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Nanoscale photophysics of Alq_3 films

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Abstract

We use near-field scanning optical microscopy (NSOM) and spectroscopy to probe the photophysics of thin films of molecular semiconductor *tris*-8-hydroxyquinoline aluminum (Alq_3) on a 10-100 nm scale. Photoluminescence NSOM is used to simultaneously map variations in emission and morphology of both solution-cast and vacuum-deposited films. Vacuum-deposited films annealed at 200°C ($T > T_g$) exhibit greater fluorescence and topographical contrast than films annealed at 100°C ($T < T_g$), with the most dramatic changes occurring in films less than 50 nm thick. These results indicate the formation of microcrystalline domains in annealed Alq_3 films, which vary with annealing temperature and film thickness. We have also used NSOM to locally photo-pattern films on a 100 nm scale and to directly measure exciton diffusion. Our results indicate very long diffusion lengths in comparison to indirect methods.

Keywords: near-field scanning optical microscopy (NSOM), organic semiconductor (Alq_3), photoluminescence, exciton diffusion, photo-oxidation

1. Introduction

Small molecule organic semiconductors such as *tris*-8-hydroxyquinoline aluminum (Alq_3) are interesting thin film materials due to the combination of their desirable opto-electronic, physical and mechanical properties.[1] Alq_3 is already being used in small opto-electronic devices, but many properties of the material, such as the formation of degradation products and charge transport are not well understood. [2] The photophysics, local order and charge transport of Alq_3 have been investigated with various bulk characterization methods, with most measurements being performed with conventional methods where the properties of the sample are spatially averaged. [3,4] For example, using XRD, it has been reported that Alq_3 films consist of microcrystalline domains with characteristic lengths well below the wavelength of visible light (50 nm).[3-5] In order to reduce spatial averaging and to probe topography concurrently with fluorescence, we use near-field scanning optical microscopy (NSOM) to probe Alq_3 films on a 100 nm scale.

2. Experimental

The transmission NSOM apparatus used in these experiments has been described in detail elsewhere.[6-8] Resolution below the diffraction-limit is made possible through the use of a standard metal-coated, tapered optical fiber tip with apertures of 100±10 nm.[9] The NSOM tip aperture is maintained in the near field of the sample surface (~ 10 nm) using optically-detected shear force feedback.[10] The NSOM tip is coupled to the 458 nm line of an Ar^+ laser as a local excitation source. A shear force feedback signal provides a topographical image of the sample simultaneously generated with the optical image. The photoluminescence from the sample is collected with a conventional microscope and routed to an avalanche photodiode (APD).

3. Results

Vacuum-deposited Alq_3 films exhibit homogeneous fluorescence (Fig. 1a) and sample topography (Fig. 1b). In contrast, drop-cast (Fig. 1c, d) and spin cast (not shown) Alq_3 films exhibit fluorescence (Fig. 1c) and morphology (Fig. 1d) variations which appear to be related to a combination of local sample morphology and film thickness.[8] We have also observed fluorescence (Fig. 1e) and topographic (Fig. 1f) inhomogeneities for Alq_3 films (film thicknesses between 10 nm and 480 nm) annealed above the Alq_3 glass transition temperature, T_g = 172°C, and films less than 50 nm thick annealed below T_g (T_{anneal} = 100°C).[11]

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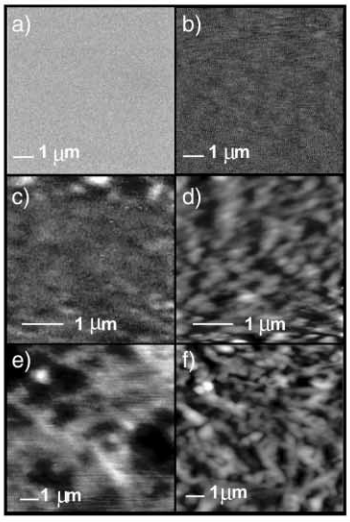


Figure 1. NSOM (left) and shear force topography (right) images of a 100 nm vacuum-deposited (a,b), 20 nm drop cast (c, d), and 480 nm (e, f) Alq_3 film on glass annealed at 200°C.

In addition to passively probing annealed, drop-cast and spin-cast Alq_3 samples, we use the NSOM tip to photo-oxidize vacuum-deposited Alq_3 thin films.[12] The photo-oxidation results in a localized decrease in the fluorescence of the film (spatial hole-burning, or SHB) which is dependent on both the illumination spot size and the exciton diffusion length. The size and shape of the photo-induced pattern is then imaged using fluorescence NSOM.

Figure 2 shows an SHB-NSOM image of a selectively photo-oxidized 100 nm Alq_3 film. The image (Fig. 2a) consists of six dark spots of varying size corresponding to increasing exposure times of the sample to the tip. The line cut in (Fig . 2b) shows the profile of the

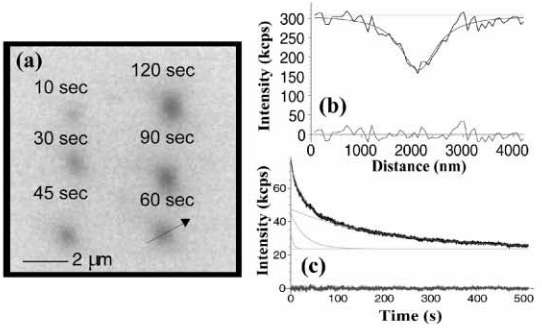
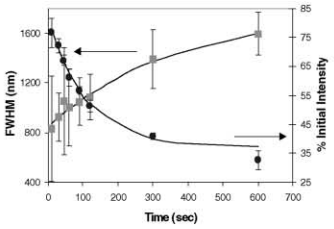


Figure 2. SHB-NSOM image (a) of an Alq_3 film, with (b) a corresponding linecut (from which we determine the fwhm and % initial intensity of each 'hole') and (c) the fluorescence yield decay. In (c), the fluorescence yield decay is characterisitic of all regions of the film. The residual for (c) is shown along the bottom of the graph.

60 s 'hole' in (a). Fitting the fluorescence yield decay curve in Fig. 2c to three decaying exponentials we obtain τ_1= 5 s, τ_2= 31 s, and τ_3= 205 s. The fast time constant is attributed to surface photo-oxidation while the slow time constants are attributed to oxidation of the bulk.

Figure 3 illustrates the measured parameters from a SHB-NSOM experiment. Extrapolation of the hole width to zero time provides a rough upper bound on the diffusion length for energy migration in Alq_3 of 400 nm; approximately a 10-fold increase over the largest exciton diffusion length reported in the literature for Alq_3. [3,13] We believe that the discrepancy between our diffusion length and those observed previously can be partially attributed to assumptions in our model which do not account for the likely formation of fluorescence quenchers.

Figure 3. The graph shows the decrease in the % initial intensity (■) from each hole, as well as the broadening of the hole diameter (●) with increasing exposure time. The exponential rise of the dark spot diameter was fit to a single exponential fit with a time constant of 360 s. The fluorescence intensity decreases with time and has been fit to two decaying exponentials with τ_1= 53 s and τ_2=205 s, which compares favorably to the larger time constants calculated from Fig. 2c.



4. Conclusions

We have shown that NSOM techniques can be successfully applied to Alq_3 films to probe optical and transport properties on a mesoscopic scale. Although the fluorescence in as-deposited films is uniform, the fluorescence and morphology of Alq_3 films (a) annealed above its glass transition temperature and (b) under 50 nm thick are shown to vary on a 100 nm scale. In addition, the SHB-NSOM technique provides a means for probing photo-oxidation on a local scale, free from spatial averaging. This advantage is important in order to observe subtle changes in the fluorescence spectrum as a function of exposure time as well as any spatial variation of the photo-oxidation kinetics.

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