

High resolution and time resolved photoemission spectroscopy for developing more efficient materials to reduce energy consumption and increase renewable energy production.

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Abstract. Due to the increase of energy consumption and the resulting ecological challenge, a collective awareness leads to the development of renewable energies and more efficient materials to increase the green energy production. Development of efficient photovoltaic materials is very closely related to their chemical and electronic properties. A better knowledge of these imbricated properties is needed, in addition to a better comprehension of their interplay with charge transport mechanisms. Exciton creation and recombination processes, charge transfer and charge collection processes take place at the surface and interface of the photoactive materials. Photoemission spectroscopy as chemical specific and surface sensitive spectroscopic technique is a method of choice on the study of physical phenomena at the origin of photoconversion efficiency. Time resolved photoemission spectroscopy has been recently renewed interest covering time scale from fs to more than seconds. It permits to probe the dynamics of relaxation of photoexcited charges and determine their lifetime. It finds application in various materials used in solar photovoltaics. In this paper, we define the physical and chemical properties determined by the combination of high resolution and time resolved photoemission spectroscopy. We show examples dealing with the development of renewable energy and energy consumption reduction in agreement with the current ecological trend for a better future.

1 Introduction

The primary energy consumption has increased by 5.8% in 2021 and fossil fuels accounts for 83% of the global primary consumption.¹ Use of fossil energy leads to irrevocable phenomena as temperature increase which could led to dramatic events. International awareness led to ecological chart (Paris agreement of the *Paris climate conference (COP21)*) which actively participates in the development of renewable energy and in energy consumption reduction. The share of renewables continuously increases to represent 13% in global power generation.¹ To develop, renewable energy must be economically competitive. Energy production cost reduction is needed. Due to the huge effort done the last 10 years, the photovoltaics energy cost has been divided by a factor of four, by reducing the material cost, by improving the efficiency and reliability.²

Promising new materials such as colloidal nanoparticles³ and perovskite^{4,5} have been developed. As charge creation and collection processes take place at the surface and interfaces of materials, core level photoemission spectroscopy is a powerful tool due to its chemical selectivity and surface sensitivity. It is possible to determine the chemistry of the surfaces and interfaces. The location of the different chemical species at the interface can be assessed by varying the kinetic energy of the probed photoelectron. This is allowed by

synchrotron radiation sources and their capability to tune the incident photon energy. In the early 2000s, time resolved photoemission spectroscopy (TR-PES) has been used to probe the charge dynamics in semiconductors through surface photovoltage measurement.^{6,7} With third generation synchrotron centres, new beamlines combining high resolution photoemission and time resolved photoemission spectroscopy offer new capabilities appealing for the development of photoactive materials.⁸⁻¹⁰ Based on new delay line detectors¹¹ high resolution photoelectron analysers¹² combined to high resolution, soft X-ray beamline offers resolving power better than 15000 and time resolutions down to 10ps.¹³ The covered temporal range benefits of exploring charge carrier recombination dynamics, charge diffusion and thermal diffusion.¹⁴ New setups based on HHG and XFEL offer better time resolutions in the fs range to probe carrier excitation and thermalization processes.¹⁴ In this paper we will focus on the capabilities offered by synchrotron-based experiments taking advantages of high resolution and time resolution photoemission spectroscopy. We will show different results on bulk materials with use in photovoltaic applications, hybrid materials as organic-inorganic heterojunctions, colloidal nanoparticles, and their applications.

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2 Photoemission process

Basic concepts of photoemission spectroscopy will be described, more details can be found in literature.^{15, 16} Photoemission spectroscopy is based on photoelectric effect. The surface of the sample is irradiated with X-rays. Photoelectrons are ejected from the sample with a kinetic energy verifying the equation [1] in agreement with the law of conservation of energy.

$$h\nu = E_B + E_K + \phi \quad [1]$$

Where $h\nu$ is the incident photon energy, E_B is the binding energy, E_K is the kinetic energy and ϕ is the work function of the material. The photoelectrons will be collected through high resolution photoelectron analyser and sorted according to their kinetic energy. The photoelectrons will stem from three main processes. An elastic signal made of sharp peaks whose energy varies with the incident photon energy originates from given atomic orbitals. Broader peaks with kinetic energy independent on incident photon energy come from Auger deexcitation processes. A background originates from inelastic processes. From the elastic process, chemical and electronic properties can be determined that helps provide a better understanding and optimisation of material for renewable energy.

2.1 Core level photoemission spectroscopy

Core level photoemission spectroscopy is focused on the collection of the photoelectrons coming from given atomic orbital. The photoelectrons are collected as a function of their kinetic energy. The number of contributions needed to fit given core level spectrum give the number of non-equivalent chemical species in the material. The position in energy of the peaks (chemical shift) provides information on the nature of the chemical bond and of the surrounding atoms of the species. The spatial origin of the collected photoelectron into the bulk can also be determined by changing the kinetic energy of the photoelectrons. Photoelectrons have an inelastic mean free path varying as a function of their kinetic energy and the nature of the materials crossed. The inelastic mean free path can be calculated using Tanuma Powell and Penn algorithm.¹⁷ About 95% of the collected photoelectrons are coming from 3 times the electron mean free path. By varying the incident photon energy, it is possible to vary the kinetic energy of the photoelectrons and carry out a depth profiling. By comparing the variation in relative intensities of the core levels as a function of the incident photon energy, it is possible to determine the nature, number and amount of inequivalent chemical species in the material as well as their location at the interface. From the variation in intensity of the C1s core level spectra measured as a function of the incident photon energy, the intercalation process of silicon at graphene/SiC interface has been successfully determined.¹⁸

2.2 Valence band maximum and cut off

The determination of the band diagram energy is of great importance for efficient charge carrier creation and collection. It allows to determine the type of band alignment for semiconductor heterojunction. The position in energy of the valence and conduction bands between two materials involved in active P-N or donor-acceptor junctions provides information on the ability to dissociate the photocharge carriers. From the measurement of the valence band, the valence band maximum energy position is determined. The work function of the material is determined from the photoemission signal Cut Off corresponding to the photoelectrons measured at lowest kinetic energy.¹⁹ It is also possible to evidence the formation of interfacial dipole between two materials, by comparing the evolution in energy position of the work function and of the core levels before and after deposit of a second material on top of a first one (atoms, organic molecules, 2D materials on semiconductor or metal).²⁰ Interfacial dipole formation can drastically affect the electronic properties of the formed heterojunction.

2.3 Surface photovoltage effect

The surface photovoltage (SPV) effect is a powerful contactless and non-destructive technique to determine the minority charge carrier lifetime.²¹ The measurement of SPV in photoemission is based on band bending phenomenon.²² Band bending comes from the difference in charge between the surface and the bulk. The position of the Fermi level into the gap of semiconductors, in the bulk, is directly related to the doping level of the material. The position of the Fermi level at the surface depends on the surface termination. At the equilibrium, an electric field is created in the depletion layer (DL). Under light excitation with an energy higher than the gap of the material, charges are promoted from the valence band to the conduction band. Due to the electric field in the DL, the electrons are attracted or repelled from the surface to compensate the excess of charges and flattened the bands. The spectroscopic signature of this phenomenon is a rigid shift of the core levels. The direction of the energy shift depends on the substrate doping. The doping of a material can be determined from the direction of the shift observed under illumination. The time needed to come back to the steady state position after illumination gives the lifetime of the photoexcited charges.

3 Materials for photovoltaic and LED applications

3.1 Bulk semiconductors

3.1.1 Silicon

Silicon is a material of choice in photovoltaic application and represents 90% of photovoltaic market.²³ Silicon solar cells has reached an energy

conversion efficiency of 25% in 1999 and new architectures have been developed to exceed this value. It has been shown that minority charge carrier lifetime plays a key role in photoconversion efficiency. A minority charge carrier lifetime optimum exists.²⁴ Nevertheless, the parameters driving the minority charge carrier lifetimes remain unclear. Experimental works paved the way to formalisms^{6,7}, but no systematic studies were done to determine the influence of the key parameters governing photocarriers lifetime. Taking advantages of new time resolved photoemission setup at synchrotron, systematic studies on surface termination and substrate doping have been performed. Their influence on SPV effect has been determined and theoretical models have been evaluated to fit the experimental data.

High resolution and time resolved photoemission spectroscopy has been performed on In/Si(111) surface as a function of indium coverage and surface reconstruction.²⁵ Depending on the surface termination, a broad dispersion in energy of the position of the Si2p core level has been obtained corresponding to a variation in band bending. The SPV relaxation exhibits two deexcitation lifetimes. A fast deexcitation process (≤ 100 ns) corresponds to a tunnelling transport process. The photoexcited charges cross the surface potential barrier through tunnel effect. The size of the depletion layer increases, the tunnel recombination is then no more allowed. A second longer deexcitation process occurs based on thermionic effect (≥ 100 ns). This works evidenced the key role played by the size of the depletion layer in the relaxation process and relaxation lifetime.

The influence of silicon substrate doping and surface termination on SPV has also been systematically studied by time resolved photoemission spectroscopy.²⁶ Water saturated and thermally oxidized Si(001) surfaces have been studied as a function of bulk doping. It has been shown that bulk doping has the highest influence on charge carrier lifetime. Thermionic relaxation model is in good agreement with experimental data for low laser fluence and bulk recombination becomes preponderant at high laser fluence as proposed in literature.²⁷ Experimental SPV shift as a function of the laser fluence agrees with current theoretical model at low fluence but differs at high fluence. New model is needed to account for SPV shift saturation observed at high fluence.

3.1.2 wide band gap semiconductors

ZnO as n-type wide band gap semiconductor (3.4eV) with high electron mobility²⁸ is a promising material as transparent electrodes or as active layer for solar cell application.²⁹ It nevertheless suffers from persistent photoconductivity. Its origin is attributed to oxygen vacancies.³⁰

SPV effect in ZnO has been investigated by time resolved photoemission spectroscopy (TR-PES).²² The implication of oxygen vacancies in SPV effect in ZnO has been evidenced by changing the surface preparation procedure. The annealing of the ZnO surface in partial pressure of oxygen for different times has shown dramatic changes in the relaxation lifetime of SPV.

Annealing of 20 min and 10 min in $1.2-1.4 \times 10^{-7}$ mbars of oxygen at 703 K led to relaxation lifetime of 150 μ s and 1.2 ms, respectively. For sub bandgap excitation of ZnO at 405 nm (3.06 eV), a small SPV shift is still observed. Even if the laser pulse energy is too small to photoexcite the charges through the band gap, ZnO presents SPV effect. These results indicate that the photoexcitation process involves in-gap states associated to ionized oxygen vacancies. This work has corroborated the involvement of ionized oxygen vacancies with persistent photoconductivity in ZnO.

3.2 Heterostructures

The combination of different materials is of great interest to build efficient photoactive heterostructures made of donor-acceptor junction for organic-organic junction³¹ or p-n junctions for inorganic heterojunction. Due to their high tunability, it is possible to match the electronic properties of organic materials with the electronic properties of inorganic semiconductor. The formation of organic-inorganic heterostructure is a promising approach. Inorganic material as ZnO can act as active layer or only play part of transparent electrode.²⁹ A key process in charge generation and collection is the charge transfer occurring at the interface between two materials.

3.2.1 hybrid heterostructures

Model donor-acceptor organic junction made of ZnPc/C60 multilayers has been investigated by TR-PES to probe the charge dynamics at the ps time scale.³² To be sensitive to the molecular orbitals of the molecules, valence band measurement has been performed at the carbon absorption edge. Working at the resonance, signal coming from the molecular orbital in the valence band is enhanced. A special care on the cleanness of the optics of the soft X-ray beamlines is needed to allow photoemission measurement at Carbon K edge with high photon flux.^{33, 34} Time resolved photoemission spectroscopy measured with time resolution of 50 ps as a function of laser flux has evidenced two photoexcitation processes. A rigid shift of the VB at high laser flux coming from space charge effect and a variation in intensity of the valence band at high energy attributed to a modification of the interface dipole.

Charge relaxation in C60/CuPc system appears complex. Different studies using TR-PES evidenced various behavior depending on the stacking of C60/CuPc and also on the nature of the substrate underneath. TR-PES measured on C60 on thin CuPc film evidenced localized photoexcited charges on C60 layer.³⁵ C1s core level contribution coming from the C60 was shifted under laser excitation when the contribution coming from CuPc remained unchanged. This result evidenced the capability to TR-PES to probe charge transfer localized on specific chemical species. The time relaxation of photoexcited charges has been investigated on C60/CuPc/TiO₂ and CuPc/C60/TiO₂ heterojunctions.³⁶ The experiments have evidenced

different relaxation behaviors for the two systems. A delay in exciton dissociation is observed for C60/CuPc/TiO₂ compared to CuPc/C60/TiO₂. This indicated the role of charge blocking of the CuPc layer disabling the exciton relaxation through TiO₂. This work has highlighted the influence of molecular stacking order in organic junction on relaxation process.

3.2.2 colloidal quantum dots

Colloidal Quantum Dots (CQDs) present advantageous characteristics as tuneable electronic properties (bandgap, doping,) and low-cost material production.^{3, 37} CQDs find application in solar cell application as active material but also application in the energy consumption reduction in efficient structure for LED applications³⁸. CQDs take advantages of high resolution and time resolved photoemission spectroscopy to optimise the production process and material tuning to adapt the electronic properties and to match electronic properties of their counterparts (P-N junctions).

Carrying out depth profiling by measuring the evolution of the relative intensity of core levels as a function of incident photon energy, it is possible to have a qualitative idea of the repartition of chemical species in the nanoparticles. The synthesis of InP/ZnS core shell nanoparticles has been investigated by high resolution core level photoemission spectroscopy (HR-PES).³⁹ By comparing the spectroscopic signature for two synthesis methods, it has been possible to determine the chemical species repartition inside the nanoparticles. While a single-step synthesis method has led to a homogenous repartition of Indium species forming InPZnS alloyed core nanoparticles, the two-step method has led to the synthesis of InP/ZnS core shell structure. Photoemission spectroscopy has also evidenced interfacial states induced by species interdiffusion at core/shell interface.

It is also possible to determine quantitatively the thickness of the shell according to the core diameter by HR-PES.⁴⁰ Using analytical model developed by Shard et al.^{41, 42} considering the spherical geometry of the nanoparticles, by plotting the variation in intensity between two chemical species coming from the core and the shell and by comparing that to the calculation, it is possible to determine the thickness of the shell. HR-PES is also very efficient in the optimisation of ligand exchange process. Ligand exchange process permits to exchange long Carbon chain used during the CQDs synthesis with shorter conductive ligands used to dope the nanoparticles. Anchor is usually of different chemical nature. For instance, in the case of PbS/CdS CQDs,⁴⁰ long carbon chains were linked through nitrogen atoms while shorter ligands were linked through Sulfuric atoms. HR-PES spectra have evidenced two kinds of nitrogen atoms and two kinds of sulfuric atoms corresponding to ligands linked to the nanoparticles and free ligands present into the media. By comparing the ratio of the different chemical species, it is possible to determine the amount of remaining ligands and to examine the ligand exchange process efficiency.⁴⁰

The doping of CQDs can be performed by ligand exchange or by changing the CQDs stoichiometry. The

doping of the CQDs can be determined by measuring the VBM and by determining the energy band diagram. The doping can also be directly determined from the direction of SPV shift under laser excitation. Both ligand exchange process and chemical composition modification take advantages of HR- and TR- PES to evidence doping variation in CQDs. n to p doping of HgTe CQDs by ligand exchange process has been evidenced by combination of HR-PES and TR-PES.⁴³ Continuous variation in Hg_{1-x}Se_xTe_{1-x} nanoparticles doping from n to p type by varying the nanoparticle composition has been evidenced by energy band diagram determination and TR-PES measurement.⁴⁴

Development of CQDs based solar cells strongly depends on charge collection efficiency. Determining the CQDs/electrode electronic coupling is of high interest. To evidence indirect substrate excitation via charge transfer from the CQDs to the substrate, PbS QDs absorbing in red light have been deposited on clean ZnO substrate.⁴⁵ An illumination in red light of PbS/ZnO surface produced a shift in energy of the PbS core level comparable to an excitation in UV light above the ZnO band gap. No shift in energy was visible for red illumination of ZnO clean surface. These results indicated that QDs photoexcitation allows for charge transfer into the ZnO conduction band at the origin of transient core level energy shift. TR-PES allowed to evidence charge transfer from QDs to ZnO surface and indirect ZnO excitation under illumination.

4 Conclusion and perspectives

To increase the photoconversion efficiency and go beyond the Shockley–Queisser limit⁴⁶, corresponding to the maximum theoretical efficiency of a single p-n junction solar cell, new materials and new architectures are developed.³ High resolution and time resolved photoemission spectroscopy has proved its capability to determine the chemical and electronic properties of complex nanomaterials and their chemical and electronic coupling with the substrate underneath. Synchrotron based photoemission spectroscopy combining variable incident photon energy, high energy resolution and time resolution down to 10 ps, is a powerful and unique spectroscopic technique able to correlate chemical and electronic properties to charge carrier lifetime. New technological advances in TR-PES experimental setup arise. Higher time resolution at fs time scale is now available and allows to probe faster excitation and fast decay processes as thermalization effects (carrier-carrier and carrier-phonon scattering)¹⁴. Time resolved near ambient pressure environment⁹ is also developed with use in photocatalysis and photochemistry. Both will participate to develop more efficient materials to decrease the energy consumption and especially in the scope of catalysis as catalytic processes account for 25% of industrial energy use.⁴⁷

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