Energy level alignment at molecular semiconductor/GaAs(100) interfaces: Where is the LUMO?

T.U. Kampen, H. Méndez, and D.R.T. Zahn
Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany

Abstract. The energy position of the lowest unoccupied molecular orbital (LUMO) in 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and dimethyl-3,4,9,10-perylenetetracarboxilic diimide (DiMe-PTCDI) was determined by investigating the energy level alignment at molecular semiconductor/GaAs(100) interfaces. Interface dipoles are found to form at the interfaces of both organic materials and consequently, the vacuum level alignment rule does not hold. The interface dipoles vary as a function of the difference in electron affinities of substrate and organic layer and the HOMO-LUMO transport gap of PTCDA is determined to 2.44 ~ 2.55 eV. Taking into account the difference in the optical band gaps of PTCDA and DiMe-PTCDI the transport gap of DiMe-PTCDI is determined to 2.36 ~ 2.47 eV.

1. Introduction

At semiconductor interfaces the alignment of energy levels may result in barriers for the injection of charge carriers. In inorganic semiconductors like silicon or gallium arsenide the respective energy levels important for the transport of charge carriers are the valence band maximum (VBM) and the conduction band minimum. The corresponding energy levels in molecular semiconductors for the transport of electrons and holes are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. One widely used technique for the investigation of the energy position of occupied states, for example the VBM or the HOMO, with respect to the Fermi level is photoelectron spectroscopy. In inorganic semiconductors the position of the CBM can be deduced by simply adding the band gap to the experimentally determined position of the HOMO. Band gaps are usually determined from the optical absorption where the formation of excitons have to be taken into account. In inorganic semiconductors exciton binding energies amount to a few meV and can be neglected in the simple approach described above for the determination of the energy position of the CBM. In molecular semiconductors the "band gap" is defined as the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Depending on the experimental technique employed to determine the band gap there is a difference between the so called optical and transport band gap, which amounts to the exciton binding energy being of the order of 1 eV.

3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and dimethyl-3,4,9,10-perylenetetracarboxilic diimide (DiMe-PTCDI) belong to a class of aromatic molecules with a filled π-electron system showing properties similar to those of wide band gap semiconductors [1]. From optical absorption measurements the optical band gap of PTCDA is determined to 2.22 eV [2,3]. Hill *et al.* performed combined photoemission and inverse photoemission measurement from which they determined the energy positions of the maximum in the density of states of the highest occupied and lowest unoccupied states. Using their energy difference and taking into account polarization effects at the surface and in the bulk of the organic film they estimated the transport gap to (3.2 ± 0.4) eV [4].
In an earlier publication we have presented a direct and more accurate determination of the position of the LUMO by using differently prepared GaAs(100) substrates [5]. The electronic surface properties of GaAs, i.e. electron affinity and surface band bending, can be changed using different surface treatments. The interface dipole at PTCDA/GaAs(100) interfaces changes as a function of the electron affinity of the substrate. For equal electron affinities, i.e. the valence band-maximum of the GaAs and the HOMO of the molecular semiconductor align, the interface dipole vanishes. Here, we will use these results for the investigation of the energy level alignment at DiMe-PTCDI/GaAs(100) interfaces.

2. Experimental

Ultraviolet photoemission (UP) measurments were performed either using synchrotron radiation or a He discharge lamp for excitation. The overall resolution was measured to be better than 0.2 eV. For the determination of the sample work function, a sample bias of –9V was given to allow the observation of the secondary electron onset position. The ionisation energy IP of the substrate surfaces (IP_s) was systematically varied from (5.23±0.10) eV, (5.55~5.92±0.10) eV, to (6.40±0.10) eV for GaAs(100)-c(4×4), wet chemically S-passivated GaAs(100), and Se-passivated GaAs(100)-(2×1) surfaces, respectively. Homoepitaxially grown n-type GaAs(100) layers ($n=1\times10^{18}$ cm^{-3}) capped with a thick amorphous As layer served as substrates for the preparation of GaAs(100)-c(4×4) and Se-GaAs(100) surfaces. Selenium was produced by decomposition of $SnSe_2$ at 340 °C according to $SnSe_2 \longrightarrow SnSe + Se \uparrow$ [6] and evaporated onto the substrates kept at 330°C. Te-doped n-type GaAs(100) ($n=2\cdot10^{17}$ cm^{-3}) was used as substrate material for wet chemically etched S-GaAs(100) surfaces. The samples were first degreased and then etched in a 3:1 mixture of CCl_4 and S_2Cl_2 for 10 s. The etching is followed rinsing the samples successively in CCl_4, acetone, ethanol and deionized water for 5 s each. After transferring the samples into a UHV system they are annealed at 430°C. Both passivation procedures lead to a well ordered, (2x1) reconstructed surface as revealed by LEED [7]. PTCDA and DiMe-PTCDI were deposited onto these different surfaces from a Knudsen cell operating at 280°C. The nominal thickness of the organic films was controlled by a quartz microbalance located in the vicinity of the sample. The typical evaporation rate was 0.5~1 nm/min. For the measurement of the optical absorption PTCDA and DiMe-PTCDI films with 40 nm thickness were grown on quartz glass substrates. The optical absorption was measured *ex situ* using a SPECORD M40 UV/VIS spectrometer.

3. Results and discussion

Figure 1 presents the optical absorption of PTCDA and DiMe-PTCDI films grown on glas substrates. Both spectra look very similar due to the fact that the molecules only

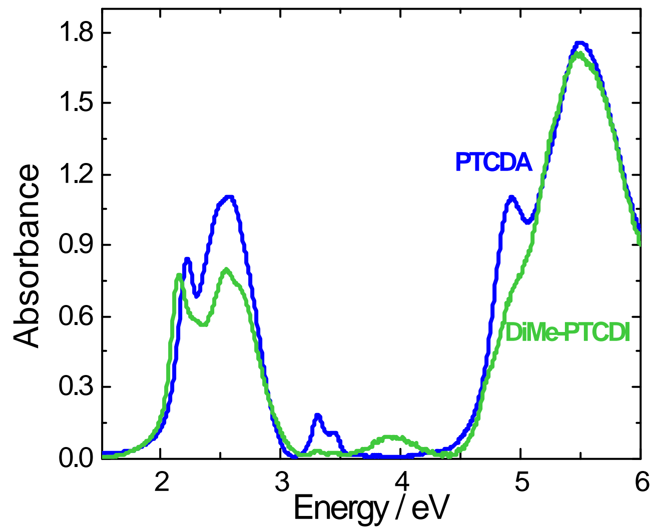

Figure 1. Absorption spectra of 40 nm films of PTCDA and DiMe-PTCDI grown on quartz glass.

differ in DiMe-PTCDI having $N-CH_3$ end groups instead of the anhydride groups in the case of PTCDA. For PTCDA the absorbance is larger in the energy range around 2.5 eV and 3.2 eV. At about 5 eV a distinct peak can be seen in the case of PTCDA compared to DiMe-PTCDI films. The most important result is the different energy position of the first maximum in the absorbance at low photon energies which is attributed to HOMO-LUMO transitions. These peaks are at 2.22 eV and 2.14 eV for PTCDA and DiMe-PTCDI, respectively. This indicates that the optical band gap of DiMe-PTCDI is by 80 meV smaller than the optical band gap of PTCDA.

Figure 2 presents an example of UP spectra with binding energy scale for the clean S-passivated GaAs(100) surface and after subsequent deposition of PTCDA.. The left and right panels show the onset of the low kinetic (high binding) energy secondary electron peak and the valence band structures, respectively. IP_S is obtained by subtracting the

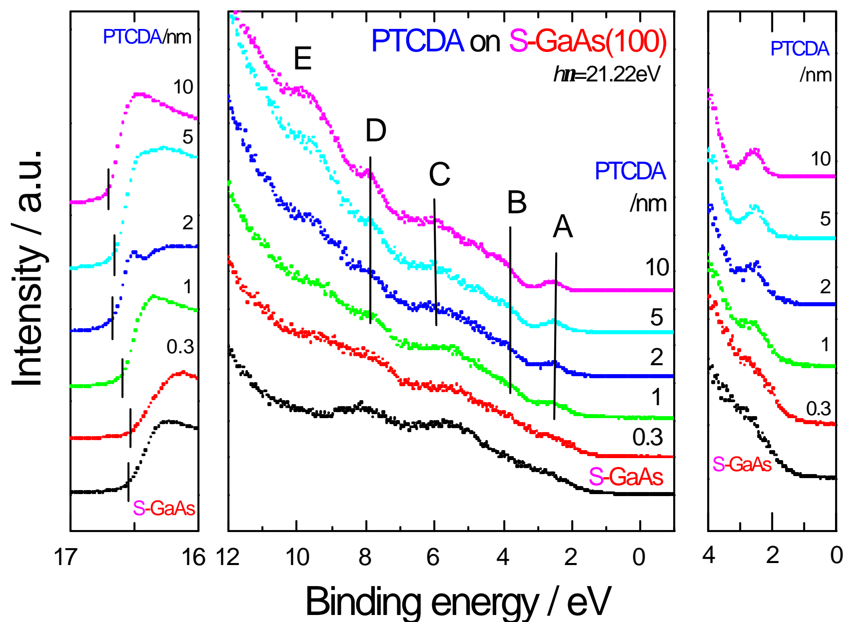

Figure 2 VB spectra upon deposition of PTCDA on S-GaAs(100) surfaces. The spectra were measured using a He discharge lamp (*hn* = 21.22eV).

total width of the valence band spectra from the photon energy, i.e. $IP_S = h\nu - (E_{cutoff} - E_{VBM})$. Here, E_{cutoff} and E_{VBM} represent the energy positions of the secondary electron onset and the VBM of the substrate surfaces relative to E_F, respectively. IP_{PTCDA} was obtained by replacing E_{VBM} by the low binding energy edge of HOMO (E_{HOMO}) in the previous equation. The shifts in E_{cutoff} upon PTCDA deposition can be interpreted as interface dipoles while the energy barrier for hole transport is obtained by $E_{VBM} - E_{HOMO}$. The only energy positions that are not directly obtained from the measured UP spectra are E_{CBM} of the substrates and E_{LUMO} of the PTCDA films. In order to determine E_{CBM} the optical gap (1.42eV) of GaAs may be added to the position of the VBM.

In the spectra of thick PTCDA films, four features from π occupied molecular orbitals (A,B,C,D) and an σ orbital (E) of PTCDA are clearly seen. This is in good agreement with previous work [8,9,10]. According to a molecular orbital calculation for the PTCDA molecule by Kera *et al.* [10], the HOMO band (A) consists of a single molecular orbital of π character distributed over the perylene core. The next three bands (B,C,D) are related to some of π character from perylene core and molecular orbital derived from oxygen $2p_x$ and $2p_y$ atomic orbitals. The feature E is ascribed to π character from perylene core and C=O and involves contribution of some σ states.

Additional core level spectra of the substrate components (Ga 3d, As 3d, Se 3d and S 2p) measured upon the PTCDA deposition on S-GaAs(100), Se-GaAs(100) as well as GaAs(100)-c(4×4) surfaces show no change in the lineshape and energy position, indicating that no chemical reaction occurs between the films and the substrates and that the band bending of the substrate surfaces does not change upon PTCDA deposition [11]. In addition, the energy position corresponding to the centre of the PTCDA HOMO in UP spectra for each sample does not appear to change during the stepwise deposition also indicating that there is no band bending in the organic film. The measured IP_{PTCDA} amounts to 6.56 - 6.67 eV, probably due to slight variations in surface morphologies and molecular orientation. For all substrates used the HOMO is found to be below the

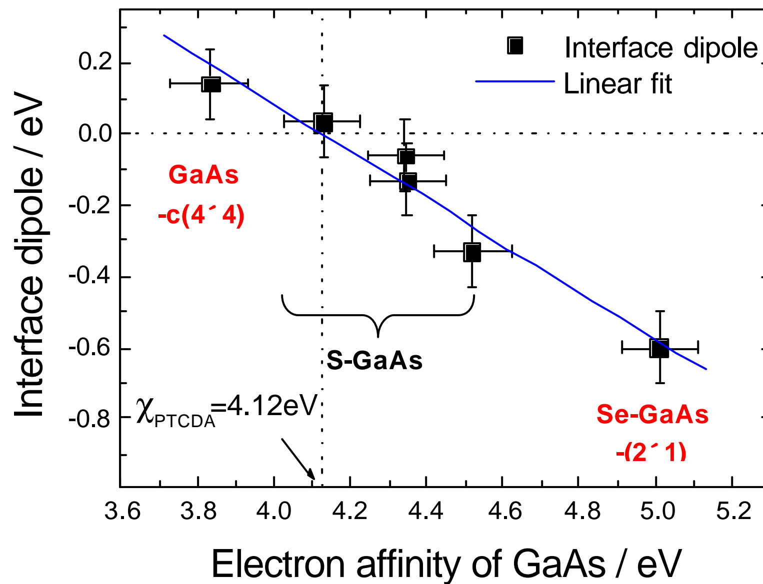

Figure 3: The interface dipole formed at PTCDA/GaAs(100) interfaces vs. χ of GaAs(100) surfaces.

VBM of GaAs(100). In the case of the PTCDA/S-GaAs(100) the VBM-HOMO offset amounts to 0.97 eV. The position of the vacuum level, on the other hand, changes upon PTCDA depostion, the amount of shift and its direction depending on the substrate treatment. For the data shown in fig.1 the vacuum level determined form the energy position of the secondary electron peak shifts to higher binding upon PTCDA deposition. This indicates that the vacuum level of PTCDA is below the vacuum level of the S-passivated GaAs(100) substrates. For the deposition of PTCDA on non passivated substrates the opposite trend was observed.

A strong correlation is found between the interface dipole and the relative energy position between E_{LUMO} and E_{CBM}, respectively the electron affinities of the PTCDA film (χ_{PTCDA}) and substrates (χ_s). At the PTCDA/GaAs(100)-c(4×4) interface where a positive interface dipole is formed, E_{LUMO} is located below E_{CBM}. The situation is reversed when a negative dipole is formed, as in the case of the PTCDA/Se-GaAs(100) interface. Consequently, the interface dipole formed at PTCDA/S-GaAs(100) varies from positive to negative depending on IP_s (or χ_s). It can therefore be deduced that the formation of the interface dipole at PTCDA/GaAs(100) interfaces is possibly driven by the difference in EA_S and EA_{PTCDA} and that in general the vacuum level alignment rule is not applicable for those interfaces.

In fig. 3 the interface dipole is presented as a function of χ_s. It can be seen that the interface dipole formed at PTCDA/GaAs(100) interfaces is linearly dependent on χ_s. Using a linear fit, the interface dipole is found to be zero at χ_s=(4.12±0.10) eV. This value also represents χ_{PTCDA} assuming that the formation of the interface dipole is driven by the difference in χ_S and χ_{PTCDA}. Using χ_{PTCDA}=(4.12±0.10) eV, the energy offset between E_{CBM} and E_{LUMO} at the interfaces can be estimated to be (–0.17±0.10) eV for PTCDA/GaAs(100)-c(4×4), (0.05~0.08±0.10) eV for PTCDA/S-GaAs(100), and (0.27±0.10) eV for PTCDA/Se-GaAs(100) interfaces. In addition, assuming that the

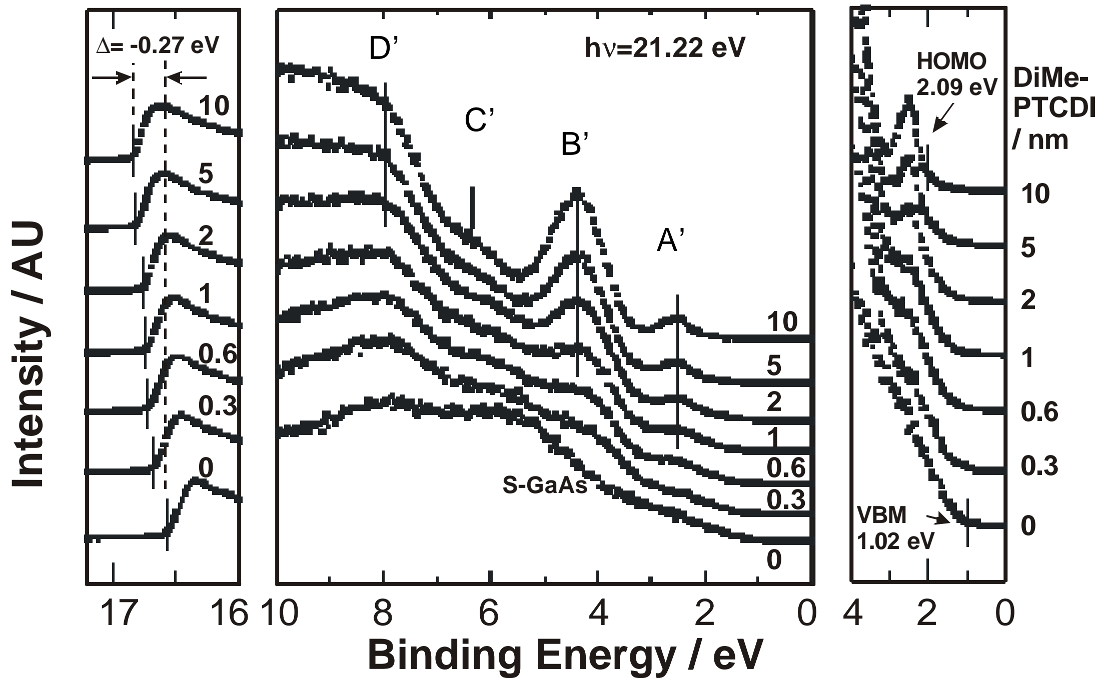

Figure 4. Valence band spectra of DiMe-PTCDI deposited on S-GaAs for several thicknesses.

.

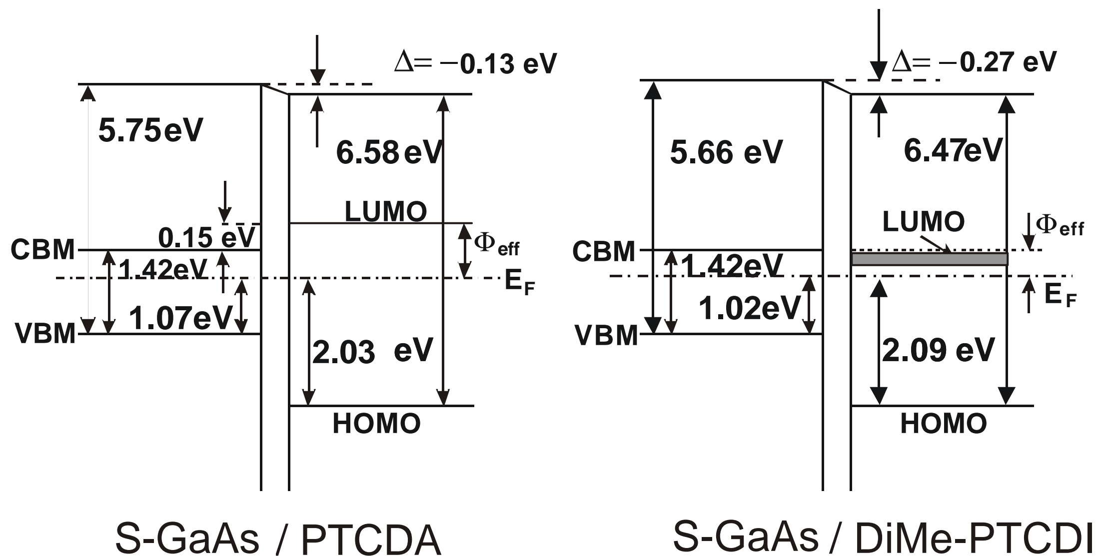

Figure 5: Energy level alignment at PTCDA/S-GaAs and DiMe-PTCDI/S-GaAs interfaces.

energy level of the PTCDA films extends up to the interfaces without energy shifts we can estimate the HOMO-LUMO gap to be in the range of 2.44~2.55 eV. This value is larger than the optical gap of PTCDA but still smaller than the transport HOMO-LUMO gap proposed by Hill *et al.*[4].

With the values for the absolute energy positions of the HOMO and the LUMO the energy band diagram of the PTCDA/S-GaAs(100) can be drawn as presented in fig. 5. With a transport band gap of 2.44~2.55 eV the LUMO is found is found to be 50 ~ 160 meV above the CBM of GaAs(100). The consequence of this small barrier is directly evident from the IV measurements performed on Ag/GaAs(100) Schottky diodes with PTCDA interlayers. The results reveal an increase in barrier height when a very thin PTCDA interlayer is inserted which in excellent agreement with the photoemission results presented here [12].

The band diagram for the DiMe-PTCDI/S-GaAs(100) interface will now be determined by analysing UP spectra for the growth of DiMe-PTCDI on S-GaAs(100) and taking into account the energy difference in optical absorption edges of PTCDA and DiMe-PTCDI.

Comparable UP spectra for the DiMe-PTCDI case are shown in fig. 4. The VB spectrum of the thick film shows four bands centered at 2.5, 4.4, 6.3 and 8 eV which are labeled A', B', C', and D', respectively. The origin of these four bands can be obtained by comparison of the VB spectra of DiMe-PTCDI and PTCDA. For both molecules, features corresponding to HOMO (A,A') appear centered at 2.5 eV, which was assigned to emission from C=C in perylene core. Another similarity can be found in a feature at 6.3 eV (D, C'). Most distinct feature for the DiMe-PTCDI film is the appearance of strong bands B' and D' compared with bands B, C and E of PTCDA which are not well resolved. Hence it can be deduced that the bands B' and D' originate from methylimide group ($N\text{-}CH_3$) in the DiMe-PTCDI molecule. As in the case of PTCDA on GaAs(100) surfaces, no detectable shift is observed in the energy positions of the four VB bands during growth of the DiMe-PTCDI film, indicating the absence of band bending in the organic layer. After 10 nm of DiMe-PTCDI the HOMO position is (2.09±0.05)eV relative to E_F. Therefore the HOMO is located (1.07±0.05)eV below VBM. Meanwhile

ϕ determined from the secondary electron onset position moves towards higher binding energy, due to the formation of an interface dipole at the interface. As judged from the spectrum of 10 nm DiMe-PTCDI film, the interface dipole amounts to (0.26±0.05) eV. The respective energy level alignment at the DiMe-PTCDI interface is presented in fig. 5. The position of the LUMO can be estimated taking into account the difference of 80 meV in optical band gaps. Assuming that the differences in optical band gaps and transport band gaps of PTCDA and DiMe-PTCDI are the same the transport band gap of DiMe-PTCDI is determined to 2.36~2.47 eV. Since the VBM-HOMO offset is by 100 meV larger in the case of DiMe-PTCDI the LUMO of DiMe-PTCDI is at same level or below the CBM of S-GaAs(100). The result is supported by IV measurements of Ag/DiMe-PTCDI/GaAs(100) Schottky diodes. Starting with thin DiMe-PTCDI the barrier height of these contacts decrease indicating that the LUMO of the DiMe-PTCDI is below the CBM of S-GaAs(100) [13].

4. Summary

The energy level alignment at interfaces between the molecular semiconductors PTCDA and DiMe-PTCDI and GaAs(100) substrates was determined by photoemission and optical absorption spectroscopy. From photoemission spectra the VBM-HOMO offset is determined to be 0.97 eV and 1.07 eV for PTCDA/S-GaAs(100) and DiMe-PTCDI/S-GaAs(100) interfaces, respectively. In the case of the PTCDA/S-GaAs(100) an interface dipole forms according to the electron affinity difference χ_{GaAs} - χ_{PTCDA}. The eletron affinity of PTCDA is determined to (4.12 ± .1) eV and, using this value, the transport gap of PTCDA is determined to 2.44 ~ 2.5 eV. Taking into account the difference in optical band gaps the transport gap of DiMe-PTCDI determined to be 2.36 ~ 2.47 eV. While for PTCDA/S-GaAs(100) interface the LUMO is found above the CBM, for DiMe-PTCDI/S-GaAs(100) interface the LUMO is at same level as or even below the CBM.

5. Acknoledgements

Financial support by the *Bundesministerium für Bildung and Forschung* (BMBF contract no. 05 KS1OCA / 1) and the EU DIODE network (HPRN-CT-1999-00164) is gratefully acknowledged.

6. References

[1] S. R. Forrest, Chem. Rev. 97 (1997), 1793.

[2] R. Kaiser, M. Friedrich, T. Schmitz-Hübsch, F. Sellam, T. U. Kampen, K. Leo, D. R. T. Zahn, Fresenius J. Anal. Chem. **363** (1999) 189.

[3] V. Bulovic, P. E. Burrows, S. R. Forrest, J. A. Cronin, M. E. Thompson, Chem. Phys. **210** (1996) 1.

[4] I. G. Hill, A. Kahn, Z. G. Soos, R. A. Pascal, Jr., Chem. Phys. Lett. **327** (2000) 181.

[5] S. Park, T. U. Kampen, D. R. T. Zahn, Appl. Phys. Lett. **79**, 4124 (2001).

[6] Z. S. Li, W. Z. Cai, R. Z. Su, G. S. Dong, D. M. Huang, X. M. Ding, X. Y. Hou and Xun Wang, Appl. Phys. Lett. **64**(25), 3425 (1994).

[7] M. D. Pashley, and D. Li, J. Vac. Sci. Technol. **A12**, 1848 (1994).

[8] Y. Azuma, S. Akatsuka, K.K. Okudaira, Y. Harada, and N. Ueno, J. Appl. Phys. 87 (2000) 766.

[9] Y. Hirose, W. Chen, E.I. Haskal, S.R. Forrest, A. Kahn, Appl. Phys. Lett. 64 (1994) 3482.
[10] S. Kera, H. Setoyama, M. Onoue, K.K. Okudaira, Y. Harada, N. Ueno, Phys. Rev. B 63 (2001) 115204.
[11] S. Park, T. U. Kampen, D. R. T. Zahn, and W. Braun, Appl. Phys. Lett. **76** (2000) 3200.
[12] T. U. Kampen, S. Park, and D. R. T. Zahn, Appl. Surf. Sci. **190** (2002) 461.
[13] D. R. T. Zahn, T. U. Kampen, and Henry Méndez, Appl. Surf. Sci., submitted.