Electronic and Structural Properties of Thin Films of Phthalocyanines and Titanium Dioxide

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Abstract

This thesis is based on experimental studies in chemical physics. Titanium dioxide (TiO_2) and phthalocyanine’s (Pc’s), interesting in many future perspectives, have been deposited as thin films and studied as follows. Information has been obtained on e.g. molecular orientation, crystal structure, depth profile of the chemical composition, electrochemical properties and electronic structure. This has been achieved by means of a combination of techniques: X-ray photoelectron spectroscopy (XPS), near edge x-ray absorption fine structure (NEXAFS), density functional theory calculations (DFT), UV-visible absorption spectroscopy (UVVIS) and cyclic voltammetry (CV).

Metal-free phthalocyanine (H_Pc) has been shown to form films with different crystal structure and molecular orientation depending on deposition method, evaporation/sublimation or powder deposition, on commercial conducting glass (fluorine doped tin oxide, FTO), which is used e.g. in solar cells and organic light emitting devices (OLEDs). The unoccupied molecular orbitals are divided in x, y and z space coordinates of the molecule and also divided in inequivalent nitrogen components.

The electronic structure is also studied for a sublimated titanyl phthalocyanine (TiOPc) film and related to the metal-free phthalocyanine. The ligand field around the titanium atom in TiOPc is compared with that of TiO_2 to delineate the unoccupied levels recorded by means of x-ray absorption spectroscopy.

Nanostructured TiO_2 films were manufactured by screen printing/doctor blading on FTO. Such films were additionally covered with lutetium diphthalocyanine (LuPc_2) by means of surface assembly from solution. LuPc_2, LuPc_3 and LuPc_2H were identified and the stability of the electrochromic reactions in this system was monitored.

Chemical vapor deposition (CVD) has been used to grow nanometer sized anatase TiO_2 crystals on pre-oxidized Si (111) without formation of interfacial carbon and with an interface layer of the size of 15-25Å. The interface layer was found to be amorphous TiSi_O with graded stoichiometry.

Keywords: photoelectron spectroscopy, x-ray absorption spectroscopy, phthalocyanine, titanium dioxide, electronic structure, electrochromic reactions, thin films, chemical vapor deposition, evaporation

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To Stefan & Vilgot

Om du tror att du vet allt är du dåligt underrättad.

Kinesiskt ordspråk
List of papers

This thesis is based on following papers, which will be referred to in the text by their Roman numerals. The papers are for simplicity ordered chronologically. Reprints were made with permission from the publishers.

I Electrochromic Properties of bis(phthalocyaninato)lutetium(III) Sensitized Nanostructured Anatase TiO₂ Thin Films
L. Vayssieres, Y. Alfredsson and H. Siegbahn

II Titanium dioxide thin film growth on silicon (111) by chemical vapor deposition of titanium(IV)isopropoxide

III Metalorganic chemical vapor deposition of anatase titanium dioxide on Si: Modifying the interface by pre-oxidation
Surface Science 530(1-2) 63-70 (2003)

IV Equivalent core-hole time-dependent density functional theory calculations of carbon 1s shake-up states of phthalocyanine

V Phase and molecular orientation in H₂Pc films on conducting glass: characterization of two deposition methods
Submitted to Thin Solid Films
The papers presented here are based on teamwork. In general, my contribution to the papers is reflected by the position of my name in the author list. In paper I I was responsible for all experiments (except for the synthesis of Pc2Lu). I also contributed to the analysis of the results. In papers II and III I was involved in the measurements and took part in the analysis of data and preparation of the manuscript. In paper IV I was involved in the planning of the work and the preparation of the manuscript. In papers V and VI I was responsible for the XPS and UV-Vis measurements, experimental data analysis and writing of the manuscript. In paper VII I had the main responsibility for all experimental measurements, data analysis and writing of the manuscript.
4 Summary of the results .............................................................................31
  4.1 Pc2Lu sensitized nanostructured TiO2.............................................31
  4.2 TiO2 thin film growth.....................................................................35
  4.3 Properties of metal-free phthalocyanine ......................................38
  4.4 Properties of titanyl phthalocyanine thin film..............42

5 Summary in Swedish
   Elektrontillstånd och struktur hos tunna filmer av ftalocyaniner och
titandioxid........................................................................................................45
  5.1 Varför man studerar grönt, blått och vit färg...............................45
  5.2 Snabbgenomgång av artiklarna..................................................46

Acknowledgements.......................................................................................48
References.....................................................................................................49
Abbreviations

B.E. binding energy, often rel. to $E_F$
CVD chemical vapor deposition
DFT density functional theory
ESCA electron spectroscopy for chemical analysis
EXAFS extended x-ray absorption fine structure
FTO fluorine doped tin oxide
FWHM full width at half maximum
HOMO highest occupied molecular orbital
I.P. ionization potential, equivalent to $E_B^V$
LEED low-energy electron diffraction
LUMO lowest unoccupied molecular orbital
ML monolayer
MOCVD metallo-organic chemical vapor deposition
NEXAFS near edge x-ray absorption fine structure
NHE normal hydrogen electrode (25 °C, activity =1)
OLED organic light emitting diode
PD powder deposited
PES photoelectron spectroscopy
PVD physical vapor deposition
SEM scanning electron microscopy
STM scanning tunneling microscopy
TDDFT time-dependent density functional theory
TTIP titanium(IV)isopropoxide
UHV ultra high vacuum
UV-Vis ultraviolet and visible absorption spectroscopy
UV-VisAS ultraviolet and visible absorption spectroscopy
VD vapor deposited
XA x-ray absorption
XAS x-ray absorption spectroscopy
XP x-ray photoelectron
XPS x-ray photoelectron spectroscopy
Symbols

- $E_{b}^{F}$: binding energy rel. to $E_{F}$
- $E_{b}^{V}$: binding energy rel. to the vacuum level
- $E_{F}$: Fermi level
- $E$: electrode potential
- $E^{o}$: normal potential
- $E^{o}$: formal potential
- $h$: Planck’s constant
- $v$: frequency
- $\AA$: Ångström ($10^{-10}m$)

Chemical formulas

- CH$_2$Cl$_2$: dichloromethane
- H$_2$Pc: metal-free phthalocyanine, free-base phthalocyanine
- LuPc$_2$, Pc$_2$Lu: lutetium diphthalocyanine, bis(phthalocyaninato)lutetium
- Pc: phthalocyanine
- SiO$_2$: silicon dioxide
- SnO: tin oxide
- TiO$_2$: titanium dioxide
- TiOPc: titanyl phthalocyanine
Chapter 1
Introduction

Green, blue and white colors. This is by far the shortest way of describing the substances investigated in this thesis. The blue and green ones are the phthalocyanines, which are artificial substances slightly resembling chlorophyll in nature (the photoactive site), while the white is titanium dioxide. They are interesting owing to several special properties that make the substances useful within several important areas. Among the most important areas for the future is alternative electricity production. Within this area there is both research on solar cells based on nanostructured titanium dioxide as well as thin film solar cells with phthalocyanines. Other research areas for phthalocyanines are organic light-emitting diodes, gas sensors, displays etc. (you can also manufacture novel displays based on titandioxide). There also exists cancer therapy research with phthalocyanines. For a brief overview see Figure 1 and also paragraphs 1.1 and 1.2.

In this thesis, studies have been performed of importance for the development of these novel areas. To gain information on e.g. the depth profile of the chemical composition, the crystal structure, electrochemical properties, molecular orientation, the HOMO and the LUMO levels a combination of techniques have been used: X-ray photoelectron spectroscopy (XPS), different photoabsorption spectroscopies (UV-VisAS, NEXAFS) and cyclic voltammetry (CV). These methods are described briefly in the thesis. Density functional theory (DFT) calculations have also been performed to provide comparison to the experimental data of the thesis, and a very brief descrip-
1.1 Why phthalocyanines?

Phthalocyanines, Pc’s, are organic dyes that are used in a number of different ways, from cancer therapy to solar cells. There is ongoing research to make use of Pc’s in gas detection [1], in cancer treatment within the area of light-activated chemotherapy [2,3,4], as semiconductor in field effects transistors [5,6] and as replacement for platinum in solid polymer fuel cells [7].

Phthalocyanine pigments are also used to manufacture recordable CD’s, as an ordinary printing dye in color printing devices and in artist paint. They are organometallic complexes that have strong color, are stable at temperatures up to a few hundred degrees Celsius and exhibit a high resistance to chemicals. The large organic molecule is built up of one or more flat and square-shaped ligands with the chemical formula \(H_{16}C_{32}N_8\) together with a central positive ion, mostly a metal ion (Figure 2). This central ion gives the properties of the specific phthalocyanine. There exists one phthalocyanine without an ion center, the metal-free phthalocyanine (H\(_2\)Pc), where there are instead two hydrogen atoms in the center of the molecule binding to the ligand. H\(_2\)Pc is, together with titanyl phthalocyanine, TiOPc, and lutetium di-
phthalocyanine, LuPc₂, the cases studied in this thesis. TiOPc belongs to the group of oxometal phthalocyanines having a metal oxide in the complex center. Lutetium diphthalocyanine is instead an example of a sandwich-type complex, having two phthalocyanine ligands surrounding the lutetium ion. The three Pc’s are shown in Figure 2.

Several Pc’s have earlier been used for sensitizing nanostructured TiO₂ solar cells [8,9,10]. LuPc₂ has in addition to its semiconducting properties also several different colors, orange, green and blue, related to the different electrochemical charge of the molecule [11,12]. Furthermore LuPc₂ has been reported as one of the first stable free radical phthalocyanines [13]. H₂Pc is together with other Pc’s used on conducting glass in thin film solar cells [14,15,16], and several Pc’s including TiOPc are used in OLEDs [17,18,19]. A general mapping of electronic properties important for applications of the molecules has been the main goal of the phthalocyanine studies presented here.

Figure 2. (a) Metal free phthalocyanine, H₂Pc, (b) Titanyl phthalocyanine, TiOPc, (c) Lutetium diphthalocyanine, LuPc₂.
1.2 Why titanium dioxide?

Titanium dioxide, TiO$_2$, is a harmless white material that you find in many forms in everyday life. It appears in a number of common substances like white paint, toothpaste, sun lotion, soap, and colored food. You can also find it as a top layer on the metal titanium, which is a popular metal in vehicles, jewelry and medical implants. In this thesis two aspects of TiO$_2$ have been studied: i) the growth of a very thin TiO$_2$ layer (ca 5 nm) in the form of nanocrystallites and ii) the electrochromic properties of a thicker (ca 5 μm) layer of nanostructured TiO$_2$ dyed with a solar (and visible) light absorber, lutetium diphthalocyanine.

The growth of TiO$_2$ crystallites on silicon has probably its largest interest within research on new extremely small transistors where the old gate material silicon oxide is limiting the size, however also for other applications nanocrystalline TiO$_2$ growth is of relevance, e.g. for solar cells. The results from the nanostructured TiO$_2$ film dyed with LuPc$_2$ are of specific interest for display applications.

TiO$_2$ is normally white but if very small grains are used (a few nanometers) the substance turns transparent due to the low light scattering efficiency. The nanostructured TiO$_2$ is like a sponge of nanometer sized particles with nanometer sized cavities. One of the most remarkable features of such a structure is the large inner surface area. Since the grains are so small most of the atoms are in the outermost layers and react as surface atoms. Nanostructured TiO$_2$ has been used in solar cell research [20,21] and displays, often dyed/sensitized with a colored substance e.g. a ruthenium polypyridine complex [22]. Electrochemically tuned "smart windows" is another application. In most of these cases a view-through back-contact is required and conducting glass, i.e. glass with a deposited transparent doped and thus conducting SnO layer, is the most common alternative.
Chapter 2
Deposition methods

In the following I describe some deposition methods and how they are used in the present work. First, evaporation deposition and chemical vapor deposition are presented, where each molecule adsorbs individually (gas phase methods). Then self assembly (a low concentration solution method) is presented followed by the deposition methods screen-printing (high concentration solution/emulsion method) and powder deposition (solid state method).

2.1 Evaporation

Evaporation is classified as a physical vapor deposition (PVD) technique together with different kinds of ion plating and sputtering techniques. The comparison between PVD and CVD is presented under paragraph 2.2.

Evaporation is briefly exactly what the name says. The material is heated above its boiling/sublimation point in vacuum. In vacuum the evaporated atoms/molecules have a long mean free path and can therefore travel in straight paths to the sample. There they condense on the surface. One consequence of this line-of-sight transport of the particles is that the shape of an aperture the particles are passing through is pictured on the sample. Shadowing effects could also evolve on corrugated surfaces.

In the evaporation of Pc onto conducting glass in paper V,VI, and VII a Pc filled molybdenum foil pocket with a needle pin hole aperture was resistively heated in a base pressure in the low $10^{-9}$ mbar range. The pocket was
thoroughly degassed up to the deposition temperature before the deposition. The pressure was raised to the low $10^{-7}$ mbar range creating a multilayer thin film of $\text{H}_2\text{Pc}$ on the substrate situated 2 cm from and facing the aperture. The sample was then transported in vacuum to the XPS analysis chamber. The thickness of the $\text{H}_2\text{Pc}$ film was subsequently estimated to $1.0 \cdot 10^2$ nm by comparing the intensity of the 620 nm absorption peak in UV-vis spectrometry with reference [23].

2.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is a method where one or several gases are allowed to chemically react in close proximity to a heated substrate surface. The by-products are then pumped out of the system. For a chemical reaction to occur spontaneously on the surface it is necessary to have reactive precursors with quite high vapor pressure which makes the handling of the precursors delicate. It is also common to dilute the precursor by an inert carrier gas. Since the by-products often are reactive, corrosive and toxic an appropriate pumping system is required to remove and neutralize them.

There are several varieties of chemical vapor deposition, from ordinary thermal CVD to newly developed variants such as plasma-enhanced processes and glow-discharge sources. The thermal process could be performed in a hot-wall system where both the substrate and the chamber are heated, or in a cold wall system where only the substrate is heated, the latter giving less by-products. The pressure may vary from atmospheric pressure to low pressure with an ultrahigh vacuum background and the temperature is usually quite high, often above 600°C.

One aspect separating CVD from physical vapor deposition (PVD) is that a chemical reaction occurs in CVD while PVD proceeds by condensation. Another aspect is that CVD usually is endothermic whereas PVD is exothermic [24]. With CVD, the film is also generally more uniform on non-flat samples than with PVD. The film could also stick better to the surface if the chemical reaction leads to chemical bonds to the substrate. Finally, as mentioned above, since chemical reactions are intended to occur and thus the precursors must be reactive, the substances are more difficult to handle than the substances used in PVD.

The use of the CVD technique has been continuously growing and major areas of applications have rapidly developed within the semiconductor and metallurgical-coating industries [25]. In parallel with this development the CVD and PVD techniques have evolved and approached each other. CVD uses for instance plasma techniques and now there exists also "reactive PVD". A rapidly growing field is metallo-organic CVD, MOCVD. The use of organometallic compounds allows for lower deposition temperature and uses a broad spectrum of substances.
The growth of TiO$_2$ on Si in paper II and III is performed by MOCVD. The precursor titanium(IV)isopropoxide (TTIP) absorbs the energy from the heated silicon surface and decomposes into TiO$_2$ and hydrocarbons, C$_x$H$_y$:

\[
\text{Ti(OCH(CH$_3$)$_2$)$_4$ (gas) + heat } \leftrightarrow \text{TiO}_2 (s) + \text{C}_x\text{H}_y (gas) \quad (1)
\]

If the reaction is pure, all bi-products are in the gas phase and continuously pumped off.

Prior to the experiment, the inlet system for TTIP(Aldrich) was baked out and passivated by several flushes with TTIP. The TTIP was purified from residues with low boiling point by freeze-pump-thaw cycles. The silicon substrate was thoroughly cleaned prior to film deposition and the resulting (7x7) reconstruction of Si(111) was checked with LEED.

### 2.3 Surface assembly from solution/self assembly

Self assembly is a surface/low dimensional assembly from a dilute solution. It is primarily used for large organic molecules that order themselves in a fluid with or without the presence of a substrate. Substrates could be both solid surfaces and fluid surfaces, as in organized Langmuir-Blodgett films. The molecules may also be dispersed in a fluid forming micelles or DNA molecules. One important issue concerning all self assembled systems is that the process stops after certain time, when the structure is complete and no further molecules are added. Often the complete structure is a homogenous monolayer denoted SAM, self assembled monolayer.

In paper I the nanostructured TiO$_2$ films were covered with LuPc$_2$ by immersing the thin films in a $10^{-4}$ M CH$_2$Cl$_2$ solution of Pc$_2$Lu for at least 24 h. The soaking was performed directly after a cleaning/heat treatment was carried out on the TiO$_2$ film, directly after the sintering process for a new film, or after a re-sintering treatment to burn off contaminants of an older (approx. 1 h - 2 weeks) film.

By letting the solution soak the nanoporous structure, a homogenous coloration by Pc molecules was achieved which was stable to solvent rinse. Since the increase of the coloration by the phthalocyanines stops after approximately one day, it may be assumed that the surface deposition process from solution actually is a self assembly process. The amount of adsorbed phthalocyanine derived from the absorption peak compared with the inner surface of the nanostructured TiO$_2$-film also confirms the surface coverage to be approximately a monolayer.
2.4 Screen print/ doctor blading

Screen print is a method to adsorb/deposit a fluid substance with certain properties in a thin layer in a specific pattern with the edges shielded. The fluid is then dried or heat-treated to fixate the substance and remove the solvent. Often the expression screen print is exclusively used for large-scale printing whereas the small-scale laboratory screen print method is referred to as doctor blading. In doctor blading, the shielding is not crucial and the thickness of the deposited suspension could instead be set by a device lifting the blade to a specific height.

The nanostructured TiO₂ film in paper I was made with a small-scale screen printing method, see Figure 3, to deposit a colloidal suspension with nanosized TiO₂ particles prepared according to O’Regan and Grätzel [20]. The viscous liquid was spread on a piece of conducting glass (FTO) with scotch tape on the edges to shield the conducting layer in a narrow area from the non-conducting TiO₂ and to set the height between the FTO substrate and the glass rod used to spread the suspension. After approximately three minutes to dry in air the electrodes were heat-treated at 450°C for 30 min. leading to well-crystallized porous anatase TiO₂ thin film of about 5 μm in thickness.
2.5 Powder deposition

In paper V, in addition to the samples manufactured by evaporation, samples prepared by spreading the molecular powder manually on the substrate surface were studied. The samples prepared directly with H₂Pc powder were gently polished with H₂Pc under ambient conditions using a stainless steel spatula leaving a thin layer homogeneous in color on the surface. The samples were then subsequently mounted on the sample holder and transferred into the spectrometer introduction chamber. The thickness of powder deposited films was estimated to be approximately the same as that of the sublimated film since the absorption in the total Q-band was of similar magnitude. (Q-band absorptions for the different deposition methods are shown in Figure 17.)
Chapter 3
Characterization methods

3.1 X-ray photoelectron spectroscopy

In XPS, x-ray photoelectron spectroscopy, electrons are emitted from the sample as a response to incoming x-ray photons as illustrated in Figure 4. A general acronym independent of photon energy is PES (photoelectron spectroscopy). The electrons acquire enough energy from the photons to enable escape from the atom and its environment. If the energy of the photon is well defined, $h\nu$, it is possible to use the kinetic energy of the outgoing electron outside the sample, $E_{K'}$, to derive the electron binding energy, $E_{B}^{V}$, via the photoelectric law [26]:

$$E_{K'} = h\nu - E_{B}^{V}$$  \hspace{1cm} (2)

The electrons are ejected from the sample atoms in all directions. Due to inelastic scattering processes, emission of electrons normal to the surface originate further down in the sample than electrons emitted at grazing angles from the sample surface. The electrons emitted in the direction of the spectrometer input are first retarded (or accelerated) and focused by an electron lens system (see Figure 5) and then dispersed in terms of kinetic energy by a hemispherical electrostatic analyzer. The photoelectrons are subsequently detected via a multichannel system consisting of multichannel plates (MCP’s), a phosphor screen and a CCD camera.
Figure 4. In XPS the x-ray photons have enough energy to remove the core electrons of the material, i.e. to lift them energetically above the vacuum level.

Figure 5. Schematic picture of an XPS system with the x-rays originating from a rotating anode.
3.1.1 Binding energy definitions

The kinetic energy in (2) is the kinetic energy of the electron just outside the sample. The detected kinetic energy is however the kinetic energy inside the spectrometer, which is generally different. This difference is due to the difference in work function of the sample, $\phi_s$, and the spectrometer, $\phi_{sp}$. This implies that the vacuum levels will be different as illustrated in Figure 6, since the sample and the spectrometer are in electrical contact, i.e. the Fermi level is pinned the same for both. This means further that the electrons are accelerated or retarded into the spectrometer due to the work function difference of the sample and the spectrometer. The relation between the kinetic energies is then:

$$E_K = E_K' + \phi_s - \phi_{sp}$$  \hspace{1cm} (3)
Table 1. Examples of atom specific peak energies and chemical shifts.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Explanation to the chemical shift</th>
<th>$E_B^F$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s</td>
<td>in SiO$_2$</td>
<td>532</td>
<td>Papers II and III</td>
</tr>
<tr>
<td></td>
<td>in TiO$_2$</td>
<td>531</td>
<td>Papers II and III</td>
</tr>
<tr>
<td>Si 2p</td>
<td>unoxidized</td>
<td>99.5</td>
<td>Papers II and III</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>103</td>
<td>Papers II and III</td>
</tr>
<tr>
<td>Ti 2p$_{3/2}$</td>
<td>$\text{Ti}^{4+}$</td>
<td>459</td>
<td>Papers II and III</td>
</tr>
<tr>
<td></td>
<td>$\text{Ti}^{3+}$</td>
<td>458</td>
<td>Papers II and III</td>
</tr>
<tr>
<td>Au 4f$_{7/2}$</td>
<td>(inert)</td>
<td>84.0</td>
<td>[27]</td>
</tr>
</tbody>
</table>

This is the reason why most binding energies for solid metallic samples are presented with the Fermi level as zero of the binding energy scale instead of the vacuum level. The relation between the binding energies is:

$$E_B^F = E_B^V - \phi_s \quad (4)$$

where $E_B^F$ is often called simply the binding energy (without specification) whereas $E_B^V$ is called the ionization potential, I.P. For nonmetallic solid samples where the Fermi level is less clearly defined, there is, however, no definite standard choice of binding energy.

3.1.2 Atom specific peaks and their chemical shifts

With XPS one can map all the occupied electronic levels reachable with the photon energy used, from the innermost core orbital to the outermost valence orbital. One main reason to use XPS is its atomic specificity. The binding energies of the core orbitals are always atom specific, since such electrons are not involved in molecular or solid state bonding. Thus it is relatively straightforward to make an elemental compositional analysis of the sample. The core levels however vary in binding energy depending on chemical environment (chemical shift), see table 1. To a first approximation, the chemical shift may be explained in terms of changes in the electrostatic potential of the core orbital upon chemical changes. On the basis of such a model, the chemical shifts provide information on the oxidation state and chemical environment of the atoms.
3.1.3 Surface sensitivity

XPS is a very surface sensitive technique. The photons penetrate quite far into the sample (at least several hundred nm) but since the XPS peaks are due to electrons that have not been inelastically scattered, the investigated depth is limited to the value of the inelastic mean free path of the electrons in the material. A typical value is about 25 Å, but it varies in the interval 3 Å - 40 Å depending on the kinetic energy of the electrons. By tuning the photon energy one can then make a non-destructive depth profile of the chemical composition. This can in principle also be achieved by changing the escape angle of the electrons with respect to the sample surface, as mentioned in 3.1.1.

3.1.4 Intensity

To be able to make a quantitative analysis it is necessary to have control of the intensity parameters. The cross section for the photon – electron orbital interaction gives the primary contribution to the photoelectron intensity. It may differ by several orders of magnitude depending on the photon polarization direction and energy. The surface sensitivity has already been mentioned above and if the studied atoms have a depth distribution into the material it is necessary to compensate for this in quantitative analysis. An important factor is also the instrument transmission which depends on the electron kinetic energy. The electron lens generally has a variable transmission function, which may lead to considerable effects over a wider kinetic energy range.

3.1.5 Additional spectral features

Photoionization not only leads to core and valence photoelectron peaks in the observed electron spectrum. Peak due to secondary processes also occur, such as Auger and autoionization peaks. These result from radiationless decay of core hole vacancies created in the photoionization process. The Auger peaks have atomic specific kinetic energies independent of the photon energy (cf. 4 in Figure 7).

On the high binding energy side of the core level peaks there are often satellite peaks. The satellite peaks are due to additional excitations/ionizations among the valence electrons upon core ionization (shake-up and shake-off). For solids such processes involve e.g. interband transitions or collective electron excitations (plasmons).
Figure 7. Some of the outcomes from when an x-ray photon has been absorbed in an atom. The different kinds of emitted electrons have been denoted 1-4. The core XPS electrons denoted 1 and the Auger electrons denoted 4 are described in this chapter while the electrons denoted 2 and 3 are covered in the next chapter (3.2).

3.1.6 Resolution

To be able to use the photoelectric law, the energy of the x-ray photons must be well defined. Narrow bandwidth photons are obtained using characteristic x-rays as in Figure 5 or synchrotron radiation from an electron storage ring coupled to a monochromator. Other variables that influence the resolution in an electron spectrum are the spectrometer specific variables, here presented for a hemispherical analyzer:

- the pass energy ($E_p$) - the lower the kinetic energies of the electrons in the spectrometer the better the resolution (smaller $\Delta E$)
- the radius of the hemispherical analyzer ($R_0$) - the larger the radius the better the resolution
- the width of the entrance slit to the spectrometer (b) - the smaller the width the better the resolution.

These instrumental factors are summarized in equation (5):
A common way to specify the resolution is to measure a standard peak, such as the FWHM of the Au 4f peak or the width of the Ag Fermi edge.

3.1.7 Equipment

ESCA 300 is a commercial instrument (Gammadata Scienta) using a rotating anode high-power x-ray source and quartz crystal monochromator delivering Al Kα radiation. It is thoroughly described in reference [28]. This instrument has a 300 mm radius hemispherical electron energy analyzer and a swift sample transport system from air to UHV. The binding energy scale of our spectra recorded with ESCA 300 was referenced to the Fermi edge of an Ag sample.

Synchrotron radiation has the advantage of being tunable at very high intensity but has the disadvantage of the limited access of the synchrotron facility compared to a home instrument. The ability to tune the photon energy allows for x-ray absorption spectroscopy recording (see next section) and makes it possible to achieve a very high surface sensitivity by adjusting the photon energy to keep the mean free path low. It also gives the possibility to record valence band spectra at different photon energies to identify components in the band due to variations in photoelectric cross section. The high intensity of the photon beam allows for fast recordings, which is of extra relevance for gas phase measurements. The beam lines I 411, I 511 and D1011 used in this work are located at the MAX-Lab synchrotron radiation facility in Lund, Sweden. The beam lines are described in references [29, 30, 31, 32]. All three are undulator-based and equipped with Zeiss SX700 plane grating monochromators providing high-intensity synchrotron radiation in the photon energy range from around 30-100 eV to 1500 eV. The end stations feature SES-200 hemispherical electron energy analyzers. At beamlines I 411 and I 511 the analyzer can be rotated around the incoming beam for polarization dependent measurements. The manipulator at I 411 may also be mounted perpendicular to the incoming beam which is the geometry used in the measurements of this thesis.

3.2 Near edge x-ray absorption fine structure

NEXAFS is an acronym for Near Edge X-ray Absorption Fine Structure. It is an x-ray absorption spectroscopy technique, where one studies the structure of an absorption spectrum over the range within approximately 10 eV
around the onset of absorption from a specific core level. One example is thus the structure obtained from the transitions from N1s to the unoccupied molecular orbitals in phthalocyanines. The photon energy is tuned over the edge so that the absorption of photons starts when the energy is sufficient to excite electrons into unoccupied states. All unoccupied states are however not allowed due to the dipole selection rules. For example, for a 1s core level, XAS maps the local p-character of the unoccupied states. An oscillating structure in the absorption spectrum at higher photon energies may also be observed for molecules and solids. Such structure is due to scattering of the outgoing electron against nearest atomic neighbors and is referred to as EXAFS, extended x-ray absorption fine structure.

Examples of different ways to record photoabsorption spectra are:

- collect Auger electrons = partial electron yield (a surface sensitive technique)
- record current = total (electron) yield
- record fluorescence photons = fluorescence yield (a moderately surface sensitive technique)
- record transmitted photons (thin sample necessary)

In the first mode it is specifically the electrons denoted 2, 3 and 4 in Figure 7 (section 3.1.5) originating from decays of the excited (and ionized) atoms that are recorded. The number of such electrons is proportional to the number of excited atoms.

The most efficient way of recording NEXAFS is the use of synchrotron radiation, allowing also the use of polarized light. The latter feature implies that molecular orientation may be studied e.g. for molecules adsorbed on surfaces or other molecular arrangement at solid/vacuum interfaces. Paper V and VII contain applications of this technique.

### 3.2.1 Experimental details

NEXAFS was obtained by collecting the Auger electrons from the sample as function of the incoming photon energy. This was done by collecting all electrons within a chosen kinetic energy range, an energy window. At beamline I 511 in MAX-lab the chosen kinetic energy window was 371-392 eV during the N1s NEXAFS recordings. At beamline I 411 the kinetic energy window was 361-390 eV during the Ti2p NEXAFS and 357-386 eV during the N1s NEXAFS. At beamline D 1011 in MAX-lab the kinetic energy window had only a low kinetic energy limit of 270 eV from a retarding potential during the Ti2p NEXAFS recordings. A large energy window makes the method less sensitive to disturbances from non-Auger electron peaks, which do not have a fixed kinetic energy but could enter the kinetic window during
3.3 Cyclic voltammetry

In electrochemistry the potential $E$ (versus NHE) is given by the Nernst equation [33]

$$E = E^o - \frac{RT}{nF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}}$$

(8)

where $a_{\text{ox}}$ and $a_{\text{red}}$ represent the chemical activities of oxidized and reduced side of the reaction, respectively, $R$ is the molar gas constant, $T$ the absolute temperature, $n$ the number of electrons involved and $F$ the Faraday constant. $E^o$ is termed the normal potential and is redox-couple specific. A simplified variant at low concentration aqueous solutions is given by

$$E = E^o - \frac{RT}{nF} \ln \frac{[\text{red}]}{[\text{ox}]}$$

(9)

where $[\text{red}]$ and $[\text{ox}]$ are the products of the ion concentrations in the electrolyte and $E^o$ is the formal potential, which thus is approximately equal to the normal potential.

In cyclic voltammetry, CV, the potential of the electrode (versus NHE via...
a reference electrode) is cyclically scanned typically with a rate of 1-100mV/s between two endpoints and the resulting current is monitored. In this way, it is possible to observe at which potential an electrochemical reaction occurs in terms of a current peak. In order to derive the redox (formal) potential $E^\circ$, an interpolation is made between the oxidation and the reduction peak, see Figure 8 [34]. A cyclic voltammogram also contains information about the reversibility and the kinetics of the system.

When the redox reaction is not reversible, when the reaction is slow due to slow diffusion or there are several reactions going on simultaneously, the CV will look very different from this. Systems having a limited level of these anomalies are those best suited for cyclic voltammetry.

In the present study, the reference electrode in the three electrode set-up was Ag/AgCl. The counter electrode was a sheet of platinum. Inert oxygen-free gases, Ar or N$_2$, were bubbled through the solution before each experiment and kept at a slight overpressure in the cup covered by a teflon lid. All parts in contact inside the cup were made of glass, titanium or teflon to avoid unwanted reactions. A potentiostat was used to drive the potential between the substrate working electrode and the counter electrode.

### 3.4 UV-visible optical absorption spectroscopy

UV-visible optical absorption spectroscopy is a technique where light with wavelengths between 300 nm and 1100 nm illuminates the material, and the light passing through is recorded obtaining an absorption spectrum for the wavelength interval used. For solutions, approximately all the light that does not travel through the substance is absorbed electronically. For a film on a piece of glass, however, light could also be reflected in the surfaces causing an overall decrease of the light or interference phenomena related to the film thickness. If the particles in a film are large compared to the wavelengths involved scattering losses may also be quite important. In the present study, the UV-visible optical absorption spectra were recorded using a Hewlett Packard UV-Visible ChemStations 8453.

### 3.5 Spectroelectrochemistry

In spectroelectrochemistry the UV-Visible optical absorption measurements are performed in situ during cyclic voltammetry. In our case, the absorption measurements were made during the potential scan, which was possible since the scan rate was slow compared to the absorption measurement time. A 10 mm x 50 mm fluorescence quartz cell was used to host the three electrode system coated with teflon to protect the electrolyte from oxygen. The cell is illustrated in Figure 9.
3.6 Density functional theory

The development in electronic structure theory has during recent years lead to dramatically improved possibilities for calculations on larger molecular systems. Density functional theory (DFT) was first formulated in theorems by Hohenberg and Kohn [35] and further developed by Kohn and Sham [36]. With DFT the total electron density for the molecule is calculated instead of the wavefunctions for each orbital of the molecule. The calculations of the individual orbitals is more correct and reliable, but when the molecular size increases, the number of variables increases dramatically and the size of the equations becomes astronomical. If one instead computes the total electron density the mathematical problem increase at a much smaller rate. The theory is based on the fact that the ground state electron density has a direct correlation to the ground state energy of the system. To solve the Kohn-Sham equation for different kinds of systems, several theories and approximations have been presented and many computer softwares have been written using different iteration schemes. In paper IV a combination of equivalent core hole approximation and time dependent DFT has been used to simulate the shake-up structure of C1s. In paper VI DFT was used to optimize the molecular geometry and simulate the I.P. for N1s for the different nitrogen atoms, the XAS for the nitrogen atoms and the valence band. The softwares used were Gaussian03 and deMon.
Chapter 4
Summary of the results

I have chosen to present the research results from the papers in the same order as in the list of papers (chronological). Paper I is presented in paragraph 4.1, papers II and III in paragraph 4.2, papers IV, V and VI in paragraph 4.3 and paper VII in paragraph 4.4.

4.1 Pc2Lu sensitized nanostructured TiO2

In paper I a nanostructured TiO2 film has been dye-sensitized with Pc2Lu. Since Pc2Lu has three oxidation states with completely different colors it was of interest to investigate if it was possible to achieve these colors for the sensitized film and to tune them by altering the potential or the acidity in the electrolyte. The nanostructured titanium dioxide was of the same kind used in electrochemical solar cells, so called Grätzel cells [20,21].

In Figure 10 a typical cyclic voltammogram of Pc2Lu on nanoporous TiO2 is shown, where different chemical reactions could be identified. This CV could be divided into three parts: (i) the first single peak at -0.4 V, (ii) the pair of peaks centered around -0.55 V, (iii) the increase in current at lower potentials:
Figure 10. A cyclic voltammogram on Pc2Lu dyed nanostructured TiO2. The scan rate was 1 mV/s and the electrolyte 0.5 M KCl, pH ca 6. The spectrum could be divided into three major contributions explained in the text.

(i) The first reduction peak appears at -0.4 V versus Ag/AgCl. This peak was largest in the first scan and diminished during repeated scanning. If the sample was held at open circuit potential for 24 hours the reaction had reversed so that the peak could appear again. A minor peak at about the same voltage was also observed in the first scan on bare TiO2. This indicates that the peak could be composed of two overlapping peaks, one from Pc2Lu and one related to the substrate.

(ii) The pair of peaks centered at around -0.55 V. Both peaks had roughly the same area, which implies a reversible reaction. Decreasing the potential, the film color changed from green to brown. Increasing the potential, the reaction proceeded substantially slower, but the green color returned before the potential reached 0 V.

(iii) The increase in current at lower potentials is probably due to proton intercalation in TiO2. At pH = 1 the current increases to the mA range at -0.7 V and the film turns dark blue for both Pc2Lu on TiO2 and bare TiO2.
Figure 11. UV-Vis optical absorption spectra of the a) "Irreversible" change during CV, scan rate 10 mV/s (fast to react, 24 hours for the back reaction). The spectra are from a new film before and after the first cyclic voltammetry scan, close up of the most characteristic changes. The green color is improved afterwards. b) Reversible change. The most characteristic changes are the growth of an absorption peak at around 540 nm and the increase in absorption at 800 nm - 900 nm.

Another small peak is observed at 0.51 V during increasing potential in the case of acidic electrolyte (pH=1), which did not seem to be due to Pc2Lu. This peak appeared not only on the nanoporous film but also on bare conducting glass without TiO2.

The spectroelectrochemical results are presented in Figure 11. The absorption spectra give information about the molecular states at the different potentials. In the absorption interval 400 nm - 1000 nm the negatively charged blue colored state, Pc2Lu−, is characterized by two peaks at 620 nm and 700 nm as shown in table 2 [37]. This agrees well with the result shown
Table 2. Previously measured peaks for thin film of Pc2Lu [37].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Peaks, nm (between 400 nm and 1500 nm)</th>
<th>Color</th>
<th>Transition</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pc2Lu+ (+ Pc2LuH due to disproportionation)</td>
<td>450, 700, 855</td>
<td>orange</td>
<td>radical ligand, Pc·</td>
<td></td>
</tr>
<tr>
<td>Pc2Lu-</td>
<td>620, 700</td>
<td>blue</td>
<td></td>
<td>as PcM (metal-monophthalocyanine)</td>
</tr>
<tr>
<td>Pc2Lu</td>
<td>460, 660, 904, 1382</td>
<td>green</td>
<td>2e_g(\pi)\rightarrow\alpha_{1a}(\pi)</td>
<td>radical ligand, Pc·</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1e_g(\pi)\rightarrow\alpha_{1a}(\pi)</td>
<td>radical ligand, Pc·</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>interligand</td>
<td>Pc· AND Pc·</td>
</tr>
</tbody>
</table>

in Figure 11 a. The behavior shown in Figure 11 a may then be interpreted such that Pc2Lu transforms to Pc2Lu- after the first scan on a new electrode. The film does not however, turn blue, but the yellow-green shade turns to more distinct green. Since the complementary color to these two wavelengths is green, this is not surprising even if others workers have observed a blue color.

Figure 11 b shows the UV-visible optical absorption spectra during CV obtained for the Pc2Lu dyed film in neutral electrolyte after the first scans, i.e. the faster reaction. The electrolyte used was 0.5 M KCl at pH=6. The peaks observed are identified based on Pc2Lu disproportionation [38]:

\[
2 \text{Pc2Lu} + \text{H}^+ \rightleftharpoons \text{Pc2Lu}^+ + \text{HPc2Lu}
\]

If Pc2Lu disproportionates, the resulting absorbance is thus a combination of both Pc2Lu+ and Pc2LuH. Markovitsi et al [37] have observed bands at 450 nm, 700 nm and 855 nm for such a case (see table 2). Pc2Lu+ has an orange color and Pc2LuH a blue color according to Plichon et al [39]. This makes it likely that the result observed in Figure 11 b, the rising peaks, is due to a combination of Pc2Lu+ and Pc2LuH, which also would give the brown color observed. The peaks in Figure 11 b are situated at (i) 540 nm, (ii) 640 nm, (iii) 700 nm and (vi) a broad feature around 850 nm. The overlaying periodicity between 800 nm and 900 nm does not seem to be related to molecular states. These wiggles changed positions for different films and different an-
gle of incidence of the light, which is expected if they are due to film thickness interference. The first peak is expected to correlate to the band at 450 nm for the disproportionated case, the difference however with respect to 540 nm is large. The second peak, which corresponds to Pc2Lu as mentioned above, diminishes slightly. The third and the forth peaks fits very well with the disproportionated case.

In summary, for electrochemistry of Pc2Lu on nanostructured TiO2 in a water-based electrolyte, the three-color system (blue, green, orange) characteristic for Pc2Lu, does not occur. Instead a reversible reaction from green to brown color occurs. This brown state could be interpreted as a mixture of the blue and orange states due to disproportionation in the presence of H+. This, together with the slow reactions, makes the studied system less interesting for display purposes.

The pH dependence, however, is an advantage since it then becomes possible to shift the potential range of the reaction to desired values. It makes it also possible to let the reaction occur just by altering pH, keeping the potential fixed. One disadvantage though, is that if the TiO2 proton intercalation (with the color changing between transparent and dark) has the same H+ dependence as the Pc2Lu color scale, it will not be possible to adjust the two color scales separately. If this, however, could be achieved the system would be powerful for display purposes. The good cycling stability of the system was a promising result, since this property is important for display purposes.

4.2 TiO2 thin film growth

One prospective use of TiO2 thin films is as high dielectric constant replacement of SiO2 as gate insulator. The dimensions of transistors are decreasing and so is the thickness of the gate insulator that now has reached a critical limit where quantum mechanical tunneling becomes a problem. To improve them further it is thus necessary to modulate another variable instead - the dielectric constant of the insulating material.

In this work the initial stages of a TiO2 growth made with CVD technique on Si(111) under UHV conditions is studied. Several different investigation techniques show the same result; the uppermost layer is pure anatase TiO2 crystals with no contaminations left of the precursor. The interface between pure TiO2 and pure Si is also very thin, in total 3 nm (paper II) or less (paper III). The composition of the interface was found to be TiSi1/2O2 with graded stoichiometry, and the amount of pure SiO2 in the interface which could jeopardize the use of the film as replacement for SiO2 in gates in transistors was found to have sufficiently low values.
Figure 12. STM picture of the grown nanocrystalline TiO₂ film. The topographic cross section shows height differences of about 3 nm on top of a distinct base level.

An STM picture of the TiO₂ film obtained in paper II is shown in Figure 12. It shows the final result after growth. Along the dashed line a topographic cross section is taken, presented in the bottom of the graph showing height differences of about 3 nm on top of a distinct base level. In the surface plane the size of the particles in the picture is approximately 10 nm. The STM picture thus shows approximately 3nm x 10nm sized particles on top of a flat intermediate layer. The total film thickness is estimated by PES to be 5.5 nm, which gives a thickness of the interface region below 3 nm.

In Figure 13 the ratios derived between the amounts of oxygen atoms, oxidized silicon atoms and titanium atoms are shown, as function of film thickness. This gives values for the expression TiSiₓOᵧ, from TiSi₂O₄ in the first atomic layer to the final TiO₂. The ratios were obtained from integrated XPS core peaks of Ti2p, O1s and Si₂p corrected for the different photoelectric cross sections. The value x in the stoichiometric expression is
Figure 13. The ratios derived between O 1s, Si ox 2p and Ti 2p throughout the growth. The dashed x-curve has been compensated for the surface sensitivity.

given in two curves where the dashed curve has been corrected for the surface sensitivity. Since the O1s recordings had the same probing depth as for Ti 2p no correction is necessary for the y-value.

From the graphs in Figure 14 it is possible to conclude that during the deposition from 22 Å up to 34 Å thickness pure anatase crystals begins to form. The Ti 2p NEXAFS spectrum from the 34 Å thick film is deconvoluted into one contribution having the shape of a pure crystalline anatase phase [40] and the contribution left (termed "TiSi\textsubscript{x}O\textsubscript{y}") with a striking resemblance to the 22 Å Ti 2p NEXAFS spectrum. The anatase part of the spectrum appears quite large compared to the amorphous part. This is because the anatase layer is lying on top of the amorphous layer and thus increases the intensity of the detected Auger electrons.

The amount of pure SiO\textsubscript{x} in the film is crucial for the possibilities of using the film as replacement to SiO\textsubscript{2} in gate insulators. It has been shown that if more than 2 nm pure SiO\textsubscript{2} is formed, the improvement of the gate will be lost [41,42]. In our case the amount of SiO\textsubscript{x} is estimated to be less than 1 nm and is also mixed with silicate TiSi\textsubscript{x}O\textsubscript{y}. This conclusion is based upon the fact that the Si\textsubscript{ox}2p XPS peak shifts to lower binding energy relative to the Si\textsubscript{bulk}2p XPS peak during the growth, as in the case of ZrSi\textsubscript{x}O\textsubscript{y} [43]. A shift in the opposite direction relative to the Si\textsubscript{bulk}2p XPS peak would instead have implied the formation of SiO\textsubscript{2} [44]. The conclusion is also supported by the estimated compositions presented in Figure 13 and the Ti 2p XPS peak structure at low coverages where evidence of Ti\textsuperscript{4+} is shown.
Contaminations from a metal-organic precursor, primarily carbon in various forms can be detected in the C1s core level XPS peak. In our TiO$_2$ film growth there was no C1s peak prior to growth nor on the TiO$_2$ film. The largest amount of carbon detected was at a film thickness of 5.7 Å in the beginning of the growth of the interface layer. It was estimated to be less than 0.15 ML (paper II). In paper III, where the Si surface was pre-oxidized, no carbon was detected in any step of the growth.

4.3 Properties of metal-free phthalocyanine

Two different methods have been used in to deposit H$_2$Pc films on conducting glass substrates (see paper V) and the obtained films have been characterized by a variety of spectroscopic methods, XPS, XAS and UV-Vis toget-
Figure 15. The two almost identical C1s core level spectra of evaporated and powder deposited H2Pc on FTO, Al Ka 1487 eV photon, and a curve fit of experimental spectrum for vapor deposited film together with computed bars for main peaks and shake-up structure.

her with theoretical DFT calculations (paper IV and VI). According to our knowledge, it is the first time a detailed discussion of the different atomic contributions to the intensity of the observed XAS peaks is reported (paper VI). The study also presents comprehensive results on both the occupied and unoccupied electronic orbitals by means of the methods used.

The XPS overview displays differences between the two preparation methods: in the case of an evaporated overlayer, the obtained results indicate a more homogeneous film than for the powder-deposited film since no photoemission from the substrate could be detected (paper V). The XPS spectra of C1s and N1s core levels are however almost identical for the molecular overlayers obtained by the two methods (cf. Figure 15 and Figure 16). A detailed description of the C1s shake-up profile of H2Pc is reported and excellent agreement between the theoretical simulation and experimental data was obtained (paper IV).

The DFT calculations performed here give the possibility to identify the different components and the symmetry character of the main NEXAFS features due to the different N atoms in the molecule as shown in Figure 16 (paper VI). The theoretically generated XPS spectrum is in good agreement with the experimental results. The valence photoemission data were likewise found to be in good agreement with previous results and theory (paper VI).
Figure 16. The two almost identical N1s core level spectra of evaporated and powder deposited H$_2$Pc on FTO, Al Kα 1487 eV photons, compared to the shape structure of a curve obtained by Gaussian broadening of the three calculated transitions with split according to the calculations/theoretical outcome.

Figure 17. UV-Visible absorption spectra for the indicated samples. These spectra are e.g. useful for phase identification. Theoretical transitions according to reference [45] are indicated by dashes.
A crystal structure characterization of the differently deposited samples was made by means of UV-Vis measurements (paper V). These indicate that the two methods used for the deposition result in two different films in terms of polymorph: α-polymorph in the case of an evaporated overlayer [46] and x-polymorph for a powder-deposited film [47], cf. Figure 17. The method also measures the band gap for the molecular films since the HOMO-LUMO transition is energetically in the range of ultraviolet and visible light.

The XAS results for the powder-deposited films reveal that the molecules are oriented parallel to the surface. The vapor-deposited film instead revealed an orientation perpendicular to the surface (paper V). This is concluded from the series of spectra recorded as function of photon polarization direction with respect to the surface plane (cf. Figure 18).

Computed XAS spectra are in excellent agreement with the experimental results even though the theoretical calculations were performed by considering only a single H$_2$Pc molecule, i.e. neglecting the intermolecular interactions. Furthermore, the theoretical data allowed assignment of the contributions of the different N atoms and the symmetry character of each XAS feature (cf. Figure 19) (paper VI). In particular, it is worth noticing that the first two peaks (of 398.4 eV and of 400.0 eV) are not to be interpreted as due to the shift in the N1s XPS, but contain substantial contributions from all nitrogen sites.

Figure 18. NEXAFS spectra for the H$_2$Pc powder-deposited and vapor-deposited film taken at three different incidence angles of the radiation used in the excitation.
4.4 Properties of titanyl phthalocyanine thin film

Figure 20 shows three N1s XAS spectra for TiOPc thin film vapor deposited on conducting glass recorded at different incidence angles with respect to the surface plane (paper VII). These correspond to near parallel/in plane (84°) and near normal (6°) orientation of the photon polarization vector with respect to the surface plane. As can be seen, the N1s → π* resonances at 398 eV and 400 eV are strongest relative to the higher lying σ excitations (beyond 405 eV) for near normal orientation of the photon polarization vector with respect to the surface plane. This implies that the molecules are oriented preferentially parallel to the surface plane similar with studies on other substrates [48].
Comparing the N1s NEXAFS spectra of TiOPc with that of H$_2$Pc, the spectrum of TiOPc contains additional structure in the second resonance at 400 eV as well as further resolved resonances at higher energies (Figure 18 and Figure 20). The fact that the TiOPc and H$_2$Pc N1s NEXAFS spectra are very similar in the near edge region, while the TiOPc N1s XPS spectrum differs in terms of chemical shifts from that of H$_2$Pc, supports the qualitative assignment of the two first resonances in the XAS spectra presented in paper VI (cf. Figure 19).

Turning next to the Ti2p XAS spectrum of TiOPc, a comparison with the corresponding spectrum of anatase TiO$_2$ is shown in Figure 21. These two spectra are seen to be substantially different both in peak positions and relative intensities. The differences of the Ti2p XAS spectrum between TiOPc and TiO$_2$ may qualitatively be described in terms of the crystal fields surrounding the titanium. If we focus on the 2p$_{3/2}$ XAS manifold from 456 eV to 462 eV we have the following simplified picture: The anatase TiO$_2$ spectrum has two main contributions due to the near octahedral coordination of the titanium atom, a t$_{2g}$ peak at 458.2 eV and an e$_g$ structure around 460 eV. Five-fold coordination with the central titanium atom in the plane of four surrounding nitrogen atoms and a fifth oxygen atom on top, will split the e$_g$ into b$_1$ at higher energy and a$_1$ at lower energy.
If the central titanium atom is moved upwards along the Ti-O-axis $t_{2g}$ will also split into $e$ at higher energy and $b_2$ at lower energy [49]. Since the titanium atom in TiOPc has been found to have such five-fold symmetry [50] we assign the four peak structure in the $2p_{3/2}$ manifold to these four resulting orbital levels. The prepeak at 455.5 eV we ascribe to a triplet state corresponding to the preedge peaks observed in the TiO$_2$ case below the $t_{2g}$ peak [51,52].

Valence spectra at N1s and Ti2p resonances for TiOPc thin film were also recorded. These spectra have been analyzed in terms of the molecular orbital parentage of the valence levels.

Figure 21. XAS at the Ti2p edge for TiOPc sublimated multilayer on FTO. A spectrum from anatase TiO$_2$ is included for comparison.
Chapter 5
Summary in Swedish
Elektronstillstånd och struktur hos tunna filmer av ftalocyaniner och titandioxid

5.1 Varför man studerar grön, blå och vit färg


Det jag har gjort är att studera dessa substanser med hjälp av (röntgen-) fotoelektronspektroskop (XPS), olika fotoabsorptionsspektroskopier (UVVis,
Figur 1. Några av användningsmöjligheterna varav vissa är kommersialiserade (titandioxid till vänster och ftalocyanin till höger). Detta är en mycket förenklad bild, eftersom titandioxid har olika egenskaper på grund av struktur och ftalocyaniner finns i så många varianter beroende på centralatom och substituenter.

NEXAFS) och cyklisk voltametri (CV). Densitetsfunktionalberäkningar (DFT) har även gjorts för att möjliggöra jämförelser. Studierna i avhandlingen är intressanta för utvecklandet av dessa nya användningsområden.

5.2 Snabbgenomgång av artiklarna

Här följer en mycket kort genomgång av de tidskriftsartiklar som tillhör denna avhandling:

Tunna filmer av titandioxid har tillverkats på kisel i artiklar nr II och III genom att låta kemikalier reagera med ytan under uppvärmning. Resultatet visar att titandioxidfilmen som skapats på detta sätt är ren, tunn, och av kristallformen anatas. Genom att passivisera ytan innan, vilket gjordes i artikel nr III, fås ännu renare film* med mer distinkt övergång. Den distinkta övergången bestod av ett 15-25Å** tunt mellanskikt av TiSiOy.

I metallfri ftalocyanin som deponeras på ledande glas ställer sig molekylerna huvudsakligen på högkant om man förångar i vakuum och man får kristallformen α-fas***. Om man deponerar molekylerna i pulverform utan

---

* Filmen var helt fri från kol under hela deponeringen. Den var även fri från andra föroreningar, men kolet brukar vara svårast att få bort.
** En atom är ca 3Å.
*** En kristallfas där molekylerna ligger tillsammans som en kortlek tiltad/ skjuvad 26°.
vakuum lägger sig istället molekylerna i stor utsträckning parallellt med ytan. Detta resultat presenteras i artikel nr V.

De olika elektronstillstånden hos den metallfria ftalocyaninen studeras i artikel nr VI, såväl de inre nivåerna, som valensnivåerna och de ickeockupera-de nivåerna, det vill säga från de innersta mest bundna elektronerna till de obundna.

För metallfri ftalocyanin har även shakeup-strukturen, det vill säga extra-excitationerna vid excitationer av de innersta elektronerna, analyserats. Detta i artikel nr IV.

Dubbeldäckaren lutetium diftalocyanin **** har använts i artikel nr I för att färga in nanostrukturerad titandioxid för att senare analysera dess elektrochemiska egenskaper i olika elektrolyter.

Tunn film av titanylftalocyanin på ledande glas har studerats i artikel nr VII. Den utgör en intressant jämförelse med både titandioxid och andra ftalocyaniner och har studerats med avseende på möjliga energinivåer hos elektronerna. Där har vi bland annat sett hur molekylen ligger på ytan (molekylorienteringen), samt fått information relaterad till molekylgeometrin.

**** Denna molekyl har extra kul färger. Grön, blå och orange har blivit rapporterade, vilket gör att den teoretiskt skulle vara mycket skoj att göra displayar av.
Acknowledgements


Min andre handledare Anders Sandell har också varit till stor hjälp. Utan dig skulle jag nog slitit mitt hår för att få bra resultat av och ordning på ostrukturerade mätningar.

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Min väggväggbonushandledare (oh vilket fint ord) Håkan Rensmo, som varit ett bra stöd i att få saker genomförda ”Det är bara att köra på.”, men även att prata om viktiga ting med.

Alla doktorander i gruppen och angränsande grupper att utbyta olika saker med (från igor-makron och mätdata till seriestrippor och felaktiga noter till Staffansvisan) och utföra saker tillsammans med (som t.ex. att försöka få vågröralabbarna att funka innan studenterna kommer eller att i ett tankspritt ögonblick testa, om vakuum kan få en atmosfärsfylld provhållburk att öppna sig, det gick), ganska kronologiskt presenterade: ”Åka”, Sven, Karin, Greger, Ingela, Annika, Mikael, Elisabeth, Anders H och Anders H, Emma, Maria, Anna-Lena, Erik, Boriss, Patrik, Jan, Anna, Katharina, John, Barbara. (Guldstjärna till dig som kan lyckas läsa det där utan att tappa bort dig.)

Alla andra som får saker att rulla och fungera, sekreterare, tekniker, dataansvariga, vaktmästare med flera, även från Fysikalen och MAX-lab. Utan er skulle det vara svårt.

Vänner, nya och gamla, sjungandes eller inte, för att ni är som ni är.

Sist men inte minst vill jag tacka min familj, särskilt Stefan för allt och Vilgot för allt möjligt.

Uppsala 6 februari 2005

Ylvi Alfredsson
References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title "Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology".)