Available online at www.sciencedirect.com
SCIENCE DIRECT®
Applied Surface Science 234 (2004) 138–143
applied surface science
www.elsevier.com/locate/apsusc

Thickness dependence of the LUMO position for phthalocyanines on hydrogen passivated silicon (1 1 1)

M. Gorgoi[a,*], W. Michaelis[b], T.U. Kampen[a], D. Schlettwein[b], D.R.T. Zahn[a]

[a]Institut für Physik, Technische Universität Chemnitz, Chemnitz 09126, Germany
[b]Physikalische Chemie 1, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany

Available online 15 July 2004

Abstract

Inverse photoemission spectroscopy (IPES) was employed to study the density of unoccupied electronic states of fluorinated and non-fluorinated cooper phthalocyanine layers deposited onto hydrogen passivated Si(1 1 1) substrates. For the non-fluorinated cooper phthalocyanine (CuPc) the lowest unoccupied molecular orbital (LUMO) is found to shift gradually towards the Fermi level with increasing film thickness. The shift amounts to 400 meV and appears for film thicknesses between one monolayer and 10 nm. This finding complements previous results obtained using ultraviolet photoemission spectroscopy where the highest occupied molecular orbital (HOMO) was found to shift as a function of film thickness. Fluorinated cooper phthalocyanine (F_{16}CuPc) shows the opposite behaviour, that is the distance between LUMO and Fermi level is increasing by 1.2 eV.

PACS: 79.20.Kz; 71.20.Rv

Keywords: Copper phthalocyanine; Fluorinated copper phthalocyanine; Inverse photoemission; LUMO

1. Introduction

In the last years the class of phthalocyanine materials has received a considerable attention because of its increasing importance in organic electronic devices. Phthalocyanines attributes such as chemical and thermal stability and the tendency to form highly ordered layers positively influence the device efficiency [1]. Therefore, phthalocyanines are promising candidates in applications such as organic light emitting diodes [2], solar cells [3], organic field effect transistors [4], and gas sensors [5]. Another application of organic molecules is the modification of semiconductor surfaces and interfaces. Ultra-thin layers of organic molecules have been used for the passivation of semiconductor surfaces, such as Si(1 1 1)–(7 × 7) and GaAs(1 0 0) [6]. For example, a C_{60} monolayer on a Si(1 1 1)–(7 × 7) surface inhibits chemical attack by water and atmospheric oxygen. Moreover, Forrest et al. demonstrated that organic molecules, in particular, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and *N*,*N*′-dimethyl-3,4,9,10-perylenetetracarboximide ($C_{26}H_{14}O_4N_2$, DiMe-PTCDI) are useful for characterization of inorganic semiconductor surface state distribution and the modification of barrier

* Corresponding author. Tel.: +49 371 531 3009;
fax: +49 371 531 3060.
E-mail address: mihaela.gorgoi@physik.tu-chemnitz.de
(M. Gorgoi).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2004.05.065

heights in Schottky contacts [7,8]. The often observed decrease in barrier height can be explained by an increase in image force lowering due to the presence of PTCDA [9,10]. Such devices are applicable for applications in the GHz frequency regime [11–14].

While a large number of articles were published on the characterization of metal phthalocyanines, only very few studies focused on the fluorinated phthalocyanines. The fluorination increases the ionization potential by about 1 eV. For example, Peisert et al. determined the ionisation energy of CuPc, F_4CuPc, and F_{16}CuPc to be 5.05, 5.7 and 6.1 eV, respectively [15]. The optical band gap, on the other hand, seems to be unaffected by the fluorination (CuPc: 1.6 eV, F_4CuPc: 1.6 eV, F_{16}CuPc: 1.5 eV). Due to large exciton binding energies optical band gaps in organic materials are by about 1 eV smaller than transport gaps [16]. The transport gap E_t can be determined by combining photoemission and inverse photoemission (IPES) experiments. Using this combination of techniques and taking into account polarization effects the transport gap for CuPc and ZnPc has been determined to be 2.3 [16] and 1.94 eV [17], respectively.

Besides the energy position of hole and electron transport levels in organic materials, organic/inorganic interfaces play an important role in thin-film based devices. The electronic structure of organic/inorganic interfaces depends strongly on the crystalline structure of the organic films and the interface bonding. These properties have been found to be determined by the substrate surface [18–26]. Therefore, metal–organic interfaces have received considerable attention [15,16,27,28]. Quite often the vacuum level alignment is used to determine the energy level alignment at interfaces. Here, it is assumed that the vacuum levels of the materials in contact align at the interface and the interface barrier heights can simply be calculated using the ionisation potentials (IP) and electron affinities (EA) of semiconducting materials and work functions of metallic materials. For metal–organic interfaces a conclusion that in general the vacuum levels do not align has been reached [29–31]. The difference in vacuum levels is attributed to interface dipoles and using photoemission spectroscopy values between 0.5 and 1 eV have been found for several metal–organic interfaces. Another important issue is the occurrence of a ‘‘band bending’’-like electrostatic energy shift in organic layers which has been observed in many metal–organic systems [32]. In most cases this shift is confined to a regime of only a few nanometers, which cannot be accounted for using the conventional band bending theory of inorganic semiconductors. Shifts occurring in such small thickness ranges can be due to a change in the intermolecular interaction, namely, due to a change in the molecular orientation as a function of the film thickness. The change in the molecular orientation thus produces a band bending or energy level shift that plays an important role in the actual device properties. This observation has been made for copper phthalocyanine (CuPc) films grown on MoS_2 substrates. Angular resolved ultraviolet photoemission spectroscopy using synchrotron radiation has been used to determine the energy position of the HOMO and the orientation of the molecules as a function of the film thickness. For a layer thickness of 0.4 nm the HOMO is found $\approx$1.05 eV below the Fermi level, while for films of 8.4 nm thickness the HOMO shifts by about 0.3 eV to higher binding energies. Following the intensity of the HOMO as a function of emission angle and azimuth the tilt angle of the CuPc molecular plane with respect to the substrate surface is determined to be 0° and 10° for the 0.4 and 8.4 nm films, respectively.

In the present work, IPES investigations on CuPc and F_{16}CuPc deposited on hydrogen passivated silicon are presented. In the case of silicon, atomically flat and ideally H-terminated Si(1 1 1) surfaces can be obtained by wet chemical etching [33]. This type of non-reactive surface is preferred for organic molecular beam deposition (OMBD) since it favours ordered arrangement of the molecules.

2. Experimental

Hydrogen passivated p-type Si(1 1 1) with a doping concentration of 1.5×10^{15} cm^{-3} was used as the substrate. The passivation process consists of a wet chemical etching in a solution containing HF (40%). After the passivation process the samples were transferred into ultra high vacuum (UHV). All measurements were performed on freshly evaporated organic layers. Sublimed CuPc (provided by Syntec GmbH Wolfen) and F_{16}CuPc were used without any further purification. The organic materials were evaporated from Knudsen-type cells at temperatures between 340 and 370 °C. During the evaporation of the organic materials the pressure was better than 2×10^{-8} mbar. The evaporation rates were in the range of 0.1–2 nm/min and the substrate was kept at room temperature. The film thickness and the evaporation rate were controlled by means of a quartz crystal microbalance and ellipsometry measurements performed subsequently. The IPES measurements were performed in an UHV system (base pressure: 8.5×10^{-10} mbar), consisting of an analysis and a preparation chamber. The IPES experimental setup works in the isochromat mode and is a ''home'' built system. The fixed-energy photon detector [34] consists of a Geiger–Müller tube with a magnesium fluoride (MgF_2) window filled with a gas mixture of ethanol and argon. The ionization energy of ethanol and the transmission function of the MgF_2 window provide an energy window 10.9 eV for the detection of photons. A low energy electron gun [35] was used to produce a mono-energetic electron beam. The overall IPES instrumental resolution, estimated from the width of the Fermi edge measured on an argon sputtered nickel sample is 0.5 eV. Spectra were recorded at normal incidence of the beam with a current density in the range of 10^{-6} A/cm^2. This value is low enough to avoid any damage of the organic film [16].

3. Results and discussion

Fig. 1 shows the IPES spectra of CuPc films deposited onto H-Si(1 1 1) as a function of thickness. The spectra were normalized with respect to the sample current and shifted vertically for clarity. Three characteristic features at 2, 3.5 and 5 eV already appear at

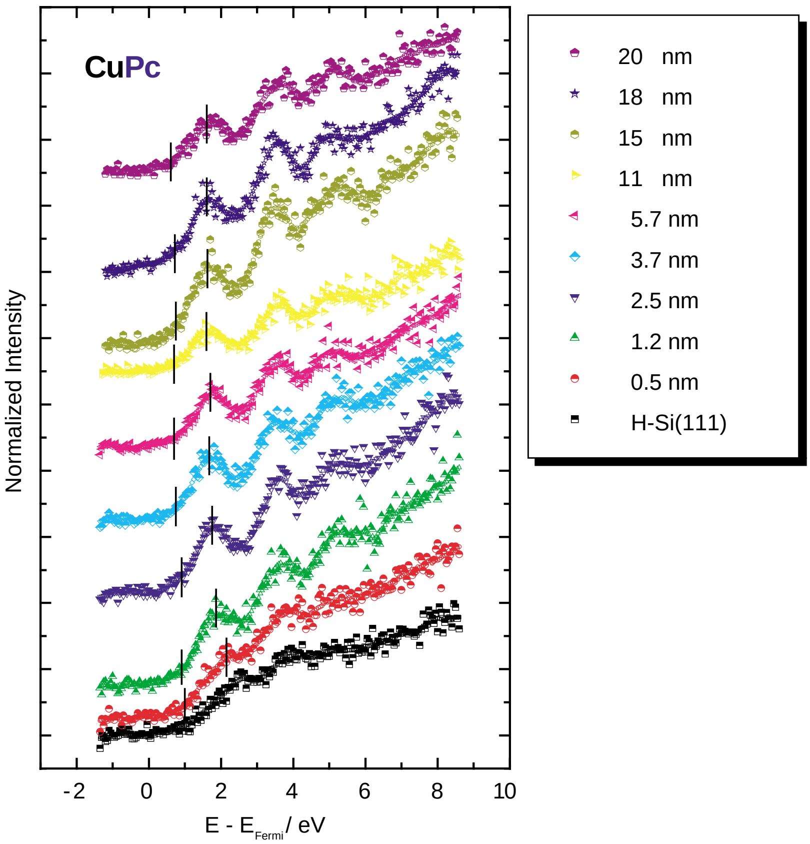

Fig. 1. IPES measurements of CuPc/H-Si(1 1 1) as a function of thickness. Peak and onset positions are marked by vertical lines.

low coverage (0.5 nm). These features are characteristic for CuPc and have been observed before by Hill et al. [16]. The appearance of these features even for low coverage is attributed to the formation of a homogeneous CuPc layer [15]. The peak having the lowest energy with respect to the Fermi level is attributed to the LUMO, which arises exclusively from π-orbitals. It should be noted, that the central metal atom does not contribute to this molecular orbital [36]. A shift of the LUMO positions towards the Fermi level can be observed with increasing thickness. The saturation of this shift occurs after approximately 10 nm. The overall shift is determined to be 0.4 ± 0.25 eV and is observed for all three features, i.e. their energy separation is constant. To determine the LUMO peak positions, a linear background was subtracted [16] and the remaining peaks were fitted with Gaussian functions. In addition, the LUMO onsets were determined with respect to the Fermi level by a linear extrapolation of the low energy edge of the LUMO feature towards vanishing intensity. In Figs. 1 and 2 the LUMO onset and peak positions are indicated by vertical bars. Opposite to CuPc, the fluorinated CuPc reveals a strong shift of the LUMO feature away from the Fermi level with increasing layer thickness (Fig. 2). The value of the shift is about 1.2 ± 0.25 eV. The saturation of the energy shift appears after 20 nm layer coverage. Figs. 3 and 4 present the dependence of LUMO peak and onset positions for the two Pc's as a function of the layer thickness. The error bars were determined from the resolution of the IPES setup. In the case of CuPc several other studies have shown that the molecules are changing their orientation as a function of layer thickness [37,38]. For a non-reactive surface such as H-passivated Si(1 1 1) the molecules within the first three monolayers are expected to lie flat on top of the substrate. This initial growth mode has been observed for the deposition of CuPc on highly

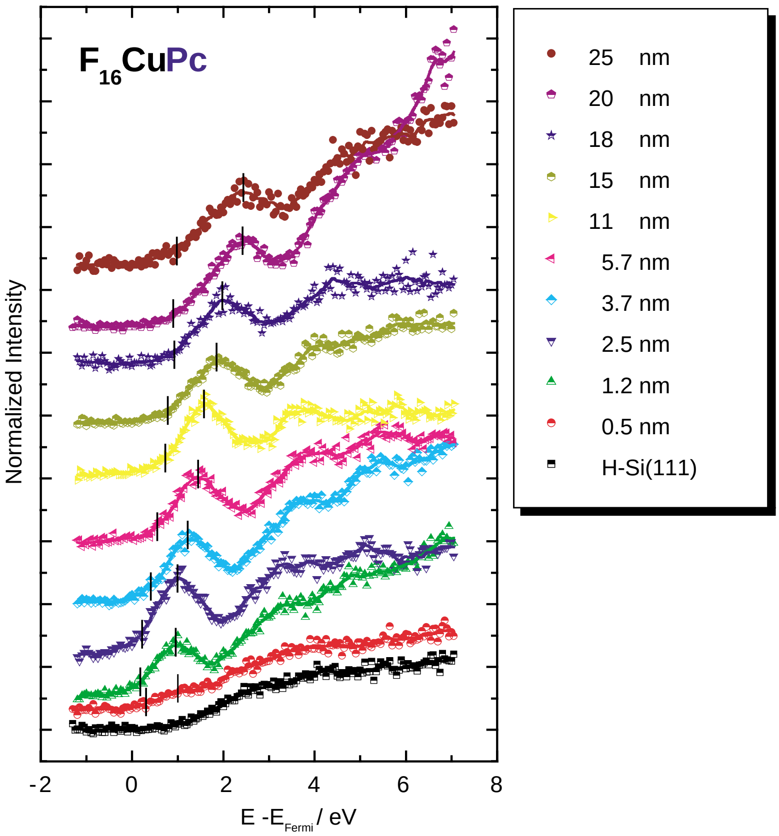

Fig. 2. IPES measurements of F_{16}Cupc/H-Si(1 1 1) as a function of thickness. Peak and onset positions are marked by vertical lines.

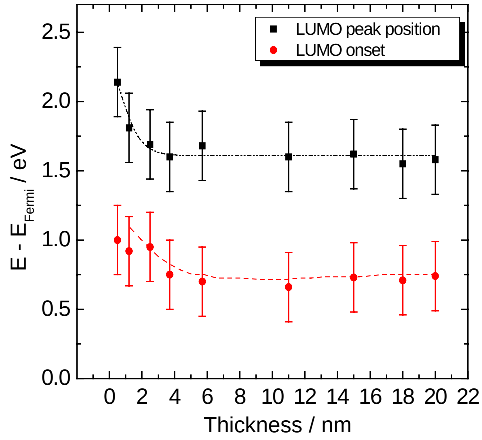

Fig. 3. LUMO peak and onset positions as a function of CuPc thickness. The dotted lines are plotted for guiding the eye.

oriented pyrolytic graphite (HOPG) [37,38]. At a higher coverage a tilt of the molecules appears leading to a molecular arrangement which is typical for the α-modification of a CuPc single crystal. The structure of the α-modification consists of alternative stacks of cofacially oriented CuPc molecules. Within each stack the molecules are aligned, shifted in position and inclined by a fixed angle of 25° [39]. An incomplete overlapping of the CuPc molecules results in a partial superposition of the π-orbitals. As a consequence, a change in molecular orientation results in a change of the intermolecular interactions and affects of the π-electron system. This change is assumed to be the main cause of the energy shift of energy levels in CuPc with increasing thickness.

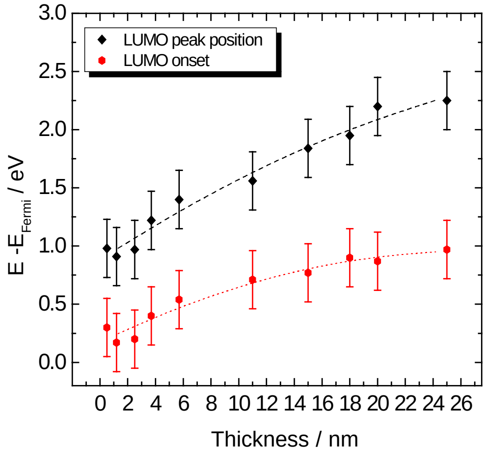

Fig. 4. LUMO peak and onset positions as a function of F_{16}CuPc. The dotted lines are plotted for guiding the eye.

Fluorination of CuPc induces a shift of energy levels towards higher binding energies [40]. Since fluorine has a higher electronegativity than carbon and nitrogen a charge transfer is expected towards the fluorine atoms. The remaining electrons at CuPc core have to screen the positive potential of the atoms, which results in a higher binding energy for the HOMO and the LUMO. At the thickness where both materials have reached the energy saturation level, the LUMO peak positions are 1.6 ± 0.25 eV for CuPc and 2.2 ± 0.25 eV for F_{16}CuPc. There is a difference of 0.6 eV in the LUMO peak positions of the two organic materials.

Unlike CuPc, F_{16}CuPc presents some major different characteristics which need to be pointed out. The value of the energy shift is three times larger than for CuPc. The direction of the shift is opposite to the one observed for CuPc. The saturation of the shift occurs at a higher coverage (20 nm) than for CuPc suggesting that the substrate is not entirely covered after 3–4 monolayers. Taking this into account it can be concluded that the F_{16}CuPc does not follow the same growth mode as CuPc that is F_{16}CuPc shows island growth mode. The deposition of the fluorinated CuPc molecules onto different substrates has been investigated in a previous study [41]. Their orientation depends strongly on the substrate reactivity and structure. For non-reactive substrates such as H-passivated Si(1 1 1) the molecules are lying flat on the surfaces. This result and the fact that fluorinated molecules show a larger electron charge density at the edges suggest that there is repulsion between the molecules increasing the intermolecular distance.

4. Summary

The interfaces between CuPc and F_{16}CuPc and hydrogen passivated silicon (1 1 1) was investigated using IPES. The LUMO peaks and onsets as a function of organic layer thickness show a shift in energy levels at the interface. The values of these shifts are 0.4 eV for CuPc and 1.2 eV for F_{16}CuPc, although the directions of the shifts are different. The LUMO peak position shifts towards the Fermi level in the CuPc

case and away from the Fermi level for $F_{16}CuPc$. The change in molecular orientation as a function of film thickness can be the main reason that produces the energy shifts considering different growth modes for the two Pc's.

Acknowledgements

The authors acknowledge the EU funded Human Potential Research Training Network DIODE (contract no.: HPRN-CT-1999-00164) for the financial support. We thank A. Fechner for his technical support.

References

[1] H. Peisert, M. Knupfer, T. Schwieger, J.M. Auerhammer, M.S. Golden, J. Fink, J. Appl. Phys. 91 (8) (2002) 4872–4878.
[2] J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo, Appl. Phys. Lett. 73 (6) (1998) 729–731.
[3] P. Peumans, S.R. Forrest, Appl. Phys. Lett. 79 (1) (2001) 126–128.
[4] M. Takada, H. Yoshioka, H. Tada, K. Matsushige, Jpn. J. Appl. Phys. 41 (2002) L73–L75.
[5] M.I. Newton, T.K.H. Starke, M.R. Wilis, G. Mc Hale, Sens. Actuators B67 (2000) 307.
[6] A.W. Dunn, P. Moriaty, M.D. Upward, P.H. Beton, Appl. Phys. Lett. 69 (1996) 506.
[7] S.R. Forrest, M.L. Kaplan, P.H. Schmidt, J. Appl. Phys. 55 (1984) 1492.
[8] S.R. Forrest, M.L. Kaplan, P.H. Schmidt, J.M. Parsey Jr., J. Appl. Phys. 58 (1985) 867.
[9] T.U. Kampen, S. Park, D.R.T. Zahn, Appl. Surf. Sci. 190 (2002) 461.
[10] A. Bolognesi, A. Di Carlo, P. Lugli, T. Kampen, D.R.T. Zahn, Organic–inorganic semiconductor interfaces, J. Phys.: Condens. Matter 15 (2003) S2719–S2728.
[11] A. Böhler, P. Urbach, D. Ammermann, W. Kowalsky, Mater. Sci. Eng. B51 (1998) 58.
[12] T.U. Kampen, S. Park, D.R.T. Zahn, Appl. Surf. Sci. 190 (2002) 461.
[13] S.R. Forrest, M.L. Kaplan, P.H. Schmidt, J.M. Parsey Jr., J. Appl. Phys. 58 (1985) 867.
[14] S.R. Forrest, M.L. Kaplan, P.H. Schmidt, J. Appl. Phys. 55 (1984) 1492.
[15] H. Peisert, M. Knupfer, J. Fink, Appl. Phys. Lett. 81 (13) (2002) 2400–2402.
[16] I.G. Hill, A. Kahn, Z.G. Soos, R.A. Pascal Jr., Chem. Phys. Lett. 327 (2000) 181.
[17] W. Gao, A. Kahn, Org. Electron. 3 (2002) 53–63.
[18] Y. Hirose, W. Chen, E.I. Haskal, S.R. Forrest, A. Kahn, Appl. Phys. Lett. 64 (25) (1994) 3482.
[19] Y. Hirose, S.R. Forrest, A. Kahn, Phys. Rev. B 52 (1995) 14040.
[20] Y. Hirose, S.R. Forrest, A. Kahn, Appl. Phys. Lett. 66 (8) (1995) 944.
[21] C. Kendrick, A. Kahn, Surf. Rev. Lett. 5 (1) (1998) 289.
[22] K. Glöckler, C. Seidel, A. Soukopp, M. Sokolowski, E. Umbach, M. Böhringer, R. Berndt, W.-D. Schneider, Surf. Sci. 405 (1998) 1.
[23] U. Stahl, D. Gador, A. Soukopp, R. Fink, E. Umbach, Surf. Sci. 414 (1998) 423.
[24] J. Taborski, P. Väterlein, H. Dietz, U. Zimmermann, E. Umbach, J. Electron Spectrosc. Relat. Phenom. 75 (1995) 129.
[25] I. Chizhov, A. Kahn, G. Scoles, J. Cryst. Growth 208 (2000) 449.
[26] H. Ishii, K. Sugiyama, E. Ito, K. Seki, Adv. Mater. 11 (8) (1999) 605.
[27] I.G. Hill, A. Rajagopal, A. Kahn, Y. Hu, Appl. Phys. Lett. 73 (1998) 662.
[28] I.G. Hill, A. Kahn, J. Appl. Phys. 86 (4) (1999) 2116.
[29] H. Ishii, K. Sugiyama, E. Ito, K. Seki, Adv. Mater. 11 (1999) 605.
[30] I.G. Hill, A. Rajagopal, A. Kahn, Y. Hu, Appl. Phys. Lett. 73 (1998) 662.
[31] Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima, K. Yamashita, Appl. Phys. Lett. 67 (1995) 1899.
[32] I.G. Hill, A.J. Makinen, Z.H. Kafa, Appl. Phys. Lett. 77 (2000) 1825.
[33] S. Bouzidi, F. Coletti, J.M. Debever, P.A. Thiry, P. Dumas, Y.J. Chabal, Phys. Rev. B 45 (1992) 1187.
[34] K.C. Prince, Rev. Sci. Instrum. 59 (1988) 741.
[35] P.W. Erdman, E.C. Zipf, Rev. Sci. Instrum. 53 (1982) 225.
[36] H. Yoshida, K. Tsutsumi, N. Sato, J. Electron Spectrosc. Relat. Phenom. 121 (2001) 83–91.
[37] H. Peisert, T. Schwieger, J.M. Auerhammer, M. Knupfer, M.S. Golden, J. Fink, P.R. Bressler, M. Mast, J. Appl. Phys. 90 (2001) 466.
[38] H. Yamane, S. Kera, S. Tanaka, H. Honda, T. Nakamura, H. Setoyama, K.K. Okudaira, N. Ueno, PC74, ERPOS, Prague, 2002.
[39] J. Simon, J.-J. Andre, Molecular Semiconductors, Springer-Verlag, Berlin, 1985.
[40] D. Schlettwein, K. Hesse, N.E. Gruhn, P.A. Lee, K.W. Nebesny, N.R. Armstrong, J. Phys. Chem. B 105 (2001) 4791–4800.
[41] J.O. Osso, F. Schreiber, V. Kruppa, H. Dosch, H. Garriga, M.I. Alonso, F. Cerdeira, Adv. Func. Mat. 12 (6/7) (2002) 455.