

### 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

アゾ色素含有のアゾポリマーを用いて,回折限 界以下のスケールでの光によるナノ加工の方法を 明かにする。配列した微小球に光照射を行った時, 微小球近傍に発生する近接場光により,ナノメー タスケールでのパターニングが可能であることを 示す。また,微小開口を有するファイバープロー

### 旨

要

ブを用いての高速光記録の例も示す。さらに,こ れらアゾポリマー表面の変形についてその変形機 構について論ずる。アゾポリマーはその高感度な 変形により,近接場光を利用した応用に魅力ある 材料となることが期待される。

キーワード

ナノ加工,近接場光,光記録,アゾポリマー,光異性化,表面変形, 微小開口ファイバープローブ

### 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 nearfield 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



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

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 nearfield 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.

### 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 backisomerization 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 photoirradiation. The cis-form of charge-transfer azobenzene back-isomerizes thermally very quickly to trans-form. A typical azopolymer with a donoracceptor 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 azobenzenecontaining 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 nearfield light source, and demonstrated a topographical nanostructure patterning technique on the surface of the azopolymer.

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

**Two-beam interference** 



**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  $Ar^+$  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  $Ar^+$  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

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



**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





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 1W/cm<sup>2</sup>). 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 mW/cm<sup>2</sup>), 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 nearfield 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,

$$\boldsymbol{F} = -\boldsymbol{\varepsilon}_0 \boldsymbol{\chi}' \left( -\nabla \left( \frac{1}{2} \boldsymbol{E}^2 \right) \right) + 2\pi f \boldsymbol{\chi}'' \boldsymbol{p}_e$$

where F is the force working on the dielectric materials,  $\varepsilon_0$  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 microsphers, 100 nm (left) and 500 nm (right). The bright region indicates a relatively strong intensity.

respectively, of the electrical susceptibility of the material, E is the electric field, f is the frequency, and  $p_e$  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 (Tg). Furthermore, decrease in Tg 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, Tg, 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-cistrans 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 Tg, 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 Tg. 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.



Fig. 12 Chemical structures of the azobenzenecontaining monomers for the sol-gel process.

the azopolymer could be erased by heating the films above Tg, but on the other hand, the structure obtained from the azobenzene-containing organicinorganic 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 Aunanoislands, 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



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.

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  $kW/cm^2$ , 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.

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 selfarrayed 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 nearfield application due to their sensitive deformation characteristics.

### References

- 1) Ohtsu, M. : Near-Field Nano/Atom Optics and Technology, (1998), Springer-Verlag, Tokyo
- 2) Ohtsu, M. and Hori, H. : Near-Field Nano-Optics, (1999), Kluwer Academic/Plenum Pub., New York
- Mansfield, S. M. and Kino, G. S. : "Solid Immersion Microscope", Appl. Phys. Lett., 57(1990), 2615
- 4) Terris, B. D., Mamin, H. J., Ruger, D. W., Studenmund, R. and Kino, G. S. : "Near-Field Optical

Data Storage using a Solid Immersion Lens", Appl. Phys. Lett., **68**(1996), 141

- 5) Tominaga, J., Nakano, T. and Atoda, N. : "An Approach for Recording and Readout Beyond the Diffraction Limit with an Sb Thin Film", Appl. Phys. Lett., **73**(1998), 2078
- Betzig, E., Trautman, J. K., Wolfe, R., Gyogy, E. M., Finn, P. L., Kryder, M. H. and Chang, C. -H. : Near-Field Magneto-Optics and High Density Data Storage", Appl. Phys. Lett., 61(1992), 142
- 7) Hosaka, S., Shintani, T., Miyamoto, M., Kikukawa, A., Hirotsune, A., Terao, M., Yoshida, M., Fujita, K. and Kämmer, S. : "Phase Change Recording using a Scanning Near-Field Optical Microscope", J. Appl. Phys., **79**(1996), 8082
- Yatsui, T., Kourogi, M., Tsutsui, K., Ohtsu, M. and Takahashi, J. : "High-Density-Speed Optical Near-Field Recording-Reading with a Pyramidal Silicon Probe on a Contact Slider", Opt. Lett., 25(2000), 1279
- Alkaisi, M. M., Blaikie, R. J., McNab, S. J., Cheung, R. and Cumming, D. R. S. : "Sub-Diffraction-Limited Patterning using Evanescent Near-Field Optical Lithography", Appl. Phys. Lett., 75(1999), 3560
- Blaikie, R. J., Alkaisi, M. M., McNab, S. J., Cumming, D. R. S., Cheung, R. and Hasko, D. G. : "Nanolithography using Optical Contact Exposure in the Evanescent Near Field", Microelectronic Eng., 46(1999), 85
- Goodberlet, J. G. : "Patterning 100 nm Features using Deep-Ultraviolet contact Photolithography", Appl. Phys. Lett., **76**(2000), 667
- 12) Todorov, T., Tomova, N., and Nikolova, L.:
  "Polarization Holography. 1:A New High-Efficiency Organic Material with Reversible Photoinduced Birefringence", Opt. Commun., 47(1983), 123
- 13) Gibbons, W. M., Shannon, P. J., Sun, Sh. T. and Swetlin, B. J. : "Surface-Mediated Alignment of Nematic Liquid Crystals with Polarized Laser Light", Nature, 351(1991), 49
- 14) Berg, R. H., Hvilsted, S. and Ramanujam, P. S. : "Peptide Oligomers for Holographic Data Storage", Nature, 383(1996), 505
- 15) Ikeda, T. and Tsutsumi, O. "Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films", Science, 268(1995), 1873
- 16) Hasegawa, M., Yamamoto, T., Kanazawa, A., Shiono, T. and Ikeda, T. : "A Dynamic Grating using a Photochemical Phase Transition of Polymer Liquid Crystals Containing Azobenzene Derivatives", Adv. Mater., **11**(1999), 675
- Natansohn, A., Azobenzene-Containing Materials; (1999), Wiley-VCH Verlag Gmbh (Weinheim)
- 18) Meerholz, K., Volodin, B. L., Kippelen, B. and Peyghambarian, N. : "A Photorefractive Polymer with High Optical Gain and Diffraction Efficiency Near 100-percent", Nature, **371**(1994), 497
- Burland, D. M., Miller, R. D. and Walsh, C. A. : " 2nd-order Nonlinearity in Poled-Polymer Systems",

Chem. Rev., **94**(1994), 31

- 20) Moerner, W. E. and Silence, S. M. : "Polymeric Photorefractive Materials", Chem. Rev., 94(1994) 127
- Ichimura, K. : "Photoalignment of Liquid-Crystal Systems", Chem. Rev., 100(2000), 1847
- 22) Delaire, J. A. and Nakatani, K. : "Linear and Nonlinear Optical Properties of Photochromic Molecules and Materials", Chem. Rev., **100**(2000), 1817
- 23) Watanabe, O., Tsuchimori, M., Okada, A. and Ito, H.
  : "Mode Selective Polymer Channel Waveguide Defined by the Photoinduced Change in Birefringence", Appl. Phys. Lett., **71**(1997), 750
- 24) Tsuchimori, M., Watanabe, O. and Okada, A. :
  "Temporal Stability of Second-Order Optical Nonlinearities Depending on Non-linear Optically Active Groups of Polyesters", J. Mater. Chem., 7(1997), 877
- 25) Batalla, E., Natansohn, A. L., Rochon, P. L. :
  "Optically Induced Surface Gratings on Azoaromatic Polymer Films", Appl. Phys. Lett., 66(1995), 136
- 26) Kim, D. Y., Tripathy, S. K., Li, L. and Kumar, J. : "Laser-Induced Holographic Surface Relief Gratings on Nonlinear Optical Polymer Films", Appl. Phys. Lett., 66(1995), 1166
- 27) Fukuda, T., Matsuda, H., Shiraga, T., Kimura, T., Kato, M., Viswanathan, N. K., Kumar, J. and Tripathy, S. K. : "Photofabrication of Surface Relief Grating on Films of Azobenzene Polymer with Different Dye Functionalization," Macromolecules, 33(2000), 4220
- 28) Labarthet, F. L., Buffeteau, T. and Souurisseau, C. : "Analyses of the Diffraction Efficiencies, Birefringence, and Surface Relief Gratings on Azobenzen-Containing Polymer Films", J. Phys. Chem. B, **102**(1998), 2654
- 29) Zettsu, N., Ubukata, T., Seki, T. and Ichimura, K. :
  "Soft Crosslinkable Azo Polymer for Rapid Surface Relief Formation and Persistent Fixation", Adv. Mater., 13(2001), 1693
- 30) Kawata, Y., Egami, C., Nakamura, O., Sugihara, O., Okamoto, N., Tsuchimori, M. and Watanabe, O. : "Non-Optically Probing Near-Field Microscopy", Opt. Commun., 161(1999), 6
- 31) Watanabe, O., Ikawa, T., Hasegawa, M., Tsuchimori, M., Kawata, Y., Egami, C., Sugihara, O. and Okamoto, N. : "Transcription of Near-Field Induced by Photo-Irradiation on a Film of Azo-Containing Urethane-Urea Copolymer", Mol. Cryst. Liq. Cryst., 345(2000), 305
- 32) Hasegawa, M., Ikawa, T., Tsuchimori, M., Watanabe, O. and Kawata, Y. : "Topographical Nanostructure Patterning on the Surface of a Thin Film of Polyurethane Containing Azobenzene Moiety Using the Optical Near Field Around Polystyrene Spheres", Macromolecules, **34**(2001), 7471
- 33) Ikawa, T., Hasegawa, M., Tsuchimori, M., Watanabe,O., Kawata, Y., Egami, C., Sugihara O. and Okamoto,N. : "Surface Deformation on Azobenzene Polymer

Film Induced by Optical Near-Field Around Polystyrene Microspheres", Synth. Metal, **124**(2001), 159

- 34) Ikawa, T., Mitsuoka, T., Hasegawa, M., Tsuchimori, M., Watanabe, O., Kawata, Y., Egami, C., Sugihara, O. and Okamoto, N. : "Optical Near Field Induced Change in Viscoelasticity on an Azobenzene-Containing Polymer Surface", J. Phys. Chem. B, 104(2000), 9055
- 35) Ikawa, T., Mitsuoka, T., Hasegawa, M., Tsuchimori, M., Watanabe, O. and Kawata, Y. : "Azobenzene Polymer Surface Deformation due to the Gradient Force of the Optical Near Field of Monodispersed Polystyrene Sphere", Phys. Rev. B, 64(2001), 195408
- 36) Kumar, J., Li, L., Jiang, X. L., Kim, D. -Y., Lee, T. S. and Tripathy, S. K. : "Gradient force: The Mechanism for Surface Relief Grating Formation in Azobenzene Functionalized Polymers", Appl. Phys. Lett., 72(1998), 2096
- 37) Bian, S., Li, L., Kumar, J., Kim, D. Y., Williams, J. and Tripathy, S. K. : "Single Laser Beam-Induced Surface Deformation on Aazobenzene Polymer Films", Appl. Phys. Lett., 73(1998), 1817
- 38) Kajiyama, T., Tanaka, K. and Takahara, A. : "Surface Molecular Motion of the Monodisperse Polystyrene", Macromolecules, **30**(1997), 280
- 39) Jean, Y. C., Zhang, R., Cao, H., Yuan, J. -P., Huang, C. -M., Nielsen, B. and Asoka-Kumar, B. : "Glass Transition of Polystyrene Near the Surface Studied by Slow-Positron-Annihilation Spectroscopy", Phys. Rev. B, 56(1997), R8459
- 40) Magonov, S. N., Elings, V. and Whangbo, M. H. : "Phase Iimaging and Stiffness in Tapping-Mode Atomic Force Microscopy", Surf. Sci., 375(1997), L385
- 41) Narita, M., Ikawa, T., Hasegawa, M., Tsuchimori, M. and Watanabe, O. : "Tg Dependence of Photo-Induced Nano-Fabrication on Azobenzene-Containing Polyurethanes", Polym. Prepr., Jpn., 49(2000), 3037
- 42) Takagi, H., Narita, M., Ikawa, T., Keum, C. -D., M., Tsuchimori, M. and Watanabe, O. : "Near-Field Induced Nanostructure Formation on the Surface of Azobenzene-Containing Organic-Inorganic Hybrids", Polym. Prepr., Jpn., **50**(2001), 2943
- 43) Hasegawa, M., Keum, C. -D. and Watanabe, O. : "Enhance Photofabrication of the Surface Nanostructure on Azobenezene Functionalized Polymer with Evaporated Au Nanoislands", Adv. Mater in press
- 44) Ikawa, T., Keum, C. -D., Takagi, H., Tsuchimori, M., Watanabe, O., Mori, W., Harada, M., Tawata, M. and Shimoyama, H. : "Near-field Optical Recording on Azopolymer Using a Sub-Microsecond Pulse", IEICE Trans. C, E85-C(2002), 1287
- 45) Mori, W., Tawata, M., Shimoyama, H., Ikawa, T., Tsuchimori, M. and Watanabe, O. : "Nano-Fabrication of Azopolymer by Scanning Near-Field Optical Microscope", IEICE Trans., (Jpn.) (in press)

- 46) Watanabe, O., Ikawa, T., Hasegawa, M., Tsuchimori, M. and Kawata, Y. : "Nanofabrication Induced by Near-field Exposure from a Nanosecond Laser Pulse", Appl. Phys. Lett., **79**(2001), 1366
- 47) Kawata, Y., Murakami, M., Egami, C., Sugihara, O., Okamoto, N., Tsuchimori, M., Watanabe, O. and Nakamura, O. : "Nonoptically Probing Near-Field Microscopy for the Observation of Biological Lliving Specimens", Appl. Phys. Lett., 78(2001), 2247

#### (Report received on Oct. 8, 2002)



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