Electronic coupling of optical excitations in organic/inorganic semiconductor hybrid structures

S Blumstengel¹, S Sadofev and F Henneberger
Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, 12489 Berlin, Germany
E-mail: Sylke.Blumstengel@physik.hu-berlin.de

New Journal of Physics 10 (2008) 065010 (17pp)
Received 15 February 2008
Published 30 June 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/6/065010

Abstract. The epitaxial growth of small conjugated molecules on ZnO-based surfaces is studied. A weak substrate interaction allows for the preparation of organic layers with well-defined morphology and electronically intact interfaces without the need for extra passivation. Nonradiative energy transfer from inorganic quantum wells to various molecules is identified by optical spectroscopy. The strength of the dipole–dipole mediated coupling between Wannier and Frenkel excitons is as large as 2 meV. In hybrid structures with type-II energy level alignment, charge separation occurs at the organic/inorganic interface as well. These findings render organic/ZnO hybrid structures interesting for light-emitting as well as photovoltaic applications benefiting from favorable properties of both material classes.

¹ Author to whom any correspondence should be addressed.
Integration of organic and inorganic semiconductors in a hybrid structure promises optoelectronic and photonic properties that cannot be achieved by the individual components alone. For instance, inorganic semiconductors exhibit large charge carrier mobilities while organic materials are known for their high yield of fluorescence, large absorption cross section, as well as easy spectral tunability. Combination of those properties would enhance the performance of devices, such as light-emitting and laser diodes or photovoltaic cells. A fundamental requirement to make that concept work is a well-defined morphology allowing for efficient coupling between the electronic excitations of the two material types. The design we consider consists of an epitaxial quantum well (QW) covered by a thin layer of organic conjugated molecules. In such a setting, it should be possible to convert Wannier excitons of the QW into Frenkel excitons of the organic overlayer via dipole–dipole interaction given that their energies are in resonance and their spatial separation is sufficiently small [1]. If the interaction strength exceeds dissipation in the subsystems, a hybrid state can even be formed comprising both types of excitons in a coherent quantum mechanical superposition [2]. Despite the large body of theoretical work [1]–[4], experimental evidence for electronic coupling between Frenkel and Wannier excitons has been provided only recently [5]–[7]. One reason for the time lag lies in the critical role of the organic/inorganic interfaces. Surface states of inorganic semiconductors cause band bending and enhanced surface recombination velocities. This manifests itself in a dramatic reduction of the luminescence yield if the QWs are located too close to the surface [8]–[10]. Such con striction increases unfavorably the interaction length in a hybrid structure. In addition, surface states can act as traps and also impair in this way exciton transfer across the interface. A second obstacle is that molecules may be chemisorbed to dangling bonds, steps or defects present on the semiconductor surface, modifying their electronic structures or even causing fragmentation of the adsorbate [11, 12]. The choice of the proper semiconductor is thus crucial. Our investigations show that ZnO is a very well-suited candidate as its surface is inert towards the deposition of conjugated molecules generating clear electronic and optical properties not influenced by surface defects.
In this paper, we will focus on two topics: first, we will describe the growth of organic molecules on ZnO or ZnMgO and discuss morphological, structural and electronic properties of the organic/inorganic interfaces. In the second part, we will summarize our experimental results on exciton transfer processes occurring between QW structures and organic overlayers in various settings and discuss the coupling mechanism. Besides excitons, single charge transfer is also observed in hybrid structures with type-II energy level alignment rendering those structures also interesting for photovoltaic applications.

2. Growth and interface properties of organic/(Zn,Mg)O hybrid structures

2.1. Epitaxial growth

The hybrid structures investigated are ZnO/ZnMgO and ZnCdO/ZnO QW structures as well as ZnO and ZnMgO epilayers covered by a thin layer of organic molecules. The QWs and the organic layer are prepared under ultra-high vacuum conditions by molecular beam epitaxy and molecular beam deposition, respectively, in a DCA apparatus equipped with interconnected growth chambers for organic and inorganic materials. In this manner, the preparation of well-defined interfaces is assured as intermittent exposure to ambient atmosphere is avoided. The QW structures as well as epilayers are grown, unless otherwise noted, on c-plane sapphire substrates inducing growth along the c-axis of the wurtzite crystal and resulting in the O-terminated (0001) surface. Conventional effusion cells are used for evaporation of Zn, Cd and Mg, while atomic oxygen is provided by an RF plasma source. The composition of the ternary compounds is controlled by the beam equivalent pressure of the molecular fluxes. The optimum growth temperature of ZnO and ZnMgO is 300–380°C, while for ZnCdO much lower temperatures (100–150°C) are required. The QW of typically 2–5 nm width, either ZnO or ZnCdO, is embedded between a 600 nm thick lower barrier layer, either ZnMgO or ZnO, and a thinner upper barrier of the same material with variable thickness \( L_s = 2–20 \text{ nm} \). The latter serves in hybrid structures as spacer between QW and organic molecules. Epilayers are typically 600 nm thick. The growth is monitored by reflection high-energy electron diffraction (RHEED) and the thickness of QW and spacer are controlled by specular beam intensity oscillations. More details on the growth of the QW structures are reported elsewhere \[13, 14\].

The chemical structures of the molecules employed in this study are depicted in figure 1. The organic component is deposited on top of the inorganic semiconductor using Knudsen-type effusion cells. The growth rate of typically 1 Å min\(^{-1}\) is controlled by a quartz microbalance and the substrate temperature \( T_S \) varied between 20 and 120°C depending on the compound. An exception is perylene, which is dispersed in a PMMA matrix and spin cast from solution to yield films typically 2 nm thick.

2.2. Interface formation

Representative atomic force microscopy (AFM) images taken in tapping mode of molecules deposited on epitaxial ZnO and ZnMgO surfaces are depicted in figures 2(a)–(c). The AFM image of the 6T/ZnO(0001) interface in the submonolayer regime (figure 2(a)) displays islands whose height corresponds approximately to the length of the molecules or half of the \( a \) lattice constant, i.e. the contact plane is the (100)-plane of the herringbone crystal \[15\]. For an isolated molecule, it was energetically favorable to lie flat on the surface. The interaction
Figure 1. Chemical structure of (a) 2,2′-p-phenylenebis(5-phenyloxazol) (POPOP), (b) α-sexithiophene (6T), (c) 2,7-bis(biphenyl-4-yl)-2′,7′-di-tert-butyl-9,9′-spirobifluorene (SP6), (d) coronene and (e) perylene.

Figure 2. AFM images of (a) 6T on ZnO(0001), $T_S = 100^\circ$C. The epitaxial Zn-terminated (0001) surface is obtained by growth on (0001)-oriented ZnO crystals. (b) POPOP on ZnO(0001), $T_S = 20^\circ$C, (c) SP6 on ZnMgO(0001), $T_S = 20^\circ$C, layer thickness 2.2 nm, (d) LEED image of coronene on ZnMgO(0001), $T_S = 20^\circ$C, layer thickness 1.5 nm, acceleration voltage 25 eV.

with the semiconductor surface is thus weak—intermolecular interactions outbalance the molecule–substrate interaction [16]. There is only one length scale regarding size of and distance between the islands suggesting formation by homogeneous nucleation. Further analysis of AFM images reveals that scaling laws apply indeed for structural quantities, such as the island size distribution $\rho$. Let $n$ be the island area size, $N = \langle n \rangle$ the average and $\Theta$ the total coverage. For a diffusion-limited growth process, it holds then $\rho_n = (\Theta/N^2)f_i(n/N)$ [17]–[19]. The scaling function $f_i$ contains the number of molecules $i$ needed to form a critical nucleus [19]. When scaled accordingly, the experimental island size distributions for different coverages transform indeed into a single curve (figure 3(a)). The shape of the curve is very well approximated by the theoretical distribution for a number $i = 3$, i.e. the smallest stable nucleus consists of four 6T molecules. A similar number was found for pentacene deposited on oxidized silicon [20]. The good quantitative agreement between the experimental data and the scaling function confirms that the growth of 6T on ZnO(0001) in the monolayer regime is diffusion limited and not perturbed by the presence of surface defects, dangling bonds or step edges. In such a growth mode, the island morphology is kinetically determined by the ratio of the diffusion constant $D$ and the incoming flux $F$, $R = D/F$, making the average island size tunable, e.g. by the substrate temperature. Figure 3(b) depicts a x-ray diffractogram (XRD) of a 25 nm thick 6T film on ZnO(0001). Well pronounced (200), (400), (600), (800), (10.00) and (12.00) reflections
of the low-temperature phase of crystalline 6T [15] certify that the growth direction with the 6T(100) plane parallel to the ZnO(0001) surface is retained under continuing deposition. Growth of 6T on ZnO(0001) thus yields crystalline layers.

The AFM image of the POPOP/ZnO(0001) interface uncovers a somewhat different morphology. Due to the arrangement of the POPOP molecules in the lattice [21], the preferred growth direction is along the b-axis resulting in layers constituted by needle-shaped crystallites with an average height of 10 nm (figure 2(b)). In contrast to 6T and POPOP, SP6 forms an amorphous layer as the spiro-linkage prevents crystallization [22]. The morphology of the 2.2 nm thick films follows exactly that of the ZnMgO(0001) surface (figure 2(c)). The steps visible in the AFM image correspond to monolayer or double layer steps of the ZnMgO crystal (c = 0.52 nm). The presence of the SP6 layer can be evidenced by employing mechanical force to the organic film by the AFM tip. Operation in hard tapping mode breaks up the formerly closed layer as seen in the 1 µm × 1 µm square in the center of the image. Even the first few layers of SP6 form thus homogeneous smooth films on the ZnMgO surface. Probably induced by the same symmetry of the molecule and the semiconductor surface, long-range order of the adsorbate is found by low-energy electron diffraction (LEED) of coronene on ZnMgO(0001). Figure 2(d) represents the hexagonal pattern of the coronene superstructure. ZnMgO diffraction spots appear at higher acceleration voltages and are used to estimate the lattice vector of the coronene surface cell to 13 ± 1 Å. Such length hints at a (4 × 4) superstructure with the unit cell rotated by 30° relative to the ZnMgO(0001) surface unit cell.

All these observations consistently demonstrate that molecules grow on different ZnO and ZnMgO surfaces in well-defined layers whose structure and morphology is mostly determined by the symmetry and crystal forming properties of the adsorbate. Surface irregularities do not perturb the assembly of the adsorbate. The x-ray photoelectron spectroscopy (XPS) confirms that the molecules are indeed physisorbed [23, 24]. In figure 4, the evolution of the O 1s and the S 2p XPS spectra of the 6T/ZnO(0001) interface with increasing thickness of the organic layer is depicted. The O 1s core level of the pristine ZnO(0001) surface is located at 530.8 eV indicative of O–Zn bonding. Upon deposition of 6T, the O 1s as well as the Zn 2p peaks (not shown) experience a rigid shift of about 0.2 eV towards lower binding energy which is
most likely caused by a change of the band bending at the ZnO(0001) surface induced by the deposition of 6T. The binding energies of the S 2p peak as well as the C 2p peak (not shown) of 6T decrease with increasing film thickness within the first ångstroms and remain almost constant for larger film thicknesses. This shift is due to more efficient photo-hole final state screening for larger 6T islands as more polarizable matter is provided by neighboring molecules [25]. The shape of all spectra remains unchanged increasing the thickness of the organic layer signifying that 6T adsorbs electronically intact on the ZnO(0001) surface. Similar results were found for the ZnO(0001) surface [23] as well as for coronene (unpublished results) and SP6 [24] deposited on ZnO or ZnMgO affirming that these surfaces can be considered as inert. The molecules are thus bound by van der Waals interaction only. This is in contrast to other semiconductors, on which chemical bond formation or even destruction of the adsorbate is observed [11, 12] and surface passivation is usually required to allow for an unperturbed growth of organic conjugated molecules [26].

3. Exciton and charge transfer processes in organic/inorganic hybrid structures

3.1. Optical properties of ZnO/ZnMgO and ZnCdO/ZnO QW structures

The bandgap of ZnO is 3.3 eV. Owing to a binding energy of 60 meV, excitons govern the optical properties up to room temperature. Alloying of ZnO with MgO or CdO is hampered by the different crystal structure of the components, namely wurtzite (ZnO) and rocksalt (MgO, CdO). Currently, the ternary bandgap can be tuned in strict wurtzite phase between 2.3 eV (ZnCdO) and 4.4 eV (ZnMgO) [13, 14]. This enables the fabrication of heterostructures with robust two-dimensional charge carrier confinement. ZnO/ZnMgO as well as ZnCdO/ZnO QW structures exhibit exciton-related photoluminescence (PL) and optically pumped lasing up to room temperature ranging from the UV to the green spectral range [27, 28]. Figure 5 depicts typical PL and PL excitation (PLE) spectra of ZnO/ZnMgO and ZnCdO/ZnO structures. In both cases, the PL comprises features of the QW and the barriers. The spectral position of
Figure 5. PL (solid line) and PLE (dashed line) spectra of the inorganic QW structures. (a) ZnO/ZnMgO ($x = 0.12$, $d_{QW} = 3.5$ nm and $L_S = 20$ nm). (b) ZnCdO/ZnO ($x = 0.07$, $d_{QW} = 2.2$ nm and $L_S = 20$ nm). A Xe-lamp with the photon energy selected by a double monochromator is used for excitation. The PL is recorded with a CCD camera after passing a monochromator or, in PLE, by a photomultiplier. Excitation in PL is always above the barrier bandgap and detection in PLE at $\hbar \omega_{det} = 3.35$ eV (a) and $\hbar \omega_{det} = 3.0$ eV (b). All spectra are taken at 5 K.

Figure 6. PL spectra of ZnO/ZnMgO QWs in dependence on the thickness of the upper barrier layer ($d_{QW} = 3.5$ nm, $x = 0.12$ ($L_S = 22$ nm), $d_{QW} = 3.8$ nm, $x = 0.12$ ($L_S = 5$ nm) and $d_{QW} = 3.5$ nm and $x = 0.11$ ($L_S = 2.5$ nm)). The excitation is above the ZnMgO band-edge and the temperature 5 K.

both features can be widely tuned by the ternary composition (given by the Mg or Cd fraction $x$) and the well thickness ($d_{QW}$). The spectral width of the QW emission depends also on these parameters and can become as small as 7 meV. The considerable Stokes shift of about 40 meV from the excitonic absorption feature visible in the PLE spectrum of ZnO/ZnMgO QWs (figure 5(a)) indicates that the emission is due to localized excitons. Localization due to well width fluctuations and alloy disorder is favored by the small exciton Bohr radius of ZnO (1.8 nm). In ZnCdO/ZnO QW structures, polarization discontinuities give rise to strong built-in
electric fields ($F \sim 10^8 \text{ V m}^{-1}$) [28]. The quantum-confined Stark effect associated with these fields defines the main contribution to the much larger Stokes shift in this case (figure 5(b)).

To achieve excitonic coupling in hybrid structures, the QW has to be in close proximity to the organic layer, i.e. the spacer length $L_S$ may not exceed the range of a few nanometers. Figure 6 displays how the PL yield of the sole QW structure decreases when the cap is thinned down. However, even for structures with cap layers as thin as $L_S = 2$ nm, pronounced QW emission is detectable. For comparison, in InGaAs/GaAs QWs, the PL yield drops by more than two orders of magnitude already at $L_S = 5$ nm [10] and in ZnCdSe/ZnSe QWs, PL practically vanishes for $L_S < 10$ nm. Unlike other semiconductors, surface states obviously play a minor role in ZnO which is a prerequisite to achieve electronic coupling across the organic/inorganic interface. Surface passivation, as suggested for other semiconductors [8]–[10], is thus also not required in this context.

### 3.2. Energy transfer in hybrid structures

The occurrence of energy transfer can be experimentally proven by a combination of PLE and time-resolved PL spectroscopy. Absorption features of the donor (QW) in the PLE spectrum of the acceptor (molecule) indicate that the acceptor is excited via energy transfer from the donor. If the energy transfer is mediated via a non-radiative process, the lifetime of the donor PL must shorten in the presence of acceptors as an additional decay channel is opened up. A risetime of the acceptor PL corresponding to the decay time of the donor PL demonstrates finally that the excitation energy indeed arrives at the acceptor. We have studied the energy transfer process for various material combinations: POPOP/ZnO/ZnMgO [5], coronene/ZnO/ZnMgO, SP6/ZnO/ZnMgO—a hybrid system with type-II energy level alignment at the organic/inorganic interface [24]—and, to extend the available wavelength range, perylene/ZnCdO/ZnMgO.

First, results for the POPOP/ZnO/ZnMgO hybrid system are summarized. It exemplifies all the above listed features. Figure 7(a) shows the spectral overlap of the QW as well as
Figure 8. Dynamics of energy transfer. (a) PL decay of the QW in a ZnO/ZnMgO reference and a POPOP/ZnO/ZnMgO hybrid structure. Solid lines are fits to the data by $I_{QW}(t) = \int_0^t dt' K(t') N(t-t')$ where $K(t)$ represents the system response to the excitation pulse. The deconvoluted exciton population $N(t)$ in the QW of both structures yields the lifetimes $\tau_{QW}$ and $\tau_{HB}$. A much weaker and slower decaying background is due to capture of long-lived carriers from the barriers. (b) PL decay of POPOP on sapphire and in the hybrid structure. Solid lines are fits to the data made as follows. Reference sample: the exciton decay in sole POPOP, $N_P(t)$, is again extracted by deconvolution of the experimental data with $K(t)$ using now a stretched exponential law. Hybrid structure: POPOP is excited (A) directly and (B) indirectly via energy transfer. The data fit is obtained by $I_P(t) = \int_0^t dt' [AK(t')+BI_{QW}(t')]N_P(t-t')$. The only free parameter is the ratio $A/B$. Experimental details: time-correlated single-photon counting with a resolution of 10 ps is used. The excitation pulses are delivered by the frequency doubled output of a synchronously pumped dye laser and spectral selectivity is provided by a double monochromator in subtractive mode. To ensure identical samples, sole QW and hybrid structure ($d_{QW} = 4 \text{ nm}$, $x = 0.1$, $L_S = 2.5 \text{ nm}$) are grown in one run. The excitation photon energy is always 3.78 eV and the temperature 5 K.

barrier emission with the absorption (PLE) spectrum of POPOP. The data are acquired with reference samples of a sole ZnO/ZnMgO QW and POPOP deposited on sapphire. PLE spectra of a POPOP/ZnO/ZnMgO hybrid structure are depicted in figure 7(b). The PLE spectrum detected at the low energy tail of the QW emission displays the exciton ground- and excited-state absorption features of the QW as well as the ZnMgO band edge. All these signatures are also prominently visible in the PLE spectrum of POPOP substantiating efficient excitation energy transfer from the ZnO QW to the organic overlayer.

PL transients verifying the non-radiative character of the energy transfer process are depicted in figure 8. Upon deposition of POPOP, the lifetime of the QW exciton shortens from $\tau_{QW} = 330 \text{ ps}$ to $\tau_{HB} = 160 \text{ ps}$ in the hybrid structure (figure 8(a)). Removing POPOP with a proper solvent recovers the original decay time. Whereas the PL of POPOP itself appears instantaneous within the 10 ps resolution of the setup, a clear risetime is observed on the hybrid structure (figure 8(b)). Data fits yield that this risetime corresponds exactly to the shorter 160 ps lifetime of the QW exciton. Moreover, a slowly decaying background of the QW PL caused by the capture of long-lived carriers in the ZnMgO barrier is also imprinted in the POPOP
Figure 9. Energy transfer in perylene/ZnCdO/ZnO hybrid structures. (a) Spectral overlap of the PLE of perylene dispersed in PMMA (1 wt. %) on fused silica and the PL of a ZnCdO/ZnO QW ($x = 0.09$, $d_{QW} = 2.2$ nm and $L_S = 3.2$ nm). PLE: $\hbar \omega_{\text{det}} = 2.8$ eV, PL: $\hbar \omega_{\text{exc}} = 3.6$. (b) PLE spectra of a perylene/ZnCdO/ZnO hybrid structure with the QW parameters (perylene: $\hbar \omega_{\text{det}} = 2.63$ eV and QW: $\hbar \omega_{\text{det}} = 3.0$ eV). The spectra are taken at 5 K.

decay. Such background is absent for direct excitation of the QW, while the shorter transients are virtually independent of whether the laser photon energy is below or above the bandgap of the barrier material. These findings unambiguously prove that the deposition of the molecular layer does not simply create a defect-related bypass but that the excitation energy withdrawn from the QW indeed reaches the organic component.

The time-resolved measurements enable a direct estimate of the time constant $\tau_{DD} = (1/\tau_{HB} - 1/\tau_{QW})^{-1} = 310$ ps as well as efficiency $\eta_{DD} = 1 - (\tau_{HB}/\tau_{DD}) = 0.5$ of the transfer process. Even higher efficiencies up to $\eta_{DD} = 0.75$ are found when POPOP is replaced by SP6. That means that three out of four excitons generated in the QW are transferred to the organic layer.

Changing composition and well width of the ZnO/ZnMgO QW structures, the spectral position of the emission can be tuned deeper in the UV. The visible spectral range can be reached by employing perylene/ZnCdO/ZnO hybrid structures. Figure 9 demonstrates that these structures are also capable of energy transfer. Appropriate choice of the QW parameters brings the emission practically in resonance with the first vibronic replica of the $S_0$–$S_1$ transition in perylene dispersed in PMMA. Again, for the hybrid structure, extra absorption features of the ZnCdO QW as well as the ZnO barrier emerge in the PLE spectrum of perylene. The Stark shift of the QW PL caused by the built-in electric field in this structure is about 300 meV. A remarkable result in this context is that almost no energy shift occurs after deposition with organic molecules. Charge flow across the interface is obviously not an essential factor and the unexcited subsystems are largely electronically isolated.
3.3. Mechanism of the energy transfer: conversion of Wannier into Frenkel excitons

The excitons of the inorganic QW, though localized, still comprise tens of unit cells and are thus of Wannier-type. The Frenkel excitons of the organic layer belong to single molecules. In this sense, the above results have shown that electronic coupling between these fundamental types of excitons can indeed be accomplished by a hybrid structure. Such coupling can originate from exchange or dipole–dipole interaction. For a ZnO/ZnMgO QW of the present design, we estimate a 1/e penetration depth of the carrier wavefunctions in the barrier of about 0.6 nm excluding a substantial exchange contribution at spacer lengths $L_S = 2$ nm and beyond. The range of the dipole–dipole interaction is considerably longer [1]. To unveil the length scale of the energy transfer in our hybrid structures, we have elaborated its time constant $\tau_{DD}$ as a function of the distance $d$ between the QW and the organic layer. The experimental data in figure 10(a) document a quick increase when $d$ changes from 4 to 10 nm. We recall that the QW exciton is quite strongly localized in the well plane. As long as the localization length does not exceed the donor–acceptor separation, it is reasonable to treat in a first approximation the dipole–dipole-mediated transfer in terms of the standard Förster model [29]. For a two-dimensional setting, the well known relation $\tau_{DD}^{-1} = \tau_{QW}^{-1}(R_0/d)^6$ translates into $\tau_{DD}^{-1} = (1/2)\tau_{QW}^{-1}N(R_0/d)^4$, where $R_0$ is the Förster radius and $N$ is the number of molecules in the cycle defined by $R_0$. Accounting for the finite QW width, an intuitive definition of the transfer distance is $d = d_{QW}/2 + L_S$. The experimental times indeed follow well a $d^4$ dependence for both types of hybrid structures investigated. The fits yield a shorter Förster radius ($R_0 = 2.6$ nm) for POPOP than for SP6 ($R_0 = 3.1$ nm). A calculation based on the spectral overlap integral provides the same tendency.
With the measured absorption coefficient spectra of POPOP and SP6, a refractive index $n = 2$, and assuming a radiative efficiency of $\eta_{QW} = 1$ for the QW, one obtains $R_0 = 3.5$ nm and $R_0 = 3.9$ nm, respectively, in fair agreement with those radii gained from the transfer times.

A Förster-type dipole–dipole mechanism is also supported by the fact that no clear signatures of energy transfer can be observed in the coronene/ZnO/ZnMgO hybrid system. This is expected from the weak transition dipole moment of the first excited state in coronene. Also for 6T/ZnO/ZnMgO, no energy transfer is expected in a configuration where the molecules stand upright on the surface, because their dipole moment is then oriented perpendicular to that of the QW exciton. On the other hand, energy transfer is found on perylene/ZnCdO/ZnO hybrid structures. Here, the electric built-in field induces a spatial separation of electron and hole in the QW. This reduces the transition dipole moment and increases the lifetime up to some nanoseconds for the specific sample of figure 9 [28]. The presence of energy transfer also on this timescale is indicative of a very low defect-related side recombination corroborating again the high quality of the hybrid interface. Direct measurements in the time domain are in progress.

The temperature dependence of the energy transfer time is depicted in figure 10(b) for a SP6/ZnO/ZnMgO hybrid structure and compared with the lifetime of the exciton of the sole QW. The latter starts to decrease above 40 K, while the energy transfer time remains practically constant. As a consequence, the efficiency of energy transfer declines with increasing temperature and, even for the smallest spacer length, we find $\eta_{DD} < 0.1$ at room temperature. The behavior of $\tau^{DD}$ is indicative of a persistence of exciton localization in the QW, as a transition to free excitons would show up in a distinct temperature dependence [30].

The above findings demonstrate the existence of dipole–dipole coupling across the organic/inorganic interface. The coupling strength $V_{DD}$ can be estimated by back translating the ensemble transfer times to a single donor–acceptor configuration by using the Förster radii deduced from the experimental data. Inserting this time in the relation $\tau^{-1}_{DD} = (\hbar/2\pi)|V_{DD}|^2 \int F_D(E) F_A(E) dE$, $F_D$ and $F_A$ being the normalized fluorescence and absorption spectra of donor and acceptor, respectively, yields $V_{DD} \approx 2$ meV for the, so far, most efficient SP6/ZnO/ZnMgO hybrid structure. The simple approach just adapting the standard Förster model to the experimental layer geometry is surprisingly successful. However, caution is advised. Improved treatments taking into consideration specific factors, such as background and polarization charges or band bending, to name only a few, are desired.

3.4. Charge separation in hybrid structures with type-II energy level alignment

The relative position of the energy states in the organic and inorganic material determines the electronic function of the interface. The energy offset between the valence band maximum (VBM) of the semiconductor and the highest occupied molecular orbital (HOMO) of the adsorbate is accessible by UV photoelectron spectroscopy (UPS). The positions of the conduction band minimum (CBM) and the lowest unoccupied molecular orbital (LUMO) follow then by adding the respective optical bandgap, derived from absorption measurements and the exciton binding energy. The energy level diagram deduced for the SP6/ZnMgO interface is depicted in figure 11(a) [24]. The offsets are such that a type-II interface is formed facilitating charge separation, a process on which photovoltaic cells rely. Specifically, the electron transfer from the organics to the semiconductor and hole transfer in the other direction is expected.
to occur for the SP6/ZnMgO hybrid system. The same holds true for ZnO with only small variations of the offsets (LUMO-CBM: 1.0 eV, HOMO-VBM: 0.8 eV) [24].

In the above study of energy transfer in SP6/ZnO/ZnMgO hybrid structures, the ZnO QW collects the optically excited electron–hole pairs before they can reach the interface so that exciton coupling becomes predominant. In order to reveal charge separation, a SP6/ZnMgO hybrid structure with no ZnO QW is studied. The optical excitation is well below the ZnMgO bandgap assuring that only Frenkel excitons in SP6 are created. These excitons diffuse towards the interface where they dissociate (figure 11(b)). The latter will show up by a shortening of the lifetime as well as a drop of the SP6 PL yield, both depending on the relation between the organic layer thickness ($d_{SP6}$) and the exciton diffusion length ($L_D$). The PL transients collected in figure 12(a) taken on specimens with SP6 films in the range $d_{SP6} = 1.6–12$ nm confirm entirely this scenario. From these data, essential parameters can be elaborated. Denoting by $D$ the diffusion constant, by $\alpha = 4 \times 10^5$ cm$^{-1}$ the absorption coefficient and by $\tau = 300$ ps the lifetime of the excitons in SP6, their volume density at incident photon flux $G_{exc}$ follows from the continuity equation

$$\frac{dn}{dt} = D \frac{d^2 n}{dx^2} + \alpha G_{exc} e^{-\alpha x} - \frac{n}{\tau}.$$ 

At the SP6/ZnMgO interface, excitons are removed with a finite surface recombination velocity $s$ due to charge separation resulting in the boundary condition $Ddn(x = d_{SP6})/dx = -sn$. Quenching at the SP6 surface can be neglected $(Ddn(x = 0)/dx = 0)$. Instead of fitting the PL transients, the efficiency of the charge transfer $\eta_{CT}$ is used as the relevant quantity. The normalized decay curves are integrated over time providing the total PL yield $I_{HB}$. The same procedure carried out on a sample where SP6 is deposited on fused silica gives the reference yield $I_R$ from which the efficiency can be calculated by $\eta_{CT} = 1 - I_{HB}/I_R$. The marked decrease of $\eta_{CT}$ when plotted versus the layer thickness $d_{SP6}$ (figure 12(b)) represents direct evidence that the rate-limiting step is indeed exciton diffusion towards the interface. On the other hand, from the standard steady-state solution $n(x)$ of the continuity equation, it follows

**Figure 11.** Charge separation at an interface with type-II energy level alignment (a) Energy level diagram of the SP6/ZnMgO interface ($x = 0.14$) derived from UPS and absorption spectra at room temperature [24]. The position of the SP6 LUMO is calculated assuming an exciton binding energy of 0.45 eV [31]. (b) Concentration profile of SP6 Frenkel excitons taking into account diffusion and dissociation at the ZnMgO interface sketched underneath.
η_{CT} = 1 \frac{N(s)}{N(0)} \text{, where } N(s) = \int_0^{d_{SP6}} dx \ n(x) \text{ at given recombination rate } s. \text{ Indeed, a very good fit to the experimental data within this simple approach is possible providing } L_D = \sqrt{D \tau} \approx 3.5-10 \text{ nm and } s \approx 20-55 \text{ m s}^{-1} \text{ between 5 and 290 K. For reasonable distances } d \text{ between the molecules and the ZnMgO surface, i.e. distances well above the van der Waals radius, } d/s \text{ yields for the charge transfer } \tau_{CT} \text{ a lower limit of about 10 ps.}

In the Sp6/ZnO/ZnMgO configuration, the excitons generated in the ZnO QW and transferred by dipole–dipole coupling to the SP6 layer are there, at least partially, subject to charge separation as well. A question of practical importance is which process—radiative recombination in the layer or charge transfer at the interface—is dominant. In the frame of the diffusion model, a positive flux \( J_{ET} = G_{exc} \eta_{DD} A_{QW} \) describing the exciton transfer has to be added to the surface recombination flux \( J_{SR} = -sn \), where in lowest order \( n \sim G_{exc} \alpha \tau \). The relevant ratio is thus \( \eta = A_{QW} \eta_{DD}/\alpha s \tau \). At given transfer efficiency \( (\eta_{DD} = 0.75 \text{ at } L_S = 2 \text{ nm}) \), \( \alpha \) and \( s \), the net outcome is controlled by the number of incident photons \( 1/A_{QW} \) needed to generate one exciton in the QW. For direct excitation, \( A_{QW} \approx 0.1 \) yields \( \eta < 1 \) and thus dominance of the charge separation. However, for optical excitation into the ZnMgO barrier and subsequent carrier capture by the well, \( A_{QW} \) increases to \( \approx 0.5 \) resulting in \( \eta > 1 \) and a positive net flux. We finally note that signatures of exciton transfer are even found for SP6/ZnMgO hybrid structures with no extra QW. Our conjecture is that exciton localization at alloy fluctuations in the ternary ZnMgO creates a barrier partly inhibiting charge separation under excitation in the inorganic part.

4. Outlook

A striking feature of the ZnCdMgO material system is that heterostructures of high crystalline perfection can be epitaxially grown in a well-defined layer-by-layer mode at temperatures
Figure 13. Energy transfer in a ZnO/SP6/ZnO double hybrid structure. (a) PL (solid line) and PLE (dashed line) of a sole SP6 film. (b) The same for the hybrid structure at 80 K ($d_{SP6} = 7$ nm). PL: $\hbar \omega_{exc} = 3.6$ eV and PLE: $\hbar \omega_{det} = 2.95$ eV.

close to room temperature [14]. By contrast, typically III–V semiconductors require growth temperature $T_S > 500$ °C. Those temperatures are not compatible with organic film growth. However, the low-temperature regime of ZnCdMgO allows in principle for overgrowth of the molecules by the semiconductor. This brings into sight stacks or even superlattice structures made of organic and inorganic materials. In this way, hybrid structures truly capable of optoelectronic function can be fabricated. In addition, novel phenomena related to resonant coupling may be expected in periodic structures. In what follows, we briefly describe our first steps in this direction.

Figure 13 compares PL and PLE data of a SP6 reference film deposited on fused silica and a ZnO/SP6/ZnO double hybrid structure. The latter consists of a 600 nm thick ZnO buffer layer, grown in standard regime, followed by a 7 nm thick SP6 layer. The organic layer is deposited after cooling down to room temperature. Finally, ZnO is grown on top of SP6 at $T_S = 100$ °C. The PL spectrum exhibits a prominent contribution from SP6 with a shape identical to that of the reference sample. Thus, despite the rather harsh environment, the organic molecules survive the overgrowth with ZnO without any visible degradation. Moreover, absorption features of ZnO appear in the PLE spectrum of SP6 indicating that the organic molecules are excited via energy transfer from ZnO. Whether the transfer is radiative or dipole–dipole-induced needs further studies.

In the above example, the RHEED pattern indicates that the upper ZnO layer is polycrystalline as expected from the amorphous nature of the SP6 film. Single crystalline growth of the inorganic overlayer is achieved in ZnO/POPOP/ZnO double hybrid structures. POPOP grows on top of ZnO in needle shaped crystallites (figure 2(b)). That is, the first ZnO layer is still partly seen during overgrowth of POPOP by the ZnO cap. Figure 14(a) shows the RHEED image taken at this stage ($T_S = 25$ °C). The streaky pattern is clearly indicative of crystalline growth of ZnO. The modulation along the stripes arises due to a roughening of the surface. The AFM image in figure 14(b) demonstrates that the ZnO overlayer follows exactly the morphology of the POPOP underneath. However, it is currently not clear whether the upper ZnO grows directly on the lower ZnO layer in the space between the POPOP islands or on a thin organic wetting layer interconnecting the islands. The PL spectrum of POPOP in the hybrid structure shows again that the molecules remain intact after overgrowth (figure 14(c)). A dip in the PLE spectrum...
Figure 14. (a) RHEED pattern taken along the (11\bar{20}) azimuth of ZnO grown on POPOP, (b) AFM image of the ZnO/POPOP/ZnO surface morphology. The thickness of the ZnO cap is 40 nm. The POPOP needle structure is still clearly present. (c) PL and PLE spectra of the hybrid structure recorded at 300 K. PL: $\hbar\omega_{\text{exc}} = 3.6$ eV and PLE: $\hbar\omega_{\text{det}} = 2.8$ eV.

(see arrow) at the position of the ZnO bandgap signifies that absorption by the overlayer reduces the direct optical excitation of POPOP. So far energy transfer at room temperature has not yet been observed in these preliminary type double hybrid structures.

5. Conclusions

The findings summarized in this paper demonstrate that organic/inorganic hybrid nanostructures with well-defined interfaces and morphology come within reach. Energy transfer in such structures can be employed for color conversion in light-emitting or laser diodes where charge carriers are injected via the ‘high mobility’ inorganic part while light is emitted subsequently from the organic overlayer. On the other hand, charge separation at the organic/inorganic interface might be exploited for photovoltaic applications. So far, most studies have been made at low temperature, however, there is in principle no obstacle for an extension to room temperature. The energy transfer in the present version is an incoherent process. A more challenging goal is the creation of true hybrid excitations based on coherent coupling between organic and inorganic components. This requires that the coupling strength is larger than the decoherence rates. The present hybrid structures exhibit coupling strengths up to $\sim 2$ meV, already beyond the radiative decay rate. Nanostructures with improved design should also make it possible to overcome the pure dephasing barrier.

Acknowledgments

We are grateful to Dr N Koch and Dr P Schäfer for the XPS/UPS and XRD measurements, respectively. We thank Professor Rabe for the use of the AFM and Dr J Puls for providing the time-resolved PL set up. Moreover, financial support of the Deutsche Forschungsgemeinschaft in the frame of Sfb 448 is acknowledged.
References

[1] Basko D, La Rocca G C, Bassani F and Agranovich V M 1999 Eur. Phys. J. B 8 353
[2] Agranovich V M, Basko D M, La Rocca G C and Bassani F 1998 J. Phys.: Condens. Matter 10 9369
[3] Engelmann A, Yudson V I and Reineker P 1998 J. Lumin. 76 214
[4] Huong N Q and Birman J L 2000 Phys. Rev. B 61 13131
[5] Blumstengel S, Sadofev S, Xu C, Puls J and Henneberger F 2006 Phys. Rev. Lett. 97 237401
[6] Zhang Q, Atay T, Tischler J R, Bradley M S, Bulovic V and Nurminko A V 2007 Nat. Nanotechnol. 2 555
[7] Itskos G et al 2007 Phys. Rev. B 76 035344
[8] Kodama S, Koyanagi S, Hashizume T and Hasegawa H 1995 Japan. J. Appl. Phys. 34/2B 1143
[9] Adlkofer K, Duijs E F, Findeis F, Bichler M, Zrenner A, Sackmann E, Abstreiter G and Tanaka M 2002 Phys. Chem. Phys. 4 785
[10] Alerken A, Hakkarainen T, Tiflikainen J, Mattila M, Riikonen J, Sopanen M and Lipsanen H 2007 J. Cryst. Growth 309 18
[11] Hughes G, Roche J, Carty D, Cafolla T and Smith K E 2002 J. Vac. Sci. Technol. B 20 1620
[12] Lin R, Galili M, Quaade U J, Brandbyge M, Bjornholm T, Degli Esposti A and Biscarini F 2002 J. Chem. Phys. 117 321
[13] Sadofev S, Blumstengel S, Cui J, Puls J, Rogaschewski S, Schafer P, Sadofyev Y G and Henneberger F 2005 Appl. Phys. Lett. 87 091903
[14] Sadofev S, Blumstengel S, Cui J, Puls J, Rogaschewski S, Schafer P and Henneberger F 2006 Appl. Phys. Lett. 89 201907
[15] Horowitz G, Bachet B, Yassar A, Lang P, Demanze F, Fave J L and Garnier F 1995 Chem. Mater. 7 1337
[16] Lang P, ElArdaoui M, Wittmann J C, Dallas J P, Horowitz G, Lotz B, Garnier F and Straupe C 1997 Synth. Met. 84 605
[17] Vicsek T 1992 Fractal Growth Phenomena (Singapore: World Scientific)
[18] Bartelt M C and Evans J W 1992 Phys. Rev. B 46 12675
[19] Strosclio J A and Pierce D T 1994 Phys. Rev. B 49 8522
[20] Ruiz R, Nickel B, Koch N, Feldman L C, Haglund R F, Kahn A, Family F and Sciles G 2003 Phys. Rev. Lett. 91 136102
[21] Ambats I and Marsh R E 1965 Acta Cryst. 19 942
[22] Johansson N, Salbeck J, Bauer J, Weissortel F, Broms P, Andersson A and Salannek W R 1998 Adv. Mater. 10 1136
[23] Blumstengel S, Koch N, Sadofev S, Schäfer P, Glowatzki H, Johnson R L, Rabe J P and Henneberger F 2008 Appl. Phys. Lett. 92 193303
[24] Blumstengel S, Sadofev S, Xu C, Puls J, Johnson R L, Glowatzki H, Koch N and Henneberger F 2008 Phys. Rev. B 77 085323
[25] Hill I G, Mäkinen A J and Kafafi Z H 2000 J. Appl. Phys. 88 889
[26] Nicoara N, Cerrillo I, Xueming D, García J M, García B, Gómez-Navarro C, Méndez J and Baró A M 2002 Nanotechnology 13 352
[27] Cui J, Sadofev S, Blumstengel S, Puls J and Henneberger F 2006 Appl. Phys. Lett. 89 051108
[28] Sadofev S, Kalusniak S, Puls J, Schafer P, Blumstengel S and Henneberger F 2007 Appl. Phys. Lett. 91 231103
[29] Kalusniak S, Sadofev S, Puls J, Wünsche H J and Henneberger F 2008 Phys. Rev. B 77 113312
[30] Forster T 1948 Ann. Phys. 2 55
[31] Kos S, Ackermann M, Klimov V I and Smith D L 2005 Phys. Rev. B 71 205309
[32] Kemerink M, Alvarado S F, Muller P, Koenraad P M, Salemink H W M, Wolter J H and Janssen R A J 2004 Phys. Rev. B 70 045202

New Journal of Physics 10 (2008) 065010 (http://www.njp.org/)