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Excitation of Thin Cyanine Films via Energy Transfer from Si Substrate

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Energy transfer from an inorganic substrate to a cyanine molecule thin film has been investigated as an excitation method for organic luminescent devices. Cyanine molecule thin films were fabricated on a Si substrate using layer-by-layer assembly and were excited from the backside of the substrate to observe the luminescence. The luminescence intensity depends on the excitation power and excitation energy. Moreover, the dependence of the luminescence intensity on excitation energy clearly shows a profile similar to the absorption spectrum of Si. These results indicate that luminescence is not due to the direct optical excitation of cyanine by the light transmitted through the substrate but due to the energy transfer from the photoexcited carriers in the substrate. Our results demonstrate that such energy transfer can be used to excite organic molecules on inorganic substrates without energy matching between the electrodes and luminescent materials.

1. Introduction

Various organic devices have been developed, ranging from transistors and solar cells.[1- 11)] In particular, organic electroluminescent devices have attracted considerable attention from the perspective of developing the low-energy-consumption displays.[12-17)] In organic electroluminescent devices, matching between the work functions in the metal electrodes and the energies of the highest occupied and lowest unoccupied molecular orbitals in the organic materials limits the material combinations that can be used. If there were no limitations to material combinations, it would be possible to use various molecules having more desirable properties, such as higher quantum efficiency.

The most conventional excitation method is optical excitation, because the optical excitation enables to obtain the luminescence from various organic molecules. However, the optical excitation causes the problem of color mixing in realistic device application. On the other hand, energy transfer has been studied as a possible method for exciting the colloidal quantum dots covered by organic insulators18-23): several studies regarding the energy transfer between organic and inorganic materials have been carried out.24-28) The energy transfer is nonradiatively caused by the overlap between the absorption spectrum of the energy acceptor and the luminescence spectrum of the energy donor without any direct contact. Therefore, if energy transfer from a semiconductor substrate to an organic molecule film can be induced, electroluminescent devices could be realized wherein the aforementioned energy matching is not required. Moreover, the energy transfer can be applicable to various systems such as optical excitation. In particular, because the radiative recombination rate in indirect gap semiconductors, such as Si, is extremely low, the problem of the color mixing is negligible.

It is possible to generate the carriers in the surface region of semiconductors using recent semiconductor processing technology, so that the optoelectronic devices based on the energy transfer can be realized. In such devices, it is expected that the energy transfer from semiconductor substrate can simultaneously provide the advantage of optical excitation (conventional for excitation of various molecules) and electroluminescence (smaller device). In addition, it would also enable the construction of luminescent devices without p-n junctions. Motivated by these, we have studied the energy transfer from a Si substrate to cyanine molecule thin film. To obtain luminescence from cyanine molecules, the back side of the Si substrate was excited. It was found that the luminescence intensity clearly depends on the excitation power. Furthermore, the excitation-energy dependence of the luminescence intensity clearly shows that carriers originally generated in the Si substrate contributed to the luminescence. The excitation mechanism of cyanine molecule thin film is discussed from a viewpoint of the energy transfer.

2. Experiment

In this study, we used a commercially used cyanine molecule $C_{25}H_{25}IN_2S_2$ (DTTCI) as the energy acceptor, which serves as the luminescent organic molecule. Its chemical structure is shown in Fig. 1. The Si substrate, which is one of the most popular semiconductors, is the indirect transition semiconductor, so that the carrier lifetime is relatively longer. If the radiative lifetime is shorter than the energy transfer time, the efficiency becomes low. In the usual energy transfer by the Förster model considering the point-to-point interaction, the rate changes with R^{-6},29) and the rate in the plane-to-plane interaction changes with R^{-4}.30) I If the radiative lifetime is short, almost zero donor-acceptor distance is required. This is not realistic condition, therefore, this longer carrier lifetime in the indirect transition semiconductors will be advantage for the energy transfer. Moreover, previously we reported the fabrication of the cyanine molecule thin film on the glass substrate.31-33) Because the same fabrication process can be used, this combination was chosen. The p-type Si substrate with the nominal resistivity of 0.01-1.00 Ω·cm, which acts as the energy donor, was polished to approximately between 500 and 200 μm, and cleaned by immersion in a fresh piranha solution (2:5 v/v mixture of 30% H_2O_2 and 98% H_2SO_4) for 60 min. To enhance the binding of the cyanine molecule layer, a polymer spacer layer was deposited by layer-by-layer assembly,34-36) which involved alternately dipping substrates into aqueous solutions of 1 wt% polydiallydimethyl ammonium chloride (cationic polymer) and 0.1 wt% polyacrylic acid (anionic polymer) for 20 min at 25ºC. The thickness of the pair of polymer layers was 5.0 or 3.5 nm. A 7.0-nm-thick DTTCI layer was adsorbed to the polymer-coated substrate by dipping it into a 0.1 wt% methanol solution at 25ºC. The thicknesses of the polymer and DTTCI thin films were determined by spectroscopic ellipsometry. The measurement was performed by the spectroscopic phase modulated ellipsometer (HORIBA Jobin-Yvon, UVISEL-TK9017TK) in the spectral range from 1.5 to 4.0 eV. Finally, the sample was covered with poly(vinyl alcohol) by spin coating to reduce photodegradation during the optical measurements.37, 38)

A continuous-wave mode Ti:sapphire laser was used as the excitation light source for luminescence spectrum measurement of the DTTCI thin film. The excitation energy was 1.65 eV and 1.88 eV. The luminescence was measured by a 35 cm single monochromator with a 2.0 nm resolution connected to a charge-coupled device. In luminescence excitation measurement, the excitation light was produced by combination of a fiber laser with the repetition rate of 20 MHz; a white light source, and a 27 cm single monochromator with a resolution of 0.2 nm. The emitted light was dispersed by a 14 cm single monochromator with a resolution of 16 nm and detected by an InGaAs diode array.

3. Results and Discussion

Figure 2 shows the luminescence spectra obtained for the two different excitation directions shown in the inset of Fig. 2. The spectral shape hardly changes with the excitation direction. Considering the substrate thickness of 500 μm and its absorption coefficient of 1×10^{3} cm^{-1} at 1.65 eV,39) the intensity of the excitation light is attenuated from 10 mW to 2.0×10^{-23} mW at the surface. Thus, although the DTTCI thin film is not directly excited by the laser light, luminescence originating from the DTTCI molecule was observed.

Figure 3 shows the dependence of the luminescence spectrum on the excitation power for the sample on Si substrate with a thickness of 500 μm. The luminescence intensity almost linearly depends on the excitation power. To clarify this dependence, the integrated luminescence intensity, normalized to that at 5 mW excitation intensity, is plotted as a function of excitation power in the inset of Fig. 3. The dotted line shows a power law fitted to the data by the least-squares method. Since the increase in the luminescence intensity is proportional to the excitation power, the luminescence intensity depends on the number of photogenerated electron-hole pairs in the substrate.

To elucidate the mechanism of DTTCI thin-film excitation via the substrate, we measured the luminescence spectra at various excitation energies using the sample on Si substrate with a thickness of 500 μm. The peak luminescence intensity, normalized by the excitation photon flux, is plotted as a function of excitation photon energy in Fig. 4 (open circles). The intensity basically increases with increasing photon energy; the spectrum is relatively different from the absorption spectrum of the DTTCI thin film (dotted curve), which was obtained from the ellipsometry data. This also suggests that the luminescence caused by substrate excitation does not result from direct optical excitation of the DTTCI thin film. As shown by the solid curve in Fig. 4, the absorption coefficient spectrum of the Si substrate, which was also obtained from the ellipsometry data, is a similar slope to the luminescence intensity spectrum.

Moreover, we focused on the dependence of the luminescence intensity on excitation photon energy in the region wherein a peak was observed at 2.12 eV, as shown in Fig. 5. The dotted curve indicates a Lorentzian fit to the peak. While a peak energy of 2.124 eV was obtained from this fit, the transition energy from the Γ valence band to the L conduction band of Si is 2.05 eV,$^{40)}$ as indicated by the gray thick line. Considering that the optical phonon energy E_{LO} (L_1) is approximately 52 meV at the L point,$^{41)}$ the energy separation of approximately 70 meV relates to phonon scattering in the L conduction band. This result demonstrates that the relaxation process of electrons generated by light excitation of Si excites the DTTCI molecules through energy transfer (the schematic dynamics is given by Supplementary figure). Regarding the small peak around 2.05 eV as the zero-phonon line, the intensity is much smaller than the one-phonon line. Unfortunately, this reason is not clear. The L point is not a singularity,$^{42)}$ so that the zero-phonon line is weak. On the other hand, the outgoing resonant process enhances the energy transfer via the L point. Therefore, the phonon scattering may drive the electron to the energy transfer.

Finally, we discuss the efficiency of luminescence via energy transfer in our measurement. The quantum yield of the charge coupled device at 1.53 eV is 53%, and the average yield in the luminescence region is approximately 45%. Moreover, the diffraction efficiency of the grating at 1.53 eV is 40%. Considering the measured count and integration time, the excitation efficiency was estimated to be 8.2×10^{-11}%, where the absorption efficiency of Si was not considered. This value could be improved by changing to a molecule with higher oscillator strength and the generation method of the electron-hole pairs. For instance, when the electrodes are fabricated near the surface or backside of the thinner substrate, diffusion loss of carriers generated in the substrate will be able to decrease. As shown in Fig. 6, the luminescence intensity increases with decreasing the Si thickness. This increase originates from an increase of numbers of carrier generated relatively near the surface, which supports our model using energy transfer. This demonstrates that the decrease in the diffusion loss increases the efficiency.

4. Conclusions

We have investigated the origin of the luminescence of an organic molecule thin film on an inorganic substrate that is induced by substrate excitation. We found that the luminescence of cyanine molecule thin film depends on the excitation power. Furthermore, the dependence of the luminescence intensity on the excitation photon energy clearly implicates the photogenerated carriers in the Si substrate. Our results indicate that the luminescence of cyanine molecule thin film originates from energy transfer, which could be used as the excitation method of the organic devices. In particular, devices without energy matching among the materials could be realized by improving the internal efficiency of the organic molecule, and the energy transfer could be used to construct devices without a p-n junction..

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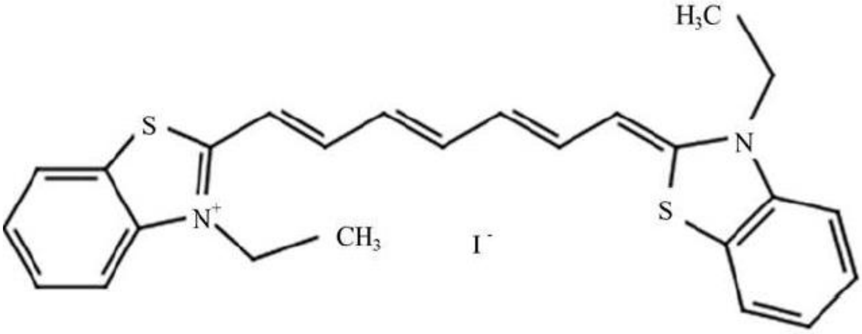

Fig. 1. Chemical structure of DTTCI.

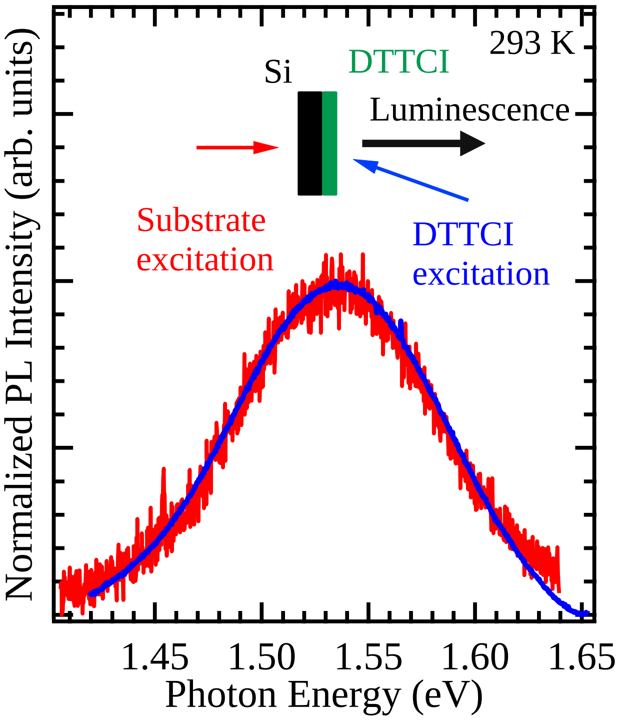

Fig. 2. DTTCI luminescence spectra obtained by excitation of the Si substrate from the back side (solid curve) and from the front side (thick curve), measured at room temperature.

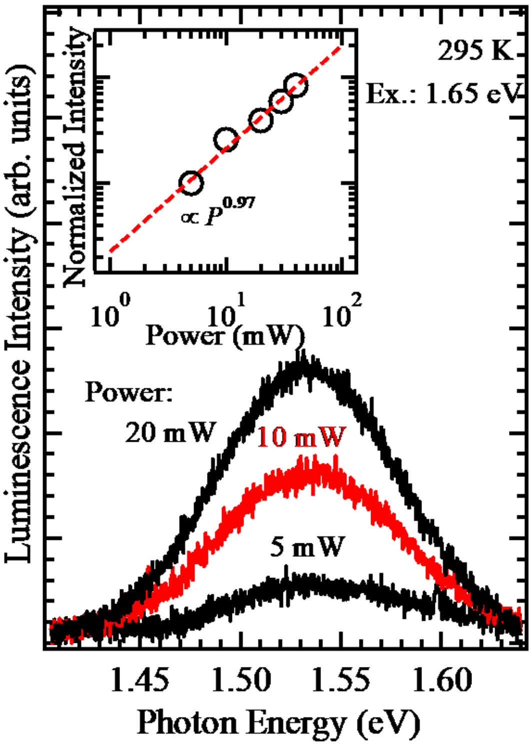

Fig. 3. Excitation power dependence of the luminescence spectrum. The integrated luminescence intensity is plotted as a function of excitation power in the inset. The dotted line indicates the fitting result.

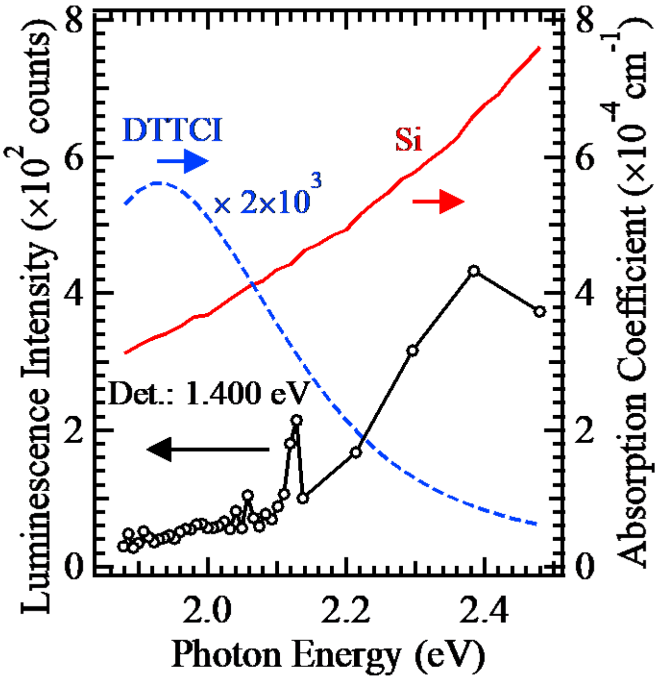

Fig. 4. Dependence of luminescence intensity on excitation photon energy (open circles). The absorption spectra of the Si substrate (solid curve) and DTTCI thin film (dotted curve) are also shown.

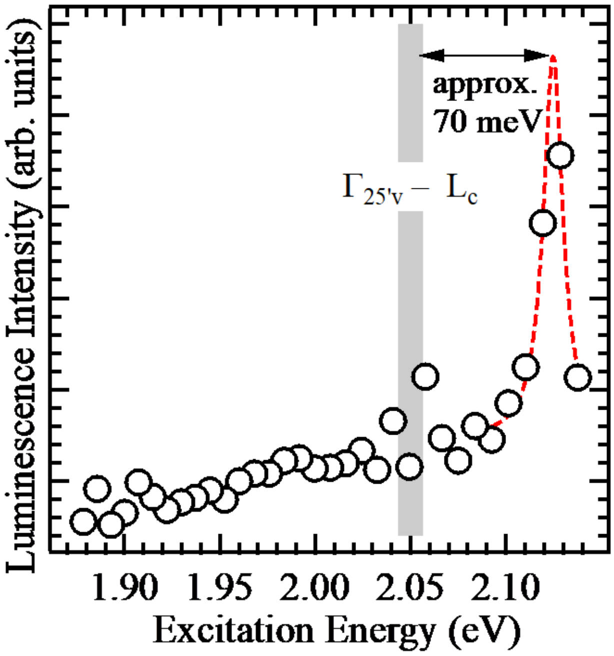

Fig. 5. Detailed excitation-energy dependence of the luminescence intensity in the region 1.88-2.15 eV. The dotted curve is the result of a Lorentzian fit and the thick grey line indicates the transition energy from the Γ valence band to L conduction band in Si.

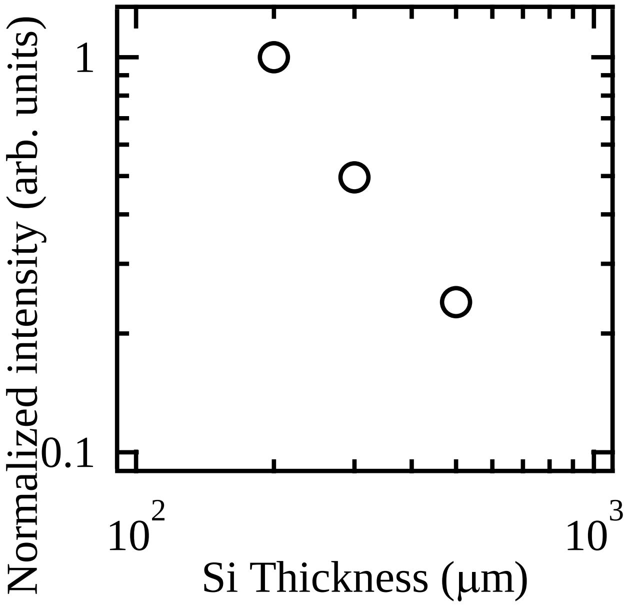

Fig. 6. Dependence of normalized luminescence intensity on thickness of Si substrate under the excitation power of 20 mW. The logarithmic scales are used.