

QUENCHING OF MOLECULAR FLUORESCENCE NEAR THE SURFACE OF A SEMICONDUCTOR

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The fluorescence efficiency of thin evaporated films of tetracene has been investigated as a function of distance from the surface of Si and GaAs utilizing LiF as a spacer. The non-radiative decay rate decreases exponentially with spacer thickness below ≈ 400 Å. These results differ from theoretical predictions based on a dipole-dipole interaction between a single molecule and the semiconductor.

The possibility of energy transfer from an excited molecule to a nearby semiconductor was recently proposed by Dexter [1], who thus extended previous work [2-5] on energy transfer from an excited molecule to a metal. Dexter's idea was that energy produced in the form of excitons in a strongly absorbing organic coating could be transferred to a semiconductor producing free electrons and holes in the semiconductor. The energy transfer occurs via a non-radiative process from the excited molecule when the excitation energy of the molecules is greater than the band gap of the semiconductor. Below we report the initial results of an experimental study of energy transfer from an organic thin film (tetracene) to a semiconductor (Si or GaAs).

Extensive theoretical and experimental investigations have been made on the interaction of an emitting dipole with a nearby metal surface [2,5]. The lifetime of an emitting dipole changes with the distance between the dipole and the metal. The dependence of lifetime on the separation has been well explained using classical electromagnetic theory [2]. Non-radiative decay of a dipole emitter at a separation

well below the wavelength of emitted light is attributed to absorption of virtual photons by the metal [3,4]. Recently, Stavola et al. [6] have performed a quantum mechanical calculation of the interaction between excited molecules and semiconductors based on the dipole-dipole interaction mechanism. They concluded that, if the distance d of the excited molecule from the semiconductor surface is much larger than the semiconductor lattice constant, the energy transfer probability is proportional to d^{-3} . This is the same result as obtained from the classical analysis [2]. If the energy of the emitted photon is in the indirect absorption region of the semiconductor, the probability is small because it is proportional to the absorption coefficient of the semiconductor. However, for distances d of the order of 10 lattice spacings or less the momentum conservation rule between photons and interband transitions of the semiconductor is relaxed and the transfer rate deviates from the d^{-3} rule. For the indirect band gap case, a probability proportional to d^{-4} is predicted.

In this paper new results are given of an experimental study of energy transfer from organic molecules to Si and GaAs single crystals. Thin evaporated films of tetracene were used as the sensitizer. The fluorescence efficiency of tetracene was measured as a function of

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distance from the surface. A strong interaction, different than predicted by the above theory, is observed between the solid tetracene film and the semiconductors.

In order to put the film of tetracene at various distances from the surface of Si or GaAs, a LiF layer to serve as a spacer was evaporated onto the room-temperature semiconductor. Deposition of previously purified tetracene was performed at ≈ 130 K or at room temperature (RT) in a clean vacuum chamber ($\approx 10^{-8}$ Torr). Optical measurements were then performed in situ without exposing the samples to atmospheric pressure. The film thickness of tetracene and LiF was measured with a quartz crystal monitor. Most measurements were then made with 50 Å thick tetracene films. Tetracene evaporated on 130 K substrates has an amorphous structure as long as it is kept at this temperature, while evaporations onto RT substrates yield polycrystalline films [7,8]. Fluorescence measurements were performed at ≈ 130 K because of the higher luminescence efficiency at low temperatures [8]. An Ar⁺ laser

(5145 Å) provided excitation incident at 45° to the surface. The intensity of fluorescence was measured normal to the surface with use of a monochromator and a photomultiplier tube. The laser beam intensity was kept sufficiently low to prevent ablation of the tetracene and thermal heating effects within the film. The measured fluorescence intensity did not change with time during exposure by the laser.

The emission spectrum of polycrystalline tetracene is similar to that resulting from singlet exciton luminescence in single crystals [9], while the spectrum of amorphous tetracene has a Stokes-shifted broad band peaked at ≈ 6000 Å. Measurements were made at the emission wavelength of 5800 Å for both amorphous and polycrystalline tetracene.

The fluorescence intensity of tetracene is shown as a function of LiF thickness in fig. 1. Dependences obtained for high-purity Si and GaAs are shown in fig. 1a, while those for three samples of Si with different doping are shown in fig. 1b. The solid curves in both figs. 1a and 1b are results for amorphous tetracene, while

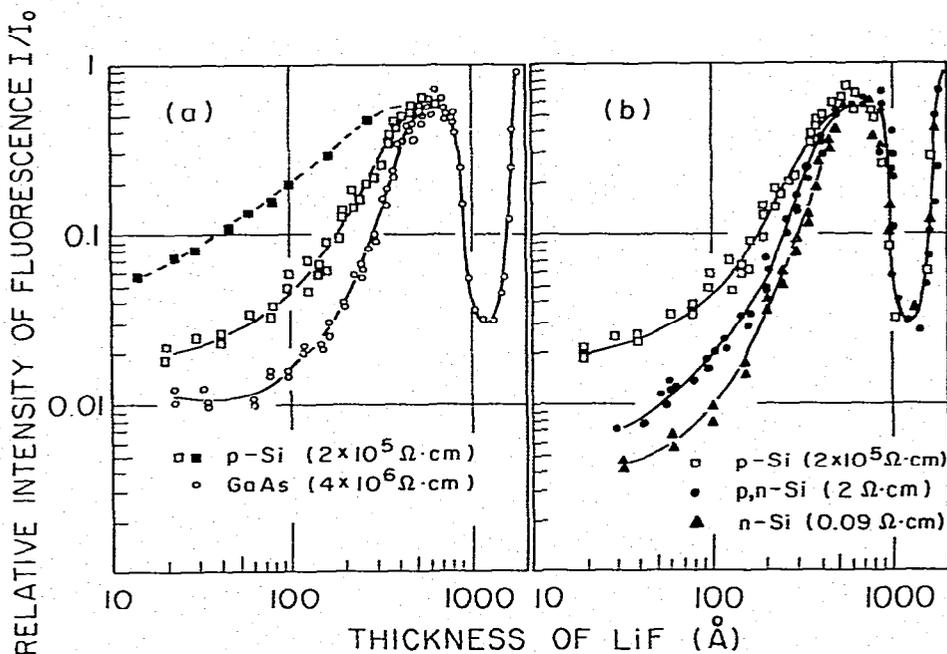


Fig. 1. Fluorescence intensity of tetracene versus LiF thickness. All curves have been normalised to unity at 2000 Å. Solid curves in (a) and (b) are for amorphous tetracene while the dashed curve in (a) is for polycrystalline tetracene. No difference is observed between n- and p-type Si of 2 Ω cm resistivity.

the dashed curve in fig. 1a is for polycrystalline tetracene on Si of resistivity $\approx 2 \times 10^5 \Omega \text{ cm}$. The intensity I for each sample was normalized to the intensity I_0 at a 2000 Å LiF thickness. In the region above 2000 Å the intensity shows an oscillatory behavior which is the result of interference between emitted light and that reflected at the semiconductor surface. The intensity does not exceed the value at 2000 Å for any LiF thickness. Therefore, we assume that the interaction which causes the non-radiative decay of tetracene is negligible at 2000 Å LiF. For spacer thicknesses less than ≈ 700 Å interference effects modify the fluorescence intensity only slightly, and hence we concentrate only on the region below ≈ 700 Å in the following analysis. Fig. 1 shows that the change in the intensity depends on the type of semiconductor. This fact tells us that an interaction exists between the tetracene film and semiconductors across the LiF spacer. Annealing of the LiF film before evaporation of tetracene did not make any change in the results of fig. 1. Measurements were also made on samples with a thick tetracene film (170 Å). In this case, excited molecules of tetracene are distributed over the thick film according to the absorption coefficient, thus the change in intensity with LiF thickness was not as sharp as shown in fig. 1. However, the behavior was qualitatively similar.

Let us express the fluorescence efficiency, η , of tetracene as $\eta = k_r / (k_r + k_1 + k_n)$, where k_r is the probability of radiative decay, k_1 is that of non-radiative decay due to interaction with the semiconductor and k_n is that of other non-radiative decay mechanisms. The quantum efficiency of fluorescence q of tetracene without any interaction with the semiconductor is given by $q = k_r / (k_r + k_n)$. The measured value of I/I_0 can be assumed to be the ratio η/q , and is given by $I/I_0 = (1 + qk_1/k_r)^{-1}$. Hence, the ratio of the decay rates k_1/k_r can be obtained as $k_1/k_r = q^{-1}(I_0/I - 1)$. Values of $I_0/I - 1$ derived from the data of fig. 1a for amorphous tetracene are plotted against LiF thickness in fig. 2. If the reduction in fluorescence efficiency near the semiconductor surface is due to energy transfer by the dipole-dipole mechanism [1,2] the dependence of k_1/k_r on the distance d should be $k_1/k_r = \beta d^{-3}$. A dotted line drawn along the data of GaAs in fig. 2 shows the d^{-3} dependence for comparison. The experimental results do not agree with theory below ≈ 200 Å LiF for either Si or GaAs. According to classical theory [2,6] the value of β can be estimated

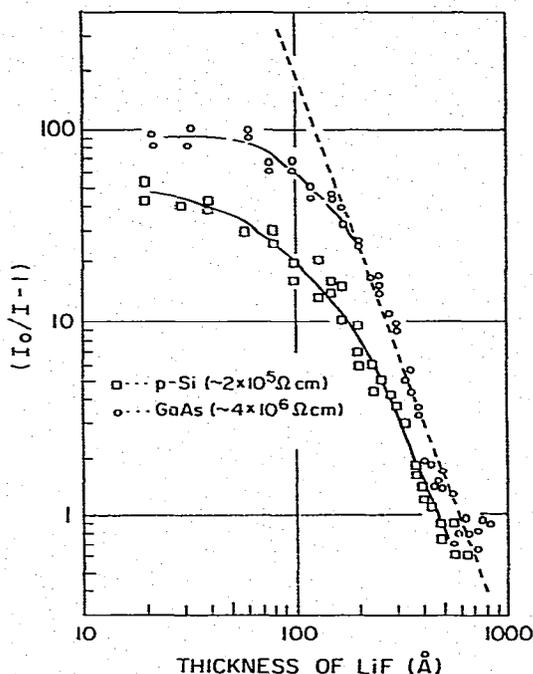


Fig. 2. $I_0/I - 1$ versus LiF thickness. The dashed line shows the d^{-3} dependence resulting from the model based on the dipole-dipole interaction.

from the optical constants of the semiconductor and LiF at the fluorescence wavelength. The calculated value for GaAs at $d = 100$ Å, for example, is $k_1/k_r \approx 5$, using the value of 10^5 cm^{-1} for the absorption coefficient of GaAs at 5800 Å. For the case of Si the value of k_1/k_r should be two orders of magnitude smaller than for GaAs because the emission band of tetracene is in the indirect absorption region of Si. Experimental values of k_1/k_r from fig. 2 are ≈ 60 for GaAs and 20 for Si at $d = 100$ Å when the quantum yield q is assumed to be unity. Therefore, it is difficult to explain the present results with the single-dipole-semiconductor model of energy transfer. Rosetti and Brus [10] have reported deviations from the d^{-3} dependence energy transfer rate for phosphorescence decay measurements of pyrazine on silver surfaces. However, they subsequently found [11] the deviations resulted from an unexpectedly wide distribution of d values. In the present work the tetracene is evaporated on top of cold LiF films of uniform thickness and there appears to be no possibility of a significant distribution

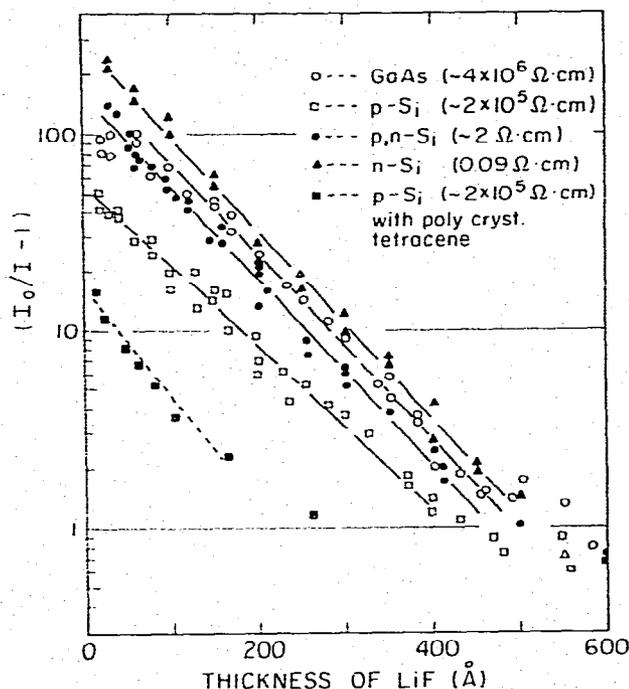


Fig. 3. $\log(I_0/I - 1)$ versus LiF thickness. The solid lines are for amorphous tetracene while the dashed line is for polycrystalline tetracene.

of d values although there is some effect resulting from the 50 Å tetracene film thickness for thin LiF films. In fig. 3, values of $\log(I_0/I - 1)$ are plotted against thickness d . Fig. 3 indicates that an exponential dependence is a good approximation. The ratio k_1/k_T can be expressed as

$$k_1/k_T = c e^{-\gamma d} \quad (1)$$

In addition, the tetracene thickness dependence of the fluorescence efficiency was measured for amorphous tetracene deposited directly on a Si surface without the LiF spacer. Fig. 4 shows the normalized intensity of fluorescence as a function of tetracene thickness on Si ($\approx 2 \times 10^5 \Omega \text{ cm}$). The normalization was made to the intensity measured for tetracene of the same thickness deposited on Si with a thick (2000 Å) LiF spacer. The normalized intensity is, therefore, assumed to be the efficiency of fluorescence at each tetracene thickness. The dashed curve in fig. 4 is calculated based on the following assumptions: (1) the tetracene film is composed of layers parallel to the

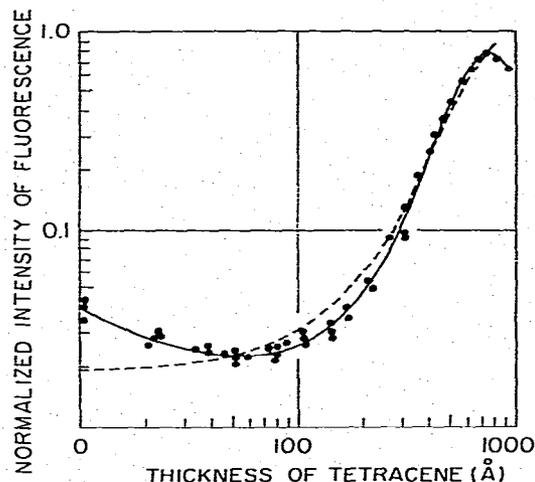


Fig. 4. Fluorescence intensity versus the thickness of amorphous tetracene deposited directly on Si ($2 \times 10^5 \Omega \text{ cm}$). Normalization was made to the intensity measured for tetracene of the same thickness deposited on Si with 2000 Å of LiF. The dashed curve is calculated as discussed in the text.

surface; (2) the density of excited states in each layer depends on the depth of the layer from the illuminated surface according to the absorption coefficient; and (3) the decay of the excited state obeys eq. (1) at each distance from the surface of Si. The contribution to the fluorescence from each layer is integrated over the entire film thickness. The absorption coefficient of tetracene used was taken as $5 \times 10^5 \text{ cm}^{-1}$, and the constants c and γ in eq. (1) were obtained from the data for Si ($\approx 2 \times 10^5 \Omega \text{ cm}$) in fig. 3. Diffusion of excitons within the tetracene film was not taken into account. The calculated curve is very close to the experimental results except below 40 Å.

The fluorescence decay time was also measured for samples of polycrystalline tetracene at $\approx 100 \text{ K}$. The excitation source was a 530 nm pulse from a frequency-doubled Nd-YAG laser whose pulse width is $\approx 30 \text{ ps}$. The fluorescence signal was detected with a low-jitter streak camera system [12]. Measurements were made on several samples with LiF spacer thicknesses (on Si) varying from 30 to 600 Å. The fluorescence decay had a fast component with a decay time of $\approx 100 \text{ ps}$ followed by a slow component whose time constant was too long to be measured by the present apparatus. The intensity of the fluorescence signal changed with the spacer thickness (consistent with the cw dependence

of $I_0/I - 1$ on spacer thickness shown above), although no change in the decay characteristics were observed in the time range from zero to 500 ps irrespective of the spacer thickness. The results of these decay time measurements indicate that the reduction of fluorescence efficiency by the interaction with the semiconductor is not due to the shortening of lifetime of the fluorescing state but to the decrease of the population of fluorescing states of tetracene molecules.

The distance dependence of fluorescence intensity in fig. 1a shows that the quenching effect is stronger in the case of amorphous tetracene than in the polycrystalline case. This fact tells us that the effect is dependent on the nature of the tetracene film. The amorphous film is considered to be a uniform film of molecules with random orientations, while the polycrystalline film has many grain boundaries [7]. In fig. 4, we can see that the fluorescence efficiency goes up as the thickness of tetracene becomes thin below ≈ 40 Å. Very thin evaporated films may not represent a uniform dielectric film, but rather a random distribution of small molecular aggregates. This fact also suggests the role of the uniformity of the film on the quenching effect. One can therefore conclude that the states interacting with the semiconductor are not the excited states of individual molecules.

Let us discuss briefly possible mechanisms for energy transfer which might explain the above results. One candidate might be charge transfer from a conducting state of tetracene to the semiconductor. Photoconductivity measurements [13] on amorphous tetracene films have shown that photoconductivity is observed over the entire region of optical absorption. However, in order for tunneling of free carriers to occur over a distance of the order of the 100 Å thickness of the LiF spacer, the potential barrier height would have to be ≤ 1 meV. Such a small barrier height is inconsistent with the large band gap energy (13 eV) of LiF.

Another explanation involves a surface excitation on the tetracene film. Electromagnetic waves propagating along the surface of a thin isotropic film can be excited by optical radiation at photon energies slightly higher than the absorption of the bulk exciton when the two media on either side of the dielectric film have different dielectric constants [14]. A surface wave on the tetracene film might be excited by the light of the incident beam reflected from the surface of the semiconductor. If the quenching effect occurs because of

a tetracene surface wave interacting with the semiconductor the effect must depend on the direction of excitation since surface wave amplitudes depend on the angle of incidence because of the momentum matching condition. We measured the dependence of $I_0/I - 1$ on spacer thickness at nominal normal incidence instead of at 45° . The result shows that the dependence is still exponential, but the constant c in eq. (1) is reduced by a factor of ≈ 2.5 . This fact supports the possibility that a surface wave excitation in the tetracene film plays a role in quenching the fluorescence. One might suppose that the energy dissipation results from the interaction with the semiconductor of the surface wave excitation before localization to excited individual molecules occurs.

With regard to the role of surface wave excitations on the energy transfer, Weber et al. [15] have investigated the energy transfer between excited molecules and surface plasmons on a metal. They report that the energy rate decreases exponentially with distance for resonance between the excited molecules and the surface plasmon. Nevertheless, further study is required to obtain a better understanding of the exponential distance-dependence of energy transfer in the present system.

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References

- [1] D.L. Dexter, *J. Luminescence* 18/19 (1979) 779.
- [2] R.R. Chance, A. Prock and R. Silbey, in: *Advances in chemical physics*, Vol. 37, eds. I. Prigogine and S.A. Rice (Wiley, New York, 1978) p. 1.
- [3] G. Vaubel, H. Bässler and D. Möbius, *Chem. Phys. Letters* 10 (1971) 334.
- [4] A. Campion, A.R. Gallo, C.B. Harris, H.J. Robota and P.M. Whitmore, *Chem. Phys. Letters* 73 (1980) 447.
- [5] A. Adams, R.W. Rendell, W.P. West, H.P. Broida and P.K. Hansma, *Phys. Rev. B* 21 (1980) 5565.

- [6] M. Stavola, D.L. Dexter and R.S. Knox, private communication.
- [7] Y. Maruyama and N. Iwasaki, Chem. Phys. Letters 24 (1974) 26.
- [8] H. Müller, H. Bässler and G. Vaubel, Chem. Phys. Letters 29 (1974) 102.
- [9] D.D. Kolendritskii, M.V. Kurik and Yu.P. Piryatinskii, Opt. Spectry. 44 (1978) 162.
- [10] R. Rossetti and L.E. Brus, J. Chem. Phys. 73 (1980) 573.
- [11] R. Rossetti and L.E. Brus, J. Chem. Phys. 76 (1982) 1146.
- [12] M. Stavola, G. Mourou and W. Knox, Opt. Commun. 34 (1980) 404; G. Mourou and W. Knox, Appl. Phys. Letters 36 (1980) 623.
- [13] W. Hofberger and H. Bässler, Phys. Stat. Sol. (b) 69 (1975) 725.
- [14] E. Burstein, W.P. Chen, Y.T. Chen and A. Hartstein, J. Vac. Sci. Technol. 11 (1974) 1004.
- [15] W.H. Weber and C.F. Eagen, Opt. Letters 4 (1979) 236.