

Electronic properties of Nano-porous TiO₂- and ZnO-Thin Films-comparison of simulations and experiments

Wilfried Wunderlich^{a,*}, Torsten Oekermann^b, Lei Miao^c, Nguyen Thi Hue^d, Sakae Tanemura^c and Masaki Tanemura^c

^aNagoya University, Dept. of Molecular Design and Eng., JST-CREST, Chikusa-ku, Nagoya 464-8603, Japan

^bUniversity of Hannover, Institute of Physical Chemistry and Electrochemistry, 30167 Hannover, Callinstrasse 3-3A, Germany

^cNagoya Institute of Technology, Dept. of Environmental Technology, Showaku Nagoya 466-8555, Japan

^dInstitute of Environmental Technology, NCST, Hoang Quoc Viet Rd 18, Cau Giay Hanoi, Vietnam

The electronic properties of anatase, rutile and ZnO thin films are of interest for many applications such as photocatalysis, or dye-sensitized solar cells. This paper describes the correlation between microstructure and electronic properties of photoactive TiO₂ and ZnO thin films, which are based on experimental data and are interpreted by *ab-initio* simulations. This study considers the influence of three main factors on the optical and electrical properties: Strain of epitaxially grown thin films, nano-particle- and nano-pore- structures, and finally the interface to adsorbed dye molecules. The first part describes the search for a suitable substrate to grow titania layers with a smaller band-gap and *ab-initio* simulations showed excellent agreement to the experimental data. A narrow band gap is predicted for strained lattice constants in the a-direction and compressed in the c-direction. The second part describes the fabrication of nano-porous thin films by sol-gel processing using appropriate precursor solutions (titanium-tetra-iso-propanol (TTIP), di-ethanol-amine (DEA)) applied on suitable nano-templates. Due to the surface curvatures the nano-porous TiO₂ has a narrow band gap, while nano-particles of titania show a larger band-gap. In the third part Dv α *ab-initio* simulations were applied to dye-sensitized solar cells (DSSC), based on ZnO and TiO₂. The results are compared to experimental data obtained for different dyes on nanoporous electrodeposited ZnO films. The ranking in efficiency found experimentally for the different combinations could be explained by the calculation results. This finding is discussed in the view of further optimization of solar cells.

Key words: *Ab-initio* calculations, band gap, electronic orbitals, epitaxial thin films, nano-porous titania, dye-sensitized solar cells, photo-catalyst.

Introduction

Excitation of electrons by photons in semi-conducting materials like TiO₂ or ZnO provides the base for many photocatalytic, photoelectric or photoelectrochemical applications. Dye-sensitized solar cells (DSSC) [1, 2], photo catalysts [3, 4], optical coatings [5] and electronic devices [6] are fabricated by taking advantage of the superior properties of these photoactive titania and ZnO materials [7-13]. This paper is concerned with optimizing these properties by changing the microstructure with the aid of simulation for three different applications, photoactive thin films, nano porous photo catalysts and dye-sensitized solar cells.

Titanium dioxide in the two phases, anatase or rutile, possesses a high refractive index and high dielectric constant, which is the basis for advanced photo-optical applications. Especially epitaxial thin films have superior optical properties compared with polycrystalline or amorphous films due to the lower defect concentration,

when they are sputtered with advanced technology, like radio-frequency (rf) helicon magnetron sputtering [14-16]. For fabrication of TiO₂ thin films, also several other methods have been applied, such as laser molecular-beam epitaxy (laser-MBE) [17, 18], pulsed laser deposition (PLD) [19, 20], metal organic chemical vapor deposition (MOCVD) [21, 22] and the sol-gel technique [23-26]. The best method for producing optical coatings is epitaxial growth with radio-frequency (rf) helicon magnetron sputtering, which has the advantages of high density, high adhesion, high hardness and good uniformity of the thickness over a large area. During epitaxial growth the lattice parameters of the thin film are adjusted to the substrate until a certain critical thickness is reached, at which point the strain in the lattice becomes so large, that the genuine lattice constants are restored. While this critical thickness is usual about three monolayers [27], titania thin films can be grown epitaxially to thicknesses of more than 150 nm [14]. By choosing a suitable substrate the lattice parameter of the thin film can be altered and the goal is to produce by this method thin films with a narrower band gap.

For purifying indoor and outdoor environments like exhaust fumes or water contaminated with bacteria or

*Corresponding author:

Tel : +81-52-789-5293

Fax: +81-52-789-3201

E-mail: wunder@mail.apchem.nagoya-u.ac.jp

other chemical and biochemical impurities flow-through reactor devices have been successfully produced, which take advantage of the photocatalytic properties of TiO_2 [2-6]. In these devices composite materials are employed, in which titania is coated on glass, tiles, alumina powders [7-10] or recently also alumina fibers [24]. The coating is usually performed by sputtering methods, but recently the cost-reductive sol-gel technique has been successfully applied as well. The photocatalytic performance of these coatings depends on the morphology of these materials, which is influenced by the preparation method, and especially a large of surface area is required. In this part we focus on the sol-gel technique, by which the pore size and distribution as well as the particles size can be adjusted by changing the processing parameters. The sol-gel technique is a suitable method to produce nano-pores, nano-particles or nano-templates [26]. The properties of these nano-structured thin films strongly depend on the distribution of the pore size and particle size and these investigations are one goal of this paper. Nano-porous titania shows a lower band-gap [28, 29], while nano-particles have a wider band-gap [30]. This controversial effect is also observed in silicon, and shows the bifurcation of physical properties, when nano-dimensions are reached. A similar splitting of physical properties is estimated in the case of Al_2O_3 , MgO : While the surface energy for nano-particles increases beyond a critical radius of curvature, the surface energy for nano-pores decreases [31]. This effect can be used as an engineering tool for developing advanced materials with enhanced properties [26].

The third application considered here in detail are the dye-sensitized solar cells based on TiO_2 or ZnO , which have gained considerable interest in recent years [1, 2]. In DSSC a highly porous inorganic semiconductor film in contact with an electrolyte is sensitized by organic dye molecules, which are adsorbed at its surface. Overall light to electricity conversion efficiencies of up to about 10% have been achieved for cells using nano-

crystalline TiO_2 electrodes, various Ru-complexes as sensitizing dyes and electrolytes containing the I^-/I_3^- redox couple [1, 2]. The conventional method for the preparation of TiO_2 electrodes for DSSC using colloidal suspensions of TiO_2 - nano-particles typically includes high-temperature sintering at 450 or 500 °C, which is necessary to remove organic sinter-additives used to establish a good connection between the TiO_2 particles. Besides TiO_2 , ZnO is a promising candidate for use in DSSC [7-13]. While Ru-complexes were found to be the best sensitizers for TiO_2 , eosin Y [11, 13] showed the best performance for ZnO with an Incident Photon to Current Conversion Efficiency (IPCE) of 92%. In recent years, one-step electrodeposition of ZnO from aqueous zinc salt solutions in the presence of water soluble dyes has been shown to provide a valuable method for the preparation of new inorganic/organic hybrid materials at low temperatures [7-13]. The influence of the dye molecules on the ZnO deposition causes a great variety of film structures and morphologies, depending on the preparation conditions, e.g. the electrode potential and the kind of dye used. While in some cases the majority of the dye molecules has been shown to end up trapped between or in the ZnO crystals [12], in most cases porous ZnO films with the dye molecules adsorbed on the ZnO surface are formed, making these materials ideal candidates for a use in dye-sensitized solar cells, because of the high interface area density between dye and semiconductor. The search for the best dye is still in progress and the performance of the various dye molecules such as tetrasulfonated metallophthalocyanines (TSPcM) [8, 9], tetrabromophenol blue [10, 11] in the DSSC is the third topic of this paper.

The conventional model of how a DSSC works can be divided into several steps as summarized in Fig. 1: The photons are absorbed with a certain absorption probability, which leads to the excitation of electrons with a certain excitation probability from the highest occupied molecular orbital (HOMO) into the lowest

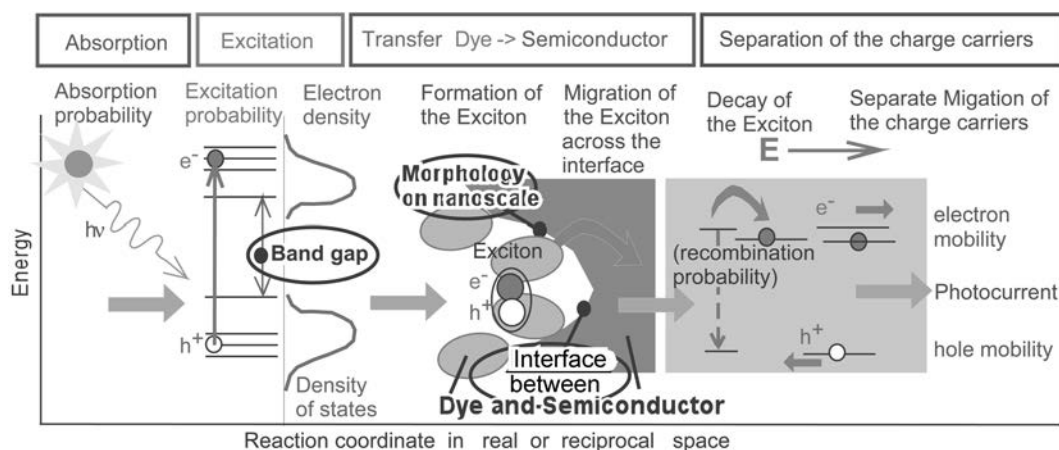


Fig. 1. Model of the origin of the photocurrent with the three main parameters considered in this study.

unoccupied molecular orbital (LUMO) of the dye. The exciton, the hole-electron pair, can be separated, if the excited electron can overcome the interface between the dye and semiconductor. The semiconductor (e.g. TiO₂) has a large band gap and the LUMO of the dye should lie close above it. At the interface the excited electrons can be injected from the dye into the conduction band of the semiconductor, and remain there. In the case of a closed electric circuit, the electrons are flowing to the conducting back contact of the semiconductor film through the outer circuit to the counter electrode, where they are transferred back to the electrolyte and from the electrolyte to the HOMO of the dye molecule. The overall light to electricity conversion efficiency is influenced by many factors such as the surface area, amount of adsorbed dye and absorption coefficient, all of which determine the light harvesting efficiency, and the electron collection efficiency, which is determined by the electron transport properties in the semiconductor including electron trapping and recombination. However, if dyes are adsorbed at the same kind of film and the dye loadings are comparable as it is the case here, the efficiency of the electron injection from the dye into the semiconductor may play a significant role. The physical reasons, however, why some dyes show high electron injection efficiencies, others not, are still largely unknown.

The goal of this paper in all three topics is the comparison between experimental data and calculation results in order to draw conclusions for improving these materials. After describing the phenomenological model of excitation by light, the experimental method and results are briefly described and compared with the simulation results for the three topics considered in this paper, the lattice distortion, the nano-porous microstructure and the dye/semiconductor interface.

Experimental

Epitaxial growth of titania thin films by sputtering

For fabrication of optical titania thin films on different substrates a radio-frequency (rf) magnetron sputtering system (ULVAC MPS-2000-HC3) with a TiO₂ target was used. The substrates were mounted onto a plate ($d = 100$ mm) rotating at 6 rpm, held at a constant temperature (RT to 600 °C) during deposition using an infrared lamp heating the plate from the backside, details are reported elsewhere [14-16]. The optimal conditions for the growth of both, epitaxial anatase and epitaxial rutile films on SrTiO₃ and sapphire substrates were $T_{\text{sub}} = 600$ °C, $P_{\text{tot}} = 0.1$ Pa, $P_t = 160$ W with about 150 nm in thickness.

The phase formation and crystallinity of films were characterized by X-ray diffraction (XRD) with Cu α_1 radiation. The pole figures were determined by a Philips MRD high resolution multi-reflection X-ray diffractometer in triple ψ -axis configuration as ψ - ϕ maps commonly

referred to as pole plots, where the azimuthal angle Φ and horizontal angle Ψ were varied in the range of 0° to 360° and 0° to 90° in steps of 5°. From this pole figure the orientation relationship was determined using a stereographic projection in a Wulff net.

The microstructure of the films was observed by high-resolution transmissions electron microscopy (HRTEM) using a JEOL JEM-2010 electron microscopy at 200 kV with a point-to-point resolution of 0.194 nm. Cross-sectional specimens of the thin films on the substrate were prepared using an ion milling system. The optical properties were measured by variable angle spectroscopic ellipsometry (VASE) using a piezo elastic modulator (UVISE, Horiba, Join-Yebon) in the spectral range of 248 to 1653 nm. The refractive indices n and extinction coefficients k of the thin films were measured as a function of the photon energy and then the optical band gaps calculated using the Tauc formula: $\text{Const}(\hbar\nu - E_g^2) = (4\pi\kappa/\lambda)\hbar\nu$ [14], where $\hbar\nu$ is the photon energy; $4\pi\kappa/\lambda(\alpha)$ the absorption coefficient at wavelength λ , κ the extinction coefficient, under the *ad-hoc* assumption of a predominant indirect allowed transition mode.

Dip-coating by sol-gel method

Nickel sheets (99.99%, Nialco, Japan) were cleaned with ethanol and then deposited with carbon-nano-tubes (CNT) or carbon layers (CL) in a plasma-enhanced chemical vapor deposition (PECVD) chamber, where the flow of ammonia and acetylene gas in a ratio of 2:1 decomposes into carbon and hydrogen with the aid of a plasma, the details are described elsewhere [26, 33, 34]. According to the processing parameters, temperature, electric field of the plasma, and the gas molecule velocity controlled by the inlet gas flow, the microstructure of the deposit changes from amorphous carbon-layers with wavy surfaces or thick or thin carbon-nano-tubes. The microstructure of the deposited layers was characterized by scanning electron microscopy (SEM, JEOL 5600 at 30 kV) and transmission electron microscopy (TEM) JEOL 3010 EX at 300 kV. Whether carbon nano tubes or carbon layers are formed, is controlled by the processing parameters [33, 34], especially the temperature controls the competition of CNT nucleation or CNT growth and only an optimum temperature of about 650 °C leads to fine CNT with a minimum thickness of about 5 nm and a dense and almost homogeneous distribution.

Using these Nickel-Carbon composites as a nano-sized template, thin films of titania were deposited by the sol-gel technique. The precursor solution contains titanium-tetra-iso-propoxide (TTIP), ethanol (both from Wako Pure Chemical Ltd.), and di-ethanol-amine (DEA, Kishida Chemical Company) and 6 h after mixing the hydrolysis reaction is completed. The specimens were dipped slowly in this liquid, removed, and dried vertically in air for 24 h, allowing the gelation to occur.

By different annealing temperatures the formation of either, anatase phase or rutile phase, can be controlled [24, 26]. This sequence of dip-coating and annealing was applied either one time or three times. The specimens were characterized by X-ray diffraction (XRD) Rigaku Rint2000 using Cu-K α and the JSPS data base for indicating the diffraction peaks.

Preparation of ZnO/dye films

Experimental data for comparison with our calculation results were taken from [13]. The film preparation is described in detail in [11]. In short, ZnO and eosin Y were deposited from an aqueous mixed solution of 5 mM ZnCl₂, oxygen (saturated), 0.1 M KCl and 50 mM eosin Y at pH = 6 and 70 °C. The working electrode was F-doped SnO₂ (FTO) coated transparent conducting glass, while a Zn counter electrode and an SCE reference electrode were used. Potentiostatic electrolysis was carried out at -1.4 V vs. SCE. The deposited films were rinsed with water and dried under air at room temperature. For re-adsorption of the dye, the films were soaked into dilute KOH solution (pH = 10.5) to extract the eosin Y molecules. Then the films were refluxed in ethanolic solutions of eosin Y or other dyes [13]. The ultraviolet-visible (UV-vis) absorption spectra of the films were measured in transmission on a Shimadzu UV-160A spectrophotometer. The amount of dye loaded into the film was determined from the UV-VIS absorption spectrum of a solution prepared by dissolving a known area of the film into a known volume of concentrated ammonia aqueous solution [11, 13].

Method of Calculation

The so-called *ab-initio* or first-principle simulation methods calculate the interaction of all electrons in the potential of the atomic cores based on the density-functional theory (DFT). The solutions are wave functions and their summation leads to the spatial charge density distribution for each orbital. The *ab-initio* method as a suitable method to calculate atomic orbitals has been applied for titania as well as dye-semiconductor interfaces. In previous *ab-initio* calculations [35-37] the electron transfer at the anatase and the N3 dye has been calculated. The number of covalent bonds between the eosine dye molecules and the zinc oxide surface was varied [38], and cases with one or two bonds were compared. For the cases with two bonds the number of electronic orbitals increased, namely the interaction of the electron wave functions between organic dye and semiconductor leads to the formation of many new molecular orbitals or abolition of atomic orbital degeneration. Changing the rotation of the dye molecule, however, has less influence on the orbitals. The goal of this paper is to compare the electronic orbitals of different interface combinations.

The Vienna *ab-initio* simulation package (VASP) [39-

41] was used to calculate the density of states (DOS) of anatase and rutile. The ultra-soft pseudo potentials for titanium and oxygen atoms from the Vasp library allow calculations of the orbital band structure with high precision. The energy versus volume $E(V)$ -plot showed almost the same equilibrium lattice constants as the literature data for both phases, anatase and rutile. This software does the calculation in reciprocal space, and the version used was limited to supercells with a size of less than $1 \times 1 \times 1$ nm, which contained about 40 atoms.

Other calculation methods used in this paper were the so-called discrete variational X-alpha (DVX α) method [42], in which a preliminary factor is assumed to solve the differential equations and in several self-consistent cycles the solution of the electron charge density and orbital occupation is calculated with not much less accuracy than in the sophisticated software programs. The software program calculates the interaction for all electrons of the atoms in real-space within a certain cluster, whose radius was chosen as 0.5 nm, a compromise between reliability and feasibility of the calculation. The cluster contains about 50 atoms with its ca. 120 wave-functions. The influence of the charge from more distant atoms was considered by the Madelung potential. This was performed by constructing a super cell of $4 \times 2 \times 2$ nm with about 570 to 700 atoms, where the crystal of the semiconductor lies in the lower part, the organic molecule in the upper part, connected with one covalent bond. The charge neutrality in the cluster and calculation cell was maintained.

Results

Bandgap of Titania thin films

The high quality of single-crystal films fabricated by rf helicon sputtering was confirmed from the appearance of the sharp peaks in the XRD scan. From the XRD pole figure plot the orientation relationship for case a) (100)_SrTiO₃//(100)_Anatase, [001]_SrTiO₃//[001]_Anatase and for case b) (110)_Al₂O₃//(100)_Rutile, [00.1]_Al₂O₃//[010]_Rutile were determined [14] and a schematic drawing of these orientation relationships is shown in the insets of Fig. 2. TEM observations confirmed the perfect crystallinity and epitaxy of the thin films [14]. The diffraction patterns were identified and could confirm the previously mentioned orientation relationships. The lattice spacings, d , of the low-index lattice planes were measured from both, diffraction as well as HRTEM micrographs as described in detail elsewhere [14]. From the d spacing values obtained, the lattice constants of the thin film were estimated as $a = 0.366$, $c = 0.970$ nm, for anatase on SrTiO₃, and $a = 0.446$ nm, $c = 0.312$ nm for rutile. Hence, in both cases, the c -spacing is contracted compared to the bulk-value, while the a -spacing is expanded.

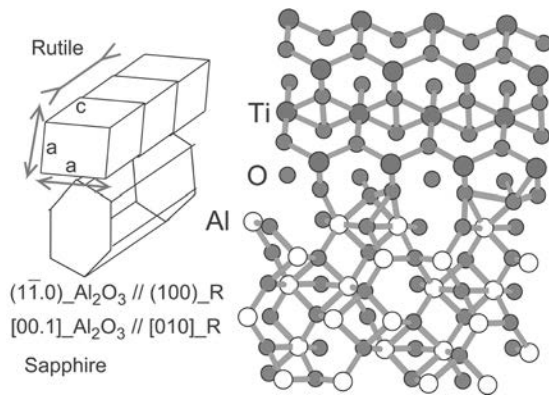


Fig. 2. Orientation relationship, strain and atomistic model of the epitaxial rutile thin film on sapphire (11.0)Al₂O₃.

The optical properties of the prepared films were characterized by spectroscopic ellipsometry; the details of the optical evaluation process are reported elsewhere [14]. By analyzing the spectral dependence of the refractive index n and extinction coefficient k according to the Tauc formula, Fig. 3 is derived, showing that the band gap of a) anatase thin films is estimated as 3.39 eV and b) rutile thin films as 3.37 eV, in both cases larger than the bulk values, 3.20 and 3.03 eV, respectively. This is in good agreement with literature data on other titania thin films [20-22].

Using *ab-initio* calculations the density of states (DOS) was plotted and the gap between the oxygen 2p-states and the titania 3d-states was estimated [32] by assuming a threshold value of 0.3 of the maximum of the DOS as shown in Fig. 3. The calibration of this value was obtained from calibrating the band gap to the experimental value of the band gap for bulk-rutile of 3.03 eV. Using this method, the band-gap of bulk-anatase was obtained as 3.20 eV in excellent agreement to the experiments. This calibration method is using the *ad-hoc* assumption, that a certain density of electrons is required to show an effect in the experiment. The *ab-initio* simulations were performed using supercells strained or compressed in a - or c -directions, which is a model for the distortion of the thin film on the substrate. The density of states as a function of the energy is shown in Fig. 3, where the lattice constant a for anatase is varied compared to the underlined bulk value of $a = 0.3785$ nm as shown on the right side of

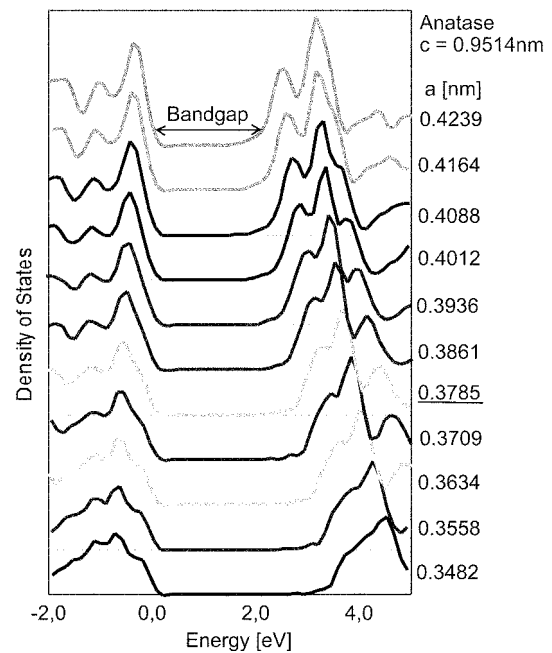


Fig. 3. Density of states as a function of the lattice constants and calculation of the band gap.

Fig. 3. The band gap increases when the lattice constant a is decreased (Table 1).

Further calculations were performed for a wide range of variations of the lattice constants a and c as shown in Fig. 4. for the three TiO₂ phases, a) anatase, b) rutile, c) brookite and d) ZnO with a Wurtzite structure. Fig. 4 shows the width of the band-gap (z -axis) as a function of the lattice constants a and c (x - and y -axis). For brookite with its orthorhombic structure the variation of the lattice constant $b = 0.5145$ nm was not considered and kept constant. The experimental data for the bulk are in excellent agreement, as well as the thin films anatase on SrTiO₃ (Fig. 4a) and rutile on Al₂O₃ (Fig. 4b) as marked with the dark dots in region A, which means a slight increase in the bad gap. The distortions in regions A and B cause a moderate increase in the lattice energy [32], while those in region C, D cause a steep increase, indicating the instability of such distorted lattices, so that they will presumably not grow epitaxially. The desired smaller band gap lies in region B, which can be achieved by decreasing the lattice constant c . For anatase and rutile the decrease in band

Table 1. Experimental results of the correlation between lattice constants and optical band gap of anatase and rutile thin films [14]

Substrate	Orientation Relationship S=Substrate, An=Anatase, Ru=Rutile	Lattice constant		Band gap [eV]
		a [0.1 nm]	c [0.1 nm]	
Anatase-bulk		3.785	9.514	3.20
Rutile-bulk		4.593	2.959	3.03
SrTiO ₃	(100)_S// (100)_An, [001]_S// [001]_An	3.660	9.760	3.51
α -Al ₂ O ₃	(11.0)_S// (100)_Ru, [00.1]_S// [010]_Ru	4.460	3.120	3.37

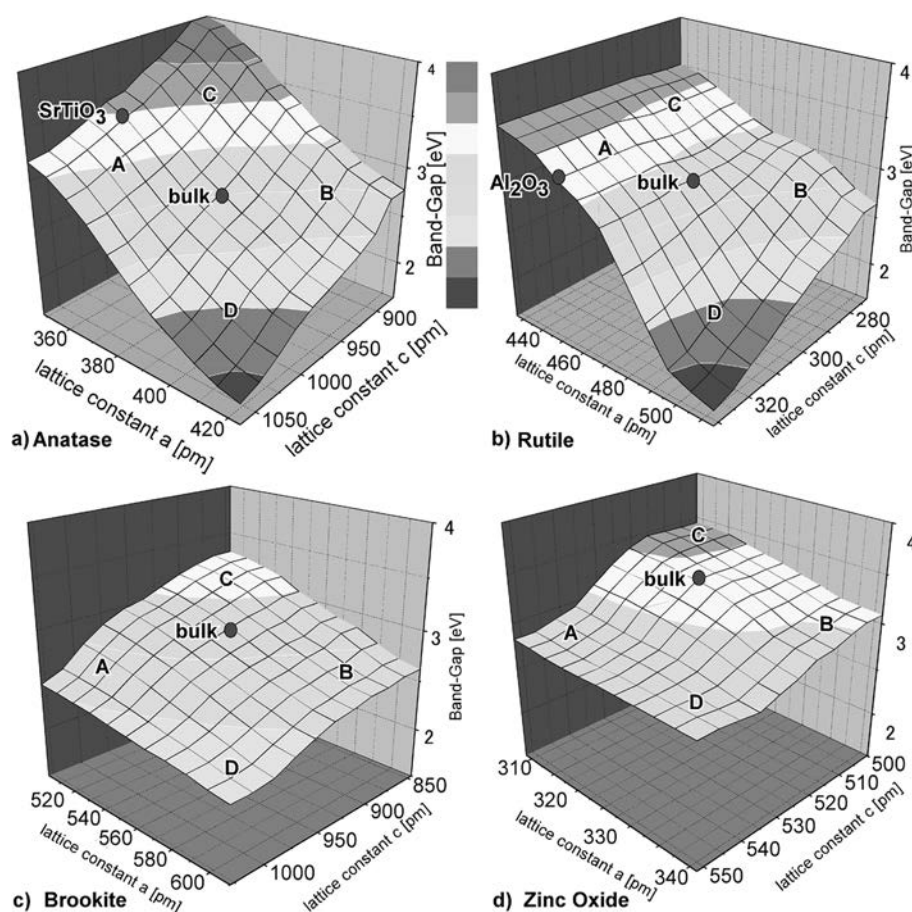


Fig. 4. Calculated band gap as a function of the lattice constants *a* and *c* for a) anatase, b) rutile, c) brookite, and d) zinc oxide. Experimental values are marked as dark dots for bulk and for thin films grown on SrTiO₃ or Al₂O₃.

gap width is rather steep, while for brookite or ZnO it is shallower.

Bandgap of Titania nano-structures

Ni-sheets deposited with Carbon layers (CL) or carbon nano tubes (CNT) show XRD peaks at 47° or at 27° and 55°, respectively [26]. After dip-coating of the titania thin films, these carbon peaks become weaker, and additionally the titania peaks, namely anatase or rutile phase appear. Specimens sintered at moderate temperatures show at 25° the anatase (101)- and at 37° the anatase (112)-peak, and specimens sintered at higher temperatures show the following rutile peaks, (100) at 24°, (110) at 27°, (100) at 32°, respectively, all peaks are in excellent agreement with bulk data. The micro-structure of the titania thin films as characterized by SEM is shown in Fig. 5 for specimens dip-coated three times and is homogenous over large areas. The surface is rough and consists of many pores, whose shape depends on the substrate (CL or CNT) or the annealing conditions. The roughness is large for anatase on CL (Fig. 5a) or rutile on CL after one time dip-coating (Fig. 5c), but rather round-shaped pores are observed for rutile on CL or CNT (Fig. 5b and d). The size as deduced from the SEM micrographs is in all specimens

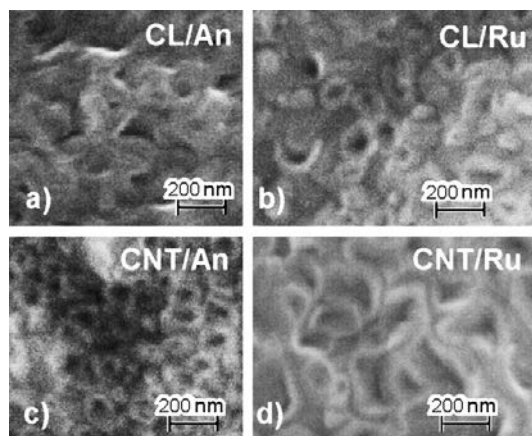


Fig. 5. Nanoporous anatase (An) and rutile (Ru) thin films on carbon layers (CL) or carbon nano-tubes (CNT).

around 50 nm, except in rutile on CNT around 100 nm (Fig. 5d). The larger pore size and the rounder shape of the pore rims in the case of rutile can be explained by the enhanced diffusion at the higher annealing temperature compared to that for anatase. The results show, that nano-porous titania thin film composites can be manufactured and the pore size and rim curvature depend strongly on the microstructure of the CL or

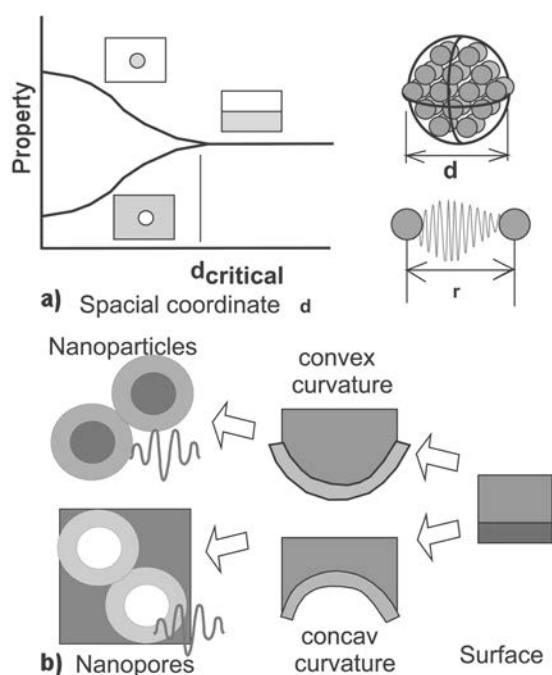


Fig. 6. Bifurcation of physical properties for nano-pores and nano-particles as deduced from previous calculation.

CNT template as further explained in the following.

The desirable band-gap of the titania films for the application in photocatalysis and some photoactive devices should in general be as narrow as possible. It is known from the literature that in the case of nano-porous titania in both phases, anatase and rutile, the band-gap is lowered [28, 29], while for titania nano-particles the band-gap increases [30]. This seems to be a general physical principle, as illustrated in Fig. 6: Concerning any physical property, like the band-gap in titania or the surface energy [31], there is a bifurcation, whether the structure consists of nano-particles or nano-pores. When the diameter d of the particles or pores drops below a critical limit, the energy is increased for nano-particles or decreased for nano-pores. This opposite behavior can be explained by the fact, that the structural diameter d of the pore or the particle becomes similar in size to the interaction distance between the atoms r (Fig. 6a). The microstructural feature, which distinguishes nano-pores from nano-particles, is the bending of the surface (Fig. 6b). If a surface is bent in a convex shape, it becomes finally a particle; when it is bent concave, a pore is formed. The conclusion from this consideration is, that a buckling thin film, like the titania films in the present experiments, with a large amount of strongly bent convex areas should behave similar to nano-particles, and those with a large amount of concave bent areas should behave similar to nano-pores. The bending of the thin film presented in this paper, can be adjusted by the spacing of the CNT s , their thickness d , and the thickness of the titania thin film t , resulting in a certain pore radius $p = s - d - 2t$ [26] and strongly bent areas of both types, concave and convex, can be

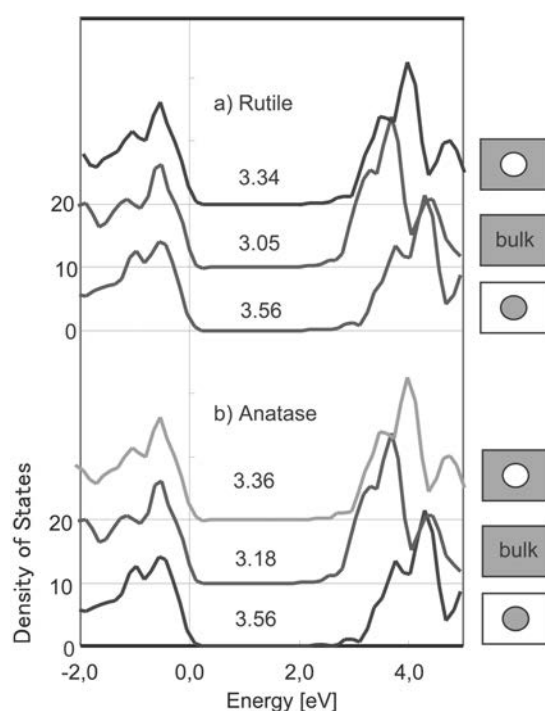


Fig. 7. Calculation results for the bandgap of a) rutile, b) anatase for nano-pores (top), bulk and nano-particles (bottom) with a radius of the pores and particles of 0.34 nm.

obtained by a narrow spacing s and small d . Comparing the experimental micrographs, this is the case for anatase films on CNT, although the value for s of about 50 nm is still far from the 10 nm limit, where the quantum size effects will occur. It is expected that only specimens with strongly bent concave areas behave like nano-porous titania, namely show a narrower band gap and, hence, are promising materials for improving the efficiency of photovoltaic devices.

The *ab-initio* calculations using VASP were performed on nano-pores and nano-particles both with a radius of 0.34 nm embedded in a supercell with $2 \times 2 \times 4$ unit cells rutile or $2 \times 2 \times 1$ unit cells anatase which corresponds to a supercell dimension of about 1 nm in each direction. The results of the DOS-calculations are shown in Fig. 7a) for rutile and Fig. 7b) for anatase. For both materials the estimated band gap for nano-particles is remarkably larger than the bulk value, while the band gap for nano-pores is only slightly larger, but the expected decrease could not be confirmed, possible reasons are discussed later.

Organic dyes on Semiconductor surface

The highest efficiencies were obtained with films made with the dye eosin Y, because in this case an extraordinarily high surface areas of nano-porous ZnO and high dye loadings were achieved [11]. When the eosin Y was extracted and absorbed again from ethanol solution, the conversion efficiency was even higher, because the dye molecules formed a well-ordered monolayer at the surface. Instead of Eosin Y, other dyes

Table 2. Experimentally measured data for short-circuit current (I_{sc}) and Incident Photon to Current conversion Efficiency (IPCE) of different substrate/dye combinations [13]

ZnO/Dye	Eosin	Coumarin	N3-Ru	TSPcSi	Tetrabromo
I_{sc}	5.9	4.0	4.0	0.8	0.7
IPCE	92	87	33	10	8

could be “re-adsorbed” as well to a film, which was prepared with eosin Y as a kind of “template” [13]. However, other dyes perform less well than eosin Y, as can be seen in Table 2, which shows the short-circuit current (I_{sc}) and Incident Photon to Current Conversion Efficiency (IPCE) of different dyes on nano-

porous ZnO surfaces. The highest photocurrent is observed for the combination eosin/ZnO (Photocurrent 5.94 mA cm^{-2} , IPCE 92%), and is similar for coumarin, but only a rather small photocurrent is observed for N3-Ru-complex, TSPcSi and tetrabromophenolblue.

The modeling of the interfaces between the organic dye molecules and the semiconductor surface considered five different organic dye species on five different surfaces, as shown in Fig. 8. In this paper one covalent bond between dye and semiconductor was assumed to occur, and the changing parameter is the organic molecule species, namely the five dye species, eosin (Fig. 8a-c, h), coumarin (Fig. 8d), tetrabromophenolblue (Fig. 8e), TSPcSi (Fig. 8g) and N3-Ru-complex (Fig. 8f, i), where large bright atoms are Br, large dark Na,

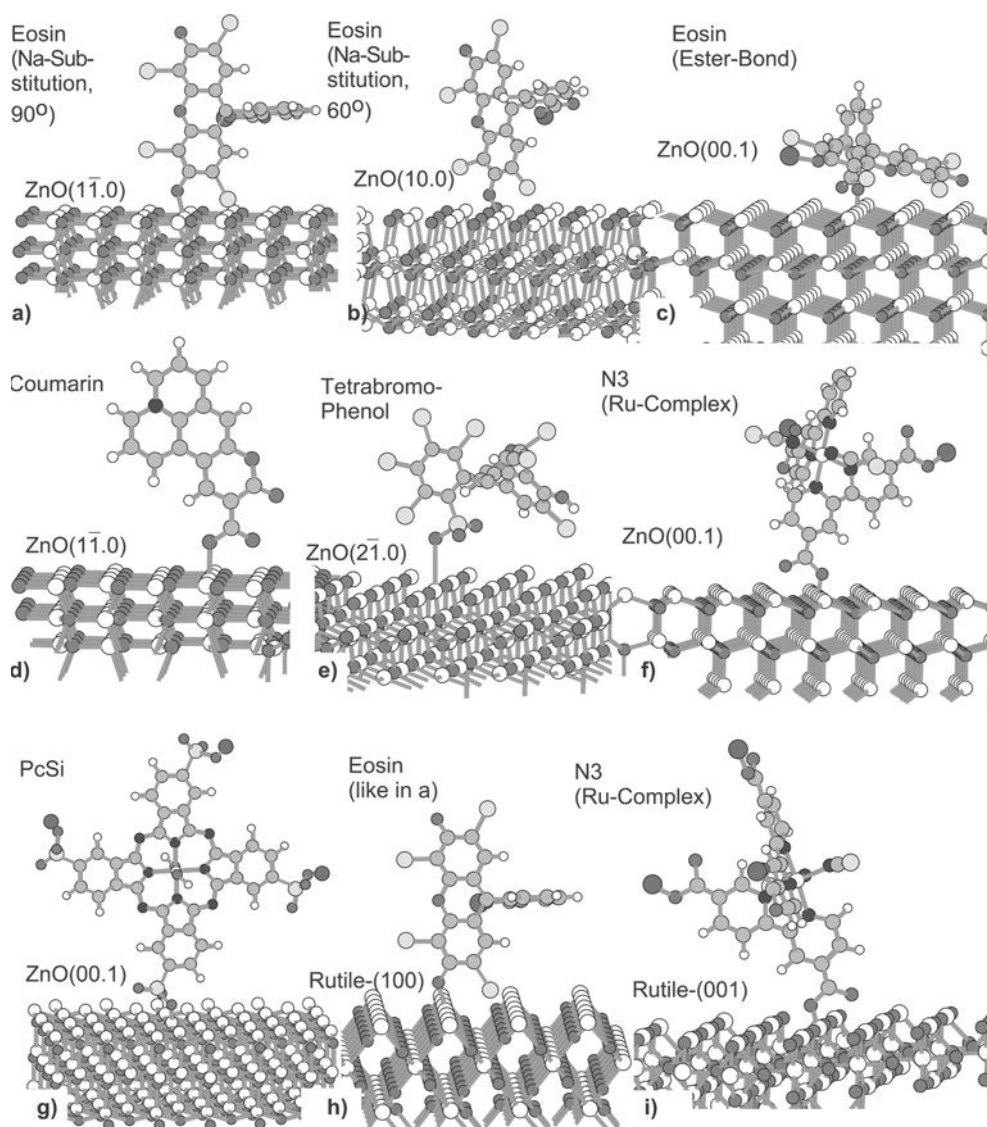


Fig. 8. Models of interfaces used for *ab-initio* calculations, upper half the dyes a, b, h) Eosin bond via OH-group, c) Eosin with Ester bond, d) Coumarin C343, e) Tetrabromophenolblue, f) N3-Bis[(4,4'-dicarboxy-2,2'-bipyridine) thiocyanato]Ru(II) Ru-Complex, g) 2,9,16,23-Tetrasulfophthalo-cyaninatodi-hydroxosilicon(IV), bonded to the surfaces a) ZnO ($1\bar{1}.0$), b) ZnO (10.0), c) ZnO (00.1), d) ZnO($1\bar{1}.0$), e) ZnO ($2\bar{1}.0$) f) ZnO(00.1), g) ZnO(00.1), h) Rutile (100), i) Rutile (001). All combinations between these molecules and interfaces were modeled.

bright C, dark O, and small H, details are shown elsewhere [38]. The molecules are optimized to the lowest energy configuration using well-known force fields. Three types of bonds occur: 1) Ester bond via one O atom of a $-\text{COOH}$ or $-\text{SO}_3\text{H}$ group, 2) bond via the O atom of an $-\text{OH}$ group, 3) breaking of a double $\text{C}=\text{O}$ bond and formation of an $-\text{O}-\text{Me}$ bond. The last case is the most unlikely to occur and only the second and the most likely to occur first case were considered here (Fig. 8c and 8a, b). The difference between the case in Fig. 8a and 8b is the bonding angle, 90° or 60° , between the ZnO surface and the outstanding bond to the Eosin molecule. These three variants occur only in Eosin, at the other four molecules the Ester bond perpendicular to the surface occurs. Hence, in total seven variants for the organic side were considered.

For the semiconductor side, ZnO with the Wurtzite structure with (11.0), (10.0), and (00.1) surfaces, and TiO_2 with the rutile structure with (100) and (001) surfaces were modeled, as shown in Fig. 8. In the case of polar surfaces like in Fig. 8c, f, h only those with the metal (Zn or Ti, white circles) on top were considered. The supercell would require at least $1 \times 1 \times 2$ nm with about 600 atoms to maintain the periodicity as shown in Fig. 9. For the *ab-initio* calculations the real space software Dvxa was used, which can treat all the electrons of about 60 atoms in a radius of 0.5 nm as marked in Fig. 9, but including the Coulomb potential of all other surrounding atoms. For comparison the calculation results of the density of states for bulk-rutile are shown in Fig. 10a together with results of the more exact Vasp (Fig. 10b) program. The band gap clearly visible in the accurate calculations is smeared out in the Dvxa calculations and in spite of this lack in accuracy, the conclusions in the following section are meaningful, because titania is one of the worst cases for the DOS with its steep descent near the band-gap (Fig. 10), while for ZnO the agreement between these calculation methods is much better.

All of these combinations between semiconductor surfaces and organic molecules (7×6 variants for the

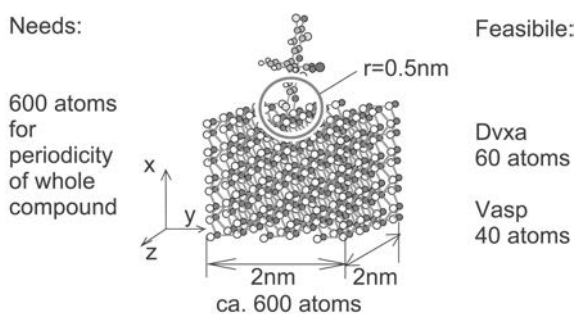


Fig. 9. Size of simulation cell for the Madelung potential and size of the cluster ($r = 0.5$ nm) for the *ab-initio* calculations.

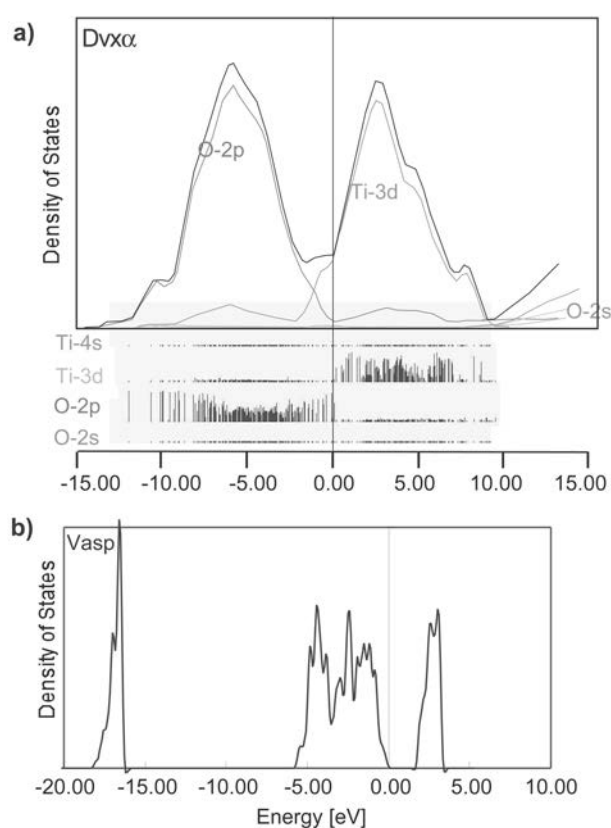


Fig. 10. Comparison of the density of states for rutile calculated with different software programs a) Dvxa, b) Vasp.

ZnO-compound, 7×2 for TiO_2) were modeled and the DOS calculated. All the three cases of Eosin on ZnO (Fig. 8a, b, c) show a significant reduction of the band gap by about 1 eV, also Coumarin on ZnO, while N3 Ru-complex, TSPcSi and tetrabromophenol blue on ZnO surfaces show about the same unchanged DOS as in bulk ZnO, indicating, that there is not much interaction between the organic molecule and the substrate. Figure 11 shows the comparison between bulk ZnO (Fig. 11a) with the ZnO-Eosin interface (Fig. 11b). Instead of the clear band gap in the case of bulk-ZnO many intermediate orbitals appear, as C-2p and O-2p, which lead to a large change in the DOS. For the TiO_2 surface, only the N3-Ru-complex on TiO_2 (Fig. 11d), shows a remarkable change in the DOS compared to bulk-rutile (Fig. 11c) indicating a strong charge exchange due to bond interaction. Comparing this result with the experimental data in Table 2, it is remarkable, that the cases with large IPCE are exactly those cases in which many new orbitals are formed and a strong interaction between the molecules occurred. This perfect agreement between high efficiency and a large number of orbitals allows some conclusions and predictions for improving the solar cells.

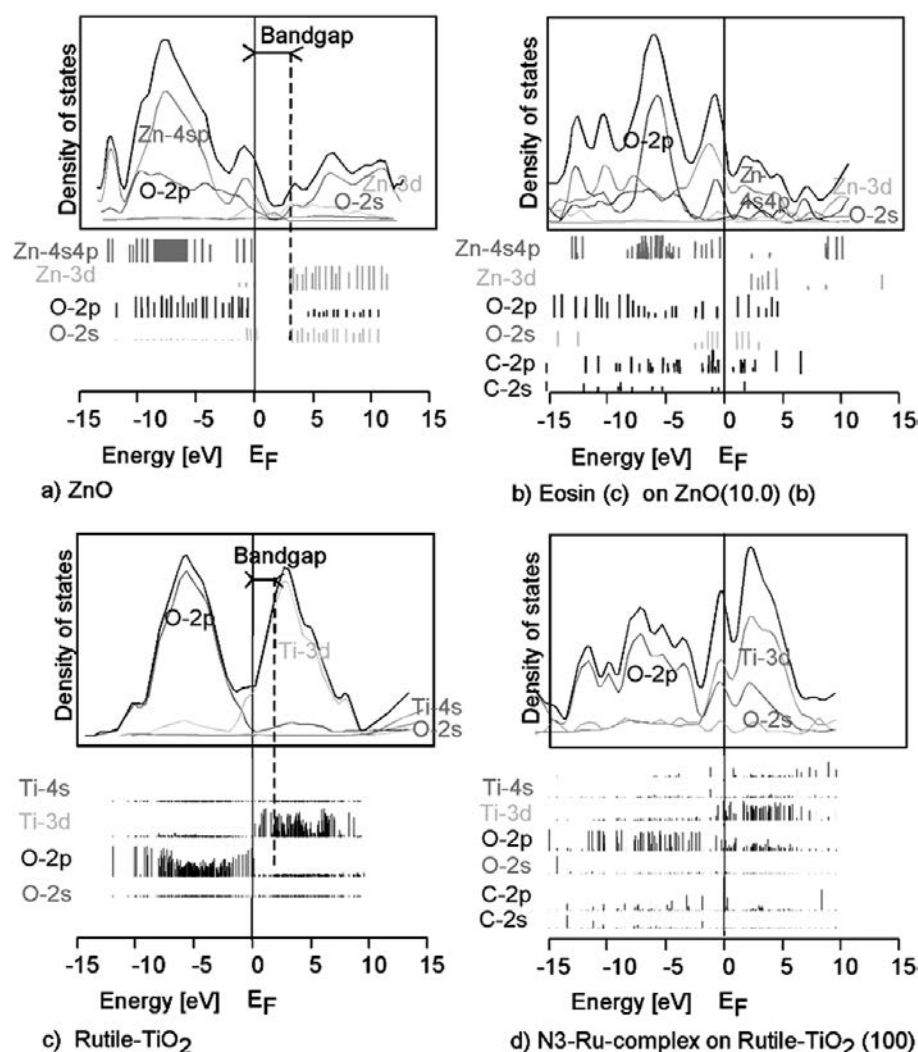


Fig. 11. Density of states and molecular orbitals for a) bulk-ZnO, b) eosin (in orientation of case in Fig. 8c) on ZnO (10.0) surface (case of Fig. 8b), c) Rutile-TiO₂, d) N3-Ru-dye on Rutile-TiO₂ (100).

Discussion

In this paper three microstructural features were considered to improve the performance of photoactive devices. A narrow band gap is considered as one important factor for increasing the efficiency of light energy into photocurrent, but also the occurrence of additional energy orbitals is helpful, as the results of the dye-semiconductor interface show. The desired decrease in the band gap width can be achieved by the three mechanism discussed in the following, lattice constant manipulation, nano-pore or nano-particles, or the choice of a suitable dye.

The band gap calculations as a function of the lattice constants (Fig. 4) show very good agreement to the experimental values, as the bulk values for anatase and rutile and those for thin films on two different two substrates match very well with the calculated values. The band gap increases due to expansion of the lattice constant c , while the lattice constant a has a smaller

value than the bulk, in agreement with the experimental results and literature values [13-16]. The calculation results show, that the desired decrease of the band gap requires the opposite, expansion in the a -direction and shrinkage in the c -direction. The decrease in band-gap can be presumably achieved in the experiment, when the lattice constants are shrunk moderately as in region B of Fig. 4, which still has only a slight increase in lattice energy due to the strain of the lattice constants and indeed the low-energy regions A and B are regions with almost no change in the volume of the unit cell and it is a challenge to find a suitable substrate sustaining these constrictions for the epitaxial film. Assuming a manipulation of lattice constants up to a limit of about 10% as usually obtained in epitaxial thin film growth experiments before misfit dislocations are formed, the predicted values for the achievable decrease in band gap is about 2.7 eV for strained rutile-thin films compared to 3.03 eV for bulk-rutile, 2.9 eV for anatase thin films compared to the bulk-value 3.2

eV for anatase, 2.8 eV compared to bulk-brookite 2.96 eV, but only about 3.1 eV for zinc oxide thin films compared to 3.2 for bulk.

The microstructure of photoactive films has also still a potential for improvement. As proposed in chapter 2, nano-porous materials are better than nano-particles, for two reasons, the smaller band-gap and the enlarged interfacial area between dye and substrate. Experimental observations [28, 29] confirmed, that in the case of the films containing nano-particles the photocurrent is larger than in large-grain specimens. The reduction of the particle size has the advantage that the connection between the particles is better than in the case of larger sized particles, and hence the electron transport properties are improved. Whether nano-pores or nano-particles support a decrease in the band-gap, needs further investigations experimentally as well as by calculations. The results presented here, which showed a band-gap increase for nano-particles but not the expected decrease for nano-pores, were performed with unrelaxed atomic positions at the surfaces and this atom shift into low-energy positions at the strongly curved surfaces seems to have another significant contribution to the electronic states to be studied. The convex curvature at nano-particles or the concave curved surfaces of nano-pores, both lead to a complicated three-dimensional inhomogeneous distribution of matter, which affects the electronic wave functions (Fig. 6). This effect, for which analytical equations are still not available in theoretical physics, becomes remarkable, when the radius of curvature is comparable to the distance of atomic interaction or the effective length of the electronic wave-functions, which is about 1 nm. In nano-size structures the atom surrounding deviates far from the periodic one in crystals and, hence, the bond length distribution becomes broader similar to the bond length increase of about 10% at grain boundaries [43]. Also atoms at the surface have enhanced vibrational modes similar to that found in grain-boundaries [44]. Both effects increase the number of orbitals by weakening their mutual bond, and this can be achieved by reducing the grain size towards nano-scale or even quantum-dot structures.

Detailed *ab-initio* calculations of the dye/semiconductor interfaces should focus on the spatial distribution of orbitals [35-37], the results obtained here give meaningful outlines, namely that the experimentally most effective combinations show characteristic features in the electronic spectra, that is an increase in the number of atomic orbitals and a high density of states, indicating a stronger interaction and the occurrence of new bonding orbitals. Hence, the main statement is, the efficiency of the light absorption and the resulting photocurrent increases, when more orbitals with a high density are available, or in other words many orbitals provided, helps to increase the photocurrent. With this statement the conclusions of a previous study about the influence

of the number of eosin bonds on ZnO [38] can be extended: Comparing the dye-semiconductor interface with one covalent bond with that with two bonds, the charge exchange increased by an increased number of orbitals in the ground and excited state. Considering now the main conclusion of the present study, namely more orbitals lead to more possibilities for excitations, leads to the conclusion, that the bonding between dye and substrate should be enforced in order to increase the solar cell efficiency. The goal of further research is to find dye molecules, which are bond strongly, rather chemisorbed than physisorbed on the ZnO surface, mainly to increase the photocurrent across the interface, but also the stability of the compound.

This conclusion stimulates the search for new promising dyes, like cyanine dyes, Carbon-derivates with dangling bonds or others. Eosin with less stable organic bonds was found to be the best candidate for this purpose in the case of ZnO. In the case of eosin the organic ring is not a genuine benzene ring, but contains an O-atom replacing one of the six Carbon atoms with their alternating valence. Hence, this electron configuration deviates rather far from the stable pure covalent bond valence and lets the electrons easily leave the molecule for migration into the bonding substrate. Taking the experience of semiconductor band structure analysis into consideration, a shift of the band gap towards negative energies means that electron pockets occur, or in other words, these electrons have a rather high effective mass in the ground state, but can easily migrate, when they are excited. This shift of the band gap to negative energies occurs, when the material is doped with electron donators. In the case of an electrolyte this occurs, when the pH is shifted to low pH values. The present calculations showed that almost all combinations with eosin have the band-gap shifted towards negative energies, indicating that electron transport seems to be the main conducting mechanism, in other words, electron injection into the n-type semiconductor and electron transport away from the interface become easier. The other possibility that electric conduction by holes is unlikely to occur and happens, when the band gap lies at positive energies, like in most of the other cases, Tetrabromol, TSPcSi and N3 dye on ZnO-surfaces. The predictions drawn from the results of this paper are rather obvious and allow the improvement of solar cell devices towards higher efficiency.

Conclusions

This paper described the correlation between optimized materials for solar energy conversion and their electronic orbital configuration. This calibration by comparing experimental data with *ab-initio* calculations could clarify the charge transfer mechanism between dye and semiconductor substrate: A strong bonding overlap leads to a decrease of the band gap and increases the

number of ground and excited states. This conclusion was confirmed for the Eosin/ZnO and N3-Ru/TiO₂ compounds with their high photo efficiency current and their large number of energy orbitals, while with other combinations with lower photo efficiency current do not show this overlap. The strong bonding exchange can be explained by the high number off-valence bonds in the Eosin molecule. These conclusions suggest that the search for new compounds should concentrate on electron-providing organic molecules strongly bonded to the substrate. Furthermore, nano-porous microstructures with large amounts of interfaces and compressive residual stresses also increase electron transport and give some valuable conclusions for optimizing the photo efficiency of photo-active devices.

Acknowledgement

Useful discussions with Prof. Tsukasa Yoshida are gratefully acknowledged.

References

1. B. O'Regan and M. Grätzel, *Nature* 353 (1991) 737-739.
2. M. Grätzel, *Nature* 414 (2001) 338-344.
3. A. Fujishima and K. Honda, *Nature* 238 (1972) 37-38.
4. A. Fujishima and K. Honda, *Bull. Chem. Soc. Japan* 44 (1971) 1148-1151.
5. H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, *Appl. Phys. Lett.* 77[4] (2000) 475-477.
6. Y.H. Lee, *Vacuum* 51 (1998) 503-509.
7. T. Yoshida, K. Miyamoto, N. Hibi, T. Sugiura, H. Minoura, D. Schlettwein, T. Oekermann, and G. Schneider, *D. Woehrle, Chem. Lett.* 7 (1998) 599-600.
8. T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura, and H. Minoura, *Adv. Mater.* 12 (2000) 1214-1217, *ibid* 1219-1222.
9. T. Oekermann, T. Yoshida, D. Schlettwein, T. Sugiura, and H. Minoura, *Phys. Chem. Chem. Phys.* 3 (2001) 3387-92.
10. T. Yoshida, T. Oekermann, K. Okabe, D. Schlettwein, K. Funabiki, and H. Minoura, *Electrochemistry* 70 (2002) 470-487.
11. T. Yoshida, T. Pauporte, D. Lincot, T. Oekermann, and H. Minoura, *J. Electrochem. Soc.* 150[9] (2003) C608-615.
12. T. Oekermann, S. Karuppuchamy, T. Yoshida, D. Schlettwein, D. Wöhrle, and H. Minoura, *J. Electrochem. Soc.* 151[1] (2004) C62-C68.
13. T. Yoshida, M. Iwaya, H. Ando, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, and H. Minoura, *Chem. Comm.* (2004) 400-401.
14. L. Miao, S. Tanemura, P. Jin, K. Kaneko, A. Terai, and N. Nabatova-Gabain, *J. Crystal Growth* 254 (2003) 100-106.
15. S. Tanemura, L. Miao, P. Jin, K. Kaneko, A. Terai, and N. Nabatova-Gabain, *Appl. Surf. Sci.* 9832 (2003) 1-7.
16. L. Miao, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, and S. Tanemura, *Appl. Surf. Sci.* 9775 (2003) 1-9.
17. C.K. Ong and S.J. Wang, *Appl. Surf. Sci.* 185 (2001) 47-51.
18. M. Murakami, Y. Matsumoto, K. Nakajima, T. Makino, Y. Segawa, T. Chikyow, P. Ahmet, M. Kawasaki, and H. Koinuma, *Appl. Phys. Lett.* 78 (2001) 2664-66.
19. S. Sugiharto, S. Yamamoto, T. Sumita, and A. Miyashita, *J. Phys. Condens. Matter* 13 (2001) 2875-81.
20. B.H. Park, L.S. Li, B.J. Gibbons, J.Y. Huang, and Q.Y. Jia, *Appl. Phys. Lett.* 79 (2001) 2797-99.
21. S. Chen, M.G. Mason, H.J. Gysling, G.R. Paz-Pujalt, T.N. Blanton, T. Castro, K.M. Chen, C.P. Fictorie, W.L. Gladfelter, A. Franciosi, P.I. Cohen, and J.F. Evans, *J. Vac. Sci. Technol. A* 11[5] (1993) 2419-29.
22. H.L.M. Chang, H. You, Y. Gao, J. Guo, C.M. Foster, R.P. Chiarello, T.J. Zhang, and D.J. Lam, *J. Mater. Res.* 7 (1992) 2495-2506.
23. Y. Masuda, T. Sugiyama, H. Lin, W.S. Seo, and K. Koumoto, *Thin Solid Films* 382 (2001) 153-157.
24. Nguyen Thi Hue, Lei Miao, and Sakae Tanemura, *J. Crystal Growth* (submitted).
25. W. Wunderlich, P. Padmaja, and K.G.K. Warrier, *J. Europ. Ceramic Soc.* 24 (2004) 313-317.
26. W. Wunderlich, Nguyen Thi Hue, and S. Tanemura, *Advances in Technology of Materials and Materials Processing (ATM)* 6[2] (2004) 264-269.
27. W. Wunderlich, M. Fujimoto, and H. Ohsato, *Thin Solid Films* 375 (2000) 9-14.
28. T. Dittrich, *Phys. Stat. Sol. (a)* 182 (2000) 447-455.
29. W. Dong, H.J. Bongard, and F. Marlow, *Chem. Mater.* 15 (2003) 568-574.
30. K.M. Reddy, S.V. Manorama, and A.R. Reddy, *Materials Chemistry and Physics* 78 (2002) 239-245.
31. W. Wunderlich and M. Takahashi, *Ceramic Transactions Am. Ceram. Soc.* 133 (2002) 189-194.
32. W. Wunderlich, L. Miao, M. Tanemura, S. Tanemura, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, and R. Belkade, *Int. Journ. Nanoscience* (accepted).
33. M. Tanemura, K. Iwata, K. Takahashi, Y. Fujimoto, F. Okuyama, H. Sugie, and V. Filip, *J. Appl. Phys.* 90 (2001) 1529-1533.
34. W. Wunderlich, and M. Tanemura, *Advances in Solid State Physics* 43 (2003) 171-180.
35. J. Schnadt, P.A. Bruehwiler, L. Patthey, J.N. O'Shea, S. Soederen, M. Odelius, R. Ahuja, O. Karis, M. Baessler, P. Persson, H. Siegbahn, S. Lunell, and N. Martensson, *Nature* 418 (2002) 620-623.
36. P. Persson, R. Bergstrom, and S. Lunell, *J. Phys. Chem. B* 104 (2000) 10348-10351.
37. L. Joubert, J.F. Guillemoles, and C. Adamo, *Chemical Physics Letters* 371 (2003) 378-385.
38. W. Wunderlich and K. Niihara, *Journal of Ceramics Processing Research* 4[1] (2003) 10-16, *ibid* 5[1] (2004) 30-39.
39. G. Kresse, and J. Hafner, *Phys. Rev. B* 47 (1993) 558-561, *ibid* 49 (1994) 14251-14269.
40. S.P. Bates, G. Kresse, and M.J. Gillan, *Surf. Sci.* 409 (1998) 336, *ibid* 385 (1997) 386-394.
41. D. Vogtenhuber, R. Podlucky, and J. Redinger, *Surf. Sci.* 402 (1998) 798-801, *ibid* 454 (2000) 369-373.
42. H. Adachi et al., "Introduction to electron orbital calculations -DvX α Method" (in Japanese), Sankyo Pub. Tokyo 1998.
43. W. Wunderlich, *Phys. Stat. Sol. (a)* 170 (1998) 99-111.
44. W. Wunderlich, *Mat. Sci. Forum* 207 (1996) 141-144.