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INTERFACE ENGINEERING
IN
ORGANIC ELECTRONICS

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Till Jesper

Viktor, Kaspar, Otto och Tuva

Abstract

Organic electronics is a field covering all applications and devices where one or several of the active components are made of organic material, such as organic light emitting diodes, organic solar cells, organic thin film transistors, organic magnets for spintronics etc. In all of the applications mentioned above, transport of charges across both inorganic/organic and organic/organic interfaces play a key role for device performance. In order to achieve high efficiencies and longer lifetimes, proper matching of the electronic energy levels of the different materials is needed.

The aim of the research presented in this thesis has been to explore different routes to optimize interface energetics and gain deeper knowledge of the mechanisms that govern charge transport over the interface. Photoelectron spectroscopy (PES) is a method well suited to study both interactions between different materials taking place at surfaces as well as interface energetics.

One way to achieve proper matching of interfaces energy levels is by adding a dipole layer. In the three first papers presented in the thesis, the method of adding a monolayer of small organic molecules to change the work function of the surface is investigated. We start with a model system consisting of a nickel surface and PPDA molecules where we have strong interaction and mixing of orbitals between the molecule and the metal surface. The second system consists of a gold surface and TDAE molecules with weaker interaction with integer electron transfer and finally in the third paper an organic surface VPP-PEDOT-Tos is modified, with TDAE, to create a transparent low work function organic electrode. In the fourth paper, we focus on gaining deeper understanding of the Integer Charge Transfer (ICT) model and the mechanisms governing the alignment of energy levels at organic/(in)organic interfaces and in the fifth paper we continue to challenge this model by using it to predict the behavior of a bilayer device, in terms of energy level alignment.

Populärvetenskaplig sammanfattning

På 1970-talet gjordes upptäckten att plast kan leda ström, vilket år 2000 kom att tilldelas Nobelpriset i kemi. Denna upptäckt blev startskottet för det helt nya forskningsfältet organisk elektronik, där fysik, kemi och elektronik samverkar. Inom detta område fokuseras det på att ta fram tillämpningar baserade på organiska material såsom lysdioder, solceller och transistorer för att nämna några. Dessa komponenter består alla av tunna filmer av olika organiska material. För att öka prestanda och livstid för organiska komponenter är det viktigt att förbättra materialen, designa bättre strukturer samt få förståelse för hur laddningar transporteras i materialen. Det är dessutom av stor betydelse att få en grundläggande förståelse för hur dessa material reagerar när de kommer i kontakt med varandra och hur laddningar transporteras över gränssytor mellan de olika materialen.

Min forskning har varit fokuserad på att få bättre insikt i de mekanismer som styr laddningsöverföring vid gränssytor mellan olika organiska material. För att få fram information om hur elektroner rör sig mellan dessa material har jag använt mig av fotoelektron-spektroskopi vilket är ett kraftfullt instrument för att studera ytegenskaper hos ett material. Med denna teknik kan man t.ex. få en bild av materialets energinivåer, eller energitillstånd som materialets elektroner är arrangerade i. Det är dessa energinivåer som styr materialets fysiska och kemiska egenskaper och är avgörande för t.ex. hur mycket energi i form av spänning som behöver tillföras en lysdiod för att få den att lysa eller hur väl en solcell fungerar.

Avhandlingen består av två olika delar, i den första delen undersöker vi möjligheten att förändra ett materials ytegenskaper med avseende på vilka energinivåer som finns tillgängliga vid laddningsöverföring till ett angränsande material. Genom att introducera en dipol på ytan av materialet, med rätt storlek och riktning, i form av ett tunt lager (monolager) med molekyler kan materialets energinivåer matchas för att förbättra möjligheterna för laddningsöverföring. Den andra delen behandlar de mekanismer som styr hur energinivåerna linjeras upp när två material som interagerar svagt (utan kemisk reaktion) med varandra bildar en

gränsyta. Vi undersöker hur avståndet mellan de olika material, samt hur ytornas polariserbarhet inverkar på energiupplinjeringen.

Preface

In this thesis, I summarize most of the work carried out during my PhD studies in the division of Surface Physics and Chemistry at Linköping University. The thesis is an extended version of my Licentiate thesis* and therefore large parts of the introductory text are directly derived from this. The introductory chapters are meant to provide a somewhat extended view of the theory and experimental methods the included papers are based on and should not be considered as a contribution to the research field on my part. The research I defend with this thesis is presented in the included papers.

During my work with this thesis I have learnt about organic electronics, experimental work and vacuum systems but more importantly, I have gotten the opportunity to meet and work with people from all over the world.

Linda Lindell

Linköping, November 2011

* Molecular Scale Interface Engineering, Licentiate, thesis 1308,

Linda Lindell, Linköping University, 2007

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During my time as a PhD student, circumstances have changed along the way in more than one way and people have both come and gone. I would like to send special thanks to:

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Papers Included in the Thesis

Paper 1:

Characterization of the interface dipole at the paraphenylenediamine-nickel interface: A joint theoretical and experimental study.

L. Lindell, M. P. de Jong, W. Osikowicz, R. Lazzaroni, M. Berggren,

W. R. Salaneck, and X. Crispin

Journal of Chemical Physics, 122, 084712 (2005).

Paper 2:

Integer charge transfer at tetrakis(dimethylamino)ethylene/Au interface.

L. Lindell, M. Unge, W. Osikowicz, S. Stafström, W. R. Salaneck, X. Crispin and

M. de Jong

Applied Physics Letters, 92, 163302 (2008).

Paper 3:

Transparent, Plastic, Low-Work-Function Poly(3,4-ethylenedioxythiophene) Electrodes.

L. Lindell, A. Burquel, F. L. E. Jakobsson, V. Lemaury, M. Berggren,

R. Lazzaroni, J. Cornil, W. R. Salaneck, and X. Crispin

Chemistry of Materials, 18, 4246 -4252 (2006).

Paper 4:

Self assembled monolayer engineered interfaces for determination of charge transfer and charge separated states

L. Lindell, C. Vahlberg, S. Braun, K. Uvdal, W. R. Salaneck and M. Fahlman

In manuscript.

Paper 5:

Energy level alignment at metal-organic and organic-organic interfaces with Alq₃ and NTCDA

L. Lindell, S. Braun, W. R. Salaneck and M. Fahlman

In manuscript.

The Author's Contribution to the Papers

Paper 1

Participating in the experimental part of the work and the process of writing the paper.

Paper 2

All experimental work, writing the first draft and responsible for the iterative process of writing the paper.

Paper 3

All experimental work, writing the first draft and responsible for the iterative process of writing the paper.

Paper 4

The spectroscopic part of the experimental work, writing the first draft and responsible for the iterative process of writing the paper.

Paper 5

All experimental work, writing the first draft and responsible for the iterative process of writing the paper.

Related Papers not Included in the Thesis

W. Osikowicz, X. Crispin, C. Tengstedt, L. Lindell, T. Kugler,
and W. R. Salaneck

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W. R. Salaneck, and O. Inganäs

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Synth. Met., 156, 1102 (2006).

F. L. E. Jakobsson, X. Crispin, L. Lindell, A. Kancierzewska, M. Fahlman,
W. R. Salaneck, and M. Berggren

"Towards all-plastic flexible light emitting diodes."

Chem. Phys. Lett., 433, 110 (2006).

P. Sehati, S. Braun, L. Lindell, X. Liu, L. M. Andersson and M. Fahlman

"Energy-Level Alignment at Metal–Organic and Organic–Organic Interfaces in Bulk-Heterojunction Solar Cells."

IEEE J Sel Top Quant., 6, 16 (2010).

R. J. Davis, M. T. Lloyd, S. R. Ferreira, M. J. Bruzek, S. E. Watkins, L. Lindell,
P. Sehati, M. Fahlman, J. E. Anthony and J. W. P. Hsu

"Determination of energy level alignment at interfaces of hybrid and organic solar cells under ambient environment"

J. Mater. Chem., 6, 21 (2011).

Content

1	Introduction	1
2	Surfaces & Interfaces.....	5
2.1	Basic Concepts and Definitions	6
2.2	Surface Modification.....	8
	Surface Dipole.....	10
	Charge Transfer Dipole.....	12
	Intrinsic Molecular Dipole	12
2.3	The Integer Charge Transfer Model.....	12
3	Photoelectron Spectroscopy	17
3.1	Basic Principles.....	17
3.2	Intensity and Resolution	19
3.3	Valence Level Spectroscopy (UPS)	21
3.4	Core Level Spectroscopy (XPS)	23
4	Equipment	27
5	Summary & Future Outlook.....	31
6	References	35
	Paper 1	
	Paper 2	
	Paper 3	
	Paper 4	
	Paper 5	

1 INTRODUCTION

The phrase "organic electronics" represents the rapidly growing branch of technology that exploits the electronic and optical properties of π -conjugated organic molecules and polymers, which are semiconducting in their undoped state. These organic semiconductors are light weight, flexible, inexpensive, soluble and their electronic properties can be modified by chemistry. For these reasons they are attractive for optoelectronics applications such as organic displays, which have indeed already found their way to the market. In the field of organic electronics, many studies have been made concerning the energetics at the interface between electrode and active organic layer in devices[1]. Parameters concerning device performance such as efficiency, turn on voltage, lifetime etc. are all highly dependent on the ability to optimize energy level alignment between the different materials and the understanding of these interfaces is therefore important[2-5].

The traditional way to estimate electron (hole) injection barriers is to take the difference between the work function of the electrode and the LUMO (HOMO) of the active organic material. This estimate is only correct if a common vacuum level is assumed which is true only for specific cases. In other cases, an interfacial dipole eD_{int} is created between the different materials, which highly affect the energy alignment. In many recent articles, possible parameters affecting the interfacial dipole that controls the electronic structure and the energy level alignment at atomically clean interfaces are provided for both metal/organic and

organic/organic interfaces[6-11]. The origin for vacuum level shifts at interfaces for weakly interacting systems of π -conjugated molecules (or polymers) on metallic contact has been more uncertain, although significant progress has been made.[12-15]. In such weakly interacting systems, direct interaction is prevented, for example, by hydrocarbon contamination and/or oxide layers. This is usually the case for devices prepared in an ambient atmosphere.

In this thesis, five papers regarding the issues mentioned above are included. The first paper deals with exploring a simple way to modify the injection barriers in devices by introducing an interfacial dipole. The interaction of a strong electron donor, *para*-phenylenediamine (PPDA) with a prototypical metal surface (polycrystalline nickel) is examined and the direction and amplitude of the work function change upon adsorption is measured. The adsorption of PPDA on Ni is expected to result in a large chemical dipole D_{chem} due to the electron donating character of PPDA, which would in turn lead to a decrease in the Ni work function.

The second paper focuses on a specific class of interfaces that is very common in a large range of applications, namely weakly interacting systems of π -conjugated molecules (or polymers) on metallic contacts. By choosing a unique model system for decoupled molecular π -orbitals and metal continuum states we present direct experimental and theoretical evidence that the interface energetics for such systems are governed by the exchange of an integer amount of electrons, as opposed to partial charge transfer in hybridized systems. The strong electron-donor molecule tetrakis(dimethylamino)ethylene (TDAE) is used in this study because of its favorable geometry: The π -orbitals of the molecule are located at the central C-C double bond surrounded by bulky methyl groups preventing any direct coupling with the metal surface. The results helped to explain several reported studies of weakly interacting interfaces, in which such a mechanism was proposed but never observed.

In the third paper the same concept as in paper one and two is used to modify the work function of the conducting organic polymer, poly(3,4-ethylenedioxythiophene) - Tosylate (PEDOT-Tos), used in organic electronics as hole injecting material. This work is of importance for the field of organic

electronics, as the availability of transparent low work function organic materials that can be used as electron injecting layer is severely limited. The work function of the conducting polymer is decreased upon chemisorption of TDAE and the origin of the low work function at the organic surface is examined.

In the fourth and fifth paper, we focus on the energy level alignment at weakly interacting organic/(in)organic interfaces and the Integer Charge Transfer (ICT)-model. In paper four, an investigation of the details of the ICT-model in terms of distance- and surface polarization effects to the Integer Charge Transfer Energy, E_{ICT} of organic materials is performed. In paper five, two commonly used organic materials are investigated in terms of their energy level alignment behavior and bilayer structures are implemented to prove the validity of the model for these materials.

Following this general introduction and overview of the included papers in Chapter 1, more detailed information about the theory behind the experiments and the experimental methods used for the papers included in this thesis will be provided. In Chapter 2, basic definitions and concepts concerning surfaces and interfaces are presented, Chapter 3 provides the reader with details about the experimental methods used for the studies and in Chapter 4, the equipment is described. In Chapter 5, a summary of the work is presented along with a brief future outlook.

2 *SURFACES & INTERFACES*

In organic electronics, devices typically contain a large number of layers with different functions. Since many of the key processes such as charge injection into light emitting diodes, and charge separation in photovoltaic cells take place at the interfaces between the materials, detailed understanding of the charge transfer process across these interfaces needs to be achieved in order to optimize device performance. It is therefore of utmost importance to understand which material parameters and fundamental physical and chemical processes are important for the various different kinds of interfaces encountered in organic electronics.

The possibility to optimize the injection barrier and interfacial properties by introducing a dipole layer at an interface governed by vacuum level alignment is demonstrated as well as information of the details affecting the mechanisms that control the interaction at interfaces where Fermi level alignment occurs.

In the following sections, the most important parameters regarding surface- and interfacial properties will be presented.

2.1 BASIC CONCEPTS AND DEFINITIONS

In organic-based devices, the most simple structure consist of a high work function hole injecting anode and a low work function electron injecting electrode with the active organic layers in between[16]. Even for such a simple construction at least two different types of interfaces are present which will have direct influence of the device performance through the energy alignment of the different materials. Figure 2.1 illustrates a single-layer Light Emitting Diode (LED) device and the corresponding energy level diagram of the LED under operation as it is traditionally considered. Parameters relevant for device operation such as Ionization Potential (IP), Electron Affinity (EA), work functions of anode and cathode, Φ_{anode} and Φ_{cathode} and electron- and hole-injection barriers, ϕ_e and ϕ_h , respectively are included in the illustration. The work function is defined as the energy required for removing an electron from the Fermi level, E_F of a material and putting it to rest at a vacuum level E_{vac} . The vertical IP of an organic material corresponds to the difference between E_{vac} and the Highest Occupied Molecular Orbital (HOMO) and EA corresponds to the difference between E_{vac} and the Lowest Unoccupied Molecular Orbital (LUMO).

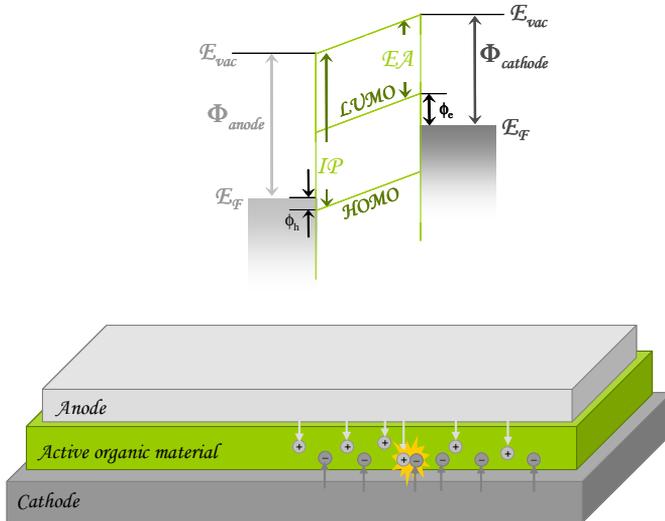


Figure 2.1 A schematic picture of the most simplified LED structure, containing one layer of an active organic material.

The energy level alignment as illustrated in the picture above is however not always true. Depending on the strength of the interaction between the materials and the position of individual energy levels relative one another at the interface between the included materials, different scenarios are possible[15]. By categorizing the type of interaction from strong, meaning chemisorption with mixing of orbitals, to weak, characterized by physisorption with no charge transfer, different models to explain the interface interaction can be applied to predict the energy level alignment. In figure 2.2 adopted from ref. [15], the different types of interfaces that are expected, depending on conditions under which it is formed and the properties of the included materials, are categorized, starting with weak interaction and ending with strong interaction.

Example of interface	Interaction type	Refs.
Nobel gas atoms or saturated hydrocarbons on clean metal surfaces	Physisorption, absence of charge transfer	[3, 17-19]
π -conjugated molecules and polymers on organic or passivated metal surfaces	Physisorption, possible integer electron charge transfer through tunneling	[14, 20]
π -conjugated molecules on non-reactive clean metal surfaces	Weak chemisorption, possible partial charge transfer	[21, 22]
(π -conjugated) molecules on reactive clean metal surfaces	Strong chemisorption, covalent bonding between molecule and metal, (partial charge transfer)	[7]
(π -conjugated) molecules with intrinsic dipole and anchoring groups on clean metal surfaces	Strong chemisorption, covalent bonding at specific sites of the molecule and metal, (partial) charge transfer, surface dipole	[23, 24]

Figure 2.2 Examples of interfaces present in organic electronics categorized according to the strength of interaction at the interface starting with weak and ending with strong interaction. The figure is adopted from Ref. [15]

In the first three included papers, the route to improve device performance by introducing an interface dipole at the substrate surface is explored. Different strength of the interaction between the substrate surface and the adsorbate are explored, from strong interaction with organic molecules chemisorbed to a nickel surface (**paper 1**) to physisorption with integer charge transfer between an organic

molecule and a gold surface (**paper 2**) and finally applying the route to an organic substrate, creating a low work function organic electrode (**paper 3**).

At interfaces where the assumption of a common vacuum level does not hold, different models have been developed to predict the energy level alignment and injection barriers, depending on the strength of the interaction. For interfaces where the interaction is weak, i.e. no chemical interaction between the different surfaces take place, the Integer Charge Transfer (ICT) model is successful in explaining the energy level alignment behavior. A more detailed description of the principles of the ICT-model is provided below. In **paper 4**, a detailed investigation on the influence of two interface phenomena on the basic principles of the ICT model is performed and in **paper 5**, the ICT-model is used to investigate interface energetics for two frequently used organic materials in both single layer structures as well as bilayer structures.

2.2 SURFACE MODIFICATION

It is well known that the work function of a clean surface can be modified by introducing a interface dipole D_{int} [6, 8, 10]. This can be used to optimize the matching energy levels at interfaces to decrease the charge injection barriers in organic-based devices. As mentioned in the introduction, the most common way to estimate the injection barrier, ϕ is to take the difference between the work function, Φ of the electrode (anode) and the ionization potential, IP (electron affinity, EA) of the organic material, assuming a common vacuum level, E_{vac} in the device. If this estimate of the injection barriers is valid it is said that the barrier is of Schottky-Mott type. In figure 2.3, a schematic picture of a device as well as a demonstration of what happens to the energy level alignment and the electron injection barrier, ϕ_e in case of an interface dipole, Δ is displayed.

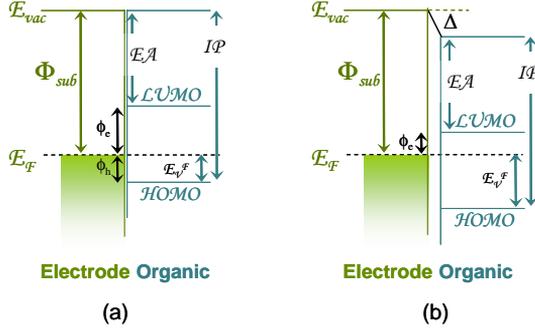


Figure 2.3 Schematic pictures of energy levels at the interface between electrode and organic material in case of vacuum level alignment in a device. In (b) a vacuum level shift is present lowering the electron injection barrier, ϕ_e . The figure is based on an illustration previously presented in Ref. [25]

The most obvious way to improve device performance would thus be to adjust the work function of the electrode to match the charge carrying level of the organic material. A direct measure of the magnitude of the interface dipole, D_{int} as a monolayer of organic molecules is deposited onto the electrode surface is the change of the surface work function[7], $\Delta\Phi$. An interface dipole with its positive pole pointing towards the organic layer and its negative pole towards the metal decreases the metal work function. It also lowers the LUMO in the organic layer, with respect to the Fermi energy[11] in the metal, by adding an electrostatic energy. As a result, the electron injection barrier, ϕ_e is reduced, as illustrated in figure 2.2(b) above. Reversing the interface dipole leads to a reduction of the hole injection barrier ϕ_h . Thus, a work function decrease (increase) is associated with an improvement of electron (hole) injection.

The interface dipole is usually considered to depend mostly on three contributions[7, 26]: i) ΔD_{surf} , a reduction of the electron density tail (push-back effect) of the electrode surface[27, 28], ii) D_{chem} , a chemical dipole due to (partial or integer) charge transfer between the molecule and the electrode surface[29, 30] and iii) D_{mol} , an intrinsic dipole perpendicular to the surface of the adsorbed molecule[1, 31]. The interface dipole can thus be expressed as a function of the three contributions according to:

$$eD_{int} = \Delta(\Phi) = f(e\Delta D_{surf}, eD_{chem}, eD_{mol}). \quad (2.1)$$

The three different contributions will be discussed and explained further in the following sections but it can be kept in mind already at this point that the contribution due to shrinking of the electron density tail always acts to reduce the initial work function of the surface and is a contribution that is always present when adsorbing any species at a metallic surface. In other words, this contribution is present whether both of the other two cases apply or not. The second and third contributions, a chemical dipole and an intrinsic molecular dipole can cause work function changes in both directions depending on the direction of charge transfer or intrinsic dipole of the molecule.

SURFACE DIPOLE

One of the most basic parameters in surface science is the work function, Φ of a material. The measured work function can however differ for a single crystal material depending on what crystal plane the electron is removed through. Since the Fermi level is a common energy level inside the surface, the difference in work function originates from the different potential felt by the electron when passing the surface. At all surfaces a tailing of a negatively charged electron cloud into the vacuum appears at the surface, leaving the inside of the surface positively charged while the vacuum side is negatively charged. Hence, a surface dipole is created. This phenomenon is well described within the Jellium model[32] where the positively charged ion cores are described as a uniform positive background represented by a step function that drops to zero at the metal surface while the electrons are described to try to screen out the positive background. At the point where the step function drops to zero the electron density decreases exponentially at the vacuum side of the surface, leaving a net positive charge inside the surface and a negative charge at the vacuum side. A schematic picture of the electron density profile at a Jellium surface is demonstrated in figure 2.4.

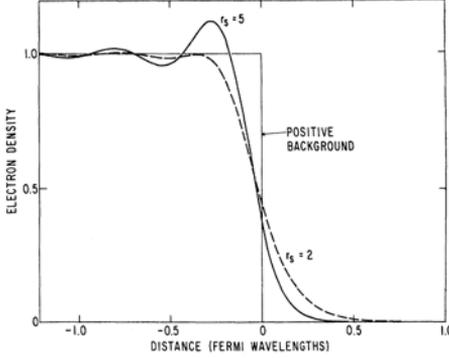


Figure 2.4 Electronic density profiles at a Jellium surface for two choices of background density, r_s . The figure is adapted from Lang and Kohn[32].

The work function is written as a sum according to

$$(\Phi) = \mu + eD_{met} \quad (2.2)$$

Where μ represents the internal chemical potential, which is a bulk component and eD_{met} the surface dipole potential of the metal, which is a surface property due to the tailing electron density. The different work functions measured for different crystal planes mentioned above are explained by different tailing of the electron cloud depending on the surface structures.

It has been shown that the presence of for instance Xe atoms at monolayer coverage, which are expected to interact weakly with the metal surface via van der Waals interaction and physisorb at the surface, leads to work function decrease[3, 27]. It is explained by a shortening of the electron density tail (push-back effect) at the metal surface and thus a reduction of the surface dipole potential, eD_{met} mainly due to an exchange-like effect usually referred to as Pauli repulsion. Recent theoretical work has shown that this purely physical effect outweighs additional chemical contributions due to polarization and charge transfer, which is to some degree always present even in the case of physisorption[27, 28].

The surface dipole contribution to the work function is calculated to be small for alkali metals (tens of an eV) while for transition metals it can be a major contribution[33].

CHARGE TRANSFER DIPOLE

In the situation of physisorption mentioned in the section above, the contact is made via pure van der Waals interaction. In the case of chemisorption the interaction is stronger and a surface chemical bond is formed between the atom or molecule and the surface. Depending of the character of the interaction, both ionic (integer charge transfer) and covalent (mixing of electronic orbitals) bond formation can occur. For chemisorption, an adsorption-induced change in the work function of a surface is seen in addition to the effect of Pauli-repulsion discussed above.

INTRINSIC MOLECULAR DIPOLE

When molecules carrying an intrinsic dipole are adsorbed on a surface, the work function will be affected by the net molecular dipole perpendicular to the surface. In addition, the chemical interaction that may occur between the surface and the adsorbed molecule contributes to the work function changes according to the case of a charge transfer dipole described above.

One of the most widely used ways to change the work function with an intrinsic molecular dipole is to use self-assembled monolayers (SAMs) of molecules that carry a large intrinsic dipole moment along the molecule[1]. Since SAMs are usually characterized by a high degree of structural ordering, the individual molecular dipoles are well-aligned and sum up to give a large shift in the vacuum level. The magnitude of the work function change can easily be tuned by chemically changing the polarity of the molecule.

2.3 THE INTEGER CHARGE TRANSFER MODEL

The general picture has for long been that vacuum level alignment occurs at the interface where direct coupling between the electrode and the organic material is prevented because of contamination of hydrocarbons and/or oxide layers. At these interfaces, the injection barrier should follow the Schottky-Mott rule, i.e. the injection barrier can be estimated by the difference between electrode work function and the charge carrying state of the organic material. This behavior has indeed been observed for many polymer/metal interfaces prepared under ambient

conditions, for which the metal surfaces are “passivated” by hydrocarbon contamination and/or oxides and the interface is governed by weak interaction. Recent studies show that the situation for these interfaces is different and that significant interface dipoles may be formed[12-15].

In this situation, the contributions to the interface dipole from Pauli repulsion (has already occurred due to passivation) and intrinsic molecular dipoles (typically absent) as well as chemisorption due to mixing of orbitals are for obvious reasons not an issue. The only probable origin for the dipole is thus charge transfer between the organic material and the electrode across the surface, which is consistent with the observed trends that depend on the initial work function of the substrate and the ionization potential (or electron affinity) of the organic material[12-14].

The Integer Charge Transfer (ICT) model was developed to explain and predict the energy level alignment behavior at organic-inorganic interfaces where direct overlap between the organic π -system from the metal bands is prevented due to presence of oxides and/or hydrocarbons, as well as for organic-organic interfaces, where the interaction between the materials is weak (physisorption). An extended description of the ICT-model is given by Braun et. al in Ref. [15].

In the ICT-model, three separate regimes are identified to control the interface energy level alignment behavior. In figure 2.5, the characteristics of the three regimes are displayed along with a short description of the charge transfer process that occurs.

The Schottky-Mott regime, characterized by vacuum level alignment has been described above and is depicted as case 2 in figure 2.5. From this, an abrupt transition is made into a region characterized by creation of a positive (or negative) interface dipole that scales with a decrease (or increase) of substrate work function, case 1 and 3. The transitions occurs when the substrate work function crosses the threshold values of the positive or negative integer charge transfer energies E_{ICT+} and E_{ICT-} as demonstrated in figure 2.5 where the charge transfer process and interface dipole formation upon contact between the electrode and the organic materials is displayed.

1. $\Phi_{\text{sub}} < E_{\text{ICT-}}$ *Transfer of e^- to organic*
2. $E_{\text{ICT-}} < \Phi_{\text{sub}} < E_{\text{ICT+}}$ *Vacuum level alignment*
3. $\Phi_{\text{sub}} > E_{\text{ICT+}}$ *Transfer of e^- from organic*

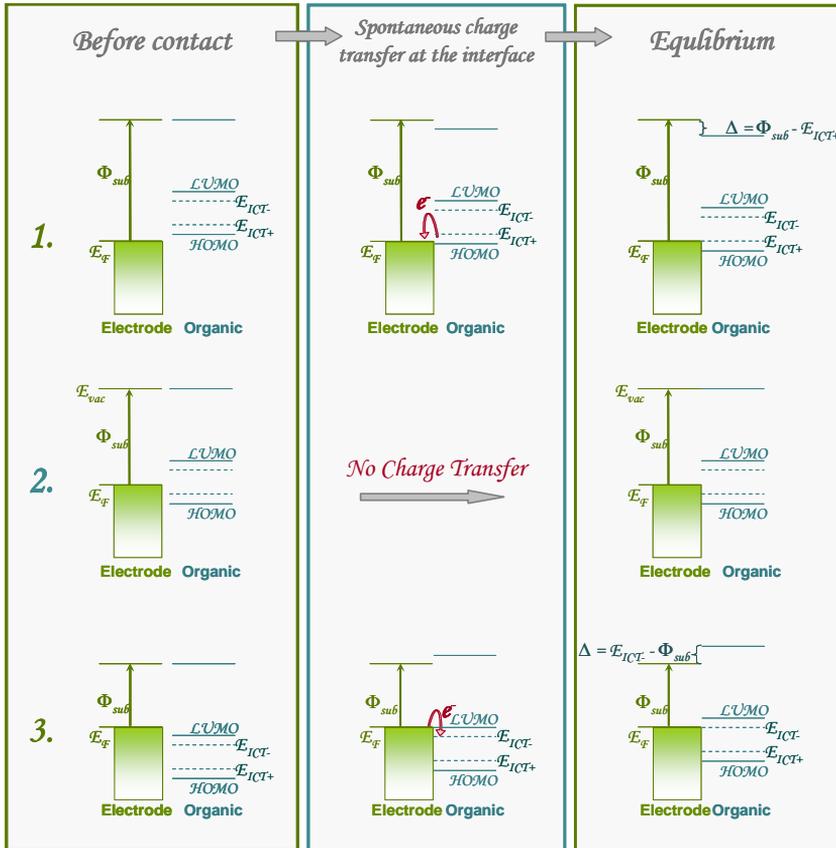
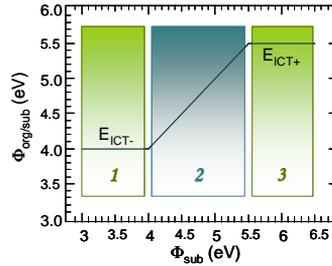


Figure 2.5 A schematic illustration of the different energy level alignment regimes possible at weakly interacting organic/(in)organic interfaces and the charge transfer process and interface dipole formation upon contact between an electrode materials with work function lower than the $E_{\text{ICT-}}$ value. The illustration is based on a model previously published by Braun et.al in Ref. [15]

The origin of the interface dipole is explained by spontaneous integer charge transfer across the interface from/to the Fermi level of the substrate to/from the organic, creating a fully relaxed charge transfer state. The process results in what is referred to as Fermi level pinning due to the alignment that occur between the

E_{ICT} value and the Fermi level of the substrate. The energy of the charge transfer state, E_{ICT} corresponds to a charged state that is fully relaxed regarding electronic and geometric interaction with the surrounding.

3 *PHOTOELECTRON SPECTROSCOPY*

This chapter aims to provide a more extensive description of the experimental technique used for the research presented in this thesis. Photoelectron Spectroscopy (PES) is based on the photoelectric effect discovered by Hertz in 1887. The basic idea of the photoelectric effect is that electrons escape from a material when it is irradiated by photons. The principle was first explained theoretically by Einstein in 1905 by the introduction of the concept of photons carrying a quantized energy $h\nu$. From this principle a new spectroscopic technique evolved, photoelectron spectroscopy or Electron Spectroscopy for Chemical Analysis (ESCA)[34]. By studying the energy of the ejected electrons, information about the inner electron structure of the material can be gained. As the experimental possibilities have developed, increasing accuracy can be achieved, yielding more detailed information[35, 36]. Nowadays PES has developed into a widely used technique used for routine surface analysis as well as for research purposes.

3.1 BASIC PRINCIPLES

A general description of the principle of PES[36, 37] can be given as follows. Light with a specific energy $h\nu$, is incident on a sample (gas, liquid or solid surface), if the energy of the light is large enough, photoelectrons are emitted and

can be analyzed with respect to their kinetic energy, E_{kin} . The process can be described by the following equations:

$$E_0 + h\nu = E_+^* + E_{kin} \quad (3.1)$$

where E_0 is the total energy of the neutral atom or molecule, $h\nu$ is the photon energy as mentioned above and E_+^* represents the total energy of the ionized molecule. The binding energy of an electron is represented by:

$$E_B = E_+^* - E_0 \quad (3.2)$$

Combining the two equations (4.1) and (4.2), we get the binding energy of the electron from:

$$E_B = h\nu - E_{kin} \quad (3.3)$$

In the process of analyzing the results from PES, it is important to keep in mind what state the examined system is in due to the dynamic effects of the PES process[38]. When a photoelectron is emitted, it leaves the molecule within 10^{-15} s. Intramolecular relaxation (relaxation within the molecule) cause the remaining electrons to relax in order to screen the hole, with a relaxation time of the order of 10^{-16} s while the nucleus geometric relaxation time is in the order of 10^{-13} s. This means that the main line corresponds to the energy of a system where the hole is fully screened but frozen in its molecular geometry[37]. The intramolecular relaxation results in a shift of the electron binding energy to lower values. When a solid is considered, intermolecular relaxation provides additional screening of the hole due to electronic response from the surrounding molecules and shift of the binding energy towards a lower value as compared to a gas-phase measurement. Under normal conditions, the initial state of the sample will always be the ground state of the material of energy E_0 while a variety of excited final states of energy E_+^* are possible. Some of the most common final states are shown in figure 3.1.

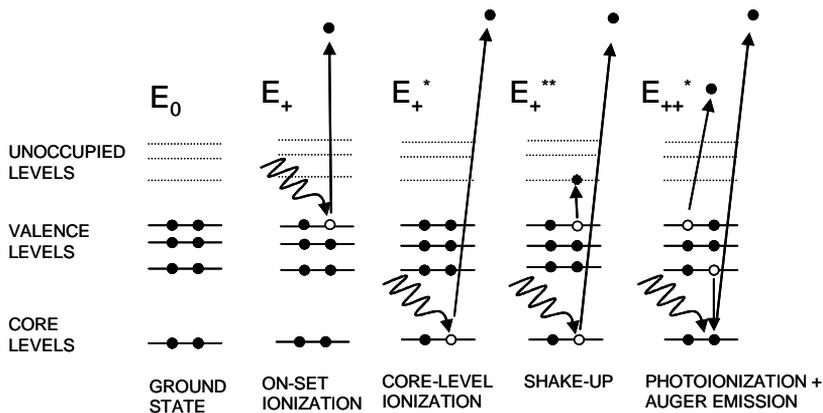


Figure 3.1. A schematic representation of various final states created in a system upon photoionization. The illustration is based on figures presented in Ref. [2, 39]

In the ground state of the atom or molecule, all electrons are in their lowest allowed energy levels. At the on-set ionization, the electron occupying the highest energy valence level is photo ionized and the molecule is still in its molecular ion ground state. In a PES spectrum, the most pronounced features are a result of the most probable photo ionization processes such as the core level ionization resulting in an excited state E_+^* . The shake-up event includes a dynamic response from the remaining electrons[40] where the final state, E_+^{**} include an electron excited into an empty state. This is a much less probable process, resulting in a low intensity peak as illustrated in figure 3.2 below. Photo ionization followed by Auger emission[41], create a final state, E_{++}^* where the molecule is doubly ionized. Since the kinetic energy of the Auger electrons are independent of the photo ionization energy, the Auger lines will appear at different binding energies, depending on what excitation energy is used in a normal PES spectrum.

3.2 INTENSITY AND RESOLUTION

A schematic picture of the electronic structure of a material and its corresponding PES spectrum is provided in figure 3.2 below. The most dominant features of a PES spectrum originate from simple ionization events, which produce the most probable final states, characterized by a single hole in a core- or valence level (C_1 ,

C_2 and V_1, V_2, V_3). The less probable events appear as much smaller features such as the shake up event described above that appear to the left of the C_2 peak.

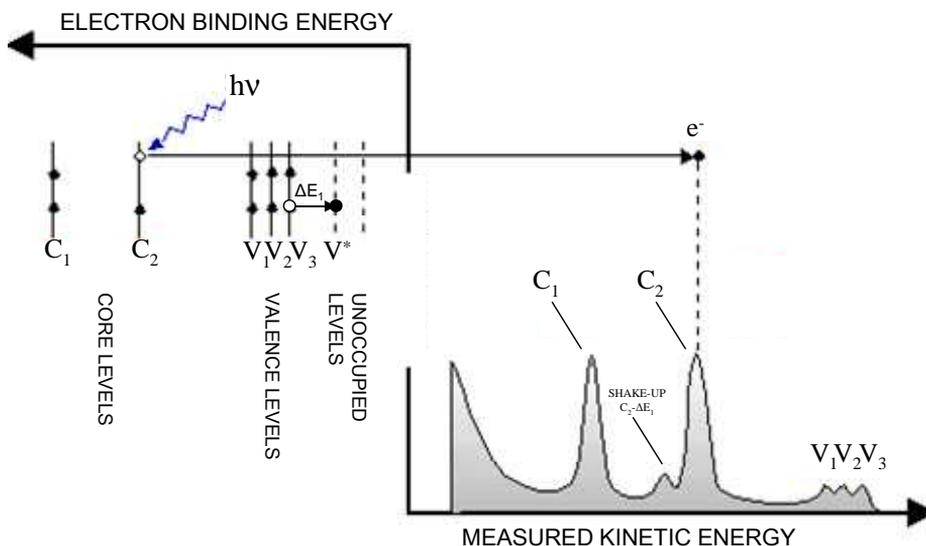


Figure 3.2 Simplified picture of how a spectrum is obtained through the ionization of the various electron levels. The figure is based on illustrations from Ref. [2, 39]

For PES, the resolution of the spectra, i.e. broadening of the peaks, depends on both instrumental parameters and factors originating from the photoemission process itself. Among the instrumental parameters, the line width of the X-ray photons is one of the most important factors and by using a monochromator in the instrumental set-up, the resolution can be improved substantially. Another contribution is the resolution of the energy analyzer. Broadening due to the photoemission process originates from life time of the ionized state, surface roughness, molecular order, and sample charging among other things. The intensity of the photoemission peaks is related to factors such as mean free path of the photoelectrons, photo ionization cross section and elemental concentration which makes it possible to estimate elemental composition and layer thickness[42] (see further information in section 3.4 below).

The probing depth of PES is determined by the mean-free-path of the ejected photoelectrons, which in turn is determined by electron-electron and electron-phonon interactions within the sample. The mean-free-path corresponds to the distance the electron travel before losing energy by inelastic scattering and depends on both the kinetic energy of the emitted electrons and the character of the material they travel through. The electrons that escape to the surface undisturbed result in the main peaks of the spectra while electrons that experience energy losses on their way to the surface (secondary electrons) give rise to the background noise of the spectra. The probing depths typically range from a few Ångströms for low kinetic energy electrons (E_{kin} 20-100 eV) up to 100 Å for both higher and lower kinetic energy electrons according to the so-called universal curve of electron mean-free-path[35, 43]. The technique is thus very surface sensitive, which sets high requirements on the quality of the vacuum in order to get spectra from clean surfaces. A typical estimation is that a pressure better than $1 \cdot 10^{-10}$ mbar is needed to keep the surface free from contamination for the timeframe of the experiment but of course this number is dependent of the surface properties of the sample.

3.3 VALENCE LEVEL SPECTROSCOPY (UPS)

Ultraviolet Photoelectron Spectroscopy (UPS) is a PES technique where a light source emitting low energy photons, in the ultraviolet range, is used. The light is usually produced by rare gas discharge lamps or comes from monochromatic synchrotron radiation. For the work in this thesis HeI radiation is used with a photon energy of $h\nu = 21.2$ eV.

One of the parameters affecting the cross section for photo ionization of an electron is the energy of the photon compared to the ionization energy of the electrons. In general, the probability of photo ionization increases as the energy of the photons comes close to the ionization energy of the electrons which makes UPS in particular well suited for measurements of valence electronic states[2]. In addition, the technique is highly surface sensitive due to the low kinetic energies of the emitted electrons that result in a short mean-free path, which makes it suitable for the determination of surface electronic structure as well as for the

investigation of interfacial properties. In figure 3.3, the valence band spectrum of gold is displayed.

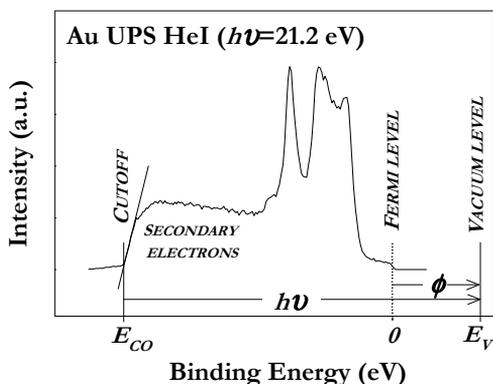


Figure 3.3 The figure displays a schematic UPS spectrum of gold where some of the most important sources for information to be gained from these measurements are marked. Figure adopted from Ref.[2]

As can be seen, the position of the Fermi level, E_F for a metal can easily be detected and the work function, Φ of a material is deduced from the cut-off of the secondary electrons, E_{CO} according to:

$$\Phi = E_{vac} - E_F = h\nu - E_{CO} \quad (3.4)$$

For organic materials, the vertical Ionization Potential (IP) of the material is accessed by adding the work function to the position of the Highest Molecular Orbital (HOMO). UPS can also provide direct information on vacuum level shifts due to *e.g.* interfacial dipoles seen as a shift of the work function. When performing UPS measurements of an organic material (or any sample with limited conductivity), special care has to be taken to avoid charging of the sample due to accumulation of positive charge at the sample surface because of high flux of emitted photoelectrons. This effect reveals itself as a shift of the spectrum towards higher binding energy and broadening of features.

In my thesis, UPS has been used to follow the work function changes due dipole formation at surfaces from monolayer adsorption in **paper 1**, **paper 2** and **paper 3**. The technique is used to investigate the nature of the bonds that are formed and

the amount of charge transfer in **paper 2**. In **paper 4** and **paper 5**, UPS is used to follow the interface energy level alignment.

3.4 CORE LEVEL SPECTROSCOPY (XPS)

For X-ray Photoelectron Spectroscopy (XPS) the most commonly used light sources are Mg(K_{α}) or Al(K_{α}) radiation which produces X-rays with photon energies of 1253.7 eV and 1486.6 eV respectively. With XPS, the core levels of the material are investigated and since each element has a unique binding energy, information regarding elemental composition of the sample is provided. Since changes in the chemical environment of an element affect core- and valence level binding energies, processes such as doping, oxidation and molecular adsorption can be followed and are detected as core level shifts. In figure 3.4 below, the S(2p) spectrum of the substance referred to as Vapor-Phase Polymerized poly(3,4-ethylenedioxythiophene)-tosylate (VPP-PEDOT-Tos) in **paper 3** is demonstrated. The S(2p) line is a doublet, S(2p_{1/2,3/2}) due to spin-orbit coupling and this figure provides a good example of how both spin-split and chemical shift present themselves in a XPS spectrum. In the figure we see one S(2p) doublet originating from the sulphur located in the PEDOT chain and two contributions from sulphur located in the tosylate units. Even if the position of the sulphur atom in the tosylate molecule is identical, they are seen at separate binding energies due to the different chemical environments surrounding the molecules.

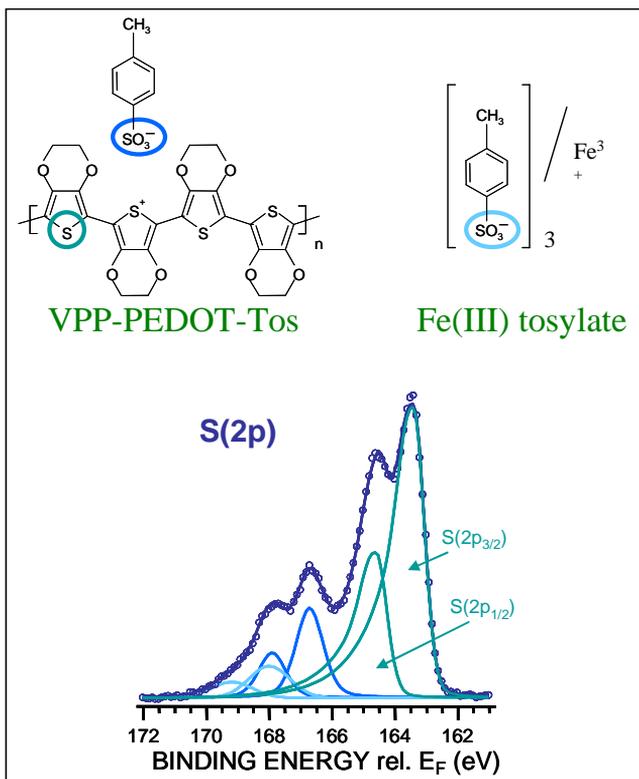


Figure 3.4 An XPS spectrum of S(2p) where the appearance of spin-split and chemical shifts is demonstrated. Spectroscopic results from Ref. [44].

Using Atomic Sensitivity Factors[45] (ASF) a quantitative analysis of the relative concentrations of different elements in the surface region is possible to perform (with limited accuracy). The ASF take into account the elemental specific cross-sections (emission probability), the mean-free path of the emitted electrons, the detection efficiency of the emitted electrons etc.

From the XPS analysis, the thickness of a thin film can be estimated from the attenuation of the substrate signal intensity after e.g. vacuum sublimation according to:

$$I = I_0 \exp\left(-\frac{d}{\lambda}\right) \quad (3.5)$$

Where I is the attenuated signal intensity, I_0 is the original signal intensity, d is the film thickness and λ is the mean-free-path[42].

In **paper 1**, **paper 2** and **paper 3**, XPS is used to investigate the interaction between an adsorbate and a substrate surface. In **paper 1**, information of adsorption geometry, bond formation, and eventually decomposition of the adsorbed molecule is extracted. In **paper 2**, the technique is used to monitor film formation even if not shown in the paper and in **paper 3**, the doping level is estimated using relative peak intensities and the amount of charge transfer between molecule and organic substrate is estimated.

4 *EQUIPMENT*

The photoelectron spectroscopy measurements made for this thesis have been carried out in laboratories of the Division of Surface Physics and Chemistry at IFM, Linköping University. The equipment consists of two photoelectron spectrometers, a commercially available Scienta ESCA 200 spectrometer and a custom designed and built spectrometer, Moses. Below, a more detailed description of the spectrometers along with the experimental details provided by the two spectrometers is presented.

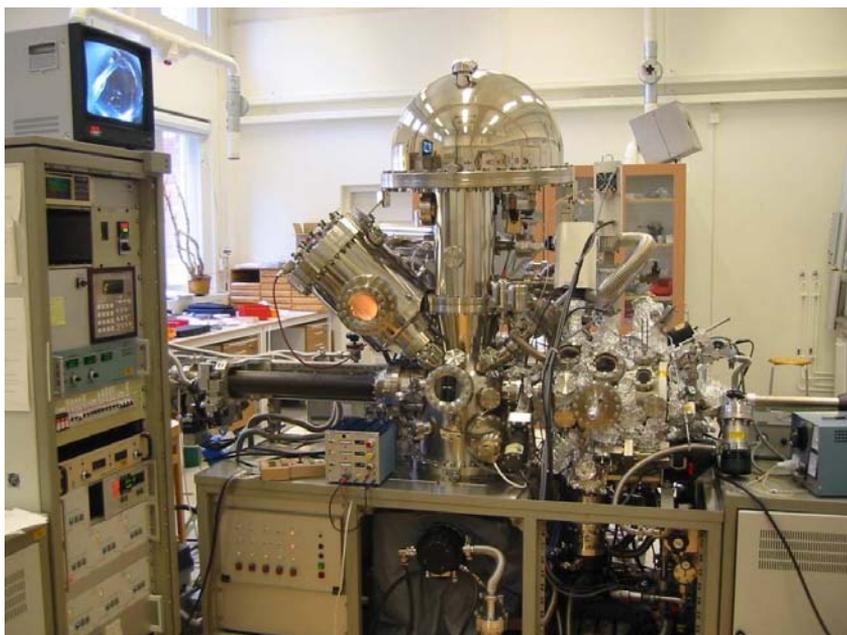


Figure 4.1. A picture of the Scienta ESCA 200 spectrometer in the lab of Surface Physics and Chemistry division in Linköping.

SCIENTA

The Scienta ESCA 200 spectrometer consists of three separately pumped vacuum chambers, an introduction-, a preparation- and an analysis chamber. The base pressure of the preparation and analysis chambers are in the order of 1×10^{-10} mbar maintained with a combination of ion getter-, titanium sublimation- and turbo molecular pumps. The preparation chamber is equipped with an ion sputter gun for preparation of atomically clean surfaces and is connected with a separately pumped gas-handling system and allow for insertion of a Knudsen-cell for preparation of thin films. The sample temperature control ranges from -190°C to 300°C . The analysis chamber is equipped with a monochromatic $\text{Al}(\text{K}_{\alpha})$ light source providing photons with an energy of 1486.6 eV for XPS measurements. A UV-light source consisting of a differentially pumped UV lamp with unfiltered radiation provide photons at 21.2 eV and 40.8 eV (He(I) and He(II) respectively) for UPS measurements. The detector system consists of a high transmission electron lens system combined with a hemispherical analyzer (Scienta SES 200 electron energy analyzer) and a multi-channel plate detector resulting in high

resolution XPS and UPS measurements. The resolution of the system is such that the XPS Au(4f) line is recorded with a full width at half maximum (FWHM) of 0.65 eV when operated at standard conditions. The resolution of UPS is 0.1 eV, measured from the Fermi edge of gold.

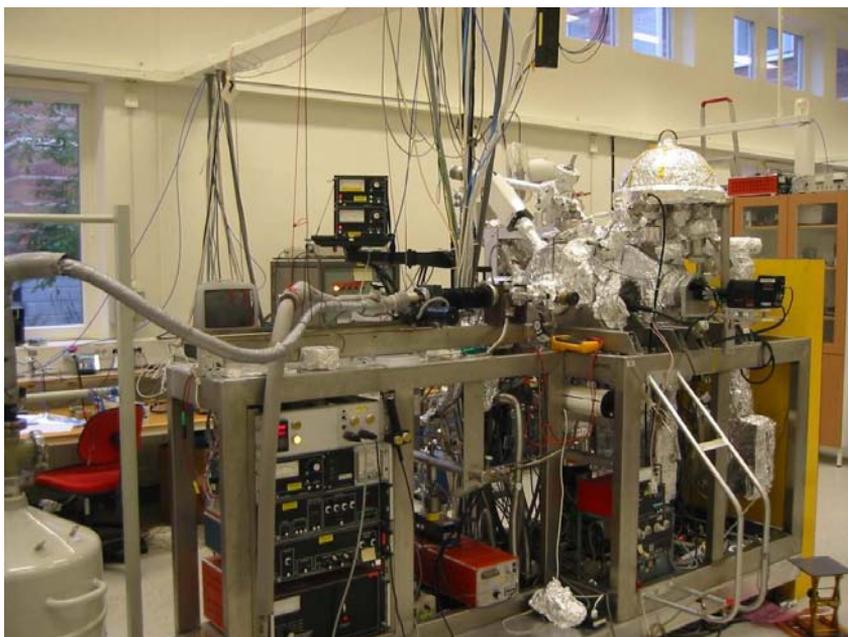


Figure 4.2. A picture of the Moses spectrometer in the lab of Surface Physics and Chemistry division in Linköping.

MOSES

The custom designed and built spectrometer, Moses, is a spectrometer for XPS and UPS analysis. It is equipped with a monochromatic UV-light source ($h\nu=21.2$ eV and 40.8 eV for He(I) and He(II) respectively) for UPS measurements and unfiltered Al(K_{α}) X-rays ($h\nu=1486.6$ eV) for XPS. Like the Scienta ESCA 200 spectrometer, it consists of three vacuum chambers. The base pressure in this spectrometer is $1 \cdot 10^{-9}$ mbar maintained with a combination of turbo molecular-, ion- and cryo pumps. The preparation chamber allows for ion sputtering of sample surfaces, vacuum sublimation of thin films and temperature control of the

substrate. The spectrometer is equipped with a hemispherical analyzer and a multi-channel plate detector. The resolution for XPS under normal operation is such that the Au(4f) line has a FWHM of 1.3 eV. The UPS resolution is 0.1 eV estimated from the width of the Fermi edge of a Au sample.

5 SUMMARY & FUTURE OUTLOOK

Summary

The aim of this thesis has been to gain deeper understanding of the different types of interaction that take place at both inorganic/organic as well as organic/organic interfaces. In order to optimize device performance and life-time, it is of great importance to find routes to minimize the energy required for a charge to pass through an interface. Photoelectron spectroscopy is an excellent tool to gain knowledge of the energy level alignment at interfaces and to study interactions at surfaces since it allows for direct probing of the occupied electron energy levels and interface dipoles are easily revealed.

As I summarize, the work for this thesis it becomes clear that the understanding of interface interactions in the field of organic electronics has developed a lot since I started. The common understanding was that the interface energy level alignment was governed by vacuum level alignment unless a strong interaction between materials were involved e.g. by using self-assembled monolayers or small molecules to create interface dipoles.

In the first paper included in this thesis, the goal was to achieve a better understanding of the fundamental origin of the interface dipole created upon chemisorption of a small electron donor molecule, *para*-phenylenediamine (PPDA) and a poly-crystalline nickel surface. The study was a joint experimental

and theoretical investigation of the system where I participated in the experimental part of the work. The results from the theoretical investigation revealed that PPDA chemisorb on the nickel surface in two different conformations, and a flat conformation (a) where the interaction happens via C-Ni and N-Ni bonds and a tilted conformation (b) where the interaction happens via one of the nitrogen lone pair of the molecule as displayed in figure 5.1.

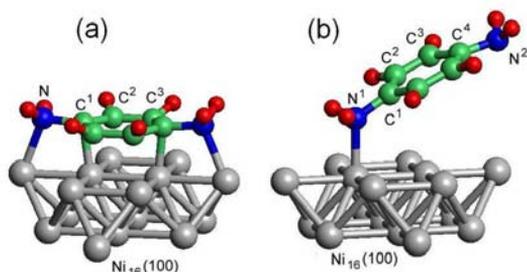


Figure 5.1 The calculated geometry conformations of PPDA on a nickel surface. Figure adopted from Ref. [25]

The experimental results show that PPDA form a monolayer mostly consisting of the flat conformation at low temperatures (-40°C) while, at higher temperatures the monolayer rearrange to the tilt conformation where the interaction eventually leads to decomposition of the molecule as the temperature rise from 20°C to 200°C . An interface dipole is created due to chemisorption of PPDA on the nickel surface which together with modification of the electron density tail leads to a substantial decrease of the nickel work function.

In the second paper, the interaction between another small organic electron donor molecule, tetrakis(dimethylamino)ethylene, TDAE and a poly-crystalline gold surface is investigated in a joint experimental and theoretical study. The aim of this study is to use the system as a model for weakly interacting organic/inorganic interfaces where direct overlap between the π -orbitals of the organic and the metallic surface is prevented and charge transfer is limited to integer charge transfer over the interface. TDAE is a strong donor but the electron-rich central $\text{C}=\text{C}$ bond is surrounded by eight outer methyl groups which prevent direct overlap between the molecular orbitals and the metal surface. A monolayer of TDAE results in a work function decrease due to an integer amount of charge transfer from TDAE, supported by both theoretical and experimental results

showing that interface dipoles as a result of charge transfer at weakly interacting organic/inorganic systems are governed by an integer amount of electrons.

The third paper aims at producing a flexible transparent low work function organic electrode using the strong donor TDAE, mentioned above, by creating an interface dipole. The organic electrode consist of vapor-phase polymerized poly(3,4-ethylenedioxythiophene)-tosylate, here denoted as VPP-PEDOT-Tos with an initial work function of 4.3 eV which is decreased to 3.8 eV upon surface modification with TDAE. The origin of the interface dipole is investigated with both experimental and theoretical methods revealing a surface redox reaction where two electrons are transferred from TDAE to the PEDOT chain whereupon parts of the PEDOT chain become undoped.

Following the first three papers where the detailed interaction and origin of dipole formation upon interface formation between substrates with different character and organic molecules is investigated, the interface energy level alignment on a macroscopic scale, at weakly interaction interfaces according to the ICT-model (described in chapter 2), is considered in the two last papers.

In the fourth paper, the basic properties of the ICT-model are investigated in terms of how the distance between the materials across an interface influences the absolute value of E_{ICT} and hence the efficiency of the charge transfer process, and also how the surface polarizability of the substrate affect E_{ICT} . Alkanethiol-based SAMs ($HS-(CH_2)_n-X$) of different lengths (n) and end-groups (X) are used as spacer-layers between a gold substrate and the small organic molecule 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ) to simulate the different interfacial properties of interest. The results indicate that both physisorption distance and local polarizability of the substrate surface have an influence on the E_{ICT} values, suggesting that fine tuning of injection barriers can be achieved by varying these two parameters.

In the fifth paper, two frequently used organic materials are investigated in terms of energy level alignment to test the validity of the ICT model and shed light on the effect of strong intrinsic molecular dipoles on the model. The E_{ICT} values are experimentally derived for tris-(8-hydroxyquinoline)-aluminum (Alq_3) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and bilayer structures were fabricated and measured for different sequential orders of the film deposition. The results are in agreement with the ICT model predictions and the

intrinsic molecular dipole is shown to introduce a vacuum level shift in the absence of charge transfer across the interface. A small but significant spread in the measured dipole energy is attributed to variations in the intermolecular order at the different interfaces, with rougher surfaces likely leading to a smaller dipole due to a decrease in intermolecular order.

Future Outlook

The ICT model is based on the fact that if it is energetically favorable to transport charges across the interface from/to the most easily oxidized/reduced state, an interface dipole is created. The energy of the charge carrying state will have an energy distribution that depends on the polarizability of the surrounding medium and the strength of the Coulomb interaction between electron and hole. The E_{ICT} values are linked to this distribution and most likely correspond to the values of the accessible states that lie deepest in the gap.

A future challenge for research on interface energy level alignment is to derive a relation between photoelectron spectroscopy derived properties such as E_{ICT} values, vertical IP, HOMO edge width etc., and device data such as injection barriers for OLEDs and OFETs and open circuit voltage for organic photovoltaic cells.

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