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Electric Field Induced Second Harmonic Generation from Vacuum Evaporated Metal-Phthalocyanine Film/Metal Electrode Interface

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1. Introduction

As one of the most widely used electronic functional materials, Phthalocyanine (Pc) and its derivatives have been investigated for many years due to their excellent thermal and chemical stability [1]. Recently, the Pcs have attracted many attentions in nonlinear optics, as well. Although under the electric dipole approximation, the second harmonic generation (SHG) is forbidden because of the centro-symmetry of Pc molecular system (fig. 1), the extensive delocalized 2-demensional π electrons of Pcs induces high order nonlinear polarizations and an effective second order dipole polarization gives rise to the radiation of SHG. Kumagai and Hoshi *et. al.* [2,3] have detected the SHG from copper phthalocyanine (CuPc) film. According to Yamada *et. al.* [4], the SHG from CuPc film was attributed to the resonant enhancement of the electric-quadrupole transition based on an orientation gas model. In our recent work [5], it has been found that static electric field broke the symmetry of Pc film and electric field induced second harmonic generation (EFISHG) could be detected. In this article, we report and analyze the second harmonic (SH) signal generated respectively by external applied bias and space charges at the interface of Pc film/metal electrode.

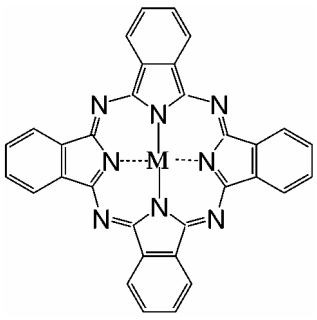

Figure 1. Chemical structure of metal-phthalocyanine molecule (M: Cu, Zn *etc.*).

2. Experiment

Preparation of sample

As described in our previous paper [6], copper phthalocyanine (CuPc) or Zinc phthalocyanine (ZnPc) was deposited on glass slide coated with metal (Au, Al etc.) electrode. Considering the SHG measurement, we prepared two kinds of samples: (1) ZnPc/Al and (2) Au/CuPc/Au.

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. SH signal was recorded by a photomultiplier tube (PMT) and integrated by the boxcar. The incident angle θ of the fundamental light was 45°.

(1) *ZnPc/Al sample.* The thicknesses of Al and ZnPc were about 30 nm. The reflected SHG was measured while a red light LED (wavelength: 660 nm, power: 0.4 mW) was used to illuminate the ZnPc film to cause changes of space charges.

(2) *Au/CuPc/Au sample*. The thicknesses of Au and CuPc were about 5 and 100 nm respectively. The transmitted SHG was measured while a DC bias was applied to both top and bottom Au electrodes.

3. Results and Discussion

In refs. [5, 6], it has been pointed out that in Pc film, the effective electric dipole polarization consisted of two terms when there was static electric field inside of Pc film: electric quadrupole induced and static electric field induced terms, as given by following expressions:

$$\mathbf{P}^{\mathrm{Q}}(2\omega) = -\nabla \cdot [\chi^{\mathrm{Q}}(2\omega;\omega,\omega) : \mathbf{E}(\omega)\mathbf{E}(\omega)], \quad (1)$$

$$\mathbf{P}^{\mathrm{dc}}(2\omega) = \chi^{\mathrm{dc}}(2\omega;\omega,\omega,0) : \mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}^{\mathrm{dc}}(0). \quad (2)$$

Where E^{dc} is the static electric field (external bias induced or space charge induced), E(ω) is the electric field of incident fundamental laser, χ^{Q} and χ^{dc} are the nonlinear susceptibilities of electric quadrupole effect and EFISHG effect, respectively.

The SHG optical waves in Pc film obey the following electromagnetic wave equation

$$\nabla\times\nabla\times\mathrm{E}(2\omega)+\frac{\varepsilon}{c^2}\frac{\partial^2\mathrm{E}(2\omega)}{\partial t^2}=-\frac{4\pi}{c^2}\frac{\partial^2\mathrm{P}^{\mathrm{NLS}}(2\omega)}{\partial t^2}, \quad (3)$$

where $\mathbf{P}^{NLS}=\mathbf{P}^{Q}+\mathbf{P}^{dc}$. By solving eq. (3) under appropriate boundary condition, one can get the electric field amplitude

E(2ω) and the intensity *I*(2ω).

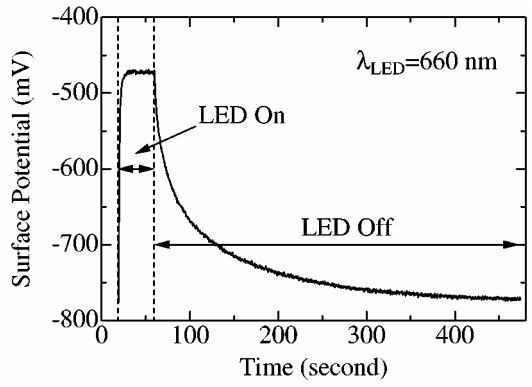

Figure 2 surface potential of ZnPc/Al sample.

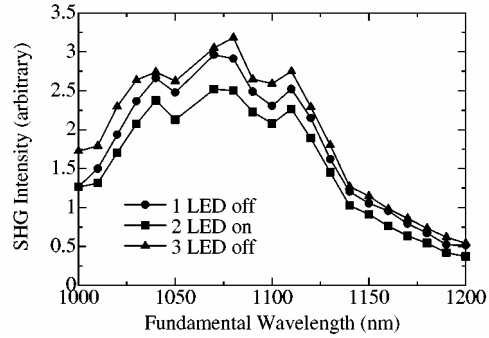

Fig. 3 SHG spectra of ZnPc/Al sample.

Figure 2 shows the experimental result of light response of surface potential built at ZnPc film and Al interface measured by Kelvin probe method. Obviously, the electric field induced by surface potential varies between two stable states when the LED light switched on/off for enough time. Consequently, it is expected to detect the change of SHG intensity when the light is on/off. In fig. 3, one can find that under the illustration of LED light, the SHG intensity decreases due to the change of electric field, as shown in fig.2. After turning off the light and waiting for about 10 minutes, the SHG intensity increases.

Figure 4 is the experimental and theoretical data of SHG intensity versus the external applied bias. In experiment, the wavelength of fundamental laser was 1100 nm, a dc bias was applied to the top and bottom Au electrodes. The thickness of CuPc film was about 100 nm after calibration. In theoretical simulation, the four-layer model was used to analyze the linear and nonlinear process, where the thickness of normal region is 0 (for detail, see ref. [5]). The dielectric constant of Au film is ε(ω)=-53.5+3.8i, ε(2ω)=-5.84+2.1i [7]. Other parameters can be found in ref [5]. In fig. 4, the dots represent our experimental data and the dashed line is the simulation result. The calculated result shows a quadratic relation between SHG intensity and external voltage. A good agreement can be found between the experimental data and theoretical simulation.

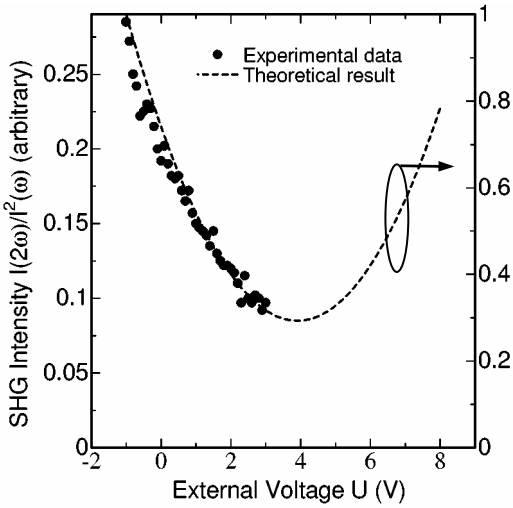

Figure 4. SHG intensity versus external bias

4. Conclusion

In this article, the EFISHG from vacuum evaporated metal-phthalocyanine film was examined both in experiment and theoretical analysis. Reasonable results were obtained in cases of space charge induced electric field and external applied bias.

Acknowledgment

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