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Photothermal Signal Detection on the Optical Waveguide

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A new detection technique of photothermal signal on the slab optical waveguide (SOWG) was demonstrated. Photothermal deflection of probe laser beam transmitted in the core layer of the SOWG was detected. Dependence of signal intensity and phase change on distance between the excitation and probe beam positions was measured. This method has high sensitivity to sample on the surface.

Slab optical waveguide (SOWG) has been applied to sensitive spectro-photometer and sensors. ¹⁻³ In these cases SOWG was used as an internal-reflection-element (IRE) of internal reflection method. In the present study SOWG is used as media in which photothermal effects such as photothermal deflection and thermal lensing effect occur.

Photothermal beam deflection method as well as thermal lensing method has so far been applied to the optical absorption measurement of sample surface. 4.5 In these methods signal generation is not efficient because cross section of the probe beam is much larger than the area where thermal signal generation occurs. The efficiency, however, becomes higher, if they are combined with the slab optical wave guide (SOWG) technique.

In the SOWG after the absorption of the exciting beam, two different types of photothermal effects will be produced. One is the ordinary photothermal effect as in the photothermal deflection spectroscopy and another is the effect characteristic to the SOWG. The former photothermal effect is considered to arise from the distribution change of refractive indices (along the direction) parallel to the optical waveguide surface. These effects come from the temperature distribution which is due to the thermal diffusion and the distribution of beam intensity, so that the photothermal signal can be detected even at relatively low chopping frequency. The latter effect will appeare as the change of light propagation in the waveguide due to the change of distribution of refractive indices in the waveguide. This effect is considered to arise from the change in distribution of refractive indices perpendicular to the optical waveguide surface, so that this could be detected at rather high chopping frequency. Since the thickness of core layer of single-mode SOWG is estimated as about 1 to 2 μ m,⁷ and to make the distribution of refractive indices within the thickness, the chopping frequency would be needed as high as 100 KHz or higher.

In either of detecting method presented here, the sensitivity of signal detection near the surface of SOWG would become higher than those in the ordinary bulk method of photothermal spectroscopy.

The optical waveguide was prepared by the ion exchange of a slide glass (Matsunami, S-3314) of microscopic use by dipping it in fused potassium nitrate for about 30 min at 400 $^{\circ}$ C. The wave guide thus prepared is appropriate for single-mode waveguide for the wavelength of He-Ne laser. As for the sample specimen 10 μ L rhodamine6G solution (100 μ mol/dm³) was dropped and dried on the waveguide surface. The diameter of the dried sample

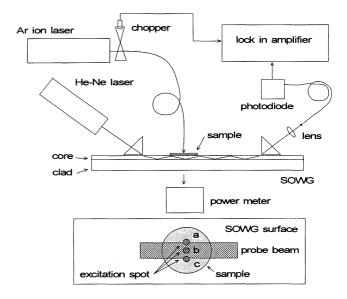


Figure 1. Schematic diagram of the photothermal signal detection system on slab optical waveguide. The sample was placed on the SOWG surface. The excitation beam from an Ar ion laser was introduced onto the SOWG through an optical fiber. The probe beam from He-Ne laser was coupled into the SOWG and outcoupled with prisms. Insert shows the relative position of the pump beam against the probe beam.

spot was about 8 mm. Figure 1 shows the experimental arrangement, where the Ar ion laser beam chopped at 120 Hz was lead through an optical fiber and was irradiated downward upon the optical waveguide as an excitation beam where the He-Ne laser beam was propagating. The spot size of the excitation beam on the SOWG surface was about 0.15 mm. The intensity of the excitation was varied in the range 0 to 10 mW which was monitored at the site of the irradiated spot.

The position of the irradiation spot of excitation beam was adjusted by using the mechanical stage. The He-Ne laser was used as a probe beam which was lead into the optical waveguide with the use of a coupling prism. The output beam from the decoupling prism on the waveguide was received by an objective lens (\times 10) and was lead through an optical fiber to the photodiode detector for the intensity measurement. The width of probe beam in the SOWG is about 0.7 mm. A lock-in amplifier (NF circuit block, LI575) was used for signal amplification.

Figure 2 shows the intensity of modulation of the probe beam and the phase change of the probe beam propagating in SOWG. When the position of excitation beam of Ar ion laser was swept as shown in Figure 1, two large peaks are found in the intensity change. The central position of the two large peaks, where the intensity is relatively low, corresponds to the instant when the excitation beam is near the center of the probe beam. The two

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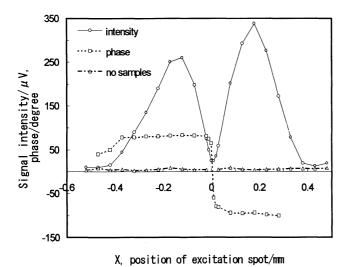


Figure 2. Intensity and phase change of photothermal deflection signals versus X, position of the excitation spot.

peaks correspond to the situation where the excitation beam is about 0.2 mm off the center point. For the plain SOWG surface without sample spot, no significant signals were observed.

On the contrary, the curve of the phase change show the opposite phase for the two peaks. The phase difference for the two peaks is exactly 180 degrees, and the turning position of the phase is exactly the instant when the excitation beam is near the center of the probe beam. These experimental results will be interpreted as follows: the instant when the excitation spot comes to the positions a and c, a little off the spot b the probe beam deflects most effectively. The direction of beam deflection at position a is opposite to that at c. This is consistent with the fact that the phase turns at the position b. These effects shows that the modulation of probe beam is caused by the photothermal beam deflection effect. Since the signal has non-zero intensity at the position b, there could be occurring a sort of thermal lensing effect. This effect, however, is considered to be small because the phase change from the position a to c is exactly 180 degrees, and the signal at the two positions has similar intensity.

Figure 3 shows the plots of the intensity of the beam deflection of probe laser with respect to the power of the irradiating beam. The proportional relationship is seen, as is considered to be supporting that the ordinary photothermal

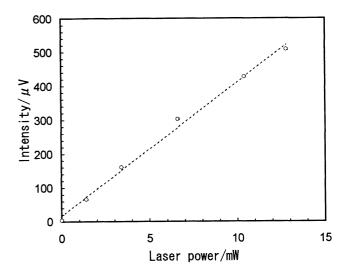


Figure 3. Relation between intensity of the photothermal deflection signal and power of the excitation beam.

phenomena is observed. Background signals for the conditions without the sample spot and without the excitation beam were 3.8 μ V and 3.5 μ V. The standard deviations were 0.03 μ V and 0.09 μ V, respectively. About 0.4 pmol of rhodamine6G is calculated to be in the spot area of the excitation beam using the values of the excitation spot size, the sample spot size and the volume of sample solution. The detection limit was about 10 fmol (S/B=2). This calculation was based on the assumption that sample was spread uniformly in the sample spot. Conclusively, the photothermal effect have been successfully observed in the optical waveguide and this method presented here using SOWG can detect ultra-low amount of substance on the waveguide surface.

References and Notes

- 1 K. Kato, Bunseki, 1995, 133.
- 2 P. W. Bohn, Prog. Anal. Spectrosc., 12, 41 (1989).
- 3 K. Kato, A. Takatsu, N. Matsuda, R. Azumi, and M. Matsumoto, *Chem. Lett.*, 1995,437.
- 4 L. Aamodt and J. Murphy, J. Appl. Phys., 52,4903(1981).
- 5 L. Aamodt and J. Murphy, J. Appl. Phys., 54,581(1983).
- 6 K. Tsunoda, H. Itabashi, and H. Akaiwa, *Anal. Chim. Acta*, **276**,133 (1993).