**Doctoral (Ph.D.) theses**

# Optical, sorptional and sensorial properties of hybrid thin layers containing zinc peroxide and zinc oxide


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## 1. Introduction

*„Concern for mankind and it's destiny – that should stand in the center of attention of all the technician effort."* (Albert Einstein)

Nanotechnology and the related inter- or multidisciplinary sciences are undergoing explosive growth, producing so many new results in weeks or months than earlier in decades. Nanosciences are based on the results of colloid chemistry, thus on the borderline between physics and chemistry will lead the way to achieve the objectives. Today biology, biotechnology and medicine is an important creator and user of research results. The investigations are mainly for the production of nanoparticles, nanostructured materials, and the usability of these materials for the purpose of a scientific or common problem identification. We meet in our everydays more and more achievement of nanoscience (nanoelectronics, sensors, anti-bacterial effect, fotocatalysis, etc.).

Production of nanoparticles and nanostructured materials with regulated size, shape and high specific surface require mainly colloid chemistrial methods, but their special electrical and optical properties can be explained by this knowledge. Semiconductor nanoparticles has prominent importance. In the latter decades the growth of electronics was triggered by the appearance and exponential developement of semiconductor industry, with the main trend of miniaturisation, and beyond it theres is many options by the specific characters of nanoparticle size range. It can be synthesized particles with properties controlled by the size, shape, refractive index, porosity, surface modification etc. and can be produced practical tools (e.g. sensors, coatings) and materials (e.g. pharmaceuticals, composites) from them. Thus we can say that after one and a half centuries waiting colloid chemistry and nanosciences have revolutionized and enrich every day the results of physical-chemistry, electronics and medicine.

One of the objectives of my work was to synthesize zinc peroxide nanoparticles in aqueous medium and to prepare porous hybrid thin films by Layer-by-Layer self-assembly method from the particles and opposite surface charge „binding materials" on the surface of solid substrate. The build-up of the films were investigated by UV-visible absorption and/or reflection techniques and quartz crystal microbalance, the structural and morphological properties were studied by X-ray diffraction (XRD) and atomic force microscopy (AFM).

Other important aim of my studies were to develop methods to measure and characterize the optical properties of the prepared thin layers, mainly the wavelength-dependent refractive index and film thickness. The latter's importance lies in the fact that in the presence of gases, vapors the spectrum of the films is shifting toward the higher wavelength range because of the increasing refractive index. My further goal was to investigate the applicability of the original and surface modified thin layers as sensors in a self-developed flow system, in presence of vapors with different polarity.

## 2. Experimental

### *Materials*

Zinc oxide nanoparticles were synthesized in aqeous medium by photolysis of zinc acetate dihydrate. ZnO nanoparticles were obtained by calcination of the prepared zinc peroxide particles, indirectly in thin films.

$ZnO_2$/PSS and $ZnO_2$/Na-hectorite hybrid thin films were built up using 0.01 % poly(styrenesulfonate) solution and 0.1 % Na-hectorite suspension on the surface of Si and glass substrate by Layer-by-Layer immersion method. The amount of organic and inorganic binding materials was varied during the pre-experiments, and after determining the optimal concentrations $ZnO_2$ thin films were prepared, and ZnO thin layers were obtained by 400 °C calcination.

During the surface modification experiments the thin films were treated by 0.01 M buthyl trichlorosilane solution (in hexane) and octanethiol coated nanogold 0.01 % sol (in hexane).

$ZnO_2$/acrylamide and $ZnO_2$/N-isopropyl acrylamide hybrid thin films were built up using 1 M acrylamide and N-isopropyl acrylamide solutions on the surface of glass and gold coated quartz substrate (QCM sensor) by Layer-by-Layer immersion method combined with in-situ photopolymerization. The layers were polymerized after treating with 0.05 M N,N-methyl-bisacrylamide (as cross-linker) and Irgacure 651 (as photoinitiator), using UV radiation under nitrogen atmosphere, thus zinc peroxide/poly(acrylamide) and zinc-peroxide/poly(N-isopropyl-acrylamide) films were obtained.

All of the starting materials were analytical or reagent grade without any further purification.

### *Methods*

The optical properties of nanoparticles and thin layers were determined by UV-Vis spectrometry (absorption, transmission, reflection) measurements.

The crystalline structure of different samples was investigated by X-ray diffraction (XRD).

Thermogravimetric (TG, DTG) measurements were used reveal the thermal behaviour of $ZnO_2$ samples.

Transmission and scanning electron microscopy (TEM, SEM) and atomic force microscopy (AFM) were used to structural and morphological studies.

The average diameter of the particles was determined by dynamic light scattering (DLS).

The interfacial electric properties of the particles and the charge of polyelectrolyte macromolecules and layer silicates were characterized by streaming potential and zeta potential measurements.

The build-up and the vapour adsorption of thin layers prepared by LbL method were monitored by UV-Vis reflection spectrometry and quartz crystal microbalance (QCM) at 25±0.1.

Hydrophobicity and surface energy of thin films were characterized by contact angle measurements.

## 3. Summary of the novel scientific results

### T1. Preparation of zinc peroxide nanoparticles by photolysis of zinc acetate dihydrate

**1.1.** Photolysis of zinc acetate dyhydrate in aqueous medium leads to the formation of $ZnO_2$ nanoparticles with a diameter range of 15-60 nm, with increasing size during the synthesis. The bandgap energy determined from optical properties varies between 4.46 and 3.76 eV during the synthesis. During high temperature heat treatment ($T > 200$ °C) there is a structural change of zinc peroxide and the result of thermal degradation are ZnO particles.
**1.2.** The heat treatment (200-800 °C) results a systematical primary size change from 15 nm to 60 nm (calculated by Debye-Scherrer equation).

### T2. Optimizing the concentration of binding materials by streaming potential measurements

The binding materials of [zinc peroxide / PSS or Na-hectorite] films were poly(styrenesulfonate) (as organic) and synthetic Na-hectorite (Optigel ®) (as inorganic). For the preparation 0.85 % $ZnO_2$ dispersion, 0.1 % Na-hectorite suspension and 0.01 % solution of PSS were used.
**2.1.** Choosing the concentration of components I used streaming potential measurements to determine the specific surface charge, to optimize the rate of component's amount during the build-up. The results are the following:

**Table 1.** *Charge ratios in case of $ZnO_2$/PSS and $ZnO_2$/Na-hectorite thin films, at different rate of amounts of binding materials*

| | **$ZnO_2$** | **PSS** | | | **Na-hectorite** | | |
|---|---|---|---|---|---|---|---|
| ***Concentration (%)*** | 0.85 | 0.005 | **0.01** | 0.05 | 0.05 | **0.1** | 0.2 |
| ***Rate of charge ($ZnO_2$ : X)*** | - | 1:10 | **1:5** | 1:1 | 1:10 | **1:5** | 1:2.5 |

**2.2.** I observed that using 0.005% PSS solution and 0,05% Na-hectorite suspension (1:10 rate) for preparation resulted a non-uniform build-up (the absorbance measured at the same wavelength increased nonlinear with layer number), or the system saturated before reaching the wanted layer number, because the electrostatic attractiveness - required to alternating build-up - was to low (from binder).

**2.3**. Using 0.05% PSS solution and 0.02% Na-hectorite suspension (1:1 and 1:1.25 ratio) also resulted the saturation of electrostatic forces (compensating the surface charge of the zinc peroxide particles), and/or due to the high quantity of binder the layers became opaque with high light scattering.

**2.4.** Using 0.01% solution of PSS or 0.1% Na-hectorite (charge ratio of 1:5) the layers were well-ordered and absorbance increased linear, so I have determined, that the optimal charge ratio is 1:5 (between zinc peroxide and binder components), therefore in the course of my work this ratio was used.

### T3. Influencing the value of bandgap energy by the material of binder in $ZnO_2$/PSS and $ZnO_2$/Na-hectorite thin films

The bandgap energy in semiconductors also appears in nanoparticles, thus also in thin layers. In contrast to the bulk phase (ZnO: 3.2-3.3 eV, $ZnO_2$: 3.7-3.8 eV) it is not a constant value, but depends of the size parameters of the nanostructured material. So this value can be influenced by varying the size, this is called *size quantization effect*.

**3.1.** I observed that in the case of zinc peroxide/Na-hectorite thin layers the energy of the bandgap remained independent of the number of layers, it is a constant 3.98 eV, because the particles intercalated between the silicate lamellae are in confined space. This property is also characteristic of ZnO/Na-hectorite films, but according to the phase transition it changes to the value of 3.2 eV.

**3.2.** In the case of the polymer films the bandgap energy is decreasing with layer number from 4.12 to 3.74 eV. This is possible because the polymer chains are able to bind to the surface of the particles and size quantization effect can dominate at low layer numbers. But at higher layer numbers the effect is weakening, so the bandgap energy decreases to the value of bulk phase.

### T4. Method to determine the optical properties of thin hybrid films

Determining the refractive index and layer thickness is one of the most important object during characterization of thin films. I have developed a technique that calculates the refractive index by fitting analytical (trigonometrical) functions onto the measured curves (the sensorial importance of that appears later at the real-time determination of refractive index change, see T.7). For the calculation of the optical parameters three cascading model was applied:

**4.1.** The solid state model I used has three components: a solid component with a wavelength-dependent refractive index (particles), a solid component with constant refractive index (binder) and pores with constant refractive index, which value is set to air's value.

**4.2.** The effective medium approach, which has two component also in the simplest case with surface roughness. As a result, I received a constant layer thickness with a homogeneous refractive index. I chose the effective medium approximation called Bruggeman model extended to three component. This is one of the most common model, on the other hand, it was easily built into the computer system evaluation software.

**4.3.** The wave propagation model determines the equations used for describe the ray propagation in the thin film. I used two-ray interference model which I summarized by complex amplitude method. The other beams of light increase the intensity but do not change the location of extrema on the curves.

**4.4.** Using the three models above cascading at the same time I received an equation between the wavelength and reflected intensity:

$$I_R \simeq a^2 \cdot \left[ r^2 + r'^2 (1-r^2)^2 + 2rr'(1-r^2)\cos\left(\frac{4\pi n_e d \cos\beta}{\lambda}\right)\right] \qquad (1)$$

Using the resulted (1) equation in simulation software - based on the best match - I could determine the effective index of refraction and layer thickness.

**T5. Application of in-situ photopolimerization in thin film preparation**

**5.1.** In addition to the traditional layer-by-layer (LbL) immersion technique I prepared zinc peroxide/cross-linked polymer hybrid thin films by combining the LbL method with photopolymerization.

**5.2.** By Fourier-transform infrared absorption spectroscopy was proved that $ZnO_2$/acrylamide and $ZnO_2$/N-isopropyl-acrylamide hybrid films became polymerized to $ZnO_2$/poly(AAm) and poly(NIPAAm) thin layers after the adsorption of cross-linking agent and irradiation with UV light.

**T6. Controlling the hydrophilic/hydrophobic properties by the material of binding polymers in $ZnO_2$/PAAm and $ZnO_2$/PNIPAAm thin films**

Water and ethanol adsorption experiments were done to investigate the similar or different properties of the cross-linked polymers in thin films. I have found that the specific adsorbed amount decreased in all cases as a result of polymerization. This is explained by the fact that while many of the binding location of the monomers are available for water and ethanol molecules in case of monomers, until many of them disappears during the polymerization. Only in case of adsorbed ethanol amount was observed benefit of the poly(acrylamide) polymerized form. The partially hydrophilic/hydrophobic hybrids (NIPAAm) adsorbed almost equal amount of water and ethanol, significantly larger quantities of water was adsorbed by the hydrophilic thin layers based on acrylamide (PAAm). The results are in good accordance with the data received at bulk phase.

**T7. Detection and characterization of adsorption of vapors by optical method**

The technique described in T.4 is able to determine optical parameters of well ordered thin films in dry atmosphere. However, if the thin layers are in an environment that is rich in vapor of water or organic liquid then the reflection spectra of the films shift toward the higher wavelength because of the increased refraction index due to the adsorption. I developed a sensor - utilizing this phenomenon – that is able to detect and characterize adsorption of vapors.

**7.1.** I have determined that the reflection spectra of the prepared $ZnO_2$/PSS hybrids shifts toward the higher wavelengths if they are in atmosphere that contains water or ethanol vapor. Quotient of reflection spectrum measured at the actual time and measured at t=0 resulted a group of curves which minimum locations and amplitudes increased with the progress of time. The latter gives that how many times higher the reflected intensity is in case of adsorption compared to the dry atmosphere.

**7.2.** Based on the phenomenon described in 7.1 I developed a 4-channel flow system gas sensor that consists of a light source, a sampler unit with temperature determination, a gas mixing unit (the vapor concentration can be varied by changing the rate of pure nitrogen and gas containing vapor), a film holder and measuring cell, and a spectrometer as detector.

**7.3.** The system is capable to record reflection spectra in every second and converts the wavelength shift to the change of the refractive index.

**7.4.** One of the cornerstones of the measurements is to find the minimum intensity location in the curves, because the noise level exceeds many times the value of the intensity difference at two neighboring pixels, thus finding the right value can be missed easily. To find the right values I used nine degree polynomial fitting of reflection curves and it resulted a high quality smoothing in the monitoring of minimum wavelengths measurement data.

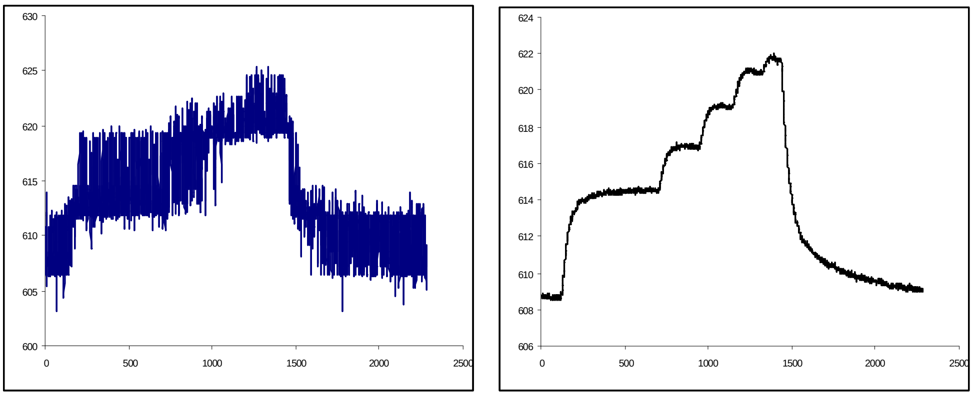


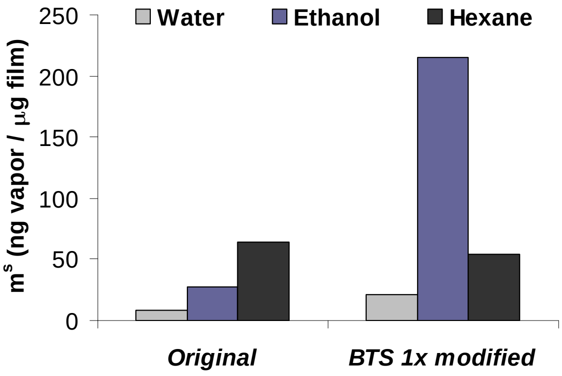

**Fig. 1.** *Extrema of the original curves (left) and the fitted curves (right) as the function of time*

## T8. Controlling the selectivity and hydrophobicity by surface modification

Surface of $ZnO_2$/PSS thin layers were modified by buthyl trichlorosilane and gold nanoparticles covered by octanethiol, thus the specific sensitivity and hydrophobicity were controlled.

**8.1.** I found in the course of surface modifying by butyl trichlorosilane that the surface became hugely sensitive for the vapor of ethanol. After modification the specific adsorbed amount of ethanol was nine times higher than the original, while water amount only tripled, so the quantity of adsorbed ethyl alcohol were four times higher than water quantity. The adsorption of the hexane has not changed significantly as a result of the surface treatment.

**8.2.** The treatment by gold nanoparticles covered by octanethiol caused that the surface became completely hydrophobic, the adsorbed water vapor amount decreased significantly, while the amount of adsorbed hexane tripled, thus 28 times higher refractive index change was observed in the case of hexane adsorption as water vapor.



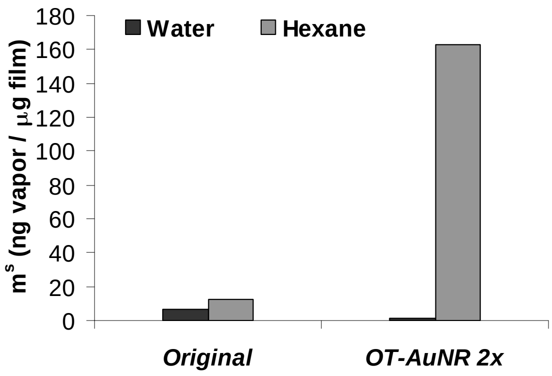




**Fig.3.** *Refractive index changes in original and modified (by BTS and OT-AuNR) $ZnO_2$/PSS thin films at $p_r = 0.5$ relative vapor pressure*

**Scientific Publications**

**Publications related to the scientific topic of the dissertation**


1. **Dániel Sebők**, László Janovák, Imre Dékány
*Optical, structural and adsorption properties of zinc peroxide/hydrogel nanohybrid films*
Applied Surface Science 256 (2010) 5349-5354

**$IF_{2010}$: 1.793**

2. **Dániel Sebők**, Tamás Szabó, Imre Dékány
*Optical properties of zinc peroxide and zinc oxide multilayer nanohybrid films*
Applied Surface Science 255 (2009) 6953-6962

**$IF_{2009}$: 1.616**

3. Edit Pál, **Dániel Sebők**, Viktória Hornok, Imre Dékány
*Structural, optical, and adsorption properties of $ZnO_2$/poly(acrylic acid) hybrid thin porous films prepared by ionic strength controlled layer-by-layer method*
Journal of Colloid and Interface Science 332 (2009) 173-182

**$IF_{2009}$: 3.019**

4. **Dániel Sebők**, Krisztina Szendrei, Tamás Szabó, Imre Dékány
*Optical properties of zinc oxide ultrathin hybrid films on silicon wafer prepared by layer-by-layer method*
Thin Solid Films 516 (2008) 3009-3014

**$IF_{2008}$: 1.884**

5. **Dániel Sebők**, Imre Dékány
*Sensorial application of zinc peroxide ultrathin hybrid films with modified surfaces for detection of ethanol and n-hexane vapours*
Nanotechnology: Sensing and actuating (submitted, 2012)

*$IF_{2010}$: 3.652*


**ΣIF = 8.312**

*(11.964)*

**Other publications**

6. N. Ábrahám, **D. Sebők**, Sz. Papp, L. Kőrösi, I. Dékány
*Two-dimensional arrangement of monodisperse ZnO particles with Langmuir–Blodgett technique*
Colloids and Surfaces A: Physicochemical and Eng. Aspects 384 (2011) 80-89

*$IF_{2010}$: 2.130*

7. Edit Pál, Viktória Hornok, **Dániel Sebők**, Andrea Majzik, Imre Dékány
*Optical and structural properties of protein/gold hybrid bio-nanofilms prepared by layer-by-layer method*
Colloids and Surfaces B: Biointerfaces 79 (2010) 276-283

*$IF_{2010}$: 2.780*

8. Cs. Vass, **D. Sebők**, B. Hopp
*Comparing study of subpicosecond and nanosecond wet etching of fused silica*
Applied Surface Science 252 (2006) 4768-4772

*$IF_{2006}$: 1.436*

**Összesített hatástényező: 14.658**
*(18.31)*

**Lectures and posters in international conferences**

**Lectures**

1. I. Dékány, R. Kun, E. Pál, L. Kőrösi, K. Szendrei, **D. Sebők**
*Optical and photocatalytical properties of ZnO and ZnAl double hydroxide nanoparticles stabilized in ultrathin films by LbL method*
$12^{th}$ International Conference on Surface and Colloid Science (IACIS), Peking, 2006. október 15-20., p. 22

2. I. Dékány, E. Pál, V. Hornok, T. Aradi, **D. Sebők**
*Nanostructured ultrathin hybrid layers prepared by LBL method*
COST D43 Meeting, Cracow, Poland, 2007. március 18-21.

**3. Dániel Sebők**, Krisztina Szendrei and Imre Dékány
*Changing of optical properties of $Zn(OH)_2$ / polymer nanofilms prepared by LbL method under various ethanol vapor pressure*
9th Conference on Colloid Chemistry, 2007. október 3-5., Siófok, p. 62.

**4. Daniel Sebők**, Edit Pál**,** Robert Kun, Tamas Szabó, Judit Ménesi, Andrea Majzik, Viktoria Hornok, Imre Dékány
*Functional and reactive surfaces prepared by layer-by-layer assembly of nanohybrid materials*
22nd ECIS Conference and Workshop of Cost action D 43, 2008. augusztus 31- szeptember 05., Cracow, Poland, p. 58.

**5. Sebők Dániel**, Janovák László, Dékány Imre
*In situ fotopolimerizációval előállított cink-peroxid / hidrogél hibrid vékonyrétegek optikai és adszorpciós tulajdonságainak vizsgálata*
VII. Országos Anyagtud. Konferencia, Balatonkenese, 2009. október 11-13.

**6. Dániel Sebők**, Laszló Janovák and Imre Dékány
*Optical and adsorption properties and sensorial application of thin films containing ZnO and* $ZnO_2$
2011. október 24., Kairó, Egyiptom

7. Imre Dékány, Tamás Szabó, Viktória Hornok and **Dániel Sebők**
*Self-assembled nanohybrid thin films prepared from inorganic colloids, polyelectrolytes and proteins*
Beyond Self-Assembly, 2012. január 22-25., Bad Gastein, Ausztria

**Posters**

**1. Dániel Sebők**, Krisztina Szendrei and Imre Dékány
*Changing of optical properties of* $Zn(OH)_2$ *nanoparticles / layer silicate nanofilms prepared by LBL method under ethanol vapour*
$20^{th}$ Conference of the European Colloid and Interface Society and $18^{th}$ European Chemistry at Interfaces Conference (ECIS-ECIC), Budapest, 2006. szeptember 17-22., p. 397

2. Krisztina Szendrei, **Dániel Sebők**, Tamás Szabó, and Imre Dékány
*Optical Properties of ZnO nanoparticles in ultrathin films prepared by LBL method.*
$20^{th}$ Conference of the European Colloid and Interface Society and $18^{th}$ European Chemistry at Interfaces Conference (ECIS-ECIC), Budapest, 2006. szeptember 17-22., p. 399

3. É. Bazsó, J. Ménesi, **D. Sebők**, N. Buzás, L. Reich, and I. Dékány
*Photocatalytic destruction of methylene blue and sudan red dyes in* $TiO_2$ *suspensions and films*
$20^{th}$ Conference of the European Colloid and Interface Society and $18^{th}$ European Chemistry at Interfaces Conference (ECIS-ECIC), Budapest, 2006.

**4. Sebők Dániel**, Patzkó Ágnes, Fodor Krisztina, Erdőhelyi András, Dékány Imre
*A metán adszorpciós tárolása*
Szeged, Ipari Kapcsolatok Napja, 2006.

5. E. Pál, **D. Sebők**, R. Kun, V. Hornok**,** A. Majzik, I. Dékány
*Layer-by-layer self-assembly of organic/inorganic colloids*
Gordon Conference, Italy, 2007

6. A. Majzik, R. Patakfalvi, E. Pál, **D. Sebők**, I. Dékány
*Surface functionalization and self-assembly of metal oxide and gold colloids*
$21^{th}$ ECIS Conference, 2007. szeptember 10-15., Geneve, Switzerland

**7. D. Sebők**, L. Janovák, E. Pál, I. Dékány
*Adsorption and reflection properties of functional hybrid nanofilms*
22nd ECIS Conference and Workshop of Cost action D 43, 2008. augusztus 31- szeptember 05., Cracow, Poland, p. 606.

8. Edit Pál, **Dániel Sebők**, László Janovák, Imre Dékány
*Self-assembled hybrid nanostuctured films*
Workshop of Cost action D 43 „Functionalizes materials and Interfaces”,
2008. április 2-4., Berlin, Germany

9. Edit Csapó, **Dániel Sebők** and Imre Dékány
*Detection of gases/vapours and proteins on the surface of functionalized gold nanoparticles and thin layers*
ISIRR 2010, Szeged

10. Edit Csapó, **Dániel Sebők,** Viktória Hornok and Imre Dékány
*Detection of gases/vapours and proteins on the surface of functionalized gold nanoparticles and thin layers*
Euronanoforum 2011, 2011. május 30 – június 1., Budapest

**11. D. Sebők**, E. Csapó, J. Homola, I. Dékány
*Immobilization of amino acids and proteins on pure and modified gold surface using Surface Plasmon Resonance (SPR) technique*
25$^{nd}$ ECIS Conference, 2011. szeptember 4-9., Berlin, Németország