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Probing Depth of Soft X-ray Absorption Spectroscopy Measured in Total-electron-yield Mode

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Two series of experiments on well-characterized systems were performed to examine the probing depth of soft x-ray absorption spectroscopy (XAS) measured in total-electron-yield (TEY) mode. First we measured the Ni 2p_{3/2} absorption spectra of Ni(100) covered with Tb as a function of the overlayer thickness. Secondly we recorded the O 1s absorption spectra of Ta₂O₅ films produced by controlled anodic oxidation of Ta foils as a function of the oxide thickness. The mean probing depth (MPD) was found to be much shorter than previously assumed (for O 1s, only 1.9 nm). The relative importance of those cascade mechanisms that lead to the electron current measured in TEY is discussed.

INTRODUCTION

The purpose of this paper is to contribute to the rather scarce knowledge about the probing depth of soft x-ray absorption spectroscopy (XAS) measured in total-electron-yield (TEY) mode. Traditionally, XAS measurements were made in transmission mode, i.e. by measuring the intensity of the x-ray beam before and after the transmission through a thin film.¹ This method of measurement is very well suited for hard x-rays, where the mean absorption lengths are long and the production of thin films is not problematic. However, for soft x-rays with energies of <2 keV the mean absorption lengths near the threshold may be very short. A few tenths of a nanometre is typical but in some cases, like the rare earth (RE) M_{4,5}-edges, characteristic absorption lengths as short as 1.5 nm have been calculated.² Such short absorption lengths set impossible requirements for the production of free-standing and pinhole-free thin films. Thus, since the recognition in 1972³ that the yield of electrons from a sample was proportional to the x-ray absorption cross-section, it has become normal to measure soft XAS in diverse photoyield modes.⁴ The only restriction on the use of photoyield methods is that the escape depth of the particles

being detected must be short by comparison to the mean absorption length.

At the present time the most commonly used photoyield mode for XAS involves the detection of all electrons emitted by the sample. However, one may also use fluorescence yield,^{5,6} energy-selected electron yield (partial electron yield)^{7,8} or even ion yield.⁹ It is known⁹⁻¹¹ that the mean probing depth (MPD) for fluorescence yield is >total electron yield > partial electron yield > ion yield. However, very little quantitative information exists on the value of the MPD for the TEY method. Indeed, very little literature exists on the mechanism controlling the probing depth of XAS in TEY mode and the only substantial paper that we are aware of is that of Erbil *et al.*,¹² which we consider below.

Until recently the general consensus of opinion was that the MPD of XAS in TEY mode was ~20–50 nm. However, several observations lead us to believe that this estimate was in many cases much too high. Such observations include:

- (1) Failure to observe saturation effects in TEY measurements of RE metals and compounds where we know that the mean absorption length at the RE M_{4,5}-edges can only be a few nanometres.² This does not meet the basic precondition for yield measurements that the absorption length must be much larger than the escape depth of the particles being detected.
- (2) The sensitivity of our spectra to surface contamination was too high to be compatible with an MPD of 20–50 nm.

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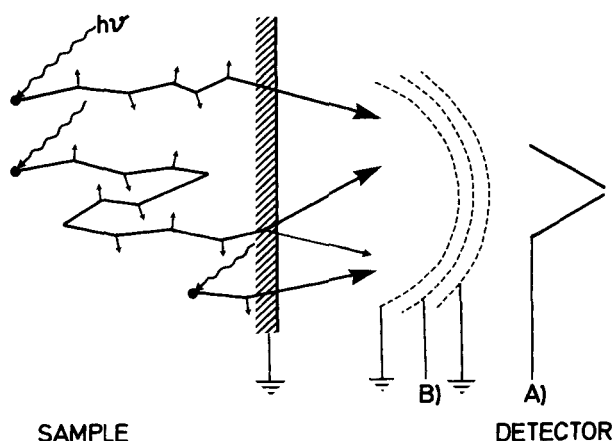


Figure 1. Schematic layout of the detection system and of the electron cascade processes.

- (3) In work on monolayers, and even submonolayers, of RE the signal was too high when compared to that of bulk RE for an MPD of 20–50 nm to be tenable.
- (4) We became aware of the little known paper of Esteve *et al.*,¹³ whose quantitative measurements indicate that the MPD of soft XAS in TEY mode was only 1 nm at the $M_{4,5}$ -edges of La and Gd.

These indications were so strong that we felt compelled to get more data on the MPD of soft XAS taken in TEY mode. To that end we adopted two approaches, namely to monitor the intensity of the Ni 2p XAS signal of an Ni(110) substrate covered with Tb as a function of the overlayer thickness and to monitor the O 1s XAS signal from a Ta_2O_5 overlayer produced by controlled anodic oxidation of Ta foils as a function of the oxide thickness. Our final conclusion will be that the MPD of soft XAS measured in TEY mode is indeed often very short (~ 2 nm). We will then discuss what has to be done in order to provide the quantitative information that already exists for photoemission^{14,15} and the same level of physical understanding that exists for XPS and AES.^{16,17}

EXPERIMENTAL DETAILS

In this paper we report the results of two separate series of experiments. In the first experiment we used a Knudsen cell to evaporate Tb onto an Ni(110) single-crystal surface cleaned by repeated cycles of sputtering and annealing. The thickness of the Tb overlayers was measured using an oscillating quartz balance (one Monolayer (1 ML) ~ 0.53 nm). We chose this system because it is known to grow homogeneously in a layer-by-layer mode and because interdiffusion is not important at room temperature.¹⁸ The Ni 2p XAS signal was measured using the double beryl crystal monochromator at beam line SA-22 in super-ACO.¹⁹

In the second experiment we used Ta_2O_5 films produced by controlled anodic oxidation of Ta foils with a thickness accuracy of better than 10%.^{20,21} These oxides are grown to such a high quality that they have become the standard for measurements of sputter depth profiling.^{20,21} The films are very stable against further

oxidation for thickness above 2 nm. Nevertheless, as an additional precaution we kept the foils in a vacuum before the measurements. The O 1s edges of these samples were measured using the SX700/I monochromator in BESSY.²²

In both experiments we used the same electron detection system, which is illustrated schematically in Fig. 1. The set-up consisted of three insulated grids placed in front of a channeltron. In standard operation the spectra were recorded with the grids and the front end of the channeltron set to earth. In some experiments a positive potential was applied to the front end of the channeltron to enhance the detection efficiency for low-energy electrons.

RESULTS AND INTERPRETATIONS

Tb on Ni(110)

The Ni 2p_{3/2} x-ray absorption spectrum of clean Ni(110) is shown in Fig. 2. As expected the intensity of the Ni peak decreases as Tb is evaporated onto the surface but the shape of the peak remains essentially unchanged. Thus we take the peak height as being representative of the XAS signal, normalizing the intensity to the background in the pre-edge region. This normalization procedure is equivalent to the usual photon flux normalization because the Tb edges occur at higher energies and do not influence the background at the Ni edge.

In Fig. 3 we show the coverage dependence of the Ni 2p_{3/2} peak height for the Tb/Ni(110) system (1 ML ~ 0.53 nm). We observe that the signal intensity falls very rapidly with increasing Tb coverage, and it is less than half the value of pure Ni after < 2 ML (~ 1 nm) of Tb has been evaporated. This fact indicates that the MPD of soft XAS-TEY in this system is comparable to that found in XPS. This is a surprising result but it is actually in agreement with the results of Esteve *et al.*¹³ The precise functional form of the decay of the signal strength with coverage is unknown. In particular, Erbil *et al.*¹² have shown that non-exponential decay can be expected for hard x-rays, i.e. Beer–Lambert behaviour should not be assumed *a priori*. However, we note that

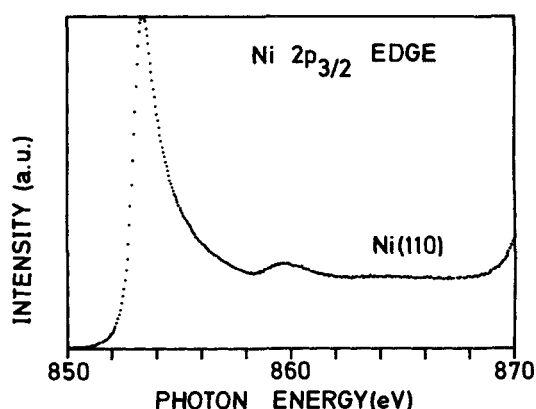


Figure 2. Ni 2p_{3/2} x-ray absorption spectrum of a clean Ni(110) surface.

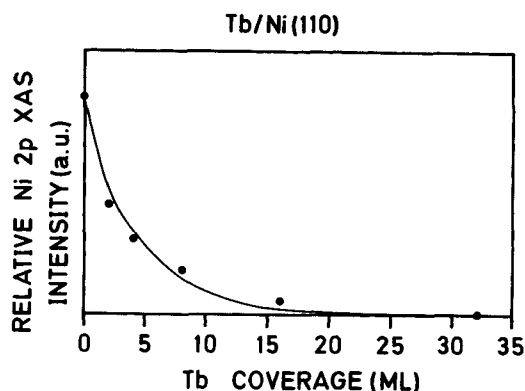


Figure 3. Relative Ni $2p_{3/2}$ peak height of the Tb/Ni(110) system as a function of Tb coverage (dots); exponential interpolation (solid line).

in this particular case the exponential interpolation shown in Fig. 3 follows the experimental points reasonably well. The approximate value of MPD obtained from the interpolation is 2.5 nm, which is in agreement with the results of Esteve *et al.*¹³

We also monitored the Tb intensity as a function of thickness and the results were consistent, with a similar MPD. However, in this case the normalization procedure based on the ratio peak/pre-edge intensity leads to distortions because the Tb peaks are mounted on the background of the Ni peaks. The artifact is caused by the decrease in pre-edge intensity at the Tb peaks as the signal from the Ni substrate is attenuated by the Tb overlayer.¹⁸

Thin Ta_2O_5 films

Here, we extend our study of the MPD in soft XAS-TEY to the case of insulator materials, namely the O 1s edge of thin Ta_2O_5 films. The purposes of this extension are twofold: to obtain more data in order to support the finding made in the Tb/Ni(110) system; and to investigate the influence of a large bandgap on the MPD. We show below that a similar value of MPD is obtained in this case, supporting the previous finding in Tb/Ni(110).

To cover all the possibilities we studied samples with an overlayer thickness in the range 2–120 nm. The spectra were taken within one injection cycle of the BESSY storage ring and with the same set of monochromator and detector parameters in order to avoid systematic errors. In addition, the spectra were taken many times to ensure reproducibility and consistency. In these particular experiments the front end of the channeltron was biased positively to enhance the detection efficiency for low-energy electrons. The spectra were divided by the electron current in the ring to obtain a relative normalization.

The O 1s x-ray absorption spectrum of the 120 nm sample is shown in Fig. 4. We note that the spectra taken for all the different thicknesses have the same form. This indicates that in all cases we probe a well-defined slab of stoichiometric oxide and no interdiffusion takes place. Based on this fact we take the O 1s x-ray absorption intensity to be proportional to the relative edge jump. First we measured films of 8, 16, 30,

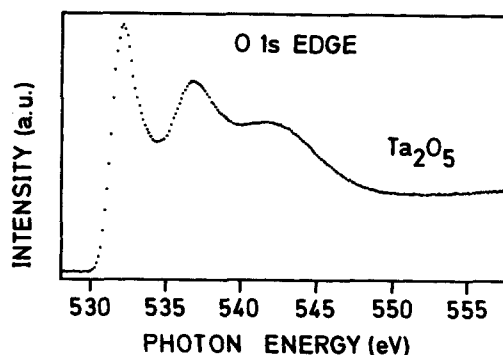


Figure 4. O 1s x-ray absorption spectrum of a 120 nm Ta_2O_5 film.

60 and 120 nm, but the spectra were exactly the same in all cases. This indicated that the MPD in this system was < 8 nm, so we decided to study thinner films of 2, 3, 4, 5 and 8 nm.

The relative O 1s edge jump as a function of the oxide thickness in the second series of films is shown in Fig. 5. As a null reference, and to avoid the possibility of spurious signals, we check that no O 1s absorption was observed in a clean Ta foil. We observe in Fig. 5 that the relative O 1s intensity saturates very rapidly and remains approximately constant for oxide films of > 5 nm. The dependence of the signal intensity as a function of the oxide thickness indicates again that the MPD is indeed very short. As in the case of Tb/Ni(110), we used an exponential interpolation to derive a value of 1.9 nm for the MPD in Ta_2O_5 (see Fig. 5).

DISCUSSION

We have found a value of 2.5 nm for the MPD of soft XAS-TEY at the Ni $2p_{3/2}$ edge of Tb/Ni(110) and a value of 1.9 nm at the O 1s edge of Ta_2O_5 . The possibilities of obtaining misleading results are extremely limited because we worked in well-defined systems. For the evaporation of Tb on Ni(110) the films were made *in situ* so oxidation effects can be ruled out. Diffusion of Tb in Ni could only lengthen the MPD and we find a result that is surprisingly short. Likewise, island formation will result in an anomalously high Ni signal after evaporation of thick Tb layers, and this is not seen. For

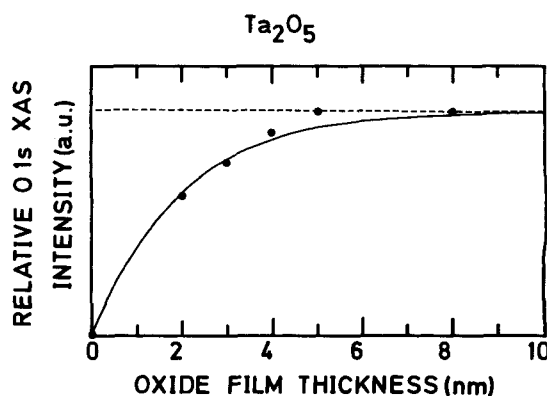


Figure 5. Relative O 1s edge jump of Ta_2O_5 as a function of the oxide thickness (dots); exponential interpolation (solid line).

the Ta₂O₅ layers the stability of the films has been discussed and further oxidation after anodic production of the films would produce a distortion in the results that is only minor in the present context. Taken together with other preliminary evidence,¹³ these results indicate that the MPD of soft XAS-TEY is very short and not of the order of tens of nanometres as is often assumed.

These values of MPD for soft XAS-TEY are only slightly longer than those found for XPS at comparable energies. For instance, at the Ni 2p_{3/2} level of Tb/Ni(110) (~ 870 eV) the values are: MPD_{XPS} = 1.8 nm¹⁵ and MPD_{XAS} = 2.5 nm; whereas at the O 1s level of Ta₂O₅ (~ 530 eV) the values are: MPD_{XPS} = 1.9 nm¹⁵ and MPD_{XAS} = 1.9 nm. This similarity with XPS is at first sight rather puzzling because the cascade processes that yield the signal in XAS-TEY are completely different. We must now consider such processes in an attempt to understand why these surprising results are observed.

First of all we note that the TEY signal in soft XAS studies consists of several contributions with different depth distributions. In general, the sum of these contributions might not show an exponential decay into the bulk, as shown by Erbil *et al.*¹² for hard x-rays. We now consider the role of the different contributions, starting with the primary processes and later analysing the effect of low-energy secondary electrons.

In XAS, a core electron is excited to unoccupied states above the Fermi level. This photoelectron may actually be detected if the final energy is above the vacuum level but is not central to the photoyield methods. More important are the one or more high-energy Auger electrons that result from the decay of the core hole. In what follows we restrict ourselves to the case of soft x-rays and we assume that there is only one important Auger decay. In Auger yield measurements one selects those Auger electrons that have not suffered energy losses and therefore detect a signal proportional to absorption events within an inelastic mean free path (IMFP) of the surface. This is the typical mode for adsorbates and SEXAFS studies.^{7,8} By contrast, in TEY we are interested in measurements with no energy selection, collecting all the electrons emitted by the sample. Then it becomes relevant to contrast the contributions of absorption events near the surface and deeper within the bulk, as is indicated schematically in Fig. 1.

The first contribution comes directly from the primary Auger electrons. These electrons may undergo many inelastic scatterings on their way towards the surface. The mean energy loss in each inelastic scattering depends primarily on the electron density of the material; typical values are of the order of 20 eV.^{23–26} As is illustrated in the top diagram of Fig. 1, the momentum transfer associated with these inelastic events is very small. Thus, a 1 keV electron might undergo an average of 50 forward scattering events before losing all its energy, which would suggest that the MPD in TEY-SXAS would be of the order of 50 IMFP (or 50–100 nm if we take an IMFP of 1–2 for 1 keV electrons). Of course, this estimation is far too naive.

There are several factors that have not been taken into account in the above analysis. Most obviously the estimate did not take into account the energy dependence of the IMFP. In particular, the IMFP has a

minimum of ~0.5 nm at lower energies. This effect alone will significantly shorten the estimate of the MPD made above. The excitation of core electrons by the primary Auger electrons contributes also to the decrease in the MPD, although this effect is not very important. Elastic scattering does not change the energy of the electrons significantly but results in a large transfer of momentum, as indicated in the middle diagram of Fig. 1. These events increase the path travelled by the electrons, decreasing even more the range of the primary Auger electrons. This is a factor seldom considered in any detail and unfortunately the relative weights of elastic and inelastic events is rather unclear.

The second contribution comes from low-energy secondary electrons produced in the inelastic scattering events. The role of these electrons can be very important, as pointed out by Erbil *et al.*¹² We note that the typical IMFP curve shows an upturn at low energy;^{14,15} this would suggest a large escape depth for low-energy electrons. We also note that the transport of low-energy electrons might be dependent on the material being studied, i.e. dependent on whether the material is a metal or a large band-gap insulator. In a metal, low-energy electrons can always attain thermal equilibrium by losing energy in Auger-like decay channels. In a material with a bandgap this is not the case, and an electron at the bottom of the conduction band may propagate larger distances because radiative decays are far less probable. This becomes especially significant in large bandgap insulators where the bottom of the conduction band is actually above the vacuum level, so in principle all the electrons excited in the conduction band can escape from the solid. However, we note that even electrons above the vacuum level may be reflected by the potential barrier at the surface.

In summary, the TEY signal consists of contributions from primary Auger electrons and low-energy secondary electrons produced in inelastic scattering events. The depth distributions of these contributions can be different and their sum might not decay exponentially into the bulk, but in general the MPD would be expected to combine the escape depth of both primary and secondary electrons. However, we note that both the similarity between MPD_{XAS} and MPD_{XPS} and the apparent exponential decay of the TEY signal can be rationalized by assuming that the MPD of soft XAS-TEY is dictated by the range of the primary Auger electrons. By contrast, the role of low-energy secondary electrons seems to be less relevant than previously assumed. This conclusion is also supported by the experimental fact that the MPD does not depend strongly on whether the material is a metal or a large band-gap insulator.

The reduced contribution of low-energy secondary electrons can be due to several factors, the most important being:

- (1) The IMFP of low-energy electrons might be shorter than suggested by the usual IMFP curves. In fact, the amount of experimental evidence in this energy region is very limited and recent results indicate that the IMFP is indeed short.²⁷
- (2) Reflection by the potential barrier at the surface can significantly reduce the escape probability of low-energy electrons. By contrast, the primary Auger

electrons are hardly affected by this potential and most of them go through.

- (3) The channeltrons are the most commonly used detectors in TEY and are, in general, quite insensitive to low-energy electrons. So even if a lot of secondary electrons are emitted by the sample they might not be detected very efficiently. In our case this effect was not important because, in some cases, the electrons were accelerated by a positive potential applied to the front end of the channeltron.

We are now investigating the influence of a negative potential in the intermediate grid to obtain information on the MPD of soft XAS measured in partial electron yield mode.

From the discussion above it is clear that the experimental results are rather puzzling. We hope that these results will stimulate more work in the field; the aim of such a work should be to understand the physical basis of TEY. In particular, the role of elastic scattering and the transport of low-energy secondary electrons needs further investigation.

SUMMARY AND CONCLUSIONS

In summary we performed two series of experiments to obtain more data on the MPD of soft XAS measured in TEY mode. Extreme care has been employed throughout the experiments to ensure working in well-characterized systems. In the first experiment we recorded the Ni $2p_{3/2}$ absorption spectra of an Ni(110)

single crystal covered with Tb as a function of the over-layer thickness. In the second we measured the O 1s absorption spectra of Ta₂O₅ produced by controlled anodic oxidation of Ta foils as a function of the oxide thickness. We used an exponential fit of the signal intensities as a function of the respective thicknesses to derive values of the MPD. We found values of the MPD that are only slightly larger than those found in XPS for the same levels. These values contradict strongly the general consensus of opinion.

The data can be rationalized by assuming that the MPD of soft XAS measured in TEY mode is dictated by the escape depth of the primary Auger electrons generated in the decay of the core hole. By contrast, the role of low-energy secondary electrons seems to be less important than previously assumed. We conclude that more work will have to be done to understand the cascade processes that initiate the electron current measured in TEY, especially the effect of elastic scattering and the transport of low-energy secondary electrons.

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