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Dynamics of molecular excitons near a semiconductor surface studied by fluorescence quenching of polycrystalline tetracene on silicon

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ABSTRACT

Tetracene, a molecule that undergoes singlet fission, is deposited on Si with variable thickness LiF spacer layers. In agreement with earlier work (Hayashi et al., 1983 [10]), the fluorescence intensity of the tetracene greatly increases as the LiF thickness approaches 100 nm. This increase is partly due to a 30% increase in the prompt fluorescence decay time but mostly results from weaker coupling of the luminescence into the Si substrate. A decrease in the prompt fluorescence lifetime is observed as the tetracene thickness is increased on bare Si. We find no evidence for triplet energy transfer to the Si.

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1. Introduction

Singlet fission (SF) represents a promising strategy for surpassing the Shockley–Queisser limit for energy conversion efficiency in singlet junction photovoltaic cells [1]. In SF, a single high-energy photon generates a singlet state that then splits into two lower energy triplet excitons. Once the triplet excitons are produced, they must then be harvested and turned into electron–hole pairs to generate photocurrent. Triplet excitons can be directly ionized by electron acceptors [2–4], and external quantum efficiencies greater than 100% have been demonstrated for organic photovoltaic devices where SF is operative [5]. Despite this success in ionizing the triplet excitons, there is interest in finding other ways to utilize the triplets produced via SF. Ideally, the SF phenomenon could be integrated into existing silicon photovoltaic technology without having to develop an entirely organic-based photovoltaic system. One approach would be to use energy transfer from excitons in the organic layer to create excitons in an inorganic substrate, which would then dissociate into electron–hole pairs. Dexter originally suggested that it might be possible to utilize Frenkel triplet excitons in an organic material to photosensitize Wannier excitons in an inorganic semiconductor [6]. Agranovich has recently summarized theoretical and experimental work on energy transfer in hybrid excitonic systems [7]. In related work, it has been shown that triplets produced by SF in pentacene can

be ionized by PbSe nanocrystals, and the resulting charge carriers injected into an amorphous Si layer [8]. However, it is an open question whether the triplet excitons produced by SF could be directly harvested in the manner suggested by Dexter.

Tetracene is a prototypical SF material [9] whose $S_0 \rightarrow T_1$ energy gap is close enough to Si's bandgap that triplet energy transfer should be possible. In 1983, Boyd and coworkers investigated the photoluminescence of tetracene layers deposited on crystalline Si both with and without a LiF spacer layer [10]. They concluded that a distance-dependent energy transfer mechanism, possibly mediated by surface plasmons in the tetracene layer, resulted in strong luminescence quenching. While most of their results concerned amorphous tetracene layers grown on low-temperature substrates, quenching was also observed for crystalline tetracene layers grown on room temperature substrates. However, that work left many unanswered questions, including an anomalous dependence on tetracene layer thickness and an apparent lack of change in the fluorescence lifetime. Given the interest in harvesting the triplet excitons produced by SF, we decided to revisit the tetracene-Si system to gain an improved understanding of the fluorescence quenching mechanism. In this Letter, we report the results of experiments on polycrystalline tetracene layers deposited onto a clean hydrogen-terminated Si 100 crystal, with and without a variable thickness LiF spacer layer. We look at how both the steady-state and time-resolved photoluminescence signals change as a function of LiF spacer layer thickness. Because tetracene exhibits prompt fluorescence (due to the decay of the initially excited singlets) and delayed fluorescence (due to triplet–triplet fusion

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back into a singlet), the dynamics of both singlet and triplet excitons can be monitored in a singlet, time-resolved photoluminescence experiment. We find that the fluorescence changes can be explained by singlet energy transfer to the Si, combined with dielectric effects that affect the ability of the fluorescence to escape the sample. We find no evidence of triplet exciton quenching by the Si. Our results highlight the complexities of hybrid organic–inorganic materials and suggest that transferring excitons between the two phases may require new chemical approaches.

2. Experimental

2.1. Sample preparation

A lightly doped (resistivity, ρ = 20 Ω-cm) n-type (100) Si substrate was cut into 1.5 cm $\times$ 1.5 cm squares, followed by ultrasonic cleaning with acetone, isopropyl alcohol, and de-ionized (DI) water (ρ = 18 MΩ-cm), each for 5 min. The substrate was then immersed in piranha solution (H_2SO_4:H_2O_2 = 3:1 in volume ratio) at 80 °C for 5 min, followed by DI water rinsing [11]. Then, a buffer oxide etching solution (NH_4F:HF = 6:1) was used to remove the oxide on the silicon wafer for 5 min, creating a hydrogen terminated surface [12]. The substrate was transferred into vacuum chamber with base pressure of 10^{-6} torr and the LiF and tetracene thin films were deposited by thermal evaporation [13]. After thin film deposition, the samples were directly transferred into a N_2 glove box with (O_2 and H_2O < 1 ppm) for encapsulation. A cleaned glass substrate with UV sealant on the periphery covered the sample, followed by UV light illumination to seal the sample under a pure-N_2 atmosphere. With encapsulation, the samples exhibited stable optical characteristics even after storage for 6 months.

2.2. Fluorescence Measurements

Steady-state excitation and emission spectra were obtained on a Horiba Jobin Yvon-Spex Fluorolog-3 fluorimeter using front-face detection with an excitation wavelength of 470 nm. Time-resolved fluorescence data were obtained using front-face detection with a Hamamatsu C4334 Streakscope picosecond streak camera at an excitation wavelength of 400 nm. The 400 nm excitation was provided by focusing the 800 nm output of a 40 kHz Spectra-Physics Spitfire Ti:sapphire regenerative amplifier into a 0.4 mm thick BBO crystal. The pulse length was less than 200 fs, and the excitation fluence at the laser focus was typically on the order of 4 microjoules/cm^2 per pulse. A 420 nm cutoff filter was used to remove scattered laser light before the detector. The streak camera data captures the decay dynamics of the entire fluorescence spectrum with 2 nm wavelength resolution and 15 ps temporal resolution.

3. Results and discussion

Both LiF and tetracene were deposited on a clean Si substrate using thermal evaporation under high vacuum. Figure 1 shows AFM images of a bare Si 100 surface before and after deposition of tetracene layers with nominal thicknesses of 3 and 27 nm. It is clear that the tetracene does not form a uniform coating, but instead forms islands distributed across the surface. This type of island growth has been observed previously for vacuum deposited tetracene [14,15] and is commonly seen for conjugated organic molecules that crystallize easily and have high surface mobility at room temperature. We chose to do most of our luminescence experiments with a tetracene thickness of 27 nm since the AFM images show that this thickness provides a reasonably even surface coverage. It should be emphasized, however, that the film itself is not a perfectly homogeneous layer and is quite 'bumpy' on nanometer lengthscales.

The crystalline nature of the tetracene islands is confirmed by the fluorescence lineshapes shown in Figure 2a. For LiF buffer layer thicknesses of 0, 5 and 10 and 35 nm, the fluorescence lineshape has the characteristic features of polycrystalline tetracene, with an enhanced 0–0 peak at 535 nm and a 0–1 vibronic replica at 550 nm. The roughly 3:1 ratio of the two peak intensities is characteristic of the delocalized singlet exciton that has been previously observed in ultrathin tetracene films and crystals [16–18]. The time-resolved fluorescence decays of tetracene on Si samples are also qualitatively similar to those observed for tetracene on inert substrates like glass. The set of data shown in Figure 2b is typical, with a prompt fluorescence decay on the order of 80–250 ps followed by a much longer delayed fluorescence with a lifetime on the order of 200 ns. To fit the entire fluorescence decay, including intermediate timescales, at least three exponential functions would be required [19]. In order to simplify our analysis, we concentrate only on the two separate time domains. The prompt fluorescence (reflecting the singlet lifetime) is characterized by τ_1 and the delayed fluorescence (proportional to the triplet lifetime) is characterized by τ_2. These two time constants can be thought of as parameterizing the data on very short timescales (<1 ns) and very long timescales (>100 ns). The two decays generated by τ_1 and τ_2 are shown as straight lines overlaid with the appropriate data ranges in Figure 2b.

Figure 3a shows the variation in the integrated steady-state fluorescence intensity as a function of LiF spacer layer thickness d_{LiF}. Also shown are data points for 5 nm thick crystalline tetracene on a p-doped Si crystal (orientation not specified), taken from the
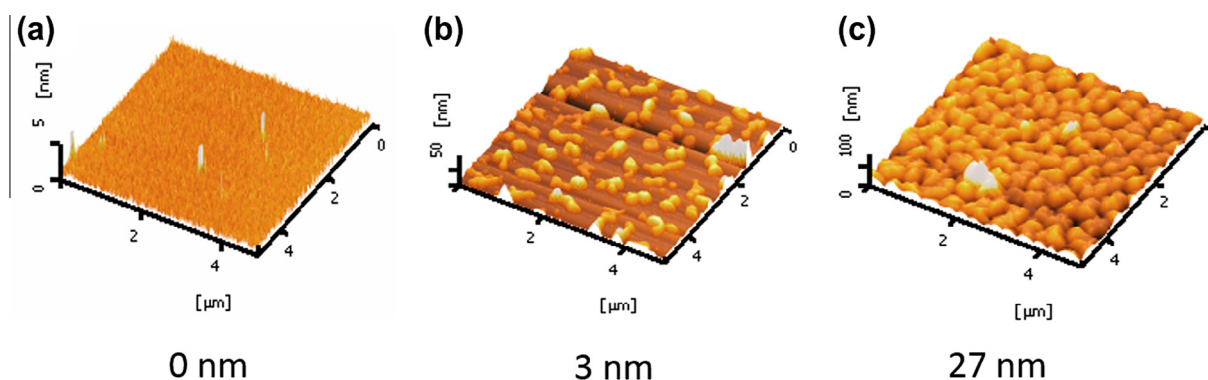

(a) 0 nm **(b)** 3 nm **(c)** 27 nm

Figure 1. AFM images of the tetracene/Si surface for thicknesses of (a) 0 nm, (b) 3 nm, and (c) 27 nm. For thinner layers of tetracene, uniform coverage is not achieved due to island formation.