Luminescence quenching of an ultrathin tetraphenylporphyrin film on a conductive SnO$_2$ substrate

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(Received 16 June 1986)

Absorption and luminescence spectra of ultrathin tetraphenylporphyrin (H$_2$TPP) films evaporated on SnO$_2$ substrates have been measured *in situ* in a vacuum of 2×10^{-6} Pa at 100 K. The luminescence intensity from a H$_2$TPP film on a SnO$_2$ substrate having a conductivity of 77 Ω^{-1}cm^{-1} is found to be 10 times smaller than that from a H$_2$TPP film on a substrate of conductivity 4.5×10^{-3} Ω^{-1}cm^{-1}. This quenching of the luminescence intensity occurs in films thinner than 10 Å, where most of the H$_2$TPP molecules are directly attached to the SnO$_2$ substrate. We propose a modified charge-transfer model for the quenching mechanism, in which the transfer efficiency depends on the charge density of conduction electrons in the SnO$_2$ substrate.

I. INTRODUCTION

Certain kinds of dye molecules adsorbed on semiconductor surfaces behave as spectral sensitizers. In such an interface system, photocarriers can be generated in the semiconductor through excitation of dye molecules with photons of energies less than the band-gap energy of the semiconductor. Recently, this effect, called dye sensitization, has become very important in the development of solar-energy conversion systems with high efficiency.[1] The mechanism of this effect has been explained in terms of the following processes. First, the π electron of the dye molecule is excited to the lowest singlet state by a photon. This molecular excitation induces a charged carrier in the semiconductor. Two phenomenological models have been proposed to explain the carrier generation. One is a charge-transfer model[2] in which the electron photoionized from the molecule is directly transferred into the conduction band of the semiconductor. The other is an energy-transfer model[3] in which electron-hole pairs are created through energy transfer by deexcitation of the photoexcited molecule. In the field of photoelectrochemistry, dye sensitization has been studied primarily with the use of photovoltaic cells because the photocurrent can be directly measured using such cells.[1,4] Many of these experimental results[4] support the charge-transfer model. Tanimura et al.[5] have measured the fluorescence-excitation spectra of tetraphenylporphyrin (H$_2$TPP) films on SnO$_2$ in order to investigate the first and the second steps of the photosensitization process. They have observed luminescence quenching caused by the charge transfer from H$_2$TPP to SnO$_2$. In this interface system, however, the electronic structure is not fully analyzed, partly because absorption measurement is very difficult to carry out for a very thin film. There have been only a few experimental studies which investigate the electronic properties of this system through impurity doping of the semiconductor. Hitherto, the nature of the semiconductor electrode has not been well characterized.

We have measured absorption and luminescence spectra of the H$_2$TPP film on SnO$_2$ substrates. It is found that the luminescence intensity depends on the conductivity of SnO$_2$. Our experimental results support the charge-transfer model in which the previous model is somewhat modified. We discuss the charge-transfer mechanism by taking the conductivity of the semiconductor into account.

II. EXPERIMENTAL

Figure 1 shows our experimental set up for *in situ* measurements of absorption and luminescence spectra of ultrathin films. The bell jar is evacuated down to a pressure of 2×10^{-6} Pa by an oil-diffusion pump with a liquid-nitrogen trap. Reagent-grade ultrasensitive colorimetric H$_2$TPP obtained from Tokyo Kasei Co. is purified by the method reported by Barnett et al.[6] It is subsequently recrystallized twice in a chloroform solvent. As shown in Fig. 1 the purified H$_2$TPP molecules are evaporated in vacuum by heating them on an alumina boat by a tungsten filament. Two substrates of optically flat fused-quartz (SiO$_2$) plates, one bare and the other covered with the SnO$_2$ film, are placed at the center of the copper-metal shield which is cooled to about liquid-nitrogen temperature in order to minimize contamination of the film by residual gas. The substrate temperature is kept at 100 K. The substrate covered with SnO$_2$ film is prepared by evaporation in another vacuum bell jar, where a pellet of
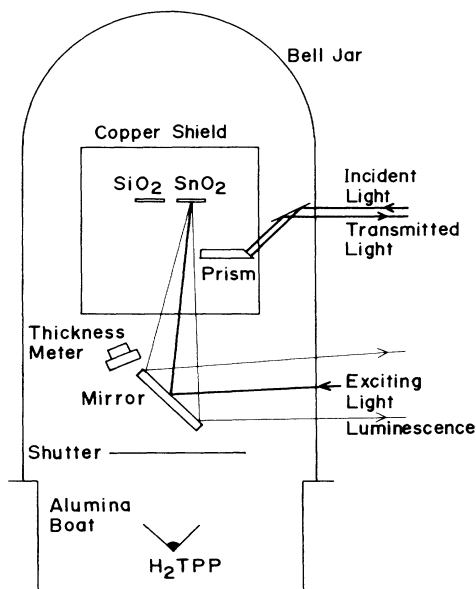
FIG. 1. Schematic drawing of the sample preparation and experimental set up for absorption and luminescence measurements in the ultrahigh vacuum bell jar. Two quartz plates with and without SnO_2 evaporation are set side by side as the substrates. A rotatable mirror and a trapezoidal prism are used for the luminescence and absorption measurements, respectively.

99.99% pure SnO_2 is heated by an electron beam. This SnO_2 film has a thickness of about 1000 Å and conductivity of 4.5×10^{-3} Ω^{-1}cm^{-1}. For the preparation of SnO_2 with a high conductivity of 77 Ω^{-1}cm^{-1}, 5 mol% of WO_3 is added to the SnO_2.[7] The evaporated SnO_2 film is annealed for several hours at 750 K to increase the conductivity and to improve the uniformity of the films. In our measurements, the bare SiO_2 plate is used as a reference for the SnO_2-coated plate. The average thickness of the film is measured by an ULVAC-CRTM-1 deposition monitor with a quartz oscillator. The deposition rate of H_2TPP is 0.5 Å/sec.

For the luminescence measurement, 514.5-nm light from an Ar$^+$ laser is focused on the film through a rotatable mirror. The output power of the laser is kept at about 10 mW to prevent the film from heating up. The luminescence is analyzed using a Nikon G-250 monochromator with a grating blazed for 750 nm. The spectral resolution is 5 nm.

For the absorption measurement, the highly conductive SnO_2 and H_2TPP molecules are evaporated at the bottom of a trapezoidal quartz prism by the method mentioned above. Absorption spectra of films as thin as 1 Å are successfully obtained by measuring the light which is totally reflected 24 times at the bottom of the prism. A tungsten halogen lamp is used as the light source and a Nikon G-250 monochromator with the reciprocal dispersion of 3 nm/mm as the spectral analyzer. The details of this method have been reported previously.[8]

III. RESULTS AND DISCUSSION

A. Absorption spectra

Figure 2 shows absorption spectra of the H_2TPP films with average thicknesses between 1 and 40 Å on the SnO_2 substrate. The temperature is kept at 100 K to prevent crystallization of the H_2TPP film. The ordinate represents the optical density measured by the total-reflection method. It should be noted that absorption spectra of ultrathin films with an average thickness of only 1 Å can be measured by this method.[8] The spectrum exhibits Q absorption bands corresponding to the π-π^* transition of H_2TPP molecules in solution.[9] The Q band is split into two subbands named Q_x and Q_y because of the twofold symmetry of two hydrogen atoms located near the center of the H_2TPP molecule, as shown in the inset of Fig. 2. Following the notation by Platt,[10] the Q_x band consists of a zero-phonon band $Q_x(0,0)$ and a one-phonon band $Q_x(1,0)$. Similarly, the Q_y band consists of $Q_y(0,0)$ and $Q_y(1,0)$, the zero- and one-phonon bands, respectively.[9,11] The first number in parentheses represents the phonon number in the excited state, while the second number, 0, corresponds to that in the ground electronic state. The peak energies of all the four bands shift slightly to the lower-energy side with increasing thickness in the range below 13 Å, while the full widths at half maximum of all the absorption bands are independent of film thickness over the measured range up to 40 Å. Even et al.[12] have reported that the broadening of the Q absorption band of H_2TPP dissolved in benzene is caused by superposition of many intramolecular vibrations of small energies and also inhomogeneity associated with random orientation of neighboring molecules. The observed linewidth is nearly equal to that of our results
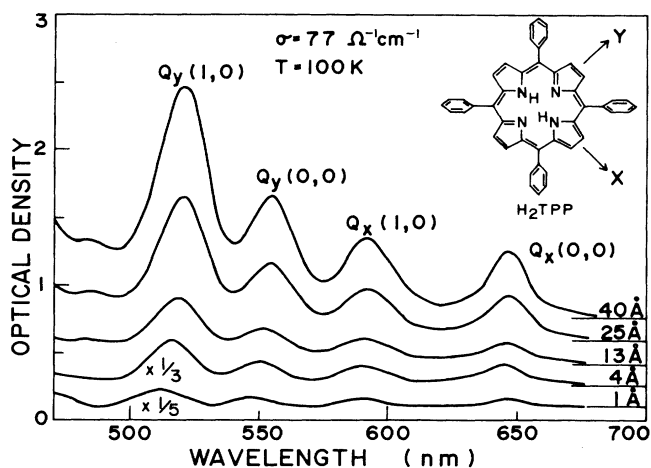

FIG. 2. Absorption spectra of the H_2TPP films with different thicknesses on the SnO_2 substrate at 100 K. The conductivity of the SnO_2 substrate is 77 Ω^{-1}cm^{-1}. Inset shows the structure of the H_2TPP molecule. The connected four phenyls are perpendicular to the plane of a porphyrin skeleton.

shown in Fig. 2. These observations suggest that the broadening in our system is also due to the mechanism similar to that in solution, where the inhomogeneity comes from random orientation of H_2TPP molecules with respect to the SnO_2 substrates in the case of thin films and with respect to neighboring H_2TPP molecules in the case of thick ones.

B. Luminescence spectra

Luminescence spectra of the H_2TPP films with thicknesses between 1 and 100 Å are shown in Fig. 3. The intensity of each spectrum is reduced according to the ratio given in the figure. The reabsorption of the luminescence is negligible, because the light absorption in the thin films is very small. There appears a zero-phonon band $Q_x(0,0)$ and its one-phonon side band $Q_x(0,1)$ at the energies corresponding to those bands which have been identified by Gouterman.[9] The peak positions shift to the lower-energy side and the bandwidths become larger with increasing film thickness.

The peak shift and the broadening of these luminescence bands give us information about the electronic structure of the H_2TPP film on SnO_2. In Fig. 4, data points A (open circles) represent the peak energies of the $Q_x(0,0)$ absorption band as a function of film thickness, B (open triangles) the $Q_x(0,0)$ luminescence band, and C (open squares) the $Q_x(0,1)$ luminescence band. Solid circles denoted by D show the bandwidth of the $Q_x(0,1)$ band. In the ultrathin film with the average thickness of 1 Å, the peak energy of the $Q_x(0,0)$ luminescence band is slightly lower than that of the $Q_x(0,0)$ absorption band.
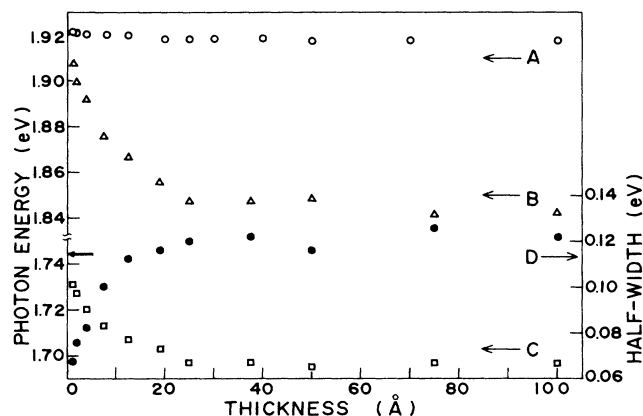
FIG. 4. Open circles (denoted by A) represent peak energies of the $Q_x(0,0)$ absorption band. Triangles (denoted by B) and squares (denoted by C) are peak energies of the $Q_x(0,0)$ and $Q_x(0,1)$ luminescence bands, respectively. Solid circles (denoted by D) denote full widths at half maximum of the $Q_x(0,1)$ luminescence band. The short arrow indicates the calculated energy position one phonon energy lower than the $Q_x(0,0)$ absorption band.

The energy extrapolated to 0 Å seems to coincide with the peak energy of the $Q_x(0,0)$ absorption band. With increasing thickness, the $Q_x(0,0)$ luminescence band shifts to the lower-energy side. The extrapolated peak energy of the $Q_x(0,1)$ luminescence band to 0 Å is approximately one phonon energy lower than that of the $Q_x(0,0)$ absorption band. This energy position is indicated by a short arrow on the ordinate of the left-hand side with the phonon energy of 175 meV as estimated from the energy separation between the $Q_x(0,0)$ and $Q_x(1,0)$ absorption bands in Fig. 2. The thickness dependence in the intensity of the $Q_x(0,1)$ luminescence band is weaker than that of the $Q_x(0,0)$ luminescence band. The Stokes shifts of both $Q_x(0,0)$ and $Q_x(0,1)$ bands increase sharply up to 5 Å, gradually around 10 Å, and then saturate to 75 and 221 meV, respectively. Such thickness dependence of the Stokes shift suggests the structural change of the film with increasing thickness. If the $Q_x(0,0)$ luminescence is associated with the intrinsic electronic state of the free H_2TPP molecule, the peak energy should coincide with that of the $Q_x(0,0)$ absorption band. In fact, the extrapolated energy of the $Q_x(0,0)$ luminescence band to 0 Å coincides with that of the $Q_x(0,0)$ absorption band. In the film with finite thickness, however, the Stokes shift is observed. Hence, this fact suggests the presence of intermolecular interactions among the excited molecules in the film. Here, we propose that the $Q_x(0,0)$ luminescence originates from the excimer in the multimolecules and we try to interpret its Stokes shift by applying a configuration coordinate model.[13] In this model, the Stokes shift of the $Q_x(0,0)$ luminescence band should be equal to the sum of the relaxation energies in the ground and excited states. The larger Stokes shift in thicker films suggests that the relaxation energy increases with increasing number of neighboring molecules. In the film with thickness above
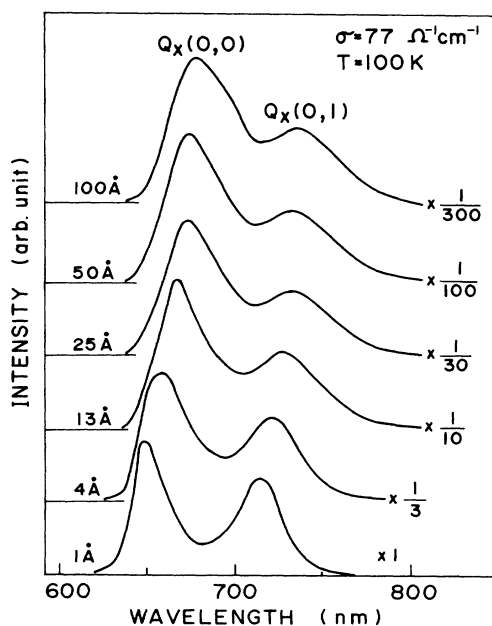

FIG. 3. Luminescence spectra of the H_2TPP films with various thicknesses on the SnO_2 substrate at 100 K. The conductivity of the SnO_2 substrate is 77 $\Omega^{-1}cm^{-1}$. The reduction ratio in intensity of each spectrum is shown at the right-hand edge.

25 Å, the molecule becomes surrounded completely by other molecules and the environment may be independent of the film thickness. Hence, we observe a constant Stokes shift. The H_2TPP molecule is plateletlike as shown in the inset of Fig. 2. If we take this geometrical structure into account,[14] the 10-Å-thick film should have a filling factor of 3 or 0.8. The former value corresponds to molecules adsorbed parallel to the SnO_2 surface and the latter to those adsorbed perpendicular to it. As H_2TPP molecules are evaporated at 100 K, they presumably are deposited randomly and do not form islands on the SnO_2 substrate. Hence, it may be reasonable to take the average filling factors of 1.3 at 10 Å and 3.3 at 25 Å. These filling factors are consistent with the thickness dependence of the Stokes shift. The weak thickness dependence of the Stokes shift in the $Q_x(0,1)$ band in comparison with that in the $Q_x(0,0)$ band might be due to the difference in the interacting phonon modes between the molecular excited state and the excimer state. On the other hand, the width of the $Q_x(0,1)$ luminescence band increases with film thickness and reaches 0.12 eV at 25 Å, while that of the $Q_x(0,0)$ absorption band is independent of the film thickness. From these facts, it is suggested that the broadening of the luminescence band is caused by excimers with varieties of different relaxation energies caused by random orientation of molecules in the film. The origin of the broadening is the same as that of the Stokes shift.

C. Luminescence intensity

Open circles in Fig. 5 show luminescence quenching of the $Q_x(0,0)$ and the $Q_x(0,1)$ bands in the H_2TPP film on low-conductivity SnO_2 as a function of the film thickness. The conductivity of SnO_2 film is 4.5×10^{-3} $\Omega^{-1} cm^{-1}$. The luminescence intensity of this film (I_{SnO_2}) is compared with that of H_2TPP film (I_{SiO_2}) evaporated directly onto the quartz plate. The ordinate, $(I_{SiO_2} - I_{SnO_2})/I_{SiO_2}$,
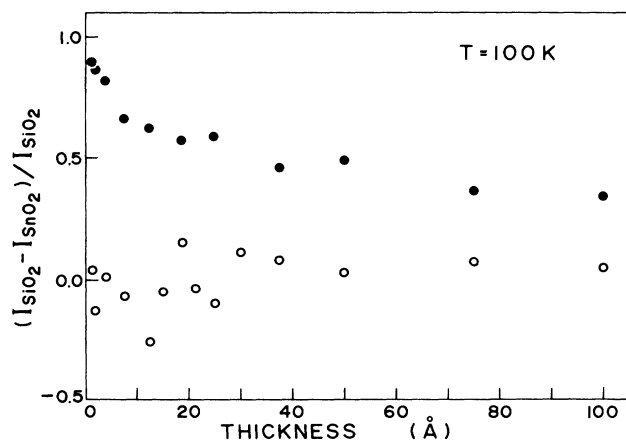

FIG. 5. Luminescence quenching ratio, $(I_{SiO_2} - I_{SnO_2})/I_{SiO_2}$, of the H_2TPP film on the SnO_2 substrate to that on the SiO_2 substrate at 100 K. Open and solid circles represent the quenching ratios on the SnO_2 substrates having the conductivity of 4.5×10^{-3} and 77 $\Omega^{-1} cm^{-1}$, respectively.

represents the quenching ratio of luminescence from H_2TPP on SnO_2 substrate to that on the SiO_2 substrate. The measured points in the thicknesses between 1 and 20 Å are scattered somewhat because the luminescence intensity is very weak in this region. However, it is clear that the quenching ratio is nearly zero over the measured thickness range from 1 to 100 Å. Namely, the luminescence intensities from the above two H_2TPP films are nearly the same. Solid circles show the quenching ratio in the H_2TPP evaporated on the highly conductive SnO_2 substrate. The SnO_2 film is a n-type semiconductor whose conductivity is 77 $\Omega^{-1} cm^{-1}$. A finite quenching ratio is observed and it depends much on the film thickness in contrast with the case of the low-conductivity film. From these results, it is suggested that electronic interaction of H_2TPP film with the low-conductivity SnO_2 substrate is very small, while the interaction is appreciable between the H_2TPP film and the highly conductive SnO_2 substrate. Namely, the conduction electron in the SnO_2 substrate plays an essential role for the luminescence quenching.

Tentatively, we divide the H_2TPP films into two kinds on the basis of the results shown in Fig. 4. The first kind of films are those with thicknesses between 1 and 25 Å. The second kind of films are those between 25 and 100 Å. In the first kind, some of H_2TPP molecules are expected to be directly adsorbed on the SnO_2 substrate. Three processes are considered for possible mechanism of the luminescence quenching in these films. The first one is enhancement of the intersystem crossing in the H_2TPP molecule adsorbed on SnO_2. The second one is the energy transfer from H_2TPP to SnO_2. The last one is the charge transfer from the H_2TPP molecule to SnO_2. The first mechanism is called external heavy-atom effect,[15] where tungsten atoms in SnO_2 film may enhance the spin-orbit interaction of the dye molecule. This mechanism is not plausible for the following reasons. The tungsten is not a material which is known to induce the external heavy-atom effect. Moreover, the Q-band luminescence of the H_2TPP molecule has not been quenched even in the dye adsorbed on KI,[5] although the iodine atom is known as a typical element where the external heavy-atom effect has been found.

Next, we discuss a possibility of the second mechanism, i.e., the energy-transfer mechanism. For the luminescence quenching by this mechanism to occur, a donor state should exist near the surface of the SnO_2 film. Moreover, the absorption band due to the donor state should overlap the $Q_x(0,0)$ and/or $Q_x(0,1)$ luminescence band. Apparently, the low-conductivity SnO_2 film does not have such a donor state, because the luminescence quenching is not observed. The 5% tungsten in SnO_2 may introduce donor states in highly conductive SnO_2 film. We have measured the absorption of the highly conductive SnO_2 film with thickness of 500 Å evaporated at the bottom of trapezoidal prism but no absorption band is detected. Hence, the optical density measured by multiple total reflections (24 times) of the incident light is less than 0.01 (the detection limit of our measurement), even if donor states exist. This value seems to be too small for the luminescence to be quenched by the energy transfer.

To induce the charge transfer in the third mechanism, the energy levels of the Q states should be higher than the conduction-band edge of the SnO_2 film in the energy level. This condition is satisfied in the n-type SnO_2 electrode. Our highly conductive SnO_2 film exhibits the character of n-type SnO_2. As shown by the solid circles in Fig. 5, the quenching ratio sharply decreases with increasing thickness up to 10 Å. This result shows that the quenching originates not only from the direct contact of isolated monomolecules with the highly conductive SnO_2 film, but also from the contact of the molecules with other neighboring H_2TPP molecules. The Q bands are not associated with an ionized state but an excited state so that no electric field is induced upon photoexcitation. The local electric field, however, may be induced in the vicinity of interface by excess electrons from SnO_2 and induce transfer of the electron from excited states of H_2TPP to the conduction band of SnO_2 by a Pool-Frenkel process.[16] In this case, the conduction electron in SnO_2 can recombine with the hole of H_2TPP molecules. As a result, the Q-band luminescence decreases. Thus, the last mechanism, i.e., a charge-transfer model modified to include the Pool-Frenkel process, is most plausible for the explanation of the conductivity-dependent luminescence quenching.

An exciton migration may contribute to the gradual decrease of the luminescence quenching in the thickness region from 10 to 100 Å in Fig. 5. Since the laser light of 514.5 nm penetrates through the film without appreciable attention, it excites H_2TPP molecules uniformly over the film. The energies of the excited molecules are transferred to the interface by a Förster-type mechanism[17] with a finite efficiency and then are lost without radiation by the Pool-Frenkel process.

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