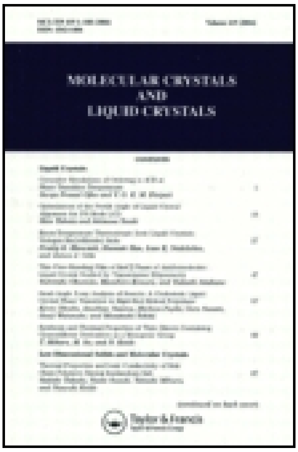

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In-Situ Observation of SHG and its Origin in Vacuum Deposited Copper Phthalocyanine Film

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IN-SITU OBSERVATION OF SHG AND ITS ORIGIN IN VACUUM DEPOSITED COPPER PHTHALOCYANINE FILM

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Abstract In situ observation system of second harmonic generation (SHG) during vacuum deposition has been constructed. It allows us to observe SHG from transmitted and reflected directions. The advantages of the system is summarized in the following two points: (1) Detailed dependence of SHG on film-thickness can be easily obtained. (2) The measurement can be achieved without exposing films to the atmosphere. This system was applied to vacuum evaporated films of copper phthalocyanine (CuPc) to clarify the origin of SH activity in such a centrosymmetric molecule. We suggest the importance of quadrupolar contribution on the basis of the thickness dependence of SHG and the comparison with the theoretical analysis.

INTRODUCTION

Second harmonic generation (SHG) provides us with a useful tool for assessing surface molecular orientation and its symmetry. Among several advantages of SHG technique, the possible application to in-situ condition is one of the most important features in addition to its high sensitivity. Because of the coherent nature of SHG process, the signal has good directionality, which enables us to use this technique in a variety of circumstances such as at the air/water interface and in high vacuum.

In this paper, we report an in-situ observation system of SHG during vacuum evaporation. The main advantages are: (1) The precise film-thickness dependence of SHG can be measured. (2) We can always use a fresh sample surface without exposing it to the atmosphere. As the first set of examples, we will present the preliminary experimental result in copper phthalocyanine (CuPc) films.

CuPc is a planar π-conjugate molecule with the centrosymmetric D_{4h} structure, so that SHG is not allowed by the usual electric dipolar response mechanism. Recently, however, relatively strong SHG activity, $\chi_{ZYY} = 4.51 \times 10^{-8}$ esu,was reported in its vacuum deposited films.[1,2] Kumagai et al.[2] proposed a model that the film structure is asymmetric along the direction of thickness, which corresponds to the point group symmetry of $C_{\infty v}$ structure, so that SHG is allowed by the electric dipolar mechanism. However, the details of the asymmetric structure is unknown at present.

On the other hand, Qin et al.[3] succeeded in explaining SHG observed in thin films of the C_{60} molecule,[4,5] by taking into account a quadrupolar mechanism. Since both CuPc and C_{60} are π-conjugated molecules, this mechanism may also contribute to the SHG in CuPc films. Thus, under this mechanism, SHG activity in CuPc arises in centrosymmetric structure without requiring the existence of the asymmetry along the direction of thickness, as suggested by Kumagai et al.[2]

We will report the film-thickness dependence of SHG experimentally observed in the transmitted direction and the simulated results in the same geometry. The comparison between the experimental and simulated results suggests the quadrupolar mechanism.

EXPERIMENTAL SETUP

Figure 1 shows optical arrangement around a vacuum chamber for evaporation (Kitano Seiki Co. Ltd.). A substrate glass plate is placed in a Cu mount whose temperature can be regulated by liquid flow. The mount can be rotated by 90°, so that the substrate normal can be oriented toward the evaporation source in the bottom and can be faced

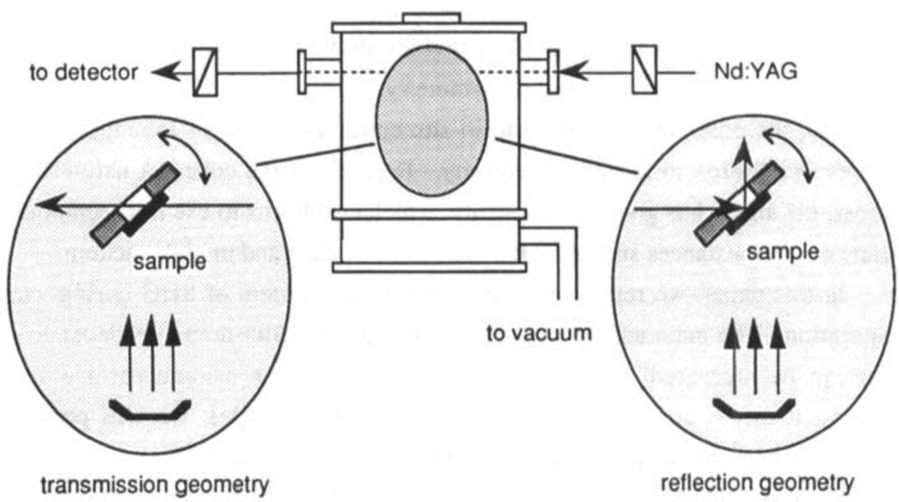

FIGURE 1 Optical arrangement for in-situ SHG observation during vacuum deposition.

toward the beam propagation direction. In the present experiment, the angle was fixed so that the incident radiation beam and the evaporating material beam made 45° with respect to the substrate normal. The substrate temperature was kept at room temperature without special temperature regulation.

The vacuum chamber was evacuated down to 1.5×10^{-5} Torr by an oil diffusion pump. CuPc after purification by sublimation was evaporated at the rate of about 5 nm/min. Since windows for optical observation have cover guides to prevent the deposition of CuPc on the window surfaces, the transmittance change through the optical view ports is negligible. The fillm thickness was monitored by Leybold Inficon XTM/2 and was calibrated by direct observation of the cross section of the film by scanning electron microscopy (Hitachi S900).

SHG was observed in transmission and reflection geometries through the optical view ports. For the transmission geometry, the fundamental beam from a Nd:YAG laser (1064 nm, 12 Hz, Quanta-Ray DCR-11) was cast upon the sample surface, and the emitted SHG was observed through a glass substrate. For the reflection geometry, the fundamental beam was cast upon the sample through the glass substrate, and the reflected SH light after passing through the glass substrate was detected.

EXPERIMENTAL RESULTS

Figure 2 shows the thickness dependence of SH light intensity observed in

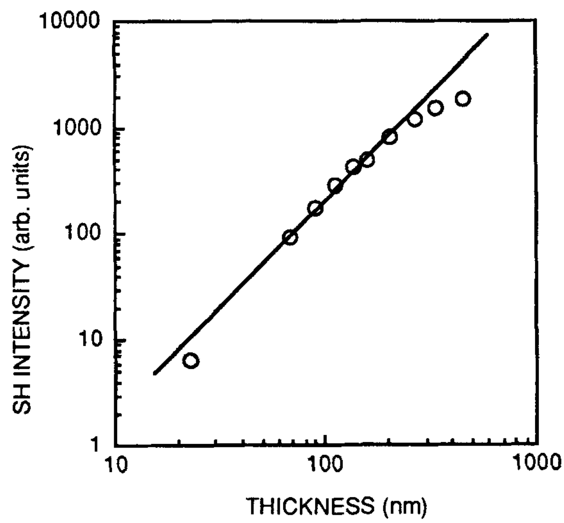

FIGURE 2 Thickness dependence of SH light intensity observed in transmission geometry.

transmission geometry. The polarization condition used was s-p; p-polarized SHG by s-polarized incident radiation. As shown by a solid line, a quadratic dependence is observed in the middle region between 70 nm ~ 200 nm. However, the deviation from the quadratic dependence is observed in thiner and thicker thickness regions.

The deviation from the quadratic dependence in the thicker region was observed below 100 nm by Kumagai et al.[2] in reflection geometry.. We have observed essentially the same thickness dependence in reflection geometry. The totally different thickness dependences in transmission and reflection geometries are explainable within the framework employed by Kumagai et al.[2] The details will be reported in a separate paper.

ANALYSIS AND DISCUSSION

We consider a three-layer model where the top and bottom layers are isotropic linear material and the middle layer is uniaxial nonlinear material whose optical C_∞ axis is normal to the layer surface. Kumagai et al. used this model with the assumption of the electrical dipolar mechanism.[2] According to this mechanism, nonlinear polarization is expressed as

$$P_i = \Sigma\, \chi_{ijk} E_j E_k \tag{1}$$

where $\chi_{113}=\chi_{223}$, $\chi_{311}=\chi_{322}$, and χ_{333} are nonzero components for $C_{\infty v}$ system, where 3 corresponds to the C_∞ axis. On the other hand, Qin et al. used a three-layer model with the assumption of the electrical quadrupolar mechanism,[3] where nonlinear quadrupole moment is expressed as

$$Q_{ij} = \Sigma\, \Gamma_{ijkl} E_k E_l. \tag{2}$$

For $C_{\infty v}$, $D_{\infty h}$ and K_h symmetries, there are 21 nonzero components that have the forms Γ_{iiii}, Γ_{iijj}, Γ_{ijij}, and Γ_{ijji}. For $C_{\infty v}$ and $D_{\infty h}$ symmetries, there are four independent components. For K_h symmetry, there is only one independent component. In the present study, we reduced the independent components into one according to K_h symmetry, for simplicity; $\Gamma_{iiii} = -2\Gamma_{iijj} = (4/3)\Gamma_{ijij} = (4/3)\Gamma_{ijji}$.

We calculated the thickness dependence of SHG based on these two models. The middle layer was treated as a uniaxial and absorbing medium by using Kumagai et al.'s dielectric constants of CuPc film.[2] In the middle layer, a fundamental electric field is expressed as the sum of forward and backward waves. All nonlinear polarizations that arise from the products of these waves were considered. The dielectric constant of the glass substrate was 2.2.

Figure 3 shows the calculated result of the thickness dependence of SHG (s-p polarization condition) in transmission geometry. The result clearly shows the difference between two mechanisms. In the figure, relative SH intensities in two mechanisms cannot be compared, since the absolute values of χ's and Γ's are not known. In the electrical dipolar model (dotted curve), SH light intensity increases quadratically with the thickness below 60 nm thickness, as shown in Fig. 3. On the other hand, the electrical quadrupolar model (solid curve) shows that the quadratic dependence occurs only tranisiently within the middle thickness range around 80 nm, as shown in Fig. 3, or more strictly the dependence is 2.6th power below about 70 nm.

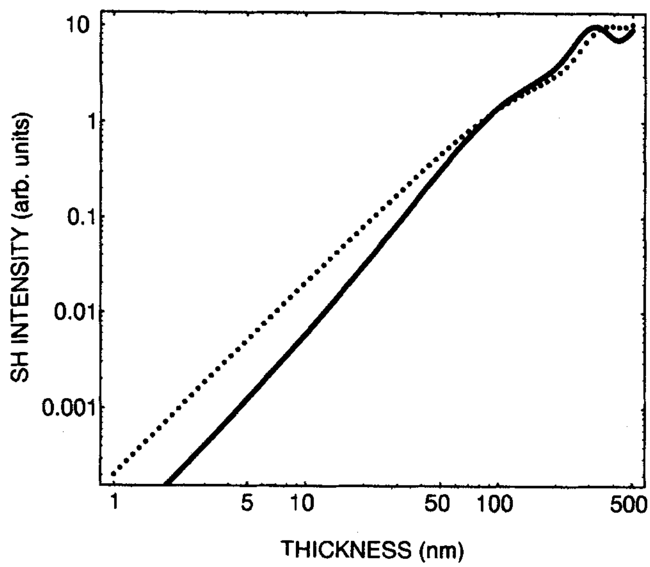

FIGURE 3 Simulated results of thickness dependence of SH light intensity in transmission geometry. Dotted and solid curves are for electric dipole and electric quadrupole models, respectively.

According to the preliminary data shown in Fig. 2 and the simulation shown in Fig. 3, we can conclude that SHG in CuPc film originates from quadrupolar mechanism. Further experiments, particularly in thin films, are now going on in our laboratory.

CONCLUSION

In-situ observation system of SHG during vacuum evaporation was constructed. The system allows us to measure precise thickness dependence of SH light intensity without exposing the film to the atmosphere. Preliminary experiment in vacuum deposited CuPc films and the comparison with the theoretical analysis suggest the origin of SHG to be quadrupolar mechanism.

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