

# Photoluminescence characterization of vacuum deposited PTCDA thin films

W. BAŁA<sup>1</sup>, Z. ŁUKASIAK<sup>1</sup>, M REBARZ<sup>\*1</sup>, P. DALASIŃSKI<sup>1</sup>, A. BRATKOWSKI<sup>1</sup>,  
D. BAUMAN<sup>2</sup>, and R. HERTMANOWSKI<sup>2</sup>

<sup>1</sup>Institute of Physics, N. Copernicus University, 5/7 Grudziądzka Str., 87-100 Toruń, Poland

<sup>2</sup>Faculty of Technical Physics, Poznań University of Technology, 13A Nieszawska Str.,  
60-965 Poznań, Poland

---

*We investigated photoluminescence (PL) under steady state excitation and photoluminescence excitation (PLE) spectra of thin 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) films deposited on (001)Si substrate with various layer thicknesses grown at different substrate temperatures. The PL and PLE spectra have been measured at various temperatures, ranging from 10 K to 325 K. The PTCDA films exhibit strong luminescence at all mentioned ranges of temperature and for different values of excitation energy. The vibronic structure of PL spectra is clearly resolved at different temperatures. The position of peaks on energy scale depends on the temperature. We have observed a blue-shift of peaks with the decrease in the temperature. In all the investigated samples, the thermal quenching of PL has been observed. Analysis of the temperature dependence of the intensity bands, their position and full width half maximum (FWHM) allowed to find the energy barriers between the excited state and defect state. We propose a schematic potential energy diagram which explains mechanism of PL recombination.*

---

**Keywords:** PTCDA, photoluminescence, excitons.

## 1. Introduction

The growing interest in molecular organic materials as the basis for creating optoelectronic devices has led to an increasing interest in the structure and growth dynamics of organic molecular thin films. Molecular organic semiconductors are promising materials for organic light-emitting diodes [1,2], thin-film transistors [3], and photovoltaic devices [4]. One of the most intensively studied molecules is 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), forming well ordered polycrystalline films on a variety of substrates. The distance between the molecular planes is 0.337 nm for the PTCDA. For this reason PTCDA and its derivatives can be regarded as a model system for quasi-one-dimensional molecular crystal. The interesting optical and electronic properties of PTCDA in the crystalline phase are due to the significant intermolecular interaction of the  $\pi$ -electron systems. Understanding of the microscopic models of recombination transitions in PTCDA crystals and thin films is rather limited [5]. In spite of various optical and electronic studies, a clear picture of the electronic band structure is still under debate.

Organic/inorganic interfaces are suitable for building and testing new electronic devices that could be used in nanotechnology [2,6,7]. Organic molecules modify semi-

conductor density of states, introducing new states in the gap, or inducing other changes in the electronic behaviour. Particularly, this is the case for PTCDA molecules absorbed on semiconductor surfaces. These systems show electronic characteristics like a diode and have been extensively studied due to their application in new organic/inorganic optoelectronic devices.

In this paper, we present the results of photoluminescence emission spectra and photoluminescence excitation spectra under steady-state conditions at different temperatures and different energy of excitation for PTCDA layers grown on n-type Si substrates. The obtained results show dependence of luminescence properties on the temperature.

## 2. Experimental

The 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) layers have been prepared in vacuum chamber at the pressure of about  $p = 2 \times 10^{-4}$  Pa on n-type (001) oriented Si substrate at temperature 410 K. Purified PTCDA powder (99.99% Sigma Aldrich Co.) was loaded into a quartz effusion cells with a nozzle of 3 mm in diameter on the top. The n-type (001) Si substrates were located 10 cm from the source. The Si substrates were first sonificated in acetone, distilled water, isopropanol, and finally in distilled water. Next, the substrates were moved into the deposition chamber where PTCDA layers were deposited onto heated sub-

\* e-mail: mateo@phys.uni.torun.pl

strates. Substrates were held at different temperatures at the range from the room temperature to 523 K during evaporation. By fixing the temperature of the effusion cell at  $T = 540$  K, the evaporation rate was kept at about 2 nm/min.

For photoluminescence (PL) and photoluminescence excitation spectra (PLE) experiments, the samples were placed in a closed cycle He cryostat (HC2 – APD Cryogenics Inc.). The PL and PLE spectra of the PTCDA layers were measured at different temperatures at the range from 10 K to 325 K. PL was excited with a He-Cd laser ( $\lambda = 325$  nm) and detected by photomultiplier (R-928 HAMAMATSU). The monochromator (SPM2-Zeiss) was employed for the spectral selection and the signal was processed and analysed by a personal computer. For PLE experiments, a halogen tungsten lamp (250 W) was used. PL and PLE spectra were checked with black body radiation from a halogen tungsten lamp with known emission spectrum.

### 3. Results and discussion

PL and PLE spectra of PTCDA layer grown on Si substrate for the temperature of 25 K are presented in Fig. 1. The vibronic structure of these spectra is visible. Besides, a classical Stokes shift between the lowest PLE band and the highest PL band can be seen. Figure 2 shows typical PL spectra of PTCDA thin film at a few values of temperature. Luminescence was excited at 325 nm (3.8 eV). These spectra were measured at the wavelength range from 500 nm to 850 nm. We observed a strong PL emission at about 2.14 eV at 13 K. The integral PL emission is nearly constant in the temperature range of 13–80 K. Next it drops slowly and when the temperature increases to above 100 K, the integral PL emission is thermally quenched very quickly, accompanied by a large shift to lower energy. The contributions of different recombination centres connected with emission peaks for selected temperatures are shown separately in Fig. 3. We used a sum

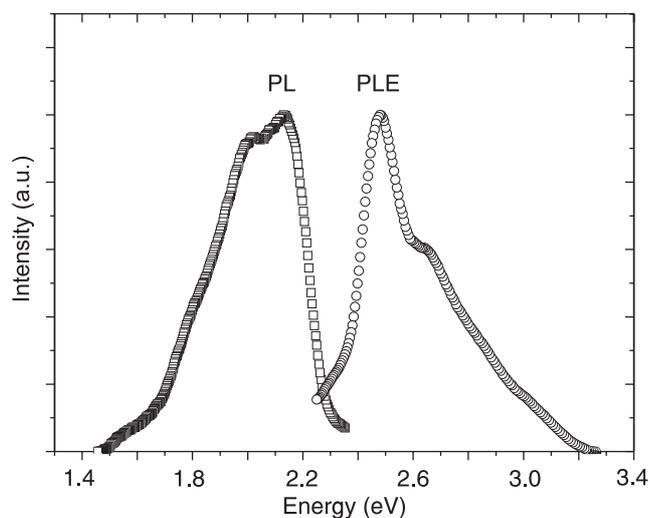


Fig. 1. Photoluminescence and photoluminescence excitation spectra of a PTCDA layer at 25 K.

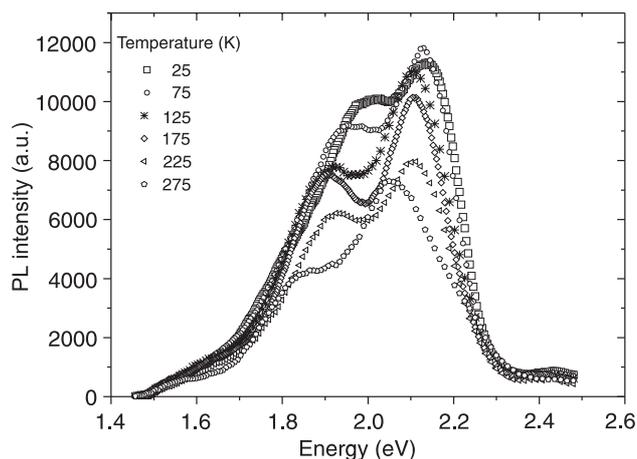


Fig. 2. Photoluminescence emission spectra of PTCDA at different temperatures.

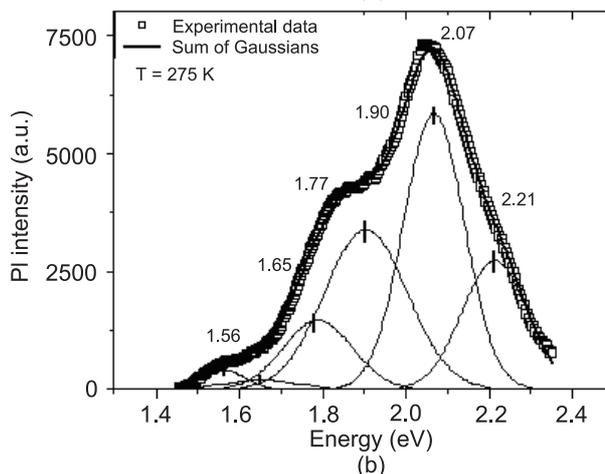
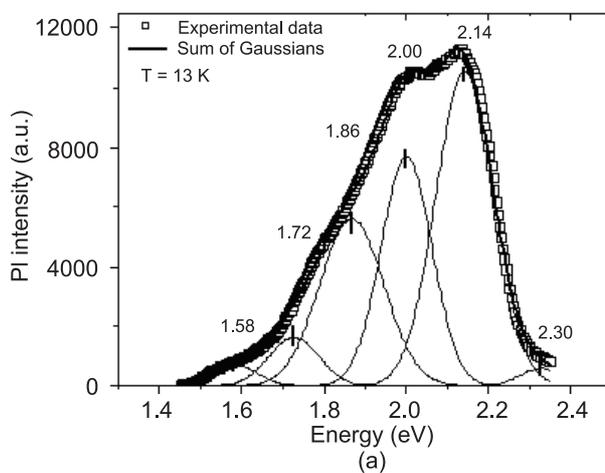


Fig. 3. Photoluminescence spectra of PTCDA with the fit (solid curve) based on Eq. 1 at 13 K (a) and 275 K (b).

of the normalized Gaussians as a model function for the line-shapes of PL peaks [5]

$$I_{PL}(\hbar\omega) = \omega^3 \sum_j \frac{a_j}{\sigma_j \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\omega - \omega_j}{\sigma_j} \right)^2 \right], \quad (1)$$

where  $j$  is the number of a peak,  $\omega_j$  is the position,  $\sigma_j$  is the width, and  $a_j$  is the area. Besides, the multiplicative factor  $\omega^3$  is related to the density of states of the emitted photons [5,8]. By performing a simultaneous fit of the PL spectra taken at different temperatures, a temperature red-shift of the main peak position by 0.267 meV/K was obtained. The temperature dependence of position for individual peaks can be described by the following expression [9]

$$\hbar\omega = \hbar\omega_0 - \frac{A}{\exp\left(\frac{\hbar\omega_0 B}{kT}\right) - 1}, \quad (2)$$

where  $\hbar\omega_0$  is the position of the peak at 0 K temperature,  $A$  and  $B$  are the imposed fitting parameters.

Figure 4 presents the position of the main peak (2.14 eV) versus temperature with fitting using Eq. (2). In inset we present the temperature dependence of position for other components. We have also observed that full width half maximum of the PL peaks is constant at low temperatures and increases when the temperature increases to above 125 K. This dependence can be approximated by the formula [10]

$$\Gamma = \Gamma_0 \left( 1 + \frac{2}{\exp\left(\frac{\hbar\omega_0}{2kT}\right) - 1} \right), \quad (3)$$

where  $\Gamma_0$  is the full width half maximum at the temperature 0 K and  $\omega_0$  is the phonon frequency. The biggest broadening was observed for 2.00 eV peak. The temperature dependence of FWHM for the mentioned peak and data fitted by Eq. (3) are shown in Fig. 5. A plot of the integral PL emission versus inverse temperature for typical PTCDA samples is presented in Fig. 6. As we can see, the intensity of PL emission is independent of temperature below 80 K and decreases rapidly above 100 K. For this reason, the

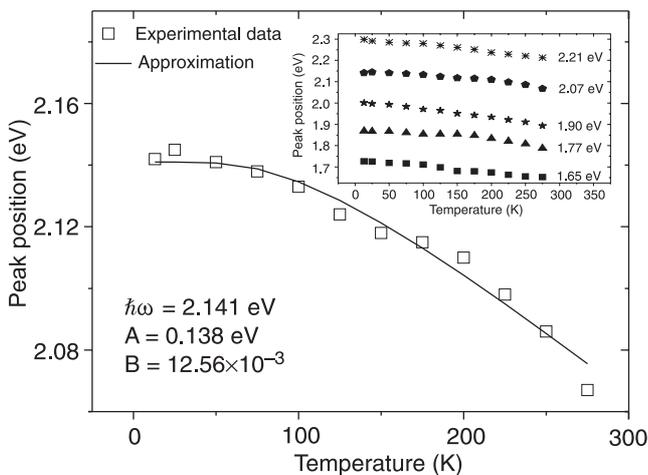


Fig. 4. Peak position of 2.14-eV contribution as a function of temperature. In inset: the temperature dependence of other indicated peaks.

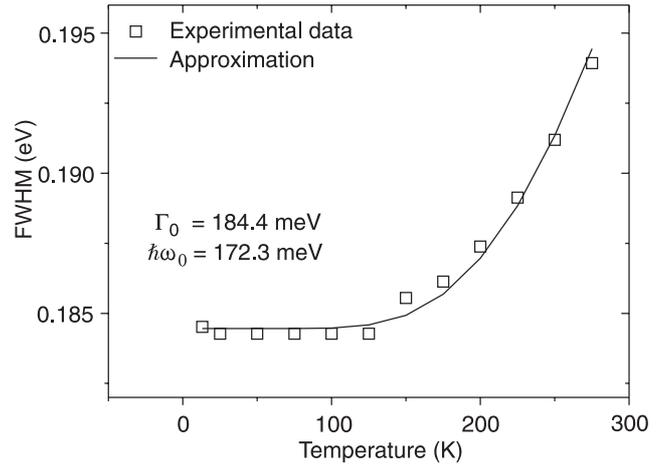


Fig. 5. Temperature dependence of full width half maximum (FWHM) of 2.00 eV peak. Fitting by Eq. (3) is shown in a solid line.

quenching of PL emission can be described by means of a two-step process and experimental data are fitted by the following expression [11]

$$I = \frac{I_0}{1 + A \exp\left(\frac{-E_1}{kT}\right) + B \exp\left(\frac{-E_2}{kT}\right)}, \quad (4)$$

where  $E_1, E_2$  are the thermal activation energies and  $A$  and  $B$  are the constants connected with the lifetime in the excited state of a molecule and the effective scattering time from the excited state to the nonradiative centre. The calculated activation energies for all investigated samples were about  $E_1 = 20$  meV and  $E_2 = 130$  meV, respectively.

The thermal quenching of photoluminescence in PTCDA structure can be described by the configuration coordinate model. This is schematically shown in Fig. 7 where  $S_0$  and  $S_1$  curves are the adiabatic potentials of the

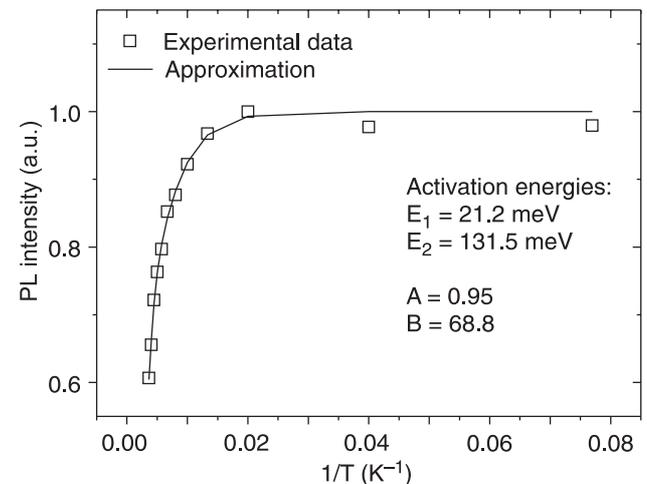


Fig. 6. Dependence of the integral PL intensity on inverse temperature for PTCDA. The fitting with a two-step thermal quenching process is shown in a solid line.

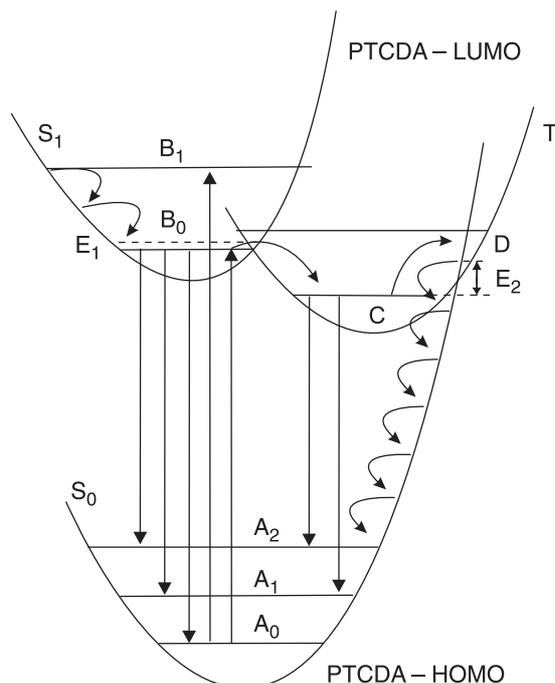


Fig. 7. Configuration coordinate model.  $S_0$  and  $S_1$  curves are related to ground and excited states of PTCDA molecule. Consecutive vibronic levels are labeled as  $A_i$  and  $B_i$ .  $T$  curve corresponds to self-trapped exciton state connected with the defect. Arrows represent absorption transitions ( $A_0B_i$ ), emission radiative transitions ( $B_0A_i$  and  $CA_i$ ), thermal excitations ( $B_0C$  and  $CD$ ) and nonradiative phonon emission ( $DA_i$ ).

ground and excited state of molecule. The  $T$  curve is the exciton state connected with the defect state of a molecule. The  $AB_i$  arrows correspond to absorption transitions. The  $B_0C$  transition over  $E_1$  barrier corresponds to capture of carrier by a defect and relaxation of the lattice around defect brings it into an excited state. The radiative emission from the excited state  $S_1$  and the exciton state  $T$  is shown by means of  $B_0A_i$  and  $CA_i$  arrows, respectively. The  $CD$  transition is the thermal excitation of the defect over the crossover of the curves  $S_0$  and  $T$ , after which a nonradiative recombination takes place (the  $DA$  transition). At high temperature, a lot of carriers have sufficient energy to overcome  $E_2$  barrier and we observe photoluminescence drop.

#### 4. Conclusions

We have investigated systematic temperature dependence of the photoluminescence emission under steady-state conditions for PTCDA layers obtained by thermal evaporation

deposition. The investigated samples exhibit strong luminescence in the temperature range from 13 K to 325 K. PL peaks positions, their width and relative intensity depend on temperature. When the temperature increases, PL peaks are red-shifted and this shift increases for higher temperatures. The full width half maximum of peaks increases when the temperature increases. The integral emission above the temperature of 100 K indicates quenching with activation energy of about 130 meV. Exciton-phonon interactions provide a nonradiative transition path leading to luminescence quenching at higher temperatures.

#### Acknowledgements

This work has been supported by the University N. Copernicus Research Program (project UMK 436 F, 443-F).

#### References

1. W. Brutting, S. Berleb, and A.G. Miickl, "Device physics of organic light-emitting diodes based on molecular materials", *Org. Electron.* **2**, 1 (2001).
2. S.R. Forrest, "Ultrathin organic films grown by organic molecular beam deposition and related techniques", *Chem. Rev.* **97**, 1793 (1997).
3. H.E. Katz, "Organic molecular solids as thin film transistor semiconductors", *J. Mater. Chem.* **7**, 369 (1997).
4. J. Simon and J.J. Andre, *Molecular Semiconductors*, Springer, Berlin, 1985.
5. A.Yu. Kobitski, R. Scholz, G. Salvan, T.U. Kampen, H.P. Wagner, and D.R.T. Zahn, "Time-resolved photoluminescence study of excitons in thin PTCDA films at various temperatures", *Appl. Surface Science* **212/213**, 428 (2003).
6. L. Torsi, A. Dodabalapur, L. Rothberg, A. Fung, and H.E. Katz, "Intrinsic transport properties and performance limits of organic field effect transistors", *Science* **272**, 1462 (1996).
7. F. Gamier, R. Hajlaoui, A. Yassar, and P. Srivastava, "All polymer field effect transistor realized by printing techniques", *Science* **265**, 1684 (1994).
8. R. Loudon, *The Quantum Theory of Light*, Clarendon Press, Oxford, 1983.
9. M. Liu, L. Bursil, S. Praver, K. Nugent, Y. Tong, and G. Zhang, "Temperature dependence of Raman scattering in single crystal GaN films", *Appl. Phys. Lett.* **74**, 3125–3127 (1999).
10. K. Akers, R. Aroca, R. Ah-Mee Hor, and R.O. Loutfy, *J. Phys. Chem.* **91**, 2954 (1987).
11. H.J. Lozykowski and V.K. Shastri, "Excitonic and Raman properties of ZnSe/Zn<sub>1-x</sub>Cd<sub>x</sub>Se strained-layer quantum wells", *J. Appl. Phys.* **69**, 3235–3242 (1991).