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Intense photoluminescence from pentacene monolayers

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Sharp and intense excitonic photoluminescence is observed at low temperatures in highly uniform pentacene monolayers deposited on a compliant polymeric substrate. The free exciton (FE) emission displays characteristic intensity that grows quadratically with the number of monolayers N . The energy of the FE band redshifts with increasing N revealing impact of molecular overlap on the FE state. © 2010 American Institute of Physics. [doi:10.1063/1.3458816]

Pentacene, with formula $C_{22}H_{14}$, is a benchmark device material in the large organic semiconductor family. It is a material for high mobility organic thin film transistors (OTFTs).^{1,2} Thin films of pentacene are of great current interest for optoelectronic devices such as organic light-emitting diodes (OLEDs),^{3,4} photodetectors,⁵ and photovoltaic cells.^{6–8} Optical characterization and understanding of the physical properties of pentacene ultrathin films down to the submonolayer limit are critical to the fabrication of high quality OTFTs and highly efficient optoelectronic devices.^{9–11}

This paper reports the observations of sharp and intense excitonic transitions in photoluminescence from highly uniform pentacene monolayers and submonolayer films deposited on polymeric substrates. We find that the intensity of the free exciton (FE) band increases with the number of pentacene layers N . For $N \leq 5$ the intensity is proportional to N^2 . This quadratic dependence of the intensity on the number of monolayers in the device is interpreted as evidence that in the few monolayer limit the probabilities for absorption and emission processes are each proportional to the number of layers N .

Significant redshifts in the energy of the FE photoluminescence band are recorded as N increases. Given that in thicker films the interlayer distance is smaller, the redshifts seem to be linked to stronger interlayer interactions that lower the FE energy.^{12–15} The FE bandwidths in optical emission of the ultrathin films are larger by more than a factor of 3 than that of a good quality pentacene crystal. The enhanced broadening may be linked to the formation of clusters and grains in the films.

It has been reported that ultrathin pentacene films prepared on molecular or polymeric substrates exhibit enhanced quality and reliability.^{10,16–20} We use poly alpha-methylstyrene (PAMS) as a suitable compliant substrate. Prior to deposition of pentacene, a 2–3 nm thick PAMS layer was spin coated on thermally oxidized Si wafers. The left panel in Fig. 1(a) describes the structure of the specimens.²¹ The optical experimental setup is similar to that in prior work.²² Luminescence measurements were conducted at temperatures slightly below 10 K. The excitation laser photon energy (~ 2.1 eV) was chosen to be above the expected

energy of the singlet FE absorption but below the highest occupied molecular orbital-lowest unoccupied molecular orbital gap (~ 2.2 eV).²³

Figure 1(a) (right) shows an atomic force microscopy (AFM) image of a submonolayer (sub-ML) film. About 70% of the substrate is covered by pentacene islands with typical

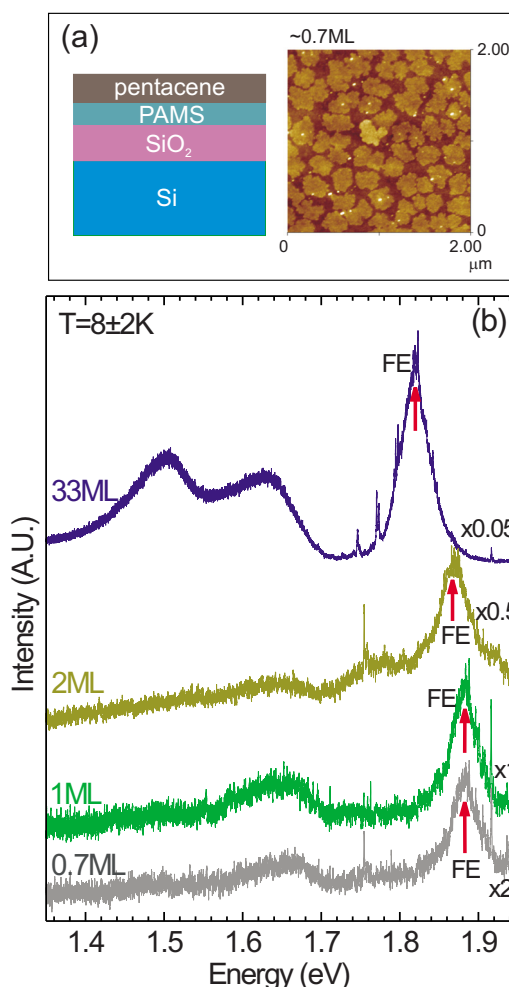


FIG. 1. (Color online) (a) Left: schematic drawing of the configuration of a pentacene film grown on PAMS. The drawing is not to scale. Right: AFM image of a pentacene submonolayer film with 70% coverage (0.7 ML). (b) Photoluminescence spectra from pentacene films with different values of N . The vertical arrows mark the positions of FE bands.

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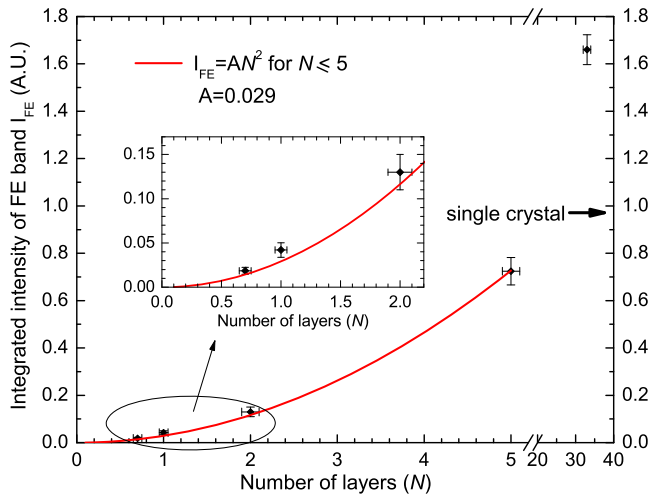


FIG. 2. (Color online) Integrated intensity of FE band I_{FE} as a function of layering. The solid curve is a fit of the data to the equation shown as a legend. The circled region is expanded in the inset. I_{FE} of single crystal of pentacene is indicated by an arrow.

lateral size of $\sim 0.2 \mu\text{m}$. In the single monolayer (1 ML) film the pentacene clusters connect and densely cover the substrate. The average thickness of the first layer is about 1.7 nm which is close to the length along the long axis of a pentacene molecule.^{13,24} It suggests that the pentacene molecules stand almost vertically with long axes nearly perpendicular to the substrate.²⁵ In a two-monolayer (2 ML) film the first layer completes before the second layer grows.²¹ The second layer is composed of large islands with average thickness of about 1.7 nm and lateral dimension approaching $1 \mu\text{m}$. In an even thicker film of 33 monolayers (33 MLs, $\sim 50 \text{ nm}$) there is formation of pyramid-like three-dimensional grains.

Figure 1(b) displays luminescence spectra from the pentacene layers. The major features in the spectra are the emission bands (identified by red arrows) that occur in the energy range 1.8–1.9 eV. The bands are relatively sharp and their energy is above the FE state in single crystal pentacene (see Fig. 3 below). We interpret the dominant optical emission bands in Fig. 1(b) as arising from FE states. Luminescence from the higher energy component of the Davydov doublet of the first singlet exciton transition, seen in cluster films,²² was not observed in these more uniform films grown on PAMS. The absence suggests that charge carriers thermalize more effectively to their lowest energy states in superior films.

Figure 2 shows that for $N \leq 5$ the integrated intensity of the FE optical emission band I_{FE} scales as N^2 . For larger N , the quadratic relation breaks down as indicated by the last point in Fig. 2 for $N=33$. The N^2 dependence seems to be a characteristic property of the intensity of FE optical emission in the few monolayer limit. The N^2 -dependence is interpreted within a simple model in which the FE optical emission intensity is proportional to the intensity of absorbed excitation light and to the probability that the photoexcited electrons and holes thermalize to the FE state.

In this model the intensity of light absorbed by the monolayers is proportional to $[1 - \exp(-Nt\alpha)]$, where t is the thickness of each layer, and α is the absorption coefficient. In the few monolayer limit N is small and the intensity of absorbed light is proportional to $Nt\alpha$. To get the other factor of

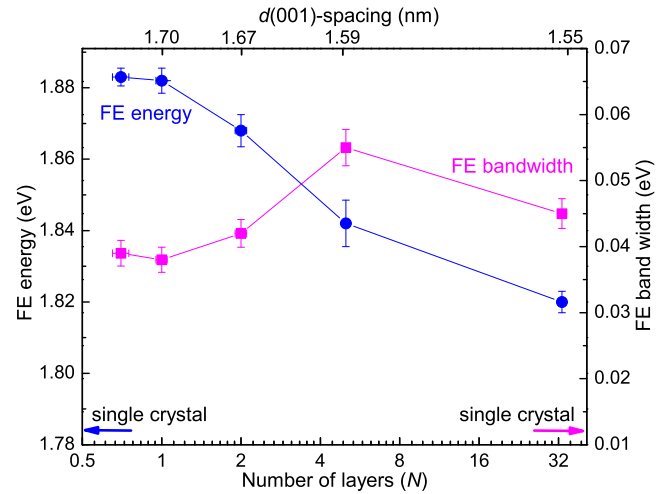


FIG. 3. (Color online) FE energy and bandwidth as a function of the number of monolayers. The arrows label the position and width of FE band in the single crystal. The solid lines are guides to the eye. The $d(001)$ -spacings are measured by XRD at room temperature. (For $T < 10 \text{ K}$ these values are expected to decrease by 1% to 2%.) For the case of 1 ML, the spacing refers to the thickness of the first layer measured by AFM.

N we propose that the probability of thermalization of photoexcited charges into the FE state is proportional to the number of layers N . To support this assumption we note that an exciton created by absorption of light can be trapped by defects or it can relax to the FE state and optically recombine. In the sub-ML and 1 ML films in which all the pentacene molecules are in contact with the substrate surface, the probability of exciton trapping by defects at the interface is high. This probability is reduced as N increases (because in thicker layers an exciton has lower chance to be trapped by interface defects). This picture for nonradiative exciton trapping is valid for small N , when the thickness of the film Nt is smaller than the diffusion length of singlet excitons in pentacene thin films.²⁶ The optical emission intensity within this simplified model is thus proportional to N^2 . The assumptions of this model break down for large N .

In Fig. 2 we show that at low temperatures the FE luminescence intensity of the monolayers can be comparable to that of the high quality single crystal when measured with similar excitation. The FE emission intensity of the 5 ML sample reaches $\sim 70\%$ of that of the crystal. To some extent the relatively lower FE emission intensity in single crystal could be linked to competition with the self-trapped exciton that dominates the optical emission at low temperatures.²⁷

Figure 3 displays the evolution of FE energy and bandwidth as a function of N . While the sub-ML and 1 ML samples display similar luminescence spectra, the FE band redshifts significantly as N increases. The results indicate that the lateral size of pentacene clusters (e.g., different in sub-ML and 1 ML films) does not affect FE transition energy while the thickness of the film has crucial impact.

To consider the interplay between the number of layers N and the lateral size of pentacene clusters we note that Bohr radii of FE states ($\leq 0.6 \text{ nm}$) are significantly smaller than the thickness of a single pentacene molecular layer ($\sim 1.7 \text{ nm}$).²⁸ The blueshift in the FE energy with decreasing N is thus unlikely to arise from quantum confinement in the perpendicular z -direction. As shown in Fig. 3 room temperature x-ray diffraction (XRD) measurements indicate that the

interlayer $d(001)$ -spacing slightly changes with layering. For 2 ML, 5 ML, and 33 ML films the $d(001)$ -spacings are 1.67 nm, 1.59 nm, and 1.55 nm, respectively.

While the in-plane molecular packing remains the same as that in the thin film phase of pentacene in the first tens of monolayers,^{21,29,30} the interlayer distance actually reduces slightly with increasing N . Smaller interlayer distance in thicker layers suggests stronger interlayer molecular interactions (larger overlap integrals) that may lower the FE transition energy.^{12–15} We conjecture that the significant redshift in the FE transition energy with increasing N is linked to the reduction in the interlayer distance and the concomitant larger interlayer interactions.

The FE luminescence bands are fit with Gaussian line-shape functions. The width can be linked to the degree of inhomogeneous broadening in the nanoscale films. The FE bandwidths of the films are broadened by a factor of between 3–5 compared to that of the single crystal. The sub-ML and 1 ML pentacene films have similar width and the narrowest (~ 38 meV) FE bandwidth which could be attributed to the high uniformity of the growth of the first pentacene layer on PAMS. The slightly enhanced broadening of FE bandwidth in films with $N > 1$ may be linked to the imperfect two-dimensional growth of the second and subsequent layers and the presence of high density of grain boundaries in multilayer structures.²⁵

Figure 1(b) reveals that the pentacene monolayers exhibit optical emission bands below the FE. The sub-ML, 1 ML, and 2 ML films have a weak band centered at about 1.65 eV. This band is better defined in the thick film of ~ 33 ML. Another weak band centered at about 1.76 eV is observed only in the 2 ML sample. The 33 ML film has a well-defined low energy band centered around 1.5 eV. Definitive assignments of the bands below the FE remain open. Self-trapped excitons may not occur in monolayers. It is possible that the optical emission observed below the FE band in the pentacene monolayer films is linked to extrinsic excitonic transitions.

In summary, photoluminescence of pentacene monolayer films grown on a highly compliant polymeric substrate reveals sharp and intense FE bands. In the few monolayer limit the intensity of FE emission band increases quadratically with the number of layers. The redshift in FE energy in thicker films may be linked to reduced interlayer distance that enhances molecular overlap. The width of FE optical emission band could be due to nonuniform islands and grains formed in the films.

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