—Communication—

Monitoring of Photoinduced Surface Reactions by Using Glass Optical Waveguides

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1 INTRODUCTION

Techniques of optical waveguide (OWG) are useful for spectroscopies at surface,[1] besides they are indispensable for promising integrated optical devices. Itoh and Fujishima first applied OWG technique to electrochemical measurements.[2] They also reported the utility of OWG to monitor the photoinduced reaction at light-scattering particles by giving an example of the deposition of Ag onto laser-flashed TiO_2 powder.[3] We have been studying the chemical kinetics occurring at semiconductor surface by using transparent ultrasmall particles in solution.[4] In order to compare the kinetics, monitoring of the electron transfer at light-scattering larger particles was intended in the present study by using the OWG technique.

2 METHOD

According to the reported procedure,[2,3] an OWG layer was made by doping a glass plate (Matsunami, S-7224) with K^+ ions in molten KNO_3 at 370℃ for 0.5 - 8 h. Of the glass plate, only one side was employed because the OWG characteristics were different from those of the other side. A polarized 632.8 nm beam of 0.7 mW from an He-Ne laser (NEC, GLD-5370) was introduced into the OWG layer through an LaSF-08 coupler prism and then taken out by another prism. The length of the guided light was 18 mm. On the surface of the OWG, a container of 11 mm long was made for solution with a rubber frame and a thin Pyrex plate. The light intensity was monitored by a power meter (Advantest, TQ-8210) or a photomultiplier tube.

3 RESULTS AND DISCUSSION

In order to find the proper doping period, the sensitivity of OWG was measured as the change in the intensity of the guided light (I_{OWG}) by contacting the surface with aqueous solution of 1 mmol/dm^3 methylene blue (MB). For the OWG of two-hour doping, the sensitivity of m=0 mode was a maximum value as shown in Fig. 1 and this OWG was used in the

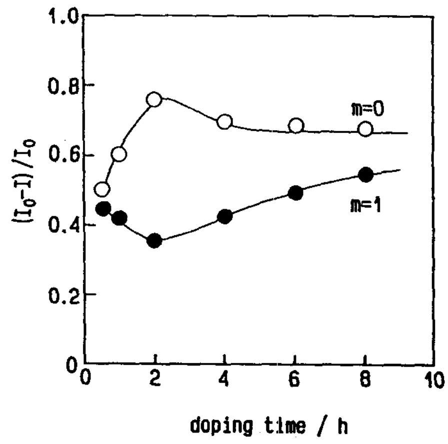

Fig. 1 Change in the intensity for the two modes of guided light with the adsorption of methylene blue on the surface is plotted as a function of doping time in the waveguide preparation.

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following experiments. The sensitivity factor, which is defined by the ratio of the absorbance for OWG to that of normal incidence, was about 40 cm^{-1}. This value is close to the reported maximum for alkaline-ion-exchanged glass OWG.[5)]

Monitoring of photoinduced surface reaction was performed by preparing the OWG adsorbed with TiO_2 powder (P-25)[3)] The adsorption of powder decreased I_{OWG} to 47 %. When MB was adsorbed on the powder, it was further reduced to one tenth. Figure 2 shows that the relative intensity of the guided light increases by the irradiation with UV-light (367 ± 16 nm) which is obtained from a 250-W Hg lamp through Toshiba UV-D36C and UV-35 glass filters. The part 10 mm long of OWG was irradiated from solution side similarly to the reported experimental set-up.[3)] By alternating filters, it was confirmed that MB was reduced by the electrons transferred from irradiated TiO_2. By adding 10 mmol/dm^3 of triethanolamine, the change in I_{OWG} increased by four times and it was proportional to the intensity of the UV-light.

When an N_2 pulse laser beam of 337 nm (ca. 4mJ) was used to irradiate the sample though a cylindrical lens, no change in I_{OWG} was observed for the TiO_2 OWG. Detectable I_{OWG} change in the experiment was estimated to be 0.05 % and 2 % in ms and μs regions, respectively. Because of the short duration and high density of the laser beam, the efficiency of electron transfer at the semiconductor surface may be extremely low, compared with the Hg lamp irradiation. This explanation is consistent with the size-dependence of the quantum yield in the previous paper.[4)]

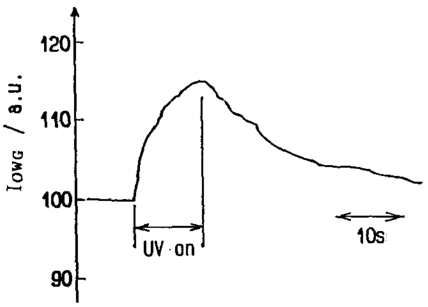

Fig. 2 Effect of UV-light irradiation on the relative light intensity of the dye-adsorbed TiO_2-OWG.

By using OWG, surface reaction can be monitored at a high sensitivity by a factor of several hundreds in principle.[5)] In actual experiment, however, S/N ratio is roughly proportional to the intensity of the monitoring light. In the present OWG with TiO_2 powder, it was only 23 μW. For transparent samples, monochromatic light of 30 mW can be used to monitor the absorption change. For light-scattering sample, the diffuse reflectance monitoring[6)] could be applied by using a similar intense light. In conclusion, the OWG method seems to be useful to monitor the absorbance only for the sample whose thickness is limited to less than the wavelength of the light.

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