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XPS for Quantitative Analysis of Surface Nano-structures

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X-ray photoelectron spectroscopy (XPS) is one of the most widely used techniques for surface analysis. In the technique, which has been applied by industry for more than 30 years, atom core electrons are excited by soft X-rays and the kinetic energy of the emitted electrons is measured. Peaks occur corresponding to the binding energy of the core electrons and their position gives therefore direct identification of atoms. Since the inelastic mean free path for electrons in the energy range studied (typically ~ 0.1 to 1.5 keV) is 0.5 – 3 *nm*, the peak intensity originates from electrons excited from atoms that are within a 2-5 *nm* thin surface layer. The core electron binding energy varies slightly depending on the chemical environment of the atom, and this is used to get information on the chemical bonds. Scanning XPS has been increasingly more used in the past decade driven by substantial improvements in lateral resolution. The interpretation of XPS has largely been based on simple peak intensity measurements and this strongly limits the quantitative accuracy of XPS. The depth resolution of XPS has usually been done by ion-etching the surface. In the past decade, significant advancements has however been done in the development of improved algorithms for quantitative XPS and non-destructive atom depth distribution analysis in the 0-10 *nm* depth range [1].

Lateral resolution

The lateral resolution in XPS-mapping has in general been inferior to scanning techniques based on electrons or ions partly because these are easier to focus to a small spot-size and partly because of a low photoelectron yield. Improvements have been done by new designs of the X-ray source and the electron energy analyzer and the resolution has improved gradually from ~1 *mm* resolution 20 years ago to ~ 3 μm today. With the construction of the third generation synchrotron radiation sources, which provide very intense photon beams it is now possible to get better than 100 *nm* resolution and this is expected to be further reduced to better than 5 *nm* in the near future [2].

Depth resolution.

Since the electron inelastic mean free path is ~1*nm*, the XPS signal attenuates strongly with the depth on the nano-meter scale. It is this property that makes XPS interesting and powerful because it gives the technique its high surface sensitivity. However this is also the source of the high uncertainty in quantitative interpretation of XPS unless it is accounted for. The fundamental problem is illustrated in fig.1 which shows spectra for different depth distributions of Cu in a Au matrix. Due to the attenuation, the Cu2p XPS-peak intensity from all four different surface morphologies is exactly identical although the surface compositions are very different. Quantification based on the peak intensity alone is thus subject to a large error. However, the energy distribution in a wider energy range below the peak depends critically on the depth distribution of atoms. These are electrons that originate from the peak but lose energy on their way out of the solid. It is then very easy to distinguish between the spectra in a 50 eV energy range on the low kinetic energy side of the peak. Much more accurate quantification can therefore be achieved if the dependence of the peak shape on the surface structure is taken into account. The problem was basically solved by developing models for the detailed analysis of the energy distribution of emitted electrons leading to algorithms summarized in [1]. The validity of these algorithms have been extensively tested experimentally and found to be able to determine both the quantitative amount of atoms as well as their in-depth distribution within the outermost ~ 10 *nm* of surfaces [1]. Practical application of these algorithms has increased after ready to use software

packages were made available [3] and they are now used in labs worldwide. Fig.2 shows a practical example of such analysis. These software packages are easy to use but they need operator interaction. They are not well suited for automatic data processing and there is a need for simplified strategies that can be automated and also used in e.g. XPS-imaging where the huge amount of data hinders manual data analysis. For this purpose, a new algorithm that automatically takes the XPS-peak attenuation effect into account was recently developed [4]. The algorithm is less accurate than those in [1] but it is substantially more accurate than using peak intensities and it is well suited for automation.

These advanced algorithms are now increasingly used for quantitative XPS analysis of surface nano-structures. In the talk we will discuss several practical examples and we will also discuss how data analysis automation might be implemented in practical XPS-mapping in the near future.

References

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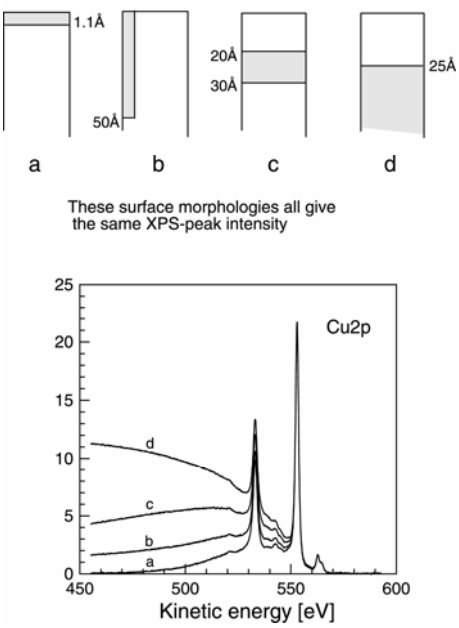

Fig.1 Four widely different surface structures of Cu atoms in Au that give identical XPS peak intensities.

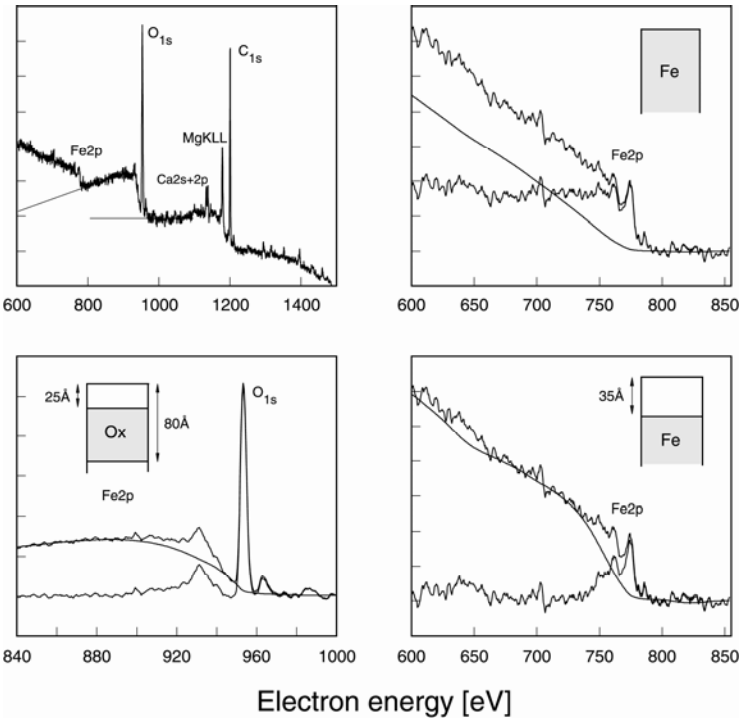

Fig.2 XPS of an oxidized iron surface. By analysis of the distribution of electrons on the low energy side of the peaks the nano-structure can readily be determined.

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