Introduction to the Quantsol 'Novel concepts and 3rd generation photovoltaics' session

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The term third generation photovoltaics is related to the sequence of photovoltaic technologies that have been developed up to the present. Definition of first generation solar cells refers to single crystal wafer related photovoltaic devices reaching up to 25% conversion efficiency (lab) and, thereby, approaching the theoretical efficiency limit of 31% for single cell devices. This was predicted by the first detailed balance model calculation of Shockley and Queisser for the photovoltaic conversion of solar irradiance in an ideal two level system with only radiative recombination [1]. In the thermodynamic model calculation it is assumed that the excess energy of those photons is lost whose energy exceeds that of the band gap. Scattering processes of the corresponding hot charge carriers result finally in the uptake of the excess energy as heat by the lattice of the respective material. The result is an equilibrium energy distribution for electrons and holes that is controlled by the lattice temperature. Only charge carriers thermalized at the lattice temperature can leave the device through the electrical contacts and contribute to the outer photovoltage and photocurrent. It is further assumed that they can recombine only via the radiative channel. The thermodynamic model calculations have been extended from the two-level system to multi-gap systems, where the solar irradiance is absorbed by several materials with different band gaps. By combining different materials with different band gaps in one photovoltaic device the output from the different materials can be summed up to yield a higher photovoltage than is possible in a device with just one band gap and at the same time the magnitude of the photocurrent can be maintained. The limiting case of this concept is reached when an arbitrarily large number of different energy gaps with infinitesimal small energy differences are absorbing the whole solar spectrum and where all the photovoltages and photocurrents are summed up [2]. The latter fictitious maximum photovoltaic conversion efficiency is in the range of 86 percent for maximum concentration. The assumption is here that all the photon energies can be converted into charge carriers that are thermalized without losing any energy. The remaining losses are just the consequence of the well-known thermodynamic limitations of an energy converter. This is, of course, a fictitious case. Nevertheless, employing the method of converting the solar spectrum with materials of different band gaps (multi-junction cells) has remained until now the only approach whereby on has surpassed the thermodynamic limit of a one gap solar cell by producing a certified 40 percent conversion efficiency in the laboratory. The corresponding multi-junction solar cells are grown as single crystals from III-V materials such that three or more different band gaps are realized in the complete solar cell for converting sunlight into electrical output. The cells are built as two or more in series coupled pn-junctions that are grown from different materials with the appropriate differences in their band gaps.

Several complementary scenarios have been advanced that aim at conversion efficiencies beyond the Shockley-Queisser limit where at the same time the above sketched demands with respect to the quality of the light absorbing materials and their arrangement in a necessarily highly ordered and structured device (multi-junction cell) can be relaxed. Such scenarios have been addressed as so-called 3rd

generation solar cells [3]. So far, none of these scenarios has been thoroughly tested even though they appear of great interest for different reasons. Firstly, each of these scenarios is envisaging the exploitation of a specific physical effect of the photogenerated hot charge carriers that has not yet been utilized for solar energy conversion but should be tested, e.g. charge carrier multiplication. Secondly, several such scenarios are connected with so-called quantum structures, i.e. material of small dimensions whose bulk properties deviate from those of the same material when filling a large space. Quantum size effects arising in these small units of mostly semiconductor material appear of interest not only for photovoltaic applications but hold the promise of additional spin-off applications. An interesting scenario is based on the recently discovered generation of multi-excitons from one hot carrier via a scattering process that occurs with high efficiency in a low band gap material when structured as quantum dots [4]. It is postulated that the generated multi-excitons can be converted in a suitably structured device into charge carriers thus achieving charge carrier multiplication. Another scenario is the capture of the hot carriers in hitherto only postulated energy selective contacts before they can lose much of their excess energy via scattering processes. It has been taken up recently also by other authors. It has been postulated that the lifetime of hot carriers could be enhanced in quantum dot devices and quantum well devices compared to the corresponding bulk materials and this effect has been postulated to help in achieving higher photovoltages. Hitherto such scenarios have been discussed and investigated in the photovoltaic community without being able to test the underlying assumptions rigorously with appropriate experimental tools. The latter have become available in recent years mainly in the form of various laser spectroscopies with femtosecond resolution, like transient absorption, two-photon photoemission, Tera-Hertzspectroscopy, etc. These powerful measuring techniques can be employed for investigating hot carrier dynamics in nano-structured materials like guantum-dots and quantum-wells and go far beyond interpreting stationary data with dynamic models. In this field it is important to be able to separate bulk and surface/interfaces dynamics. All these possibilities have not yet been fully realized in the field of photovoltaics. Their utilization can bring the discussion of the so-called 3rd generation photovoltaic devices on a more stable and realistic ground since the corresponding scenarios and the underlying assumption can be clarified concerning hot carrier dynamics in guantum structured materials with a particular focus on such processes that have been considered for photovoltaic applications.

References

- 1 W. Shockley, H. J. Queisser, J. Appl. Phys 32 (1961) 510-519.
- 2 A. Marti, G. L. Araujo, Solar Energy Mater. Solar Cells 43 (1996) 203.
- 3 M. A. Green, Prog. Photovolt.: Res. Appl 9 (2001) 123-135.
- *R. D. Schaller, V. I. Klimov, Physical Review Letters 92 (2004) 186601.*

Thermodynamics of losses in photovoltaic conversion

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Since the invention of the first modern solar cell, considerable attention has been given to the understanding of fundamental losses that occur in photovoltaic conversion. The classical paper by Shockley and Queisser¹ (with a previous partial result by Trivich and Flinn²) has laid down the basic framework in terms of a detailed balance between photons absorbed and emitted by the cell, and the work (electricity) produced in the conversion process. The best solar cells today achieve some 80% of the theoretical Shockley-Queisser maximum, and interest is being turned to devices that exceed this limit by the use of new mechanisms, outside the realm of the present generation of photovoltaics.

The aim of this paper is to revisit the detailed balance argument and analyse the fundamental losses in an "ideal" solar cell from a thermodynamic point of view. To this end, the conversion process can be pictured as the transformation

$$photon[T_s, \mathcal{E}_s, \mu_s(=0)] \to photon[T_o, \mathcal{E}_o, \mu_o(=qV)]$$
(1)

where *T* is the temperature, \mathcal{E} is the étendue of the beam, μ is the chemical potential, and the subscript *s* refers to the incident solar radiation and *o* to the emitted beam at temperature T_o of the converter, assumed equal to the ambient temperature. For a solar cell where non-radiative recombination is absent, the conversion process takes place subject to conservation of the combined number of photons and electron-hole pairs:

$$\dot{N}_{s} - \dot{N}_{so} = \frac{1}{q}I + \left(\dot{N}_{o} - \dot{N}_{oo}\right)$$
(2)

where q is the electron charge, I is the current generated by the converter, \dot{N}_s and \dot{N}_o are the incident and emitted photon flux and \dot{N}_{so} and \dot{N}_{oo} are the equilibrium black-body photon fluxes with étendue \mathcal{E}_s and \mathcal{E}_o which maintain the temperature T_o of the converter. The

$$qV = u_s \left(1 - \frac{T_s}{T_o}\right) - T_o \sigma_i \tag{3}$$

resulting voltage can be written in the thermodynamic form

where u_s is the energy of an incident solar photon which carries "reversible" entropy $s_s = u_s/T_s$, giving rise to the Carnot factor in the first term. The term σ_i is the internal entropy generation in the conversion process, consisting of three contributions:

$$\sigma_{kin} = k_B \ln\left(\frac{I_{\ell}' - I}{I_{\ell}'}\right) \qquad \sigma_{cool} = k_B \left(\frac{T_s}{T_o} - 1\right) - k_B \ln\left(\frac{T_s}{T_o}\right) \qquad \sigma_{exp} = k_B \ln\left(\frac{\mathscr{E}_s}{\mathscr{E}_o}\right) \tag{4}$$

where $I_{\ell}^{\prime} = I_{\ell} + I_{o}$, I_{ℓ} is the photogenerated current $q(\dot{N}_{s} - \dot{N}_{so})$, $I_{o} = \dot{N}_{oo}$ is the dark saturation current, σ_{kin} is the entropy generation on account of a finite "turnover rate" of the photovoltaic "engine", σ_{cool} is the entropy increase due to "isochoric" (at constant étendue) cooling of the beam, and σ_{exp} is the entropy generation due to the isothermal étendue expansion. The last term (which describes also the increase of voltage upon concentration of sunlight) is absent if the étendues of the incident and emitted beam are equal.

Equation (3) with (4) represent the thermodynamic analogue of the Shockley solar cell equation. The resulting voltage-current characteristic is plotted in Figure 1. One can contemplate which of the losses described above are fundamental and which can, at least in

principle, be eliminated. As already noted étendue expansion can be avoided by focusing the incident beam or by restricting the aperture of the emitted beam. It is suggested here that, in contrast, the "reversible" entropy s_s and the irreversible kinetic entropy term σ_{kin} are fundamental and unavoidable part of the conversion process: the former a direct consequence of the entropy balance and the latter a necessary contribution if conversion is to proceed at a finite velocity.

We shall explore the idea that it is possible, at least in principle, to eliminate the cooling term σ_{cool} . This type of device would be a hot-carrier solar cells where photogenerated hot electronhole pairs produce additional work *w* as they are cooled to the ambient temperature (Fig. 2). The energy *w* takes a maximum value if the process takes place reversibly, and the total free energy (voltage) generated per photon is then equal to

$$qV_{oc}(hot) = u_s \left(1 - \frac{T_s}{T_o}\right)$$
(5)

It is interesting to note that the voltage (5) may exceed the bandgap of the semiconductor.



Fig. 1. The voltage-current characteristic for the different types of solar cells discussed in this paper.



Fig. 2. Schematic diagram of a hot electron solar cell where energy produced by each photon can be characterised in terms of the étendue \mathcal{E} temperature *T* and the chemical potential μ of the incident and emitted photon beams.

¹ Shockley, W. and Queisser, H.J. Detailed balance limit of efficiency of p-n junction solar cells, J. Appl. Phys. 32, 510 (1961)

² Trivich, D. and Flinn, P.A, Maximum efficiency of solar energy conversion by quantum processes, in: F. Daniels and J. Duffie (eds), Solar Energy Research, Thames and Hudson, London, 1955.

PHOTON MANAGEMENT FOR FULL SPECTRUM UTILIZATION WITH FLUORESCENT MATERIALS

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Motivation

Fluorescent concentrators are a concept well known since the late seventies [1] to concentrate both direct and diffuse radiation without tracking systems. In a fluorescent concentrator dyes in a matrix absorb radiation and emit light with a longer wavelength. Most of the emitted light is internally totally reflected and therefore trapped and guided to the edges of the concentrator, where it is utilised by solar cells. Stack designs with several concentrator plates with different dyes allow for a full spectrum utilisation. An additional advantage is the splitting of the solar spectrum, so the different parts can be converted more efficiently with different, bandgap matched cells [1]. This study investigates system designs to maximise the output of fluorescent concentrator systems with today available dyes and solar cells. In addition we explore the possibilities to overcome the principal efficiency limiting problem of the loss cone of total internal reflection, which causes losses of at least 30% [2]. Rugate filters, which serve as a band reflection filter for the emitted light are a promising option to reduce these losses.

Approach

Today organic fluorescent dyes are available, which have quantum efficiencies above 95% for the visible spectrum. There are no such dyes for the infrared. As we have shown in Ref. 3 transmission of typical materials for fluorescent concentrators is high in the near infrared, the spectral range in which the spectral response of a silicon solar cell is the highest. This enables a system design where a silicon solar cell at the bottom of the fluorescent concentrator converts the infrared radiation. Since the spectral response of GaInP solar cells matches the photoluminescence of most dyes, GaInP is the obvious choice for the solar cells at the edges of the fluorescent concentrator. The typical open circuit voltage (V_{OC}) of a GaInP solar cell is in the region



Figure 1: Fluorescent concentrator system design with silicon bottom cell and GaInP solar cells at the edges of the concentrator.

above 1300 mV. This compares to a V_{OC} of a typical silicon solar cell of about 600..660 mV. That is, assuming the same fill factor, nearly twice the energy can be utilised if a photon is converted by the GaInP solar cell instead by the silicon cell.

Experimental Results

A first experimental realisation of the system shown in Figure 1 consisted out of one $2x^2$ cm² back-contact silicon solar cell under a fluorescent concentrator plate of 2x2cm² and 3mm thickness. Four 2x2cm² GaInP solar cells were optically coupled to the edges of the concentrator and connected in parallel. The remaining cell area was covered with black material. Figure 2 shows that without the concentrator the silicon solar cell had an efficiency of 16.7%. Under the fluorescent concentrator the efficiency dropped to 14.0%. The parallel interconnection of the four GaInP solar cells had an efficiency of 3.7% in reference to the 4cm² area of the fluorescent concentrator. Therefore the total system efficiency was 17.7%, which is significantly higher than the silicon solar cell alone. Figure 2 b) shows the spectral efficiencies of the system. It can be seen clearly how the fluorescent concentrator system increases the efficiency in the region of 400 to 500nm. We expect much higher efficiencies with optimised GaInP solar cells with the correct geometric dimensions, which are currently in production.



Figure 2: Efficiencies of a system as delineated in Figure 1 in comparison to a single silicon solar cell



Figure 3: Another fluorescent collector concept with photonic band-stop filter. The photonic structure helps to minimise losses due to the escape cone of internal reflection. It reflects light in the emission range of the dye but transmits the light in the absorption range of the dyes. Therefore no incoming light is lost in the usable wavelength range

Rugate filters are multilayer systems with continuously varying refractive index profiles. They can serve as band reflection filters for the emitted light which leaves the fluorescent concentrator in the loss cone of total internal reflection. Because of unwanted reflection in the absorption range of the fluorescent dye (Figure 4) no significant net-increase of system efficiencies could be achieved yet. Weighted with the AM1.5-spectrum and the absorption spectrum of the fluorescent concentrator the losses due to this reflection are 10% of the light being otherwise absorbed by the fluorescent concentrator. Thus the filter effectuated no significant net increase of the efficiency when it was applied to a fluorescent concentrator/ GaInP solar cell system. As the efficiency remained unchanged, it could be calculated that the filter increased the internal light guiding efficiency after the light has been absorbed by 11% at least. Measurement of the angular distributions of the light which is coupled out at the edges of a fluorescent concentrator of 5x5cm² showed also a beneficial effect of the Rugate structure for the collection of light, which is emitted into the loss cone of total internal reflection. Thus, significant efficiency enhancements can be expected from structures without the unwanted reflection in the absorption range



Figure 4: Reflection spectrum of a so called Rugate filter and the absorption and photoluminescence of the fluorescent concentrator the filter was designed for. The filter was produced at Fraunhofer IST by chemical vapour deposition. The reflection band of the filter very nicely fits the emission peak of the dye in the concentrator. However, there is still some unwanted reflection in the absorption range of the dye.

References

[1] A. Goetzberger, W. Greubel, "Solar Energy Conversion with Fluorescent Collectors", Appl. Phys. 12, 123 (1977)

[2] V. Wittwer, K. Heidler, A. Zastrow, A. Goetzberger, "Theory of fluorescent planar Concentrators and experimental results" Journal of Luminescence 24/25 (1981)

[3] J. C. Goldschmidt, S. W. Glunz, A. Gombert, G. Willeke "Advanced Fluorescent Concentrators", Proc. of the 21st Europ. PV Conf., Dresden (2006)

LOW DIMENSIONAL STRUCTURES IN PHOTOVOLTAICS

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Although the study of nanostructures such as quantum wells (QWs) and quantum dots (QDs) have dominated optoelectronic research and development for the past two decades, photovoltaic (PV) applications of these low dimensional structures have been less extensively studied. Our group has pioneered the study of both QWs and QDs for PV applications. The properties of QWs are exploited in the strain-balanced quantum well solar cell (SB-QWSC), which offers a way to extend the spectral range of the highest efficiency single-junction cell, the GaAs cell. This can in principle lead to higher efficiency and, in addition, the wide spectral range and small cell size make these devices particularly attractive for high concentration, building integrated applications utilising direct sunlight. The properties of QDs offer advantages for the luminescent solar concentrator (LSC), which is non-tracking and concentrates both diffuse and direct sunlight. The QD-LSC is therefore complementary to the SB-QWSC for building integrated concentrator PV applications.

In the SB-QWSC, illustrated schematically in Fig. 1a, the low-band-gap, higher-lattice-constant (a₂) alloy $In_xGa_{1-x}As$ wells (In composition $x \sim 0.1 - 0.2$) are compressively strained. The higher-band-gap, lower-lattice-constant (a₁) alloy $GaAs_{1-y}P_y$ barriers (P composition $y \sim 0.1$) are in tensile strain [1]. This approach solves the problem that there are no lattice matched binary or ternary III-V compounds with *lower-band-gap* than GaAs. Of the many possible balance conditions we find that *zero-stress* gives the best material quality [2] and enables at least 65 wells to be grown without relaxation [3]. The QWs extend the absorption from the bulk band-gap, E_g , to a threshold energy, E_a , determined by the confinement energy as in Fig. 1b, providing a broader spectral response.



Figure 1. a) Schematic of the SB-QWSC. b) Energy band-edge diagram of the p-i-n SB-QWSC. c) Spectral response of a 50 well SB-QWSC.

We have shown that the SB-QWSC offers further advantages in that at high concentration (>200×) it is inherently subject to the fundamental radiative efficiency limit whereas good homojunction cells are well described by the ideal Shockley picture, in which the limiting efficiency is determined by radiative and non-radiative recombination in the charge neutral layers of the cell. We analyse SB-QWSCs in terms of a light and dark current model [4]. The model calculates the spectral response (SR) from the field bearing regions, charge neutral layers and from the QWs as in Fig. 1c by first calculating the confined densities of states and absorption coefficient from first principles, assuming unity quantum efficiency for carrier escape from the QWs, and then solving the transport equations analytically [5]. The total dark current, J_d , is self-consistently expressed as the sum of depletion layer and charge neutral radiative and nonradiative currents with parameter values extracted from the SR fits to experimental data. Integrating the convolved SR and incident light spectra then gives the short-circuit current, J_{SC} . Assuming that the additivity condition holds the device current-voltage characteristic, J(V), is given by $J(V) = J_{SC} - J_d$. Finally, the device efficiency is determined from the maximum power point of the J(V) curve.

Radiative recombination can be estimated by a detailed balance argument relating the photons absorbed to the photons radiated. The electroluminescence (EL) of the device in an electrostatic field is determined by integrating the generalised Planck equation over the device geometry and depends on the quasi-Fermi level separation, ΔE_F . By fitting absolute EL measurements we find, as expected, that $\Delta E_F = qV$ in the bulk, but that, surprisingly, $\Delta E_F < qV$ in the QWs [6]. In Ref. [7] it is argued that this suppression of ΔE_F in the QWs violates the second law of thermodynamics. This may be resolved by postulating the existence of hot carriers in the QWs and indeed, a strong dependence of the carrier temperature in QWs on both carrier density and electric field has been reported in several papers [8]. The generalised Planck equation predicts that ΔE_F suppression in the QWs will result a reduction in the EL intensity whereas an increased carrier temperature in the QWs will result in a change in the shape of the EL spectrum. Recent EL measurements on SB-QWSCs at high biases show a change in the shape of the QW EL spectrum that is consistent with

a carrier temperature in the QWs up to 80K higher than that in the bulk [9]. If this thermoelectric effect is proven to play a significant role in the efficiency enhancement, the challenge would then be to maximise the driving force responsible for the reduction of J_d [8].

In practice the number of QWs that can contribute to the photocurrent is limited by background doping in the iregion so photon-recycling (PR) schemes are necessary to achieve complete absorption of incident photons with energies between E_g and E_a . We have demonstrated enhanced efficiency in SB-QWSCs grown on distributed Bragg reflectors (DBRs) [10], in which incident photons not absorbed by the device initially are reflected back into the device. Another benefit of growing SB-QWSCs on a DBR substrate is that J_d is suppressed when compared to devices grown on GaAs substrates. Both J_d and device EL are well described by the models outlined above when PR effects are taken into account and, it is predicted that optimised DBR designs could lead to efficiency increases of >2% absolute [10].

LSCs concentrate light in addition to reducing spectral losses, and simply consist of transparent polymer sheets doped with luminescent species [11]. Sunlight incident on the top surface is first absorbed by the luminescent species and is then re-radiated, ideally with high luminescence quantum efficiency (Q_e) , such that a fraction of the emitted light is trapped in the sheet and can be converted by a solar cell at the edge. A stack of sheets can separate the light, as in Figs. 2a and 2b, in order to maximise the power conversion efficiency. In addition to avoiding the need for expensive solar tracking and the ability to collect both direct and diffuse sunlight, a further advantage of the LSC is that it reduces thermalisation losses and heat dissipation in an attached solar cell by converting the incident spectrum to improve the match with the absorption spectrum of the cell. However, the development of this promising concentrator was initially limited by the performance of the luminescent dyes available. Particular problems were their poor stability under solar irradiation and the large re-absorption losses owing to significant overlap of the absorption and emission.

QDs have advantages over dyes in that: (i) their absorption spectra are far broader, extending into the UV, (ii), their absorption properties may be tuned simply by the choice of nanocrystal size, and (iii) they are inherently more stable than organic dyes. Moreover, (iv) there is a further advantage in that the red-shift between absorption and luminescence is *quantitatively* related to the *spread* of QD sizes, which may be determined during the growth process, providing an additional strategy for minimising losses due to re-absorption [12]. However, the Q_e s of QDs cannot yet match the near unity values achieved for some dyes but, an encouraging result of $Q_e > 0.8$ has been reported [13] for core-shell QDs.



Figure 2. a) Schematic of a three-stack LSC. b) Ideal cell band-gap, absorption and luminescence for each layer in the stack. c) Predicted average fluxes escaping the top and right-hand surfaces of a mirrored $L \times W \times D = 42 \times 10 \times 5$ mm acrylic QD-LSC with $Q_e = 0.75$ together with the normalised observed luminescence escaping the right-hand surface.

We have developed thermodynamic models for planar luminescent concentrators [14,15], modules [16] and stacks [17] by applying a detailed balance argument to relate the absorbed light to the spontaneous emission using selfconsistent three-dimensional (3D) fluxes. Comparison with measurements on small test slabs [14,15], modules [16] and stacks [17] show that our 3D flux models can predict both the room temperature red-shift and the total flux escaping each surface, providing a tool for optimisation of the LSC. More recently, we have developed a simplified linearised model [18] in order to facilitate calculations on practical sized devices. For an idealised mirrored $40 \times 10 \times 0.5$ cm LSC doped with QDs matched to an InGaP cell we calculate that 78% of the luminescence will be lost through the top surface. Recently, pioneering use has been made of wavelength-selective cholesteric liquid crystal coatings applied to the top surface in order to reduce these losses [19]. The chiral cholesteric coatings are transparent to incoming light but reflect the emitted light and, experimental results [19] suggest that a significant increase in light output can be achieved.

References

p160.

- [1] N J Ekins-Daukes et al., Appl. Phys. Lett. 75, 1999, p4195.
- [2] N J Ekins-Daukes et al., Cryst. Growth Des. 2, 2002, p287.
- [3] M C Lynch et al., J. Mater. Sci. 40, 2005, p1445.
- [4] J P Connolly et al., Proc. 19th EUPVSEC, (Paris, France, 2004), p355.
- [5] M Paxman et al., J. Appl. Phys. 74, 1993, p614.
- [6] A Bessière et al., Proc. 31st IEEE PVSC, (Orlando, USA, 2005), p679.
- [7] A Luque et al., *IEEE Trans. Elec. Devices*, **48**, 2001, p2118.
- [8] M Mazzer et al., *Proc.* 3^{rd} WCPEC, (Osaka, Japan, 2003), p2661.
- [9] M Führer et al., *Proc.* 21^{st} *EUPVSEC*, (Dresden, Germany, 2006),
- [10] D C Johnson et al., Proc. 31st IEEE PVSC, (Orlando, USA, 2005), p699.
- [11] A Goetzberger and W Greubel, Appl. Phys. 14, 1977, p123.
- [11] K W J Barnham et al., Appl. Phys. Lett. 76, 2000, p1197.
- [12] A P Alivisatos, MRS Bulletin, February, 1998, p18.
- [13] A J Chatten et al., Proc. 3rd WCPEC, (Osaka, Japan, 2003), p2657.
- [14] A J Chatten, et al., Semiconductors **38**, 2004, p949.
- [15] A J Chatten et al., Proc. 19th EUPVSEC, (Paris, France, 2004), p109.
- [16] A J Chatten et al., *Proc. 31st IEEE PVSC*, (Orlando, USA, 2005), p82.
- [17] A J Chatten et al., *Proc. 21st EUPVSEC*, (Dresden, Germany, 2006),
- p315.
- [18] M G Debije et al., Proc. WREC IX (Florence, Italy, 2006).

Si/SiO₂ Quantum Well Structures: Preparation and Characterization

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Introduction. Bandgap engineering of silicon based material provides a promising way towards 3rd generation photovoltaic devices such as tandem solar cells [1]. It has been recognized that multiple bandgaps can be achieved by control of the layer thickness in Si/SiO_2 quantum layer superlattices. In the present study we focus on preparation and characterization of $SiO_2/Si/SiO_2$ single quantum layers, which represent the building block of such superlattices. The aim is to gain control of the matter at the atomic scale and to understand its low-dimensional physics and, thus, to provide a gateway to the enhancement of solar cell efficiencies by making use of quantum size effects.

Preparation. SiO₂/Si/SiO₂ single layer structures were prepared under ultrahigh vacuum conditions (base pressure $< 2?10^{-9}$ mbar) by thermal deposition of Si onto cleaned quartz glass (SiO₂) wafers kept at room temperature and subsequent oxidation with O neutrals from a RF plasma source (RF power: 300 to 600W, substrate temperature: 600°C). Nominal Si coverages down to about 1 nm can be precisely controlled by monitoring the particle flux with a water-cooled quartz microbalance. Surface and interface analysis is performed by X-ray photoelectron specroscopy (XPS) without breaking the vacuum. Raman scattering and photoelectrical measurements are performed under ambient conditions.



Fig. 1: Si 2p XPS spectra of 10 nm Si films after RF plasma oxidation with O neutrals at (a) 200 W and (b) 600 W (substrate temperature: 600°C). The curve fittings reveal a superposition of solely Si and SiO₂. Estimated SiO₂ layer thickness: (a) 1.1 nm, (b) 4.0 nm.

Si/SiO₂ interface. Si layers deposited onto the quartz glass substrate at 600°C have an amorphous structure. RF plasma oxidation allows the growth of oxide films with nm thickness at these a-Si layers at moderate temperatures (<600°C). Fig. 1 shows the Si 2p XPS spectra of two 10 nm Si films after RF plasma oxidation. Both spectra contain two distinct peaks, which change their relative intensities when the RF power is increased from (a) 200 W to (b) 600 W. Peak analysis by appropriate curve fitting allows a clear assignment of these two peaks to the oxidation states Si⁰⁺ and Si⁴⁺, corresponding to Si and SiO₂, respectively [2]. At 200 W all suboxide species (i.e., oxidation states Si¹⁺, Si²⁺, Si³⁺) are absent, at 600 W only trace amounts can be detected. Accordingly, under the applied conditions pure SiO₂ is formed on top of the Si layers with a nearly abrupt interface. The thickness of the SiO₂ layers is estimated from the curve analysis under the assumption of a constant inelastic mean free path of 3 nm [2]. Supposing a consumption of 0.45 nm Si per 1nm SiO₂, the resulting sample configurations are as follows: (a) 9.5 nm Si + 1.1 nm SiO₂ and (b) 8.2 nm Si + 4.0 nm SiO₂ superlattices.

Ultrathin Si layer. Annealing of the oxidized a-Si layer is necessary for crystallization of Si and the improvement of the interface quality. Generally, temperatures to anneal ultrathin a-Si layers sandwiched by SiO_2 are higher compared to common crystallization of bulk a-Si [3].



Fig. 2: Raman spectrum of oxidized 10 nm Si layer (cf. Fig. 1a). (a) Effect of RF plasma oxidation and subsequent annealing at 1000°C. (b) Line shape analysis elucidating the multicomponent film structure.

The Raman spectra shown in Fig. 2(a) indicate that 1000°C annealing leads to a crystallization of the Si layers. Before annealing the sample produces a broad peak centered at around 480 cm⁻¹ characteristic for a-Si (grey line). After annealing this signal transforms into a rather sharp peak with a maximum around 517 cm⁻¹ (black line). Comparison of this signal with the TO vibration mode of single-crystalline silicon located at 520 cm⁻¹ (dotted line) reveals two distinct features: (i) an asymmetric lineshape which indicates different components, (ii) peak shift and broadening which implies a nanocrystalline (nc) film structure. Curve analysis, presented in Fig. 2(b), elucidates the multi-component structure of the layer. Besides the convolution of crystalline and amorphous material, a third contribution centred at around 500 cm⁻¹ is observed, which is assigned to strained or nc-Si. From this data a lower limit of the crystalline fraction of ~74 % is determined, which proves the highly crystalline structure of the quantum layers [4]. As indicated in Fig. 2(a) the signal of Si layer exhibits a FWHM of 10 cm⁻¹ and a peak downshift of 2-3 cm⁻¹. Theoretical calculations have correlated these values to a mean nanocrystal size of 60-80 Å [5], which coincides well with the effective Si layer thickness. From these findings it is concluded that the Si layers are composed of Si nanocrystals embedded in an a-Si matrix. First photoelectrical measurements demonstrate that a photocurrent can be detected in these single Si quantum layers, even if the nominal Si layer thickness is decreased to 2 nm. In Fig. 3 the quantum efficiencies of photoconductivity for Si layers of 10 nm and 2 nm nominal thickness are plotted vs. the photon energy. It is seen that for both samples photoconductivity sets on in the range of the direct c-Si band gaps at 3.6 eV and 4.2 eV.



Fig. 3: Quantum efficiency of photoconductivity for Si quantum layers with a nominal thickness of 10 nm and 2 nm at 300 K. Onset of photoconductivity appears in the range of the direct c-Si bandgap.

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References

- [1] Green, M.A.: Third Generation Photovoltaics. Advanced Solar Energy Conversion (Berlin, Springer, 2005)
- [2] Joong Kim, K., Park, K.T., Lee, J.W.: Thin Solid Films 500 (2006), 356; Himpsel, F.J., McFeely, F.R., Taleb-Ibrahimi, A., Yarmoff, J.A., Hollinger, G.: Phys. Rev. B 38 (1988) 6084.
- [3] Zacharias, M., Streitenberger, P.: Phys. Rev. B 62 (2000), 8391.
- [4] Viera, G., Huet, S., Boufendi, L.: J. Appl. Phys. 90 (2001), 4175.
- [5] Campbell, I.H., Fauchet, P.M.: Solid State Commun. 58 (1986), 739.

Microscopic modelling of quantum well solar cells

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We present a microscopic model of the photocurrent in quantum well solar cells (QWSC), based on the nonequilibrium Green's function formalism (NEGF) for a multiband tight binding Hamiltonian. The quantum kinetic equations are self-consistently coupled to Poisson's equation. Relaxation and broadening mechanisms are considered by the inclusion of acoustic and optical electron-phonon interaction in a self-consistent Born approximation of the scattering self energies.

I. INTRODUCTION

Since the pioneering work of Barnham and coworkers [1], the potential efficiency enhancement by the introduction of quantum wells in the intrinsic region of a *pin* solar cell has attracted considerable interest both from the photovoltaic community and within a broad spectrum of fundamental research [2]. An accurate description of the physics of QWSC, including the processes shown in Fig. 1, requires the combination of a microscopic material model with a formalism for nonequilibrium quantum transport in interacting systems. The NEGF formalism together with a tight-binding or Wannier basis matches these requirements and has been successfully applied to similar systems like quantum cascade lasers [3]



or resonant tunneling in layered semiconductor heterostructures [4].

FIG. 1: Characterizing structure and processes of a *pin*-QWSC.

Generation and recombination

- 1. Photogeneration of electron-hole pairs between confinement levels
- 2. Radiative recombination
- 3. Nonradiative recombination (Auger-/trap)

Transport

- 4. Resonant and nonresonant tunneling
- 5. Thermal escape from quantum wells and sweep out by built in electric field
- 6. Relaxation by inelastic phonon scattering

II. MODEL

The QWSC system is described by the total Hamiltonian

$$H = H_0 + H_{int}, \quad H_{int} = H_{ep} + H_{e\gamma} + H_{other}, \tag{1}$$

where H_0 denotes the multiband (e.g. two-band sp_z or 10-band sp^3s^*) tight-binding Hamiltonian for the noninteracting system, H_{ep} and $H_{e\gamma}$ stand for the interaction of carriers with phonons and photons, respectively, and H_{other} contains further types of elastic scattering (from interface roughness, ionized dopants, alloy composition inhomogeneities, etc.), inter-carrier scattering and nonradiative recombination terms. The Hamiltonians of the extended contact regions are absorbed into respective boundary self energies Σ^B reflecting the openness of the system. Interactions such as carrier-phonon and carrierphoton scattering are included perturbatively in terms of interaction self energies Σ on the level of a selfconsistent Born approximation. For polar-optical phonons, which are the main relaxation mechanism, the standard Fröhlich Hamiltonian is used, and the acoustic phonons are modelled by the deformation potential approach. The coupling to photons is described within the dipole approximation and for monochromatic illumination. For both phonons and photons, an equilibrium distribution is assumed. Carrier-carrier interactions are considered by solving Poisson's equation with the carrier densities from the Green's functions and a given doping profile, which corresponds to a Hartree level approximation. The self-consistent electrostatic potential is contained in the exactly solvable Hamiltonian H_0 .

In layered semiconductors, a suitable representation of the carrier wave function is obtained from Bloch sums of planar orbitals,

$$|\alpha, L, \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_{t}^{L,\alpha}} e^{i\mathbf{k}\cdot\mathbf{R}_{t}^{L,\alpha}} |\alpha, L, \mathbf{R}_{t}^{L}\rangle, \tag{2}$$

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where α denotes the localized orbitals, L indicates the layer and $\mathbf{R}_t^{L,\alpha}$ the location within the layer. N is a normalization factor and \mathbf{k} the transverse wave vector. The real time nonequilibrium Green's functions $G_{\alpha,L;\alpha',L'}(\mathbf{k};t,t')$ are defined as nonequilibrium ensemble averages of the corresponding single-particle operators [5, 6]. In steady state, it is possible and more convenient to work with the Fourier transform $G^{<}_{\alpha,L;\alpha',L'}(\mathbf{k}; E)$. Within the NEGF formalism, the steady state equations of motion for the Green's function are given

(in matrix notation) by the Dyson equations

$$G^{R} = \left[\left(G_{0}^{R} \right)^{-1} - \Sigma^{R} - \Sigma^{RB} \right]^{-1}, \quad G_{0}^{R} = \left[(E + i\eta) \mathbb{1} - H_{0} \right]^{-1}, \tag{3}$$

$$G^{\lessgtr} = G^R \left(\Sigma^{\lessgtr} + \Sigma^{\lessgtr B} \right) G^A, \quad G^A = (G^R)^{\dagger}.$$
⁽⁴⁾

Together with the self-energies from boundaries and interactions, they form a closed set of equations for the Green's functions that has to be solved self-consistently.

Once the Green's functions are known, macroscopic quantities can be derived, such as carrier and current densities at a given layer L, which for a nearest-neighbor coupling tight-binding model are given by

$$n_{L} = \frac{-2i}{A\Delta} \sum_{\mathbf{k}} \int \frac{dE}{2\pi} tr\{G_{L;L}^{<}(\mathbf{k};E)\}, \quad J_{L} = \frac{2e}{\hbar A} \sum_{\mathbf{k}} \int \frac{dE}{2\pi} 2Re\{tr[t_{L;L+1}G_{L+1;L}^{<}(\mathbf{k};E)]\}, \quad (5)$$

where A is the cross sectional area.

III. RESULTS

Apart from the nonequilibrium carrier and current densities given by Eqs. (5), interesting quantities that can be derived from the Green's functions are e.g. the local density of states and the photocurrent response, which for a given structure reveal the location of confinement levels, the effects of electronphonon scattering, tunneling of carriers out of the wells and the characteristics of optical transitions, as displayed in Fig. 2 for a generic quantum-well *pin* structure.



FIG. 2: Self-consistent local density of states (left and right) and photocurrent response (middle) for 25 ML quantum well pin-diode $(V_{bias} = -0.01V)$ with acoustic and polar optical electron-phonon interaction.

IV. CONCLUSIONS

The nonequilibrium Green's function formalism applied to quantum well solar cells allows for the study of the microscopic processes involved in the generation and transport of carriers under nonequilibrium conditions and at the same time for the extraction of observable quantities that can be compared to experimental results.

- [1] K. Barnham and G. Duggan, J. Appl. Phys. 67, 3490 (1990).
- [2] K. Barnham et al., Physica E 14, 27 (2002).
- [3] S.-C. Lee and A. Wacker, Physica E 13, 858–861 (2002).

- [5] L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics, Benjamin-Cummings, 1995.
- [6] L. Keldysh, Sov. Phys.-JETP. 20, 1018 (1965).

2

^[4] R. Lake, G. Klimeck, R. C. Bowen, and D. Jovanovic, J. Appl. Phys 81, 7845 (1997).

III/V Multijunction Solar Cells

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Single-junction solar cells have a low theoretical efficiency limit (37%) compared to the theoretically possible one (95%) due to the inability to properly match the sun's spectrum with a semiconductor material having a single bandgap. Photons with energies smaller than the bandgap energy are lost completely, whereas photons with larger energy loose their energy in excess of the bandgap of the semiconductor via thermalization processes. These processes decrease the efficiency considerably. Stacking semiconductor materials, which have different bandgaps one on top of each other, the highest bandgap material on top, one can increase efficiency tremendously. All these cells are connected in series by tunnel junctions. Maximum efficiencies increase with the number of junctions, however there is a reasonable compromise between the maximum possible efficiency and the cost-intensive and complex manufacturing process. Realistic calculations, also taking losses into account, predict a maximum efficiency under an AM1.5 spectrum in the range of 40% for a three junction stack (Ge, (InGa)As, (GaIn)P) and of 52% for a stack, where a material, having a 1eV bandgap would be introduced between the substrate and the (InGa)As. The novel, metastable compound semiconductor system (GaIn)(NAs) would be an optimal candidate as 1eV solar cell material in these multi-junction solar cell concepts, as it can be grown lattice matched to GaAs or Ge-substrates. Up to now, however, the short minority carrier diffusion in the devices limit the performance of such cells. Minority carrier diffusion lengths as low as 10 -20 nm have been observed. With minority carrier diffusion lengths shorter than the depletion widths, the carrier collection in such a device is dominated by field-aided collection rather than by diffusion collection, which is common for other III/V materials. This results in low short circuit currents and low quantum efficiencies of the devices. It is crucial to determine whether these short diffusion lengths are due to extrinsic, growth related defects or are an intrinsic property of this material system. Another important issue in these films is the high background carrier concentration in the order of $10^{17}/\text{cm}^3$, which is mainly observed for material grown by metal organic vapour phase epitaxy (MOVPE), influencing the doping characteristics and carrier concentrations, the carrier mobility as well as the performance of the devices. Also, several structural characteristics, as outlined in the following, are intrinsic to the dilute-N-containing material systems and influence carrier transport, optoelectronic properties and finally device performance.

The present paper presents these specific intrinsic structural and compositional properties of the metastable quaternary material, such as the chain like N-ordering in growth direction. In addition, this study discusses up to which extent optimised growth and annealing conditions can be found to circumvent these properties of the material and hence improve device performance.

All (GaIn)(NAs) bulk structures or multi quantum well samples used for this study have been grown on (100) GaAs substrates in a commercially available horizontal reactor system (AIX200) by MOVPE (metal organic vapour phase epitaxy) using hydrogen carrier gas at a low reactor pressure of 50 mbar. Due to the large difference in covalent radius between Nitrogen and Arsenic, the material system under investigation is metastable, low substrate temperatures have to be chosen in order to achieve significant N incorporation. Substrate temperatures are usually fixed to 550°C. The substrate temperatures are calibrated to the Al/Si eutectic formation occurring at 577 °C. As a consequence of the low growth temperatures, MO sources efficiently decomposing at lower temperatures like the group V sources tertiarybutylarsine (TBAs) and the unsymmetric dimethylhydrazine (UDMHy) have to be used. As group III sources, trimethylgallium (TMGa) as well as triethylgallium (TEGa) and trimethylindium (TMIn) are applied. For solar cell device structures Te (from diethyltellurium (DETe)) was used as n-type dopant and Mg (from dicyclopentadienylmagnesium (Cp₂Mg)) as p-dopant, respectively. For van der Pauw-Hall measurements 1 to 2 µm thick test films have been grown and measured as grown and after annealing at 77 K and 300 K. Secondary Ion Mass Spectrometry (SIMS) analysis has been performed on selected samples in order to examine the actual incorporation of the dopants in comparison to the activated amount, measured by Hall effect measurements.

To anneal defects from the quaternary, metastable material, it needs to be thermally treated at elevated temperatures after growth. These annealing procedures have been varied in this study. We have applied annealing steps consisting of a 5 - 120 min TBAs stabilized anneal at 700° C - 800° C and a subsequent unstabilized annealing step at 625° C - 700° C for 25 min in the MOVPE reactor.

It will be shown by transmission electron microscopy, employing special dark field techniques, in combination with valence force field modelling of stable crystal structures as well as optoelectronic characterization of the material, that one is close to fulfilling material characteristics necessary for embedding the material into a 4-junction solar cell stack.

Hybrid Carrier Multiplication Quantum Dot Solar Cells

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The one-to-one relationship between absorbed photon and generated electron-hole pair is the key limitation to the conversion efficiency of existing solar cell approaches. Recently, various semiconductor nanocrystals have shown to exhibit highly efficient carrier multiplication, a process wherein a single incident photon is converted into multiple electron-hole pairs, or multiexcitons.¹ Semiconductor nanocrystals have consequently been the target of intensive research efforts, not only due their potential application as active materials in third generation solar cells, but also as an experimental testbed for the fundamental study of the carrier multiplication mechanism. Traditionally, carrier multiplication has been described by impact ionization. In this process a high energy photogenerated electron in the conduction band collides with an electron in the valence band which is then promoted to the conduction band by gaining the excess kinetic energy of the first electron. Recent ultrafast photoinduced absorption measurements however have shown that the carrier multiplication occurs within less than 200 fs, suggesting that other mechanism such as the direct photogeneration via-multiple virtual single-exciton states² or coherent superposition of multiple excitonic states³ may be responsible for the carrier multiplication.

The aim of our work is to exploit the process of carrier multiplication in PbSe and PbTe nanocrystals in photovoltaic devices with enhanced photocurrents and hence higher conversion efficiencies. To estimate the efficiency enhancement that can be expected from such solar cells we have calculated the ultimate and detailed balance efficiencies for the thermodynamic limit and the semiempirical limit based on the experimentally observed quantum efficiency in PbSe nanocrystals.¹ In the first case we assumed that the energy distribution of the photogenerated electrons and holes resulting from carrier multiplication is given by a room-temperature Fermi-distribution. The detailed balance limit calculated with empirical quantum efficiencies showed only marginal enhancement over the Shockley-Queisser limit (\sim 31%) known for conventional solar cells. However. if the carrier multiplication occurs via impact ionization, the above mentioned assumption is invalid and the energy distribution of the photogenerated carriers is instead given by a Fermi-distribution with no separation of the quasi-Fermi-energies and an effective temperature exceeding the lattice temperature. Under the assumption of a maximum multiplicity of 2 (i.e. maximally 2 excitons generated per incident photon) these calculations showed that thermodynamic and semi-empirical conversion efficiencies to be 53% and 41%, respectively.

The PbSe and PbTe nanocrystal building blocks used in our work are synthesized via the simple, low-cost, highly tunable hot-injection method. Figure 1A shows a transmission electron micrograph of a hexagonally close packed array of 3.5 nm PbSe Simple adjustments of the synthesis conditions allow the average nanocrystals. nanocrystal diameter to be tuned between 3.5 and 10 nm. Since the particles are far smaller than the Bohr exciton radius, their electronic properties are dominated by strong quantum confinement effects. The absorption spectra in Figure 1B show that the first exciton peak $(1S_e-1S_h)$ with energies is tunable between 0.5 to 0.9 eV as well as higher level transitions attributed to $1S_{h}-1P_{e}$ and $1P_{h}-1S_{e}$. Additional photophysical characterization of the PbSe nanocrystals was performed to confirm the optical signature of carrier multiplication. In photoinduced absorption measurements PbSe nanocrystals were excited with a pump laser pulse ($h\omega=3E_g$) and showed photoinduced multiexciton decay dynamics with biexcitonic decay times ranging from 40-60 picoseconds and quantum efficiencies of approximately 125%.



Figure 1: (A) TEM image of PbSe nanocrystal array (top inset: nanocrystal diameter distribution, bottom inset: high resolution image of a single PbSe nanocrystal with resolved (100) lattice planes.), (B) Size dependent absorbance spectra, and (C) carrier multiplication schematic.

In order to benefit from the additional excitons generated by carrier multiplication, the charges have to be removed from the nanocrystal at a rate faster than biexcitonic decay rate (see Figure 1C). In addition to these kinetic limitations, the application of these nanocrystals in photovoltaic devices requires knowledge of position of the valence and conduction band levels. The valence and conduction band levels of conducting polymers are commonly determined from the oxidation and reduction potentials measured with cyclic voltammetry (CV). We have performed CV measurements on PbSe and PbTe nanocrystal films in an effort to correlate the difference in oxidation and reduction potential with the optically determined band gap. While the measurements allowed a rough approximation of the position of the nanocrystal valence and conduction band levels, a clear correlation with nanocrystal size could not be established due to difficulties related to an irreversible electrochemical degradation of the nanocrystal film. Complimentary to the CV measurements we have employed Kelvin probe force microscopy (KFPM) to measure the surface potential of the nanocrystal film. These measurements allow a direct determination of the average work function of the nanocrystal film and furthermore permit the mapping of the surface potential with high spatial resolution.

With the nanocrystal building blocks in hand, our current research efforts focus on identification photovoltaic device configurations which may allow the utilization of multiexcitons. We are currently exploring two parallel device configurations: the first approach is based on the well known bulk heterojunction cell architecture, in which the nanocrystals are mixed with a conducting polymer to form a bicontinuous network allowing charge generation and transport. The parallel approach focuses on the electron transport through all-inorganic nanocrystal films consisting of a blend of PbSe and PbTe nanocrystals.

References

(1) Schaller, R. D.; Klimov, V. I. *Physical Review Letters* **2004**, *92*, 186601/186601-186601/186604.

- (2) Klimov, V. Journal of Physical Chemistry B 2006, 110, 16827-16845.
- (3) Shabaev, A.; Efros, A. L.; Nozik, A. J. *Nano Letters* **2006**, *6*, 2856-2863.

PbSe/PbS and PbSe/PbSe_xS_{1-x} core-shell nanocrystals used as Q-switches and gain devices

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PbSe Nanocrystals (NCs) exhibit strong size quantization effects and activity in the IR spectral regime, having a recent interest as useful components in telecommunication, biological imaging and opto-electronic applications. The current paper discusses the growth of PbSe/PbS and PbSe/PbSe_xS_{1-x} core-shell structures carried out in colloidal solutions. The PbSe/PbS structures were prepared by a post precipitation of the PbS on a pre-prepared cores. This two stage procedure occasionally results in broadening of size distribution, accompanied by additional byproducts and complexity of the reaction. Altenatively, this document discusses a unique single-step technique for the growth of PbSe/PbSe_xS_{1-x} core-shell NCs, by the injection of precursors into a single mother solution. The faster nucleation of PbSe NCs permitted the creation of the core constituent, followed by the formation of the PbS shells, with ~1% crystalline mismatch. The crystallographic properties of the and core-shell NCs were examined by a high-resolution transmission electron microscopy, showed the formation of a high quality PbSe/PbS interfaces with an overall rock salt cubic structure.

The optical properties of the PbSe/PbS and PbSe/PbSe_xS_{1-x} NCs showed that an integration of appropriate stiochoimetric amounts of sulfur in the reaction, improved substantially the absorption quantum efficiency (up to 60%), with a very small red shift of the first exciton band. While, an increase of the PbS shell thickness caused a large red shift of the absorption curve with a reduction of the exciton intensity. Theoretical estimations suggest that a shell with a three monolayer thickness should have a band gap rapping that of a core size <7 nm, leading to a direct band gap transitions within the PbSe core. While an increase of the shell thickness may create an indirect semiconductor PbSe/PbS and PbSe/PbSe_xS_{1-x} composite. Furthermore, the comparison of the absorption and photoluminescence bands of NCs with various sizes showed a transfer from a Stokes shift into an anti-Stokes shift of the luminescence energy with the decrease of the NCs size.

The saturable absorbing properties of PbSe core NCs and their corresponding PbSe/PbS core-shell and PbSe/PbSe_xS_{1-x} core-shell structures, were examined at an energy of 1.54 μ m. These NCs act as a passive Q-switch and were integrated into near infra-red pulsed lasers. Saturation fluence values in the order of a few hundreds mJ/cm² were obtained, leading to a laser power output of 2.0-3.5 mJ with a pulse duration of 40-53 nsec. We demonstrated a substantial decrease of the saturation fluence values, when using PbSe/PbS and PbSe/PbSe_xS_{1-x} core-shells structures, in comparison with the corresponding PbSe core NCs. A quasi-three level energy manifold was used for the simulation of saturation fluence curves, suggesting absorption cross sections of ~10⁻¹⁶ cm², and an excited lifetime of a few picoseconds, due to the formation of multi-excitons under an intense pumping required for the saturation conditions, suitable properties for mode-locked devices.

Organic Bulk Heterojunction Solar Cells: Scientific and Technological Challenges for the future

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Low-cost photovoltaic (PV) cells, which are light and flexible, could open up many new applications for solar cells, from self-powered electronic newspapers to self sufficient buildings. Among the various thin film techniques, solution processed organic solar cells have the highest potential for a true low cost technology since production demands only low temperature, solution coating or printing processes with low resolution. Organic photovoltaics in general has come into the international research focus during the past three years ^[i, ii, iii]

Up to now main efforts have focused on the improvement of the solar conversion efficiency, and the demonstration of 5 % efficient solar cells under true AM1.5 conditions were regarded as an important milestone to prove the technology's potential. ^[iv]

Despite this in comparison to inorganic technologies low efficiency, organic photovoltaics is evaluated as one of the future key technologies opening up completely new applications and markets for photovoltaics. Photovoltaic elements based on thin plastic carriers, manufactured by printing and coating techniques from reel to reel, and packaged by lamination techniques is not only intriguing but highly attractive from a cost standpoint.

In this contribution we give an overview of technological challenges which were overcome during last years, and analyze future challenges. Technological concepts as well as new materials are introduced, which will raise efficiencies beyond the 5% range. Alternative electrode systems, replacing high cost ITO electrodes on films, are presented. The lifetime of organic solar cells, which is considered as the main challenge, is addressed in more detail. Due to improvements in packaging, materials, interface engineering and an improved understanding of failure mechanisms, operational lifetimes of over 1000 hours under 1 sun at elevated temperatures are reached with relative ease.

i N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, Science 1992, 258, 1474.

ii J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, *376*, 498.

iii G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, *270*, 1789. iv NPEL certificate for Kaparka solar cell ES 6 from July 18th 2005

iv NREL certificate for Konarka solar cell E8-6 from July, 18th, 2005

Plastic solar cells based on PCBM:P3HT and ThCBM:P3HT blends

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Solar cells based on composites of conjugated polymers and fullerene derivatives continue to be of interest as promising candidates for low cost and large area photovoltaic devices. Up to now the 'state of the art' polymer solar cells are based on a combination of a regioregular poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM). For these cells it was demonstrated that a thermal annealing process of the complete devices resulted in an enhancement of the solar cell performance.^[11] This enhancement of the power conversion efficiency has been attributed to an increase of the hole transport in the blend due to crystallization of P3HT, an improved film morphology, and a red shift of the absorption spectrum that results in a better overlap with the solar spectrum.^[2-6] Li et al. have recently reported plastic solar cells based on a P3HT:PCBM mixture with a power conversion efficiency up to 4%, which was realized by controlling the growth rate of the photoactive layer.^[7] The influence of slow film growth on the morphology and electronic properties of the blend has recently been studied by several groups.^[8-10]

We have recently synthesized an efficient acceptor-type fullerene that can be used in solar cells based on P3HT and other donor-type materials, as a replacement for PCBM. This fullerene derivative was designed to improve the compatibility with polythiophene donors by replacing the phenyl group of PCBM with a thienyl one, resulting in 1-(3-methoxycarbonyl)propyl-1-thienyl-[6,6]-methanofullerene(ThCBM). Previous results indicate that ThCBM provides for the same charge carrier mobility as PCBM and that a highly functional bulk heterojunction morphology can be readily obtained with P3HT. These cells were fabricated with active layers that were thermally annealed. ^[11]

We now present investigations of morphology and electrical properties of photovoltaic devices based on a P3HT:ThCBM active layer, obtained by the 'slow evaporation method'. The solar cells were fabricated by depositing the photoactive layer from solvents with different boiling points, which determine the grow rate of the films. Atomic force microscopy analysis reveals a more granular structure in case of quick grown (thermally annealed) films, as well as a well-defined fibrilar and crystalline structure for slowly grown films. Furthermore, electrical characterization of the solar cell devices indicates a clear advantage for the slow growth procedure. This is mainly represented by an order of magnitude enhancement in the hole mobility through the P3HT phase, resulting in a more balanced transport of electrons and holes in the blend, and its consequent 0.4% (absolute) increase in power conversion efficiency. Additionally, is shown experimentally that optimum device performance, for the slow growth procedure, is obtained at film thicknesses of approximately 300 nm, making it possible to maximize light absorption in these blends.

AFM was used to investigate the morphology of the active layer of regioregular P3HT:ThCBM blends that were grown at different rates by using solvents having different boiling points. Figure 1 shows the AFM images of the P3HT:ThCBM blend films cast from three solvents with different boiling points:

chloroform (61 °C), 2-methyl-thiophene (113 °C), and ODCB (173 °C). As can be clearly seen in Figure 1, the fast grown film is far less structured compared to two



slowly grown films. A red shift of approximately 37 meV appears in more ordered films due to better inter chain π overlap.

The hole mobility in the various blends was determined through analysis of the space-charge limited current (SCLC) in hole-only devices (made with Pd top electrode). The hole mobility of P3HT in a blend with ThCBM turned out to be the same for the films prepared by the slow growth method from methylthio-

Figure 1. The $1x1 \mu m$ AFM height and phase images of P3HT:ThCBM blend films: fast grown spun from CHCl₃ (a), slow grown spun from methylthiophene (with the schematic representation for the whisker formation) (b), and slow grown spun from ODCB (c). The AFM images were thickness invariant.

phene and ODCB solution, and amounts to $\mu_h = 2 \times 10^{-7} \text{ m}^2/\text{Vs}$. For the fast dried and thermally annealed P3HT:ThCBM blend films, the hole mobility of P3HT phase was $2 \times 10^{-8} \text{ m}^2/\text{Vs}$. Hence, applying slow drying, the hole mobility in the P3HT phase increases one order of magnitude with respect to the thermally annealed films, and it is in perfect balance with the electron mobility.

The best device prepared by a fast drying procedure had a power conversion efficiency $\eta = (3.1\pm0.2)$ %, $J_{sc} = 90.8 \text{ A/m}^2$, $V_{oc} = 0.59 \text{ V}$, and a filll factor FF = 59.3%. For the slowly dried films the best performance is obtained using an ODCB solution; with values of $\eta = (3.5\pm0.3)$ %, $J_{sc} = 99.5 \text{ A/m}^2$, $V_{oc} = 0.55 \text{ V}$ and FF = 63%. The best device prepared from 2-methylthiophene showed a similar η of (3.4 ± 0.2) %.

<u>References</u>

1. F. Padinger, R. S. Rittberger, N. S. Sariciftci, Adv. Funct. Mater. 13, 85 (2003).

- 2. V. D. Mihailetchi, H. Xie, B. de Boer, L. J. A. Koster, P. W. M. Blom, Adv. Funct. Mater. 16, 699 (2006).
- 3. W. Ma, C. Yang, X. Gong, K. Lee, A. J. Heeger, Adv. Funct. Mater. 15, 1617 (2005).
- 4. X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels, R. A. J. Janssen, *NanoLett.* 5, 579 (2005).
- 5. D. Chirvase, J. Parisi, J.C. Hummelen, V. Dyakonov, Nanotechnology 15, 1317 (2004)
- 6. A. Swinnen, I. Haeldermans, M. vande Ven, J. D'Haen, G. Vanhoyland, S. Aresu, M. D'Olieslaeger, J. Manca, *Adv. Funct. Mat.* **16**, 760 (2006)

8. J. Huang, G. Li, Y. Yang, Appl. Phys. Lett. 87, 112105 (2005)

9. V. D. Mihailetchi, H. Xie, B. de Boer, L. M. Popescu, J. C. Hummelen, P. W. M. Blom, L.J. A. Koster, *Appl. Phys. Lett.* **89**, 012107 (2006)

10. V. Shrotriya, Y. Yao, G. Li, Y.Yang, Appl. Phys. Lett. 89, 063505 (2006)

11. L. M. Popescu, P. van't Hof, A. B. Sieval, H. T. Jonkman, J. C. Hummelen, Appl. Phys. Lett. 89, 213507 (2006).

^{7.} G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nature Mater.* 4, 864 (2005).

Novel Approaches to an Efficient Organic Photovoltaic Solar Cell using the concept of exciton path in Bacterial Photosynthesis

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Introduction

The power conversion efficiency of the bulk hetero-junction (BHJ) polymer solar cell has been increased markedly in the last few years and achieved up to $4 \sim 5\%$ and is attractive because of its advantages: lightweight, low cost, wide application, and environmental suitability. Our group has investigated independently the BHJ solar cell to give the power conversion up to 4.05% and a very high fill factor (0.70) by insertion of the amorphous TiO₂ prepared by sol-gel process as a buffer layer. The TiO₂ layer fabricated easily without a vacuum process or a high-temperature treatment is expected to work as an efficient hole and exciton-blocking layer. Furthermore, TiO₂ between the active layer and Al electrode markedly improved the stability of polymer solar cell because TiO₂ layer is expected to inhibit the reaction between the active layer and Al electrode, resulting in high durability (only 6% loss of photocurrent under 100 hr irradiation of AM 1.5 sun) under atmospheric air without sealing of the device. This finding will make history of organic photovoltaic cell (OPV) for practical use. However, "exciton bottleneck" is an important problem together with charge-recoupling of electron and hole to be solved for supplying highly efficient OPV.

Bacterial photosynthesis system fulfills these key points enable novel approaches to an efficient OPV. It has an elegant light-harvesting apparatus as an antenna system and an efficient photo-electric conversion apparatus as a reaction center, suggesting a concept of separated pathway of electron from exciton. Introduction of bacteriochlorophyll (BChl) *e* naro-rod aggregates prepared from *Chlrobium phaeobacteroides* as an exciton pathway shown in Fig. 1 into the BHJ layer of a regio-regular poly(3-hexylthiophene) (P3HT) and PCBM sandwich cell resulted in a remarkable improvement of photo-electric conversion efficiency up to 2 times.



Fig. 1. Structure of chlorosome in green sulfur bacterium and BChl *e* nano-rod **Results and Discussion**

Treatment of acetone vapor of the BChl *e* solid film prepared on the PEDOT:PSS coated ITO promoted the further aggregation to form a nano-rod aggregates absorbing at 720 nm (red line) as shown in Fig. 2.



Fig. 2. Absorption (left: red line) and IPCE (right: blue line) spectra of BChl *e* solid films before and after acetone vapor treatment. The structure of cell: ITO/PEDOT:PSS/BChl e/Al.

The nano-rod structures of BChl *e* aggregates was confirmed by SEM pictures (data not shown). BChl *e* nano-rod aggregates might work as light-harvesting antenna in chlorosomes of *Chlorobium phaeobacteroides* as shown in Fig. 1. And also BChl *e* nano-rod aggregates might work as photoactive layer of the OPV cell from the IPCE spectra for ITO/PEDOT:PSS/BChl e/Al as shown in Fig. 2 and enhancement of the efficiencies for the bulk hetero-junction solar cell, ITO/PEDOT:PSS/P3HT:PCBM:BChl-*e*/Al, as shown in Fig. 3. Acetone vapor treatment induced not only transformation of BChl *e* to higher aggregates but also crystallization of P3HT polymer to higher crystalline states, and both effects improved markedly the OPV cell efficiencies.



Fig. 3. Effect of acetone vapor treatment on the efficiency of the bulkhetero-junction OPV cell, ITO/PEDOT:PSS/P3HT:PCBM:BChl-*e*/Al, introduced by BChl *e* nano-rod aggregates.

Optical Simulation of the Light Distribution in Organic Bulk-Heterojunction Solar Cells with ZnO:AI Transport Layer

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Organic solar cells based on a polymer-fullerene bulk-heterojunction typically consist of a stack of different semiconducting thin films of with individual thickness in the range of a few 100 nm. The device is capped with a metal electrode back reflecting the incident light into the absorber, *Fig. 1 (a)*. Hence, the attenuation of the light intensity in this kind of device is not of Lambert-Beer-type as the electric field must vanish at the metal electrode, *Fig. 1(b)*, and part of the absorber layer remains unused for exciton and charge carrier generation. The generation profile within the active layer is thus rather dominated by superposition of interfering electric fields of incident and reflected photons, thus creating a position dependent generation profile $G \sim |E \cdot E^*|$ within the absorber, *Fig. 1(b)*. Accordingly, the relative variation of the thickness of individual layers shifts the distribution and directly modifies the generation profile within the active layer.



Fig. 1: (a) Conventional architecture of a bulk-heterojunction photovoltaic device with 80nm thick absorber. (b) Light intensity distribution for various wavelengths due to internal reflection at the metal electrode (right).

To investigate the effect of thin film interference and to derive the optimal configuration of the device, we performed an analysis based on the transfer-matrix formalism. With knowledge of the complex index of refraction and thickness L of individual layers one calculates the interference pattern of the incident light for each wavelength. It is shown that the integral photocurrent becomes highest for two particular thicknesses (*L=80nm, 230nm*) of the absorber film, whereas it is reduced from its maximum value for other values of L due to a positional mismatch of the integral intensity distribution. *Fig. 2* depicts the variation of the photocurrent in a conventional BHJ device as function of the absorber thickness. The two local maxima reflect the presence of thin film interference in the device resulting in the best superposition of incident and reflected light waves for *L=80nm, 230nm*. For higher absorber thickness the relevance of interference effects becomes less important and the absorption becomes Lambert-Beer-type.

To overcome the optical losses due to thin film interference the concept of the optical spacer (OS) has been suggested in the literature (A.J. Heeger et al., Adv. Mat., **18**, 572, 2006). The OS is an n-type wide gap semiconductor, e.g. titania or titanium dioxide (TiO_X , TiO_2), introduced as a transparent transport



Fig. 2: Calculated photocurrent (100 mW/cm², AM1.5G) as function of the thickness of the light absorber of a conventional bulk-heterojunction device as depicted in Fig. 1(a).

layer between the absorber film and the metal electrode, thus redistributing the light propagation within the absorber. The thin film accounts for a high optical transmission in the visible range of the solar spectrum and provides good electron transport from the fullerene acceptor to the metal cathode. Introducing such material expands the intensity profile over a larger distance and, if properly adjusted. centres the maximum of the generation profile in the absorber layer. Based on the concept of the optical spacer we have synthesized aluminium doped zinc-oxide nanoparticles (ZnO:Al) which can be processed from solution to give a transparent n-type semiconductor film which acts as an optical spacer. The advantage of this approach is that the material can be derived and processed without residual organic contaminants as compared to sol-gel precursors like TiOx. Characterization of the ZnO:Al films yielded a high optical transmission (T>90%) in the relevant spectral range and sufficiently high conductivity (σ ~10⁻³ S/cm). The ZnO:AI is processed via spin coating from alcoholic suspension giving highly conductive and resistive coatings. To fine tune the relative thicknesses of the active layer and the optical spacer we have performed optical simulations on basis of experimentally determined dielectric function of all functional materials in the cell. We present first experimental results on solar cells with an ZnO:Al optical spacer and discuss the effect of the functional layer by simulation of the light propagation through the cell. The optimal thickness of the spacer was calculated for given absorber thickness to achieve the highest photocurrent. Improvement on the device performance by incorporation of OS can only be achieved for specified thickness of the absorber. In contrast to results reported in the literature our simulations demonstrate that the highest gain in photocurrent achieved by means of the OS is less than 20%, Fig. 3. Further improvements in the device efficiency might arise from an enhanced selectivity of the cathode.



Fig. 3: Optimal thickness of the optical spacer for a given absorber thickness calculated to give the highest photocurrent (blue circles). The red curve shows the relative gain (right axis) in photocurrent with respect to the absorber thickness for a device without optical spacer.

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Can MEH-PPV be photostable in a donor-acceptor blend?

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A major drawback of organic solar cells is their fast photodegradation. Photooxidation of the working layer gives one of the main contributions to degradation of polymer/fullerene solar cells [1]. On the other hand, the photooxidation rate of a soluble PPV derivative in the donor-acceptor blend with fullerene in oxygen atmosphere decreases by an order of magnitude as compared with the pristine polymer [2]. We have found that the photooxidation rate of a prototype conjugated polymer, MEH-PPV, in an appropriate donoracceptor blend can be dramatically reduced as compared with the polymer/fullerene blends. As electronic acceptors we used 2,4,7-trinitrofluorenone (TNF) or 1,5-dinitroantraguinone. We recorded evolution of IR spectra of MEH-PPV/acceptor films under green laser irradiation with intensity up to 330 mW/cm² and observed monotonic decreasing the photooxidation rate with increasing the acceptor content. For 1:0.4 MEH-PPV/TNF blend we did not observed any change in the MEH-PPV characteristic bands during 6 hours of irradiation. The photoluminescence intensity and photooxidation rate in the MEH-PPV/acceptor blends as functions of the acceptor content were correlated implying that triplet excitons are a key intermediate of photooxidation in these blends. We discuss possible photooxidation mechanisms in blends of MEH-PPV with TNF, DNAQ, fullerenes and the means of their reduction.

- 1. K. Norrman and F.C. Krebs, Sol. Energy Mater. Sol. Cells. 90, 213 (2006).
- 2. H. Neugebauer, C. Brabec, J.C. Hummelen, and N.S. Sariciftci, Sol. Energy Mater. Sol. Cells. **61**, 35 (2000).

Organic Tandem Solar Cells

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Supra-hierarchical Nano-structured Organic Solar Cells

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Polymer solar cells are attracted all over the world because of its low cost and easy process in fabricating solar cells. Recently, intensive research on organic thin film solar cells have been devoted to improve the efficiency and to understand its mechanisms. The power conversion efficiency has been increased to $4\sim5\%$ under A.M. 1.5 [1-4]. These high efficiencies have been achieved by bulk-heterojunction structure, which is contained micro-separated p-type semiconductor (polymer) and n-type semiconductor (fullerene) in order to compensate for the small depletion area of organic materials. Bulk-heterojunction structure is formed by only mixed p-type and n-type semiconductor in solvent and coated its solution on substrates. Therefore the fabrication process is very easy and its cost is very low. To improve the efficiency and stability of polymer solar cells, we have developed a new hole blocking layer of titanium oxide, and also a new method to optimize the morphology of the active layer (P3HT:PCBM) using mixed solvent system. Additionally, TiO_x layer between active layer and Al electrode may prevent the degradation of polymer solar cells. The main reasons for degradation of photocurrent are the reaction between the conjugated polymer and the Al electrode, diffusion of the Al from the electrode into the active layer, and oxidation by oxygen in air.

For organic solar cell fabrication, commercial indium-tin oxide (ITO) on glass substrates ($5\Omega/cm^2$) were used. The substrates were sonicated with purified water, acetone, and ethanol, respectively. After drying, the substrates were spin-coated with poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) at 3000 rpm. Active layer of the blended P3HT:PCBM in chlorobenzene was spincoated at 2000 rpm. The active layer was immediately annealed at 140°C for 4 min. The TiO_x layer was prepared by spincoating titanium(IV)isopropoxide solution in ethanol at 2000 rpm. The titanium(IV) isopropoxide was hydrolyzed from moisture in air and changed to TiO_x. The film thickness was investigated by using Tencor Alpha-step Profiler. The thickness of TiO_x layer was controlled by varing the concentration of Ti alkoxide solution. The Al layer (100 nm) was finally deposited by thermal evaporation in vacuum (5×10^{-3} Pa).Photocurrent-voltage characteristics were measured by using CEP-2000 (Bunkoh-Keiki Co. Ltd.) in the ambient atmospheric at room temperature under simulated solar light, AM1.5, 100mW/cm².

Generally, polymer solar cells without hole blocking layer have been used. However, it is well known that if Fermi level of a metal is higher than that of p-type semiconductor, Schottky barrier is formed between semiconductor and metal. This barrier could prevent holes in p-type semiconductor from transporting into a metal electrode. Fig. 1 shows I-V curve of the Au/P3HT/Al cell measured under illumination of light and dark condition. The efficiency of attained 0.0002% with Isc of 0.00143 mA/cm², Voc of 0.58 V, and FF of 0.22. In dark condition, the high rectification was obtained due to the effect of Schottky barrier between Al and P3HT. However, the rectification turned to be less and the reverse current increases under the illumination of light. This behavior may be explained by the reason that holes are activated by illumination and more holes can leap the Schottky barrier. This result indicated that the hole blocking barrier formed by Schottky barrier between Al and P3HT is insufficient and hole blocking layer is needed to improve the cell performance.



Fig. 2(a) shows the influence of the thickness of TiO_x layer on the efficiency of solar cells. The efficiency of cells without TiO_x layer is in the range from 1.4 to 2.0%. The efficiency for the cell with TiO_x layer of 5-11 nm showed the maximum value, approximately 4%. More thick TiO_x layers led to a lower efficiency, for the r eason of increase in series resistance. Fig. 4(b), (c) and (d) show the effects of the thickness of TiO_x layer on Voc, Isc, and FF, respectively. V_{oc} and FF increased dramatically from 0.4 V to 0.6 V and from 0.5 to 0.7, respectively, whereas Isc increased only a little.

Fig.3 shows the stability of the polymer solar cell with TiO_x layer of 7 nm and without TiO_x layer. The transverse axis is the time of illuminated sunlight at AM 1.5 (the light intensity 100 mW/cm²) on the device without sealing under the ambient atmosphere. The vertical axis is the normalized short-circuit current density under illumination. Isc of the device with TiO_x decreases to only 0.94 in 100 hour, whereas Isc of the device without TiO_x decreases to approximately 0. Fig.4 shows the UV-Vis absorption spectrum of glass/P3HT:PCBM and glass/P3HT:PCBM/TiO_x as soon as fabrication and after 150 h of illumination of simulated sun light. Absorbance of glass/P3HT:PCBM/TiO_x at wavelength 500 nm was decreased to 0.25 whereas absorbance of

P3HT of glass/P3HT:PCBM decrease to smaller than 0.1. The mechanism of this photo-bleaching may be the oxidation of active layers by oxygen in air and photo-degradation. From Fig. 4, the results indicated that only TiO_x cannot block all oxygen in air. These can be implied that the thin TiO_x layer plays an important role to prevent reaction of active layer with Al and diffusion of the Al into the active layer. Therefore, Al layer prevents the incursion of oxygen in air into active layer.



Fig.2 (a) The efficiency , (b) FF, (c) Voc, and (d) Isc of the photovoltaic device with several thickness of TiO_x layer.





Fig.3 Normalized short-circuit current density of the device with (closed circle) and without (open circle) TiO_x layer v.s. time of illuminating the A.M. 1.5, 100 mW/cm² simulated sun light.

Fig.4 UV-Vis spectrum of glass/P3HT:PCBM as soon as fabrication (thin grey line : a) and after illuminated for 150 h (thick grey line : b) and glass/PCHT:PCBM/TiOx as soon as fabrication (thin black line) and after illuminated for 150 h (thick black line : d).

In summary, we achieved 4% conversion efficiency together with high durability under ambient air by inserting thin TiO_x layer between the active layer and Al electrode. TiO_x layer serves as hole blocking layer and also prevents the contact between Al and the active layer. This technique will come to play an important role in the practical application of the polymer solar cells.

REFERENCES

- Li G., Shrotriya V., Huang J., Yao Y., Mariarty T., Emery K. and Yang Y. (2005) High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends, *Nature Materials*, 4, (11), pp. 864-868.
- [2] Reyes-Reyes M., Kim K. and Carroll D.L. (2005) High-efficiency photovoltaic devices based on annealed poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C61 blends, J. Appl. Phys. Lett., 87, (8), pp. 1-3.
- [3] Ma W., Yang C., Gong X., Lee K. and Heeger A.J. (2005) Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, *Adv. Funct. Mater.*, 15, (10), pp. 1617-1622.
- [4] Padinger F., Rittberger R.S., Sariciftci N.S. (2003) Effects of postproduction treatment on plastics solar cells, Adv. Funct. Mater., 13, (1), pp. 85-88.

Femtosecond Laser-induced Nanoscale Phase Transitions

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Abstract

Femtosecond laser investigations of phase separations and transitions of numerous composites are reviewed. Self-organization phenomena led to nano-sized periodic structures which can be controlled by the substrate chemistry and the condensed phase contact.

Laser Ablation basically is a phase separation process driven by laser radiation. A certain component which can attain any aggregate state such as solid films, inter-matrix phases, liquid films, particulates, are removed from a solid sub-The strate phase [1]. advantage of sub-picosecond laser pulses such as the high thermal energy localization and the possibility to tune the nonlinear absorptivity of transparent foreign phases in a wide range by the laser intensity attracted vivid attention since more than a decade [1-4]. In this context, femtosecond laser investigations of the separation and phase transitions of inorganic, organic and biological composites, films and coatings are reviewed [3-19].

The possibility to generate submicrometer structures is limited by the laser wavelength in the far field. Self-organization phenomena triggered by sub-picosecond laser treatments, however, led to interesting nano-sized periodic structures which could be manipulated by the substrate chemistry [11,12] and the liquid containment [13-15].



Fig. 1 fs-Laser-induced phase separation of a TiN film from silicon. 150 fs, 800 nm, F = 3.0 J/cm², circular polarization. Increasing laser pulse number (a) N = 50; (b) N = 80; (c) N = 100; (d) N = 200. [16]

High precision of ablation can be normally reached in homogeneous phases as e.g. in the bulk of a TiN layer (Fig. 1a). Average ablation rates below 10 nm per pulse can be achieved. However, complications arise in the case of silicon as a substrate. Once the coating layer to be separated has been perforated, silicon cannot be ablated efficiently and columns of redeposited and converted material (mainly SiO_x) are formed (Fig. 1b-d) [16].

Fig. 2 fs-laser-treated TiN.



(a) $F = 3.8 \text{ J/cm}^2$, N = 10, 130 fs.(b) $F = 0.3 \text{ J/cm}^2$, N = 100, 130 fs [17]

Femtosecond laser irradiation in the multi-pulse regime of various compound ceramic materials led to periodic nanostructures [11-15]. A cavity on aluminium nitride generated by N = 100pulses with a fluence of $F = 3.8 \text{ J/cm}^2$, well above the ablation threshold, $F_{\rm th} = 0.5 \, \text{J/cm}^2$, showed ripples perpendicularly oriented to the field vector (Fig. 2a [17]). Two periodicities could be discriminated: above the threshold, at 3.8 J/cm², grooves (ripples) with lengths of few µm's and a period of 590 nm are formed. Near the threshold, at 0.3 J/cm², however, a new type of ripples with a period around 170 nm much less than the laser wavelength occurs. This observation indicates a correlation between the order of periodicity and the laser fluence. Actually, only these two types of structures were observed: no transient index gratings were created as a result of the intensity variation.

Phase separations by laser ablation can be accompanied by chemical and morphological surface conversions. They may be attractive for surface technological and nanotechnological purposes. The remaining roughnesses are self-assembled being not only detrimental to micromachining applications but also opening a range of nanotechnological applications.

A ripple type with periodicities <200 nm could be generated near the ablation threshold of TiN but also of SiC and Si in air contact. This phenomenon can be correlated with surface energy changes triggered by femtosecond-laser-induced non-ther-

mal melting processes on the 100fs scale. A clear dependence on the chemical composition of the bulk and/or the conversion layer could be detected [11,12,14,15]. Materials with high surface energy exhibit a strong tendency to relax to the nano-ripples. At higher fluences, these chemical differences were masked and classical ripples with periodicities approaching the laser wavelength (800 nm) occurred.

Bonding of foreign ligands e.g. in a surface conversion reaction like oxidation of the TiC or TiB_2 grains or a ligand addition/exchange to the surface atoms in fluid contact may affect this mechanism drastically. Water contact reduces the surface energy practically independent of the nature of the solid and releases the need of surface rearrangement so that no self-assembled regular nano-ripples occur at threshold fluences.

In contrast, wavelength-sized ripples were detected on polyimide for linear polarization. The application of circularly polarized light led to a cone-like pattern also with a period equal to the wavelength and topped with nano-sized (100 nm) craters. Again, this self-organization depended strongly on the chemical composition, i.e. on the glass temperature, of the respective polymer [19].



Fig. 4 fs-laser-treated polyimide. Circular polarization, $F = 1.3 \text{ J/cm}^2$, N = 50, 150 fs [18]

Further systematic studies of these phenomena are under way in the author's laboratory.

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References

- D. Bäuerle, Laser Processing and Chemistry, Third Edition, Springer-Verlag, Berlin, Heidelberg, New York 2000.
- 2) S. Küper, M. Stuke, Appl. Phys. B 44 (1987) 199.
- 3) W. Kautek and J. Krüger, SPIE Proceedings 2207 (1994) 600.
- 4) J. Krüger and W. Kautek, Laser Physics 9 (1999) 30.
- W. Kautek, J. Krüger, M. Lenzner, S. Sartania, C. Spielmann, and F. Krausz, Appl. Phys. Lett. 69 (1996) 3146.
- T. von Woedtke, P. Abel, J. Krüger, W. Kautek, Sens. Actuators B 42 (1997) 151.
- 7) J. Bonse, S. Baudach, J. Krüger, W. Kautek, SPIE Proceedings 4065 (2000) 161.
- 8) S. Baudach, J. Krüger, W. Kautek, The Review of Laser Engineering 29 (2001) 705.
- G. Daminelli, P. Meja, A. Cortona, J. Krüger, M. Autric, W. Kautek, SPIE Proceedings 4760 (2002) 239.
- J. Krüger and W. Kautek, in "Advances in Polymer Science", Vol. 168, "Polymers and Light". Ed. Thomas Lippert, Springer-Verlag Berlin Heidelberg, 2004, p. 247.
- P. Rudolph, K.-W. Brzezinka, R. Wäsche, W. Kautek, Appl. Surf. Sci. 208-209 (2003) 285.
- 12) P. Rudolph, W. Kautek, Thin Solid Films 453-454 (2004) 537.
- 13) G. Daminelli, J. Krüger, W. Kautek, Thin Solid Films, 467 (2004) 334.
- 14) W. Kautek, P. Rudolph, G. Daminelli, A. Hertwig, S. Martin, J. Bonse, J. Krüger, SPIE Proceedings 5448, 213.
- W. Kautek, P. Rudolph, G. Daminelli, J. Krüger, Appl. Phys. A 81 (2005) 65.
- 16) J. Bonse, M. Geuß, S. Baudach, H. Sturm, W. Kautek: Appl. Phys. A 69 399 (1999) 399.
- 17) J. Bonse, H. Sturm, D. Schmidt, W. Kautek: Appl. Phys. A **71** (2000) 657.
- 18) S. Baudach, J. Bonse, and W. Kautek, Appl. Phys. A 69 (1999) S395.
- 19) W. Kautek, in "Laser Ablation and its Applications", Ed. C. Phipps, Springer Series in Optical Sciences, Norwell, Mass. USA 2007. 215-229..

Ultrafast interfacial carrier dynamics

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Charge carrier dynamics at interfaces is of fundamental interest for a broad range of applications such as photovoltaics and optoelectronics. The interface between different materials can behave as a charge separating boundary but also control the recombination of electron-hole pairs. The impact on the specific application can be completely contrastive and interfacial engineering is often necessary to develop the materials towards their typical designation. Femtosecond real time measurements provide relevant information of the ultrafast processes occurring at interfaces in inorganic or organic compounds and help to enhance the performance of the specific interface when incorporated into a functional device.

ZnO is a promising semiconductor material intended for use as a charge transport electrode in low-cost nano-composite solar cells and may eventually replace the widely used colloidal TiO_2 in such devices in the future [1]. Electrodes can be perpared as μ m thick films consisting of ordered crystalline ZnO nanorods [2] with a mean diameter much larger than their colloidal counterparts and thus allowing for a cross-sectional potential field gradient [3]. This and also the absence of grain boundaries in nanorod layers is expected to improve the carrier transport properties in comparison to colloidal semiconductor films. However, ZnO based solar cells have not yet met the long-standing efficiency values obtained with dye sensitized solar cells on the basis of TiO₂. Charge separation at the heterogeneous dye/ZnO interface is still poorly understood and interfacial carrier dynamics at TiO₂ and ZnO nmstructured electrodes differ considerably in the femtosecond time window (Fig. 1,2). Perylene was used as a model sensitizer chromophore adsorbed to the semiconductor surface via a propionic or acrylic acid group where the latter acts as a spacer/binding group. Fs transient absorption (fs-TA, Fig. 1) and time-resolved two-photon photoemission (TR-2PPE) (Fig. 2) spectroscopy was applied for monitoring interfacial charge transfer using 20 fs laser pulses supplied by novel type low power NOPAs operating at 150KHz repetition rate.



Fig. 1: Transient absorption (perylene cation absorption) of sensitized colloidal electrodes



The two methods represent complementary experimental tools for comparative studies of the different semiconductor/dye systems. TR-2PPE addresses surface reactions with energy selectivity whereas fs-TA can be tuned to probe a specific fingerprint of the electron transfer reaction such as the cationic state or injected electron intraband absorption. First experimental results suggest that the interfacial dynamics are controlled by the nature of the molecular species on the TiO₂ electrode and by the semiconductor surface properties for ZnO electrodes (Fig. 3).



Fig. 3 Comparison (perylene cation transient absorption) of colloidal and nanorod electrodes

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References

- [1] Law, M., Greene, L. E., Johnson, J. C., Saykally, R., Yang, P. Nat. Mater. 4, 455 (2005)
- [2] Yamabi, S., Imai, H. J. Mater. Chem. 12, 3773 (2002)
- [3] Galoppini, E., Rochford, J., Chen, H., Saraf, G., Lu, Y., Hagfeldt, A., Boschloo, G. J. Phys. Chem. B, 110 (33), 16159 (2006)

Ultrafast Interfacial Carrier Dynamics in UV-Blue Photoluminescing ZnSe Nanoparticles

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The charge carrier dynamics in semiconductor nanocrystals (NCs) has attracted much interest during the last years [1,2]. The dynamics of carrier cooling in semiconductors is an extremely important factor for many applications such as molecular electronics, quantum dot lasers and solar energy conversion ([3] and references therein). When the size of the semiconductor particle is small in comparison with the Bohr radius of the bulk exciton, the electronic energies of nanoparticles or quantum dots (QDs) become size and shape dependent. As a result QDs have atomic-like discrete energy spectra and higher exciton energies. Because of a large energy spacing and an enhanced surface-to-volume ratio, the carrier dynamics are significantly different from those in bulk materials [1].

The post-preparative irradiation of the water soluble thiol-stabilized ZnSe colloidal nanocrystals (2-3 nm in size) leads to a strong increase of the photoluminescence quantum yield of UV-blue emission. The changes of the photoluminescence properties of the colloidal samples have been explained by changing in particle composition, size, and crystal structure accompanying the irradiation treatment [4].

Recently, we carried out a femtosecond transient absorbance study of relaxation dynamics of these ZnSe NCs samples [5]. Fig.1 shows the changes in the absorption and PL spectra of the ZnSe QDs during "white light" illumination: before irradiation (solid lines) and after 150 min of irradiation (dashed lines).



Fig. 1. (left) Changes in the absorption and PL properties during post-preparative treatment. Excitation wavelength for the emission measurements was λ_{exc} =342nm. Inset: Magnified PL spectra of the sample before irradiation. Fig. 2. (right) Transient absorbance change for untreated ZnSe NCs. Signal amplitudes are color coded: red indicates positive, green zero and blue indicates negative absorbance changes. The scale is linear for $\tau < 1$ ps and logarithmic for longer delay times.

The absorption spectra of the obtained ZnSe QDs exhibit a shoulder in the region of 325-400nm, which is assigned to the transition to the first exciton state. The absorption edge of NCs are shifting to the red spectral region during post-preparative phototreatment. Since the NCs are in the regime of size – confinement, we can conclude that the colloidal particles grow under irradiation. Two bands of PL are observed for the samples under investigation. The narrow emission band, which is close to the first exciton absorption peak has been ascribed to the band-edge emission, while the broad band in the spectral region 400-600 nm can be assigned to the recombination of trapped charge carriers. The red shift of the exciton absorption band and drastic increase of the band-edge emission can be explained by formation of ZnS passivating shell upon post-preparative treatment.

The time-resolved transient absorbance spectra mainly reflect the formation and decay of the optical transient bleaching in the region of the lowest exciton transition (region of the spectrum marked with the letter (**a**) in Fig. 2). The broad featureless positive absorption change in the region from 390 nm to 680 nm (marked with (**b**) in Fig. 2) most likely has contributions from band edge carriers, trapped carriers and solvated carriers [6].

In order to directly assign observed dynamics to the electron or to the hole relaxation processes and study effect of the passivation shell on charge carrier dynamics we used MV^{2+} , which is well known as a very effective electron acceptor [7]. Upon mixing of the NC sample with MV^{2+} the PL of the NCs has been quenched completely. The quenching of the PL of the NCs/ MV^{2+} system can be explained by very effective and fast electron transfer from the conduction band of the semiconductor NCs to MV^{2+} . Figs. 3 and 4 show the results of the transient absorbance experiments for the unpassivated and passivated ZnSe/ MV^{2+} systems respectively.



Fig. 3. (left) and Fig. 4 (right) Transient absorbance change for unpassivated (left) and passivated (right) ZnSe NCs with electron quencher MV²⁺.

The presence of the electron acceptor MV^{2+} leads to reduction in the relaxation time of the excitonic transition bleach of ZnSe NCs samples, also a new absorption bands with maxima at 400 nm and 600 nm are observed. These bands correspond to the absorption bands of the MV^{++} radical. From the comparison of the experimental results for different ZnSe NCs samples it can be seen that the ET rate is increased for the colloidal samples after the post preparative treatment (compare Figs. 3 and 4). Indeed, the interfacial ET time of 640 fs and 2.6 ps for the "bare" ZnSe and ZnSe(ZnS) core (shell) samples mixed with MV^{2+} have been obtained from a global fit analysis. Interestingly, the residual signal in the region of the excitonic bleach remains at long delay time for the ZnSe(ZnS)/ MV^{2+} system (see Fig. 4), while it has not been observed in the case of "bare" ZnSe(ZnS) core (shell) NPs, which leads to the slower relaxation dynamics. Finally, the detailed analysis on relaxation kinetics of the charge carriers in the ZnSe QDs and the influence of the ZnS passivating shell on the interfacial electron transfer will be presented.

Acknowledgements

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6. References

- [1] V.I. Klimov, J. Phys. Chem. B **104**, 6112-6123 (2000).
- [2] C. Burda, X.B. Chen, R. Narayanan, M.A. El-Sayed, Chemical Reviews **105**, 1025-1102 (2005).
- [3] A.J. Nozik, Annu. Rev. Phys. Chem. **52**, 193-231 (2001).
- [4] A. Shavel, N. Gaponik, A. Eychmuller, J. Phys. Chem. B 108, 5905-5908 (2004).
- [5] V.V. Matylitsky, M.O. Lenz, J. Wachtveitl, A. Shavel, N. Gaponik, A. Eychmüller, in Ultrafast Phenomena XV, Springer, Berlin / Heidelberg / New York (2006).
- [6] T.W. Roberti, N.J. Cherepy, J.Z. Zhang, J. Chem. Phys. 108, 2143-2151 (1998).
- [7] T. Watanabe, K. Honda, J. Phys. Chem. **86**, 2617-2619 (1982).

Confocal Photoluminescence and focused Optical Transmission for the Identification of Spatial Inhomogeneities in Polycrystalline Cu(In,Ga)Se₂

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Inhomogeneities of Cu($In_{1-x}Ga_x$)Se₂ are analyzed by confocal room temperature photoluminescence and by confocal optical transmission with sub-/one-µm lateral resolution. According to Planck's generalized law for the emission of radiation from matter we deduce

i) the laterally resolved chemical potential of the electron hole ensemble (splitting of

quasi-Fermi levels) and the respective spectral absorptivity/emissivity, as well as ii) the laterally resolved spectral optical transmission which, of course, can be translated into spectral absorptivity, too.

In particular for the alloy (Ga-admixture) with x = 0.3 we observe local fluctuations of Fermi-Level splitting (ϵ_{Fn} - ϵ_{Fp}) corresponding to \approx 50 meV for 300K and AM1-equivalent photon fluxes which contribute to additional entropic terms in the process of quantum solar energy conversion.

We visualize lateral patterns of pl-yield, of quasi-Fermi level splitting and of optical threshold energies for absorption via 2D-scans, their 2D Fourier transforms, and Minkowski opening functions.

In addition, lateral fluctuations of optical threshold energies (equivalent to optical band gaps ϵ_g) in the range of (20-30)meV have been detected and were correlated in the particular local regimes with (ϵ_{Fn} - ϵ_{Fp}) (correlation coefficient of lateral variation of optical threshold energy with lateral variation of splitting of quasi-Fermi levels is + (0.5-0.6)). We furthermore observe lateral fluctuations of local short circuit currents which are explained in terms of lateral gradients of the chemical potential of minorities.



Figures 1,2: Confocally recorded PL-yield from a $Cu(In_{0.70} Ga_{0.30})Se_2$ absorber (I.h.s.), and local fluctuations of quasi-Fermi-level splitting (r.h.s., a), and of speed of minority carrier extraction across the heterojunction (Mo / Cu(InGa)Se₂ / CdS / ZnO) (r.h.s., b; after L. Gütay et al. 2006)


Figure3: Local scan of PL-yield in $Cu(In_{0.7}Ga_{0.3})Se_2$ and according spectral distribution of a line scan (spot 1)(after L. Gütay et al. 2006).



Figure 4a,b: Lateral variation of local quasi-Fermi level splitting $\Delta(\epsilon_{Fn}-\epsilon_{Fp})$ in a Cu(In_{0.7}Ga_{0.3})Se₂ absorber from spectrally resolved confocal luminescence (upper part) and according histogram of quasi-Fermi level splitting $\Delta(\epsilon_{Fn}-\epsilon_{Fp})$ (lower part).

Figure 5 : Lateral spectral transmission of a $Cu(In_{0.7}Ga_{0.3})Se_2$ absorber from focused transmission / absorption / reflexion analyses with sub-micron resolution

Thin Film Solar Cells: Nucleation Control and Growth Morphology

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Thin film solar cells are strongly influenced by inhomogeneities. The known effects related to grain boundary behaviour will be shortly summarized and discussed with respect to possible electronic effects which is of importance for the solar cell performance. As an experimental example the properties of CdTe solar cells will be presented.

CdTe is a promising material for low cost thin film solar cells. To achieve high conversion efficiencies, the structure and morphology of the CdTe layer has to fulfil some elementary requirements such as a large lateral grain size without pinholes. Therefore a good knowledge of the involved growth mechanisms is necessary. We have systematically investigated the growth of CdTe thin films by Close Spaced Sublimation (CSS) using our dedicated system DAISY-SOL. Thin films of CdTe were deposited on CdS substrate held at temperatures in the range 270°C to 560°C. The effect of substrate temperature on structure and surface morphology of CdTe films were investigated. To show kinetic influences on film growth the vapour fluxes were varied by choosing different source temperatures. Different CdS-substrates were used to investigate the influence of the substrate on CdTe-film growth. Growth rate as a function of substrate temperature was studied. Up to 450°C the growth rate was almost constant depending only on the source temperature. For higher temperatures it is exponentially decreased to zero. Structure of CdTe films was determined by XRD and a strong (111) orientation was observed within the temperature range $270^{\circ}C - 480^{\circ}C$. Above 480°C the texture changed to a mixture of (311) and (220) orientations. Surface and crosssectional morphology of CdTe growth was determined with SEM. The morphology of the layers showed three major modes: Columnar grains with a diameter of 0.2µm and a length of $6\mu m$ for temperatures from $280^{\circ}C - 300^{\circ}C$, pyramidal grains with a diameter of $0.5 - 1.5\mu m$ up to 480°C and irregular shaped grains with a diameter of 3 - 4.5µm for temperatures up to 560°C.

CdS-substrates were deposited at different temperatures and XRD-measurements revealed temperature dependent orientation. CdTe deposited on these varying substrates showed major differences. For highly oriented CdS the CdTe was also highly oriented. For more random oriented CdS the CdTe layer exhibited substrate temperature dependent changes in structure and morphology. At intermediate temperature region a high impact of the substrate on the absorber layer has been identified.

Modifications of the CdTe-structure and morphology are observed after CdCl₂activation of the layers, which are dependent on substrate orientation as well as on CdTe deposition temperature.

The influence of growth parameters on CdTe film morphology and on cell efficiency will be discussed. It turns out that grain boundary recombination or related reduced parallel resistances are one dominant loss mechanism for the solar cell performance. We will present the morphology needs for high solar cell performance using thin film materials and will address the research fields to be addresses for controlling nucleation and growth of thin film solar cell materials.



substrates. CdTe was deposited at three different source temperatures



Figure 2: SEM-pictures (surface and cross section) of exemplary samples for the three different growth modes (first growth mode: picture *a*) and *b*), second growth mode: picture *c*) and d), third growth mode: e) and f))

Analysis of the Chemical and Electronic Structure at the Solid-Liquid Interface of Dye Sensitized Solar Cells with Synchrotron Induced Photoelectron Spectroscopy

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At BESSY we run the experimental station SoLiAS, dedicated to solid-liquid interface analysis. SoLiAS allows for the transfer of wet chemically prepared surfaces to the ultra high vacuum without contact to ambient air. In addition in situ (co)adsorption of volatile solvent species onto liquid nitrogen cooled samples is possible. SoLiAS proves to be very useful in analyzing the chemical and electronic structure of the solid-liquid interface of dye sensitized solar cells. Ru(N3)-dye was adsorbed from ethanol solution under clean N₂ atmosphere in an UHV-integrated electrochemical cell (EC). Acetonitrile or benzene were adsorbed from the liquid in the EC or in situ from the gas phase. Ex situ sintered nanocrystalline anatase substrates as well as in situ deposited polycrystalline TiO₂ samples were used. Distinct reversible changes occur in synchrotron induced photoelectron valence band and core level spectra when the solvent is adsorbed to pristine and dye covered TiO₂ substrates. Based on the experimental results the alignment of electronic states ^[1] and a model on the dye-solvent interaction are deduced ^[2].

The valence band maximum of nc-TiO₂ is found at $E_B = 3.6$ eV binding energy while the fundamental gap is 3.2 eV only. In the gap states are found with a maximum at $E_B = 1.3$ eV. In addition surface states just below the Fermi level are found. In the rigid band model these states are assigned to occupied conduction band states but may be due to substochiometric TiO_{2-x}. Adsorption of acetonitrile is accompanied by quenching of surface gap states related to Ti³⁺3d-orbitals (Fig. 1). This finding is confirmed in Ti2p core orbital spectra by the quenching of the Ti³⁺ low binding energy shoulder of the Ti⁴⁺ bulk emission. On nanocrystalline samples full quenching is obtained by adsorption from the liquid. By adsorption from the gap states the gap states are partially quenched. Also with adsorption of Ru(N3)-dye and coadsorption of acetonitrile the gap states are quenched (Fig. 2). Coadsorption of acetonitrile shifts the dye HOMO by 150 meV from 2.0 eV binding energy to 2.15 eV.





Fig. 1: SXPS spectra of the gap states of nanocrystalline anatase TiO_2 in the course of acetonitrile adsorption and desorption.

Fig. 2: SXPS spectra of the gap states of nanocrystalline anatase TiO_2 in the course of Ru(N3)-dye adsorption and acetonitrile coadsorption and desorption.



Fig. 3: Schematic of the photovoltaic-relevant valence states in the rigid band model a) the as prepared nanocrystalline TiO_2 anatase film, b) after dye adsorption from ethanol solution with HOMO position, c) after coadsorption of the solvent acetonitrile with the HOMO shifted by 150meV to higher E_B . Using the optical absorption maximum the LUMO is found 0.17 eV above the Fermi level.

A schematic representation of the photovoltaic-relevant valence states as deduced in the simple rigid band model is displayed in Fig.3. The measured HOMO corresponds to the position of the lowest energy hole-state created by the photoemission of an electron i.e. the HOMO of the molecular cation. Except for a Franck Condon shift of approximately 0.1 eV away from the Fermi level due to vibrational excitation in the photoemission process, this is the relevant energy position for rereduction by the redox system. For the electron injection process the alignment of the LUMO to the conduction band edge is crucial. Using the energy of the optical absorption maximum (535nm=2.32eV), the LUMO is found 0.17 eV above the Fermi level.

As expected the S2p emission of the dye NCS group is just damped when benzene is coadsorbed (Fig 4a right). In contrast the S2p emission counterintuitively sharpens upon CH_3CN coadsorption (Fig 4a left). In a simple model (Fig. 4b left) the polar solvent acetonitrile penetrates the dye layer and the interaction of the dye NCS groups with the TiO_2 surface or with neighbouring dye molecules is suppressed due to solvation. The S2p intensity development in the course of CH_3CN adsorption suggests reorientation of the dye molecules pointing the NCS groups away from the surface towards the electrolyte. On the other hand nonpolar benzene just covers the dye layer (Fig. 4b right). The solvation and orientation of the dye by acetonitrile may be important for obtaining vectorial charge transfer.



Fig. 4a: Ru(N3)-dye S2p level in the course of acetonitrile (left) and benzene (right) coadsorption and desorption.

- Fig. 4b: Cartoon of the Ru(N3)-dye/solvent interaction in the course of acetonitrile (left) and benzene (right) coadsorption and desorption.
- K. Schwanitz, U. Weiler, T. Mayer, and W. Jaegermann J.Phys.Chem. C, 111, 849-854
- [2] K. Schwanitz, E. Mankel, R. Hunger, T. Mayer, W. Jaegermann BESSY Highlights 2005

Recombination in Microcrystalline pin Solar Cells

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Microcrystalline silicon (μ c-Si:H) is a thin-film silicon morphology which is superior to conventional crystalline silicon (c-Si) with regard to material consumption and cost effectiveness. Unfortunately, state-of-the-art μ c-Si:H suffers from an inferior electronic quality compared to the crystalline counterpart. It consists of small crystalline grains with dimensions of up to a few 10 nm, which are surrounded by an amorphous silicon (a-Si:H) tissue. It is assumed that the a-Si:H tissue and the grain boundaries induce localised states in the band gap of μ c-Si:H which deteriorate the electronic properties through trapping and recombination. Due to the poor diffusion lengths, μ c-Si:H solar cells are



Figure 1: µc-Si:H solar cell (1mm x 1mm) with thin film contact structure specially designed to minimize microwave distortion.

designed in a pin arrangement rather than as a pn junction. In the pin cell a 1-2 μ m thin nominally undoped μ c-Si:H (i) layer acts as absorber. This i layer is sandwiched between p and ndoped contact layers. Since the absorber of the cell is identical with the space charge region, the high density of localised states of μ c-

Si:H will induce strong recombination that limits the solar cell performance. Efficiencies as high as 10 % have been reported for μ c-Si:H single junctions cells. However, it is unclear which type of defect through what type of recombination process limits the device performance. It is therefore of great importance to identify and, in the long run, eliminate the relevant defects.

In this lecture we will show that the coherent manipulation of the electron spin of charge carriers and defects that participate in recombination of μ c-Si:H pin solar cells can be directly observed in the photocurrent. The electron spin can be addressed selectively by means of electron spin resonance, a method that is sensitive to the local environment of the specific spin. This magnetic fingerprint of the electron spin in the macroscopic observable reveals many details of recombination not accessible by other experimental



Figure 2: (a) Current change as a function of excitation length reflecting the coherent spin motion during the resonant excitation at g = 1.9975. (b) Fast Fourier Transform spectrum of the Rabi oscillations.

techniques, such as details of the recombination mechanism and its dynamics or the distributions of coupling strengths between recombining charge carriers [1-4]. From the latter, information can be deduced about distance distributions between electrons and holes prior to recombination and their localization length. We will review the basic idea of the experiment and discuss the latest experimental results achieved on μ c-Si:H solar cells. The state-of-the-art μ c-Si:H pin solar cells were prepared on ZnO coated glass by RF-PECVD [5]. The coherent measurements were made possible through a special contact design established by laser scribing techniques (Fig. 1). Such a design strongly reduces inhomogeneities of the driving microwave field and enables the direct observation of Rabi oscillations in the photocurrent of the pin solar cell at T = 10 K (Fig. 2a). By Fourier transformation of the data it is possible to discriminate experimentally between different spin-coupling regimes of the recombining charge carriers due to their Rabi frequency, Ω (Fig. 2b). Strongly coupled spin pairs that indicate a direct capture process at deep defects



Figure 3: Microwave induced change of measured charge as a function of external magnetic field $3.5\mu s$ after a 320ns long microwave pulse. The inset shows the same spectrum for a broader range of the magnetic field which reveals an additional resonance with a line width of 20mT.

are expected at Ω = 50 MHz and weakly coupled pairs which are characteristic for a tunnelling process between shallow tail states and deep defects are expected at half that frequency [6]. In contrast to our previous results achieved on ECR-CVD grown µc-Si:H thin films [4], we find a much stronger signal originating from weakly coupled spin pairs in the measurements on µc-Si:H solar cells. In addition to the well known µc-Si:H pEDMR resonances as shown in Figure 3, we also observe a very broad resonance (insert of Fig. 3). This signal is believed to be associated with shallow band tail states of the valence band. It dynamics has the same as the resonance at g=2.0045, which is believed to be associated to a specific dangling bond defect of µc-Si:H. The results will be discussed with regard to different possible recombination and transport mechanisms in µc-Si:H pins.

- 1. C. Boehme, K. Lips, Phys. Rev. Lett., 91 (2003) 246603
- 2. A. R. Stegner, C. Boehme, H. Huebl, M. Stutzmann, K. Lips and M.S. Brandt Nature Physics 2, (2006) 835 - 838
- 3. C. Boehme, K. Lips, J. Non-Cryst. Solids, 338-340 (2004) 434
- 4. K. Lips, C. Boehme, Quantsol 2004
- 5. B. Rech, T. Roschek, T. Repmann, J. Müller, R. Schmitz, W. Appenzeller, Thin Solid Films, 427, (2003) 157
- V. Rajevac, C. Boehme, C. Michel, A. Gliesche, K. Lips, S.D. Baranovskii, and P. Thomas, Phys. Rev. B 74 (2006) 245206

Ultrafast Dressing and Coupling of Single Quantum Dot Excitons

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There has been considerable debate about the nature of the energy transfer processes in biological systems on the one hand and in man-made systems such as quantum dots on the other hand. In particular, the role of coherence and the coupling mechanisms in photosynthesis as well as in quantum dot systems remains to be clarified. Here the dipole-dipole coupling plays a central role, being an elementary interaction responsible for the structure and function of many atomic, molecular, and solid state systems. There is a very wide range of dipole-dipole interaction strengths, depending on the spatial arrangement and the microscopic interaction mechanism, such as permanent dipole couplings, van der Waals dispersion forces, or Förster dipole energy transfer.

In order to investigate such elementary coupling mechanisms we have employed a bottom-up aproach, in chosing a model system with isolated quantum dot excitons, which we manipulate coherently by ultrashort laser pulses. In particular, we use interface quantum dots (QD) formed in thickness fluctuations of a 5.1 nm (100) GaAs quantum well (QW) grown by molecular beam epitaxy between two AlAs=GaAs superlattice barriers on a (100) GaAs substrate and buried 120 nm below the surface. Differential reflectivity (Δ R/R) spectra are recorded as a function of pump-probe time delay Δ t with a spatial resolution of < 250 nm in a near-field pump-probe setup at 12 K.

By excitation with non-resonant subpicosecond pump pulses we show that the energy levels of isolated excitons can be shifted in a controlled way, a phenomenon known as optical Stark effect (OSE) in atomic physics. In this phenomenon the strong field of the exciting light couples to the excitonic states leading to modified, socalled "dressed states". Since the pump pulse is detuned from the exciton energy levels (Fig.1), this is a virtual excitation and the shifting of energy levels occurs on a time scale limited by the length of the pump pulse only. Analysis of the experiment with optical Bloch equations using a density matrix formalism for a quasi-atomic two-level system leads to very good agreement with the experimental data, showing that this Stark shift can be used to shift the phase of the coherent polarization of the quantum dot in a controlled way.



Figure 1. Optical Stark effect: The exciton transition is detected with a resonant probe pulse, during the virtual excitation by a detuned strong pump pulse.



Figure 2. The pump pulse resonenting excites quartering dot A, which we monitor by probing the biexcitonic transition of this quantum dot. A_{Bx}^{H} denotes the biexcitonic shift. The dipole dipole interaction shifts the energy levels of a neighboring quantum dot (ΔE_{DG} , which is probed signature vitaneously.

energy levels of a neighboring quantum dot (ΔE_{DQ}), which is probed simultaneously. For resonant excitation several times are able to demonstrate coherent superpositons of the single exciton states, when light pulses much shorter than the decoherence time T₂ of the excitonic transitions are used. A note that are used. A note that the pulses in Figure 2. The relevant excitonic transitions in an isolated QD can be represented by an effective four-level system, consisting of the crystal ground states 00>, two nearly degenerate single-exciton states with orthogonal polarization orientation, 10) and 01), and the biexciton state (1). Increasing the pump field leads to Rabi oscillations of the excited quantum dot, which we can detect by probing the biexcitonic resonance of this quantum dot. Moreover, monitoring the first excited state transition of a neighboring quantum dot (B) was find an energy shift of this transition which directly depends on the occupation of the exprised guantum dot (A). This shift is due to the dipole-dipole interaction between the two neighboring quantum dots. Generally, two different mechanisms can contribute to this coupling: resonant Förster energy transfer and direct Coulomb interaction between permanent excitonic dipole moments. To determine which of these two interaction mechanisms is relevant for our experiment, nonlinear-optical spectra are calculated from the time evolution of the density matrix in rotating wave approximation. The QDs are treated as two-level systems that interact with the pump and probe fields and are coupled via the dipole-dipole interaction. Most of the parameters of the calculations are guantitatively known. From the comparison of the lineshape and temporal dynamics of the ΔR spectra of the experiment with the calculations we conclude that coupling between permanent excitonic dipole moments is the dominant interaction mechanism in our experiment. The Förster coupling between the guantum dots on the other hand is weak, due to the too large distance (> 20nm) and detuning (3meV) between two neighboring guantum dots.

References:

"Space and time resolved coherent optical spectroscopy of single quantum dots", Thomas Unold, Kerstin Mueller, Christoph Lienau and Thomas Elsaesser, Semicond. Sci. Technol. 19 (2004) 260.

"Optical Stark Effect in a Quantum Dot: Ultrafast Control of Single Exciton Polarizations", Thomas Unold, Kerstin Mueller, Christoph Lienau, Thomas Elsaesser, and Andreas D. Wieck, Phys. Rev. Lett. 92 (2004) 157401.

"Optical Control of Excitons in a Pair of Quantum Dots Coupled by the Dipole-Dipole Interaction" T. Unold, K. Mueller, C. Lienau, T. Elsaesser, and A. D. Wieck, Phys. Rev. Lett. 94 (2005) 137404.

Ferromagnetic semiconductors for improved photovoltaic conversion

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Present photovoltaic devices, based on p/n junctions, are limited from first principles to maximal efficiencies of 31% (respectively 40% under full solar concentration) [1]. However, more innovative schemes may overcome the Schockley-Queisser limit since the theoretical maximal efficiency of solar energy conversion is higher than 85% [2]. To date, the only practical realisation of such an innovative scheme has been multi-junction devices, which presently hold the world record efficiency of nearly 41% at significant solar concentration [5]. It has been proposed to make use of the solar spectrum in much the same way as the multi-junction devices does but in a single cell, using impurity induced intermediate levels to create gaps of different sizes. This intermediate band semiconductor (IBSC) concept [3,4] has a maximal efficiency similar to that of multi-junction devices but suffers from prohibitively large non-radiative recombination rates.

We here propose to use a ferromagnetic impurity scheme, see Figure 1, in order to possibly reduce the non-radiative recombination rates and concurrently increase the theoretical maximum efficiency to 54% without concentration, as compared to 46% for the IBSCs. Using *ab initio* methods, the electronic and energetic properties of transition metal impurities in GaN and CuGaS₂ has been studied. For the large gap GaN, it was found that inclusion of Cr and Mn, respectively, induces bandstructures providing efficiencies potentially close to 40% with Curie temperatures reaching up to 140K. The chalcopyrite CuGaS₂ has a priori a better bandgap and it is shown that inclusions of Cr or Co on Ga respectively Cu sites gives potentially higher efficiencies, over 40%, improving slightly on GaN. The calculated Curie temperatures for the CuGaS₂ compounds are lower than for the GaN, reaching about 120K at the most. The calculations of the magnetic transition temperatures are complicated by the fact that the exchange interaction between impurity atoms is decreasing with distance and thus one configuration cannot be considered completely representative.





Neither of the two investigated compounds have optimal electronic properties but do still show significant maximal efficiencies and enables us to, at this level of approximation, refine the selection criteria for the construction of an optimal ferromagnetic photovoltaic device. The most optimal configuration is when there is an intermediate level at about one third of the total gap in one of the spin channels, while in the other spin channel the gap is somewhat closed in comparison to an unperturbed gap. This could be realized in an optimal bandgap material by inserting a transition metal element with optimised spin splitting.

References:

- [1] W. Shockley and H.J. Queisser, 1961 J. Appl. Phys. 32 510.
- [2] N.-P. Harder and P. Würfel, 2003, Semicond. Sci. Technol. 18 S151.
- [3] M. A. Green and S. R. Wenham, 1994, Appl. Phys. Lett. 65, 2907.
- [4] A. Luque and A. Martí, 1997, Phys. Rev. Lett. 78, 5014.
- [5] U.S. DOE news site: http://www.energy.gov/news/4503.htm

N-TYPE DOPING CONCEPT OF CHALCOPYRITE CuG aS e₂ WIDER-GAP MATERIAL: CHALLENGE AND LIMITS

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The development of thin film solar cells based on chalcopyrite wider-gap CuGaSe₂ and CuInS₂ material with high energy conversion efficiency has inspired research efforts towards doping techniques using extrinsic dopants. It has been found that the wider-gap members of semiconductor series such as diamond \rightarrow Si \rightarrow Ge or AlN \rightarrow GaN \rightarrow InN cannot be doped n-type at equilibrium. The difficulty to n-dope chalcopyrite CuGaSe₂ (CGS) and CuInS₂ wider-gap material is another example of the general trend, while the doping of lower-gap chalcopyrite CuInSe₂ (CIS) results into an n-type conductivity [1,2]. The highly efficient chalcopyrite based lower band gap cells are dominated by bulk rather than interface recombination losses, but the wide band gap cells such as CuInS₂ and CGS show an opposite recombination behavior over a barrier [3,4]. Concepts for the minimization of the interface recombination losses of the window - absorber heterojunction cell are doping of the absorber and window layers, electrical charge and band line-up at the interface [5]. Hence, amajor task to overcome the limited efficiency of such interface losses limited n-ZnO/n-CdS/p-CGS heterojunction cells has been to achieve the type inversion at the CGS / CdS interface. Therefore, an extrinsic ntype doping of the near surface region of the p-type CGS has become a challenge [6,7].

High-energy ion implantation of Zn, Ge or Sn ions is *one approach* of n-doping the p-type CGS semiconductor under non-equilibrium conditions. The preparation of n-type CGS material requires shifting of the Fermi level close to the conduction band gap. This can be in theory completed by introducing additional donor-like defects. Theore tical first-principles methods have been applied by Persson et al. [2] to study the doping effects in chalcopyrite CIS and CGS by divalent cationic dopants (Mg, Zn, Cd) or anion-site doping with halogens (Cl, Br, I). It has been found that the formation of intrinsic In_{Cu} double donor in CIS under Se-poor growth conditions results in net n-type doping. Due to the low formation energy of the compensating acceptor V_{Cu} , even at Cu-rich conditions, a high degree of compensation will always be present for n-type doping in CIS. Due to the fact that the formation energy of V_{Cu} becomes zero in CGS it is theoretically



found not to shift the Fermi energy towards the conduction band minimum under equilibrium conditions. So far, it has been concluded that n-type doping of CGS is impossible under equilibrium conditions, but could be possible if one prevent Cu outdiffusion at high $E_{\rm F}$ via non-equilibrium effects. Hall measurements carried out on polycrystalline CGS thin films in a wide temperature range from 25 K up to 300 K show conductivities of 0.10 up to 0.35 S/cm with charge carrier concentration of 10^{17} /cm³ up to 10^{18} /cm³ but with a very strong variation of the deduced Hall coefficient and mobility which points to a high degree of compensation of the extrinsic intrinsic donors by acceptors. The

complementary ontinuous-wave electron paramagnetic resonance (EPR) and photoluminescence (PL) spectroscopy have been used to detect the doping induced electronic structure of additional defect levels in the band gap of the CGS chalcopyrite host lattice [9]. Our recent studies on the Ge-implantation of polycrystalline CGS thin films prepared by chemical close spaced vapor transport (CCSVT) technique [9] suggest that an extra donor-acceptors-like emission at 1.47 eV appears in the near-surface doping region [7] with a new donor-like state 360 meV below the conduction band minimum (CBM). The intensity of this new Ge-related PL emission depends on the concentration of implanted Ge ions. Additionally, a new Ge-related EPR signal is observed which shows an increase with the doping concentration. It was found that only 0.3 atom% of Ge ions contributes to the EPR signal. Nevertheless, the doping-related EPR signal exhibits a Curie-like temperature dependence up to 300 K assigned to localized magnetic moments likely due to electrons trapped by donors.

The chemical equilibrium crystal growth by chemical vapor transport with some few weight percents of doping material like Ge or Sn has been used as the *second approach* of n-type doping the CGS chalcopyrite [8]. It is found that the co-growth results into ~0.1 atom% of Ge and Sn in the crystalline CGS indicating that the dopants are incorporated into the chalcopyrite host lattice either on cationic or anionic sites. EPR studies performed on the Ge- and Sn doped single crystalline CGS show novel dopant-related paramagnetic contributions of 0.3 atom% for CGS:Ge and 0.2 atom% for CGS:Sn, which are in the same order of magnitude of the 0.1 %atom doping concentration. As in the case of the polycrystalline CGS:Ge, this doping -related EPR signal shows a Curie-like temperature dependence up to 100 K of a localized defect state.

In order to obtain insights not only on the defect electronic structure of the extrinsic doping, very recent Ge K-edge X-ray absorption fine structure spectroscopy applied to poly- and single crystalline Gedoped CGS has been used as an atom specific structural probe to obtain information on the locally structural coordination of the incorporated Ge-atoms in the chalcopyrite host lattice [10].

In this contribution we will discuss and summarize our experimental results and will give some concluding explanations on the limits of the n-type doping.

References

- [1] A. Zunger, Appl. Phys. Lett. 83 (2003) 57.
- [2] C. Persson, Y.-J. Zhao, S. Lany, A. Zunger, Phys. Rev. B 72 (2005) 035211.
- [3] I. Hengel, A. Neisser, R. Klenk, M. Ch. Lux-Steiner, Thin Solid Films 361-362 (2000) 458.
- [4] M. Rusu, S. Doka, C.A. Kaufmann, N. Grigorieva, Th. Schedel-Niedrig, M. Ch. Lux-Steiner, Thin Solid Films 480-481 (2005) 341.
- [5] R. Klenk, Thin Solid Films **387** (2001) 135.
- [6] J. Krustok, J. Raudoja, J.H. Schön, Physica Status Solidi (a) 178 (2000) 805.
- [7] S. Doka, M. Rusu, A. Meeder, E. Arushanov, N. Fabre, S. Fiechter, Th. Schedel-Niedrig, M.Ch Lux-Steiner, Mater. Res. Soc. Symp. Proc. Vol. 865 (2005) F5.27.1; PhD Thesis (Freie Universität Berlin, 30.10.2006).
- [8] J. Hofstetter, Diploma Thesis (Freie Universität Berlin, 03/2006).
- [9] M. Rusu, S. Wiesner, D. Fuertes Marrón, A. Meeder, S. Doka, W. Bohne, S. Lindner, Th. Schedel-Niedrig, Ch. Giesen, M. Heuken, M. Ch. Lux-Steiner, Thin Solid Films 451-452 (2004) 556.
- [10] S. Doka, V. Koteski, H.-E. Mahnke, Th. Schedel-Niedrig, M. Ch. Lux-Steiner, in preparation.

InGaAsP/InGaAs tandem solar cells

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Recently, a III-V triple junction solar cell grown on a Ge(100) crystal has exceeded the 40% conversion efficiency barrier. Even higher values can be achieved, if more than three appropriate subcells were realized with optimized band gaps. Calculations [1] show that a band gap in the range of 1eV is highly desirable in optimized solar cells with multiple junctions. Currently, Ge(100) bottom sub-cells are employed in high-performance multi junction solar cells. Our idea of an InGaAsP-InGaAs tandem solar cell with low band gaps is to replace the bottom Ge sub-cell by a more efficient double junction bottom cell and to combine the top and bottom tandem cell by means of metamorphic growth, mechanical stacking, wafer bonding, or separation of the solar spectrum. As shown in Fig.1 the serial connection between the InGaAs bottom cell ($E_{gap} = 0.7eV$) and the InGaAsP top cell ($E_{gap} = 1.1eV$) was realized by employing an Esaki-diode-like tunneling junction including thin layers of highly n-doped InGaAs and highly p-doped GaAsSb. This asymmetric material combination was used because of their favorable band offsets. Here, for achieving the best performance of the tunnel junction

	front contact			
	n-InGaAs	ARC	n-InGaAs	
window	n+	InP	20 nm	
top cell		InGaAsP	2 µm	
BSF	p	InP	50 nm	
tunnel	p++	GaAsSb	15 nm	
contact	n++	InGaAs	15 nm	
barrier	n+	InP	30 nm	
bottom cell		InGaAs	3 µm	
BSF	р	InGaAs	25 nm	
buffer	р	InP	150 nm	
substrat	p	InP	350µm	
back contact				

and the solar cell, the interfaces of the tunnel junction have to be as sharp as possible.

For all interfaces currently under investigation, the atomic and the electronic structure is by far not as precisely known as the respective bulk properties. As the atomic configuration of an interface defines the respective system under study [2] and, thus, is one of the most fundamental physical properties, continued improvements in device performance require strict control over growth conditions. Most other physical quantities sensitively depend on the interface structures. Therefore, each and every investigation of any interface property adds to the understanding of

Fig.1 Layer structure of the MOVPE-grown low bandgap double junction solar cell. For the serial connection of the bottom cell (InGaAs) and the top cell (InGaAsP) a tunnel diode, made up of n-InGaAs and p-GaAsSb, was used.

its particular atomic structure at the same time. Thus, in these studies, the influence of different preparation procedures on the InGaAs/GaAsSb-interface was investigated in detail by optical in-situ spectroscopy, i.e. reflectance difference/anisotropy spectroscopy (RDS/RAS). These in-situ signals were then benchmarked via a contamination-free transfer from MOCVD to UHV and surface science tools like low energy electron diffraction (LEED) and photoelectron spectroscopy (XPS/UPS).

Here, the monolithically grown tandem solar cell was prepared via metal organic chemical vapor deposition (MOCVD) using non-gaseous precursors that are much less toxic than the conventional gaseous precursors. It was found that a sharper InGaAs/GaAsSb-interface was achieved, if the GaAsSb layer growth was performed (in an unusual manner) on a III-rich (i.e. InGa-rich) surface reconstruction. Starting on As-rich InGaAs resulted in a much too low Sb content within the first monolayers of the GaAsSb layer, which was detected by XPS (see Fig.2). Analysis of the Sb 4d and the As 3d core level peak areas revealed, that the Sb to As ratio was more than three times higher for the GaAsSb grown on InGa-rich InGaAs, than for the GaAsSb grown on As-rich InGaAs [4].



Fig.2 As 3d and Sb 4d core levels, measured with XPS on 2nm GaAsSb, grown on As-rich (blue) and on InGa-rich (orange) InGaAs surface. The growth on the InGa-rich InGaAs surface leads to more Sb in the GaAsSb layer.

Direct comparison of these results to a standard Asrich GaAsSb surface [5] showed that the Sb to As ratio of the III-rich interface preparation was much more suitable than the V-rich preparation.

I-V measurements (Fig.3) were performed with an inhouse solar simulator. It shows the characteristics under full AM1.5g spectrum (blue curve) and additionally the response to the filtered AM1.5g illumination (red curve). For the filtered measurement

a RG850 (Schott) filter was used for simulating the illumination conditions for the operation of the double junction solar cell below a GaAs-based top cell. An open circuit voltage of 840mV, a short circuit current density of 12.1mA/cm², a fill factor of 73% and a solar conversion efficiency of 7.3% were obtained without an antireflection coating (ARC). Comparing the conversion efficiency with the

efficiency of a germanium bottom-cell (4.6%) employed in the record triplejunction solar cell (GaInP/GaInAs/Ge) a significant improvement is possible. In combination with a GaAs-based high bandgap tandem solar cell, an overall conversion efficiency beyond 45% could be reached.

Fig.3 I-V characteristic of an InGaAs/InGaAsP double junction solar cell measured under a full (blue curve) and a RG850-filtered (red curve) AM1.5g spectrum.



References

[1] A. Marti, G.L. Araujo, Solar Energy Materials and Solar Cells 43 (1996) 203

[2] J. Pollmann, Surf. Sci. 601 (2007) 88

[3] F. Dimroth, C. Baur, A.W. Bett, K. Volz, W. Stolz, Journal of Crystal Growth 272 (2004) 726

[4] U. Seidel, H.-J. Schimper, Z. Kollonitsch, K. Möller, K. Schwarzburg, T. Hannappel, J. Cryst. Growth 298 (2007) 777

[5] Z. Kollonitsch, H.-J. Schimper, U. Seidel, K. Möller, S. Neumann, F.-J. Tegude, F. Willig, T. Hannappel, J. Crystal Growth 287 (2006) 536

[6] C. Baur, M. Meusel, F. Dimroth, A. W. Bett, Conference Record of the 31st IEEE PV Specialists Conf., IEEE, Piscataway, NJ, USA 2005 675

Characterization and Modelling of Dye-sensitized Solar Cells LM Peter Department of Chemistry, University of Bath Bath BA2 7AY, United Kingdom

Recent progress towards understanding the processes taking place in dye-sensitized nanocrystalline solar cells (DSC) will be reviewed, and some areas characterized by controversy or poor understanding will be highlighted. Thermodynamic and kinetic criteria for successful cell design will be summarized, and experimental results obtained by several novel methods for characterizing the stationary and dynamic properties of DCS will be discussed. These methods include direct measurement of the quasi Fermi level using an indicator electrode following up an idea of Uli Würfel [1,2] (See **Figures 1 & 2**) and charge extraction measurements to determine the energetic distribution of electron traps in the nanocrystalline oxide [3] (see **Figures 3-5**). The influence of electron trapping on dynamic measurements of electron transfer and transport will be examined within the framework of the *quasi-static assumption*, and a new assessment of the electron diffusion length in the DSC will be given, which suggests that collection of photoinjected electrons should be considerably more efficient than previously assumed.



Figure 1. Cell design for measurement of quasi-Fermi level on the electrolyte side of the TiO_2 films in a DSC

Figure 2. QFL measurement at 1 sun

The charge extraction method involves allowing the open circuit voltage of the dye cell to decay at open circuit in the dark up to a pre-determined time, when the cell is short circuited to extract the remaining charge. The results obtained are illustrated by **Figure 3**, which shows how the experiment is repeated for different delay times to obtain the trapped charge as a function of potential.



Figure 3. The top panel shows a series of five experiments in which the open circuit decay was interrupted by short circuiting the cell. The lower panel shows the integrated current transients obtained, which give the stored charge at the open circuit voltage value chosen.

The open circuit decay also provides information about shunting of the dye cell via the conducting glass substrate. In the absence of a blocking layer, the decay is rapid as electrons transfer via the fluorine-doped tin oxide layer to the idodide/tri-iodide electrolyte. This process can be prevented by using a thin (50 nm) blocking layer of compact TiO_2 as illustrated in **Figure 4**

Analysis of the photovoltage decay for cells with a blocking layer provide information about the rate constant for electron transfer from the nanocrystalline oxide to I_3^-/I^- as well as about the energetic distribution of electron traps in the oxide [4]. **Figure 5** shows an example of the fit used to obtain these parameters (here T_c is a temperature that characterizes the energetic width of the exponential trap distribution).



Figure 4. Open circuit photovoltage decay for dye cells with and without a compact TiO₂ blocking layer



Figure 5. Photovoltage decay shown on a log-lin plot together with the fit to theory used to obtain information about the kinetics of electron transfer and the distribution of electron trapping states.

References.

- 1. Lobato, K; Peter, L.M; Würfel, U., J. Phys. Chem. B, 2006, 110, 16201.
- 2. Lobato, K.; Peter, L. M. Journal of Physical Chemistry B 2006, 110, 21920.
- 3. Bailes, M.; Cameron, P. J.; Lobato, K.; Peter, L. M. Journal of Physical Chemistry B 2005, 109, 15429.
- 4. Walker, A. B.; Peter, L. M.; Lobato, K.; Cameron, P. J. Journal of Physical Chemistry B 2006, 110, 25504.

Semiconductor-sensitized solar cells: comparison with dye-sensitized cells

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The dye-sensitized solar cell (DSSC) is the most studied of the various nanocrystalline solar cell types. An obvious alternative is to replace the dye by a relatively low bandgap semiconductor as light absorber (the semiconductor-sensitized solar cell or SSSC, which we define here as containing an electrolyte to distinguish it from the extremely thin absorber solar cell – the ETA cell). In studies of this cell type, advantages of using a semiconductor rather than a dye are often stressed. In spite of these perceived advantages, the DSSC possesses one major advantage at this time over the SSSC: the maximum obtained efficiency of the DSSC is ca. 11% compared to < 3% for the SSSC (5% if the ETA cell is included). This major difference cannot be simply attributed to the greater body of research carried out on the DSSC, since right from the early days of the DSSC, efficiencies over 9% were obtained.

The purpose of this contribution is to consider the fundamental differences between the two cell types. In particular, characteristic charge-transfer times for the different steps are compared. To simplify nomenclature, the term 'semiconductor' refers to the absorbing semiconductor while we use the term 'oxide' to denote the porous oxide.

Charge transfer times in the SSSC can be divided, like the DSSC, into a number of processes:

- 1. Electron injection from semiconductor to oxide (typically ps scale).
- 2. Back electron transfer from oxide to semiconductor (not well studied).
- 3. Electron/hole recombination time in semiconductor (very variable but typically ns scale for the common semiconductors used).
- 4. Electron injection from oxide to electrolyte (indirect recombination).
- 5. Electron injection from substrate to electrolyte (indirect recombination).

Processes 4 and 5 are essentially the same for the DSSC and SSSC, although perhaps modified by different coverages of the oxide surface by a molecular dye or a larger-volume solid semiconductor. The first 3 processes can be different for the two types of cell. While there is much less fast-time data for semiconductor-to-oxide electron transfer times compared to dye-to-oxide times, there is evidence that the former may be at least an order of magnitude slower. However, since electron/hole recombination in the semiconductor is typically two to three orders of magnitude slower than the injection time, this may not be very important.

An important clue to the difference in performance between the two types of cells lies in the fact that high monochromatic photocurrent efficiencies – often 70-80% - have been seen for *small* amounts of deposited semiconductor, but that the efficiency usually decreases when the amount of the semiconductor deposited increases above a certain optimum. For highly quantized semiconductors, like FeS_2 or PbS, this loss may be due mainly to change in energy level structure and inability to inject electrons into the oxide. However in many cases, the quantum efficiency loss in these cells, when enough semiconductor is deposited to give a strong absorption of the incident light, is in a transfer process not listed above – electron transfer from semiconductor to semiconductor before being injected into the oxide. In other words, the efficiency can be high for semiconductor particles directly contacting the oxide, but drops considerably when semiconductor-to-semiconductor charge transfer is necessary. If this is true, then the strategies to improve SSSCs would be either to increase the thickness of the layers; to increase the surface area (decrease the size of the oxide particles) or conversely to increase the size of oxide particles, allowing larger pores and deposition of larger crystals of the semiconductor. The optimal thickness of semiconductor will depend on the properties of the semiconductor itself, in particular on recombination time between electrons and holes in the semiconductor and the transit time for electrons generated relatively far from the oxide to reach the semiconductor/oxide interface where they can be rapidly injected into the oxide. The hole transfer from semiconductor to electrolyte is also particularly important, since if holes are very rapidly extracted from the semiconductor (and this applies equally to a semiconductor particle in contact with the oxide or one father away, as long as the electrolyte can reach the surface of all particles), then clearly electron/hole recombination in the semiconductor will be reduced.

Another issue for both the DSSC and the SSSC, particularly important for solid state cells, but often relevant also for liquid ones, is the 'passivating layer' sometimes deposited onto the oxide surface which reduces electron injection from the oxide to the electrolyte (liquid or solid). In the SSSC, the semiconductor itself may act as a passivating layer to a greater or lesser extent. Thus the beneficial effect of CdS deposited either before or after the 'absorbing' semiconductor could be explained by this passivation. It is also notable that if CdS itself is used as an absorbing semiconductor, additional higher-bandgap oxide passivating layers on TiO₂ do not appear to make an appreciable difference to the efficiency, presumably since CdS itself acts also in this capacity.

In conclusion, the present limit of < 3% is not seen as fundamental and large increases in efficiency are expected from the SSSC.

Light-harvesting host-guest antenna materials for photonic devices

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In natural photosynthesis, light is absorbed by photonic antenna systems consisting of a few hundred chlorophyll molecules. These devices allow fast energy transfer from an electronically excited molecule to an unexcited neighbour molecule in such a way that the excitation energy reaches the reaction centre with high probability. Trapping occurs there. The anisotropic arrangement of the chlorophyll molecules is important for efficient energy migration. In natural antennae the formation of aggregates is prevented by fencing the chlorophyll molecules in polypeptide cages. A similar approach is possible by enclosing dyes inside a microporous material and by choosing conditions such that the cavities are able to uptake only monomers but not aggregates. In most of our experiments we have been using zeolite L as a host because it was found to be very versatile. Its crystals are of cylindrical shape and consist of an extended one-dimensional tube system. They can be prepared in wide size range. We have filled the individual tubes with successive chains of different dye molecules and we have shown that photonic antenna materials can be prepared, not only for light harvesting within the volume, but also for radiationless transport of electronic excitation energy to a target molecule fixed at the ends of the nanochannels as well as with an injector molecule fixed at their "entrances". The molecule which has been excited by absorbing an incident photon transfers its electronic excitation to another one. After a series of such steps the electronic excitation reaches a luminescent trap. The energy migration is in competition with spontaneous emission, radiationless decay, guenching, and photochemically induced degradation. Fast energy migration is therefore crucial if a trap should be reached before other processes can take place. - The supramolecular organization of the dyes inside the channels is a first stage of organization. It allows light harvesting within a the volume of a dye-loaded zeolite L crystal and radiationless transport to both ends of the cylinder or from the ends to the centre. The second stage of organization is the coupling to an external acceptor or donor stopcock fluorophore at the ends of the zeolite L channels, which can trap or inject electronic excitation energy. The third stage of organization is the coupling to an external device via a stopcock intermediate. The wide-ranging tunability of these highly organized materials offers fascinating new possibilities for exploring excitation energy transfer phenomena, and challenges for developing new photonic devices for solar energy conversion and storage. A dyesensitized solar cell which employs energy transfer instead of electron injection is of great interest. The advantage of such a cell is that the dyes do not require regeneration. This is in contrast to cells working by electron injection, in which the dyes have to be regenerated by a redox couple.

A dye-zeolite composite prepared as a monodirectional antenna opens possibilities for novel sensitized solar cells. Arranging small composite crystals with their c-axes perpendicular to the surface of a semiconductor allows transport of the excitation energy towards the zeolite-semiconductor interface by energy migration. Stopcock molecules are placed only at one channel end to allow energy transfer. The semiconductor layer can be very thin, because the electron-hole pairs form near the surface. The transfer of electrons from antenna to semiconductor is prevented by introducing an insulating layer.

Energy can also be transferred from an appropriately chosen semiconductor to the antenna composites by reversing the current and putting a voltage over the semiconductor. The dye-zeolite composites on the semiconductor surface subsequently lose their energy by emitting light. The colour of the emission can be tuned by adapting the ratio of blue, yellow, and red fluorescent dyes, hence also white light emission is possible. Higher energy efficiency is expected for such a system compared to conventional LEDs.

- Photon-Harvesting Host-Guest Antenna Materials
 G. Calzaferri, S. Huber, H. Maas, C. Minkowski, Angew. Chem. Int. Ed. 42, 2003, 3732.
- Trapping Energy from and Injecting Energy into Dye-Zeolite Nanoantennae H.Maas, G. Calzaferri, Angew. Chem. Int. Ed. 41, 2002, 2284-2287.
 Sequential Functionalization of the Channel Entrances of Zeolite L Crystals S. Huber, G. Calzaferri, Angew. Chem. Int. Ed. 43, 2004, 6738-6742.
- [3] Förster-Type Energy Transfer along a Specified Axis C. Minkowski, G. Calzaferri, Angew. Chem. Int. Ed. 44, 2005, 5325.
- [4] Organizing supramolecular functional dye-zeolite crystals
 A. Zabala Ruiz, H. Li, G. Calzaferri, Angew. Chem. Int. Ed. 45, 2006, 5282.
- [5] Light-harvesting host-guest antenna materials for photonic devices
 Gion Calzaferri, Stefan Huber, André Devaux, Arantzazu Zabala Ruiz,
 Huanrong Li, Olivia Bossart, Le-Quyenh Dieu, Proc. of SPIE, Organic Optoelectronics and
 Photonics II, Vol. 6192 2006 619216-1 619216-9.

Nano-Structured Solar Cells Based on Aligned ZnO Nanowires

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The report of a dye-sensitized solar cell with a light to electric conversion efficiency of around 10% by O'Regan and Grätzel¹ has generated intense research in the field of nanostructured solar cells. Even though big efforts have been made, it was not possible within the last 15 years to increase the conversion efficiency significantly above 10%.² One reason might be the enormously enhanced interface area between the TiO₂ nanocrystalline film and the electrolyte, which is needed to provide sufficient absorption sites for the light harvesting dye. On the other hand electron transport through the TiO₂ network is slow and recombination at that large interface decreases the cell efficiency.

Our approach is to replace the mesoporous nanocrystalline TiO₂ film by an array of aligned ZnO nanowires. Electron transport along the nanowires is improved because of a lower trap density due to the absence of grain boundaries. The smaller surface to volume ratio requires the use of long wires in conjunction with a dye absorber or alternative absorber materials with a larger absorption coefficient. Dye-sensitized ZnO nanowire solar cells with a liquid electrolyte have been reported^{3,4} as well as solid state nanowire cells with a CdSe absorber and a CuSCN hole conductor.⁵ We present ZnO nanowire solar cells with a Cu₂O absorber which acts also as a hole conductor. Cu₂O has the big advantage that it is not hazardous, relatively cheap and available in large quantities. We discuss the band structure of the solar cell including band discontinuities and electrostatic fields in terms of the cells working principle and its performance.

References:

- (1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
- (2) Grätzel, M. Prog. Photovolt: Res. Appl. 2006, 14, 429.
- (3) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. *Nature Materials* **2005**, *4*, 455.
- (4) Law, M.; Greene, L. E.; Radenovic, A.; Kuykendall, T.; Liphardt, J.; Yang, P. J. Phys. Chem. B 2006, doi: 10.1021/jp0648644.
- (5) Lévy-Clément, C.; Tena-Zaera, R.; Ryan, M. A.; Katty, A.; Hodes, G. Adv. Materials 2005, 17, 1512.

Optoelectronic switching devices based on semiconducting nanocomposites

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Recent development in nanoelectronics¹⁻³ and information processing in chemical systems^{4,5} has turned our attention towards application of semiconducting nanocomposites as materials for construction of optoelectronic devices. Currently used computing devices are based on monolithic semiconductor structures fabricated on the surface of silicon wafers.⁶ All these devices use binary logic for information processing and utilize electric signals for communication. Logic gates are basic elements processing information: they function as switches whose output (0 or 1) depends on input conditions. Further development (i.e. miniaturization) of semiconductor devices is limited by technological and physical factors.⁷ Application of chemical structures for information processing seems to bypass, at least temporarily, the limitations of classical silicon technology and sustain the development of information technologies.

Nanocomposites incorporating semiconductor particles and coordination or organometallic compounds are novel materials with numerous extraordinary properties. Various synthetic methods are applied in preparation of semiconductor nanocomposites, including electrodeposition, wet impregnation, suspension polymerization, mechanical mixing, chemical vapor deposition, sputtering and others.⁸ Nanocomposite materials usually show improvement of performance as compared with neat constituents concerning such properties as stability, (photo)catalytic activity, solar energy conversion and others. Semiconductor nanoparticles usually serve as light harvesting antennae or (photo)catalytic centers, while matrices apart from purely mechanical support may function as electron buffers, photosensitizers, protecting layers etc.

This presentation concerns a series of nanocomposites based on titanium dioxide and iron species like Prussain blue and ferrocene. These materials are characterized spectroscopically and electrochemically. The experimental data are supplied with quantum-chemical modeling using ZINDO (STO-3G) and DFT ($b3pw91/6-311++g^{**}$) approaches. These studies reveal the binding modes of the modifiers with the semiconductor surface and their mutual electronic interactions. Detailed photoelectrochemical studies enabled elucidation of the photocurrent generation mechanism and identification of processes responsible for photocurrent switching.

Spectral and electrochemical studies of the Prussian blue-titanium dioxide nanocomposite reveal only a weak electronic interaction between the components. This interaction is manifested in a slight increase of band gap energy of the composite as compared with neat titanium dioxide (Degussa P25): 3.22 and 2.35 eV for TiO₂ and PB@TiO₂, respectively. Furthermore, a bathochromic shift of ca. 40 nm for the MMCT (Fe^{II} \rightarrow Fe^{III}) transition of Prussian blue is observed.

Even weaker interaction was observed in the case of ferrocene-titanium dioxide nanocomposite. The only observable change consists in the hypsochromic shift of the lowest energy ferrocene transition of ca. 5 nm.

Despite these very weak interaction, discussed modifications of titanium dioxide have dramatic influence on photoelectrochemical properties of these materials. At positive polarization of photoelectrodes the photoelectrochemical response of the electrode closely resembles that of neat titanium dioxide. Reduction of Prussian blue to Prussian white or negative polarization of the photoelectrode in the case of ferrocene-based composite results in photocurrent reversal. This effect, however, is observed only in the presence of molecular oxygen dissolved in the electrolyte. Furthermore, in the case of ferrocene-based material an enormous increase of photocurrent intensity is observed.

Detailed analysis of electrochemical behavior and photocurrent kinetic studies supplemented with quantum chemical modeling indicate that the photocurrent switching in these materials results from two different mechanisms. For the Prussian blue modified titania the photocurrent switching results mostly from the electrostatic interaction of charge carriers within the semiconductor particle with the surface polymeric species. Formation of inversion layer is responsible for the photocurrent reversal. The photocurrent switching in the case of ferrocene-based material is a consequence of photocatalytic ferrocene oxidation by holes from the valence band. High intensity of cathodic photocurrent results from a very efficient charge separation at ferrocene (p-type semiconductor) – titania (n-type semiconductor) bulk heterojunction.



Equivalent circuit for ITO-nanocomposite-electrolyte junction.

Despite chemical diversity and mechanistic differences both systems can be used for construction of prototypical optoelectronic devices.

The composite materials generate photocurrent only upon UV and blue irradiation (300-450 nm), but the photocurrent character depends on the photoelectrode potential. In the case of ferrocene and Prussian blue materials the cathodic-to-anodic switching occurs in the range 100-150 mV and at 200 mV vs. Ag/AgCl, respectively. At potentials higher than the switching potential range the electrodes generate anodic photocurrent, while at lower potentials cathodic photocurrents are observed. One can assign the logic values of "0" and "1" to the negative and the positive polarization of the photoelectrode, respectively. The switching characteristics allows for using it as an optoelectronic two channel demultiplexer (data selector). This device collects information in form of light pulses and converts it into photocurrent pulses. Furthermore, the sign (direction) of photocurrent pulses can be directed into two output channels: cathodic or anodic. An electronic equivalent of this logic device is composed of two AND and a NOT logic gates. The input data signal (light pulses) is applied to one input of both AND gates, the control signal goes to one AND gate directly while to the other via an inverter. In this configuration one of the AND gates is in the ON and the other is the OFF state.



Electronic equivalent circuit of nanocomposite photoelectrode working as two channel optoelectronic demultiplexer.

References

(1) Luo, Y.; Collier, C.P.; Jeppesen, J.O.; Nielsen, K.A.; Delonno, E.; Ho, G.; Perkins, J.; Tseng,

H.-R.; Yamamoto, T.; Stoddart, J.F.; Heath, J.R. ChemPhysChem 2002, 3, 519.

(2) Moore, G.E. *Electronics* **1965**, *38*, 114.

(3) Stan, M.A.; Franzon, P.D.; Godstein, S.C.; Lach, J.C.; Ziegler, M.A. *Proc. IEEE* **2003**, *91*, 1940.

- (4) Zauner, K.P. Crit. Rev. Solid State Mat. Sci. 2005, 30, 33.
- (5) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines A Journey into Nanoworld*; WILEY-VCH: Weinheim, 2003.

(6) Hillis, W.D. *The pattern on the stone. The simple ideas that make computers work*; Perseus Publishing: Boulder, 1999.

- (7) Keyes, R.W. *Proc. IEEE* **2001**, *89*, 227.
- (8) Rajeshwar, K.; de Tacconi, N.; Chenthamarakshan, C.R. Chem. Mater. 2001, 13, 2765.

Charge transport in dye sensitized solar-cells: An electrochemical STM-study

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Dye sensitized solar-cells (DSSCs) are a low cost alternative to conventional solar cells and gain more and more interest in science and development [1]. The elementary processes in these cells are highly attractive for researchers because of their role as model systems for photon to electron conversion. A dye serves as the absorber of the sunlight in the Grätzel cell and injects an electron to the conduction band of a nanoporous network of TiO₂-nanoparticles. The nanoporosity is chosen to maximize the surface area of the material. TiO₂ is a very suitable material due to its large bandgap. The regeneration of the dye is done by an electrolyte, most suitable is an iodide/triiodine redox couple. Besides the optimization of materials, understanding of the charge transport mechanism in these cells is of special interest and still not completely resolved.

One important part in the transport phenomena of the cell is the transport between individual TiO_2 -nanoparticles in the nanoporous network. Cahen et al. suggest a hopping process between surface states for the transport between single TiO_2 -nanoparticles [2]. Another model is a tunnelling process for this transport with a barrier width of around one nanometer [3].

Very common methods of solar cell characterization are averaging properties of the whole particle network or at least a large number as an ensemble. Instead of averaging the properties of the semiconductor network we have chosen scanning tunnelling microscopy and spectroscopy as a spacially resolved method to investigate transport mechanism in the TiO₂-nanoparticle network. With Scanning Tunnelling Spectroscopy one can determine band positions and the Fermi level of TiO₂ relative to different substrates (Fluoron doped tinoxide as transparent electrode and platinum as the metallic counter electrode of the DSSC), as shown in Figure 1. The tunnelling spectra (tunnelling current as a function of bias voltage) show hysteresis like-behaviour with varying bias sweep direction which is attributed to the slow kinetics of the occupation of surface states. Tunnelling spectra have also been recorded in the DSSC-electrolyte under potential control. In this case the tunnelling process is mainly determined by the semiconductor/electrolyte interface. The interpretation of *in situ* tunnelling spectra requires taking into account Faradaic currents at the semiconductor electrolyte interfaces.

The minimization of Faradaic currents at the STM-tip for *in situ* measurements was established with a special technique of tip-preparation. A well defined geometry of electrochemically etched tips lead to a reproducible coating of STM-tips.

Light induced currents of dye sensitized TiO_2 -layers can also be measured with an STM by applying an illumination path to the set-up. The light-induced part of the tunnelling current can be separated from the bias-induced part by amplitude modulation of the laser illumination. The dependence of the frequency of this modulation can be compared to the dependency from a bias modulation. Both signals are correlated and therefore the light induced current was attributed to a photovoltage.



Figure 1: Tunneling spectra of a thin layer of TiO₂ on two different substrates [4].

- a) 100 nm layer of TiO_2 on FTO
- b) 100 nm layer of TiO_2 on platinum

References

[1] O'Regan, B, Grätzel, M.: A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO₂ films, Nature 353, 737 (1991)

[2] Cahen D., Hodes, G., Grätzel, M., Guillemoles, J.F., Riess, I.: Nature of Photovoltaic action in Dye Sensitized solar cells, J. Phys. Chem. B 104, 2053 (2000)

[3] Rühle, S., Cahen, D.: Electron Tunnelling at the TiO₂ Substrate Interface can determine Dye-Sensitized Solar Cell Performance, J. Phys. Chem. B 108, 17946 (2004)

[4] Wendling, B.: Ortsaufgelöster Ladungstransport an photoelektrochemischen Solarzellen: Eine EC-STM Studie, Dissertation TU Clausthal, Papierflieger-Verlag Clausthal-Zellerfeld (2006)

Electron and energy transfer processes in heterogeneous photocatalysis

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Photoelectrochemical and photocatalytic behavior of titanium dioxide depends strongly on surface properties of this semiconductor. Chemical modification of the titania surface may induce several effects – band bending and shifting, changes in the lifetime of surface-trapped charges, changes in efficiencies of the electron and energy transfer processes, or photosensitization.

Visible light photosensitization consists in the photoinduced electron transfer. It can be achieved by four main approaches: (i) bulk doping, (ii) surface modification, (iii) formation of composite semiconductors and (iv) metal-semiconductor composites. Bulk doping results in formation of intra-band gap donor or acceptor levels which render the effective band gap smaller (Fig. 1a). The modification usually involves introduction of p (N,¹ $C_{2,3}^{2,3}$ S, Cl, Br, I, Pb), d (V, Cr, Au, Rh, Ni, Pt,⁴⁻⁸ etc.) or f (Eu, Pr, Yb, Ce, Nd etc.) block elements into TiO₂ (or other wide band gap semiconductor) matrix. Surface modification, in turn, involves formation of covalent or ionic bonds between semiconductor surface and chromophoric molecules or formation of chromophoric surface species upon interaction with chromogenic molecules. In the first case diverse organic dyes (porphyrins, phtalocyanines, thiacarbocyanine dyes, various natural dyes) and metal complexes undergo photoexcitation with visible light and inject electrons into the conduction band (Fig. 1b). Chemisorption of chromogenic molecules onto the TiO₂ surface results in formation of ligand-to-metal charge transfer (LMCT) or metal-to-metal charge transfer transitions (more precisely referred to as metal-to-particle or ligand-to-particle charge transfer; MPCT and LPCT) involving surface Ti^{IV} ions and surface bound ligands or transition metal complexes, respectively. Photoexcitation of these systems results in a direct electron injection into CB as a consequence of photon absorption (Fig. 1c). Composite semiconductors are formed when TiO₂ particles interact with particles (or are covered with layers) of semiconductors of smaller band gap and different band edge potentials. Visible light irradiation leads to charge separation only in the smaller band gap semiconductor and subsequently electron can be injected into CB of TiO_2 (Fig. 1d). This process results not only in photosensitization, but also in more efficient charge separation and suppression of recombination processes. Similar processes take place upon excitation of metal nanoparticles within their plasmon resonance bands. In this presentation selected examples of various types of the photosensitized TiO₂ systems (based on original works of the authors) will be presented.



Figure 1. Modes of band gap "narrowing": bulk doping resulting in formation of acceptor or donor levels (a); photosensitization with organic or inorganic chromophores chemisorbed onto semiconductor surface (b); formation of surface complexes exhibiting MMCT or LMCT transitions (c); and formation of composite semiconductors (d). E_{bg} stands for the bandgap energy.

Although the charge transfer processes govern the photocatalytic and photoelectrochemical properties of TiO_2 and other broad-bandgap semiconductors, the energy transfer may also play an important role in photocatalysis. Our studies have shown, that relative efficiencies of the electron and energy transfer processes may be controlled to some extend by a simple surface modification. Exchange of the surface hydroxyl groups by inorganic ions, complexes and organic groups can effectively suppress an interfacial electron transfer and improve the energy transfer processes. In this presentation the photoinduced generation of singlet oxygen at modified TiO_2 materials, as an example of energy transfer process, will be considered.

Recently Nosaka *et al.* reported for the first time detection of singlet oxygen photogenerated at TiO₂ surface using gated photon counting method.⁹ This direct method is based on emission properties of singlet

oxygen in its ${}^{1}\Delta_{g}$ state. Although the results of Nosaka prove singlet oxygen generation at TiO₂ it is not clear which conditions favor ¹O₂ generation at titanium dioxide surface. In our opinion studies on cyanuric acid (CA) photodegradation may shine some light on this problem. CA is a very stable compound, resistant towards oxidation. It does not undergo degradation neither in the presence of neat TiO2 photocatalyst upon UV-light irradiation nor under sonolysis, *i.e.* under conditions where oxygen-centered radicals are formed. ¹⁰⁻¹² However, photodegradation of cyanuric acid was observed in the presence of TiO_2 modified with $[PtCl_6]^{2-}$ complex.⁸ There are also reports on photocatalytic degradation of cyanuric acid by fluorinated titanium dioxide (F-TiO₂).^{13,14} In this photocatalyst the surface -OH groups were substituted by F⁻. The unusual reactivity of F-TiO₂ was explained by generation of "bulk" hydroxyl radicals which are expected to be stronger oxidants than OH' bound to the surface of unmodified TiO2.^{15,16} Lower efficiencies of interfacial electron transfer processes – like direct hole oxidation, reduction with electrons from the conduction band, photocurrent generation – were observed for $F-TiO_2$ as compared to neat TiO_2 .¹⁴ On the other hand the lifetime of OH[•] photogenerated at unmodified TiO_2 is long enough to allow its diffusion to distances of few micrometers away from the photocatalyst surface.¹⁷ These arguments against the mechanism of CA degradation by "bulk" OH led us to check the possibility of singlet oxygen photogeneration in $F-TiO_2$ suspension and to explain its possible role in CA decomposition. The results of our experiments, which will be presented to the audience of this talk, support the possibility of two basic mechanisms taking place at the surface of irradiated titanium dioxide particles – the electron transfer and energy transfer (Fig. 2). The first one leads to generation of hydroxyl radical, superoxide radical and other reactive oxygen species, while the second one may be responsible for singlet oxygen formation. Modification of the titanium dioxide surface (or its structure) enhances the energy transfer pathway and suppresses the interfacial electron transfer, although a complete inhibition of the latter does not take place. At the surface of unmodified TiO_2 the electron transfer processes prevail, while singlet oxygen may be formed with lower efficiencies.



Figure 2. Primary processes at neat TiO₂ (upper scheme) and at TiO₂ with substituted surface –OH groups (lower scheme).

References:

- (1) S. Sakthivel, H. Kisch, ChemPhysChem 2003, 4, 487.
- (2) C. Lettmann, K. Hildenbrand, H. Kisch, W. Macyk, W. F. Maier, Appl. Catal. B: Environ. 2001, 32, 215.
- (3) S. Sakthivel, H. Kisch, Angew. Chem. Int. Ed. 2003, 42, 4908.
- (4) L. Zang, W. Macyk, C. Lange, W. F. Maier, C. Antonius, D. Meissner, H. Kisch, Chem. Eur. J. 2000, 6, 379.
- (5) W. Macyk, H. Kisch, Chem. Eur. J. 2001, 7, 1862.
- (6) H. Kisch, G. Burgeth, W. Macyk, Adv. Inorg. Chem. 2004, 56, 241.
- (7) G. Burgeth, H. Kisch, Coord. Chem. Rev. 2002, 230, 40.
- (8) W. Macyk, G. Burgeth, H. Kisch, Photochem. Photobiol. Sci. 2003, 2, 322.
- (9) Y. Nosaka, T. Daimon, A.Y. Nosaka, Y. Murakami Phys. Chem. Chem. Phys. 2004, 6, 2917.
- (10) T.A. Tetzlaff, W.S. Jenks Org. Lett. 1999, 1, 463.
- (11) K. Lanyi, Z. Dinya Microchemical J. 2003, 75, 1.
- (12) C.L. Bianchi, C. Pirola, V. Ragaini, E. Selli Appl. Catal. B: Environ. 2006, 64, 131.
- (13) Y.-C. Oh, W.S. Jenks J. Photochem. Photobiol. A: Chem. 2004, 162, 323.
- (14) H. Park, W. Choi J. Phys. Chem. B 2004, 108, 4086.
- (15) C. Minero, G. Mariella, V. Maurino, E. Pelizzetti Langmuir 2000, 16, 2632.
- (16) C. Minero, G. Mariella, V. Maurino, D. Vione, E. Pelizzetti Langmuir 2000, 16, 8964.
- (17) Y. Kikuchi, K. Sunada, T. Iyoda, K. Hashimoto, A. Fujishima J. Photochem. Photobiol. A: Chem. 1997, 106, 51.

Transport in Disordered Semiconductors: The Variable Range Hopping Model Revisited

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Photogalvanic Cells in Chemistry Education

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A fundamental demand on chemical education today is to communicate core principles of chemistry in close combination with everyday life experiences of students as well as with convincing applications from modern science and technology.

Photogalvanic cells described in this lecture are suitable to fulfill this requirement. They are the basis of a curricular concept that bridges the gap between galvanic cells and compact cells made of semiconductors. By use of these cells students gain an understanding of the process of light conversion into electric energy and work on optimizing the experimental setup. The focus is on the key steps of a photogalvanic device: (i) the light-induced charge separation by photoexcitation of electrons from the valence band to the conduction band, leading to the formation of electrons, e⁻, and holes h⁺, in opposite directions to generate a photo-induced current. The efficiency of the so called "2-pot-cell" and the "1-pot-cell" will be demonstrated and discussed as well as the sensitization of a TiO₂ photoelectrode with anthocyanin dyes from red wine.





Fig. 1: The photogalvanic "2-pot-cell" and the photogalvanic "1-pot-cell"

Literature

- [1] D. Wöhrle, M. W. Tausch, W.-D. Stohrer: PHOTOCHEMIE, Wiley-VCH, Weinheim (1998)
- [2] C. Bohrmann-Linde, M. W. Tausch, J. Chem. Educ. 80 (12), 1471 (2003)
- [3] M. W. Tausch, M. v. Wachtendonk (editors) CHEMIE 2000+, C. C. Buchner, Bamberg (2006)

Transport through organic monolayers on Si

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Interfaces are known to dominate electrical transport across electronic junctions such as semiconductor / metal junctions (which are also relevant for photovoltaics). Recently it was recognized that interfaces control transport across molecular based devices as well. Therefore, finding ways to control the molecule/electrode interface behaviour can make a major contribution to the field of molecular electronics.

I will present experimental transport results on Si-alkyl layer/metal junctions, in which the alkyl chain monolayers are bound to Si by the mostly covalent Si-C bond. This bonding is strong and directional so as to direct the molecules to the appropriate sites on the Si surface, something that results in a well defined and organized interface.

Our transport results through these organic layers, agree well with 1970s theoretical simulations for a Si/SiOx/metal MIS system by Green and Shewchun for solar cells applications ^[1](see figure). This agreement implies that these molecular systems act as nearly ideal insulators and give near-ideal metal/insulator/ semiconductor (MIS) junctions, something that was not achieved with inorganic insulators of comparable thickness^[2].

This then raises the question if this type of molecular junctions can be of interest for photovoltaic cells. Our preliminary results on these molecular junctions suggest that they may indeed be useful for revisiting the MIS idea as very rough measurements on make shift structures already show an open circuit voltage of about 480 mV, comparable to the Si/Au V_{oc} that was measured at the time that MIS cells were still en vogue.



M. A. Green, F. D. King, J. Shewchun, *Solid-State Electronics* 1974, *17*, 551.
 A. Salomon, T. Boecking, C. K. Chan, F. Amy, O. Girshevitz, D. Cahen, A. Kahn, *Physical Review Letters* 2005, *95*, 266807/1.

Nanostructured Semiconductor Films for DSCs by Electrostatic Layer-by-Layer Deposition

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Electrostatic layer-by-layer (ELBL) deposition is a simple technique in which a substrate is alternately immersed in aqueous solutions (or suspensions) of cationic and anionic materials, which build up in successive layers by electrostatic attraction.¹ The technique has most often been used to produce organic films from alternating cationic and anionic polymers. However, semiconductor films can be produced using a suspension of charged semiconductor particles and a solution of an oppositely charged polymer. The particles are easily charged by controlling the pH of the suspension. An advantage of this method is that once a monolayer of particles has adsorbed onto the preceding polymer layer, additional particles in suspension are electrostatically *repulsed* from the surface. The ELBL technique therefore deposits approximately one monolayer of particles per cycle. This allows for fine control of film thickness.

TiO₂ films. In this work, TiO₂ nanoparticulate films were deposited on conducting glass (precoated with F:SnO₂) by dipping the substrate alternately in a solution of cationic poly(diallyldimethylammonium chloride) (PDAC) and a suspension of anionic 17-nm TiO₂ particles at pH 11 due to the addition of 5 mM triethylamine, with intermediate rinsing steps. After 50 deposition cycles, the film is sintered at 500 °C for 30 min in order to both induce interparticle necking and burn away the polymer. The resulting film thickness is typically 1.5 μ m.

TiO₂ films prepared in this way can yield good solar cells after soaking in dye, sealing against a platinized counterelectrode, and filling with a suitable electrolyte.^{2,3} Cells in this study yielded solar energy-to-electricity conversion rates under full-sun AM1.5 irradiation of 1.4% and 3.0% when sensizited with N719 [(*cis*-di(thiocyanato)-*N*,*N*'-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium(II)] and the organic dye D5 [3-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid], respectively.

Films that are not sintered after ELBL deposition still give working solar cells, albeit with much reduced efficiency compared to sintered films: 0.7% with N719 and 0.8% with D5. That they work at all is somewhat surprising given that the TiO₂ particles remain separated by polymer layers. The cells were therefore studied by transient techniques.

Electron kinetics. The kinetics of electron transport and recombination were studied by measuring the transient decay of current under short-circuit conditions (yielding the transport time, τ_{tr}) and of voltage under open-circuit conditions (yielding the electron lifetime, τ_e) during illumination by a 530-nm LED laser under square-wave intensity modulation.

A plot of τ_{tr} vs. J_{SC} (the short-circuit current) gives a clear and reproducible difference between sintered and unsintered films, with the former exhibiting faster transport (Figure 1). This result is consistent with expectations given that an unsintered film will consist of unfused TiO₂ particles that still contain polymer. Subjecting an unsintered film to high pressure to cause particle necking without removing polymer does not reduce the film's transport time, suggesting that the interference from the polymer is the primary factor hindering transport. On the other hand, the choice of dye makes no significant difference in the transport time, although N719 and D5 are quite different. This suggests insensitivity of the particles to species at the particle surfaces. When the electron lifetime τ_e is measured against V_{OC} , the picture is somewhat different (Figure 2). Longer lifetimes are observed in sintered samples, especially at high light intensities (high V_{OC}). However, a dye effect also appears, with N719 resulting in slightly longer lifetimes than D5. Dyes serve to insulate the particle surface from the electrolyte and thus different dyes would be expected to result in different rates of recombination. Our results suggest that the choice of dye has an effect on electron transfer from the TiO₂ into the electrolyte, but not on electron transfer between particles even in the unfused (unsintered) condition, where the electron must pass through the surface of each particle.



Figure 1. Electron transport time vs. shortcircuit current for sintered and unsintered films dyed with N719 and D5.



ELBL conformal TiO₂ coatings. TiO₂ nanoparticles can coat larger structures quite nicely by ELBL deposition. We shall present work in progress toward exploiting the ELBL technique for conformal coatings, focusing on two systems.

First, we are exploring the formation of structured films by coating TiO_2 particles over an organic template. The controlled evaporation of solvent (CS₂) from a solution containing poly(9,9'-dihexylfluorene) can result in an organic film with very regularly spaced pores.⁴ Coating such a film with the ELBL technique, followed by burning away the organic template, leaves a thin, highly structured TiO₂ film.

Second, there has been much interest in using ZnO nanorod architectures in DSCs. However, they face the disadvantages of (1) the lack of good dyes compatible with ZnO and (2) low surface area. We have attempted to use ELBL deposition to coat ZnO nanorods (grown by chemical bath deposition) with TiO₂ nanoparticles. The goal is a system where TiO₂, loaded with a standard dye (such as N719), absorbs light with high efficiency and transfers the injected electron to ZnO, where the electron can take advantage of fast transport to the collector. The system also has the advantage that the TiO₂ particles would significantly increase the roughness factor of the film.

References:

(1) Decher, G. Science 1997, 277, 1232-1237.

- (2) He, J.-A.; Mosurkal, R.; Samuelson, L. A.; Li, L.; Kumar, J. Langmuir 2003, 19, 2169-2174.
- (3) Agrios, A. G.; Cesar, I.; Comte, P.; Nazeeruddin, M. K.; Grätzel, M. Chem. Mater. 2006, 18, 5395-5397.
- (4) Vamvounis, G.; Nyström, D.; Antoni, P.; Lindgren, M.; Holdcroft, S.; Hult, A. *Langmuir* **2006**, *22*, 3959-3961.

TOWARDS BIOMIMETIC SOLAR CELLS

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From all known photosynthetic organisms the green sulfur bacteria are able to survive under the lowest illumination conditions, illustrating the effectiveness of their photosynthetic apparatus. The highly efficient transport of excitons, formed on absorption of solar light, through their chlorosomes towards the reaction centers originates from self-assembly of the bacteriochlorophyll molecules. Excitons are able to make typically $5 \cdot 10^2$ hops from one to an adjacent bacteriochlorophyll molecule before decay to the ground state would occur, which is sufficient to collect most excitation energy at the reaction centers. Crucial for self-assembly of the bacteriochlorophyll molecules are the coordinative bonds between electron-donating side groups and the electron-accepting metal atom in the center of the molecule, combined with π - π interactions between the bacteriochlorophyll macrocycles. An intriguing question is whether this self-assembled structure could be mimicked in order to realize efficient exciton transport in artificial light-harvesting systems. In this work we studied the relationship between self-assembly of artificial chromophores and the ability to transport excitons efficiently to an active interface, where excitons are dissociated into charges. One of the self-assembling porphyrin derivatives investigated is {meso-tetrakis[3,5-bis(methoxymethyl)phenyl]porphyrinato}zinc(II) (CH_2-O-CH_3) (Fig. 1). Self-assembly is accomplished by the coordinative bonds formed between the electron-donating side group at the 3 or the 5 position of the phenyl groups and the electron-accepting metal atom in the center of the porphyrin molecule.

The molecular organization in thin spin-coated films has been elucidated using various optical techniques combined with X-ray diffraction. From these results it turns out that CH_2 -O- CH_3 molecules form self-assembled stacks. In contrast, {*meso*-tetrakis[3,5-bis(t-butyl)phenyl]porphyrinato}zinc(II) (*t*- C_4H_9) (Fig. 1) molecules that lack the electron-donating groups do not self-assemble. Exciton transport through the porphyrin film (2) and dissociation at the interface with TiO₂ (3), resulting in the formation of charges, has been studied using the Time-Resolved Microwave Conductivity (TRMC) method.[1] Excitons formed in the self-assembled CH_2 -O- CH_3

film on TiO₂ are dissociated efficiently into charges; the Incident Photon to Charge Separation Efficiency (*IPCSE*) at the absorption maximum equals 16%. In contrast, the isotropic non-assembling $t-C_4H_9$ film on TiO₂ shows an *IPCSE* at the absorption maximum of only 4%. Fitting a model for the photo-induced charge separation efficiency to the TRMC data yields an exciton diffusion length equal to 15 nm for CH_2 -O-CH₃, while for t-C₄H₉ a much shorter exciton diffusion length of only 3 nm is obtained. Combining these data with exciton lifetimes of 160 ps and 74 ps yields exciton diffusion coefficients equal to $1.4 \cdot 10^{-6}$ m²/s and $1.2 \cdot 10^{-7}$ m²/s, respectively. As a consequence, excitons in isotropic t-C₄H₉ layers are only able to make 9 hops before decay to the ground state occurs, while with $3 \cdot 10^2$ hops the transport of excitons in the self-assembled CH_2 -O-CH₃ film appears to be as efficient as in natural chlorosomes. This difference demonstrates the importance of the molecular self-assembly for the light-harvesting efficiency, both in natural organisms as well as in artificial biomimetic systems. The results unambiguously show that the principle of selfassembling chromophores, possessing highly efficient exciton transport in natural chlorosomes, is mimicked successfully in the present artificial light-harvesting system and holds a high potential for future photovoltaics.



Figure 1. Molecular organization of CH_2 -O- CH_3 and t- C_4H_9 on TiO₂ and its influence on processes occurring on optical excitation; 1: illumination resulting in the formation of an exciton, 2: exciton transport and 3: exciton dissociation by injection of an electron into TiO₂. Also shown is the chemical structure of the porphyrin derivatives investigated.

(1) A. Huijser, T.J. Savenije, A. Kotlewski, S.J. Picken and L.D.A. Siebbeles, *Adv. Mater.* **2006**, *18*, 2234-2239.

Nano-structures for improved light management in thin-film solar cells.

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Manipulation of light propagation in solar cells is of great importance in order to further improve their performance. Optical reflection or transmission in a selected wavelength region of the illumination spectrum at particular interfaces in the structure and light propagation in selected directions other than specular is often desired. In this contribution two thin-film based nano-structures are introduced, which have a potential for the manipulation of light propagation in thin-film solar cells: (i) one-dimensional photonic-crystal-like structures and (ii) diffraction gratings.

The photonic-crystal-like structures (PC) based on thin layers such as a-Si:H, ZnO, SiN_x, SiO_x, and TiO₂ demonstrate wavelength-selective high reflection or transmission in the visible and infra-red part of the spectrum. The advantage of these materials is that they can be deposited at low temperature (< 200°C). We show that the key issues for manipulation of reflection or transmission in a selected wavelength region are thicknesses, refractive indexes and a number of the individual layers used in the PC structures. The design rules for 1-D PC that result in a high broad-band reflection will be presented. The application of these 1-D PC as highly reflective back reflectors in thin-film silicon solar cells results in a noticeable increase of photo-generated current.

Periodic diffraction gratings have a large potential for efficient light scattering into large angles. These gratings are based on periodic perturbations of the surface morphology. The effect of the height and period of simple periodically-structured rectangular gratings on light scattering parameters – haze and angular distribution function of scattered light – is presented. Rectangular metal gratings based on thin aluminium layers with the period in a micrometer range have been fabricated and optically characterised. Optimal properties of such gratings for their implementation as a back reflector in thin-film silicon solar cells will be presented.