surface were observed using the SNOM, as shown in **Fig. 15**. Although the problem of artifacts occurring due to edge effects remains, the possibility of optical reading was demonstrated.

The use of low power pulsed irradiation, which was selected to avoid thermal effects, enables us to record marks on the azopolymer surface using a long irradiation time. In this case, the size of marks was larger than the aperture size. The shape of the mark changed depending on the polarization character



**Fig. 15** AFM image (above) and optical image measured with SNOM (below). The deformed structure was obtained by the optical near-field recording technique with the fiber probe.



**Fig. 16** AFM images showing the polarization dependency for the linearly polarized light (above) and the circularly polarized light (below).

when the polarized light was coupled into the probe. **Figure 16** shows the different shaped marks obtained by coupling with linearly polarized light and circularly polarized light, respectively. The periphery of the dent formed a large hump along the direction of the irradiated light, and the hump rotated along with the rotation of the polarization of the incident light. In the fabrication technique using the probe, the deformed structure depended critically on the irradiation power, the irradiation time and so forth. If all of these processes can be characterized, it is expected that the probe technique can be developed as a new nanometric fabrication method.

## 7. New application<sup>46, 47)</sup>

Laser ablation is an attractive technique from the viewpoint of the optical fabrication. We demonstrated that nanofabrication beyond the diffraction limit can be attained by near-field exposure using a nanosecond laser pulse having a high peak power density through a system of self-arrayed microspheres. The microspheres were scattered into the air during irradiation by an ablation process.

The nanostructure patterning technique allows us to record a moving specimen on the azopolymer surface as a deformation reflecting the shape of specimen by employing continuous pulsed laser irradiation. We demonstrated the observation of a moving paramecium and euglena gracilis.

## 8. Conclusion

In conclusion, we have demonstrated a photoinduced nanofabrication method, applicable to dimensions beyond the diffraction limit, using azobenzene-containing polymers. Azopolymers are expected to become attractive materials for near-field application due to their sensitive deformation characteristics.

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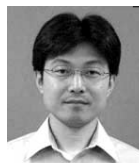
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