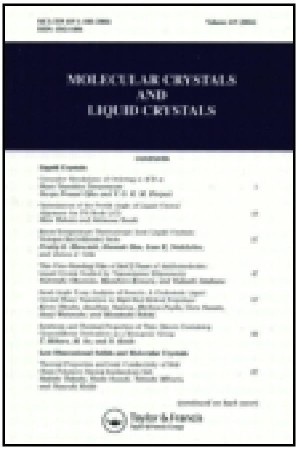

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SURFACE PLASMON RESONANCE ENHANCED SECOND-HARMONIC GENERATION IN POLED POLYMER THIN FILM

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SURFACE PLASMON RESONANCE ENHANCED SECOND-HARMONIC GENERATION IN POLED POLYMER THIN FILM

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In this paper we report surface plasmon resonance (SPR)-enhanced second-harmonic generation (SHG) in a poled polymer thin film using an attenuated total reflection (ATR) configuration (Kretschmann configuration). The second-harmonic (SH) light generated in this configuration is about 7000 times larger than that in the reflection geometry. This result is in agreement with the enhancement predicted by theoretical calculation.

Keywords: attenuated total reflection; SHG; surface plasmon resonance

INTRODUCTION

Surface plasmon resonance (SPR) is widely used as probes for ultirathin films and affinity sensors of biological molecules [1,2]. The SPR condition is achieved in an attenuated total reflection (ATR) configuration where a 40 nm-thick Au or Ag thin film is vacuum-evaporated at an ATR surface of a

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prism (Kretschmann configuration). In the resonance condition, we have more than 10-fold enhancement of the electric field of the incident light at the surface of the metal thin film. If we can use the field for second-harmonic generation (SHG), we can observe huge SHG intensity on resonance.

There have been several attempts that use SPR in a Kreteschmann configuration for SHG experiments. The SPR-enhanced SHG from a nonlinear optical dielectric medium was firstly reported by Quail *et al.* [3]. An x-cut quartz crystal was attached at the bottom of the prism and the SPR-enhanced SHG from the quartz crystal was observed. Although 20 years have passed since the first report, there are few reports on the SPR-enhanced SHG from nonlinear optical organic thin films [4,5]. If we can use 10^4-fold enhancement of SHG on resonance resulting from 10-fold enhancement of the fundamental field, the SHG intensity from 1 μm-thick poled polymer thin film will be equal to that from a 1 mm-thick the $LiNbO_3$ crystal in the angle phase matching condition. Such large enhancement can be used for the potential application for micrometer or nanometer sized optical devices.

In this paper we report about 7000-fold enhancement of SHG in a 28 nm-thick poled polymer thin film of PILC, whose chemical structure is shown in Figure 1 [6], in the SPR condition using a Kretschmann configuration. This value is constant with the enhancement of 10^4 predicted by the theoretical calculation using a Transfer Matrix technique [7].

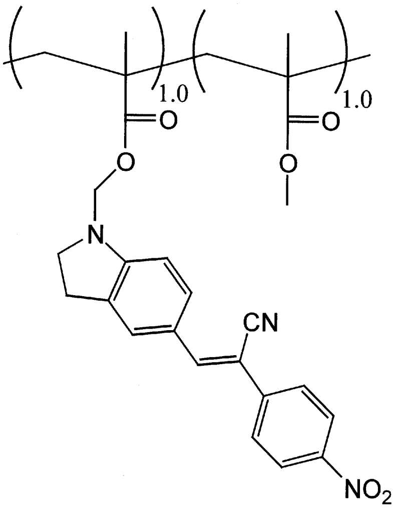

FIGURE 1 Chemical structure of PILC.

EXPERIMENTAL

The polymeric material, PILC, has a cyanostilbene type push-pull nonlinear optical chromophore as a side chain group as depicted in Figure 1 [6]. It has been reported that PILC shows a large second-order nonlinear suspectibility $\chi^{(2)} = 120\,\mathrm{pm/V}$ for the fundamental light at $\lambda = 1064\,\mathrm{nm}$ [6]. The average molecular weight M_w and glass transition temperature T_g was reported 1.4×10^4 and 127°C, respectively.

The polymeric material was dissolved in chloroform and was spin-coated at 2200 rpm on a glass substrate whose surface was covered with a 40 nm-thick Au thin film vacuum-evaporated. The thickness of the PILC film was estimated to be 28 nm by an SPR measurement with a semiconductor laser light ($\lambda = 635\,\mathrm{nm}$) assuming that the refractive index of the polymer thin film $n = 1.52$. The film was Corona-poled at 5 kV at a temperature of $T > T_\mathrm{g}$ [8]. The film was attached to the bottom of a BK7 prism with index matching oil as shown in Figure 2 (a).

The SPR-enhanced SHG measurement was performed with an Nd:YAG laser running at its fundamental wavelength $\lambda = 1064\,\mathrm{nm}$ at a reputation rate of 10 Hz. *p*-polarized incident light was chosen with a combination of a Gran-Laser prism and a half wave plate. The intensity was reduced less than $0.3\,\mathrm{mJ/mm^2}$ to avoid damage of the Au thin film. *p*-polarized second-harmonic (SH) light generated in the poled polymer thin film was detected with a photomultiplier in the total reflection direction after removal of the fundamental light with color and interference filters.

RESULTS AND DISCUSSION

Figure 3 shows the reflectivity profile (open circles) together with that of the SHG intensity (filled circles). The resonance condition was observed at approximately 42.5 degrees, where the incident light was absorbed in the Au thin film. The SHG intensity has a peak at around the resonance angle due to the enhancement of the fundamental field on resonance. The slight

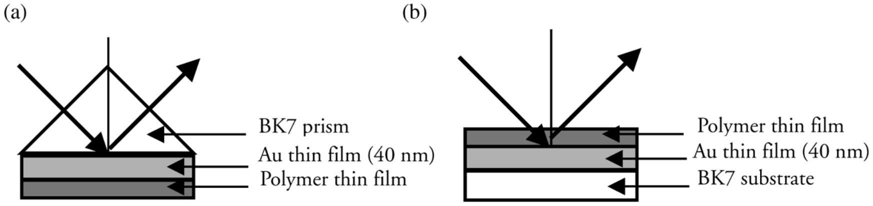

FIGURE 2 Optical setup for (a) the SPR-enhanced SHG geometry and (b) a Fresnel reflection geometry.

shift of the SHG peak to the lower angle of incidence with respect to the ATR dip is predicted by simulation using the Transfer matrix calculation [6]. We observed 7000-fold enhancement compared with the SHG intensity in a Fresnel reflection geometry illustrated in Figure 2 (b).

When the thickness of the polymer thin film is smaller than coherence length, the SHG intensity from the film, ${I_{\mathrm{polym}}}^{2\omega}$, can be described as

$$ {I_{\mathrm{polym}}}^{2\omega} = A\, d^{2}{}_{\mathrm{polym}} (F^{2\omega} \chi^{(2)}{}_{\mathrm{polym}} : (F^{\omega} E^{\omega})(F^{\omega} E^{\omega}))^{2}, \tag{1} $$

where E^{ω} denotes the electric field of the incident light and F^{Ω} does a factor of the enhancement at frequency Ω [9], A is a certain constant, and d_{polym} is a thickness of the polymer thin film. $F^{2\omega} \sim 1$ because the angle of incidence at 42.5 degrees was off resonance for 2ω light. Transfer matrix calculation [7] gives $F^{\omega} \sim 10$, resulting in the enhancement of 10^{4}. This value is in line with our result, the 7000-fold enhancement, shown in Figure 3.

The SHG intensity from a 1 mm-thick the $\mathrm{LiNbO_3}$ crystal in the phase matching condition, ${I_{\mathrm{LN}}}^{2\omega}$, can be described as

$$ {I_{\mathrm{LN}}}^{2\omega} = A\, {d_{\mathrm{LN}}}^{2} (\chi^{(2)}{}_{31} : E^{\omega} E^{\omega})^{2}, \tag{2} $$

where $\chi^{(2)}{}_{31} = 10\,\mathrm{pm/V}$ [10] is the susceptibility of the $\mathrm{LiNbO_3}$ crystal effective in the angle phase matching condition. The Eq. (1) and Eq. (2) suggest that the 1 μm-thick PILC polymer film with $\chi^{(2)}{}_{\mathrm{polym}} = 120\,\mathrm{pm/V}$ [6] in the SPR condition ($F^{\omega} \sim 10$) shows SHG activity almost equal to

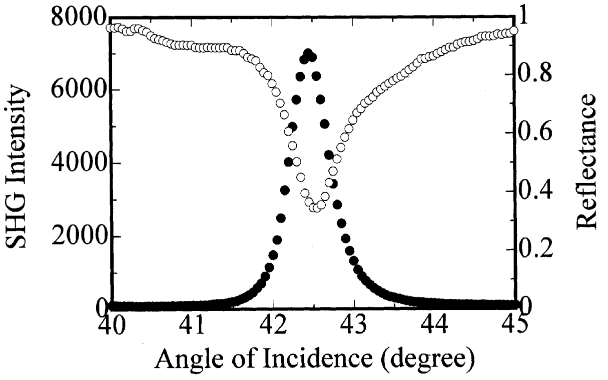

FIGURE 3 The ATR-scan profile for reflectance (open circles) and the SHG intensity (filled circles).

that from the 1 mm-thick $LiNbO_3$ crystal in the phase matching condition. Since the SPR-enhancement technique is quite simple, it will be compatible with the micrometer or nanometer sized optical integrated circuits in future.

CONCLUSION

We have reported the SPR-enhanced SHG in poled polymer thin film in a Kretschmann configuration. The SH light generated in this configuration is about 7000 times larger than that in a Fresnel reflection geometry. This technique will be compatible with the micrometer or nanometer sized optical integrated circuits.

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