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Inelastic background analysis of HAXPES spectra: towards enhanced bulk sensitivity in photoemission†

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We report on quantitative inelastic background analysis in hard X-ray photoelectron spectroscopy at high excitation energy (12–18 keV) using the Tougaard method implemented with careful optimisation of the inelastic scattering cross section. Such a method enables the determination of the in-depth elemental distribution over depths up to 70 nm. We studied three parameters and investigate their influence on the results: the depth of the layer increases the uncertainty, the thickness and composition of the layer has an influence on statistics, and the excitation energy that must be chosen as a trade-off between high probing depth and low photoionization cross section. We show how this promising method can be used to follow diffusion of a 1-ML La layer after annealing a technologically relevant sample. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: inelastic background; Tougaard method; HAXPES; high-k; metal gate

Introduction

The reliable determination of buried elemental depth distributions in a non-destructive way is of importance in material science and especially in nano-device technology where thin active layers are covered by electrode overlayers up to 100 nm thickness. The main parameter limiting the probing depth in photoelectron spectroscopy is the inelastic mean free path (IMFP) that is the averaged distance travelled by an electron without suffering any energy loss. This IMFP value that may be obtained by the TPP-2M formula[1] increases with increasing kinetic energy of the photoelectron. Classical XPS is performed with the use of soft X-rays (the most used laboratory source is Al Kα with hv = 1487 eV); the probed depth is then around 3 nm.[2] The use of harder X-rays (a few keV nowadays) increases the IMFP, and analysis can be performed on core level spectra of buried layer up to a depth of 20 nm[3] but increases the uncertainty of the value.[4] The subshell photoionization cross section (σ) is also decreasing with increasing photon energy,[5] but nowadays, third generation synchrotron sources provide enough brilliance to ensure practical use of photoelectron spectroscopy at such high excitation energies. The use of inelastic background analysis extends the probing depth up to around eight times the IMFP, which turns into a 10 nm depth with soft X-rays.[6] Recently, it was shown that 50-nm probing depth can be accessible with hard X-rays[7] using this method. In the present paper, we report inelastic background analysis of hard X-ray photoelectron spectroscopy (HAXPES) spectra to analyse the diffusion processes of a ML-thick layer and investigate the effect of the burying depth and initial amount of substance on the results.

Experimental

The study is performed on different technologically relevant multi-layer ‘high-k/metal gate stack’ samples typically used in advanced complementary metal-oxide semiconductor device fabrication and having the overall structure detailed in Fig. 1. This structure includes a thick, top Si gate. The thickness of each layer is a nominal parameter limiting the probing depth in photoelectron spectroscopy. A second series of samples with a 50-nm-thick Si capping layer, the influence of high temperature activation annealing (1065 °C, N2 ambient, 1.5 s) typically used in device processing, on the La diffusion process is studied with a sample having significantly thicker active materials (HfSiON high-k layer: 11.5 nm; LaOx control layer: 1 nm) covered by the thinnest Si overlayer (20 nm). Hard X-ray photoelectron spectroscopy experiments were performed at the ID-32 beamline of the European Synchrotron Radiation Facility (Grenoble, France)[8] using photon energies of 12, 15 keV.
Inelastically scattered background analysis of HAXPES spectra

An overall energy resolution of 4.7 eV was achieved without any use of post-monochromator in order to obtain maximum photon flux to perform fast data acquisition. A SPECS PHOIBOS 225 (SPECS GmbH, Berlin, Germany) high resolution spectrometer allowing detection of photoelectrons with maximum kinetic energy of 15 keV was used. All spectra presented here were corrected for variation because of photon flux and spectrometer transmission. A clean Au foil was used to calibrate the energy scale by peak fitting the Au 4f7/2 for 12 keV measurement and by energy shift of the Ti 1s peak calculated IMFP takes into account corrections at high energy.[4]

Analyze software.[9] The method relies on knowledge of the IMFP and the inelastic scattering cross section,[10,11] and neglect surface excitations and elastic scattering, which are less present at these high energies.[12] For a specific sample and element, the calculated IMFP takes into account corrections at high energy[13] and is a weighted average of individual IMFPs according to the nominal thicknesses of the crossed layers; the estimated error of the resulting IMFP is lower than 15%. The inelastic scattering cross section can be either computed[13] or derived from Reflective Electron Energy Loss Spectroscopy (REELS) measurements[14] but needs to be carefully optimised.[7] Here, it is taken from REELS measurements of pure silicon at 10 keV that has been shown to be effective for this particular kind of samples.[7] The depth distribution is determined following a trial and error procedure by varying step-by-step the depth of both the top and bottom interfaces of the layer until a good match between the calculated and the measured background is obtained. The error is estimated by the depth yielding significant differences by visual inspection.

Results and discussion

Inelastic background analysis of deeply buried interfaces

Influence of the photon energy

Figure 1 shows the La 2p3/2 HAXPES spectra measured at 12, 15 and 18 keV photon energy. The spectra consist in the no-loss peak located at 5523 eV binding energy and of inelastic loss features extending over typically 150 eV to lower kinetic energy. When the photon energy increases, the IMFP and thereby the escape depth (3 × IMFP) increases; but at the same time, the photoionization cross section decreases drastically.[5] These two quantities influence in opposite ways the intensity of both the no-loss peak and the inelastic signal above the background at higher kinetic energy. At 12 keV, the no-loss peak is not detected because, with a calculated IMFP of 10.3 nm, the escape depth is still much lower than the thickness of the Si overlayer. A closer look at 17 eV below the position of the no-loss La peak shows another peak due to a primary bulk plasmon loss in the silicon overlayer.[13] With background analysis, it could be possible to probe the whole La buried layer; however, the background region around 5450 eV is not flat due partly to the poor signal to noise ratio and partly to the tail with loss features originating from the Ti 1s peak at 4966 eV binding energy,[15] which may introduce limitations in the inelastic background analysis. In the spectrum at 15 keV, the corresponding IMFP is 15.5 nm; and the no-loss peak can be clearly seen because the escape depth is close to the overlayer thickness. Also, the inelastic background signal to noise ratio is now better and not affected too much by the decreased photoionization cross section. At 18 keV, the very low intensity of the no-loss peak is due to the decreasing photoionization cross section despite an escape depth of nearly 60 nm (IMFP of 19.6 nm); also, at this particular energy, the intensity is lower because of beamline setup. The best signal/noise and IMFP/σ ratios ensuring to probe and analyse in a suitable way the ML-thick La buried layer is therefore found at the intermediate energy of 15 keV, which is the excitation energy used in the following. Therefore, the accessible information contained in the no-loss peak is valid up to ~45 nm, whereas the inelastic losses features can be used to extract in good conditions the in-depth distribution at larger depths. Therefore, the optimised photon energy must be a trade-off between the escape depth and the photoionization cross section, both affecting the signal to noise ratio of the inelastic background in HAXPES.

Analysis of the diffusion of the deeply buried La layer

In Fig. 2, the La 2p3/2 core levels and loss spectra at 15 keV are displayed before and after annealing of the sample. We see clear...
changes in the inelastic background shape, along with the attenuation of the no-loss peak, before and after annealing, indicating a diffusion of La deeper below the surface. In the following, these changes are analysed quantitatively using background analysis.

Figure 2 shows the best modelling of the La 2p3/2 inelastic background region before (upper panel) and after (lower panel) annealing at 1050 °C for both samples with a 50-nm-thick (left panel) and a 30-nm-thick overlayer (right panel). Overall, the inelastic background is well reproduced. Below the no-loss peak, the first plasmon is also well accounted for. At first sight, this is unexpected because the intensity from intrinsic plasmon excitations will still be present after background correction, which only removes the extrinsic excitations. However, photoexcitation of the La 2p3/2 peaks takes place in the La layer and therefore it does not have contribution from the intrinsic Si plasmon excitation; the full intensity at the Si plasmon loss peak is therefore extrinsic, and i.e. it is entirely caused by the transport of the La 2p3/2 photoelectron through the a-Si overlayer. The depths and error estimation of the top and bottom interfaces of the La layer determined from the modelling by the trial and error process are summarised in Table 1. Before annealing, the depth distribution of La is found to extend over 2 and 4.5 nm for 30- and 50-nm-thick capping, respectively. The expected 0.4-nm-thick La layer is consistent with these results, within the error bars. The depth of the top interface is determined as 41 and 57.3 nm, respectively, in good agreement with the nominal values of 36.5 and 56.5 nm also confirmed by direct measurements by electron energy loss spectroscopy performed in a transmission electron microscope.[7]

The results also show very similar trends regarding the annealing effect on both samples. In both cases, the annealing induces lanthanum diffusion toward the Si substrate down to 71 nm for both 30- and 50-nm samples as determined by the depth of the bottom interface; this effect is actually expected to happen up to the SiON/HfSiON interface in the processing of such gate stacks samples. For the 50-nm-thick capping, these results are in good agreement with a preliminary Auger depth profiling experiment showing a thin La layer located at 61 nm before annealing[7] and diffusing up to 70 nm after annealing (not shown). The present model also shows a smaller depth of the top interface after annealing that would highlight an upward La diffusion, inside the Si gate, however not seen from the Auger data. Thus, possible artefact in the analysis should be responsible for this arising from the very small amount of La (<1 nm) diffusing during the annealing process, as will be discussed after. The variations on the interface positions have different effects on the changes of the modelled inelastic background; a small change of the top interface...
interface depth increases drastically the intensity around 17 eV below the no-loss peak (the energy of the first plasmon); a clear difference can be made between two different top interface positions with a good precision, whereas the same change of the bottom interface gives a smaller change in the intensity around 100 eV below the no-loss peak. This increases the difficulty to make the distinction between two different bottom interface depths. For these reasons, the error is lower for the top interface than for the bottom interface; but it is not clear at this point how both interfaces are affected by the burying depth of the La layer. In the next section, we tentatively clarify this issue.

**Influence of overlayer thickness and amount of substance**

**Overlap thickness**

We now focus on the effect of the burying depth of the La layer on the determination of the depth distribution. We have performed background analysis of the La 2p3/2 inelastic background on HAXPES spectra at 15 keV for samples capped with a 20-nm-thick Si overlayer and have compared the results with what was found for 30- and 50-nm-thick overlayers (Table 1). We observe a strong influence of the overlayer thickness on the analysis: indeed, the determined La depth distribution is much narrowed, and thus more accurate, when the burying depth is decreased with a thinner overlayer.

The top and bottom interface positions are overestimated compared with the expected depths for all samples presented; this is likely because of uncertainties in the IMFP values used for the analysis, without excluding elastic electron scattering effects (which is neglected in this analysis). Also, the choice of the inelastic scattering cross section derived here from REELS measurements of pure Si despite being suitable for the analysis does not correspond exactly to the real composition of the overlayer. When decreasing the burying depth of the layer, the small change on depth distribution performed by the step-by-step process (for both top and bottom interface) gives a stronger modification of the inelastic background. It is then easier to see differences between two modelled backgrounds; therefore, the error on the interface position decreases when decreasing the overlayer thickness. While performing background analysis, the supposed 0.4-nm-thick lanthanum is found to be 4.5, 2 and 1 nm thick for the 50-, 30- and 20-nm samples, respectively. The difference between the expected and modelled thickness is mainly dominated by the low statistics of the spectra and the error of the determined bottom interface depth. However, for all three samples, a 0.4-nm-thick layer is compatible within the estimated error bars of the analysis.

**Effect of the initial amount of substance**

Figure 3 displays HAXPES spectra of the two samples showing improved signal intensity for the thick La layer by increasing the amount of substance (AOS). The two spectra show different behaviours depending on the AOS, the two samples being different only for their thicknesses of the LaOx layer (0.4 and 1.0 nm) and HfSiON layer (1.7 and 11.5 nm). The Si 1s no-loss peak has the same intensity (not shown here) for both samples confirming that overlayer thicknesses are comparable. At 15 keV, the HfSiON layer is not within the 3-IMFP range (IMFP calculated at 8.3 nm) for the thick sample, but very intense Hf 2s,p no-loss peaks and background distortions are seen. This HfSiON layer is more visible, despite its location under the LaOx layer, through Hf 2s,p peaks that have higher photoionization cross section than the La peaks and through higher AOS.

The inset in Fig. 3 shows the La 2p3/2 region, where the increased thickness of the La layer yields an increased intensity of the no-loss peak and a much better signal to noise of the inelastic background. Modelling of depth distribution for La in the thick layer sample gives a top interface located at 43.2 nm and a bottom interface at 45.4 nm below the surface. The overestimation of interfaces positions from the surface is again possibly attributed to the choice of the IMFP, elastic electron scattering and inelastic scattering cross section. The lanthanum thicknesses modelled are now closer to the expected value, for the thick sample where a 2.2-nm-thick lanthanum layer is found with an expected thickness of 1 nm and for the thin layer sample where the analysis gives a 1-nm-thick La layer (expected value of 0.4 nm). The AOS has a strong effect on the estimated error; both the top and bottom interface position errors are decreasing with increasing AOS.

**Conclusion**

We report on the first use of inelastic background analysis of HAXPES spectra using the Tougaard method in order to determine the depth distribution of elements buried up to 71 nm below the surface and to quantitatively study the diffusion due to annealing. We have investigated three parameters: the
influence of the layer thickness, which decreases the uncertainty of the interfaces positions; the chosen excitation energy, which should be a compromise between escape depth and photoionization cross section; finally, we found that the depth of the layers play a crucial role for the sensitivity of the method (the closer to the surface, the lower the error). We have shown that even with low statistics in the HAXPES spectra, the background analysis method is suitable to determine elemental depth profiles of ML-thick layers in technologically relevant samples and can be used to follow diffusion before and after an annealing process.

References