Evidence for Exciton Confinement in Crystalline Organic Multiple Quantum Wells

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Multiple-quantum-well structures based on two crystalline organic semiconductors, namely, 3,4,9,10 perylenetetracarboxylic dianhydride and 3,4,7,8 naphthalenetetracarboxylic dianhydride, have been grown by organic molecular-beam deposition. Both optical-absorption and time-resolved photoluminescence measurements reveal a significant effect on the binding energy and the radiative recombination probability of excitons due to localization of carriers. Variational calculations of the ground-state exciton energy in quantum wells have been done, and the results agree with the experimental data. This provides evidence for exciton confinement in organic quantum-well structures.

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Inorganic semiconductor multiple-quantum-well (MQW) structures have been a subject of intense study in the past decade due to their interesting electronic and optical properties which have many promising applications in optoelectronic device technology.[1] However, epitaxial growth of semiconductor heterostructures is limited to materials with small lattice mismatch.[2] In contrast, organic crystals are bonded together by the relatively weak van der Waals force,[3] which allows for the layering of materials of widely differing crystal lattices whose strain energy is insufficient to create lattice defects. In principle, therefore, it is possible to grow defect-free heterostructures with a wide range of crystalline organic semiconductors. Recently, highly ordered organic MQW structures based on 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) and 3,4,7,8 naphthalenetetracarboxylic dianhydride (NTCDA) have been grown by the ultrahigh-vacuum process of organic molecular-beam deposition (OMBD).[4,5] The so-called "quasiepitaxial" growth of organic thin films has also been demonstrated on a variety of substrate materials including inorganic semiconductors such as InP and Si. More surprisingly, highly ordered organic thin films can be grown on noncrystalline substrates such as fused quartz and glass. Thus, new opportunities for engineered heterostructures consisting of a wide range of organic material combinations layered without regard to lattice match provide exciting possibilities in the field of optoelectronics.

Both the optical and electronic properties of organic semiconductors are governed by the nature of excitons in the crystal. Excitons in most organic crystals are thought to be Frenkel-like,[3] although there are a few reports suggesting that excitons in anthracene crystals are Wannier[6,7] in nature. Therefore, it is important to determine the characteristics of excitons in the archetype compound PTCDA in order to understand its optical and electronic properties. Crystalline organic semiconductor heterojunctions (HJs) have been grown previous to this work, and their electrical and optical properties indicate that the HJ band offsets control the flow of charge between the contacting semiconductors in a manner similar to inorganic heterostructures.[8-10] Thus, MQW structures based on PTCDA and NTCDA provide the ideal tools for a study of the nature of excitons in crystalline organic semiconductors.

In this paper we report the measurement and analysis of optical-absorption spectra of organic multiple-quantum-well structures grown by OMBD. An increase of the singlet ground-state exciton energy in PTCDA with decreasing layer thickness has been observed, and the results can be understood in the context of a change in exciton binding energy due to quantum confinement in a potential well[11,12] formed by the energy-band offsets between the contacting materials. The results of our variational calculations on the well-width dependence of exciton binding energy are in good agreement with experimental data. Time-resolved photoluminescence measurements were also done for organic MQW structures, and the exciton lifetimes were found to decrease with decreasing PTCDA/NTCDA layer thickness. The decrease in exciton lifetime is explained in terms of a shrinkage in exciton volume in the MQW's,[13] and is also a result of quantum confinement of charge carriers.

The organic MQW structures investigated in this work consist of ultrathin, alternating layers of PTCDA and NTCDA of equal thickness, with layer thicknesses in the several samples ranging from 10 to 200 Å. Layer thicknesses are estimated to be uniform to within about two molecular layers (i.e., $\approx 6-7$ Å). Organic MQW structures reported in this paper were grown on glass substrates by organic molecular-beam deposition[4]—a process analogous to conventional molecular-beam epitaxy used to grow inorganic semiconductor heterostructures. The key to achieving good surface morphology and sharp interfaces was to keep the substrates at about 90 K during growth. Low-temperature quasiepitaxial growth of crystalline organic thin films on inorganic substrates has been demonstrated for a number of crystalline organic materials.[4,14,15] Under such conditions, highly ordered molecular stacks are observed for our PTCDA/NTCDA MQWs using both birefringence and
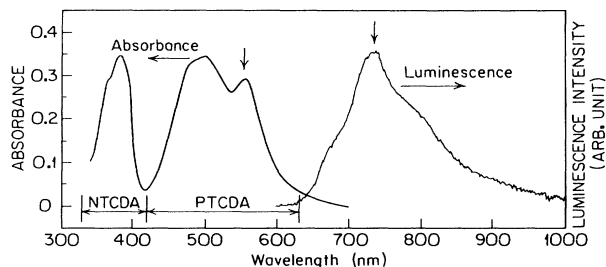
FIG. 1. Typical room-temperature optical-absorption and low-temperature (20 K) photoluminescence spectra of a PTCDA/NTCDA multiple-quantum-well sample.
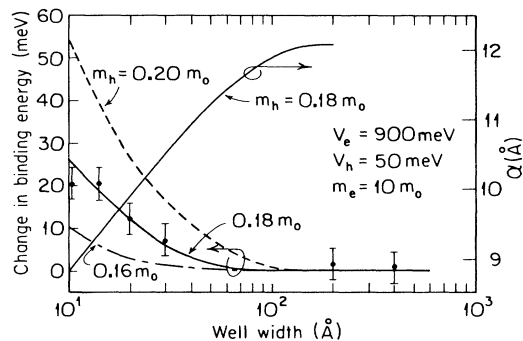

FIG. 2. Exciton line shift as a function of well width. The solid line is the result of variational calculations. The variational parameter α is also shown.

x-ray measurements in the multilayer structure consisting of PTCDA and NTCDA.[4,16]

Optical-absorption measurements were done at room temperature using a spectrophotometer. Time-resolved photoluminescence measurements of organic quantum-well samples were done at 20 K using a multiline cw Ar-ion laser with an output of 400 mW. At this energy, excitons were generated only in the PTCDA layers since the NTCDA layers are transparent to the incident light. Laser pulses were generated using an acousto-optic modulator with a rise and fall time of less than 4 ns. The laser-pulse width was 10 ns. The time decay of the monochromatic luminescence signal was measured using a double-pass 0.75-m Spex monochromator in conjunction with a multichannel photon counting averager. Deconvolution of the measured luminescence signal from the instrumental temporal response at the shortest times measured ($\sim$5 ns) has been carried out in all data analysis.

The room-temperature optical-absorption and low-temperature (20 K) photoluminescence spectra of a five-period symmetric PTCDA/NTCDA organic MQW sample with an individual layer thickness of 40 Å is shown in Fig. 1. The characteristic absorption spectra of both PTCDA and NTCDA are present, and the absorption bands are due to exciton generation in the corresponding crystalline layers. The absorption bands are relatively broad because of the strong exciton-phonon interaction characteristic of organic crystals.[7] From the lowest-energy cutoffs of the spectra, the "energy gaps" are determined to be 2.2 and 3.1 eV for PTCDA and NTCDA, respectively. We have found that the lowest-energy (0-0) singlet-exciton absorption peak in PTCDA (indicated by the arrow) shifts to higher energy as the layer thickness is decreased. No apparent shifts in the higher-energy exciton lines were observed, possibly as a result of the broad nature of these lines. The dependence of the ground-state-exciton energy shift with well width is shown by the data points in Fig. 2.

The blueshift in the exciton energy in PTCDA can be due to molecular polarization in the presence of an exciton which extends into the NTCDA in the multilayer structure.[4] It has been shown that the first-order exciton

energy correction due to polarization arising from the multilayer structures decreases the total exciton energy by a quadratic function of increasing layer thickness. However, the observed dependence on layer thickness is much weaker than that predicted from the polarization model.

Alternatively, the exciton energy shift can be due to the change in exciton binding energy as a result of quantum confinement. As the layer thickness decreases, the exciton motion becomes two dimensional. The exciton is "squeezed" in the potential well formed in the PTCDA layer, resulting in an increase in exciton binding energy. In this model, the small-band-gap PTCDA layer is treated as a potential well bounded by the large-band-gap NTCDA layers in a type-I superlattice configuration. This picture is consistent with observations made for single PTCDA/NTCDA heterojunctions using current-voltage measurements similar to those used to determine the properties of other PTCDA-based heterojunctions.[8] Thus, electrons and holes are confined in PTCDA layers of width L_z. The total Hamiltonian[11] for an exciton in a quantum well is

$$H_{tot} = H_e + H_h + H_{xy} , \tag{1}$$

where H_e and H_h describe the motion of electrons and holes along the z axis in the quantum well, and H_{xy} describes the two-dimensional motion of excitons in the x-y plane (parallel to the heterointerfaces). The relative dielectric constant of PTCDA used in this calculation is 3.6,[16] assuming the crystal is an isotropic dielectric continuum. While it is known that dielectric anisotropies in such films are large, the isotropic continuum model nevertheless has been found to provide a very accurate description of charge-transfer exciton dynamics in similar organic crystals such as anthracene.[6]

The Schrödinger equation can then be solved by the variational principle using the following trial wave function:

$$\Psi_{tot} = \Psi_e \Psi_h \exp[-(r^2/\alpha^2 + z^2/\beta^2)^{1/2}] . \tag{2}$$

Here, $z = z_e - z_h$ and $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$, where z_e, $\mathbf{r}_e$, z_h, $\mathbf{r}_h$ are the positions for electrons (e) and holes (h) in the z direction and the x-y plane. In Eq. (2), the total wave function Ψ_{tot} consists of the hydrogen $1s$-like wave function (Ψ_{1s}), modulated by the harmonic part of the wave function, i.e., the electron (Ψ_e) and hole (Ψ_h) wave functions. Also, α is a variational parameter in the trial solution, and β is set equal to a_0, where a_0 is the exciton Bohr radius in the bulk crystal.

It should be noted that the trial wave function used is assumed to be ellipsoidal with $\beta = a_0$. Such an ellipsoidal trial wave function is consistent with the results of the theoretical calculations done by Shinozuka and Matsuura.[12] For very small well widths, the harmonic part of Eq. (2) dominates the exciton z dimension.

To solve the Schrödinger equation, the binding energy is minimized as a function of α. The results of the calculation are shown by the solid line in Fig. 2. The parameters used in this model are listed in Table I. Here, the sum of the electron potential (V_e) and the hole potential (V_h) is equal to the difference in energy gaps of PTCDA and NTCDA. Of all the parameters used in the calculation, the results are only sensitive to the choice of the effective hole mass m_h. Using these parameters, a good fit to the experimental data is obtained for $m_h = 0.18 m_0$, where m_0 is the electron rest mass. Note that a small value of m_h and a relatively large value of effective electron mass m_e were chosen in the calculation. A large difference in electron and hole effective masses is common in organic crystals such as naphthalene and anthracene.[17] Indeed, in previous work, it has been shown that PTCDA is a preferentially hole-transporting material, indicating that m_h is substantially less than m_e.[4] The effect of different values of m_h are shown for comparison in Fig. 2. Note that the fit to the data is good except for the 10-Å sample. This can have several causes, including nonuniform layer thickness and penetration of the exciton wave function into adjacent PTCDA layers.

The calculated values of α, as shown in Fig. 2, increase monotonically with increasing well width, and asymptotically approach the free-exciton Bohr radius of 12 Å, indicating that the exciton is confined in the quantum wells. The dependence of α on L_z for the ellipsoidal exciton can be understood as follows: As well width decreases, Ψ_{1s} becomes a 2D wave function resulting in a decrease in its extent in the z direction. At the same

TABLE I. Parameters used in the variational calculations.

Parameters	Symbol	Unit	Value
Hole mass	m_h	m_0	0.18
Electron mass	m_e	m_0	10.0
Electron potential	V_e	meV	900
Hole potential	V_h	meV	50
Relative dielectric constant of PTCDA	ε_p		3.6

time, the effective Bohr radius (α) in the x-y direction also decreases with decreasing L_z in order for the wave function to retain spherical symmetry. In the case of an extremely narrow well, the exciton is squeezed to the extent that its wave function is forced to deviate from spherical symmetry.

To test this conclusion of quantum confinement, photoluminescence (PL) measurements were carried out by optically pumping the MQW's with an Ar-ion laser. From the absorption spectrum in Fig. 1, it is apparent that NTCDA is transparent to the excitation from the Ar-ion laser, and therefore the PL spectrum for a MQW sample shown in the figure is due to PTCDA alone. Also, no PL signal is obtained when NTCDA is optically pumped by the Ar-ion laser. From the PL spectrum, we can identify two major emission bands at 720 and 800 nm, and a shoulder at about 680 nm. From the energy difference between the absorption and luminescence spectra (indicated by arrows), we obtain a Franck-Condon shift of 4050 cm^{-1}. Indeed, such a large Franck-Condon shift in PTCDA is observed in MQW samples as well as in the bulk PTCDA crystal. To our knowledge, this is the largest value reported for a Franck-Condon shift in organic crystals, and is indicative of an extremely strong exciton-phonon coupling along the tightly packed PTCDA molecular stacks.

Time-resolved PL measurements were made by monitoring the time decay of the luminescence signal at 720 nm (the 1-0 singlet transition). The PL-signal decay transients for two MQW samples obtained at 20 K are shown in the inset of Fig. 3. The inset shows the response for the two samples under equal excitation intensity. Here, the exponential decay over several decades in intensity of the transient is apparent. In addition, the PL decay time is found to decrease as the layer thickness decreases. The dependence of the exciton lifetime on well width is shown in Fig. 3. The exciton lifetime τ_{ex} is found to be 10.8 ± 0.5 ns for $L_z = 20$ nm, decreasing to 5.7 ± 0.5 ns for $L_z = 1$ nm. The change in exciton lifetime in the MQW samples could be due to traps at the interface. The overall recombination rate can be written as $\tau^{-1} = \tau_r^{-1} + \tau_{\text{nr}}^{-1}$, where τ_r is the exciton radiative lifetime and τ_{nr} is the trapping time. If the nonradiative recombination rate is such that $\tau_{\text{nr}} \leq \tau_r$, the observed lifetime should decrease due to traps. The results of our PL measurements show that the time-integrated luminescence intensity was found to be constant with sample layer thickness, indicating that nonradiative recombination is not important. Further, if the exciton lifetime in molecular crystals is dominated by traps, it should decrease with increasing temperature.[18] However, our time-resolved measurements show that the radiative decay time is independent of temperature from 20 to 295 K, indicating again that the PL signal here is not due traps.

The decrease of τ_{ex} with decreasing L_z, therefore, can result from an increase in the spontaneous recombination
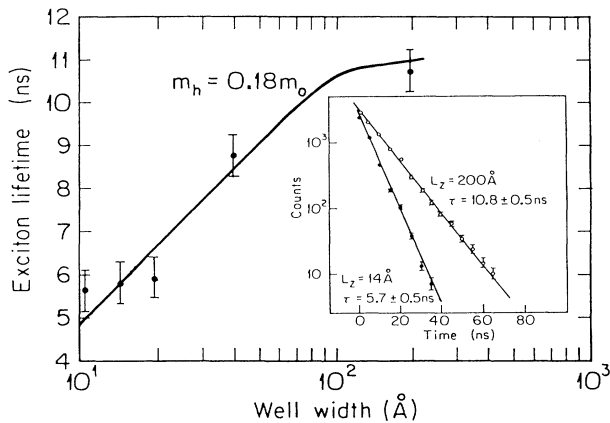
FIG. 3. Exciton lifetime τ_{ex} as a function of well width. The solid line is the fit to the data based on the theory described in the text. Inset: PL-signal time-decay transients for two MQW samples. Note that the transient for the $L_z = 200$ Å sample has been shifted upward by 10% of a decade in this plot.

rate due to an increase in the overlap of the electron and hole wave functions in the PTCDA potential wells. A similar explanation of the observed dependence of the exciton lifetime on well width has been observed in GaAs/GaAlAs quantum wells.[13] For the hydrogenic $1s$ state, R_{sp} can be shown to be proportional to the exciton volume[19] (given by $\int |\Psi_{tot}|^2 d^3r$, which differs significantly from $a_0^2 L_z$ used in previous work[13]). Using the results of the calculation of α discussed above (Fig. 2), the exciton volume in a MQW is observed to decrease with decreasing well width. The shrinkage of the exciton due to quantum confinement can thus account for the decrease in exciton lifetime. Based on the above analysis and using the parameters given in Table I, the dependence of exciton volume, and hence τ_{ex}, on well width is shown by the solid line in Fig. 3. The results of the calculation are in good agreement with the exciton lifetime data, indicating the exciton quantum-confinement model can quantitatively account for the change in both exciton binding energy and exciton lifetime using the model given above and the parameters in Table I.

In summary, we have characterized PTCDA/NTCDA organic quantum-well structures by both optical-absorption and time-resolved photoluminescence measurements. The exciton binding energy was found to increase with decreasing well width, whereas its lifetime decreased with decreasing well width. The dependence of exciton binding energy and lifetime on L_z can both be understood in terms of confinement of Wannier-like molecular excitons in quantum wells. To our knowledge, these results provide the first evidence for exciton quantum confinement in organic MQW structures. From the results of our calculation, the effective exciton Bohr radius is 12 Å, indicating that the exciton wave function extends to three or four molecular layers in PTCDA.

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