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HAXPES studies of solid materials for applications in energy and information technology using the HIKE facility at HZB-BESSY II

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Abstract

In the present work we will review the research directions addressed at the HIKE end-station of the BESSY II storage ring of HZB using hard x-ray photoelectron spectroscopy (HAXPES). The emphasis of this review is on the specific techniques properties required by the diverse scientific questions addressed at the HIKE applied in the various experiments performed there.

Introduction

When synchrotron radiation (SR) based photoelectron spectroscopy was in its infancy in the middle of the 1970s only VUV energies up to a few tens of eV were available. Very few core levels could be studied. Nevertheless this field expanded rapidly, and with the subsequent generations of SR facilities the usable X-ray energies increased. However, x-rays of suitable intensity and energies of a few keV were not used very much until the third generation facilities were developed. An exception was the ground breaking study of the Au4f levels by Lindau and coworkers [1]. Advances in accelerator technology, new monochromators and also high energy electron spectrometers opened up a new field of research called Hard X-ray Photoelectron Spectroscopy (HAXPES). The pioneering work was made in Hamburg in the group of Wolfgang Drube [2]. In this paper the acronym THE-XPS (Tunable High Energy X-ray Photoelectron Spectroscopy) was used but it did not survive. Very soon after the acronym HAXPES was introduced, which was also used at the first workshop on the subject. When Wolfgang Drube opened the HAXPES conference in Hamburg 2011 he stated that "I strongly believe that HAXPES is the ESCA for the future". We believe that this statement is correct, but the situation is more complex. The acronym ESCA was introduced by Hagström, Nordling and Siegbahn [3] in the famous paper where the core level chemical shift was established. In this paper CuK α (8.6 keV) and CrK α (5.4 keV) radiation were used to excite the spectra. ESCA used HAXPES excitation energies in the beginning and this point has recently been reviewed [4, 5].

The use of modern tunable high brilliance and high energy x-ray sources opens up a large number of prospects to study important problems in materials research. The information depth can be varied up to tens of nanometers, and consequently real devices can be profiled rather than model systems. At moderate x-ray flux HAXPES is not destructive and the possibility to study buried interfaces is of course of great importance. Modern technology often demands the use of carefully designed multilayer structures and HAXPES is capable of studying the interdiffusion of atoms through the interfaces and films. The list of applications can be made very long.

The HAXPES facility at BESSY II, named HIKE (which is an acronym for high kinetic energy), was commissioned at the end of 2005 [6]. The facility uses the dipole magnet beamline KMC-1 as source [7]. This beamline is provided with a double crystal monochromator that can operate in almost back scattering angles thus attaining a high energy resolution in the tender x-ray range of 2 to 6 keV. The HIKE end-station is equipped with a high energy electron spectrometer R4000 from VG Scienta. The resolving power of such a combination gives values of $E/\Delta E$ of about 10000 at those energies where the monochromator works in backscattering conditions. The photon flux available at a bending magnet facility is much lower than at an undulator source. However, by using post focusing elliptical capillary optics [8] it is possible increase the brilliance by a factor of 5. Due to radiation damage it is in many cases impossible to use all the flux from a modern high energy undulator facility. Therefore, there is a wide class of research problems connected to materials studies for energy and information technology development that are very suitable for studies performed at the HIKE facility in Berlin. The studies concern depth profiling of different materials in real devices such as solar cells or modern batteries, interdiffusion of

atoms in layered devices, quality control of devices, and of course also fundamental scientific problems that can be addressed using hard x-rays and photoelectron spectroscopy.

In the present report we will review the activities at the HIKE facility at BESSYII and will focus on the relation between instrument capabilities and development of fundamental science and of applications to systems of technological importance.

Solar cells

One of the most intense contemporary research fields connects to the solar energy harvesting. In this case the behavior of interfaces in a layered structure of a solar cell is the main factor determining the final power conversion efficiency of the devices. To be more specific: the energy barriers for the carriers found at the interfaces are the main factors that decide if a structure is efficient or not. Due to this reason these interfaces require a quite comprehensive investigation in terms of their energy level alignment. However to spectroscopically investigate a buried interface in a real device is a scientific challenge. Reproducing the interface with tailored thicknesses to match the probing of spectroscopic techniques in a laboratory environment proved to be the solution. Due to the possibility of extended depth profiling and non-destructivity HAXPES has become an important tool to provide information on local chemistry as well as structural properties. Using HAXPES it is possible to study systems where the top layer of the investigated structures is sufficiently thick to form the same interface structure as in a “real-device” thin-film solar cell layer stack.

The systems investigated at the HIKE end-station in HZB Berlin are also quite varied in terms of solar cell applications. Nevertheless, we can distinguish two classes, namely: organic and inorganic based solar cells. Within the organic solar cells investigations [9-16] we choose an example of a study where the authors look at polymer based solar cells.

The example concerns devices that are composed of a light absorbing and hole conducting polymer, and an electron conducting fullerene derivative [9]. In this case the polymer was poly((2,7-(9,9-(di-n-octyl)fluorene)-alt- 5,5-(40,70-di-thienyl-20,10,30-benzothiadiazole)) (F8DTBT) , and the fullerene derivative [6,6]- phenyl-C61-butyric acid methyl ester (PCBM). There has been a discussion in the literature on how the PCBM would be aggregating; e.g would there be a vertical phase separation present. The system has been studied by different techniques such as Atomic Force Microscopy (AFM), dynamic secondary ion mass spectroscopy (ToF-SIMS). However the question on the morphology was still open. HAXPES gives the possibility of non-destructive depth profiling, but in this case the chemical shift cannot be used. Both the polymer and the fullerene derivative contain a multitude of chemically inequivalent carbon atoms, and consequently there is no possibility to disentangle the carbon atoms. The solution was to use another property of an electron spectrum: the shakeup satellites. When the blended samples were studied, using laboratory x-ray photoelectron spectroscopy and photon energies of around 1500 eV, no shakeup satellites could be found. However, as has been investigated earlier the fullerene system is characterized by a relatively strong shakeup satellite at about 4 and 6 eV from the main line[17]. The

polymer does not have satellites at this position. The HAXPES of this material was studied at two different excitation energies 2010 eV and 6000 eV. The result is displayed in Figure 1.

Figure 1 Left: the HAXPES of a blend between the polymer F8DTBT and the fullerene derivative PCBM. Right: the shakeup spectrum of pure PCBM taken at 6 keV excitation energy. The strong satellites at 4 and 6 eV from the main line are clearly visible.

As can be seen the shakeup satellites do not show up in the 2010 eV spectrum but they are clearly visible in the spectrum taken with 6 keV photon energy. The conclusion is unambiguous. The fullerenes do not aggregate at the surface, but are found in a phase between 6 nm - 20 nm below the surface.

Beyond demonstrating the power of the technique in separating the information on a vertical scale this study was one of the first HAXPES investigations of organic semiconductors without any radiation damage.

Within the inorganic solar cells we can distinguish now 3 main directions given by the materials involved namely silicon [18-21], chalcopyrite [22-28] and emerging new materials such as perovskite [29, 30] based thin films.

Next we chose to illustrate the silicon based solar cells. Wimmer et al.[18] investigated the buried interface between the high quality absorber Si and a transparent conductive oxide ZnO:Al. The structures are prepared by depositing amorphous silicon (a-Si), which is subsequently solid-phase crystallized (SPC) during an annealing process at 600–650° C on top of the ZnO:Al transparent conductive oxide. By varying the excitation energy between 2010 and 8040 eV, the authors were able to probe the Si/ZnO:Al interface buried below 12 nm Si before and after the SPC process. The results of this investigation are shown in Figure 2 where the Si 1s core level is displayed as a function of excitation energy and sample types. The Si 1s spectra exhibit two main contributions attributed to Si-Si and Si-OX bonds. The shown photoemission

spectra are normalized to the maximum intensity and aligned to the energetic position of the Si 1s Si-Si feature which makes direct comparison possible. After annealing, a slight narrowing of the Si 1s Si-Si signal can be observed. This can be clarified by the SPC-induced conversion of amorphous Si into polycrystalline Si. This is supported by the 6030 eV Si 1s spectrum of a single-crystalline Si wafer reference shown in Figure 2 (blue line) which exhibits a similar shape. After SPC, the Si-O_x signal increases strongly, which clearly indicates that the sample further oxidizes during ex-situ SPC. However with increasing excitation energy the Si-O_x signal decreases. This finding suggests that surface oxidation predominates. An accurate estimation of how much and where the oxidation takes place is done by the authors by referencing the ratio of oxide vs. bulk Si signal from the solar cell stack to that of the ratio of oxide vs. bulk from a Si wafer which has the oxidation exclusively at the surface [18]. It is immediately clear that the SPC treatment is mainly inducing the Si/ZnO interface oxidation and not only the expected surface oxidation even in the case of the ex-situ sample. Moreover they find indications of a possible oxidation already at the moment of deposition of Si onto ZnO. Thus the authors conclude that both findings have to be considered in the final device optimization. This investigation proves the practicality of HAXPES as a tool for characterizing buried interfaces in model systems based on real devices.

Figure 2 Si 1s core level for different excitation energies and different samples. Si-O_x indicates silicon to oxygen bonds.

The next example concerns the chalcopyrite based solar cells. Using HAXPES Mönig et al. [22] investigated the composition of the Cu(In,Ga)Se₂ (CIGSe) absorber material with emphasis on the known but not sufficiently understood Cu depletion at the surface [31, 32]. The solar cells grown with the following structure: glass/Mo/CIGSe/CdS/ZnO show very high performance only when prepared with a Cu depleted surface [33]. The extent and exact composition of this Cu poor layer was not identified and thus was the subject of Mönig et al.

work [22]. CIGSe films with 3 different Cu to (In+Ga) ratios (1.00, 0.84 and 0.73) were grown on Mo coated float glass. The films were also cleaned with KCN solutions before the HAXPES measurements; nevertheless their composition was approximately unchanged, also proven by additional XRF measurements [22]. The HAXPES depth profiling of the CIGSe samples was achieved by varying the excitation energy from 2 to 7 KeV and thus varying the information depth from approximately 6 nm to 26 nm, thus making fully use of the true bulk sensitivity of the technique. Figure 3 displays the ratio of the core level normalized intensities Cu 2p to (In 3p+Ga 2p) obtained for different energies for the 3 samples investigated. The results found by the authors are striking: while sample CGI-100 (1.00 ratio of Cu to In+Ga) shows no dependency which points to homogeneous in-depth Cu distribution as given by the elemental concentration, the other 2 exhibit a lower Cu concentration at the surface versus the bulk [22]. To estimate the extent of the depleted layer

and quantify the changes for samples CGI-084 and CGI-073 the authors use a simple model which separately describes the surface and bulk of the samples (see Figure 3 inset), specifically assigning a thickness d to the surface layer. The formula that describes the intensity ratio depends exponentially on the factor d and is directly proportional to the Cu concentration at the surface and in the bulk. This allows a reliable determination of d as well as of the concentrations of Cu through the fit of the experimentally determined ratios.

angular resolved XPS limit.

Figure 3 Ratio of the normalized intensities of Cu 2p versus (In 3p + Ga 2p) as a function of photon energy for the three samples investigated.

Within the emerging materials for solar cells, perovskite thin films are a very hot topic due to the steep quantum efficiency curve exhibited by devices containing these materials as light absorbers [34] developed in the last few years. In particular, perovskite structures with the formula $\text{CH}_3\text{NH}_3\text{MX}_3$ are used, where M is Pb and X is I, Cl or Br or a mixture of these elements. What are of course of interest in the further development of these materials are their electronic structure, interface interaction and energy level alignment. These questions have found a direct answer in the work of Lindblad et al. [29] who studied $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cell materials deposited onto mesoporous TiO_2 using photoelectron spectroscopy with hard X-rays. In this case HAXPES proves to be the perfect tool to determine the energy level alignment at the interface by making use of its extended probing depth feature and cross section selectivity. In Figure 4 the authors show the valence region spectra of two differently prepared perovskite samples, a TiO_2 film and a $\text{TiO}_2/\text{PbI}_2$ structure recorded with an excitation energy of 4000 eV. What is immediately apparent is the clear binding energy difference in the position of the valence band cut-off of the perovskite samples and the TiO_2 film. By determining these values and by using those together with

The results obtained from the fit are shown in Table 1.

Sample	d	$([\text{Cu}]/[\text{III}])_{\text{surf}}$	$([\text{Cu}]/[\text{III}])_{\text{bulk}}$
CGI-084	$(0.6 \pm 0.1) \text{ nm}$	$0.0(-0.0/+0.1)$	0.90 ± 0.02
CGI-073	$(0.8 \pm 0.1) \text{ nm}$	$0.0(-0.0/+0.1)$	0.78 ± 0.02

Table 1 Results from fit for the 2 samples.

As pointed out by the authors the significant conclusion is the presence of a completely Cu depleted surface in both sample cases which extends only to a few monolayers. These results are supported by theoretical and experimental evidence from literature and prove once more the strength of HAXPES in reliably depth profile materials beyond the

the optical band gaps of the corresponding materials the energy level diagram can be drawn and is displayed in Figure 4 B.

Figure 4 (A) Valence band spectra of TiO₂ film, TiO₂/PbI₂ and the one and two-step perovskites measured with 4000 eV excitation energy; (B) Energy level alignment derived from experiment; C – will be deleted from figure

Furthermore the authors show that samples prepared by two different methods exhibit similar electronic structure. Thus HAXPES enables them to find properties which otherwise would not be accessible by soft x-ray photoemission.

Batteries

One other heavily studied research direction due to its relevance in the present world energy need is the energy storage solution. Within this field batteries have received a

lot of attention lately. However the last update in that particular area happened in 1991 when Sony commercialized the first Li based battery [35]. Since then research has concentrated in improving their performance while reducing their scale. The structure of a battery involves a large number of materials as electrodes,

electrolytes and additives. Typically graphite is used as negative electrode, cobalt containing layered transition-metal oxides are used as positive electrodes, and lithium hexafluorophosphate (LiPF₆) is widely used as electrolyte in non-aqueous carbonate solutions [36, 37]. However the challenge now is to improve battery performance by searching for materials with better properties than the typical ones such as higher capacity, abundant, stable and able to accommodate more Li. On the other hand electrodes and electrolytes chemical reactivity upon charging/discharging (cycling) is the crucial part that influences the battery stability and performance. This characteristic can be very well traced by depth profiling HAXPES. One of the experiments performed at the HIKE end-station by Philippe et al. [38] investigates the electrochemical performances of nanosilicon-based electrodes using LiFSI as conductive salt with respect to LiPF₆ by tracking with photoelectron spectroscopy (PES) the evolution of the Li-Si compound, the surface oxide and other interfacial phases upon long term cycling. In this work PES is used in a wide range of energies from soft X-rays to hard X-rays and therefore uncovers the surface and the true bulk electronic properties, thus emphasizing the importance of HAXPES in the context of non-destructively depth profiling of model devices.

The silicon nanoparticles electrodes investigated in contact with the 2 electrolyte compounds LiFSI and LiPF₆ exhibit very different behavior. Firstly the long term exposure of the silicon electrodes to the LiPF₆ creates a fluorinated species at the surface that replaces completely the oxide while LiFSI exposure

induces no change in the Si electrode [38]. From electrochemical results the authors find a much higher capacity of the battery when LiFSI is used. The very thorough photoemission analysis done by the authors finds and describes the chemical processes that occur during cycling at the surface of the Si nanoelectrodes exposed to the two different electrolytes as well as profiles the passivation layer (SEI). As an example we show here the Si 1s and 2p core levels of the electrode exposed to LiFSI recorded at different photon energies as to allow different probing depths (Figure 5).

Figure 5 In depth evolution of Si 2p and Si 1s core levels of the Si electrode after the 1st, 50th and 100th discharge of a Li-Si cell with an electrolyte containing LiFSI. Bottom left corner: comparison with the 100th discharge using LiPF₆ as electrolyte.

The 3 main components observed are the surface oxide SiO₂, lithium silicate Li₄SiO₄ and the LiSi_x alloy. The first two are associated with the surface layer formed by exposure to the electrolyte and cycling whereas the LiSi_x is formed throughout the electrode upon charging discharging with LiFSI as electrolyte. After 50 and 100 cycles the main difference with respect to the first cycle is the steady decrease of the SiO₂/Li₄SiO₄ area ratio, indicating that the reaction of the surface oxide SiO₂ with lithium continues upon repeated cycles. The most important result is that no additional component appears. The observation is very different with LiPF₆ after 100 cycles, as shown in the bottom left corner of Figure 5 [38]. The high binding energy component is attributed to the fluorinated compound SiO_xF_y located at the surface of the particles. The absence of this component after 100 cycles with LiFSI confirms that no HF reaction of the particles surface occurs upon long cycling when this electrolyte is used. This significant difference in the chemistry of the silicon particles surface is unquestionably linked to the improved performances of Li-Si electrochemical cells using LiFSI salt.

By using HAXPES as an integrant part of the depth profiling PES tool chest the authors were able to show that unlike LiPF_6 , long term cycling with LiFSI results in the preservation of favorable interactions between the binder and the active material essentially pointing to a better performance in the battery.

Figure 6 a) Ti 2p core level recorded at 3 keV excitation energy from the LAO/STO sample of 5 unit cells (uc) from PSI as a function of x-ray incidence angle; b) Area ratios Ti^{3+} vs. Ti^{4+} for that sample.

Complex Oxides

The class of complex oxides has received a tremendous interest in research in the last years due to their potential application in microelectronics and telecommunications. More specific perovskite materials have many fascinating properties such as colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering, and spin dependent transport. These compounds are candidates for memory devices and spintronics applications. Moreover in heterostructures a baffling property has been discovered namely the presence of a metallic interface phase even though the constituents are insulating[39]. This is the case we chose to illustrate here. Sing et al. [40] accessed non-destructively the interface of LaAlO_3 and SrTiO_3 by using HAXPES in the classic approach of angular dependent XPS. The authors prove spectroscopically for the first time the presence of the 2D electron gas (2DEG) at the interface of the two oxides. The samples investigated originated from two different institutes and had a slightly different preparation but in both cases the treatment was such to avoid oxygen vacancies. In Figure 6 we show only the Ti 2p core level recorded from the sample from Paul Scherrer Institute (PSI) at fixed incident energy of 3000 eV as a function of emission angle of photoelectrons. From the Ti^{3+} signal in the 2p core-level spectra there is a

clear indication for extra electrons located at Ti sites. The authors perform an evaluation based on a standard fitting procedure which takes into account the areas of Ti^{3+} and Ti^{4+} as a function of angle (Figure 6 b)) and find the layer thickness of the 2DEG. Much smaller than the photoelectron probing depth the 2DEG is confined to only 1 uc in this case [40]. The other set of samples investigated exhibit similar behavior with the 2DEG confined within a few unit cells at most. This investigation is one of the most straightforward uses of HAXPES evidencing the extended depth accessibility and non-destructivity of the technique.

Multilayers

Diffusion plays an important role nowadays in all research fields that involve nanometer scales especially thin films. This phenomenon has been extensively studied as it influences tremendously the behavior of the thin film heterostructures and ultimately the performance of devices in different applications. HAXPES has proven to be very sensitive to diffusion and thus allowed very consistent tracking of the sharpness of interfaces in metal multilayers [41-43] as well as Heusler multilayers [44] and x-ray mirrors [45, 46]. Here we chose to illustrate a case that concerns the stability of a typical multilayer heterostructure of Mo/B₄C/Si applied in modern reflective optics. De Rooij-Lohmann et al. [45] investigated this trilayer thin film system by a combination of techniques in order to determine the diffusion rate and behavior during annealing. HAXPES brought to the investigation its sensitivity to chemical interaction and extended probing depth properties which then allowed the characterization of the buried interfaces. Samples with different B₄C thickness were studied using the HIKE system before and during annealing. While Mo and Si are chosen for their optical constants, B₄C is only used to reduce the interdiffusion between the metal and the semiconductor. Without B₄C the system forms MoSi₂ silicide [47]. The authors found that with the presence of B₄C and as a function of the film thickness the diffusion occurred in two different stages before reaching a steady state. HAXPES proved without a doubt the formation of MoSi₂ upon annealing to 500° C.

Figure 7 The Mo 3d a) and Si 2s b) HAXPES spectra of both the as deposited and the fully annealed $t^{1/2}=53$ s^{1/2}; steady state sample with 1.3 nm B₄C. All spectra were acquired with an incident photon energy of 2010 eV. c) Peak shifts of Mo 3d and Si 2s (non-oxide) as a function of annealing time.

In Figure 7 a) and b) both Mo 3d and Si 2s (non-oxide component) core levels exhibit energy shifts consistent with the formation of the silicide MoSi₂. A more detailed evolution of those shifts upon

annealing is given in Figure 7 c). The 2 stages observed are in agreement with the authors findings on the different diffusion speeds observed by low energy ion spectroscopy (LEIS) [45]. Further qualitative and quantitative evaluation of the HAXPES data on the B 1s and C 1s indicates a reduction of boron quantity consistent with a downwards diffusion into Mo while carbon remains constant in concentration. Additionally boron is found to be chemically active forming MoB_x while B_4C decomposes. This behavior cannot however explain the diffusion stages observed since all these processes have already finished before stage 2, thus the authors perform TEM investigations on the same sample system in order to investigate the morphology as a possible cause. It is found that during stage 2 crystallization takes place, amorphous structures turning polycrystalline. This then assigned to be the cause of the increase in diffusion as it is known that grain boundaries act as accelerators for diffusion [48].

With this study HAXPES is proven to be a valuable complementary technique when performing a complete investigation of a buried interface, bringing to the table its chemical sensitivity and extended probing depth.

Fundamental Science - the HAXPES of Ni1s.

A multitude of scientific experiments concerning fundamental problems have been performed during the operation of the HIKE endstation at the KMC-1 beam line at BESSY II. Out of these projects we here review is a study of an old and very important problem: the explanation of the so called 6 eV satellite in the core electron spectrum of nickel. The discussion on this satellite can be seen as the starting point for highly correlated materials in general, which nowadays forms a very active research field.

The 6 eV satellite was first observed by core photoelectron spectrum of the $\text{Ni}2p_{3/2}$ core level [49]. The satellite was assigned as a "surface plasmon". This interpretation did not survive over the years. A long debate on the assignment has been going on for almost 40 years. In 1975 Hüfner and Wertheim proposed a phenomenological model including correlation effects [50], In 1980 Mårtensson and Johansson used a Born-Haber cycle argument to describe the main lines and the satellite in terms of fully screened and localized excitonic states [51]. A very good description was obtained using this approach. A large number of papers have dealt with this satellite since then. See Ref. [52]. The model in Ref. [50] and the method in Ref. [51] became most generally accepted as a theoretical description of the core level satellites in Ni. However, as late as 2006 a report again put forward the idea of an explanation in terms of a surface plasmon [53].

Using HAXPES it is possible to observe also the Ni 1s core level photoelectron spectrum. This was made at the HIKE end station at the KMC1 beamline at BESSY II [52]. The Ni 2p core electron spectrum was studied using a photon energy of 6.03 keV to excite spectrum. The Ni 1s spectrum was excited by 12.6 keV photons. Thus, the excess kinetic energies were 5 keV and 4 keV, respectively. This makes the electron mean free path rather similar in the two cases. It is also important to notice that the high kinetic energy

implies that the result essentially is dominated by the bulk electron structure. In Figure 8 we show the spectra from Ref. [52]

Figure 8 The Ni 2p (left panel) and Ni 1s (right panel) core photoelectron spectra, including the satellite structure. The spectra were excited using 6.03 keV and 12.6 keV photons, respectively. As can be seen the satellite is observed at 4 eV in the case of the Ni 1s spectrum.

This result directly rules out the explanation in terms of a surface plasmon since such a satellite would be seen at the same energy relative to the respective main lines. The result confirms the description by [50, 51]. The difference in satellite energy is explained by the difference in multiplet structure [52].

Fundamental Science – non-destructive PES profiling

Erik Lewin 2008

Industrial applications

St Gobain

Conclusion

- [1] I. Lindau, P. Pianetta, S. Doniach, W.E. Spicer, Nature, 250 (1974) 214-215.
- [2] W. Drube, T.M. Grehk, R. Treusch, G. Materlik, Journal of Electron Spectroscopy and Related Phenomena, 88-91 (1998) 683-687.
- [3] S. Hagstrom, C. Nordling, K. Siegbahn, Physics Letters, 9 (1964) 235-236.

- [4] N. Martensson, E. Sokolowski, S. Svensson, *Journal of Electron Spectroscopy and Related Phenomena*, 193 (2014) 27 - 33.
- [5] S. Svensson, E. Sokolowski, N. Martensson, To be published 2015, in: J. Woicick (Ed.), Springer Verlag.
- [6] M. Gorgoi, S. Svensson, F. Schafers, G. Ohrwall, M. Martin, P. Bressler, O. Karis, H. Siegbahn, A. Sandell, H. Rensmo, W. Doherty, C. Jung, W. Braun, W. Eberhardt, *Nucl Instrum Meth A*, 601 (2009) 48-53.
- [7] F. Schafers, M. Martin, M. Gorgoi, *Review of Scientific Instruments*, 78 (2007) 123102.
- [8] M. Gorgoi, F. Schafers, S. Svensson, N. Mårtensson, *Journal of Electron Spectroscopy and Related Phenomena*, 190 (2013) 153-158.
- [9] M.P. Felicissimo, D. Jarzab, M. Gorgoi, M. Forster, U. Scherf, M.C. Scharber, S. Svensson, P. Rudolf, M.A. Loi, *Journal of Materials Chemistry*, 19 (2009) 4899.
- [10] E.M.J. Johansson, M. Odelius, M. Gorgoi, O. Karis, R. Ovsyannikov, F. Schafers, S. Svensson, H. Siegbahn, H. Rensmo, *Chemical Physics Letters*, 464 (2008) 192-197.
- [11] E.M.J. Johansson, M. Odelius, S. Plogmaker, M. Gorgoi, S. Svensson, H. Siegbahn, H. Rensmo, *The Journal of Physical Chemistry C*, 114 (2010) 10314-10322.
- [12] U.B. Cappel, S. Plogmaker, E.M. Johansson, A. Hagfeldt, G. Boschloo, H. Rensmo, *Phys Chem Chem Phys*, 13 (2011) 14767-14774.
- [13] E.M.J. Johansson, R. Scholin, H. Siegbahn, A. Hagfeldt, H. Rensmo, *Chemical Physics Letters*, 515 (2011) 146-150.
- [14] R. Schölin, M.H. Karlsson, S.K. Eriksson, H. Siegbahn, E.M.J. Johansson, H. Rensmo, *The Journal of Physical Chemistry C*, 116 (2012) 26300-26305.
- [15] M. Karlsson, I. Jogi, S.K. Eriksson, H. Rensmo, M. Boman, G. Boschloo, A. Hagfeldt, *Chimia (Aarau)*, 67 (2013) 142-148.
- [16] M. Pazoki, J. Oscarsson, L. Yang, B.W. Park, E.M.J. Johansson, H. Rensmo, A. Hagfeldt, G. Boschloo, *RSC Advances*, 4 (2014) 50295-50300.
- [17] C. Enkvist, S. Lunell, B. Sjögren, P.A. Brühwiler, S. Svensson, *The Journal of Chemical Physics*, 103 (1995) 6333-6342.
- [18] M. Wimmer, M. Bär, D. Gerlach, R.G. Wilks, S. Scherf, C. Lupulescu, F. Ruske, R. Félix, J. Hüpkes, G. Gavrila, M. Gorgoi, K. Lips, W. Eberhardt, B. Rech, *Applied Physics Letters*, 99 (2011) 152104.
- [19] D. Gerlach, D. Wippler, R.G. Wilks, M. Wimmer, M. Lozac'h, R. Félix, S. Ueda, H. Yoshikawa, K. Lips, B. Rech, M. Sumiya, K. Kobayashi, M. Gorgoi, J. Hüpkes, M. Bär, *IEEE Journal of Photovoltaics*, 3 (2013) 483-487.
- [20] D. Gerlach, R.G. Wilks, D. Wippler, M. Wimmer, M. Lozac'h, R. Felix, A. Muck, M. Meier, S. Ueda, H. Yoshikawa, M. Gorgoi, K. Lips, B. Rech, M. Sumiya, J. Hupkes, K. Kobayashi, M. Bar, *Applied Physics Letters*, 103 (2013) 023903.
- [21] M. Wimmer, D. Gerlach, R.G. Wilks, S. Scherf, R. Félix, C. Lupulescu, F. Ruske, G. Schöndelmaier, K. Lips, J. Hüpkes, M. Gorgoi, W. Eberhardt, B. Rech, M. Bär, *Journal of Electron Spectroscopy and Related Phenomena*, 190 (2013) 309-313.
- [22] H. Mönig, C.H. Fischer, R. Caballero, C.A. Kaufmann, N. Allsop, M. Gorgoi, R. Klenk, H.W. Schock, S. Lehmann, M.C. Lux-Steiner, *Acta Materialia*, 57 (2009) 3645-3651.
- [23] P. Pistor, N. Allsop, W. Braun, R. Caballero, C. Camus, C.H. Fischer, M. Gorgoi, A. Grimm, B. Johnson, T. Kropp, I. Lauermann, S. Lehmann, H. Mönig, S. Schorr, A. Weber, R. Klenk, *physica status solidi (a)*, 206 (2009) 1059-1062.
- [24] A. Gloskovskii, C.A. Jenkins, S. Ouardi, B. Balke, G.H. Fecher, X.F. Dai, T. Gruhn, B. Johnson, I. Lauermann, R. Caballero, C.A. Kaufmann, C. Felser, *Applied Physics Letters*, 100 (2012) 92108.
- [25] B. Johnson, J. Klaer, S. Merdes, M. Gorgoi, B. Höpfner, A. Vollmer, I. Lauermann, *Journal of Electron Spectroscopy and Related Phenomena*, 190 (2013) 42-46.
- [26] B. Ümsür, W. Calvet, B. Höpfner, A. Steigert, I. Lauermann, M. Gorgoi, K. Prietzel, H.A. Navirian, C.A. Kaufmann, T. Unold, M.C. Lux-Steiner, *Thin Solid Films*, (2014) in press.
- [27] P. Pistor, D. Greiner, C.A. Kaufmann, S. Brunken, M. Gorgoi, A. Steigert, W. Calvet, I. Lauermann, R. Klenk, T. Unold, M.C. Lux-Steiner, *Applied Physics Letters*, 105 (2014) 063901.
- [28] R. Sarmiento-Pérez, S. Botti, C.S. Schnorr, I. Lauermann, A. Rubio, B. Johnson, *Journal of Applied Physics*, 116 (2014) 093703.
- [29] R. Lindblad, D.Q. Bi, B.W. Park, J. Oscarsson, M. Gorgoi, H. Siegbahn, M. Odelius, E.M.J. Johansson, H. Rensmo, *J Phys Chem Lett*, 5 (2014) 648-653.
- [30] T. Leijtens, S.D. Stranks, G.E. Eperon, R. Lindblad, E.M.J. Johansson, I.J. McPherson, H. Rensmo, J.M. Ball, M.M. Lee, H.J. Snaith, *ACS Nano*, 8 (2014) 7147-7155.
- [31] U. Rau, H.W. Schock, *Appl Phys A*, 69 (1999) 131-147.
- [32] D. Schmid, M. Ruckh, H.W. Schock, *Applied Surface Science*, 103 (1996) 409-429.

- [33] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, *Progress in Photovoltaics: Research and Applications*, 16 (2008) 235-239.
- [34] in, <http://www.nrel.gov/ncpv/>.
- [35] T. Nagaura, K. Tozawa in: *Progress in Batteries and Solar Cells*, Vol. 9, JEC Press Inc. Brunswick, OH, 1990.
- [36] H. Li, Z. Wang, L. Chen, X. Huang, *Advanced Materials*, 21 (2009) 4593-4607.
- [37] B. Scrosati, J. Garche, *Journal of Power Sources*, 195 (2010) 2419-2430.
- [38] B. Philippe, R. Dedryvere, M. Gorgoi, H. Rensmo, D. Gonbeau, K. Edstrom, *J Am Chem Soc*, 135 (2013) 9829-9842.
- [39] A. Ohtomo, H.Y. Hwang, *Nature*, 427 (2004) 423-426.
- [40] M. Sing, G. Berner, K. Goss, A. Muller, A. Ruff, A. Wetscherek, S. Thiel, J. Mannhart, S.A. Pauli, C.W. Schneider, P.R. Willmott, M. Gorgoi, F. Schafers, R. Claessen, *Phys Rev Lett*, 102 (2009) 176805.
- [41] E. Holmstrom, W. Olovsson, I.A. Abrikosov, A.M.N. Niklasson, B. Johansson, M. Gorgoi, O. Karis, S. Svensson, F. Schafers, W. Braun, G. Ohrwall, G. Andersson, M. Marcellini, W. Eberhardt, *Physical Review Letters*, 97 (2006) 266106.
- [42] S. Granroth, R. Knut, M. Marcellini, G. Andersson, S. Svensson, O. Karis, M. Gorgoi, F. Schafers, W. Braun, W. Eberhardt, W. Olovsson, E. Holmstrom, N. Martensson, *Physical Review B*, 80 (2009) 094104.
- [43] S. Granroth, W. Olovsson, E. Holmstrom, R. Knut, M. Gorgoi, S. Svensson, O. Karis, *Journal of Electron Spectroscopy and Related Phenomena*, 183 (2011) 80-93.
- [44] R. Knut, P. Svedlindh, O. Mryasov, K. Gunnarsson, P. Warnicke, D.A. Arena, M. Bjorck, A.J.C. Dennison, A. Sahoo, S. Mukherjee, D.D. Sarma, S. Granroth, M. Gorgoi, O. Karis, *Physical Review B*, 88 (2013) 134407.
- [45] V.I.T.A. de Rooij-Lohmann, A.E. Yakshin, R.W.E. van de Kruijs, E. Zoethout, A.W. Kleyn, E.G. Keim, M. Gorgoi, F. Schafers, H.H. Brongersma, F. Bijkerk, *Journal of Applied Physics*, 108 (2010) 014314.
- [46] V.I.T.A. de Rooij-Lohmann, L.W. Veldhuizen, E. Zoethout, A.E. Yakshin, R.W.E. van de Kruijs, B.J. Thijsse, M. Gorgoi, F. Schafers, F. Bijkerk, *Journal of Applied Physics*, 108 (2010) 094314.
- [47] I. Nedelcu, R.W.E. van de Kruijs, A.E. Yakshin, F. Bijkerk, *Physical Review B*, 76 (2007) 245404.
- [48] I. Kaur, W. Gust, M. Max-Planck-Institut für Fundamentals of Grain and Interphase Boundary Diffusion, Ziegler Press, 1989.
- [49] Y. Baer, P. Heden, J. Hedman, M. Klasson, C. Nordling, K. Siegbahn, *Physica Scripta*, 1 (1970) 55.
- [50] S. Hüfner, G. Wertheim, *Physics Letters A*, 51 (1975) 299-300.
- [51] N. Mårtensson, B. Johansson, *Physical Review Letters*, 45 (1980) 482.
- [52] O. Karis, S. Svensson, J. Rusz, P.M. Oppeneer, M. Gorgoi, F. Schafers, W. Braun, W. Eberhardt, N. Martensson, *Physical Review B*, 78 (2008) 233105.
- [53] A.P. Grosvenor, M.C. Biesinger, R.S.C. Smart, N.S. McIntyre, *Surface Science*, 600 (2006) 1771-1779.