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# Characterization of deeply buried interfaces by Hard X-ray Photoelectron Spectroscopy

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"Si j'ai pu voir plus loin, c'est que je me tenais sur les épaules de géants" Isaac Newton

"If I have seen further it is only by standing on the shoulders of giants" Isaac Newton

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### Preface

This thesis describes the research carried out during my PhD project in the period from October 2014 to May 2018. This thesis is entitled "Characterization of deeply buried interfaces by HArd X-Ray Photoelectron Spectroscopy". The PhD was separated between the two sites of PFNC (Platform for NanoCharacterization) in CEA (Grenoble) and the Physics Department of the Syddansk Universitet (Denmark).

This thesis addresses the need for developing non-destructive, in-depth innovative characterization techniques suitable for deeply buried layers and interfaces. The goal has been to improve and extend to the hard X-ray range the XPS inelastic background analysis in order to obtain a technique which is fast to apply, well defined for a large range of samples and accessible to non-experts. This work is an association between the CEA (Atomic and Alternative Energy Authority) in Grenoble (France), the Syddansk Universitet in Odense (Denmark) and the ECL (Ecole Centrale de Lyon) in Ecully (France). The experiments took place at the Platform for NanoCharacterization (PFNC) of LETI (Electronics and Information Technology Institute, France), at the Spring-8 synchrotron (Japan) and at the DESY synchrotron (Germany).

The first chapter provides details about the samples used for the experiments and their technological importance and the characterization issues that it presents. It describes the characterization techniques used for the analyses presented in the other chapters and reviews the latest improvements of the inelastic background analysis.

The second chapter presents the inelastic background analysis accuracy using a reference spectrum recorded from bulk material. This investigation was done on different samples with varying thicknesses and determines the reliability of the results compared to TEM measurements. This is presented in an article published in Applied Surface Science, in 2018.

The third chapter presents a complete analysis of the elemental diffusion by inelastic background analysis. This was done on a sample before and after two annealing steps. The depth distribution and the absolute and relative concentrations of elements were determined. The results were compared to measurements with TEM, sputter depth profiling and core-level analysis. This work was submitted to Journal of Applied Physics and is in the first revision step of the publication process.

The fourth chapter is a theoretical study for determining a rule for the choice of input parameters. This was done to make the analysis simpler for unknown samples and complex stacks. We investigated very different materials in stacks of variable thicknesses.

The fifth chapter is a proof of principle for future extends of the technique to 3D mapping by HAXPEEM combined with inelastic background analysis. The experiment was done on a quite simple stack consisting of two materials and the results are compared to TEM measurements. This work was published in Applied Physics Letters, in 2016.

The sixth chapter is a review of the work done in this thesis.

### Abstract

This thesis aims at improving the inelastic background analysis method in order to apply it to technologically relevant samples. Actually, these improvements are utterly needed as they concern criteria of accuracy and time saving particularly for analysis of devices presenting deeply buried layers with different materials. For this purpose, the interest of the inelastic background analysis method is at its best when combined with hard X-ray photoelectron spectroscopy (HAXPES) because HAXPES allows to probe deeper in the sample than with conventional X-ray photoelectron spectroscopy (XPS).

The present work deals with technologically relevant samples, mainly the high-electron mobility transistor (**HEMT**), at some crucial steps of their fabrication process as annealing. Actually, it is very important that these analyses shall be performed non-destructively in order to preserve the buried interfaces. These are often the location of complex phenomena that are critical for device performances and a better understanding is often a prerequisite for any improvement.

In this thesis, the in-depth diffusion phenomena are studied with the inelastic background analysis technique (using the QUASES software) combined with HAXPES for depth up to 60 nm. The depth distribution results are determined with deviations from TEM measurements smaller than a typical value of 5%. The choice of the input parameters of the method is discussed over a large range of samples and simple rules are derived which make the actual analysis easier and faster to perform.

Finally, it was shown that spectromicroscopy obtained with the HAXPEEM technique can provide spectra at each pixel usable for inelastic background analysis. This is a proof of principle that it can provide a 3D mapping of the elemental depth distribution with a non-destructive method.

### Résumé

Cette thèse vise à améliorer la méthode d'analyse du fond continu inélastique afin de l'appliquer à des cas qui présentent un intérêt technologique. En effet, ces améliorations sont cruciales car elles portent sur des critères de précision et de gain de temps, plus particulièrement pour l'étude de dispositifs présentant plusieurs couches profondément enterrées de matériaux bien distincts.

Ainsi, l'analyse du fond continu inélastique associée à la spectroscopie de photoélectrons à rayons X durs (HAXPES) présente un grand intérêt car l'HAXPES permet de sonder plus profondément dans un échantillon qu'avec la spectroscopie de photoélectrons à rayons X classique (XPS).

Ce présent travail porte sur des échantillons technologiquement pertinents, principalement des transistors à haute mobilité d'électrons (HEMTs), à certaines étapes cruciales de leur processus de fabrication, tels que des recuits. Il est donc très important que ces analyses soient effectuées de manière non destructive afin de préserver les interfaces enterrées. Ce sont souvent l'emplacement de phénomènes complexes qui sont critiques pour les performances du dispositif et une meilleure compréhension est une condition préalable à l'amélioration des dispositifs.

Dans ce travail, les phénomènes de diffusion en profondeur sont étudiés grâce à l'analyse du fond continu inélastique associée à l'HAXPES (en utilisant le logiciel QUASES) pour des profondeurs allant jusqu'à 60 nm. Les résultats de distribution en profondeur présentent des écarts par rapport aux mesures TEM inférieures à 5%. Le choix des paramètres d'entrée de la méthode est discuté pour une large gamme d'échantillons et des règles simples en sont issues qui rendent l'analyse réelle plus facile et plus rapide à effectuer.

Enfin, il a été montré que la spectromicroscopie faite avec la technique HAXPEEM peut fournir des spectres à chaque pixel utilisables pour l'analyse du fond continu inélastique. Cela peut fournir une cartographie 3D de la distribution en profondeur des éléments de manière non-destructive.

### Abstrakt

Denne afhandling har til formål at forbedre den uelastiske baggrundsanalysemetode til anvendelser i den til teknologiske industri. Faktisk er disse forbedringer absolut nødvendige, for at opnå nøjagtighed og tidsbesparelse, især for analyse af prøver med dybt begravede lag af forskellige materialer. Til det formål er interessen for den uelastiske baggrundsanalysemetode bedst i kombination med hård røntgenfotoelektron-spektroskopi (HAXPES), fordi HAXPES gør det muligt at probe dybere i prøven end med konventionel røntgenfotoelektron-spektroskopi (XPS).

Dette arbejde beskæftiger sig med teknologisk relevante prøver, hovedsagelig høj-elektron mobilitetstransistor (HEMT), på nogle afgørende trin i deres fremstillingsproces som fx annealing. Faktisk er det meget vigtigt, at disse analyser udføres på en ikke-destruktiv måde for at bevare de begravede grænseflader. Det er ofte her de komplekse fysiske fænomener opstår, som er kritiske for fuktionaliteten, og en bedre forståelse af grænsefladerne er ofte en forudsætning for at kunne forbedre denne.

I denne afhandling studeres de dybdegående diffusionsfænomener med den uelastiske baggrundsanalyse teknik (ved hjælp af QUASES software) kombineret med HAXPES for dybder op til 60 nm. Dybdestributionsresultaterne har afvigelser fra TEM-målinger mindre end en typisk værdi på 5%. Valget af input parametre for metoden er diskuteret på bagground af et stort udvalg af prøver samt omfattende simuleringer og enkle regler er udledt, hvilket gør den praktiske analyse nemmere og hurtigere at udføre.

Endelig blev det vist, at spektromikroskopi opnået med HAXPEEM-teknikken kan tilvejebringe spektre ved hver enkelt pixel som kan anvendes til uelastisk baggrundsanalyse. Dette viser at i princippet kan en 3D-billeddannelse af den elementære dybdefordeling bestemmes ikke destruktivt.

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### Acronyms

HEMT: High Electron Mobility Transistor **XPS**: X-ray Photoelectron Spectroscopy HAXPES: HArd X-ray PhotoElectron Spectroscopy **2DEG**: 2 Dimension Electron Gas MOCVD: Metal Oxide Chemical Vapor Deposition **EBPVD**: Electron Beam Physical Vapor Deposition **RTA**: Rapid Thermal Annealing **IMFP**: Inelastic Mean Free Path **REELS**: Reflected Electron Energy Loss Spectroscopy **ESCA**: Electrons Spectroscopy for Chemical Analysis **PES**: PhotoElectron Spectroscopy **XPEEM**: X-ray PhotoElectron Emission Microscopy HAXPEEM: HArd X-ray PhotoElectron Emission Microscopy **CCD**: Charge Couple Device **EAL**: Effective Attenuation Length **HSA**: HemiSpherical Analyzer **SMA**: Spherical Mirror Analyzer **ARXPS:** Angle Resolved X-ray PhotoElectron Spectroscopy

### **Chapter 1: Introduction**

Today, there are incessant improvements in the field of nanoelectronics. In most devices, interfaces play a major role [1] and has become more and more important in the understanding of the device operation. This is due to:

- the decreasing size of the components resulting in thinner and thinner layers,
- the complexity of the stacks which contain insulators, conductors and semiconductors,
- the steps in the creation of the device which often consist of several annealings.

It is therefore necessary to better understand the phenomena happening during the creation of critical interfaces, most often deeply buried beneath the surface. This implies a need for more efficient and accurate characterizations.

Among the different characterization techniques permitting analyses without damaging the interfaces, photoemission has always had an important place because it permits to perform a large range of analyses: chemical analysis, depth profile analysis (with and without sputtering) and measurement of band structure, energy-level alignments, band bending,... etc.

Nevertheless, the analysis depth is limited around 10 nm with laboratory X-ray sources  $(hv \sim 1200 - 1500 \text{ eV})$  which is not sufficient to access buried interfaces in devices. However, using tunable hard X-ray radiation provided by synchrotron facilities, the probing depth can be drastically improved which permits to analyze deeper with photoemission.

Among the many phenomena happening at the interfaces, the elemental diffusion stays one of the most important to characterize. In the last decades, the inelastic background analysis of photoemission spectra has proved its efficiency to retrieve the elemental depth distribution. More recently, this method combined with hard X-rays has been shown as a good solution to non-destructively characterize deeply buried interfaces in complex stacks [2-4].

However, inelastic background analysis of photoemission spectra from deeply buried elements in complex stacks can be optimized and this is the purpose of this thesis.

### I. High Electron Mobility Transistors

This part exposes the motivation for using High Electron Mobility Transistors (HEMTs) devices in this work. The studied samples are described and the reason why there is a need for improved characterization on these technologically relevant structures is pointed out. The motivation also applies to any multilayer structure presenting deeply buried interfaces.

#### 1. Generalities about HEMTs devices

Today, many new technologies use power electronic devices which convert and handle electric energy. For two decades, the research has focused on new materials to replace the silicon currently used in power transistors.

Gallium Nitride (GaN) is an advantageous material since it presents better energetic efficiency, it can work at high frequency and high temperature and there are less energy losses with GaN than with Si.

GaN material presents different properties necessary for such applications. It is a semiconductor with a wide band gap of ~ 3.43 eV [5] and also a large breakdown voltage of  $3.4 \text{ MV.cm}^{-1}$  [6].

Furthermore, in the AlGaN/GaN heterostructure, there is the creation of a two-Dimensional Electron Gas (2DEG) [7] at the junction between the two materials presenting different band gaps (see Fig. 1 (right)). At the AlGaN side of the interface, a positive charge density is formed whereas at the GaN side, there is compensation by free electrons which are trapped in the potential well at the interface. These form the 2DEG as shown on Fig. 1 [8]. It turns out that these electrons have a high electron mobility that can reach 1500-2100 cm<sup>2</sup>.V<sup>-1</sup>.s<sup>-1</sup> which is better than what is obtained with Si and SiC (< 1350 cm<sup>2</sup>.V<sup>-1</sup>.s<sup>-1</sup>) [6]. This is the reason why such structures are called High Electron Mobility Transistors (HEMTs). In addition, the electron density in the 2DEG is very high [9].



Figure 1: (right) Energy band gap of AlGaN/AlN/GaN HEMT, adapted from [10] (left) Creation of the 2DEG (Psp: spontaneous polarization, Ppiez: piezoelectric polarization).

Therefore, the AlGaN/GaN interface is very interesting but it is difficult to study as it is deeply buried and it is where complex phenomena take place.

These last years, improvements were made in order to produce devices with optimized performances but still progresses are needed to insure the durability of the device.

Because of the high voltages used for power applications, lateral metallic extensions (called field-plates) are added in the transistor architecture to decrease the electric field peaks and increase the breakdown voltage [11]. A  $SiN_x$  passivation layer is deposited on the AlGaN surface as the 2DEG was shown dependent of the AlGaN surface quality [7, 8] as shown in Fig. 2.

The 2DEG is the channel of the HEMT which links the three electrodes: source and drain for the contacts and gate for the switching function of the canal. The contacts are made by first depositing metal layers (ex: AI, Ta, Ti...) and subsequently anneal the structure for a short time to create an alloy with the AIGaN substrate. This canal is localized under the AIGaN layer, also called barrier layer as shown on Fig. 2. This is a challenge for the creation of the alloy source/drain contact with AIGaN as the barrier layer must stay intact after annealing.



Figure 2: Scheme of a HEMT structure.

The source, drain and gates are metallic layers with also different band gap compared to AlGaN which participate in the stack complexity as well as surface passivation and elemental diffusion. This makes the understanding of the phenomena taking place in the device even more complicated and highlights the need for accurate and effective characterization.

In the final structure (see Fig. 2), the interesting part is the interface between the AlGaN substrate and the metallic contact. This interface is deeply buried in the device which makes the analysis very difficult. One solution to characterize this buried interface would be the removal of the top layer but this would be harmful to the interface. Therefore, it is desirable to keep the complete structure during the analysis.

For a properly working HEMT, the source/drain-contacts must be ohmic, with a low resistance and the process to create the ohmic contact by annealing must be well known in order to be reproducible. Therefore, this kind of samples needs to be characterized at every stage of the contact creation process to investigate the mechanisms taking place during the different annealing steps.

For these reasons such samples are good examples to show the advantages of being analyzed with the inelastic background analysis technique combined with Hard X-ray PhotoElectron Spectroscopy (HAXPES). Since the method allows non-destructive analysis of deeply buried interfaces [2-4]. It is the main purpose of this thesis to investigate this and to find the best way to define the input parameters in order to obtain an accurate, reliable and effective analysis.

#### 2. Fabrication of the samples

The samples studied in the following chapters are based on a GaN(4  $\mu$ m)/Al<sub>0.25</sub>Ga<sub>0.75</sub>N(22 nm) substrate epitaxially grown by Metal Oxide Chemical Vapor Deposition (MOCVD) on a Si(111). Metallic layers of Ta or Ti and Al are then successively deposited by Electron Beam Physical Vapor Deposition (EBPVD). To achieve the contact electrode, the stack is annealed by Rapid Thermal Annealing (RTA) successively at two different temperatures (depending of the deposited metal) under a nitrogen atmosphere.

The layers of the analyzed samples are thinner (~ 25 - 65 nm) than in the real device (~ 100 - 200 nm). However, proportions of Ta/Al thicknesses are kept to ensure that those are still representative of the real HEMTs. It is also much more representative than those obtained by removing most of the top electrode which would be necessary if the analysis is done by XPS with conventional X-ray sources.

Each sample was analyzed by high resolution TEM, as exemplified in Fig. 3. The details of each sample structure will be given in Chapters 2, 3 and 5.



Figure 3: TEM image of a HEMT with Ta/AI contact with thicknesses measurement.

#### 3. Motivations: critical interfaces of interest

These devices present a critical deep interface between GaN and AlGaN where the 2DEG is formed. Diffusion phenomena happen during the annealing process and can affect this interface and therefore the operation of the device. This is a particular case but more generally, diffusion phenomena happen for many devices during the fabrication process and can affect their operation.

These deeply buried interfaces are often the place of complex phenomena which need to be studied in order to understand the operation of devices and improve them.

This is the motivation for improvements of XPS inelastic background analysis method as it is a non-destructive technique to analyze the depth distribution of elements in a sample.

### II. X-ray Photoelectron Spectroscopy

#### 1. Overview of X-ray photoemission

X-ray Photoelectron Spectroscopy (XPS) was invented due to several discoveries in the 19<sup>th</sup> and 20<sup>th</sup> centuries. It is a quantitative and non-destructive method which gives chemical and elemental information about sample surfaces.

XPS is based on the photoelectric effect which consists of bombarding a material (in vacuum) with photons, discovered by Hertz in 1887 [12]. With XPS, the photon irradiation is made with X-rays which were discovered by Röntgen in 1895 (Nobel Prize of 1901). The photoelectric effect was adapted to X-rays by Thomson and Lenard [13] (Nobel Prize of 1905). Then, Einstein theoretically explained it in 1905 [14] (Nobel Prize of 1921). Karl Siegbahn (Nobel Prize in 1924) got an almost complete understanding of the electron shell.

In practice, the photoionized electrons emitted from an atom deep in a material travel into this matter until reaching the surface. The photoelectrons are then detected and filtered in energy to obtain XPS spectra, ie, photoelectron intensity as a function of their measured kinetic energy :  $I = f(E_k')$ .

#### 1.1. Three step model

The whole photoemission process is usually described by a three step model explained in 1964 by Berglund and Spicer [15]. This model permits to simply describe the XPS process in three well separated steps:

(1) Photoionization

This is the optical excitation of the electron in the bulk, where an occupied electronic state is excited by photon absorption into an unoccupied electronic state. This step has a certain probability called the photoionization cross-section,  $\sigma$ .

(2) Travel of the excited electron

The photoelectron travels in the bulk toward the surface with or without loss of energy. The electrons which travelled to the surface without inelastic losses compose the elastic peak of the spectrum and the others which underwent inelastic collisions compose the inelastic background. This attenuation of the elastic peak with the travelled distance is quantified with the Inelastic Mean Free Path (IMFP),  $\lambda$ .

#### (3) Photoelectron emission and analysis

The photoelectron crosses the surface in losing some energy related to the surface potential and travels in the vacuum toward the analyzer. The ultra-high vacuum (~  $10^{-9}$  mbar) makes the additional loss of energy that the electron could lose during the travel through the spectrometer negligible.

The three-step model is depicted in Fig. 4.



Figure 4: Illustration of the three step model for valence band photoemission [16].

In this thesis, emphasis is put on the second step in order to show how it can be used to get information from inelastic background on layers too deeply buried for classical core level analysis.

#### **1.2.** Photoelectric effect

The photoemission process is illustrated in Fig. 5. During this process, X-rays penetrate deep (micrometers) into the bulk and are absorbed by atoms which eject electrons. Only the electrons generated close to the surface can escape into the vacuum and be detected. The others loose too much kinetic energy by interacting with the material.

The electrons reach the detector only if the energy of incident photons, hv, is higher than the electron binding energy,  $E_B$ , plus the work function of the sample  $\Phi_{sa}$ . Then the photoelectric effect can be written as:

$$hv = E_K + E_B + \Phi_{sa} \tag{1}$$

where h is Plank's constant and  $\upsilon$  the photon's frequency. The electron binding energy is referenced to the Fermi level E<sub>F</sub> defined as E<sub>F</sub> = 0 [16] as explained below.

#### 1.3. Determination of the kinetic energy

Actually, the electron binding energy  $E_B$  is measured because the Fermi level  $E_F$  of the sample is assumed to be the same as that of the spectrometer,  $E_F = 0$ , as illustrated in Fig 5. However, the measured kinetic energy  $E_K$ ' is dependent on the work function of the spectrometer  $\Phi_{sp}$ . Then, the kinetic energy can be written as:

$$E_K = E'_K + (\Phi_{sp} - \Phi_{sa}) \tag{2}$$

where  $\Phi_{sp}$  can be determined by measuring the value of the Fermi level on a reference sample as gold or silver. If the sample is an insulator, the electric connection between sample and spectrometer can be insufficient, holes stay at the sample surface and the whole XPS spectra shift towards high binding energy. This can be overcome by providing electrons with a flood gun.

Figure 5 illustrates the photoelectric phenomenon and the equations (1) and (2).



Figure 5: Illustration of the photoelectric effect with the relevant energy levels in the sample.

#### 1.4. Photoionization cross-section

The photoionization cross-section represents the probability for an electron in an atomic subshell *nl* to be excited by absorption of photon energy. This value varies with the atoms, the considered core-level electron and the incident photon energy.

In XPS experiments, it is evaluated within the electrical dipole approximation. In this case, the subshell differential photoionization cross-section for a linearly polarized photon source (as is the case for synchrotron radiation) can be approximated for the solid angle  $\Omega$  and the atomic subshell *nl* by [17-21]:

$$\frac{d\sigma_{nl}}{d\Omega} = \frac{\sigma_{nl}}{4\pi} (1 + \beta_{nl} P_2 \cos \gamma) = \frac{\sigma_{nl}}{4\pi} \left( 1 + \frac{\beta_{nl}}{2} (3\cos^2 \gamma - 1) \right)$$
(3)

where  $\beta_{nl}$  is energy dependent asymmetry parameter of the atomic subshell nl.  $P_2(\cos \gamma)$  is the second order Legendre polynomial and  $\gamma$  the angle between the photon's propagation direction and the polarization vector.

For an unpolarized photon source, the subshell differential photoionization cross-section can be approximated by:

$$\frac{d\sigma_{nl}}{d\Omega} = \frac{\sigma_{nl}}{4\pi} \left( 1 - \frac{\beta_{nl}}{2} (3\cos^2 \alpha - 1) \right) \tag{4}$$

where  $\alpha$  is the angle between the propagation directions of photons and photoelectrons.

Different atomic subshell photoionization cross-sections of the Al core-levels as a function of photon energy are displayed on Fig. 6. These atomic calculations of photoionization cross-sections are extracted from references [20] and [22].



Figure 6: Atomic subshell photoionization cross-sections of Al for core-levels 1s, 2s, 2p, 3s and 3p. Data from [20, 22].

#### 1.5. Chemical shift

From details of the peak energy-position in XPS, we can get information about the chemical composition of the sample. This core-level energy-position depends of the element from which the electrons come but also on the chemical environment of the element as illustrated on Fig. 7. This effect is called "chemical binding energy shift".

Then, the chemical shift depends on the difference of electronegativity between atoms. For an electron coming from an atom bonded to another with a higher electronegativity, respectively lower, the binding energy is decreased, respectively increased.



Figure 7: Si 2p XPS spectrum with chemical composition analysis.

The chemical binding energy shift,  $\Delta \varepsilon$ , can be described by [16]:

$$\Delta \varepsilon = kQ + qV \tag{5}$$

$$E_B = E_{\varepsilon} + \Delta \varepsilon \tag{6}$$

where k is a constant, Q is the charge of the atom, V is the potential of neighboring atoms and  $E_{\epsilon}$  is the binding energy of the free atom.

The chemical shift is used to determine the chemical environment of the detected elements. The NIST X-ray database [23] gives the chemical shift of the most frequently encountered compounds.

To measure an accurate core-level binding energy by fitting the elastic peaks, one must subtract the background of the electrons that have lost kinetic energy during their travelling in the material. This is commonly done using a Shirley background approximation [24] or more accurate methods [25] (see part IV).

#### 1.6. Line shape

The shape of the elastic peak is a convolution of the natural shape of the core-level, with a Gaussian linked to the instrumental broadening. For most of the compounds, the elastic peak shape is therefore a Lorentzian function convoluted by a Gaussian function. However, for insulators, the core-levels appear as a Gaussian function because of the widening due to charge effect. For metallic materials, the excitation of conduction electrons causes energy losses for the photoelectrons and the core-level shape presents a typical asymmetry which can be modelled with Doniach-Sunjic functions [26].

Here again, the subtraction of a background is necessary as it distorts the elastic peak shape. For metals, such a subtraction is often tricky (see below in Chapter 3).

#### 1.7. Correlated effects

After the photoionization, the system is in an excited state with a hole in an atomic level (described in Fig. 8). Intrinsic contributions are due to the sudden creation of an electric field from the core hole, which appears because of photoexcitation of the core electron. The valence electrons are excited and this decreases the photoelectron energy. These processes can be plasmons or:

- Shake-up, when the photoelectron interacts with the valence band. Fig. 8 shows that an electron from the valence band is excited to a higher energy state in the valence band. This results in a loss of kinetic energy for the photoelectron and appears as a satellite peak in the XPS spectrum.
- Shake-off, this is the same principle except that the electron from the valence band is excited to a higher energy state and the photoelectron occurs at a lower energy which contributes to the general inelastic background. These contributions appear in the 15 - 25 eV to 50 eV below the elastic peak [27, 28].
- Auger transitions. In the Auger process, an electron from a higher energy level fills a core-hole and an electron from the same level is ejected.



Figure 8: Photoionization and effects shake-up and shake-off adapted from [29].

#### 2. Photoelectron transport

During the transport through the material towards the surface, the electron can undergo elastic and inelastic collisions. Both elastic and inelastic collisions modify the number of the detected electrons.

#### 2.1. Inelastic scattering effect - Inelastic Mean Free Path

For inelastic collisions, the electrons undergo energy losses and contribute to the inelastic background. Therefore, the probed depth is limited by the distance that electrons can travel through the matter. This probed depth can be evaluated as  $3\lambda$ , where  $\lambda$  is a parameter called IMFP which can be calculated via the formula stated by Tanuma, Penn and Powell (TPP-2M) [30-32].

The IMFP depends on the material and the photon energy. With laboratory sources (Al K $\alpha$  or Mg K $\alpha$ ), the probed depth is limited,  $3\lambda \sim 10$  nm, which makes XPS a surface sensitive characterization technique. However, to probe deeper in a material, we can use synchrotron sources (Hard X-ray PhotoEmission Spectroscopy, HAXPES) since this value increases with electron energy (see Fig. 9).

Equation (7) for the calculation of the IMFP for energies between 50 eV and 30 keV is given by [30]:

$$\lambda = \frac{\alpha(T)T}{E_p^2 \left\{ \beta \left[ \ln(\gamma \alpha(T)T) \right] - \frac{C}{T} + \frac{D}{T^2} \right\}}$$
(7)

with

$$\beta = -0.10 + \frac{0.944}{\left(E_p^2 + E_g^2\right)^{0.5}} + 0.069\rho^{0.1}$$
(8)

$$\gamma = 0.101 \rho^{-0.5} \tag{9}$$

$$C = 1.97 - 0.91U \tag{10}$$

$$D = 53.4 - 20.8U \tag{11}$$

$$U = \frac{N_{\nu}\rho}{M} = \frac{E_p^2}{829.4}$$
(12)

where 
$$\alpha(T)T = \frac{m_e v^2}{2}$$
,  $\alpha(T) = \frac{1 + \frac{T}{m_e C^2}}{\left(1 + \frac{T}{m_e C^2}\right)^2}$  and  $E_p = 28.8 \left(\frac{N_v \rho}{M}\right)^{0.5}$ 

Ep is the free-electron plasmon energy (in eV),  $E_g$  is the band gap energy (in eV),  $\rho$  is the density (in g.cm<sup>-3</sup>), N<sub>v</sub> is the number of valence electrons per atom or molecule and M is the atomic or molecular weight. This can be calculated with Quases-IMFP or with NIST Electron Inelastic-Mean-Free-Path Database [33, 34]. Figure 9 taken from ref [32] shows plots of the IMFP in a large energy range for some elements.



Figure 9: Plots of electron inelastic mean free paths as a function of electron energy for Mg, Al, Si, K, Sc and Ti, from [32].

#### 2.2. Photoemission peak intensity

The intensity of the photoemission peaks follows a Beer-Lambert law, when elastic scattering is neglected [35]:

$$I(d) = I_0 e^{-\frac{a}{\lambda \sin \theta}} \tag{13}$$

where I(d) is the intensity as a function of the depth, d, where the electron is excited.  $I_0$  is the initial peak intensity,  $\lambda$  the IMFP and  $\theta$  the detection angle (see Fig. 10).



Figure 10: Origin of the elastic peak intensity [16].

As seen on Fig. 10, the intensity of the elastic peak follows an exponential decay law. 63% of the signal comes from the layer between the surface and  $d = \lambda \sin\theta$ , 23% from the layer between  $d = \lambda \sin\theta$  and  $d = 2\lambda \sin\theta$  and 9% from the layer between  $d=2\lambda \sin\theta$  and  $d=3\lambda \sin\theta$ . This also means that the vast majority of the electrons composing the elastic peak come from depth  $\leq 3\lambda$ . By studying the intensity as a function of  $\theta$ , this can be used to determine if the detected element comes from the surface or deeper in the material. This is known as the Angle resolved XPS (ARXPS) technique (see part III.2.).

#### 2.3. Features due to excitation during transport

After the photoionization, the system is in an excited state with a hole in an atomic level. Several kinds of excitations can accompany the photoionization: intrinsic and extrinsic excitations, multiple excitations and interferences between extrinsic and intrinsic excitations. These excitations result in decreasing of the measured photoelectron kinetic energy and introducing particular shapes in the spectrum. The origin of these processes are summarized in ref [36].

As already mentioned, an XPS spectrum can show features due to different processes related to photoionization: shake-up, shake-off, Auger transitions etc. The spectrum without the effects due to the photoelectrons transport through the material is called the "intrinsic spectrum". However, extrinsic contributions can also contribute to an XPS spectrum. Whereas these extrinsic contributions are due to the time- and space-varying electric field from the moving photoelectron, which also cause excitations, and thereby energy losses. These contributions are mainly plasmons from bulk and surface.

The plasmons are collective oscillations of the free electrons in a solid and at the surface due to the path of the photoemitted electron through the material. The plasmon energy is typically 10 - 20 eV and depends of the photoelectron kinetic energy and of the free-electron density. The plasmon features are separated by a determined energy because they are harmonics of a resonance mode.

#### 2.4. Elastic scattering effect – corrected photoionization cross-sections

For elastic collisions, the collisions change the direction of the photoelectrons without any kinetic energy losses. The photoionization cross-section (Eq. 4) is modified as [37]:

$$\frac{d\sigma_{nl}}{d\Omega}_{elastic} = \frac{\sigma_{nl}}{4\pi} Q_{nl} \left( 1 - \frac{\beta_{eff}}{4} (3\cos^2 \alpha - 1) \right)$$
(14)

where  $Q_{nl}$  is the parameter describing the decrease of intensity due to elastic scattering and  $\beta_{eff}$  is the effective asymmetry parameter describing the decrease of anisotropy due to elastic scattering to correct Eq. 4 for these elastic losses. Note that for single crystal samples, the main effect is a modulation of the photoemission intensity due to diffraction effects.

#### 2.5. Recoil effect

The recoil effect is defined as quasi-elastic scattering of electrons on an atomic core potential. The recoil effect results in an electron energy loss and thus in a shift of the elastic peak position and a broadening of the elastic peak. This energy loss is proportional to the incident energy and therefore, in current XPS, one can neglect the "recoil" effect but in HAXPES with high photon energy, this effect cannot be neglected. This induces an energy shift  $E_R$  caused by recoil from phonon excitations [38-41]:

$$E_R = -\frac{Q^2}{2M} \tag{15}$$

with

$$Q = q - k = \sqrt{2(\hbar\omega - E_B)} \tag{16}$$

where M is the mass of the emitter atom, q the photon momentum and k the photoelectron momentum.

#### 2.6. Photoelectron transport at high energy

Electron transport in a material, in general, can be described by application of the Chandrasekhar *H*-function [42]. The single scattering albedo,  $\omega$ , can be used to determine the importance of the elastic scatterings relative to inelastic ones [43, 44]:

$$\omega = \frac{\sigma_s}{\sigma_s + \sigma_a} = \frac{\lambda}{\lambda + \lambda_{tr}} \tag{17}$$

$$\lambda_{tr} = \frac{1}{N\sigma_{tr}} \tag{18}$$

where  $\sigma_s$  and  $\sigma_a$  are the scattering and absorption cross-section, respectively,  $\lambda_{tr}$  is the transport mean free path and N is the atomic density.

The transport cross-section can be expressed, in the case of amorphous sample, as [43]:

$$\sigma_{tr} = 2\pi \int_0^{\pi} (1 - \cos\theta) \frac{d\sigma_{el}}{d\theta} \sin\theta \, d\theta \tag{19}$$

where  $\theta$  is the elastic scattering angle,  $d\sigma_{el}/d\Omega$  is the differential elastic scattering crosssection. This can be determined by NIST software [45].

#### 2.7. Effective attenuation length

The Effective Attenuation Length (EAL) is a term used to describe the rate at which the XPS signal intensities from a substrate material or an overlayer film change as a function of the film thickness. It is also an important parameter which can be expressed for practical applications as [43]:

$$EAL = \lambda (1 - 0.735\omega) \tag{20}$$

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In the case of HAXPES, elastic scattering is negligible and  $\lambda_{tr} \rightarrow \infty$  and then  $\omega \rightarrow 0$ . This give EAL ~  $\lambda$  which simplifies the calculations since the IMFP is easily obtained with the TPP-2M formula.

#### 2.8. Effect of elastic scattering on the measured spectrum

For some cases, the electron scattering effects modify the XPS spectra intensity significantly and this can be accounted for by the introduction of a correction factor,  $CF(z,\theta)$  [36, 46] in the equation of the intensity:

$$I(z) = C. e^{\frac{-z}{\lambda \cos \theta}} CF(z, \theta)$$
(21)

where C is a constant, z the depth,  $\theta$  the angle of emission with respect to the surface normal.

A simple expression of this parameter was determined for the particular geometry found in most XPS instruments, where  $\theta \le 30^\circ$ , from extensive Monte Carlo simulations [36, 46]:

$$CF(z) \cong e^{(-0.157764\tau - 1.25132)} + e^{(-0.0562417\tau^2 + 0.00698849\tau - 0.201962)}$$
(22)

with

$$\tau = \frac{z(\lambda + \lambda_{tr})}{\lambda \lambda_{tr}}$$
(23)

#### 3. HArd X-ray PhotoElectron Spectroscopy (HAXPES)

The HAXPES technique use hard X-rays which are generated by a synchrotron. A synchrotron light is an electromagnetic radiation emitted by electrons propagating on a curved trajectory at nearly the speed of light and accelerated in a storage ring.

A synchrotron facility consists of a linear accelerator where the electrons are created and accelerated, a booster to obtain relativistic electrons, a storage ring to keep them at a stable velocity and the beamline where the emitted light is transversally deflected to be used for analyses. The advantages of synchrotron light are its intensity and brightness, due to ondulators [47], and its tunable energy.

The experimental parameters do not have the same importance in HAXPES compared to XPS. For high energy photoelectron, the IMFP significantly increases (see Fig. 9 and 11) [28], this is why we may probe much deeper in the samples with a high energy synchrotron

source. However, the photoionization cross-section decreases significantly (see Fig. 11) [19, 20, 38], this is why we need a synchrotron source. The synchrotron energy must be carefully chosen to obtain a good compromise between these two parameters in order to probe deeper and keep a good signal to noise ratio.



Figure 11: comparison of IMFP and cross-section values with soft and hard X-rays for Si.

#### 4. Instrumental aspects

Kai Siegbahn received the Nobel Prize in 1981 for the development of the actual method named Electrons Spectroscopy for Chemical Analysis (ESCA) [48], nowadays currently named PES (Photoelectron spectroscopy) or XPS.

#### 4.1. X-ray laboratory sources

A current passes through a tungsten wire which is heated by it and emits electrons by thermo-ionization. These electrons are accelerated by a potential (~ 10-20 keV) to a metallic anode. Generally, the anode is made of aluminum or magnesium and these present a better photoemission intensity compared to the first source used by K. Siegbahn which was copper. Then high energy electrons are emitted from deep core-levels and when these are filled by outer electrons, the energy released is emitted as X-rays with an energy which is particular to the metal of the target. Aluminum and Magnesium emit  $K_{\alpha 1}$  rays at 1486.6 eV and 1253.6 eV, respectively.

A metallic foil separates the X-ray creation chamber from the sample chamber, it permits to absorb the secondary and diffused electrons and ensure a protective separation of the different vacuum chambers. Most X-ray sources are also equipped with a monochromator which allows to select the  $K_{\alpha}$  ray, based on Bragg diffraction of photons and eliminates rays coming from contaminations on the electrode.

#### 4.2. Electron energy analyzer

The analyzer installed in almost all the modern XPS instruments is a 180° hemispherical analyzer. It is composed of two glass half spheres, of radius  $R_1$  and  $R_2$ , covered by gold (see Fig. 12). The potentials  $-V_1$  and  $-V_2$  are applied to the external and internal sphere, respectively. An electric field is then created which separates the electron trajectory depending of their kinetic energy compared to the typical analyzer energy,  $E_a$ , and the corresponding radius trajectory,  $R_a$ .



Figure 12: 180° hemispherical analyzer description of an ESCA instrument, from ref [29].

The resulting energy resolution,  $\Delta E$ , is [49]:

$$\Delta E = E_p \left( \frac{W}{2R_0} + \frac{\delta \alpha^2}{2} \right) \tag{24}$$

where  $E_p$  is the pass energy, W is the slit width,  $R_0$  is the mean radius and  $\delta \alpha$  is the angular spread of the incoming electron beam. Novel systems for measuring the electron kinetic energy employ Time-of-Flight (ToF) drift tubes [50].

#### 4.3. Electron optical system

All modern spectrometers are fitted with electron collection electronic-lenses which are electrostatic lenses. These lenses permit to collect the photoelectrons and transfer them to the entrance slit. It also permits to have a certain distance between the analyzer and the sample which gives a room to put tools (flood gun, sputtering source, etc). It also retards the electron and brings them at the proper energy and makes an image of the analyzed area.

#### 4.4. Electron detector

The electron detector can be a channel photomultiplier or multi channel plate associated with a CCD (Charge Couple Device) camera. The multi channel plate is used to amplify the signal of electrons and convert it into photons detectable by the CCD camera. The electrons pass through a micro-canal and are then localized by resistive anodes on a phosphorescent screen where they emit light detectable by the CCD camera.

The advantages are high speed and high spatial resolution of the analysis.

#### III. XPS depth profiling

In depth information in XPS can be obtained in two different ways: ARPXS and sputter depth profiling.

#### 1. Angle Resolved X-ray Photoelectron Spectroscopy

The Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) is a technique which enables to non-destructively determine the distribution of the elements in the material. This technique permits to retrieve the depth distribution of elements in the first  $3\lambda$  by performing XPS analysis at different angles. The intensity of components contributions in the elastic peak will varies depending of the angle because of the probed depth which will be different and permits to retrieve the depth distribution of each element (see Fig. 13).

Therefore, this technique is for surface analysis as it is limited to  $3\lambda$  and it requires quite smooth surfaces.



Figure 13: Ge/GeO<sub>2</sub> XPS analysis under two different angles. ARXPS presentation.

We will not describe further this technique because it was not used during this thesis.
### 2. XPS sputtering depth profiling

In this part, the XPS sputtering depth profiling technique is presented (see Fig. 14). This technique is used to determine the depth distribution of the elements deeply buried in a material.

The current XPS technique is surface sensitive with only the first  $3\lambda$  analyzed (~ 9 nm). HAXPES with ultra high resolution gives access to information down to 57 nm depth [51]. The proportion of information from this probing depth is too small to analyze deeply buried layers and interfaces. This is why the depth profiling is used as a destructive characterization technique to get access to in-depth information.

The depth profiling technique performed in the following chapters uses sputtering. This technique can be used under two different modes:

- Continuous mode: when the core-level spectra are recorded during the sputtering.
- Alternate mode: when there are measurement/sputtering cycles.

The continuous mode is faster to perform and limits surface contamination under low pressure since the abrasion is continuous, there is less time for surface contamination. However, the sputtering beam can induce Auger electrons which modify the spectra. The alternate mode is often preferred to continuous one under ultra high vacuum because it presents less undesirable effects due to the sputtering since it is shut-down during the analysis for the alternate mode.

The spectrum is recorded in energy windows over the core-level ranges which are preselected. This decreases the recording time but it requires to know the in-depth composition of the sample in order to record all the elements.



Figure 14: scheme of principle of XPS sputtering depth profiling.

The sputtering consists in ions from a monoatomic or cluster ion-source impinging on the sample. In this thesis, a monoatomic Ar<sup>+</sup> source was used. Ions are accelerated to a few keV onto the sample surface to remove the first atomic layers by atom-ejection.

The sputter speed is dependent of the elements composing the material. There are references of sputter speeds (often made by manufacturers) but the best way to know the sputter speed for special compounds is to measure the sputtering rate on reference sample with a known thickness. The main problems with this technique are: (i) preferential sputtering can be observed on spectra, (ii) the chemical bonds in compounds can be damaged and (iii) the analysis area can also be damaged by the ion sputtering process.

The data obtained after calibration provide the atomic concentration as a function of the sputtering time or sputtering depth if the sputter rate is known.

The sputter rate dz/dt, where z is the sputter depth, is dependent on the total sputtering yield, Y (atoms sputtered per ion) following the eq. (24) [52]:

$$\frac{dz}{dt} = \frac{jY}{Ne} \tag{25}$$

where j is the primary-ion current density, N is the atomic density and e is the elementary charge  $(1.6 \times 10^{-19} \text{ C})$ .

### IV. Inelastic background analysis, Tougaard method

This method consists in analysis of the inelastic background from a measured XPS spectrum. This is a non-destructive characterization technique as it uses the XPS technique. This method enables by fitting the inelastic background to remove it from the measured spectrum in order to obtain the so-called intrinsic spectrum and improve the core-level analysis. However, by modeling the inelastic background, we can also get information about the in-depth distribution of the element.

The electrons composing the inelastic background underwent energy losses and those originate from deeper in the material than the ones composing the elastic peak which originate closer to the surface. From a detailed quantitative analysis of these phenomena, the inelastic background analysis permits to get information from deeper in a material compared to current XPS analysis. This estimated depth, around  $3\lambda$  for ARXPS, is around  $8\lambda$  [36, 53] or even higher in some cases [54] for inelastic background analysis which is more than two times deeper than for the core-level analysis.

### 1. Analysis requirements

The XPS spectrum for inelastic background analysis does not require to be a highly resolved spectrum. This makes the measurement slightly faster than the one for core-level spectra where the energy range of measurement is drastically smaller. The analysis is easier to perform when the inelastic background part below the elemental elastic-peak is not affected by peaks of other elements. This total region also has to be around 90 eV large for a reliable analysis with around 30 eV before the elastic-peak without perturbation by other peaks to get a well defined subtraction of the background line (see below).

### 2. Principle

The inelastic background is made of electrons which underwent energy-losses during their path through the sample. The shape of the inelastic background is then dependent on the energy-losses of the electrons and is subject to changes with material nature and structures [55-58]. A good example was made with 4 different depth-distributions of copper in a gold matrix [59] (see Fig.15). Note that the peaks intensities have not been normalized. The analyzed core-level is the Cu 2p, this shows that the peak intensity alone is not useful for quantitative analysis of inhomogeneous samples. This is so because these widely different

structures give the same elastic peak intensity. However, the background of inelastically scattered electrons is very different. It is the analysis of these that is used in this technique to determine the depth distribution.



Figure 15: Four widely different surface structures of copper in gold that give identical peak intensities [59].

### 3. Two step model

In the two-step model compared to the three-step model (Chapter 1 part II.1.1.), the third step is neglected. During the third step, the electron escapes through the surface and travels in the vacuum to the analyzer. In this model, the number of electrons detected per second, per unit energy and solid angle  $\Omega$  is J(E, $\Omega$ ) [60]:

$$J(E,\Omega) = \int dE_0 F(E_0,\Omega) \int f(z) G\left(E_0, \frac{z}{\cos\theta}; E\right) dz$$
(26)

where  $F(E_0,\Omega)d^2\Omega dE_0$  is the flux of electrons excited from an atom in an energy interval  $dE_0$  at  $E_0$  into the solid angle element  $d\Omega$ .  $G(E_0,R;E)dE$  is the probability that an electron with initial energy  $E_0$  has an energy between E and E+dE after having traveled the path length R. f(z) is the depth distribution profile from the surface as a function of the depth z. Landau showed that G can be expressed as:

$$G(E_0, R; E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{is(E_0 - E)} e^{-R\sum(s)} ds$$
(27)

$$\sum(s) = \frac{1}{\lambda} - \int_0^\infty K(T) e^{-isT} dT$$
(28)

with

where s is an integration variable without physical significance, K(T) is the inelastic crosssection with T the energy loss.

A solution of the eq. (26) give the equation of the intrinsic XPS spectrum  $F(E,\Omega)$  [61]:

$$F(E,\Omega) = \frac{1}{P_1} \left[ J(E,\Omega) - \frac{1}{2\pi} \int dE' J(E',\Omega) \int ds e^{-is(E-E')} \left( 1 - \frac{P_1}{P(s)} \right) \right]$$
(29)

with  $P(s) = \int f(z)e^{\left(-\frac{z}{\cos\theta}\right)\Sigma(s)}dz$  and  $P_1 = \int_0^\infty f(z)e^{-\frac{z}{\lambda\cos\theta}}dz$  (30),(31)

### 4. Inelastic scattering cross-section and IMFP

The IMFP and the inelastic scattering cross-section, K(T), appear in the expression for  $\Sigma(s)$ , eq. (27). Therefore, F(E, $\Omega$ ) and J(E, $\Omega$ ) depend on the IMFP and the inelastic scattering cross-section. The IMFP is calculated with the TPP-2M formula whereas K(T) may be calculated with the dielectric function of the solid [62]. An alternative to the calculation of K(T) is the determination of  $\lambda(E)K(E,T)$  by analysis of REELS [62, 63].

For fast and easy calculation of the energy-loss probability for electrons, the concept of Universal cross-section was introduced with the observation that  $\lambda(E)K(E,T)$  depends strongly on T, weakly on E and is not very specific of the material [64]:

$$\lambda(E)K(E,T) = \frac{BT}{(C+T^2)^2}$$
(32)

with C=1643 eV<sup>2</sup> and B $\approx$ 3000 eV<sup>2</sup>. The universal cross-section can be applied for most metals, their oxides and alloys. The use of the universal cross-section is often preferable to the REELS determination where the surface effects are overestimated due to double cross of the surface by electrons during REELS analysis unlike XPS.

For some materials like AI or Si which present a narrow plasmon structure, we have to use a three-parameter universal cross-section [25]:

$$\lambda(E)K(E,T) = \frac{BT}{(C-T^2)^2 + DT^2}$$
(33)

The parameters B, C and D have been determined for different classes of materials (see Fig. 16)



Figure 16: cross-sections for different classes of materials from [25].

### 5. In-depth profiles implemented in Quases-Tougaard software

The inelastic background analysis can be performed with the Quases-Tougaard software [34]. The Quases-Analyze software creates the modeled inelastic background (Fig. 17, pink curve) adjusted to fit the measured spectrum,  $J(E,\Omega)$  (black curve) to create the intrinsic spectrum,  $F(E,\Omega)$  (green curve).

To create the modeled inelastic background, the software needs several input parameters:

- IMFP calculated from TPP-2M formula
- Emission angle of the XPS analysis
- Inelastic scattering cross-section selected in the library provided with the software or created with B, C and D parameters (eq. 29)
- In-depth profile type selected between buried layer, islands (passive or active substrate), exponential profile or several buried layers
- Depth distribution given by parameters



Figure 17: Print screen of the Quases-Analyze software, analysis of a Si 1s spectrum.

In-depth profiles implemented in the Quases-Analyze software are shown in Fig. 18. In the following analyses, only two kinds of the implemented profiles were used:

### 5.1. Buried layer profile

This profile is described as (b) on Fig. 18. When atoms from an element A are localized as a buried layer between the depth  $z_0$  and  $z_0 + \Delta z$ , the concentration profile of element A can be written as:

$$f_A(z) = C_A \tag{34}$$

then [61], 
$$P_1 = C_A \lambda \cos \theta \ e^{-\frac{z_0}{\lambda \cos \theta}} \left[ 1 - e^{-\frac{\Delta z}{\lambda \cos \theta}} \right]$$
(35)

and

$$P(s) = C_A \frac{\cos\theta}{\Sigma(s)} e^{-\frac{z_0 \Sigma(s)}{\cos\theta}} \left[ 1 - e^{-\frac{\Delta z \Sigma(s)}{\cos\theta}} \right]$$
(36)

### 5.2. Several buried layer profile

This profile is described as (g) on Fig. 18. When N atoms are localized at depth  $z_0$ , the distribution function can be expressed as:

$$f(z) = N\delta(z - z_0) \tag{37}$$

then [61], 
$$P_1 = N e^{\frac{-z_0}{\lambda \cos \theta}}$$
(38)

$$P(s) = Ne^{\frac{-z_0 \Sigma(s)}{\cos \theta}}$$
(39)



Figure 18: In-depth profiles implemented in the Quases-Analyze software from [36].

It has to be noted that beside Quases-Analyze, another software exists which is called Quases-Generate [34]. This software enables to create spectra from references of pure materials. This is the inversed approach to the one used in Quases-Analyze. Instead of extracting the intrinsic spectrum,  $F(E,\Omega)$  from the measured one,  $J(E,\Omega)$ , by subtracting the extrinsic contributions modeled by the software; the modeled extrinsic contributions are

and

added to the intrinsic spectrum,  $F(E,\Omega)$  obtained from a bulk pure material to create the theoretical final spectrum  $J(E,\Omega)$  to be compared to the measured one.

The Tougaard method combined with HAXPES provides very useful information about deeply buried elements as demonstrated in ref [2-4]. It appears as a solution to the technological need for non-destructive in-depth characterization.

## V. XPS microscopy

### 1. Conventional XPS imaging

There are several conventional methods to perform a laterally-resolved XPS measurement developed and optimized in the last 35 years.

There are two approaches to perform XPS imaging (described in Fig. 19) [65, 66]:

- Figure 19(a) shows the scanning XPS imaging method which consists of focusing the X-ray beam into a small micro-spot and scan the surface of a sample while collecting the photoemission signal with a position-sensitive detector.
- Figure 19(b) shows the parallel XPS imaging method which uses an electron energy analyzer with the capability to simultaneously image and energy-filter the photoelectrons. The X-ray beam is larege (several 100 µm to mm size) and an electron optical column projects the image at the entrance of the electron energy analyzer.



Figure 19: Schematic description of the existing imaging methods with hemispherical (HSA) and spherical mirror (SMA) analyzers. EnL: entrance lens; ExL: exit lens; CL: coupling lens. Extracted from [65].

Conventional XPS imaging instruments have a lateral resolution around 10  $\mu$ m [67, 68] due to the limitations arising from the spot-size or the aberrations of the entrance lens. The principle of Fig. 19(c) is described below.

### 2. XPEEM using NanoESCA

X-ray PhotoEmission Electron Microscopy (XPEEM) is the most advanced XPS microscopic method as it enables the highest lateral resolution and uses the method of Fig. 19(c). The NanoESCA instrument used in this work is manufactured by Scienta Omicron. It was built to

overcome the lateral resolution limits of conventional methods explained previously (see Fig. 19 (a) and (b)).

The NanoESCA uses an electrostatic PEEM column for full-field imaging and a double hemispherical analyzer as imaging spectrometer. The second hemisphere compensates spherical aberrations occurring in the first one during image transmission.

### 2.1. Excitation sources

The photons impinge the sample at a  $65^{\circ}$ -angle with respect to the sample normal. The instrument has available several sources (UV photons, VUV photons, laboratory or synchrotron X-rays). The X-rays spot-size can be adjusted between 30 and 200  $\mu$ m. These sources permit to perform complementary analyses.

### 2.2. Details about the NanoESCA instrument

The details of the NanoECSA instrument are explained in Fig. 20. The NanoESCA allows three different operating modes (Fig. 20(a)):

- Mode 1: Direct, non-energy filtered PEEM imaging: electrons are transmitted through the PEEM column only, the signal arises mostly from secondary electrons.
- Mode 2: Area-selected XPS spectroscopy (micro-spectroscopy); here, a spectrum is recorded using the electrons emitted from an area on the sample surface defined by the field of view of the PEEM or the use of a field (iris) aperture within the field of view.
- Mode 3: Energy -filtered imaging (spectro-microscopy); in this case the PEEM image is transmitted through both hemispheres.

An objective lens working with asymmetrical voltages permits to extract at high potential and focus the photoelectrons and then decelerate them at the voltage of the PEEM column. This objective lens comes with selectable contrast apertures of different sizes located in the back-focal plane of the lens and a stigmator to avoid effect of axial astigmatism. The contrast aperture controls the instrumental lateral resolution.

A field (iris) aperture located in the first intermediate image plane permits to adjust the analysis area within the field of view in Mode 2.

Projection lenses localized before the entrance of the imaging double energy analyzer retard and project the electrons into the analyzer. These lenses also permit to magnify it onto the image intensifier in direct non-energy filtered PEEM mode.

In Mode 2, XPS micro-spectra can be measured with a channeltron detector placed after the first analyzer hemisphere.

A second set of projection lenses are located after the second hemisphere to obtain the final magnification in energy filtered imaging mode for a final field of view between 5 and 650  $\mu$ m. A description of the system is presented on Fig. 20.



Figure 20: (top Left) Scheme of the XPEEM optical system. (top Right) Scheme of an imaging double energy analyzer, from [65]. (bottom) Instrument, from [66].

### 3. XPEEM spectromicroscopy

With the energy filtered imaging mode, a stack of images can be recorded which contains at each pixel microscopic and spectroscopic information (One image per energy-step). This permits to obtain a map of the surface elemental distribution and chemical composition. The experimental lateral resolution obtained in this mode with core-level electrons was shown to be within the micron-range in routine analyses [69] and close to the instrumental resolution (<  $0.5 \mu m$ ) in the case of optimized sample [70].

In this work, we show in Chapter 5 that it possible to extend the capabilities of XPEEM by performing spectromicroscopic experiments with inelastically-scattered photoelectrons, using Hard X-rays and a dedicated instrument [71].

# VI. Previous improvements of the inelastic background analysis by HAXPES

This part presents the advances made about the analysis of the inelastic background prior to the start of this thesis work.

Before these last improvements, the inelastic background analysis was mainly used to nondestructively retrieve the structure or the amount of substance from an X-ray Photoelectron Spectroscopy (XPS) analysis using conventional Mg or Al K<sub> $\alpha$ </sub> X-ray sources [36, 53, 59, 72-74].

With the advent of device technologies at the sub-micron down to nanometric scale and the constant need for device optimization, there is a pressing need for non-destructive techniques able to provide information about deeply buried layers and interfaces. This is the reason why the XPS inelastic background analysis appeared as a solution since it is a non-destructive technique whereas it provides information more than twice deeper than ARXPS analysis.

### 1. Use of high kinetic energy XPS spectra for inelastic background analysis

As discussed previously, the main parameter limiting the probing depth in photoelectron spectroscopy is the Inelastic Mean Free Path (IMFP). Note that this value increases whereas the subshell photoionization cross-section decreases with increasing photoelectron kinetic energy.

The use of synchrotron energy to increase the probing depth appeared as a good solution to get more from the method [3]. As explained in this paper, the photoelectron energy must be carefully chosen to increase the probing depth without losing too much of the XPS signal intensity (see Fig. 21). Then, a good compromise between the IMFP and the photoionization cross-section has to be found.

Figure 21 from ref [3] illustrates this balance. XPS spectra from La buried at 56.5 nm were recorded with 12, 15 and 18 keV photons. The La  $2p_{3/2}$  spectrum is significantly better with 15 keV photons, this is because the IMFP is too small with 12 keV photons and the photoionization cross-section is too small with 18 keV photons. This perfectly illustrates the need to find a good compromise between the IMFP and the photoionization cross-section.

It has to be noted that the spectrum is very noisy and presents an energy-resolution too low for a core-level analysis but sufficient for an inelastic background analysis.



Figure 21: Left panel: structure of the sample with a 50-nm overlayer before annealing. Right panel: La 2p hard X-ray photoelectron spectroscopy spectra at different photon energies. The no-loss peak is marked by a line for clarity, from [3].

### 2. Accuracy of inelastic background analysis

### 2.1. Effect of variation of overlayer and buried-layer thicknesses on the accuracy

The study of gradual diffusion of elements during annealing has been done with XPS inelastic background analysis for many years [75]. With HAXPES, this was first done on annealed transistors with a LaO/TiN/Si stack [3]. This work shows that the thinner the overlayer is the more accurate are the results obtained on the buried-layer thickness (see Fig. 22 and Table 1). However, as shown in table 1, the results on buried-layer depths are less accurate for thin overlayers than for thicker ones.

The analysis was also tested with a thicker buried-layer (1 nm instead of 0.4 nm for La). The results show that the determined thickness of the buried-layer is slightly closer to the expected value than for a thinner buried layer (results give a 2.2 nm thickness for the 1 nm-thick layer and a 1 nm thickness for a 0.4 nm-thick layer). Note that the determined depth distribution is even more overestimated than the buried-layer thickness.

In addition, in this article, it was demonstrated that even a measured spectrum with poor signal to noise ratio can still provide information with the inelastic background analysis as shown on Fig. 22 (b).

This is in good agreement with the expected depth. However, for overlayer-thicknesses smaller than 37 nm (see Table 1) the deviation is considerably larger. As explained in this article, this could be due to the chosen Si inelastic scattering cross-section and to the chosen IMFP (in Si) which gives a reasonable description for a large Si overlayer but less accurate

description for thin layers. This can be explained by the TiN layer contribution which becomes more important with a thin Si overlayer and which is not taken into account in these input parameters.

In this thesis, it is found that the input parameters can be refined and that one can in this way obtain more accurate and reliable results.



Figure 22: La 2p<sub>3/2</sub> spectra measured at 10° from surface normal for hv = 15 keV as well as the modeled and their difference (called subtracted spectrum. The 50-nm sample (a) before annealing and (b) after annealing; 30-nm sample before annealing (c) and after annealing (d). The detailed sample structure is also shown for both samples (50-nm sample on the left panel and 30 nm on the right panel) and the annealing effect is illustrated with red arrows, from [3].

La 2p <sub>3/2</sub>		Top interface (nm)		Bottom interface (nm)		Thickness	
		Expected	Modelled	Expected	Modelled	Expected	Modelled
50-nm sample	As deposited	56.5	57.3 ± 1.6	56.9	$61.8 \pm 2.5$	0.4	4.5
	Annealed		$32 \pm 1.0$		$71 \pm 2.5$		
30-nm sample	As deposited	36.5	$41.0 \pm 1.25$	36.9	$43.0 \pm 2.5$	0.4	2
	Annealed		$27.5 \pm 0.4$		$71 \pm 2.5$		
20-nm-thin La	As deposited	26.5	$35.0 \pm 0.5$	26.9	$36 \pm 1.5$	0.4	1
20-nm-thick La	As deposited	26.5	$43.2 \pm 1$	27.5	$45.4 \pm 0.8$	1.0	2.2

Summary of the background analysis results at hv = 15 keV for the 1-ML-thick La layer (50-, 30- and 20-nm-thin La sample) and 1.0-nm-thick La layer (20-nm-thick La).

Table 1: Results of analyses of High-K LaO/TiN/Si transistors of ref [3]

### 2.2. Effect of variation of input inelastic scattering cross-section on the accuracy

A similar analysis with high photon energy was made on these High-K samples but with varying the input inelastic scattering cross-section. Figure 23 shows a comparison of inelastic background analysis for La  $2p_{3/2}$  with the universal cross-section, the Si cross-section implemented in Quases and the Si cross-section calculated from REELS analyses at 10 keV [2]. An effective IMFP was also chosen as a weighted average of individual IMFP of each layer instead of the IMFP for Si. In this article, it was proven that the inelastic scattering

cross-section has a critical influence on the inelastic background analysis and varies with electron energy and class of materials. This paper shows that the cross-section determined from analysis of a REELS spectrum recorded at 10 keV [62] provides a better fit of the inelastic background than the 2 parameters cross-section and even better than the 3 parameter cross-section [25] (see Fig. 23).

This analysis was also shown to be better for a thicker overlayer of Si since the influence of the TiN-overlayer is not taken into account when using a Si cross-section. Thus, the thicker the Si overlayer is the smaller is the relative influence of the TiN layer in the electron path.



Figure 23: HAXPES spectra of the 30 nm sample measured at 15 keV (black). The calculated background for a 2 nm-thick La layer buried at 41 nm is plotted in red, using: (a) A two parameter universal inelastic cross section; (b) a three parameter cross section for silicon; and (c) a silicon cross section derived from REELS measurement at 10 keV. Blue curves represent the intrinsic HAXPES spectrum after background subtraction, from [2].

This study on the influence of the cross-section was brought to another level with an analysis on HEMTs (see Chapter 1 part I.1.) with Ti/Al contact. When used with HAXPES, the probing depth is very large and the composition of the sample over the probing depth can vary substantially. If the materials, composing the sample, have very different inelastic scattering properties, it is not a good approximation to use the properties of either material. Therefore, it was considered in [4] to use an effective cross-section, taken as a mixture of individual cross-sections. A core-level analysis was used to determine the elements present in the stack and so thereby, the individual cross-sections that have to be taken into account.

It was found that the uncertainty on the top interface was 5% and the uncertainty on the bottom interface was around 15-20% when using the effective cross-section 0.5Ti + 0.5Al.

Figure 24 shows the inelastic background modeling for different effective cross-sections compared to the universal cross-section for a Ti 1s spectrum from a Ti layer buried under an Al overlayer.



Figure 24: Ti 1s HAXPES background analysis of the as-received stack using different inelastic scattering cross-sections: (a) Universal; (b) a blend of half Universal and AI scatteringcross-sections; (c) a blend of half Ti and AI scattering cross-sections; (d) a blend of 70% Universal and 30% AI scattering cross-sections; (e) a blend of 30% Universal and 70% AI scattering cross-sections, from [4].

This demonstrates that, at the start of this PhD project, the inelastic background analysis combined with HAXPES appeared to be a powerful and non-destructive method to analyze deeply buried interfaces. Then, it was a good characterization candidate for analysis of HEMTs.

However, in the light of the above (see for example Fig. 24), it appeared that the input parameters (IMFP and inelastic scattering cross-section) were not well determined for such analyses.

The purposes of this project were then to increase the accuracy of the method and find a rule for the determination of the input parameters for the inelastic background analysis on such complex stacks. This was investigated to make the analysis faster and more accurate to apply for a large variety of samples and for non-experts. Also, it appeared that it was of high interest to start extending this technique to imaging as most of surfaces analyzed nowadays are intrinsically heterogeneous.

## Chapter 2: Use of a reference spectrum

This chapter presents the accuracy of inelastic background analysis using a reference spectrum recorded from bulk material. This investigation was done on different samples with varying thicknesses and determines the reliability of the results compared to TEM measurements.

This is presented in a published article [76]:

C. Zborowski, O. Renault, A. Torres, Y. Yamashita, G. Grenet, and S. Tougaard, Determination of the input parameters for inelastic background analysis combined with HAXPES using a reference sample. *Applied Surface Science* **432**, p. 60-70 (2018).

# Determination of the input parameters for inelastic background analysis combined with HAXPES using a reference sample

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### Abstract

The recent progress in HAXPES combined with Inelastic Background Analysis makes this method a powerful, non-destructive solution to get quantitative information on deeply buried layers and interfaces at depths up to 70 nm. However, we recently highlighted the need for carefully choosing the scattering cross-sections in order to accurately describe the transport of photoelectrons through a complex overlayer structure with layers presenting very different scattering properties. It is found that the transport through such thick bi-layer structures can be described with an effective inelastic scattering cross-section in the form of a weighted sum of individual cross-sections of the pure layers. In this study, we have experimentally investigated this by analyzing AI/Ta/AIGaN stacks on a GaN substrate. We present a refined analytical method, based on the use of a reference spectrum, for determining the required input parameters, i.e. the inelastic mean free path and the effective inelastic scattering crosssection. The use of a reference sample gives extra constraints which make the analysis faster to converge towards a more accurate result. Based on comparisons with TEM, the improved method provides results determined with an accuracy typically better than 95% instead of around 10% without reference. The case of much thicker overlayers up to 66 nm is also discussed, notably in terms of accounting for elastic scattering in the analysis.

**Keywords:** Inelastic Background Analysis; HEMTs; Buried interface; Hard X-ray photoemission; Inelastic scattering cross-section

### I. Introduction

The rapid advance of new technologies, notably in the field of nano-electronics and energy harvesting, has intensified the need for non-destructive and fast in-depth characterization of critical buried interfaces. The device structures often consist in stacked layers of several 10 nm thickness for the top electrode covering the active part. A complete removal of the top electrode prior to surface-sensitive measurements would be harmful to the interface which is prone to subtle changes upon variations of the processing conditions. Rather, it is desirable to characterize the device structure in a state closely related to the real structure where most of the top electrode has been preserved. A typical case is the High Electron Mobility Transistors (HEMTs) [77] used in III-nitrides power devices, where a 2D electron gas is formed [78] at the interface between the AlGaN channel and the GaN substrate. Careful control is needed during the formation of the ohmic contact with the source/drain part of the device [79], highlighting the need for efficient analytical methods. The recent advances in inelastic background analysis of photoemission spectra concerned its applicability in HAXPES [2-4, 80]; it was shown that inelastic background analysis performed on multi-layer stacks could accurately determine depth distributions of deeply buried layers up to at least 50 nm with an uncertainty of 14% for the bottom interface depth and 7% for the top interface depth [4]. The energy distribution of inelastically scattered HAXPES photoelectrons [36, 81] provides information from deeply buried layers. These electrons originate from depths as high as 8 times the inelastic mean-free path (IMFP) [81] and constitute the so-called inelastic background to lower kinetic energy of the core-level photoemission peak. This combination proved its efficiency on different samples and for different thicknesses and compounds such as Si, Al, Ti and related alloys. The method requires essentially only two input parameters, namely the inelastic mean free path which can be taken from the TPP-2M formula [82] and the inelastic scattering cross-section [25]. These parameters are easy to determine in the case of single-layer samples but it was recently shown [4] that it may become more difficult when the sample consists of several overlayers having widely different scattering properties. In a recent work on HEMTs devices with Ti/AI source/drain contacts [4], the effective crosssection was determined by a trial-and-error method and the optimized model is then difficult to decide in a quantitative way. Here, we present a refined analytical method based on the use of a reference spectrum, for determining the required input parameters, i.e. the inelastic mean free path and the effective inelastic scattering cross-section. The use of a reference sample makes the analysis faster to converge towards a more accurate result because this gives additional constraints in the fitting procedure because the intensity and the shape of the corrected peak must fit to the reference on an absolute scale. The analysis provides results determined with an accuracy of typically 95% for the bottom interface depth and even

less for the top interface depth on the AI, Ta and Ga depth distributions up to 70 nm below the surface.

### II. Experimental

### Samples

The samples considered for this study are High Electron Mobility Transistors (HEMTs) based on an  $AI_{0.25}Ga_{0.75}N(22 \text{ nm})/GaN(1 \mu m)$  substrate epitaxially grown by Metal Oxide Chemical Vapor Deposition (MOCVD) on a Si(111) wafer. Metallic layers of Ta/Al are then deposited by Electron Beam Physical Vapor Deposition (EBPVD) to form the contact electrode.

In this study, we investigated different thicknesses of AI and Ta layers as seen in Fig. 25 and we performed TEM analyses on 4 different areas of each sample to precisely measure the thickness of each layer. We analyzed 4 different samples:

Al( $20 \pm 1.5 \text{ nm}$ )/Ta( $5 \pm 0.4 \text{ nm}$ )/AlGaN( $22 \pm 0.5 \text{ nm}$ ), hereafter denoted as Ta5/Al20 Al( $21 \pm 1.5 \text{ nm}$ )/Ta( $12 \pm 0.5 \text{ nm}$ )/AlGaN( $25 \pm 0.5 \text{ nm}$ ), hereafter denoted as Ta12/Al21 Al( $40 \pm 3 \text{ nm}$ )/Ta( $5 \pm 0.5 \text{ nm}$ )/AlGaN( $22 \pm 0.5 \text{ nm}$ ), hereafter denoted as Ta5/Al40 Al( $66 \pm 3 \text{ nm}$ )/Ta( $5 \text{ nm} \pm 0.5 \text{ nm}$ ) /AlGaN( $22 \pm 0.5 \text{ nm}$ ), hereafter denoted as Ta5/Al66. The industrial HEMT device structure consists of a 25 nm thick Ta layer below a 100 nm thick Al layer. The present samples are however still much more representative of real devices than the structures obtained after removal of most of the top electrode, as would be required for a traditional XPS analysis.

The reference Ta sample is a thick Ta layer (50 nm) deposited by the same technique as for the studied samples and on the same substrate AlGaN/GaN.



Figure 25: Structure of the samples and TEM determination of the layer thicknesses.

### HAXPES measurements

HAXPES spectra were recorded at the BL15XU beamline of the Spring-8 synchrotron, without any particular surface preparation. The photon energy was 7935.7 eV, according to the calibration performed on the Au Fermi level. The experimental geometry was set with x-rays impinging the sample at 45° and photoelectrons being detected at 7° from the surface normal. The spectra were recorded over an extended energy range suitable for inelastic background analysis. These extended spectra including energy loss features were taken for Ta  $3p_{3/2}$  (5744 eV kinetic energy), Al 1s (6376.7 eV kinetic energy) and Ga 2p, 2s (6818.7, 6520.7 eV kinetic energy) core-levels, over 250, 200 and 350 eV to lower kinetic energy, respectively.

The inelastic mean free path (IMFP) is chosen as an average over the value for each layer calculated with the TPP-2M formula [82], with a weight averaging corresponding to the atomic concentration used in the applied cross-section (see Table 2). The probing depth of the method is ~8 IMFP [81] and the quite high IMFP in aluminum (8.9 nm for Ta 3p<sub>3/2</sub>, 9.7 nm for Al1s and 10.2 nm for Ga 2p, 2sphotoelectrons) ensures that we probe the complete stack and reach the critical AIGaN/GaN interface. The universal two-parameter cross-section [25] gives a good description of energy loss processes in transition metals and their oxides but not for materials with a single sharp plasmon structure [25, 81]. The universal cross-section is shown in Fig. 26 together with the inelastic scattering cross-section of Al [25] and Ta where it is clear that the Al cross-section Electron Energy-Loss Spectra (REELS) from Ta at 2 keV using the procedure in ref [34, 63]. When the electrons pass through layers consisting of Ta and Al, the Al and Ta cross-sections will give a better description of the energy loss processes on the entire path than the universal cross-section. In this analysis we have therefore used a blend of two of these cross-sections depending on the structure analyzed.



Figure 26: Cross-sections of aluminum, tantalum and the universal cross-section.

Table 2 presents the IMFP applied for the different cross-sections used in the following analyses. The effective cross-sections and the corresponding IMFPs were calculated with a varying relative weight A of Ta and B of Al as:

$$K_{eff} = \frac{A}{100} \times K_{Ta} + \frac{B}{100} \times K_{Al} \tag{40}$$

$$IMFP_{eff} = \frac{A}{100} \times IMFP_{Ta} + \frac{B}{100} \times IMFP_{Al}$$
(41)

Where  $K_{\text{eff}}$  is the effective cross-section and  $\text{IMFP}_{\text{eff}}$  the effective IMFP.

Hereafter, the cross-sections will be denoted  $K_{A,B}$ .

Ta 3p <sub>3/2</sub> at 5744 eV					
A	В	IMFP <sub>eff</sub>			
100	0	5.8 nm			
0	100	8.9 nm			
50	50	7.3 nm			
33	67	7.8 nm			
20	80	8.2 nm			
40	60	7.6 nm			
	Ga 2p at 6818 eV				
А	В	<b>IMFP</b> <sub>eff</sub>			
100	0	6.6 nm			
0	100	10.2 nm			
5 nm = > 20	21 nm => 80	9.5 nm			
12 nm = > 52	21 nm => 48	8.9 nm			
	Al 1s 6376 eV				
A	В	IMFP <sub>eff</sub>			
0	100	9.7 nm			

Table 2: IMFP considered in the analysis depending on the associated cross-section.

### III. Results

### 1. Generating the reference spectrum

The inelastic background analysis needs two input parameters which are the IMFP,  $\lambda$ , and the inelastic scattering cross-section, K(T), as described in equations (42), (43) and (44) [83].

$$F(E,\Omega) = \frac{1}{2\pi} \int J(E',\Omega) dE' \int \frac{e^{-is(E-E')}}{P(s)} ds$$
(42)

with

$$\boldsymbol{P}(\boldsymbol{s}) = \int \boldsymbol{f}(\boldsymbol{z}) \boldsymbol{e}^{\left(\frac{-\boldsymbol{z}}{\cos\theta}\right) \sum (\boldsymbol{s})} d\boldsymbol{z}$$
(43)

and 
$$\sum(s) = \frac{1}{\lambda(E)} - \int_0^\infty K(T) e^{-isT} dT$$
(44)

Here,  $F(E,\Omega)$  is the primary excited spectrum, also called the atomic excitation function.  $J(E_0, \Omega)$  is the measured spectrum, T = E'-E is the energy loss,  $z/\cos\theta$  is the travelled distance, f(z) is the concentration distribution as a function of the depth z and P(s) and s are mathematical quantities without physical significance. For the numerical evaluation of eqs. (42)-(44) we have used the QUASES-Tougaard software package [34].

As we recently demonstrated [4], the effective inelastic cross-section can be described as a blend of individual inelastic cross-sections (see Fig. 26) for each individual layer composing the overlayer structure. In this study, we investigate a refined method with the objective to determine in a more reliable manner (compared to previous studies [2-4, 80]) the best effective inelastic cross-section and IMFP.

Here, a reference spectrum is used. This spectrum represents the intrinsic Ta spectrum obtained by the subtraction of the modeled inelastic background from the experimental Ta spectrum of a thick (50 nm) Ta layer. For Ta, the two-parameter universal cross-section is a good approximation to model the inelastic background and the depth distribution is known to be constant for all relevant depths. We used the universal cross-section for the creation of the reference because the Ta and the universal cross-sections are really closes (see fig. 26). Both give a similar result but the universal one is the most obvious choice when it works as well as in this case. We use as IMFP the value in Ta, 5.8 nm (Table 2). Then both the depth distribution as well as all input parameters are known and we obtain the Ta  $3p_{3/2}$  reference spectrum, F(E), which is shown in green in Fig. 27(a). Note that the fit to the background is perfect over the full energy range without using any adjustable parameters.

This reference F(E) spectrum is obtained with the same experimental settings as the F(E) from the samples. Therefore the analysis with eq. (42) of the experimental spectra must result in the same F(E), both with respect to shape and intensity. In the analysis of the sample, the input parameters in the analysis are the IMFP, the cross-section and the concentration depth profile (for the Ta this is the top and the bottom interface depth for the layer).

Fig. 27(b) shows, in black, the best F(E) obtained with the QUASES-Tougaard package [14] for the Ta spectrum of the Ta5/Al20 sample. The blue vertical lines on the right of the graph represent the range of the spectrum where the areas of the subtracted spectrum and the reference are calculated to obtain a ratio which is denoted as the scale factor. The scale factor represents the elemental concentration by comparison to the reference and must therefore be 1.00 in the case of a pure Ta buried layer. With the use of a reference spectrum, there are thus two additional criteria for the fitting procedure: the scale factor and the background shape which should be the same as for the reference F(E) of Fig. 27(a). These two additional criteria to determine the goodness of the fit make the analysis faster and more reliable since it decreases the number of possible solutions. Instead of comparing all possible depth distributions and find the resulting F(E) giving the best fit in the background region, here with the reference, we select just the depth distributions providing a 1.00 scale factor and determine the best result by additionally minimizing the area difference between the reference F(E) and the resulting F(E) on an absolute scale in a wide energy loss range below the peak.



Figure 27: (a) Analysis of the Ta reference spectrum and creation of the reference F(E), (b) Analysis of the Ta 3p<sub>3/2</sub> spectrum on the Ta5/Al20 sample, the blue lines represent the region where the scale factor is calculated.

In the following, we discuss how this best fit is obtained and how the method is implemented on the HAXPES spectra of the samples considered here. The data are presented in the form of Fig. 27(b) where the subtracted spectrum of the considered sample is compared with the reference Ta spectrum on an absolute scale.

### 2. Analysis procedure for the Ta5/Al20 sample

### a. Ta analysis

The analysis was done without taking into account the results of the TEM measurement before we obtain the final result of the depth distribution. Firstly, as shown in Fig. 28(a), an analysis was performed with the universal cross-section for different depth distributions. In all cases, the top and bottom interface depths of the Ta layer were adjusted to obtain  $F(E) \sim 0$  far from the peak and a scale factor of 1.00 calculated over the range of the main peak.

The resulting shape of the F(E) function is in all cases very different from the reference in the 3-100 eV energy loss region. If we consider that the area of the resulting subtracted spectrum over the 10-140 eV energy range should be the same as for the reference F(E), then the best fit corresponds to the 22 to 26.1 nm depth distribution (blue curve) since this has approximately equal positive and negative deviations from the reference F(E).

Figs. 28(b) and 28(c) show the subtracted Ta  $3p_{3/2}$  F(E) spectra, obtained with the AI and Ta inelastic cross-sections, respectively. The applied IMFP is chosen to be that of bulk aluminum (see table 1) because we know from a survey spectrum that we have a huge amount of aluminum in this sample. For each selected top interface depth, the bottom interface depth is varied until the area over the peak is the same as for the reference (scale factor =1.00) and F(E) ~ 0 far below the peak. From Fig. 28 it is clear that all the fits are not satisfactory, however, it is noted that the distributions found with each cross-section are very similar. The best modelings are from 22 to 26.1 nm for the universal cross-section, from 24 to 29.3 nm for the Ta one and from 22 to 25.7 nm for the AI cross-section. We note that the variation of the bottom depth of the layer is about 3.6 nm which is around 13% of the total depth. We also note that the uncertainty on the top interface depth is around 2 nm or 9% which is already satisfactory. However in our previous study [4] we found that the use of an optimized effective cross-section may provide a better fit and with an increased accuracy in particular regarding the top interface depth. In the following, we investigate the implementation of the method described above with the use of effective cross-sections.



Figure 28: Modelling of Ta3p<sub>3/2</sub> spectrum for the Ta5/Al20 sample with the universal crosssections (a) and with the cross-section of Al (b) and Ta (c) for different depth distribution presenting a scale factor of 1.00.

Fig. 29 shows the modeling with different effective cross-sections. As shown in Fig. 26, the cross-sections for the individual materials are very different and with a linear combination of individual cross-sections we might obtain a better fit and an accuracy at least as good as in our previous study [4] (93% for the top interface and 86% for the bottom interface). In each case, we calculated the IMFP as the average of the IMFP in aluminum and tantalum with weight factors corresponding to the ratio in the inelastic cross-section (see Table 2). The IMFP is 7.8 nm for  $K_{33,67}$ , 7.3 nm for  $K_{50,50}$  and 8.2 nm for  $K_{20,80}$ . Comparing Fig. 28 and Fig. 29, it is seen that the modelings are significantly better with the effective cross-sections. In this case, E, the error value (calculated as the area from the subtraction between the reference and the modeling) are sometimes too close to determine which one of the depth distributions are the best. To discriminate the results, we used also the standard deviation,  $\sigma$ here. The best fit is obtained for  $K_{50,50}$  and a depth distribution from 21 to 27.5 nm (same spectrum as shown in Fig. 27(b)). It is noted that the  $K_{33,67}$  gives a best result from 21 to 25.9 nm and K<sub>20,80</sub> gives a best fit from 21 to 25.1 nm. So all the best fit for these cross-sections give the same top interface depth of  $21 \pm 0.5$  nm corresponding to an uncertainty of 2.4% on the top interface depth and a bottom interface depth around  $26.2 \pm 1.5$  nm corresponding to an uncertainty of 5.7% on the end bottom interface depth. Therefore, the refined method with a reference spectrum implemented with effective cross-sections drastically improves the accuracy of the analysis by decreasing the uncertainties on the depth of both layer interfaces and especially for the more deeply buried, bottom interface. It is also noted that the accuracy of the determination of the top and bottom interface depths (21 nm and 26.2 nm compared to the nominal values 20 nm and 25 nm) corresponds to a deviation by 1 nm or 95 % for the top interface depth.



Figure 29: Modelling of the Ta3p<sub>3/2</sub> spectrum for the Ta5/Al20 sample with different blends of cross-sections for different depth distributions, each giving a scale factor of 1.00. (a) Modellings with the K<sub>50,50</sub> cross-section, (b) with the K<sub>33,67</sub> cross-section and (c) with the K<sub>20,80</sub> cross-section.

### b. Ga and Al analysis

Fig. 30 shows the analysis for the Ga 2p, 2s and Al 1s peaks. Here, the analyses were performed without the use of a reference because suitable reference spectra could not be recorded. The model considered for the Ga analysis is a thick Ga layer covered with an overlayer. The results were all generated with an IMFP of 9.5 nm corresponding to the found depth distribution (Ta(5.2 nm) and Al(21 nm)). It should be noted that all applied cross sections give a top interface depth around  $25 \pm 1.5$  nm and the best fit is obtained with K<sub>50,50</sub> (Fig. 30(a)). The reason why the choice of the cross-section is less important in this case is that the photoelectrons have undergone many inelastic scattering events and the sharp

structure (Fig. 26) in the cross-section is smeared out. In contrast, the IMFP still has a large influence because the determined depth scales with the IMFP value. The AI 1s analysis on Fig. 30(b) was done with the "several buried layers" model of the software [34] using a modeling for two layers because AI is present both as a top layer and in the AlGaN layer. We obtained a depth distribution with a top layer of  $20 \pm 1$  nm and a buried layer (of AlGaN) from  $25 \pm 1.5$  nm to  $47 \pm 3$  nm using an IMFP of 9.7 nm and the K<sub>45,55</sub> cross-section. The result for the gallium is thus a depth distribution as a substrate from  $25 \pm 1.5$  nm and the result for the aluminum is a depth distribution from 0 to  $20 \pm 1$  nm which is in good agreement with the Ta result from  $21 \pm 0.5$  nm to  $26 \pm 1.5$  nm and with the TEM result from 20 to 25 nm (see Fig. 30(c)).



Figure 30: (a) Best modelling of Ga (2p, 2s) spectrum, (b) best modelling of Al 1s spectrum and (c) summary of the resulting depth distribution for the Ta5/Al20 sample.

# 3. Case of thicker layer of Ta on Ta12/Al21 sample: effect on the choice of the cross-section

Here we investigate the case where a thicker Ta layer is buried underneath the same ~20 nm thick Al overlayer.

### a. Ta analysis

For this sample, the thicknesses of the AI and Ta layers as determined by TEM are 21 and 12 nm respectively (see Fig. 25). Fig. 31 shows the best results obtained for different crosssections, with corresponding IMFPs (see table 2). Fig. 31(a) shows the best results with the universal, AI and Ta cross-sections with the constraint that  $F(E) \sim 0$  far below the peak and scale factor = 1.00. Similarly to the analysis in Fig. 28, all results are non-satisfactory fits. More precisely, it is noted that the depth distributions obtained with the universal crosssection and with the AI and Ta ones are very different, from 21 to 26.4 nm for the universal, from 23 to 29.9 nm for the AI one and from 26 to 37.4 for the Ta cross-section. Fig. 31(b) shows the result of several trials using different effective cross-sections: K<sub>33,67</sub> gives a depth distribution from 22 to 33 nm,  $K_{40,60}$  from 22 to 35.3 nm and  $K_{50,50}$  from 21 to 34.1 nm. These cross-sections all give quite good fits, nevertheless it is difficult to decide which is the best fit, so the conclusion is the average of these, i.e. from  $21.6 \pm 0.5$  nm to  $34.2 \pm 1.5$  nm (2% and 4% uncertainty, respectively). This result is again close to the nominal thicknesses determined by TEM which is from 21 to 33 nm (accuracy of 99% for the top interface and 97.9% for the bottom interface) and the result is again better than what we found without using a reference spectrum in our previous study [4] (7% uncertainty for the top interface and 14% for the bottom interface). It is noted that while the  $K_{20.80}$  cross section gave a good fit for the 5 nm Ta layer (Fig. 29(c)) it gave a worse fit (not shown) for the 12 nm Ta layer sample. This is as expected because the relative proportion of Ta is larger in the latter case.



Figure 31: Best modellings of Ta 3p<sub>3/2</sub> spectrum for the sample Ta12/Al21 (a) with the universal, Al, Ta and (b) with the K<sub>33,67</sub>, K<sub>40,60</sub> and K<sub>50,50</sub> cross-sections with the corresponding depth distributions presenting a scale factor of 1.00. (c) Resulting depth distribution.

### b. Ga, Al analysis

For the Ga analysis, the effective IMFP was fixed at 8.9 nm, calculated with the above determined structure: Al(21.6 nm)/Ta(12.6 nm). All effective cross-sections applied give almost the same depth distribution, namely a substrate containing gallium with an overlayer of  $33 \pm 5$  nm. Fig. 32(a) shows the fit with K<sub>50,50</sub>. The Al analysis was done with the same input parameters on Fig. 32(b) as in Fig. 30(b) since it is a similar top layer of Al. The resulting Al depth distribution is a top layer of 21 ± 1 nm and a buried layer (of AlGaN) from 33 ± 5 nm to 55 ± 10 nm. These results are also in good agreement with the TEM results which are an Al top layer of 21 nm and a Ga substrate starting from 33.5 nm.



Figure 32: (a) Best modelling of Ga (2p, 2s) and (b) best modelling of Al 1s spectra for the sample Ta12/Al21 and (c) resulting depth distribution.

### 4. Case of thicker overlayers: effect of elastic scattering on the Ta5/Al40 sample

Here we investigate the case where a thin Ta layer is more deeply buried underneath a 40 nm thick Al overlayer. In this case the effect of elastically scattered electrons turns out to be important.

#### a. Ta analysis

In the case of such a deeply buried Ta layer, one can expect an influence of elastic electron scattering [46, 84, 85]. In order to approximately quantify the effect on the attenuation of the peak intensity, we have used a correction factor, CF, which was introduced by Jablonski and Tougaard [46, 86]. It is defined as the additional peak intensity attenuation due to elastic electron scattering events [46, 86]. For angles of emission < 30°they found that CF is slightly larger than 1 for shallow layers (due to effects of backscattering from the substrate) and slightly smaller than 1 for layers up to ~2 IMFP or more accurately  $2\lambda_{et}$  defined in eq.(46) below (see Figs. 4 and 5 respectively in ref. [86]). For larger depths the correction becomes substantial and CF can be calculated with the following formula [86]:

$$CF = \exp(-0.157764\tau - 1.25132) + \exp(-0.0562417\tau^2 + 0.00698849\tau - 0.201962)$$
(45)

where 
$$\tau = \frac{z}{\lambda_{et}}$$
 and  $\lambda_{et} = \frac{\lambda_i \lambda_{tr}}{\lambda_i + \lambda_{tr}}$  (46)

With z, the depth of the layer,  $\lambda_i$ , the inelastic mean free path and the transport mean free path  $\lambda_{tr} = 16.24$  nm for AI and 19.96 nm for Ta, taken from the NIST database [87]. We find CF= 0.38for a thin Ta layer buried in pure AI at 40 nm and we take this value as scale factor instead of 1 to take into account this attenuation due to elastic scattering at this large depth. By integrating eq. (45) over all depths from 0 to infinity and using the parameters for Ta, we

find that the value of the correction factor is 0.96 for the Ta reference, so the correction on the reference is quite small. For a thin Ta layer buried in pure AI at 20 nm we obtain CF= 0.82. This value is for a model where Ta is in a matrix of aluminum but in our case, under the Ta layer, there is an AIGaN layer which presents stronger backscattering effects compared to AI and would therefore increase this CF value. This gives a CF value close to 1.00 and explains why this correction for the previous two samples (sections 2 and 3) was not necessary.

The result for Ta is almost the same for all cross-sections tested and Fig. 33 shows the best result for  $K_{50,50}$  which gives a depth distribution from  $38 \pm 5$  nm to  $44.3\pm 5$  nm. This result is close to the expected nominal thicknesses even through the Ta is deeply buried but the uncertainty on the determined top and bottom interface depths is larger (13% and 12% respectively). We also obtain a very noisy F(E) spectrum. Despite of this, a deviation of only 5% from the TEM results (40 to 45 nm) is found. Considering that the Ta layer is at a depth of 4.5 times the IMFP of Ta in AI, this figure is rather small. Thus, the error is only on the order of the uncertainty on the IMFP.



Figure 33: Best modelling of Ta  $3p_{3/2}$  spectrum for the Ta5/Al40 sample with the  $K_{50,50}$  crosssection and the corresponding depth distributions presenting a scale factor of 1.00.

### b. Ga, Al analysis

For the analysis of the Ga spectrum from this sample, we see in Fig. 34(a) that the Ga 2s and Ga 2p peaks are extremely small because of the large depth. However, the inelastic background shape is still well described over the full energy loss range. We also tried different cross-sections for this analysis performed with an IMFP of 10.2 nm (the IMFP in Al) but here we chose to show the result with the  $K_{50,50}$  cross-section which is better than a result with the universal, Al or Ta cross-section but almost identical to the one with the  $K_{40,60}$  cross-section. The resulting depth distribution is 45 nm ± 10 nm and as indicated the uncertainty on this value is large. The result from the analysis of the Al 1s spectrum (Fig. 34(b)) gives a distribution from 0 ± 0.5 nm to 40 ± 5 nm which is in good agreement with TEM measurements from 0 to 39.9 nm. This result was obtained with the Al cross-section and with the model "one buried layer" since the AlGaN layer is deeply buried and the contribution to the Al 1s signal from this layer is negligible.



Figure 34: (a) Best modelling of Ga (2p, 2s) spectrum and (b) best modelling of Al 1s spectrum for the Ta5/Al40 sample and (c) resulting depth distribution.

## 5. Case of thicker overlayers: treatment without no-loss peak on the Ta5/Al66 sample

Here the overlayer is so thick that the no-loss peak cannot be seen. In spite of this, it is still possible to get a meaningful result from the analysis, as shown below.

### a. Ta, Al analysis

Fig. 35(a) shows the analysis of the Ta  $3p_{3/2}$  spectrum obtained with an effective (60%Universal, 40%Al) cross-section. In this figure, we show 3 different modelings for a variation of 10 nm on the layer depth: we clearly see that the best fit is obtained for the depth distribution between 65 and 70 ± 10 nm which is in fairly good agreement with the TEM measurement (66 to 71 nm). We could not use the Ta reference spectrum for this analysis because the peak is absent in the spectrum. It is surprising that although the peak itself cannot be seen, the background analysis works reasonably well, as in the case of traditional XPS. The analysis of the Ga peaks (not shown) yields a resulting overlayer depth with a very large (>10 nm) uncertainty. The analysis on the Al 1s in Fig. 35(b) was done with a

15%Universal 85%Al cross-section and a top interface depth of  $65 \pm 10$  nm is obtained, in good agreement with the TEM results.



Figure 35: (a) Best modelling of Ta 3p<sub>3/2</sub> and (b) best modelling of AI 1s spectra for the Ta5/AI66 sample and (c) resulting depth distribution.
## **IV.** Discussion

#### 1. Analysis with the use of a reference spectrum.

Table 3 shows the main results of the present analysis of the Ta layers. The accuracy of the analysis is represented by the deviation of the values of top and bottom interfaces from the values obtained with TEM. The main difference between the previous analytical framework [2-4, 80] and the one presented in this paper is the use of a reference sample in the inelastic background analysis. The uncertainty with the use of a reference can be compared with the result in our last study [4]. For the Ta12/Al21 sample, which has a structure close to the Ti10/Al15 sample of that study, the accuracy is 99% on the top interface and 98% on the bottom interface whereas it was 7% and 14%, respectively for the Ti10/Al15 sample. So there is a clear improvement by using a spectrum from a reference sample. This is a general result for all samples studied. Thus as seen in Table 3, without using a reference the accuracy is in the range from ~96 % to 88 % whereas it is in the range from 99% to 94.6 % when the analysis is done with the use of a reference. This improved accuracy is a very important point for future analyses. It also makes the analysis easier and quicker because we just have to apply a variation on the top interface depth and find the bottom depth which gives a scale factor of 1.00. Thus without a reference spectrum, the fit-criterion is that  $F(E) \sim 0$  in a wide energy range beyond  $\sim 25$  eV from the peak. However, with a reference, we have two additional criteria to take into account, i.e. both the shape and the intensity of F(E) must match the reference, and this effectively decreases the number of fits that have to be tested.

It is also important to apply an optimized effective cross section for inelastic electron scattering. Thus as seen in Table 3, using the universal cross-section and a reference spectrum gives an accuracy which is comparable to- or in some cases worse than the analysis without a reference but with an effective cross-section. This is because with the universal cross-section, the deviation of F(E) from the reference F(E) is huge (see Figs. 28 and 31) even though  $F(E) \sim 0$  far below the peak and the scale factor is 1.00. It should be noted that this effect is largest when the cross sections for the materials in the layered structure are very different as it is the case here (see Fig. 26). This is in particular the case when transition metals enter in a layered structure with materials like Al and Si but will, to a lesser extent, also be the case for materials like SiO<sub>2</sub> and polymers (see ref [25] for the variation in shape of cross-sections for different classes of materials).

The reference spectrum must be obtained from analysis of a sample with a well-known depth distribution. Such a sample is most conveniently produced by considering a pure sample of the material or a sample with a thick overlayer of the material.

The effect of elastic electron scattering is usually ignored in the inelastic background analysis. It is well known that elastic electron scattering modifies the range of path lengths traveled by the photo-excited electrons before they escape [46, 84-86]. Jablonski and Tougaard showed that this can be approximately accounted for by the use of a CF (correction factor) function which represents the additional peak intensity attenuation caused by elastic electron scattering [46, 86]. For emission angles smaller than 30° from the surface normal, the CF factor will in general (see Figs. 4 and 5 in [86]) be close to 1 for depths smaller than ~2 IMFP (or more accurately smaller than  $\sim 2\lambda_{et}$  (defined in eq.(46)). We have found in this study that for Ta layers up to ~ 20 nm it was not necessary to correct for elastic scattering. However for the deepest Ta layers ( $\geq$  40 nm), we found that elastic scattering was important and that this can be accounted for by the use of the CF correction.

It is also observed from table 3 that for depths < 40 nm the uncertainty by background analysis with a reference is smaller than that of TEM and for depths > 40 nm the uncertainty is slightly larger than that of TEM.

Sample	Layer	TEM measurement	Without reference		With reference			
			Quases with effective cross-section	Dev. from TEM	Quases with universal cross-section	Dev. from TEM	Quases with reference and effective cross-section	Dev. from TEM
Ta5/Al20	Та	From $19.9 \pm 1.5$ nm	From $21.5 \pm 1$ nm	7.5%	From $22 \pm 1$ nm	10.5%	From $21\pm0.5nm$	5.3%
		To $24.8 \pm 1.9$ nm	To $27 \pm 1.5$ nm	8.2%	To $26.1 \pm 1.5$ nm	5.2%	To $26.2 \pm 1.5$ nm	5.4%
Ta12/Al21	Та	From $21.4 \pm 1.5$ nm	From $22.5 \pm 1.5$ nm	4.9%	From $21 \pm 1$ nm	1.9%	From $21.6 \pm 0.5$ nm	1%
		To $33.5 \pm 2$ nm	To $35 \pm 2$ nm	4.3%	To $26.4 \pm 1.5$ nm	21%	To $34.2 \pm 1.5$ nm	2.1%
Ta5/Al40	Та	From 39.9 ± 3 nm	From $35 \pm 5$ nm	12.3%	From $34 \pm 5$ nm	14.8%	From $38 \pm 5$ nm	4.8%
		To $45.1 \pm 3.5$ nm	To $41 \pm 5 \text{ nm}$	9.1%	To $39 \pm 5$ nm	13.5%	To $44.3 \pm 5 \text{ nm}$	1.8%

Tableau 3: Comparison of the results with two methods of analysis with and without reference on the Ta buried layer.

#### 2. Analysis without a reference spectrum.

It is evident from the results in Table 3, that using the spectrum from a reference sample improves the accuracy of the analysis considerably. However, it is of interest to know how accurate the analysis is without a reference because this may be the only option in practical analysis if a reference sample is not available. To this end we show in Table 4 the results obtained for both the Ta layers and also for the Al overlayer and the AlGaN substrate layer. The accuracy (based on the deviation from the TEM result) is between ~ 99.5 % and 88 %. The smallest deviations are observed for the thicker layers (~5 % for the 12 nm thick Ta layer and ~ 0.5-2 % for the 20 to 66 nm Al overlayer and ~1 % for the Ga buried 25 to 45 nm in the sample) while it is 7.5 to 12.3 % for the 5 nm thick Ta layer. This indicates that the accuracy

is not strongly dependent on the layer thickness since the relative deviation drops with the thickness.

It is also observed from Table 4 that for depths < 40 nm the uncertainty by background analysis without a reference is similar to that of TEM and for depths > 40 nm the uncertainty is  $\sim$  2-3 times larger than that of TEM.

As a general result it should also be noted that as mentioned above for structures considered here which involve materials with widely different cross-sections, the effective cross-section has a great influence on the final depth distribution in the case of thin samples. However, when the depth is large (>  $\sim 2.5$  IMFP), the different cross-sections all give the same result. This is because in this case the electrons have undergone many inelastic scattering events and the structure in the cross-section is smeared out. The analysis which is used here with a blend of cross-sections has been implemented in Ver 6.0 of the Quases-Tougaard software [34]. This provides an easy tool to interactively change the blended cross-section and simultaneously see the result on the fit of the analyzed peak and background.

Sample	Layer	TEM measurement	Quases without reference and with effective cross-section	Deviation from TEM
Ta5/Al20	Al	$19.9 \pm 1.5 \text{ nm}$	$20\pm1nm$	0.5%
	Та	From $19.9 \pm 1.5$ nm	From $21.5 \pm 1$ nm	7.5%
		To $24.8 \pm 1.9 \text{ nm}$	To $27 \pm 1.5$ nm	8.2%
	Ga	$24.8\pm1.9nm$	From $25 \pm 1.5$ nm	0.8%
Ta12/Al21	Al	$21.4\pm1.5nm$	$21 \pm 1  nm$	1.9%
	Та	From 21.4 ± 1.5 nm	From 22.5 ± 1.5 nm	4.9%
		To 33.5 ± 2 nm	To $35 \pm 2$ nm	4.3%
	Ga	From $33.5 \pm 2$ nm	From $33 \pm 2$ nm	1.5%
Ta5/Al40	Al	$39.9 \pm 3 \text{ nm}$	$40\pm5nm$	0.3%
	Та	From 39.9 ± 3 nm	From $35 \pm 5$ nm	12.3%
		To $45.1 \pm 3.5$ nm	To $41 \pm 5$ nm	9.1%
	Ga	From $45.1 \pm 3.5$ nm	From $45 \pm 10$ nm	0.3%
Ta5/Al66	Al	$66.4 \pm 3 \text{ nm}$	$65\pm10nm$	2.2%
	Та	From 66.4 ± 3 nm	From $65 \pm 10$ nm	2.2%
		To $71.5 \pm 3.5$ nm	To $70 \pm 10  nm$	2.1%

Tableau 4: Global results on all the layers for the 4 different samples.

# V. Conclusion

We have performed Inelastic Background Analysis of different samples presenting different thicknesses of AI and Ta layers and we successfully retrieved the nominal thicknesses measured by TEMfor depths up to 70 nm. The accuracy using a reference sample on the determined depth distribution istypically95% and even less for the deepest buried layers. It was also shown that it is possible to retrieve the depth distribution for depths up to 70 nm. In this case, even though the no-loss peak cannot be detected, the accuracy is still good, ~98%, but with a larger uncertainty ~14%. This kind of analysis is non-destructive and it is quickto record and analyze. Thereby, we confirmed in this study that Inelastic Background Analysis combined with HAXPES using a reference spectrum in the procedure provides a powerful method to determinewith enhanced accuracy and uncertainty the depth distribution of deeply buried elements.

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# Chapter 3: Determination of concentration and structure

This chapter presents a complete analysis of the elemental diffusion by inelastic background analysis. This was done on a sample before and after two annealing steps. The depth distribution and the absolute and relative concentrations of elements were determined. The results were compared to measurements with TEM, sputter depth profiling and core-level analysis. This work was submitted to *Journal of Applied Physics* and is in the second revision step of the publication process.

This chapter shows that inelastic background analysis combined with core-level analysis provide a complete non-destructive analysis and that inelastic background analysis on complex samples can provide the depth distribution and the concentration with a good accuracy.

# Quantitative determination of elemental diffusion from deeply buried layers by photoelectron spectroscopy

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#### Abstract

The recent advances in inelastic background analysis of XPS spectra recorded with hard Xrays (HAXPES) makes this method a powerful, non destructive solution to retrieve the depth distribution of deeply buried elements. In this work, we apply this technique to study diffusion phenomena, upon annealing, in power transistor devices. We present a complete analysis of a sample under different stages of the fabrication process. We investigate the accuracy of the determination of the elemental depth distributions and concentrations with the inelastic background analysis. This is done by cross-checking with destructive techniques such as TEM/EDX and XPS depth profiling, and we shed light on the complementarities with HAXPES core-level analysis. We obtain consistent results which show the formation of an inhomogeneous structure, consisting of a blend of Al, Ga and Ta, created during annealing. The inelastic background analysis permits to successfully retrieve the depth distributions of Al, Ga and Ta as well as the concentration of these elements in each layer, over 70 nm below the surface. This is a reliable solution to investigate diffusion phenomena and improve the fabrication processes of devices with critical and deeply buried interfaces.

#### Keywords

Inelastic background analysis, HEMTs, buried interfaces, hard x-ray photoemission, TEM/EDX, depth profile analysis, core-level analysis.

## I. Introduction

High Electron Mobility Transistors (HEMTs) [77] have been the subject of research of continuous expansion for some years. This kind of transistors is used in III-nitrides power devices, where a 2D electron gas is formed at the interface between the AlGaN channel and the GaN substrate [78]. These devices involve a top electrode layer of several tens of nm thickness, which covers the active layers. Undeniably, a complete removal of this top electrode prior to surface-sensitive measurements will be harmful to the interfaces, which are prone to subtle changes upon variations of the process conditions. It is therefore preferable to keep the device in a state as closely related to the real structure as possible with the top electrode and therefore preserve the deeply buried interfaces of interest from exposure to the atmosphere and damages caused by removal of the top layer. The rapid advance in these new technologies has intensified the need for non-destructive and fast in-depth characterizations of deeply buried interfaces.

Recently, we applied inelastic background analysis to study Ta/AI electrodes from HEMT devices with different thicknesses in the as deposited state [76]. The inelastically scattered photoelectrons [36, 81] contributing to the background permitted to retrieve the depth distribution of deeply buried elements. We demonstrated the potential and the accuracy of the inelastic background analysis method when it is combined with HArd X-ray PhotoElectron Spectroscopy (HAXPES) [2-4, 80]. This permits to significantly extend the probing depth with inelastic background analysis from 10 nm with current XPS to 70 nm with HAXPES spectra. In the fabrication of the HEMT devices, series of annealings are performed to achieve the ohmic contact at the electrode/substrate interface in order to obtain good electrical properties. Therefore, it is highly important to know the details of any inter-diffusion process happening during annealing, and in particular at the source/drain region [79].

In this paper, we address this subject by analyzing the same sample at three stages of the process: before annealing, after a first annealing at 550°C and after a second annealing at 650°C. We show how a complete non-destructive and in-depth study of the sample by HAXPES combining inelastic background and core-levels analyses can give valuable insights about what happens during annealing. In this respect, the depth distributions of the elements and their concentrations have been determined. The results are compared to two more common and well-known destructive techniques: Transmission Electron Microscopy (TEM)/Energy Dispersive X-Ray (EDX) and depth profile XPS analysis. This study was done to show the reliability and the possibilities of this technique and its advantages as a non-destructive characterization technique. This can be helpful for in-line characterization between two stages in the fabrication process using new high energy laboratory X-rays

sources [11] or using it together with several complementary characterization techniques as it does not modify the sample.

# II. Experimental

#### Samples

We have studied High Electron Mobility Transistors (HEMTs) based on an  $AI_{0.25}Ga_{0.75}N(22 nm)/GaN(1 \ \mu m)$  substrate epitaxially grown by Metal Oxide Chemical Vapor Deposition (MOCVD) on a Si(111) wafer. Metallic layers of Ta and Al are then successively deposited by Electron Beam Physical Vapor Deposition (EBPVD). To achieve the contact electrode, the stack is annealed first for 300 s at 550°C and then for 300 s at 650°C under nitrogen atmosphere. As we need a Ta reference sample for the inelastic background analysis, a thick Ta layer (50 nm) has been deposited by the same technique on the same AlGaN/GaN substrate.

#### Characterization techniques

The spectra for inelastic background analysis and core-level analysis were recorded on the BL15XU beamline at the Spring-8 synchrotron. The analyses were done without additional surface preparation. The photon energy was 7935.7 eV, determined from calibration on the Au Fermi level. The x-rays impinged the sample at 45° and the photoelectrons detection angle was at 7° from the surface normal.

Core-level spectra were recorded for Al 1s (1559 eV binding energy), Ga  $2p_{3/2}$  (1117 eV binding energy) and Ta  $4f_{5/2}$ ,  $4f_{7/2}$  (24, 22 eV binding energy) with an energy resolution of 0.3 eV.

The spectra for inelastic background analyses were recorded over an extended energy range to include energy loss features. The spectra were taken for Ta  $3p_{3/2}$  (5744 eV kinetic energy), Al 1s (6376.7 eV kinetic energy) and Ga 2p, 2s (6818.7, 6520.7 eV kinetic energy) corelevels, over 250, 200 and 350 eV to lower kinetic energy, respectively.

The analysis made by TEM and EDX were performed on the PlatForm of NanoCharacterization (PFNC) of CEA-MINATEC.

The lamella for TEM and EDX analysis were prepared by Focused Ion Beam (FIB) with FIB Strata 400S from FEI. They underwent a Ga exposition to locate the area of interest before the deposition of a SiO<sub>x</sub> protection layer. These TEM analyses were done with the TEM Tecnai OSIRIS from FEI at 200 kV and the measurements were obtained based on the Si lattice ( $a_{Si} = 0.543$  nm [88]).

The STEM-EDX analyses were done with the STEM Titan THEMIS from FEI.

The measurements for TEM and EDX analyses were done on 4 different regions of the sample and the values given in this work are the average on these different regions with the mean deviation.

The depth profile analyses were done with a VersaProbe II from PHI using an AI k $\alpha_1$  source and a monoatomic argon sputtering gun at 1 kV. The analyses were performed on five different peaks: AI 2p (73 eV binding energy), Ta 4f<sub>7/2</sub> (22 eV binding energy), Ga 2p<sub>3/2</sub> (1117 eV binding energy), O 1s (543 eV binding energy) and N1s (398 eV binding energy).

#### Sample description

TEM measurements of the layer thicknesses of the as-deposited samples (Fig. 36) give: Al( $39.9 \pm 3 \text{ nm}$ )/Ta( $5.2 \pm 0.5 \text{ nm}$ )/AlGaN( $22.5 \pm 0.5 \text{ nm}$ ). Even though the actual HEMT device structure consists of a 25 nm thick Ta layer below a 100 nm thick Al layer, the present sample is thinner but with Ta/Al proportions kept. These samples are therefore much more representative of real devices than those obtained by removing most of the top electrode which would damage the interface but would be required for a traditional XPS analysis limited to 10 nm. The associated EDX measurements, discussed later, show that annealing induces diffusion of Ta and Ga into the Al top layer. A schematic of the in-depth distribution is given in Fig 36.



Figure 36: TEM cross-sectional image of the samples and schematic diagram with average values of the layer thicknesses.

These samples turned out not to be efficient devices. As can be observed on the TEM image Fig. 36 after the 650°C annealing, the contact is inhomogeneous and forms discontinuous grains. This is undesirable for an ohmic contact and electrical tests proved that this device is not functional. The analysis of each step is relevant here as it shows that the second annealing was probably made at a too high temperature. These analyses were done to improve the fabrication process and understand the phenomena happening at the deeply buried interfaces in the samples with the inelastic background analysis of HAXPES spectra.

#### Methodology: inelastic background analysis

The inelastic background analysis needs two input parameters which are the inelastic mean free path (IMFP),  $\lambda$ , and the inelastic scattering cross-section, K(T), as described in equations (47), (48) and (49) [83].

$$F(E, \boldsymbol{\Omega}) = \frac{1}{2\pi} \int J(E, \boldsymbol{\Omega}) dE \int \frac{e^{-is(E-E')}}{P(s)} ds$$
(47)

with 
$$P(s) = \int f(z)e^{\left(\frac{-z}{\cos\theta}\right)\Sigma(s)}dz$$
 (48)

and 
$$\sum(s) = \frac{1}{\lambda(E)} - \int_0^\infty K(T) e^{-isT} dT$$
 (49)

Here,  $F(E,\Omega)$  is the primary excited spectrum, also called the atomic excitation function. J(E,  $\Omega$ ) is the measured spectrum, T = E'-E is the energy loss, z/cos  $\theta$  is the travelled distance, f(z) is the concentration distribution as a function of the depth z and P(s) and s are mathematical variables without physical significance. For the numerical evaluation of eqs.(47)-(49) we have used the QUASES-Tougaard software package [34].

The IMFP used for the inelastic background analysis are chosen as a weighted average over the value for each element calculated with the TPP-2M formula [30], with a weight corresponding to the proportions used in the applied effective cross-section (see eq. (50) and (51) below and Table 5). The depth of information provided by the method is ~ 8xIMFP [81] which is higher than for core-level XPS which is estimated at 3xIMFP. Therefore, the quite high IMFP in aluminum (8.9 nm for Ta  $3p_{3/2}$ , 9.7 nm for Al 1s and 10.2 nm for Ga 2p, 2s photoelectrons) ensures that we get information from the critical electrode/substrate interface.

Previously, we found that for samples containing materials with quite different cross-sections and IMFPs, a blend of element-specific inelastic scattering cross-sections [25] gives a better description of the energy loss over the entire path of the electrons than the pure elemental cross-section [76]. For this reason, we have used effective cross-sections optimized according to the core-level analysis structure and the inelastic background shape.

The Universal cross-section as well as the element-specific cross-section of AI is implemented in the Quases-analyse software package [34] whereas the Ta cross-section was determined from analysis of a REELS spectrum from Ta at 2 keV using the procedure in ref [63].

We have used a set of effective cross-sections ( $K_{eff}$ ) and IMFPs (IMFP<sub>eff</sub>) presented in Table. 5. The effective cross-sections and the corresponding IMFPs were calculated with a varying relative weight A of Ta and B of Al as:

$$K_{eff} = \frac{A}{100} \times K_{Ta} + \frac{B}{100} \times K_{Al}$$
(50)

$$IMFP_{eff} = \frac{A}{100} \times IMFP_{Ta} + \frac{B}{100} \times IMFP_{Al}$$
(51)

where  $K_{AI}$ , IMFP<sub>AI</sub> and  $K_{Ta}$ , IMFP<sub>Ta</sub> are the cross-sections and IMFP of AI and Ta, respectively, determined with a 10-15% accuracy [30].

The universal cross-section was also used for some analyses. The Ta and Universal crosssections are very close and a 10% variation of IMFP has only a small influence on the result. Therefore, we used the Ta IMFP in the corresponding calculation of  $IMFP_{eff}$  when using the Universal- in the effective-cross section.

Ta 3p <sub>3/2</sub> at 5744 eV						
A	В	IMFP <sub>eff</sub>				
100	0	5.8 nm				
0	100	8.9 nm				
50	50	7.3 nm				
40	60	7.6 nm				
Ga 2p at 6818 eV						
А	В	IMFP <sub>eff</sub>				
100	0	6.6 nm				
0	100	10.2 nm				
50	50	8.4 nm				
AI 1s 6376 eV						
А	В					
100	0	6.3 nm				
0	100	9.7 nm				
20	80	9.0 nm				
95	5	6.5 nm				

Table 5: IMFP considered in the analyses depending on the associated cross-section

All the modeled inelastic backgrounds are shown as red in the following figures, the measured spectra are black curves and the subtraction of the modeled inelastic background from the measured spectra, also called intrinsic spectra are green curves.

The best fits are determined by minimization of the RMS deviation between the modeled inelastic background and the measured one.

## III. Results

#### 1. Analysis of the Al(40 nm)/Ta(5 nm) as-deposited sample

#### a. Inelastic background analysis

Fig. 37 shows the results of the inelastic background analysis of Ta  $3p_{3/2}$  (Fig. 37(a)), Al 1s (Fig. 37(b)) and Ga 2s, 2p (Fig. 37(c)) for the as deposited sample. The obtained structure is summarized in Fig. 37(d) and compared to the TEM measurements in Fig. 36. The analyses of Al and Ga were made without a reference. Spectra were recorded on an Al foil and a GaN bulk sample but were found to not be representative of the structures of our thin layers of Al and AlGaN. For Ta, we used a reference spectrum [76] obtained from an experimental Ta  $3p_{3/2}$  recorded on the pure Ta reference sample.

#### <u>Ta analysis</u>

Fig. 37(a) shows that the Ta  $3p_{3/2}$  peak intensity is extremely small as expected for a deeply buried Ta layer. The vast majority of the Ta  $3p_{3/2}$  electrons loose energy during their path through the overlayer and contribute to the inelastic background. Along the same line, the spectrum also presents distinct plasmons which are characteristic of an Al overlayer. We found that the effective cross-section which gives the best account of the measured background over the full energy range is the 50%Al 50%Ta cross-section with the corresponding 7.3 nm IMFP (table 5).The resulting Ta depth distribution is from 38 ± 5 nm (4.8% deviation from TEM) to 44.3 ± 5 nm (1.8% deviation from TEM) (see fig. 37(d)). This value was found using a Ta reference spectrum and the correction factor CF to account for the effects of elastic scattering, corresponding to this structure as scale factor, previously determined in ref [76] at 0.38. The Ta amount of substance is thus 6.3 nm in this sample.

#### <u>Al analysis</u>

The AI spectrum (Fig. 37(b)) also presents plasmons due to the crossing of the AI overlayer by electrons. Our first attempt using a pure AI cross-section from the software package gave a bad description of the electrons path and a bad fit of the spectrum. The reason could be that our deposition process leads to a quite different structure from the one of the sample used for the AI cross-section available in the software. That is the reason why we used the "three parameters cross-section" from ref [89] with the values  $C = 240 \text{ eV}^2$  and  $D = 8 \text{ eV}^2$ determined by fitting the region of the first two plasmons. The best result is found with the "several buried layers" mode of the Quases-Analyze software and the IMFP corresponding to AI of 9.7 nm which is more accurate than what was previously done [76]. Moreover, the "several buried layers" mode of the Quases-Analyze software permits to provide relative concentration of the layers since, with this mode, it is possible to create a modeling for several buried layers of different concentrations. The best match is obtained for 2 layers: a pure Al layer from  $1.5 \pm 0.2$  nm to  $40 \pm 3$  nm (0.3% deviation from TEM) with a concentration fixed at  $c_{AI} = 1$ , and another layer with a smaller relative Al concentration,  $c_{AI} = 0.26$ , from 40  $\pm 5$  nm to 68  $\pm 10$  nm (0.6% deviation from TEM) identified as the AlGaN layer. The upper top layer would be a native oxide about 3 nm thick. Note that the top interface depth at 40 nm of the AlGaN layer almost corresponds to the top of the Ta layer (38 nm), which indicates that there is Al in the Ta layer (even though the uncertainty on these depth values is comparable to the Ta layer thickness).

#### <u>Ga analysis</u>

In Fig. 37(c), the Ga 2p and 2s peaks are extremely small which indicates that the AlGaN layer is also deeply buried. There are also plasmons because the Al overlayer is crossed by the Ga photoelectrons. The analysis of Ga was made using the "several buried layers" mode with the 50%Al 50%Ta cross-section and the corresponding IMFP of 8.4 nm (table 5). The best adjustment is for a depth distribution that consists in an infinitely thick layer with the fixed concentration  $c_{Ga} = 1$ , beginning at 67 ± 10 nm (0.8% deviation from TEM) and a layer with a relative concentration,  $c_{Ga} = 0.72$ , extending from 40 ± 5 nm (0.2% deviation from TEM) to 67 ± 10 nm. In addition to Al, there is also Ga in the Ta layer.



Figure 37: Inelastic background analysis on the as-deposited Al(40 nm)/Ta(5 nm) sample (a) for Ta 3p<sub>3/2</sub> with a reference (b) for Al 1s (c) for Ga 2s, 2p (d) schematic average results from inelastic background analysis and comparison with TEM measurements of Fig. 36

#### b. TEM/EDX analysis and XPS depth profiling

From the High-Angle Annular Dark-Field (HAADF) image of Fig. 38 and Fig. 36, we clearly identify four regions from the top to the bottom Al, Ta, AlGaN and GaN respectively. The EDX images in Fig. 38 show that the distribution of Ga, N, Ta and Al are roughly as expected. However, in the Ta layer, there is a fair amount of oxygen and a small concentration of Ga, Al and N. There is Ga at the surface of the stack because of the FIB preparation of the sample and oxygen because of the deposited SiO<sub>x</sub> as explained before.

The main point is that the presence of Ga and Al in the Ta layer is in complete agreement with the inelastic background analyses.

The XPS depth profiles are shown in Fig. 38 as a function of time because the sputtering rate is unknown for such stacks. From top to bottom, the first region is identified as metallic aluminum with a native oxide. The next region is Ta with a small amount of Al, O, Ga and N as previously found. The composition of the third region is found to be 10% Al, 35% Ga and 55% N, which is in good agreement with the deposited Al<sub>0.25</sub>Ga<sub>0.75</sub>N composition with just ~5% excess of GaN. The last region is GaN with 55% N and 45% Ga. Here again, there is a good agreement between XPS depth profile and the inelastic background analyses whereas the Al concentration seems to be overestimated which could be due to the nitrogen excess.



Figure 38: EDX images of the as deposited Al(40 nm)/Ta(5 nm) sample for five elements (N, O, Al, Ta and Ga) and XPS depth profiling.

#### 2. Analysis of elemental diffusion after 550°C anneal

#### a. Inelastic background analysis

Fig. 39 shows the inelastic background analyses of Ta  $3p_{3/2}$  (Fig. 39(a)), Al 1s (Fig. 39(b)) and Ga 2s, 2p (Fig. 39(c)) after the first annealing. The determined structure is summarized in Fig. 39(d) with a comparison to the TEM measurements of Fig. 36.

#### <u>Ta analysis</u>

The Ta  $3p_{3/2}$  spectrum presents a much larger peak compared to that from the as-deposited sample. This peak intensity enhancement implies Ta diffusion towards the surface into the Al electrode layer. The analysis takes this mixing into account by a cross-section of 7%Ta 60%Al 33%universal and the corresponding 7.6 nm IMFP (see table 5, 60%Al 40%Ta). The resulting depth distribution is from 16.5 ± 0.5 nm to 45 ± 5nm (4.2% deviation from TEM). The Ta concentration calculated with the Ta reference spectrum gives a concentration  $c_{Ta} = 0.15$ . The total amount of Ta in the layer is thus 0.15 x (45 - 6.5) = 4.28 nm. This is 32% lower than the amount (6.3 nm) found in the as-deposited sample. For this sample, it would be difficult to calculate the CF factor because of the unknown structure of the alloy but scattering effects are expected, although smaller than for the as-deposited sample, and this explains the underestimation of the amount of substance.

#### <u>Al analysis</u>

The AI 1s spectrum presents a similar shape compared to Fig. 39(b) which demonstrates a comparable distribution of the AI. The analysis was made using a cross-section of 20%Ta 80%AI and the corresponding 9.0 nm IMFP (see table 5). The best depth distribution is obtained with a "several buried layers" mode which includes three layers with different relative concentrations  $c_{AI}$ : on top, an AI layer from 0.5 ± 0.2 nm to 15 ± 1 nm with a fixed concentration  $c_{AI} = 1$ , a second layer with a smaller relative concentration,  $c_{AI} = 0.85$ , from 15 ± 1 nm to 44 ± 5 nm (6.4% deviation from TEM) and the AIGaN layer with a relative  $c_{AI} = 0.19$  from 44 ± 5 nm to 68 ± 10 nm (1.2% deviation from TEM). These concentrations cannot be directly compared to those of the as-deposited sample due to of their relative aspect to the concentration fixed at 1 for the top layer, because of the absence of reference.

#### <u>Ga analysis</u>

The inelastic background analysis of Ga 2s, 2p spectrum was made using an 8.4 nm IMFP and the three parameter cross-section with C = 300 eV<sup>2</sup> and D = 50 eV<sup>2</sup>. The resulting depth distribution is found with the "several buried layers modeling" with three different regions: the GaN substrate which begin at 66 ± 10 nm (deviation from TEM 4%), with a fixed concentration  $c_{Ga}$  = 1, AlGaN goes from 44.5 ± 5 nm (5.3% deviation from TEM) to 66 ± 10

nm with a smaller relative concentration,  $c_{Ga} = 0.72$ . Finally the top layer goes from 15 ± 1 nm to 45 ± 5 nm (4.2% deviation from TEM) with the relative concentration,  $c_{Ga} = 0.3$ .



Figure 39: Inelastic background analysis on the Al(40 nm)/Ta(5 nm) sample after the 550°C annealing (a) for Ta 3p<sub>3/2</sub> with a reference (b) for Al 1s (c) for Ga 2s, 2p (d) average results of the analysis and comparison with TEM measurements of Fig. 36

#### b. TEM/EDX analysis and XPS depth profiling

When comparing the HAADF image of Fig. 40 with Fig. 36, we clearly see that a diffusion (white part in the top layer) happened during the annealing. From the EDX images, we see that Ta, Ga, O and N have diffused towards the surface and with the same shape as the diffusion in the HAADF image. The EDX shows a homogeneous AI depth distribution in both layers containing AI. The AIGaN and GaN layers seem unchanged. These results are in good agreement with the inelastic background analyses.

The depth profile (bottom part of Fig. 40) confirms the diffusion of Ta and Al compared to Fig. 38. The metallic Al shows that there is still a large region of pure aluminum and a native aluminum oxide. Ta and Ga have diffused closer to the surface. The AlGaN is also Gapoorer and N-richer which confirms that Ga diffused.

So we have four different regions in this sample: a pure Al layer (with native oxide); a diffusion region with Ta, Ga and Al; the AlGaN; and the GaN region. The diffusion region presents a gradient in the composition.



Figure 40: XPS depth profiling and TEM analysis on the Al(40 nm)/Ta(5 nm) sample after the 550°C annealing.

#### 3. Analysis of elemental diffusion after 650°C anneal

#### a. Inelastic background analysis

Fig. 41 shows the inelastic background analysis on the Al(40 nm)/Ta(5 nm)sample for Ta  $3p_{3/2}$  (Fig. 41(a)), Al 1s (Fig. 41(b)) and Ga 2s, 2p (Fig. 41(c)) after the second annealing. The determined structure is summarized in Fig. 41(d) which also shows a comparison to the TEM measurements (Fig. 36).

#### <u>Ta analysis</u>

Fig. 41(a) shows a more intense Ta peak compared to Figs. 37 and 39. This reveals that Ta has diffused closer to the surface during the second annealing. The analysis was made with a blend of three different cross-sections 7%Ta 60%Al 33%universal and using the corresponding 7.6 nm IMFP (see table 5). The resulting depth distribution is from 5 ± 1 nm to  $45 \pm 5$  nm (same as the TEM value) with a concentration  $c_{Ta} = 0.14$ . Ta has diffused by 11.5 nm towards the surface (from 16.5 to 5 nm). The amount of substance is 5,6 nm which is closer to the initial value of 6.3 nm (11% lower) as the Ta diffused closer to the surface and therefore the influence of elastic scattering effects is decreased.

#### <u>Al analysis</u>

Fig. 41(b) shows a very strong aluminum oxide peak compared to the other stages analyzed. The analysis was performed using the several buried layers method with the 95%Ta 5%Al cross-section and the corresponding IMPF of 6.5 nm (see table 5). The resulting depth distribution is divided into three regions; the top Al layers going from  $0 \pm 0.5$  nm to  $6 \pm 1$  nm with a fixed concentration  $c_{AI} = 1$ , the diffusion region with an Al relative concentration,  $c_{AI} = 0.42$ , going from  $6 \pm 1$  nm to  $45 \pm 5$  nm (same as the TEM value) and the AlGaN region with a relative concentration  $c_{AI} = 0.15$ , going from  $45 \pm 5$  nm to  $67 \pm 10$  nm (1.4% deviation from TEM).

#### <u>Ga analysis</u>

Fig. 41(c) shows that the Ga peaks are more intense compared to the previous stages. So Ga diffused closer to the surface. The analysis was made using the three parameters cross-section with C = 400 eV<sup>2</sup> and D = 210 eV<sup>2</sup> and an 8.4 nm IMFP. The resulting depth distribution with the several buried layers model gave: the GaN beginning at 66 nm with the fixed concentration  $c_{Ga} = 1$ , the AlGaN from 44 ± 5 nm to 66 ± 10 nm (2.9% deviation from TEM) with a relative concentration  $c_{Ga} = 0.7$  and the diffusion layer from 8 ± 1.5 nm to 44 ± 5 nm (2.2% deviation from TEM) with a relative concentration  $c_{Ga} = 0.7$  and the diffusion layer from 8 ± 1.5 nm to 44 ± 5 nm (2.2% deviation from TEM) with a relative concentration  $c_{Ga} = 0.26$ . The concentration of the AlGaN and GaN layers don't seem to have changed during the second annealing.



Figure 41: Inelastic background analysis on the Al(40 nm)/Ta(5 nm) sample after the 650°C annealing (a) for Ta 3p<sub>3/2</sub> with a reference (b) for Al 1s (c) for Ga 2s, 2p (d) average results of the analysis and comparison with TEM measurements of Fig. 36.

#### b. TEM/EDX analysis and XPS depth profiling

Figure 42 shows the EDX images recorded from the sample after the 650°C annealing. The HAADF image shows that the second annealing created crystallites compared to Fig. 38 and 40. The EDX for AI shows that the AI concentration in the AIGaN layer has decreased because AI diffused from AIGaN to the overlayer which is in good agreement with the evolution of the concentrations found by the inelastic background analysis. Ta, AI and N are in the crystallites whereas the oxygen is now only in the top layer compared to Fig. 40.

Unfortunately, the Ga was not recorded by EDX for this sample but we expect that Ga is also in the crystallites since the Ga and Ta diffusion were very similar to those in the first annealing and according to the depth distribution found by inelastic background analysis.

Figure 42 (bottom part) shows XPS depth profiling after the 650°C annealing. It shows that oxygen is present in all regions even in the AlGaN layer and the nitrogen diffused a bit in the overlayer. Ga and Ta diffused closer to the surface. The composition of the AlGaN layer is maybe almost the same, N-enriched from 5% and Ga-deficient from 5%.



Figure 42: XPS depth profiling and TEM analysis on the Al(40 nm)/Ta(5 nm) sample after the 650°C anneal.

#### 4. Core-level analysis of the Al(40 nm)/Ta(5 nm) sample

From left to right, Figure 43 shows the core-levels Al 1s, Ga 2p<sub>3/2</sub> and Ta 4f for the Al(40 nm)/Ta(5 nm) sample: as-deposited, 550°C-annealed and 650°C-annealed, respectively from top to bottom. As expected, in Al 1s, the metallic Al contribution (gray) (1558.2 eV in ref [23]) diminishes and the oxidized Al contribution (blue) increases when the sample is annealed 550°C. This oxidized Al contribution becomes even larger than the metallic part of the Al 1s spectrum after the second 650°C annealing. This contribution is more and more shifted as the oxidation increases, which indicates a modification of the oxide composition. These observations are in good agreement with the precedent analyses which show that the oxygen initially at the surface as a native oxide diffuses in the Al during annealing (Fig. 40).

For the as-deposited sample, the Ga  $2p_{3/2}$  core level shows only one contribution (green) which is attributed to AlGaN since the calculated IMFP doesn't permit to reach the GaN layer. For the 550°C- annealed sample, Ga  $2p_{3/2}$  clearly shows two contributions: one (violet) from Ga diffusing from AlGaN towards the upper layers and one (green) from AlGaN. Note that the contribution from AlGaN is not at the same binding energy: it is shifted by 0.29 eV towards higher binding energy because of a change in composition due to the Ga diffusion leading to Al-richer AlGaN. For the 650°C- annealed sample, the contribution (violet) to the Ga  $2p_{3/2}$  core level is associated with diffused Ga decreases and shows a small shift towards higher binding energies. This means that the diffused Ga which had first interacted with Ta, now also interacts with Al and thus contributes at almost the same binding energy as the Al-richer AlGaN contribution.

The Ta 4f core level overlaps with several other core levels: O 2s, Ga 3d, C 2s and N 2s. However, it shows a very different shape for the annealed samples if compared to the asdeposited one. It is sharper and therefore from a more homogeneous state. A new compound has been formed by interacting with Ga and Al. As the C 2s, N 2s core level intensities decrease when the samples are annealed, they are desorbed from the surface during annealing whereas the O 2s is mainly from Al oxide. Moreover the Ta intensity increases in the annealed samples compared to the as-deposited one which confirms the Ta diffusion towards the surface.



Figure 43: Core-level analyses of the sample Al(40 nm)/Ta(5 nm) under the three stages for Al 1s, Ga 2p<sub>3/2</sub> and Ta 4f.

		As deposited		550°C annealed		660°C annealed	
Spectrum	Component	Position (eV)	FWMH (eV)	Position (eV)	FWMH (eV)	Position (eV)	FWMH (eV)
Al 1s	Al metal	1558.22	0.57	1558.23	0.58	1558.21	0.59
	Al oxide	1561.09	1.37	1561.30	1.76	1561.83	1.98
Ga 2p <sub>3/2</sub>	AlGaN	1117.18	1.12	1117.47	1.27	1117.52	1.13
	alloy			1115.09	0.96	1115.31	0.89
Ta 4f	Ta4f7/2	20.82	1.50	20.79	0.39	20.77	0.30
	Ta4f5/2	22.52	1.22	22.70	0.35	22.68	0.33
	O2s	23.61	3.02	23.61	3.08	23.61	3.21
	Ga3d	19.40	1.60	19.39	1.19	19.53	1.31
	C2s	17.35	3.24	17.50	2.90	17.53	2.95
	N2s	15.09	1.89	15.20	2.39		

Table 6: Values from the core-level analyses of the sample AI(40 nm)/Ta(5 nm) under the three

stages for AI 1s, Ga 2p<sub>3/2</sub> and Ta 4f.

# **IV.** Discussion

Fig. 44 shows a summary of the inelastic background analysis results and Table 7 shows the comparison of the TEM results with the inelastic background analysis results. The deviation from TEM is less than 5% which is very good for an unknown sample, particularly for the deeply buried Ga around 68 nm depth. Taking into account the uncertainty of the measurement, we could even consider that there is a perfect agreement between the inelastic background analysis and the TEM measurements. It must be noted that the uncertainty is largest for the deepest buried layers that we analyzed. However, this shows that the inelastic background analysis combined with HAXPES is a reliable, non-destructive method to determine the depth distribution of deeply buried elements.

The results for the as deposited sample indicate that there is a  $\sim 3$  nm thick native Al oxide on a  $\sim 36.6$  nm thick pure Al layer. Under the Al layer, there is a 5 nm thin layer containing Ta, Al, O, and Ga on top of the AlGaN(23.2 nm)/GaN substrate. After the 550°C annealing, we have a 15.75 nm thick layer of Al on a 28.75 nm thick alloy of Ta, Al and Ga with possibly some O and N. This thick layer is formed by diffusion of Ga, Ta and O towards the surface during this annealing. After the 650°C annealing, there is a 6.3 nm thick Al oxide layer on a 38.37 nm thick alloy layer. So the Ga, Ta and O have diffused closer to the surface. We have still the AlGaN(21.83 nm)/GaN substrate underneath the alloy which is Ga-depleted and Nenriched according to the core-level analysis.

Therefore inelastic background analysis permitted to obtain the layer thicknesses with a < 5% accuracy (< 10% in ref [76]) and also the relative concentration of the layers and in the case of Ta, the absolute concentration by using a reference spectrum. This technique requires high energy photons which up to now has only been available at synchrotron facilities. However recently, laboratory sources producing hard X-rays have become available [90] which will make the technique more generally applicable and easily accessible in the near future.

The HAXPES core-level analysis is also a non-destructive technique, although it is quite time consuming but it is very useful to get information on the chemical composition of the sample. This technique is a good complementary analysis to the inelastic background which adds chemical information.

We can obtain the same information with a good accuracy also from TEM, EDX and depth profile analyses as shown on Figs. 38, 40 and 42. These analyses confirmed the results of inelastic background and core-level analyses which demonstrate that these two techniques can provide a complete and non-destructive characterization of the chemical composition, thicknesses and structures of samples.



Figure 44: results of the inelastic background analysis on every step of the HEMT processing.

	In	ТЕМ	Inelastic	Dev.
Sample	terfi		background	From
	ace	measurement	analysis	TEM
	Al Al + Ta	39.9 ± 3 nm	39.3 ± 5 nm	1.5%
Al40/Ta5 As deposited	+ Ga	45.1 ± 3.5 nm	44.3 ± 5 nm	1.8%
	AlGaN GaN	67.6 ± 4 nm	67.5 ± 10 nm	0.1%
	Al Al + Ta		15.75 ± 1 nm	
Al40/Ta5 550°C annealed	+ Ga	46.8 ± 2 nm	44.5 ± 5 nm	4.9%
	AlGaN GaN	68.6 ± 4 nm	67 ± 10 nm	2.3%
	Al Al + Ta		6.3 ± 1.5 nm	
Al40/Ta5 650°C annealed	+ Ga	45 ± 2 nm	44.67 ± 5 nm	0.7%
	AlGaN GaN	68 ± 5 nm	66.5 ± 10 nm	2.2%

Table 7: Comparison of the results from	TEM and inelastic background analyses on every
	sample.

# V. Conclusion

In this study, we have applied inelastic background analysis to HAXPES spectra to nondestructively study complex diffusion phenomena at depths up to 70 nm below the surface. We obtained results consistent with TEM measurements which show the formation of an inhomogeneous structure consisting of a blend of AI, Ga and Ta during annealing. We also demonstrated the potential of the inelastic background analysis which permits to retrieve the depth distributions of AI, Ga and Ta as well as the relative or absolute concentration of these elements in each layer. The technique was found to provide a good deviation from TEM (deviation typically smaller than 5%) while results from EDX and XPS depth profiling deviated sligtly more (typically less than 15%). Therefore, this technique is reliable to study complex diffusion phenomena at large depths without damaging the samples. With the new high energy X-ray laboratory sources [90] it is also possible to use it for in-line characterization during the frabrication process, so this is a promising method for in-line characterization and/or as a complementary analysis to other techniques.

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# Chapter 4: Theoretical study of the choice of input parameters for inelastic background analysis

The last years, the notions of effective inelastic scattering cross-section [4] and effective IMFP [76] were introduced for cases where the electrons have passed through materials with widely different inelastic scattering cross-sections (Fig. 45). It was shown that it is not obvious which effective cross-section should be used even for well-known samples [76]. It was also shown that an analysis can become very long to perform for unknown samples where lots of values of the depth distribution for lots of combinations of IMFPs and inelastic scattering cross-sections have to be tested in order to find the best modeling of the inelastic background.

In this Chapter, we made a systematic study of this by analyzing model spectra from different depth profiles created with Quases-Generate© software and analyzed with Quases-Analyze© software [34]. The goal of this study was to decide how to make the best choice of input parameters for inelastic background analysis particularly for an unknown sample. To do this, XPS spectra of virtual stacks were created and then analyzed using particular combinations of effective inelastic scattering cross-sections and effective IMFPs in part inspired by the experience acquired from [4, 76, 91].

This study provides tools to make the analysis easier for unknown samples.

# *I.* Procedure of the theoretical study

With the Quases-Generate© software, it is possible to create spectra corresponding to different depth distributions. Here, we first create spectra for a range of depth profiles and subsequently, these are analyzed by Quases-Analyze©. The best combination of effective cross-section and IMFP are determined by comparing the results to the true depth distribution.

#### 1. Creation of the spectra

To create spectra from virtual stacks composed of one buried layer and an overlayer of different materials (see Fig. 45(A)) we need two steps of creation with the Quases-Generate© software as we used different materials for each layer presenting widely different inelastic scattering cross-sections and IMFPs as seen on Fig. 45(B).



Figure 45: (A) Composition of virtual stacks used for the study (B) Cross-sections of the materials used in virtual stacks

The first step is the creation of the "buried" layer from a reference spectrum recorded on a bulk sample of the material desired for the buried layer. For this step, we also need a proper inelastic scattering cross-section for this material and its IMFP. We choose two kind of buried layers from: Au reference spectrum recorded at 1152 eV kinetic energy with conventional AI K $\alpha$  X-ray source and a calculated IMFP = 1.36 nm and Si reference spectrum recorded at 6099 eV kinetic energy with synchrotron and a calculated IMFP = 10.33 nm. We also used the Si inelastic scattering cross-section calculated from REELS analysis and recorded at 10 keV [13] for the Si buried layer and the universal cross-section for Au which is a very good approximation.

This reference spectrum,  $J_H(E,\Omega)$ , was corrected for the analyzer transmission and used as input parameter with IMFP, inelastic scattering cross-section and thickness of the layer to obtain the spectrum from the "buried" layer without the contribution of the overlayer so not yet buried (see Fig. 46).

The second step consists in the addition of the inelastic contribution due to the path of the electrons through the overlayer.

The spectrum generated from step 1 was taken as input in Quases-Generate© with the IMFP, inelastic cross-section and thickness of the overlayer material. We considered overlayers of AI, Si, Ta, polymer and Au as it presents widely different inelastic scattering cross-sections and IMFP and are well representative of a wide range of samples that are currently encountered.



Figure 46: steps for the generation of the depth profiles

#### 2. Analysis of the spectra

Figure 47 shows the analysis of a spectrum created as described previously. This figure shows the generated spectrum (black curve), the modeling of the inelastic background (pink curve) and the resulting subtracted spectrum (green curve). This figure shows exactly the same kind of analysis which was done in references [4, 76, 91].

To perform this kind of data analysis and calculate the inelastic background, the Quases-Analyze© software needs the effective IMFP, the effective inelastic scattering cross-section and the depth distribution. Ideally, the determined depth distribution should be the same as the input depth distribution used to create the spectrum in Quases-Generate© and this will be used as a criterion to determine the quality of the analysis. In addition, the modeled inelastic background shape should be close to the created spectrum shape which is also an adjustment criterion for the analysis. Therefore, combinations of effective IMFP and effective inelastic scattering cross-section are tested and the depth distribution is varied until these two requirements are fulfilled.

The IMFP for the pure materials is calculated with TPP-2M formula [30-32] and the effective inelastic scattering cross-section is created from the two individual cross-sections of the materials composing the virtual stack with the version 6.00 of the Quases-Analyze© software.

#### II. Need for an improved cross-section

As shown in references [4, 76, 91], the effective IMFP, IMFP<sub>eff</sub>, may be calculated as the average of a weighted sum of the individual IMFPs of each material. Equation (52) gives the calculation made for the IMFP chosen as input parameter in the software.

$$IMFP_{eff} = A \times IMFP_{Overlayer} + B \times IMFP_{Buried \ layer}$$
(52)

where A and B will depend on the thicknesses of the overlayer and of the buried layer.

The cross-section has also been chosen as an average of a weighted sum of the individual cross-sections of each material in references [4, 76]. Equation (53) gives the calculation made for the effective cross-section,  $K_{eff}$ , chosen as input parameter in the software.

$$K_{eff} = C \times K_{Overlayer} + D \times K_{Buried \ layer}$$
(53)

where C and D are the coefficient of the cross-sections for the overlayer and the buried layer, respectively. Many combinations of A and B, and of C and D were tested and the one giving the best fit and/or a result close to the expected profile were selected. This kind of analysis takes a long time since many combinations have to be tested and that is the reason why a general guide in the choice of the cross-section is very helpful.

Figure 47 (A) and (B) show the inelastic background analysis of spectra from two samples. The analysis in panel (A) was performed on the Si spectrum resulting from a virtual stack made of a 5 nm-thick layer of Si buried under 10 nm of Au. The analysis in panel (B) was performed on the Au spectrum resulting from a virtual stack made of a 5 nm-thick layer of Au buried under 8 nm of Si.

Figure 47 (A) and (B) show two inelastic background's modeling for each spectrum, performed with the Si cross-section and the universal cross-section, respectively. We see that the shapes of the modeling are quite bad in all cases except for the use of Si in panel (B) but the depth distribution is still far from the expected values.

Figure 47 (C) shows the results from a range of combination of  $d_1$  and  $d_2$  compared to the expected values (black line). We can see that the results deviate considerably from the expected values.



Figure 47: (A) inelastic background analysis of a spectrum created for a virtual stack of a 5 nmthick Si layer buried under 10 nm of Au (B) inelastic background analysis of a spectrum created for a virtual stack of a 5 nm-thick Au layer buried under 8 nm of Si (C) comparison of the results with the expected values.

As the modeling with the individual cross-sections gives a very bad description of the electron-path through the samples, this shows that the use of an effective cross-section is very important when two layers have very different cross-sections (Fig. 45(B)) as in this case with Si and Au (Fig. 47).

# III. Study of different combinations of input parameters

#### 1. Virtual stacks tested

Our virtual stacks are made of one buried layer of Au or Si covered by one overlayer of Au, Si, Al, polymer or Ta.

The created stacks from a reference spectrum of Au are made of a gold buried layer (1 nm, 3 nm or 5 nm thick) covered by an overlayer of Al, Si, Ta or polymer (of thickness 4 nm, 6 nm or 8 nm). So, 36 different virtual samples were tested with very different overlayer-materials which present quite different IMFP and cross-section shapes (Fig. 45(B)). These samples will be representative for laboratory experiments since the Au reference was recorded with conventional X-ray source and the peak is at 1152 eV of kinetic energy.

The created stacks from a reference spectrum of Si are made of a Si buried layer (1 nm, 5 nm, 10 nm or infinitely-thick) covered by an overlayer of Al, Au, Ta or polymer (of thickness 5 nm, 10 nm, 20 nm or 40 nm). So, 60 different virtual stacks were tested also with a large range of difference in IMFP and cross-sections. These samples will be representative for synchrotron experiments since the Si reference was recorded with hard X-rays and the peak is at 6099 eV of kinetic energy.

#### 2. Effective cross-section and IMFP

The proportions of each individual cross-sections and IMFPs in the calculation of the effective cross-section and effective IMFP are expected to be related to the thicknesses of the material layers involved in the stack.

Based on our previous analyses [76, 91], we have considered these values for the effective cross-section,  $K_{eff}$ , and effective IMFP, IMFP<sub>eff</sub>:



where  $t_A$  is the thickness of the layer of material A,  $t_B$  is the thickness of the layer of material B,  $K_A$  and IMFP<sub>A</sub> are the cross-section and IMFP of material A, respectively and  $K_B$  and IMFP<sub>B</sub> the cross-section and IMFP of material B, respectively.

As the electrons constituting the spectrum do not all come from the deeper interface of the buried layer, we should maybe consider only half the thickness of the layer for the material A. This consideration will model that the electrons come from the middle of the layer which is a good average for all the electrons coming from the buried layer, if the probing depth is sufficient to probe the entire buried layer. This gives the following equations:

$$IMFP_{eff_{-\frac{1}{2}}} = \frac{\frac{1}{2}t_A}{\frac{1}{2}t_A + t_B} \times IMFP_A + \frac{t_B}{\frac{1}{2}t_A + t_B} \times IMFP_B$$
(56)

$$K_{eff_{-\frac{1}{2}}} = \frac{\frac{1}{2}t_A}{\frac{1}{2}t_A + t_B} \times K_A + \frac{t_B}{\frac{1}{2}t_A + t_B} \times K_B$$
(57)

To investigate the exact influence of these choices, we tested all the combinations of these effective input parameters for all the virtual samples created. The analyses were done with only the shape of the fit as a criterion to determine  $d_1$  and  $d_2$ . We made it as if we did not know the expected values of  $d_1$  and  $d_2$ . The results are given in Appendix.

Figure 48 shows the comparison of different depth distributions with  $\pm 2$  nm of variation. It is clear that the fit for 10 to 20.2 nm (green curves) shows the best match with the created spectrum (black curve).



Figure 48: Inelastic background analysis on Si spectrum created for a depth distribution from 10 to 20 nm.

#### **IV. Results**

#### 1. Comparison of the results for all the samples

Figure 49 shows the resulting analysis for all considered stacks. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths, i.e. the input  $d_1$  and  $d_2$  (black lines). The results are presented for the 4 combinations of input parameters presented in eq. (54-57). Also shown are RMS deviations from the expected values calculated as:

$$RMS(d) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left(\frac{d - d_{true}}{d_{true}}\right)^2}$$
(52)

It is clear that the resulting depths deviate more from the true depth for the combinations (C) and (D) where  $K_{eff}$  is used and therefore  $K_{eff_{-1/2}}$  is the best choice. The results are also closer to the expected values (black line) for IMFP<sub>eff\_1/2</sub>.

The best combination of input parameters is therefore  $K_{eff_{1/2}}$  with IMFP<sub>eff\_1/2</sub> (smallest RMS values) and permits to obtain very accurate results for all the samples tested with RMS deviations of only 13.69% on d<sub>1</sub> and 5.57% on d<sub>2</sub>.

It should be noted that the results deviate less for small depths and that it is difficult to determine which IMFP is the best for these depths whereas  $K_{eff_{-1/2}}$  still gives the closest results to the true values.



Figure 49: start and end depth for the 4 combinations of effective input parameters and for the 96 samples.

In the following, we will study the different types of stacks individually to determine the best choice of input parameters as a function of the involved materials.

#### 2. Si buried-layer under Al overlayer

Figure 50 presents the results for stacks with varying thicknesses of Si layer buried under Al layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

As seen before,  $K_{eff_{1/2}}$  gives the best results since the analysis values are closer to the true depths (Fig. 50 (A) and (B)). The results are most accurate for small thicknesses and the use of IMFP<sub>eff</sub> or IMFP<sub>eff\_1/2</sub> does not make any significant difference (similar RMS values in (A) compared to (B) and in (C) compared to (D)). This is expected as the Si IMFP is 10.33 nm and the Al IMFP is 10.21 nm, the variations on the calculated IMFPs are smaller than 0.1 nm which makes no difference on the modeling.

To conclude,  $K_{eff_{-1/2}}$  is the best choice of input parameter and for materials with close IMFP values, the IMFP does not vary sufficiently to allow a choice between IMFP<sub>eff</sub> and IMFP<sub>eff\_1/2</sub>, as seen with the RMS values of Fig. 50 (A) and (B).



Figure 50: start and end depth for 4 combinations of effective input parameters and for a Si layer buried under AI.
### 3. Si buried-layer under polymer overlayer

Figure 51 presents the results for stacks with varying thicknesses of Si layer buried under polymer layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

Polymer IMFPs are generally higher than the Si IMFP (10.33 nm), around 12.5 nm, and the cross-sections are very different (see Fig. 45).

 $K_{eff_{1/2}}$  gives closer results ((A) and (B) better than (C) and (D)) and IMFP<sub>eff</sub> compared to IMFP<sub>eff\_1/2</sub> ((A) compared to (B)) provides closer results with  $K_{eff_{1/2}}$ , according to the RMS values of 7.86% and 4.77% for d<sub>1</sub> and d<sub>2</sub>, respectively.

For Thicknesses of Si larger than 1 nm, the shapes of the inelastic background modeling are also visibly better for  $K_{eff_{-1/2}}$ .

Then, for overlayer materials presenting a higher IMFP than the IMFP of the buried material, combination (B) is the best choice of input parameters.



Figure 51: start and end depth for 4 combinations of effective input parameters and for a Si layer buried under polymer.

### 4. Si buried-layer under Ta overlayer

Figure 52 presents the results for stacks with varying thicknesses of Si layer buried under Ta layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

The Ta cross-section is similar to the polymer cross-section (see Fig. 45) and the IMFP is small, calculated at 7.0 nm compared to Si (10.33 nm).

The results are closer to the true depths for combination (A),  $K_{eff_{1/2}}$  with IMFP<sub>eff\_1/2</sub> (see RMS values on Fig. 52 (A) compared to (B), (C) and (D)). All combinations give extremely close RMS deviation values but the shapes of the inelastic background modeling are also better with  $K_{eff_{1/2}}$ , for a Si buried layer thicker than 1 nm.

Then for a material overlayer presenting a quite small IMFP compared to Si but similar in cross-section to polymer,  $IMFP_{eff_{1/2}}$  is preferable combined with  $K_{eff_{1/2}}$ .



Figure 52: start and end depth for 4 combinations of effective input parameters and for a Si layer buried under Ta.

### 5. Si buried-layer under Au overlayer

Figure 53 presents the results for stacks with varying thicknesses of Si layer buried under Au layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

The Au cross-section is the most different from the Si cross-section compared to others cross-sections (see Fig. 45). The Au IMFP is also very small, 4.9 nm, compared to the Si IMFP (10.33 nm). This is probably the reason why the deviation of the resulting values is larger than for the previous cases.

Also for this case, the shapes of the inelastic background modeling appear to be closer to the spectrum with  $K_{eff_{-1/2}}$  for buried layers thicker than 1 nm.

However, it is clear from Fig. 53 that combination (A) presents the closest results to the true depths and smallest RMS values (31.07% and 6.77% for  $d_1$  and  $d_2$ , respectively). Then the  $K_{eff_{1/2}}$  with IMFP<sub>eff\_1/2</sub> is the best combination choice in this case.



Figure 53: start and end depth for 4 combinations of effective input parameters and for a Si layer buried under Au.

### 6. Au buried-layer under Al overlayer

Figure 54 presents the results for stacks with varying thicknesses of Au layer buried under Al layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

At the kinetic energy of Au 4d (1152 eV) the Au IMFP = 1.4 nm is very small compared to the Al IMFP = 2.6 nm. The cross-sections of Au and Al are also very different (see Fig. 45).

From Fig. 54, it is clear that combination (D) shows the worst results and combination (A) shows the closest results to the true depths, RMS deviation values are 5.88% for  $d_1$  and 5.93% for  $d_2$ . Therefore, the K<sub>eff\_1/2</sub> combined with IMFP<sub>1/2</sub> appears to be the best choice of input parameters for materials of quite different IMFPs and cross-sections.



Figure 54: start and end depth for 4 combinations of effective input parameters and for an Au layer buried under Al.

### 7. Au buried-layer under polymer overlayer

Figure 55 presents the results for stacks with varying thicknesses of Au layer buried under polymer layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

At this kinetic energy, the polymer IMFP is 3.2 nm compared to 1.4 nm for Au. We are in the case of materials of quite close cross-sections (see Fig. 45) and very different IMFPs.

Figures 55 (A) and (B) show clearly that  $K_{eff_{1/2}}$  gives the best results and the RMS deviation values are the best. However, combination (B) shows the smallest RMS deviation values 5.01% and 5.6% for d<sub>1</sub> and d<sub>2</sub>, respectively. Therefore, IMFP<sub>eff</sub> gives the best results compared to IMFP<sub>eff 1/2</sub>.

This gives the same result as for a Si layer buried under polymer. The best combination of input parameters for polymers is  $K_{eff 1/2}$  with IMFP<sub>eff</sub>.



Figure 55: start and end depth for 4 combinations of effective input parameters and for an Au layer buried under polymer.

### 8. Au buried-layer under Ta overlayer

Figure 56 presents the results for stacks with varying thicknesses of Au layer buried under Ta layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

At the kinetic energy of Au 4d, the Ta IMFP is 1.9 nm which is a close value to the Au IMFP (1.4 nm) and their cross-sections are also close (see Fig. 45).

Figure 56 (A) shows the smallest RMS deviation values of 1.05% for  $d_1$  and 6.3% for  $d_2$ . Then,  $K_{eff_{1/2}}$  combined with IMFP<sub>eff\_{1/2</sub>} is the best choice of input parameters for the method. This is the result for quite close individual cross-sections and quite closes material IMFPs.



Figure 56: start and end depth for 4 combinations of effective input parameters and for an Au layer buried under Ta.

### 9. Au buried-layer under Si overlayer

Figure 57 presents the results for stacks with varying thicknesses of Au layer buried under Si layer. The determined depths  $d_1$  and  $d_2$  are plotted against the expected depths and presented for the 4 combinations of input parameters: (A), (B), (C) and (D).

At the kinetic energy of Au 4d, the Si IMFP is 2.7 nm. The IMFPs and cross-sections of the two layer's materials are very different in this case (see Fig. 45) (Au IMFP = 1.4 nm).

We are in a similar case to the one with Au buried under an Al overlayer. Combinations (A) and (B) present the smallest RMS deviation values which indicates that the  $K_{eff_{-1/2}}$  gives the best results.

 $IMFP_{eff_{1/2}}$  is also the best choice as in the Al overlayer case but (A) RMS values are extremely close to (B) RMS values).

Then  $K_{eff_{1/2}}$  with IMFP<sub>eff\_{1/2</sub> is the best choice of input parameters in the case of materials with quite different IMFPs and cross-sections.



Figure 57: start and end depth for 4 combinations of effective input parameters and for an Au layer buried under Si.

### V. Conclusion

When the cross-section and/or the IMFP for the overlayer are very different from the values for the buried layer, an effective inelastic scattering cross-section and an effective IMFP are needed.

In this Chapter, we have studied spectra for a wide range of depth profiles consisting of a buried layer of Si and Au with an overlayer of Ta, Al, Si, Au or polymer. The goal was to determine a rule for the choice of input parameters for inelastic background analysis.

The summary of the results of this study is given in table 8.

In all cases except for polymer overlayers, it was found that the best choice of input parameters is to consider half the thickness of the buried layer in the calculation of the effective IMFP and effective cross-section. The combination was called:  $K_{eff_{-1/2}}$  with IMFP<sub>eff\_1/2</sub> from eqs. (56) and (57).

For polymers, the best solution was to consider the complete thickness of the buried layer in the IMFP calculation instead of half, combination called:  $K_{eff_{1/2}}$  with IMFP<sub>eff</sub>. However the results for IMFP<sub>eff</sub> and IMFP<sub>eff\_1/2</sub> were very closed. So, as a general rule for all the samples, we could say that the effective IMFP, the effective inelastic scattering cross-section and depth distribution have to be linked by the equations (56) and (57).

Sample	Best IMFP	Best cross-section
Al/Si	IMFP <sub>1/2</sub>	K <sub>eff_1/2</sub>
Polymer/Si	IMFP	K <sub>eff_1/2</sub>
Ta/Si	IMFP <sub>1/2</sub>	K <sub>eff_1/2</sub>
Au/Si	IMFP <sub>1/2</sub>	K <sub>eff_1/2</sub>
Al/Au	IMFP <sub>1/2</sub>	K <sub>eff_1/2</sub>
Polymer/Au	IMFP	K <sub>eff_1/2</sub>
Ta/Au	IMFP <sub>1/2</sub>	K <sub>eff_1/2</sub>
Si/Au	IMFP <sub>1/2</sub>	K <sub>eff_1/2</sub>

### Table 8: best input parameters choice for the different samples tested.

This guidance for the choice of the input parameters make the data treatment with Quases-Analyze© faster to perform as we know that the depth distribution result is linked to the effective cross-section and IMFP by the equations (56) and (57). This decreases the number of possible results and improves the accuracy of the analysis and it will be very useful for unknown samples. Now, the users can create the effective inelastic scattering cross-section in the Quases-Analyze© software and determine mathematically the best depth distribution

with the RMS calculation included in the new version of the software and we have provided a detailed guidance for the choice of input parameters of the method.

In this work we did a theoretical study for rationalizing the approach of the inelastic background analysis towards analyzing "unknown" samples. We presented a study for the choice of the input parameters testing different combination of: inelastic mean free path and inelastic scattering cross-section for a large range of samples. Different spectra were created with Quases-Generate© for spectra recorded with synchrotron and with laboratory sources. Different thicknesses of the buried layer and of the overlayer were tested for each case. Between the different combinations of input parameters tested, the best for all cases was considering half the thickness of the buried layer in the calculation of the effective IMFP and effective inelastic scattering cross-section.

This guidance for the choice of the input parameters together with the availability of the new software version make the analysis easier for unknown samples as well as for known samples by finding a rule for determining the inelastic mean free path and the inelastic cross-section linked with the element depth distribution. This make the analysis of the inelastic background faster, easier to apply and more user-friendly even for non-specialists.

# Chapter 5: Towards 3D mapping of the depth distribution

This chapter is a proof of principle for future extends of the technique to 3D mapping by HAXPEEM combined with inelastic background analysis. The experiment was done on a quite simple stack consisting of two materials and the results are compared to TEM measurements.

This work was published in [80]:

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## Quantitative spectromicroscopy from inelastically scattered photoelectrons in the hard X-ray range

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### Abstract

We demonstrate quantitative, highly bulk-sensitive x-ray photoelectron emission microscopy by analysis of inelastically scattered photoelectrons in the hard X-ray range, enabling elemental depth distribution analysis in deeply buried layers. We show results on patterned structures used in elec- trical testing of high electron mobility power transistor devices with an epitaxial Al0.25Ga0.75N channel and a Ti/Al metal contact. From the image series taken over an energy range of up to 120 eV in the Ti 1s loss feature region and over a typical 100 Im field of view, one can accurately retrieve, using background analysis together with an optimized scattering cross-section, the Ti depth distribution from 14 nm up to 25 nm below the surface. The method paves the way to multi- elemental, bulk-sensitive 3D imaging and investigation of phenomena at deeply buried interfaces and microscopic scales by photoemission.

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The advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) exploiting third generation synchrotron radiation sources has enabled a step forward in photoemission for accessing information from buried interfaces [92-94]. Recently, HAXPES was further extended to the microscopic scale with Hard X-ray Photoelectron Emission Microscopy (HAXPEEM), and the possibility to retrieve microscopic, bulk sensitive information from corelevel spectromicroscopy [95]. This technique is to date the only way to perform laterally resolved HAXPES, as small-spot methods derived from Scanning Photoemission Microscopy (SPEM) have still not been applied to the hard x-ray range. HAXPEEM further expands on previous PEEM-based, highly depth-resolved methods employing soft X-ray standing waves [96, 97], but is unfortunately restricted to a limited depth range of some nm. Particularly, it enables the analysis of buried interfaces in well-defined patterned structures as frequently encountered in device technology, where the active layer of a functional material is part of a more or less complex stacked structure with a top electrode [95-97]. Resistive memory devices are an important example in this field, where in some cases the switching mechanism from a high resistive to a low resistive state deals with an accumulation of oxygen vacancies at the oxide/electrode interface [98, 99]. This particular case illustrates the importance of spatial resolution in HAXPES, which becomes also mandatory when physical characterization and electrical testing have to be performed on the same test device structure. However, in most practical cases, the thickness of the electrode overlayer is larger than the maximal probing depth accessible with core-level photoelectrons, which is about three times the inelastic mean-free path (IMFP). With excitation energies of 3-8 keV, the probing depth is typically smaller than 20 nm, making it necessary to study model devices with a thinner electrode, which may no longer be representative of the real conditions. Moreover, quantification with core-level spectra alone from deeply buried elements can lead to large errors, especially in the case of complex distribution profiles. One way to overcome this limitation is to exploit inelastically scattered photoelectrons [36, 81] providing information from deeply buried interfaces up to 50 nm, as was recently shown in HAXPES [2]. Indeed, these latter electrons originate from typical depths as high as 8 times the IMFP [81] and constitute the so-called inelastic background to lower kinetic energy of the core-level photoemission spectrum. This background contains specific information regarding the depth distribution of the corresponding element which can be retrieved in a quantitative way, following Tougaard's theoretical and practical framework originally developed for XPS [34, 36, 81]. Applied to HAXPES, the method has, similarly to XPS, the potential to determine and quantify complex depth distributions of several elements such as diffusion profiles, but still lacks microscopic capabilities.

In this letter, we present an HAXPEEM method where the spectromicroscopic information arises from inelastically scattered photoelectrons and is treated in a quantitative

way by inelastic background analysis for probing deeply buried interfaces previously not accessible at microscopic scales by photoemission. Unlike microprobe XPS providing a spectrum from areas of interest as small as rv10 Im with laboratory X-ray sources and less than 100 nm with synchrotron radiation X-rays, the key advantage of XPEEM is the full- field, spectroscopic imaging capability, enabling one to ultimately retrieve one spectrum at each image pixel. Here, we focus on the quantitative analysis of energy-loss spectra from different areas within the HAXPEEM microscope field of view (FoV), as a necessary step for further developments regarding the mapping from analysis of spectra-at-pixels. An example is taken with a power transistor device structure based on a 2D electron gas in AlGaN with a top ohmic Ti/Al contact, the formation of which is crucial to understand for further optimizing device operation.

The study is performed on a technologically relevant stack of GaN-based High Electron Mobility Transistor (HEMT). This sample presents two metal overlayers of aluminum (15 nm) and titanium (10 nm) deposited by Electron Beam Physical Vapor Deposition (EBPVD) on a Al<sub>0.25</sub>Ga<sub>0.75</sub>N (11 nm)/AlN(1 nm)/GaN(some µm) heterostructure epitaxially grown by Metal-Organic Chemical Vapor Deposition (MOCVD) on a Si(111) substrate. Subsequently, so-called TLM (Transfer Length Method) structures used for resistivity measurements were patterned by UV lithography and the lift- off process. The resulting sample was analyzed prior to any activation annealing or sputtering so we rely on the nominal layer thicknesses shown in Fig. 58. The nominal thicknesses were further confirmed by Energy-Dispersive X-ray spectrometry (EDX) performed in a High Resolution Transmission Electron Microscope on a cross section prepared by focus ion beam milling in a TLM contact identical to that observed in HAXPEEM.

HAXPEEM was performed with a NanoESCA MkII spectromicroscope (ScientaOmicron) from Forschungzentrum Jülich [95] as a temporarily installed endstation at the P09 beam- line of PETRA III (Deutsches Elektronen-Synchrotron DESY, Hamburg) [100]. The photon energy was set to 8 keV. The image chain at the exit of the imaging spectrometer (aberration- compensated double hemispherical analyzer) consists of a double multichannel plate (MCP), a phosphor screen, and a CCD camera. Image series were recorded over the extended Ti 1s region, namely, including the core-level peak and its energy-loss tail up to 120 eV to the lower kinetic energy side. More precisely, the imaging unit was operated in the analogue mode, with the MCP acting as a linear amplifier and the CCD acquiring long exposure (30 s per image). The kinetic energy range was scanned from 2909 to 3099 eV. The energy step was 0.5 eV and the field of view (FoV) 97 lm. The pass energy of the imaging spectrometer was set to 200 eV and its entrance slit to 1 mm, yielding an overall energy resolution (photon band width included) of 2 eV. The contrast aperture was set to 500 lm, providing a theoretical lateral resolution of 500 nm. The image series obtained

provide ultimately one core-level and energy loss spectrum per pixel. However, for a better local statistics on the energy loss spectra, these latter were generated from larger regions, on the Ti/Al contact.



Depth (nm)



Figure 59 presents the Ti 1s energy-loss spectra generated over several regions on the Ti/Al contact highlighted as a bright stripe on both HAXPEEM images presented. All spectra display identical shapes, indicative qualitatively of a uniform Ti depth distribution over the stripe. We note that some Ti 1s intensity is also detected on the dark stripe where the bare AlGaN substrate is solely expected. This artifact is due to scattering in the light optical system, between the screen and the CCD camera [95]. The image taken using inelastically scattered photoelectrons in the far energy loss region (E-EF ¼ 2931 eV), 107 eV kinetic energy from the core-level peak, displays an increased intensity compared to the core-level image taken at the peak energy (E-EF ¼ 3038 eV). This image is therefore more useful to study the buried Ti layer and may also provide an enhanced effective lateral resolution through the increased counting statistics. Also, it can be guite clearly seen that the energyloss image highlights, on the right hand side, the edge of the stripe (white arrow), which is not so obvious from the core-level image. This points to the fact that substantial information can be obtained from the energy-loss image of a buried element, particularly if the corelevel peak is weak due to either a small amount of substance [2] and/or a weak photoionization cross-section. Looking closer at the Ti 1s micro-spectra on the bright stripe, we see that the first plasmon loss peak has higher intensity than the Ti 1s core level peak at 3038 eV kinetic energy, in agreement with the buried character of Ti in the region of interest. The separation between these two peaks is 15.6 eV, which is in good agreement with the plasmon excitation energy in pure AI (15.8 eV) [101].



Kinetic energy (eV)
Figure 59: HAXPEEM micro-spectra of the extended Ti 1s photoelectron energy-loss region and corresponding images at the core-level peak (3038 eV, right) and in the far inelastic energy loss region (2931 eV, left). The image field of view is 97 μm, and the size of the area of interest, 10x10 μm. Both images are displayed within the same grayscale dynamic. The arrow on the energy-loss image points to the edge of the stripe.

Next, we concentrate on the quantitative, so-called inelastic background analysis[81] of the energy-loss Ti 1s micro-spectra of Fig. 59. We have not considered the analysis of the spectra from the dark stripe, first because of the artifact on the Ti 1s emission; another reason is that regarding Al 1s, the depth distribution of Al in distinct layers makes the analysis more difficult. The principle of the quantitative analysis consists in subtracting from the photoelectron spectrum  $J(E,\Omega)$  measured within the solid angle  $\Omega$ , the extrinsic contributions to the energy losses, which depend upon the depth distribution f(z) of the considered element. One obtains a corrected or original spectrum,  $F(E_0,\Omega)$ , only accounting for intrinsic contributions, including shake-up excitations, of primary photoelectrons. This formalism relies on a two-step photoemission model [36, 81], assuming that the intrinsic and extrinsic effects are decoupled. The surface excitations are neglected in this model and replaced by a bulk excitation cross-section: this approximation is particularly suitable in HAXPES where surface excitations are less prominent. Then, we can express the measured spectrum as [36, 81]:

$$F(E,\boldsymbol{\Omega}) = \frac{1}{2\pi} \int J(E,\boldsymbol{\Omega}) dE \int \frac{e^{-is(E-E')}}{P(s)} ds$$
(53)

with

and

$$P(s) = \int f(z) e^{\left(\frac{-z}{\cos\theta}\right)\Sigma(s)} dz$$
(54)

$$\sum(s) = \frac{1}{\lambda(E)} - \int_0^\infty K(T) e^{-isT} dT$$
(55)

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where E0 is the initial energy of the photoelectron and E the final energy after having travelled the distance  $z/\cos\theta$ . K(T) is the inelastic-scattering cross-section which represents the probability of an electron to lose the energy T = E0 - E and  $\lambda$  is the inelastic mean free path which depends on E. In Eq. (47), J(E, $\Omega$ ) is the measured spectrum, while we want to determine F(E<sub>0</sub>, $\Omega$ ). The QUASES-Tougaard software [34] was developed to perform these calculations.

Figure 60 presents the background modeling of the Ti 1s HAXPEEM spectrum displayed in Fig. 59. The only input in the software is  $\lambda(E)$  and K(T) while the depth distribution f(z) is varied until a good match is obtained over typically ~30–120 eV to lower kinetic energy below the Ti 1s peak [34, 36, 81], between the calculated and the measured spectrum. The effective  $\lambda$  is taken as a weighted average of individual  $\lambda$  calculated using the TPP-2M formula [30, 32, 102] for each of the layers located above, according to their nominal thicknesses. The resulting, effective  $\lambda$  value for Ti 1s photoelectrons is determined as 5.5 nm. Therefore, the corresponding probing depth ( $\sim 8\lambda$ ) with inelastically scattered photoelectrons in the energy-loss region of interest here is up to 44 nm, and consequently, the entire 10 nm-thick Ti layer below the 15 nm-thick Al surface layer can be probed. For the choice of the scattering cross-section, we first note that the cross-section of pure AI presents a marked plasmon peak, of which both single and double excitations are clearly visible in the 35 eV energy loss region below the Ti 1s peak (Fig. 59). A universal, broad and featureless cross-section [25] is therefore not suitable in the case of sharp plasmon structures [2]. However, we found that the use of a weighted average of individual K(T) functions of pure Ti, pure AI, and universal cross-sections provides a better match (and therefore a more accurate determination of the depth distribution) than just using a single AI cross-section. This is in agreement, as explained above, with the large probing depth which includes the entire Ti buried layer, meaning that the Ti 1s photoelectron is transported across layers of Ti and Al. The blend with the two-parameter universal cross-section [25] is believed to originate from the surface AI oxide layer and maybe also be associated with particular microstructures of the deposited Ti and Al films. The cross-sections for Al [62] and Ti were determined from reflection electron energy-loss spectroscopy using the QUASES-XS-REELS software [63]. The optimal blend of individual Ti, AI, and universal cross-sections is  $K_{eff}(T) = 0.28 x K_{Univ}(T) + 0.27 x K_{Ti}(T) + 0.45 x K_{AI}(T).$ 



Figure 60: Inelastic background analysis of the Ti 1s HAXPEEM energy-loss micro-spectrum from the pink region of Fig. 59.

In other similar cases, we recently found that using such blends of cross-sections is necessary to improve the reliability of the inelastic background analysis in HAXPES of deeply buried layers [4]. Here, using this blend, the inelastic background is best reproduced, over the 25–120 eV energy loss range, for a Ti depth distribution ranging between 14 ± 0.5 nm and 25 ± 1 nm below the surface. These figures are in very good agreement with the overlayer structure determined by TEM-EDX (Fig. 58). The question arises now to which extent the modeled background is sensitive to variations, at the nm-scale, of the effective Ti depth distribution. This is because the background spectrum is quite noisy due to the microscopic character of the emitting area; we found, however, that considering a larger area by averaging over the entire Ti/Al stripe did not significantly change the result. In a previous study [2], we faced a similar issue for a different reason, namely, a small buried elemental concentration: we showed that the derived, correct depth distribution corresponded to a minimum in the X<sup>2</sup> residual of the modeling. Similarly here, we have performed several alternative modeling using different depths of both the top and the bottom Ti interface (varied by a typical ± 0.5 nm increment) and could confirm that the error (namely, the normalized integrated area of the corrected spectrum), for the 14 to 25 nm depth distribution corresponds to a minimum. The use of a smaller increment did not result in significant changes in the modeling; from this observation, we determine the uncertainty of  $\pm 0.5$  nm in the depth derived for each interface. As seen in Fig. 61, significantly increased errors are observed for deviations larger than ± 10% from the optimal 14 nm and 25 nm interface depths.



Figure 61: Calculation of the best modeling for the inelastic background analysis comparing different depth distributions using the same cross-section.

Extending the described method to the analysis of spectra-at-pixels to allow depth-resolved mapping of the Ti 1s elemental distribution is of high interest towards 3D-imaging in HAXPES. Such a development is actually ongoing in our group, and is based on previous work performed in XPS imaging [103, 104]. The challenge in HAXPES 3D-imaging is to combine a suitable automated procedure for background analysis, as the one described here, with noise reduction and multivariate methods such as Principal Component Analysis suitable for treating very low-intensity spectra. Last, but not least, it is useful to summarize the pros and cons of the technique developed here. As mentioned before, the method is able to determine precisely elemental depth distributions over several tens of nm in a non-destructive way and ultimately at the nm scale, with, as reported previously [36], similar accuracy in the case of complex distribution profiles; the microscopic capability cannot be reached by laboratory techniques such as X-ray reflectivity or spectroscopic ellipsometry. It is restricted to elemental distributions, but chemical information can be derived by complementary core-level analysis over smaller depth, cross-checked by analyzing overlapping depth distributions of different elements.

In conclusion, we have shown that spectroscopic imaging with HAXPEEM using inelastically scattered photoelectrons excited with hard x-rays enhances the sensitivity to deeply buried layers. We have performed a quantitative inelastic background analysis within Tougaard's framework to retrieve at the microscopic scale, in a reliable way, the elemental depth distribution over 14–25 nm depth below the surface. The method paves the way to the

investigation of phenomena at deeply buried interfaces at the microscopic scale by photoemission.

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## **Chapter 6: Review**

In this part, we will summarize the results of studies made during this thesis.

Previous studies [2-4] (see Chapter 1 part VI) have shown that the use of an effective inelastic scattering cross-section and an effective IMFP improve significantly the accuracy of inelastic background analysis in the case of complex stacks containing materials with different cross-sections and IMFPs.

It appeared that in these cases, many combinations of individual cross-sections together with effective IMFP have to be tested to find the optimal values. As the variation of the depth distribution can result in very small variations on the modeling which are very difficult to determine by visual inspection, a bot (to fully investigate the parameter ranges) and an error calculation (to evaluate the accuracy) were implemented. The bot was created during the previous thesis but it was significantly enhanced to reduce the calculation time from 3h down to 18 min for 1500 modelings. The original error calculation was changed for an area error calculation on a controlled range of the spectrum together with a calculation of the mean deviation. A semi-automated procedure was set to determine the best matching between the measured spectrum and the calculated spectra of different inelastic background modeling made for the various depth distributions.

In Chapter 2 [76], we investigated the use of such a reference spectrum in order to add another criterion, the scale factor, to test the accuracy of the method in a more concrete context. We studied unannealed HEMTs with Ta/Al contact with varying thicknesses of Al and Ta layers (see Fig. 62). We performed high resolution TEM measurements of the different layer-thicknesses (see Fig. 62):



Figure 62: Structure of the samples and TEM determination of the layer thicknesses [76].

A Ta reference spectrum was created (Fig. 63(a) green curve), F(E), by subtracting of the inelastic background modeling from a bulk Ta measured spectrum. The subtracted spectra obtained from the inelastic background analysis on the four samples were then compared to this reference spectrum. The match between the two curves was evaluated by the scale factor which is the ratio of the areas of the two peaks. The depth distribution was varied until the scale factor is 1.00 in addition to a perfect visual match of the shape. The Ta reference was found to be very useful to assess the accuracy of the inelastic background analysis.



Figure 63: (a) Analysis of the Ta reference spectrum and creation of the reference F(E), (b) Comparison of the Ta 3p<sub>3/2</sub> subtracted spectrum from the Ta5/Al20 sample to the reference, the blue lines represent the region where the scale factor is calculated [76].

The inelastic mean free path (IMFP) used for these analyses was calculated as a weighted average over the values for each layer calculated with the TPP-2M formula [30], with a weight averaging corresponding to the proportions used in the cross-sections.

If depth distributions were analyzed for Ta using a Ta reference sample, we were not able to obtain a good reference for Ga and Al and these peaks were analyzed without a reference sample. Actually, we measured references for these two elements but we found that the structure of our reference samples was not representative of the materials in the studied samples.

Figure 64 shows the subtracted spectra compared to the reference for varying depth distributions giving a 1.00 scale factor.  $\varepsilon$  is the error and  $\sigma$  the mean deviation of the spectra from the reference. The different figures, (a), (b) and (c), present the results for different cross-sections and their associated IMFP. In each case, the best overall agreement is blue curve. In this example, it was very difficult to determine which combination of effective cross-section and IMFP gives the best result as each gives a scale factor of 1.00 with very close calculated error and mean deviation. However, by averaging the 3 results, we get a compatible result with the distribution obtained from TEM measurement.



Figure 64: Modeling of the Ta 3p<sub>3/2</sub> spectrum for the Ta5/Al20 sample with different blends of cross-sections for different depth distributions, each giving a scale factor of 1.00 by comparison to the reference spectrum. (a) Modelings with the 50%Al 50%Ta cross-section, (b) with the 67%Al 33%Ta cross-section and (c) with the 80%Al 20%Ta cross-section [76].

Table 9 shows the main results of Ta depth distribution analyses. On the right, results are shown for analyses with the use of a reference together with an effective cross-section or the 2 parameter universal cross-section. On the left, the results for analyses without use of a reference but with an effective cross-section are shown. This shows that the effective cross-section and IMFP gives a significantly better accuracy on the results than the universal cross-section (see Deviation from TEM column on Table. 9). Also the use of a reference spectrum provides results closer to the expected values.

This demonstrates that the use of an effective cross-section is a real improvement to the analysis when the stack contains materials with quite different cross-sections and IMFPs and permits to reach a deviation under 12.3% even for the deepest depth distribution. The use of a reference spectrum together with error and mean deviation calculations makes the analysis easier to perform since the goodness of the fit is not anymore determined only by a visual inspection but also with the help of mathematical criteria. It also permits to decrease the

uncertainty and improve the accuracy of the analysis. The results appeared closer with a general deviation from the expected depth distribution typically under 5%.

Sample	Layer	TEM measurement	Without reference		With reference			
			Quases with effective cross-section	Dev. from TEM	Quases with universal cross-section	Dev. from TEM	Quases with reference and effective cross-section	Dev. from TEM
Ta5/Al20	Ta	From 19.9 ± 1.5 nm	From $21.5 \pm 1$ nm	7.5%	From $22 \pm 1$ nm	10.5%	From 21± 0.5 nm	5.3%
		To 24.8 ± 1.9 nm	To $27 \pm 1.5$ nm	8.2%	To 26.1 ± 1.5 nm	5.2%	To 26.2 ± 1.5 nm	5.4%
Ta12/Al21	Та	From 21.4 ± 1.5 nm	From 22.5 ± 1.5 nm	4.9%	From $21 \pm 1$ nm	1.9%	From 21.6 ± 0.5 nm	1%
		To 33.5 ± 2 nm	To 35 ± 2 nm	4.3%	To 26.4 ± 1.5 nm	21%	To 34.2 ± 1.5 nm	2.1%
Ta5/Al40	Та	From 39.9 ± 3 nm	From 35±5 nm	12.3%	From 34±5 nm	14.8%	From $38 \pm 5$ nm	4.8%
		To $45.1\pm3.5\text{nm}$	To $41\pm5nm$	9.1%	To $39\pm5nm$	13.5%	To $44.3 \pm 5$ nm	1.8%

Table 9: Comparison of the results with two methods of analysis with and without reference on<br/>the Ta buried layer [76].

This kind of analysis is time-consuming as many combinations of effective cross-sections and IMFPs are tested and each gives several possible depth distributions which have to be compared. But the use of an IMFP corresponding to the cross-section significantly decreases the number of tests and the use of a reference sample drastically simplifies the determination of the best modeling. This can be even truer for stacks with more than two different materials. However, the use of an effective cross-section and an effective IMFP is essential only if the materials present quite different cross-sections and IMFPs. Then the difficulty of the analysis depends on the structure of the sample and the materials composing them. In any case, a reference can be helpful to determine the best depth distribution and the atomic concentration in the layer. It has to be noted that it is not always possible to have a proper reference sample as the structure of a bulk sample can be very different from the one for a thin layer.

In Chapter 3, these improvements were then applied to study the atom diffusion during the annealing steps of HEMTs fabrication [91]. The inelastic background analysis results combined with core-level analysis were compared to sputter depth profile analyses and TEM analyses (see Fig. 65) to investigate the accuracy of the determination of elemental depth distribution induced by annealing.

In this study, the Ta(5 nm)/Al(40 nm) sample was investigated because the proportions of Ta and Al in this sample are the same as in the real HEMT device. Therefore, this sample is the most representative of the real devices. In order to obtain a good ohmic contact electrode, the stack was annealed twice for 300 s, first at 550°C and then at 650°C under nitrogen atmosphere. This is the procedure used in fabrication of the real devices.



Figure 65: TEM measurement of layer thicknesses on every step of the HEMT fabrication [91].

Figure 66 shows an example of analysis which was presented in Chapter 3 [91]. This is the complete inelastic background analysis of the sample after the first annealing at 550°C. The analysis was performed on Ta, AI and Ga spectra and the best modeling for each element is shown in the figure with the cross-sections used. The resulting depth distributions and the relative concentrations of each layer are shown for AI and Ga. For Ta, the absolute concentration has been found because we had the reference. The results are summarized in panel (d) together with TEM values. The analyses of AI and Ga were done with a different mode, i.e. "several buried layers" in the Quases-Analyze software, compared to the Ta analysis, i.e. "one buried layer" in the Quases-Analyze software. It permits to retrieve the different elemental phases of the depth distribution as a function of the relative atomic concentration of the element. These analyses could also have been done with the "one buried layer" mode as in paper [4]. In this case, we would have seen several overlaps between the depth distributions of elements and the results of thicknesses would not have been as accurate as with the "several buried layers" mode and the concentration would not have been found.

In this analysis, effective cross-sections were used with their corresponding effective IMFPs. The results were found to be coherent with sputter depth profiles, TEM analyses and corelevel analyses. The results were found with a deviation from TEM values typically smaller than 5% (see Table. 10).



Figure 66: Inelastic background analysis on the Al(40 nm)/Ta(5 nm) sample after the 550°C annealing (a) for Ta 3p<sub>3/2</sub> with a reference (b) for Al 1s (c) for Ga 2s, 2p (d) average results of the analysis and comparison with TEM measurements of Fig. 42 [91].

These analyses were performed as if the samples were unknown. The uncertainty on the determined absolute depths is  $\sim$  10%. The uncertainty on the absolute depths is about a factor of 2 larger than the uncertainty on the TEM values (see Table. 10).

Sample	Interface	TEM measurement	Inelastic background analysis	Dev. From TEM
Al40/Ta5 As deposited	Al Al + Ta	39.9 ± 3 nm	39.3 ± 5 nm	1.5%
	+ Ga	45.1 ± 3.5 nm	44.3 ± 5 nm	1.8%
	GaN	67.6 ± 4 nm	67.5 ± 10 nm	0.1%
Al40/Ta5 550°C annealed	Al Al + Ta		15.75 ± 1 nm	
	+ Ga	46.8 ± 2 nm	44.5 ± 5 nm	4.9%
	GaN	68.6 ± 4 nm	67 ± 10 nm	2.3%
Al40/Ta5 650°C annealed	Al Al + Ta		6.3 ± 1.5 nm	
	+ Ga	45 ± 2 nm	44.67 ± 5 nm	0.7%
	AIGaN GaN	68 ± 5 nm	66.5 ± 10 nm	2.2%

 Table 10: Comparison of the results from TEM and inelastic background analyses on every sample [91].

The absolute concentration of Ta has successfully been determined due to the availability of a reference for this element but only the relative concentrations have been found for AI and Ga as we did not have reference. A more accurate result could have been obtained for this sample if the absolute concentrations of AI and Ga would have been determined. AI and Ga references were recorded from an AI foil and a GaN reference. However, these references were found to not be well representative of the material structure in the sample maybe because of the different deposition technique or because of measurement conditions.

Thus, the recording of a reference can be important not only to make the analysis easier to perform but also to obtain accurate information about the absolute concentration in the layers.

However, the analysis remains delicate to perform without any rules to choose the input parameters. It is sometimes very difficult to choose between several resulting depth distributions obtained with different combinations of cross-section and IMFP that result in nearly the same spectra. It has also been observed that the best modeling can result in incoherent depth distribution compared to real values which is a problem when analyzing an unknown sample. This is why we investigated the choice of input parameters for analyses on well known samples in order to find a rule for the choice of input parameters.

Thus, in Chapter 4, we have first generated spectra using the Quases-Generate software [34] from references of Au (peak at 1152 eV kinetic energy) and Si (peak at 6099 eV kinetic energy). After that, we analyzed the spectra with Quases-Analyze software. The stacks were Au and Si buried layers under an overlayer of Ta, Al, polymer, Au or Si with varying thicknesses of both layers.

$$\mathbf{d}_{1} = \mathbf{Ta, AI, Si, Au} \quad \mathbf{t}_{B} \qquad IMFP_{eff_{-\frac{1}{2}}} = \frac{\frac{1}{2}t_{A}}{\frac{1}{2}t_{A} + t_{B}} \times IMFP_{A} + \frac{t_{B}}{\frac{1}{2}t_{A} + t_{B}} \times IMFP_{B} \qquad (56)$$

.

$$K_{eff_{\frac{1}{2}} = \frac{\frac{1}{2}t_A}{\frac{1}{2}t_A + t_B} \times K_A + \frac{t_B}{\frac{1}{2}t_A + t_B} \times K_B$$
(57)

For each sample, we investigated the results for the 4 combinations of IMFP and crosssection, K (see Fig. 67).  $K_{eff_{-1/2}}$  eq. (62) and IMFP<sub>eff\_1/2</sub> eq. (63) are the cross-section and IMFP, respectively, calculated for half the thickness of the buried layer as the electrons from the buried layer come in average from the middle of the layer.  $K_{eff}$  and IMFP<sub>eff</sub> are the crosssection and the IMFP, respectively, calculated for the full thickness of the buried layer. The combination giving the closest depth distribution to the expected one is  $K_{eff_{-1/2}}$  and IMFP<sub>eff\_1/2</sub> for all cases except for a polymer overlayer where IMFP<sub>eff</sub> is prefered.



Figure 67: start and end depth for the 4 combinations of effective input parameters and for the 96 samples.

This gives a rule for the choice of input parameters and a physical coherence between the IMFP, the cross-section and the resulting depth distribution.

Therefore, for a real-world analysis, the idea is first to determine approximately an effective cross-section where the elemental individual cross-sections to use can be determined from a survey XPS spectrum and according to the shape of the inelastic background. Then, the depth distribution and the proportions in the effective cross-section and effective IMFP can be adjusted according to this rule.

This is particularly important for materials presenting quite different IMFPs and crosssections. This is also valuable if the photon energy is sufficient to probe the full buried layer down to its lower interface. If not, the contribution of the buried layer in the effective IMFP and cross-section will be smaller than half the thickness of the buried layer in equations (62) and (63).

Previously, it was proved that inelastic background analysis can be used to create images of surfaces [104, 105]. In Chapter 5, we tested as a proof of principle for a future development of the technique, the combination of inelastic background analysis with Hard X-ray PhotoElectron Emission Microscopy (HAXPEEM). HEMTs with Ti/Al contact were

investigated. Figure 68 shows examples of Ti 1s spectra which can be extracted from small areas ( $10x10 \mu m$  for Fig. 68) on the sample.



Figure 68: HAXPEEM micro-spectra of the extended Ti 1s photoelectron energy-loss region and corresponding images at the core-level peak (3038 eV, right) and in the far inelastic energy loss region (2931 eV, left). The image field of view is 97 μm, and the size of the area of interest, 10\_10 μm. Both images are displayed within the same grayscale dynamic. The arrow on the energy-loss image points to the edge of the stripe [80].

Figure 69 shows an example of inelastic background analysis performed on the spectrum extracted from the pink region on Fig. 68.



Figure 69: Inelastic background analysis of the Ti 1s HAXPEEM energy-loss micro-spectrum from the pink region of Fig. 68 [80].

This analysis shows that it is possible to retrieve the depth distribution from small areas on a sample. This attests that a non-destructive and in-depth, depth distribution mapping can be performed with inelastic background analysis combined with HAXPEEM.

However, the area size has to be carefully chosen so as to not be too small in order to provide an acceptable signal/noise ratio for the spectrum.

## **Conclusion & Perspectives**

This work presents improvements of inelastic background analysis with Quases-software of HAXPES spectra to make the analysis easier to perform for complex stacks. Characterization of deeply buried layers and elemental diffusion in the electronic industry is very important for controlling and improving device fabrication.

Among techniques, XPS is well known for studying the chemical environment of elements and for its advantage to be non-destructive but limited to the surface analysis (~ 9 nm) with laboratory X-ray sources (< 1.5 keV). With the use of hard X-rays, the probing depth can be extended to 35 nm with synchrotron radiation. Combined with inelastic background analysis and using Quases-software, the elemental depth distribution can be determined from laboratory XPS spectra up to 20 nm depth and from HAXPES spectra up to 60 nm. With the recent advances on high energy X-ray sources for laboratory experiments [90], the depth distribution can be determined even deeper also for laboratory experiments.

The determination of the best matching between the calculated and the measured inelastic background spectra always present an accuracy issue with the numerous depth distributions presenting very close modeling.

### 1. Accuracy - use of a reference

Previously, the analysis was made with only a visual inspection as criterion for the goodness of the modeling. We implemented an error and deviation calculation as a handier criterion than visual inspection. Now, when a proper reference spectrum for the material can be measured, the intrinsic spectrum can be determined. This spectrum is compared to the resulting spectrum of the subtraction of the inelastic background modeling to the measured spectrum on the studied sample. This comparison is quantified by the scale factor which is an additional criterion to determine the best modeling and therefore the resulting depth distribution.

### 2. Additional information - elemental diffusion study

Previous studies of elemental diffusion were done with the "one buried layer" mode [4]. Elements were found to be in several different layers of different alloys without taking into account the inhomogeneous concentration of elements in the sample for the depth distribution determination. In this thesis, we used the "several buried layers" mode of the Quases-Analyze software and we were able to define the absolute concentration of elements

with a reference of at least a relative concentration because of a lack of a reference. This approach provides additional information about the layers and a more accurate and complete study of the sample.

### 3. Reliability and complementarities – comparison with other techniques

The determination of the result with error and deviation calculation makes the inelastic background analysis more reliable than with only a visual inspection. The samples were also studied by other techniques: TEM, sputtering depth profile, core-level analysis etc. The results were compared to those obtained from these techniques and found to be compatible but also complementary to these other characterization methods. This shows the reliability of the method and the advantage of the non-destructive aspect for complementarities.

### 4. Towards an easier analysis - rule for the choice of input parameters

The effective cross-section and effective IMFP are calculated from individual cross-sections and individual IMFPs of pure materials. Previously, the proportions of these individual crosssections and IMFP in the effective ones were randomly determined by testing many combinations.

In this thesis, it was shown that these input parameters are related to the depth distribution and should be calculated by considering half the thickness of the studied buried layer. This provides a rule linking the depth distribution, the IMFP and the cross-section, rule which decreases drastically the number of cases to be tested.

### 5. Perspectives - to 3D mapping

It was shown that the spectromicroscopy obtained with the HAXPEEM technique can provide spectra for small regions usable for inelastic background analysis from rather small regions on the sample surface. This can in principle provide non-destructive 3D mapping of the elemental distribution with a non-destructive method. However, to perform this kind of analysis, a large number of spectra from the analyzed region have to be treated. The analysis process is time-consuming before reaching a final elemental 3D mapping.

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#### Published papers:

- O. Renault, C. Zborowski, P. Risterucci, C. Wiemann, G. Grenet, C.M. Schneider, and S. Tougaard, *Quantitative spectromicroscopy from inelastically scattered photoelectrons in the hard X-ray range.* Applied Physics Letters. **109** (1), (2016).
- P. Risterucci, O. Renault, C. Zborowski, D. Bertrand, A. Torres, J.P. Rueff, D. Ceolin, G. Grenet, and S. Tougaard, *Effective inelastic scattering cross-sections for background analysis in HAXPES of deeply buried layers*. Applied Surface Science. 402, p. 78-85 (2017).
- C. Zborowski, O. Renault, A. Torres, Y. Yamashita, G. Grenet, and S. Tougaard, Determination of the input parameters for inelastic background analysis combined with HAXPES using a reference sample. Applied Surface Science. 432, p. 60-70 (2018).
- O. Renault, E. Martinez, C. Zborowski, J. Mann, R. Inoue, J. Newman, and K. Watanabe, Analysis of buried interfaces in multi-layer device structures with hard X-ray XPS (HAXPES) using a CrKα source. Surface and Interface Analysis, ((accepted 2018)).
- C. Zborowski, O. Renault, A. Torres, C. Guedj, Y. Yamashita, S. Ueda, G. Grenet, and S. Tougaard, *Quantitative determination of elemental diffusion from deeply buried layers by photoelectron spectroscopy.* Journal of Applied Physics, ((revision process 2018)).

#### Conference presentations:

- ECASIA'15 conference, poster: "Inelastic background analysis in HAXPES at the micron-scale", Granada, Spain (2015).
- HiSpear workshop, poster: "Study of annealing changes at buried interfaces by HAXPES combined with inelastic background analysis", Synchrotron SOLEIL, Saint-Aubin, France (2016).
- Journées Surface et Interfaces conference, poster: "Study of annealing changes at buried interfaces by HAXPES combined with inelastic background analysis", Marseille, France (2016).
- ECOSS'32 conference, oral: "Inelastic background analysis in HAXPES: application to deeply buried Ta/AI interfaces in advanced power devices", Grenoble, France (2016).
- AVS 63th conference, oral: "Inelastic background analysis of HAXPES spectra for device technology: A non-destructive tool for accessing deeply buried interfaces", Nashville, USA (2016).
- ECASIA'17 conference, oral: "Inelastic background analysis in HAXPES using a reference sample", Montpellier, France (2017).
- AVS 64<sup>th</sup> conference, poster: "Improvements of inelastic background analysis in HAXPES using a reference sample", Tampa, USA (2017).

# Appendix A: Comparison of characterization techniques

technique	TEM [106]	APT [107]	SIMS [108]
samples	Conductor	conductors and insulators	all elements
preparation	maximum thickness: 100 nm	tip	electron gun if charge effect
source	electrons (100 -200 keV)	laser impulsion	Cs, O or Ar ions (0.2 - 15 keV)
secondary beam	electrons	ions	emitted ions from material
detector	EDS	PSD (position and ToF)	ToF
invasive			no
destructive	yes	yes	yes
energy resolution	0.1 - 0.8 eV	1	1
in-depth resolution	0.2 nm	0.05 nm	0.5 nm
lateral resolution	0.2 nm	0.2 nm	100 nm
detection limit	1x10 <sup>19</sup> at/cm <sup>3</sup>	1x10 <sup>18</sup> at/cm <sup>3</sup>	1x10 <sup>12-16</sup> at/cm <sup>3</sup> 100 ppb
probing depth	1-10 nm		0.5 nm
Information	-imaging -crystalline structure -geometry, thickness -composition contrast	-3D mapping -chemical composition -concentration profile -quantitative analysis	-3D distribution mapping -in-depth concentration profile -composition, doping, diffusion

technique	Ellipsometry [109]	FTIR [110]	XRD [111]	XRR
samples	all elements flat surface	all elements transparent substrate Si	all elements except H	all elements except H
preparation	no	no	no	no
source	UV - visible (1-10 eV)	IR	X-rays (1.5 keV)	X-rays (1.5 keV)
secondary beam	UV-visible	IR	X-rays	X-rays
detector	photomultiplicator	thermal MCT	Vantec scintillator	Vantec scintillator
invasive	no	no	no	no
destructive	no	no	no	no
energy resolution	0.01 eV	1x10 <sup>-4</sup> at/cm <sup>3</sup>	5 % 75 eV	5 % 75 eV
in-depth resolution	0.5 nm	20 nm	3 nm	3 nm
lateral resolution	30 µm	1.5 µm	10 µm	10 µm
detection limit	10 <sup>15-16</sup> at/cm <sup>3</sup>	10 <sup>15-16</sup> at/cm <sup>3</sup>	1 % at ppm	1 % at ppm
probing depth	nm - µm	μm	3 nm - 10 µm	3 nm - 10 µm
Information	-material optical constants -thin film thickness -interfaces (roughness)	-chemical composition -chemical binding -surface chemistry and contaminations	-composition and structure measurement -Stress, grain size	-roughness, geometry, thickness, thermal expansion coefficient

technique	AES [112]	RBS [113, 114]	XPS [29, 115]
samples	Z<30 not for heavy elements and insulators	5 < Z < 50 heavy atoms sensibility	all elements except H and He
preparation	thickness < 1 cm	1	no
source	electrons (1 -10 keV)	light ions (MeV)	X-rays < 1.5 keV
secondary beam	Auger electrons	retrodiffused ions	photoelectrons
detector	MCD	surface barrier	MCD
invasive	no	localy	no
destructive	yes for depth profile mode	yes	yes for depth profile mode
energy resolution	0.02 - 0.2 % 2 eV	0.2 % 10 keV	0.02 % 0.42 eV
in-depth resolution	0.2 nm	2 - 20 nm	2 - 20 nm
lateral resolution	20 nm	100 µm	15 - 20 µm
detection limit	1x10 <sup>19</sup> at/cm <sup>3</sup> 0.1% at	1x10 <sup>19</sup> at/cm <sup>3</sup>	5x10 <sup>18</sup> at/cm <sup>3</sup> 0.1 % at
probing depth	3 - 5 nm	1 - 10 nm	1 - 10 nm
Information	-Auger mapping -chemical bindings -in-depth profile -quantitative analysis (composition, doping) -diffusion	-elemental analysis -in-depth profile -quantification (reference) -composition, doping, diffusion	-mapping -depth profile -chemical binding

## Appendix B: Complete table of analysis results of Chapter 4

			K <sub>eff</sub>	_1/2		K	eff
t Au	t Al	$IMFP_{eff\_1/2}$	% Au	% Al	$IMFP_{eff}$	% Au	% Al
10	40	24,93	11,11	88,89	23,80	20,00	80,00
10	60	25,37	7,69	92,31	24,53	14,29	85,71
10	80	25,60	5,88	94,12	24,93	11,11	88,89
30	40	22,87	27,27	72,73	20,89	42,86	57,14
30	60	23,80	20,00	80,00	22,10	33,33	66,67
30	80	24,34	15,79	84,21	22,87	27,27	72,73
50	40	21,45	38,46	61,54	19,27	55,56	44,44
50	60	22,60	29,41	70,59	20,55	45,45	54,55
50	80	23,31	23,81	76,19	21,45	38,46	61,54

		K	eff								
IM	FP <sub>eff_1</sub>	/2	IN	<b>ИFP<sub>eff</sub></b>		IM	FP <sub>eff 1/</sub>	2	IN	∕IFP <sub>eff</sub>	
start	end	t	start	end	t	start	end	t	start	end	t
45	57	1,2	43	55	1,2	44	55	1,1	41	52	1,1
67	80	1,3	64	77	1,3	65	77	1,2	63	75	1,2
88	101	1,3	85	98	1,3	86	98	1,2	84	96	1,2
43	77	3,4	39 75 3			42	71	2,9	38	69	3,1
65	104	3,9	60	102	4,2	63 94 3		3,1	58	90	3,2
86	128	4,2	80	124	4,4	84	117	3,3	78	111	3,3
41	100	5,9	9 35 97 6,2		6,2	41 92 5		5,1	35	85	5
61	120	5,9	9 55 138 8,3			61	111	5	54	104	5
81	138	5,7	74	145	7,1	81	130	4,9	74	130	5,6

					-	-		
-			K <sub>ef</sub>	f_1/2		К	eff	I
t Au	t Si	$IMFP_{eff\_1/2}$	% Au	% Si	$IMFP_{eff}$	% Au	% Si	stai
10	40	25,13	11,11	88,89	23,98	20,00	80,00	45
10	60	25,57	7,69	92,31	24,72	14,29	85,71	67
10	80	25,81	5 <i>,</i> 88	94,12	25,13	11,11	88,89	88
30	40	23,03	27,27	72,73	21,01	42,86	57,14	44
30	60	23,98	20,00	80,00	22,25	33,33	66,67	65
30	80	24,52	15,79	84,21	23,03	27,27	72,73	87
50	40	21,58	38,46	61,54	19,36	55,56	44,44	42
50	60	22,76	29,41	70,59	20,67	45,45	54,55	63
50	80	23,48	23,81	76,19	21,58	38,46 61,54		82

		К	eff					K <sub>eff</sub>	_1/2			
IM	FP <sub>eff_1</sub>	/2	11	<b>MFP</b> <sub>eff</sub>		IM	FP <sub>eff_1</sub> ,	/2	II	<b>MFP</b> eff		
start	end	t	start	end	t	start	end	t	start	end	t	
				54 1 2								
45	57	1,2	42,5	54	1,2	43	54	1,1	41	52	1,1	
67	80	1,3	3 64 76,5 1,3		65	76	1,1	62	73	1,1		
88	102	1,4	86	99,5	1,4	86	98	1,2	83	95	1,2	
44	80	3,6	39	75,5	3,7	42	71	2,9	37,5	67	3	
65	103	3,8	60	101	4,1	63	63 94 3,1		58	90	3,2	
87	132	4,5	80	122	4,2	84	117	3,3	,3 78 111 3,			
42	111	6,9	36	115	7,9	41	91	5	35	85	5	
63	145	8,2	55	130	7,5	61	110	4,9	55	115	6	
82	146	5 6,4 74 142 6,8		6,8	82	137	5,5	74	130	5,6		

						_	
			$K_{eff}$	f_1/2		К	eff
t Au	tPo	$IMFP_{eff\_1/2}$	% Au	% Po	$IMFP_{eff}$	% Au	% Po
10	40	29,96	11,11	88,89	28,32	20,00	80,00
10	60	30,58	7,69	92,31	29,37	14,29	85,71
10	80	30,92	5,88	94,12	29,96	11,11	88,89
30	40	26,98	27,27	72,73	24,11	42,86	57,14
30	60	28,32	20,00	80,00	25,87	33,33	66,67
30	80	29,09	15,79	84,21	26,98	27,27	72,73
50	40	24,92	38,46	61,54	21,78	55,56	44,44
50	60	26,59	29,41	70,59	23,64	45,45	54,55
50	80	27,62	23,81	76,19	24,92	38,46	61,54

		K	eff					K <sub>eff</sub>	_1/2		
IM	FP <sub>eff_1</sub>	/2	11	<b>VFP</b> eff		IM	FP <sub>eff_1/</sub>	/2	IN	<b>∕</b> IFP <sub>eff</sub>	
start	end	t	start	end	t	start	end	t	start	end	t
			43.5 54.5 1.1								
46,5	58	1,1	43,5 54,5 1,1			43	53	1	41	51	1
68	80	1,2	65	77	1,2	65	76	1,1	62	73	1,1
89,5	102	1,3	86,5	99	1,3	86	97	1,1	83	94	1,1
46	79	3,3	40	74	3,4	45	75	3	39	70	3,1
68	104	3,6	61	97	3,6	66 97 3,1		3,1	59	90	3,1
89,5	128	3,9	82	121	3,9	85	114	2,9	79	110	3,1
				,							
44	98	5,4	36	89	5,3	43	90	4,7	36	87	5,1
64	115	5,1	57	128	7,1	64	113	4,9	56	112	5,6
86	145	5,9	76	138	6,2	85	137	5,2	75	127	5,2

						_		K <sub>eff</sub>									K <sub>eff</sub>	_1/2		
			K <sub>eff</sub>	_1/2		K	eff		IM	$FP_{eff_1}$	./2	11	<b>MFP</b> eff		IM	FP <sub>eff_1/</sub>	2	II	<b>MFP</b> <sub>eff</sub>	
t Au	tTa	$IMFP_{eff\_1/2}$	% Au	% Al	$IMFP_{eff}$	% Au	% Al		start	end	t	start	end	t	start	end	t	start	end	t
10	40	18,55	11,11	88,89	18,06	20,00	80,00		39,5	49	1	38,5	47,5	0,9	40,5	50	1	38,5	48	1
10	60	18,74	7,69	92,31	18,37	14,29	85,71		59,5	69	0,9	58	67	0,9	59,5	68,5	0,9	58,5	67,5	0,9
10	80	18,84	5,88	94,12	18,55	11,11	88,89		79	88	0,9	78	87	0,9	80	89	0,9	80	90	1
30	40	17,65	27,27	72,73	16,78	42,86	57,14		40	69	2,9	38	69	3,1	40	68	2,8	38	68	3
30	60	18,06	20,00	80,00	17,31	33,33	66,67		61	92	3,1	58	89	3,1	60	88	2,8	57	84	2,7
30	80	18,29	15,79	84,21	17,65	27,27	72,73		80	107	2,7	78	109	3,1	81	111	3	77	105	2,8
50	40	17,03	38,46	61,54	16,08	55,56	44,44		39	87	4,8	36	84	4,8	39,5	91	5,2	36,5	89	5,3
50	60	17,53	29,41	70,59	16,64	45,45	54,55		59	106	4,7	56	117	6,1	59	104	4,5	56	112	5,6
50	80	17,84	23,81	76,19	17,03	38,46	61,54		79	125	4,6	75	125	5	79	123	4,4	74	110	3,6

								K <sub>eff 1/2</sub>						K <sub>eff</sub>					
_			K <sub>ef</sub>	f 1/2		K	eff	IN	1FP <sub>eff 1</sub>	./2	=	<b>MFP</b> eff	F	١N	IFP <sub>eff 1</sub>	/2	IMFP <sub>eff</sub>		F
t Si	t Al	IMFP <sub>eff 1/2</sub>	% Si	% Al	$IMFP_{eff}$	% Si	% Al	start	end	t	start	end	t	start	end	t	start	end	t
10	50	102,26	9,09	90,91	102,35	16,67	83,33	52	62	10	52	62	10	52	62	10	52	62	10
10	100	102,21	4,76	95,24	102,26	9,09	90,91	102	112	10	102	112	10	102	120	18	102	120	18
10	200	102,18	2,44	97,56	102,21	4,76	95,24	212	212 220 8			220	8	116	228	112	116	228	112
10	400	102,16	1,23	98,77	102,18	2,44	97,56	430 440 10			430	440	10	434	442	8	434	442	8
50	50	102,55	33,33	66,67	102,75	50,00	50,00	50	50 100 50			100	50	60	110	50	60	110	50
50	100	102,39	20,00	80,00	102,55	33,33	66,67	104	104 156 52		104	156	52	118	168	50	118	168	50
50	200	102,28	11,11	88,89	102,39	20,00	80,00	214	264	50	214	264	50	230	280	50	230	280	50
50	400	102,22	5,88	94,12	102,28	11,11	88,89	432	482	50	432	482	50	450	500	50	450	500	50
100	50	102,75	50,00	50,00	102,95	66,67	33,33	50	150	100	52	150	98	58	158	100	60	160	100
100	100	102,55	33,33	66,67	102,75	50,00	50,00	104	212	108	104	212	108	112	222	110	112	222	110
100	200	102,39	20,00	80,00	102,55	33,33	66,67	216	316	100	216	316	100	226	328	102	226	328	102
100	400	102,28	11,11	88,89	102,39	20,00	80,00	434 534 100			534 100 432 532 100 444 544 10				100	452	552	100	
Inf	100	102,50	67,35	32,65	102,50	80,49	19,51			11	LO			118					
Inf	200	102,50	43,86	56,14	102,50	60,98	39,02			20	208					23	30		
Inf	400	102,50	12,33	87,67	102,50	21,95	78,05	406						426					

								K <sub>eff 1/2</sub>								K	K <sub>eff</sub>			
			K <sub>ef</sub>	f 1/2		K	eff		IN	1FP <sub>eff 1</sub>	/2	I	MFP <sub>ef</sub>	f	IN	IFP <sub>eff 1</sub>	/2		<b>MFP</b> eff	f
t Si	t Au	IMFP <sub>eff 1/2</sub>	% Si	% Au	$IMFP_{eff}$	% Si	% Au		start	end	t	start	end	t	start	end	t	start	end	t
10	50	54,45	9,09	90,91	58,53	16,67	83,33		42	52	10	46	56	10	44	54	10	48	58	10
10	100	52,12	4,76	95,24	54,45	9,09	90,91		94	102	8	98	108	10	82	94	12	86	96	10
10	200	50,87	2,44	97,56	52,12	4,76	95,24		202	214	12	204	214	10	206	216	10	210	218	8
10	400	50,22	1,23	98,77	50,87	2,44	97,56		404	416	12	406	416	10	418	428	10	430	440	10
50	50	67,49	33,33	66,67	76,46	50,00	50,00		50	98	48	52	102	50	54	102	48	58	106	48
50	100	60,32	20,00	80,00	67,49	33,33	66,67		102	154	52	118	168	50	112	162	50	128	178	50
50	200	55 <i>,</i> 54	11,11	88,89	60,32	20,00	80,00		218	268	50	240	290	50	230	280	50	244	294	50
50	400	52,72	5,88	94,12	55,54	11,11	88,89		416	468	52	428	478	50	412	460	48	426	476	50
100	50	76,46	50,00	50,00	85,42	66,67	33,33		58	158	100	66	166	100	60	160	100	70	170	100
100	100	67,49	33,33	66,67	76,46	50,00	50,00		124	224	100	144	244	100	128	228	100	148	248	100
100	200	60,32	20,00	80,00	67,49	33,33	66,67		240	340	100	268	366	98	238	338	100	272	372	100
100	400	55 <i>,</i> 54	11,11	88,89	60,32	20,00	80,00		424	524	100	446	546	100	418	520	102	446	546	100
Inf	100	76,46	50,00	50,00	85,42	66,67	33,33			200			226			194			226	
Inf	200	60,32	20,00	80,00	67,49	33,33	66,67			295			320			305			335	
Inf	400	52,72	5,88	94,12	55,54	11,11	88,89			495			505			485			530	

					_			. [	K <sub>eff 1/2</sub>							K <sub>eff</sub>				
				K <sub>eff 1/2</sub>		K <sub>eff</sub>			IMFP <sub>eff 1/2</sub>			IMFP <sub>eff</sub>			IMFP <sub>eff 1/2</sub>			IMFP <sub>eff</sub>		
t Si	t Po	IMFP <sub>eff 1/2</sub>	% Au	% Po	$IMFP_{eff}$	% Au	% Po		start	end	t	start	end	t	start	end	t	start	end	t
10	50	123,03	9,09	90,91	121,39	16,67	83,33		42	52	10	42	52	10	34	44	10	38	48	10
10	100	123,97	4,76	95,24	123,03	9,09	90,91		104	114	10	102	114	12	106	114	8	102	114	12
10	200	124,47	2,44	97,56	123,97	4,76	95,24		204	214	10	208	218	10	204	212	8	210	220	10
10	400	124,73	1,23	98,77	124,47	2,44	97,56		398	408	10	398	408	10	404	414	10	404	414	10
50	50	117,78	33,33	66,67	114,18	50,00	50,00		54	104	50	56	104	48	60	110	50	64	114	50
50	100	120,67	20,00	80,00	117,78	33,33	66,67		108	158	50	102	154	52	110	160	50	106	156	50
50	200	122,59	11,11	88,89	120,67	20,00	80,00		208	256	48	212	260	48	214	264	50	212	262	50
50	400	123,73	5,88	94,12	122,59	11,11	88,89		398	450	52	394	444	50	406	456	50	404	454	50
100	50	114,18	50,00	50,00	110,57	66,67	33,33		54	154	100	52	152	100	56	156	100	60	160	100
100	100	117,78	33,33	66,67	114,18	50,00	50,00		116	218	102	114	214	100	124	224	100	128	230	102
100	200	120,67	20,00	80,00	117,78	33,33	66,67		228	328	100	220	320	100	238	340	102	224	324	100
100	400	122,59	11,11	88,89	120,67	20,00	80,00		404	506	102	398	498	100	412	512	100	418	514	96
200	100	114,18	50,00	50,00	110,57	66,67	33,33			114			110			116			114	
100	200	120,67	20,00	80,00	117,78	33,33	66,67			218			212			234			228	
50	400	123,73	5,88	94,12	122,59	11,11	88,89			424			416			436			432	

					-				K <sub>eff 1/2</sub>						K <sub>eff</sub>					
			K <sub>eff 1/2</sub>			K <sub>eff</sub>			IMFP <sub>eff 1/2</sub>			IMFP <sub>eff</sub>			IMFP <sub>eff 1/2</sub>			IMFP <sub>eff</sub>		
t Si	t Ta	IMFP <sub>eff 1/2</sub>	% Si	% Ta	$IMFP_{eff}$	% Si	% Ta		start	end	t	start	end	t	start	end	t	start	end	t
10	50	73,30	9,09	90,91	75,81	16,67	83,33		44	58	14	46	60	14	42	56	14	46	60	14
10	100	71,87	4,76	95,24	73,30	9,09	90,91		94	102	8	96	104	8	90	100	10	92	104	12
10	200	71,11	2,44	97,56	71,87	4,76	95,24		196	206	10	198	208	10	190	204	14	196	204	8
10	400	70,71	1,23	98,77	71,11	2,44	97,56		402	412	10	404	414	10	404	412	8	406	414	8
50	50	81,32	33,33	66,67	86,83	50,00	50,00		46	98	52	52	102	50	50	98	48	54	104	50
50	100	76,91	20,00	80,00	81,32	33,33	66,67		96	146	50	100	152	52	94	144	50	102	152	50
50	200	73,97	11,11	88,89	76,91	20,00	80,00		186	236	50	194	244	50	180	234	54	188	238	50
50	400	72,24	5,88	94,12	73,97	11,11	88,89		398	448	50	416	466	50	392	442	50	402	452	50
100	50	86,83	50,00	50,00	92,33	66,67	33,33		48	148	100	50	152	102	46	140	94	48	148	100
100	100	81,32	33,33	66,67	86,83	50,00	50,00		100	202	102	102	210	108	102	204	102	110	214	104
100	200	76,91	20,00	80,00	81,32	33,33	66,67		198	298	100	204	306	102	210	312	102	210	318	108
100	400	73 <i>,</i> 97	11,11	88,89	76,91	20,00	80,00		398	498	100	402	502	100	398	496	98	398	508	110
500	100	93,91	71,43	28,57	97,84	83,33	16,67			100			100			100			98	
200	200	81,32	33,33	66,67	86,83	50,00	50,00			228			244			234			240	
100	400	73,97	11,11	88,89	76,91	20,00	80,00			412			418			420			426	