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Study of SHG from CuttbPc LB film/metal Interface

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1. Introduction

As one of the most primitive nonlinear optical phenomena, second harmonic generation (SHG) has been investigated for half a century and it has become a very useful spectroscopic tool in the study of surface and interface. Under the electric dipole approximation, it was theoretically shown that SH signal cannot be generated in a centrosymmetric system. However, the generation of SH signal from the centrosymmetric molecules such as CuPc[1, 2] has been detected. In our recent experiments, an enhancement of SH signal was detected from the CuPc derivative, CuttbPc LB films deposited on metal coated glass substrate[3]. According to Yamada *et al.*[4], the SHG from CuPc film deposited on glass substrate was attributed to the resonant enhancement of the electric-quadrupole transition based on an orientation gas model. On the other hand, based on our surface potential studies, it is found that excessive charges are transferred from metal to the CuttbPc LB film until a thermodynamic equilibrium is established at the interface between LB film and metal[5,6]. Due to the presence of these exchanged charges, a very high electric field with an order of 10^7-10^8 V/m is created. The symmetry of CuttbPc LB film is broken due to the space charge induced electric field (SCIEF) and an electric field induced SH polarization is created at the space charge region of CuttbPc LB film.

2. Experiment

Preparation of CuttbPc LB film

As described in our previous papers[5,6], the monolayer of CuttbPc was formed on the pure water surface by spreading its xylene solution (1 mmol/L) using a micro syringe. A thin glass slide coated with evaporated metal electrode (Au, Al) was used as the substrate. The first layer of CuttbPc was transferred onto substrate by the conventional vertical depositing method while the surface pressure was kept on 20 mN/m. After the deposition of the first layer, the 2nd, 3rd, ..., and *n*th layer were deposited successively by the horizontal lift method. The thickness of the CuttbPc monolayer was determined about 1.7 nm by the X-ray diffraction (XRD) measurement.

SHG measurement

An optical parametric oscillator (OPO) excited by third-harmonics of YAG (yttrium aluminum garnet) laser was used as the pulsed fundamental laser light with a duration of 10 ns and repetition rate of 10 Hz. The reflection SH light was detected by a photomultiplier tube (PMT) through IR cut filter, lenses and monochromator. Finally, the signal from PMT was integrated by the boxcar, and the output values from the boxcar corresponded to the intensity of reflection SHG. The incident angle θ of the fundamental light was 45°.

3. Results and Discussion

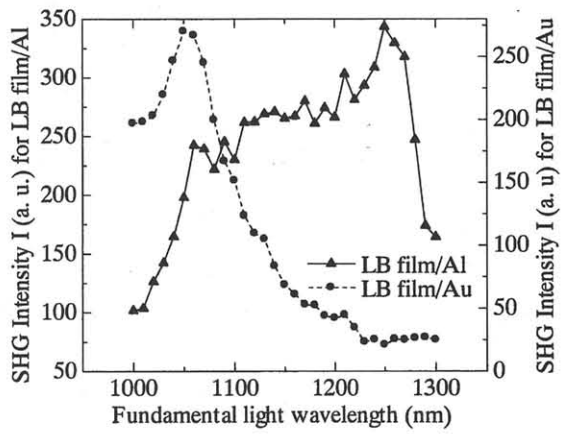

Figure 1. SHG spectra from CuttbPc LB film/Al and CuttbPc LB film/Au structure.

Figure 1 shows the reflected SHG spectra measured from CuttbPc LB film-Al and CuttbPc LB film-Au structures. It is shown that in the case of SHG from CuttbPc LB film/Al structure, relative SHG intensity has two peaks at the wavelengths around 1050 nm and 1250 nm, respectively, while in the case of SHG from LB film/Au element, only one peak at the wavelength around 1060 nm is found. The intensity of SHG from film/Au element decreases as the wavelength of fundamental optical wave increases from 1050 nm to 1300 nm. It has been known that the sharp peak observed in the SH spectra at the wavelength around 1050 nm was attributed to the resonance enhancement of the electric quadrupole transition. But what is the origin of the peak at the

wavelength of 1250 nm? The difference between these two structure is the surface potential or the SCIEF. The saturated surface potential of LB film/Al structure interface is about 1.0 V while the one of film/Au interface is near zero. Consequently, the SCIEF inside of LB film on Al electrode is about 1.0V/20nm=5×10^7 V/m while the SCIEF inside of LB film on Au is 0. Then we suppose that the SHG from the LB film/Al structure is contributed by electric quadrupole and EFISHG effects while the one from the LB film/Au structure is only generated by the electric quadrupole process.

The SHG optical wave in the SCR of LB film will obey the following electromagnetic wave equation

$$\nabla\times\nabla\times E(2\omega)+\frac{\ddot{\varepsilon}(2\omega)}{c^2}\frac{\partial^2 E(2\omega)}{\partial t^2}=-\frac{4\pi}{c^2}\frac{\partial^2 P(2\omega)}{\partial t^2} \quad ,(1)$$

Where P(2ω) is the SH polarization contributed by electric quadrupole and SCIEF and can be written as

$$P(2\omega)=\chi^D E(\omega)E(\omega)E^s+\chi^Q : E(\omega)E(\omega)ik$$

E^s is the SCIEF, E(ω) is the electric field of incident light, χ^D and χ^Q are the nonlinear susceptibilities of electric field induced SHG effect and electric quadrupole effect, respectively.

In order to proof our hypothesis, we then calculated the nonlinear susceptibilities of electric quadrupole and EFISHG process. Our calculation is based on the angular dependence experiment. In the experiment, we fixed the polarizer (analyzer) angle γ (δ) at 0 or 90° and changed the analyzer (polarizer) angle δ (γ) from 0 to 90°, and we can get four groups of SHG intensity as function of the polarized angle. After the calculation based on the experimental data, we can get the components of χ^D and χ^Q[7]. It is shown that with the fundamental wavelength increasing from 1100nm to 1200nm, the electric quadrupole effect becomes weak while the SCIEF makes a main contribution to the SHG from LB film/Al structure.

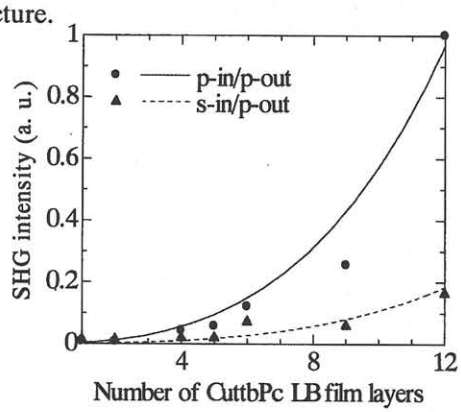

Figure 2 Reflected SHG intensity as a function of LB film thickness. Lines are the calculated data, dots represent the experimental results.

Figure 2 shows the SHG intensity as a function of the thickness of LB film *d*. In the figure, the dots present the experiment results and the lines are the calculated data normalized to experiment results. A good agreement between the calculated and is shown between the analysis and experiment.

In our present study, only the electric field induced by the space charges gives rise to a contribution to what we analyzed EFISHG. An external static electric field is about to be applied to the element and it is expected that the SCIEF would be determined by such a method. Furthermore, the surface plasmon effect at the interface need to be examined although we found that the SHG generated by bare metal film is very weak as be compared with that from CuttbPc LB film/metal interface. Further investigation is under proceeding.

Acknowledgments

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