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New Reference Material for Imaging XPS (X-ray Photoelectron Spectroscopy) Instrument Characterization

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Abstract:
Reference materials without variations in topography are essential for the characterization of imaging XPS (X-ray Photoelectron Spectroscopy) Instruments. Therefore a new fabrication process for this kind of zero-topography reference material was developed at PTB and resulted in first prototypes. The fabrication process and first measurement results will be presented in this paper.

Key words: Imaging XPS, Reference material, topography free, micro technology

Introduction

Imaging XPS has great potential to address the requirement of surface analytical technology to deliver combined information about the lateral topography and the chemical composition of nano-structured components. For the improvement of reproducibility, precision and accuracy of imaging XPS instruments reference materials tailored to the special demands of those methods are required. Currently no appropriate reference materials for imaging XPS are available, but are highly demanded for quality control in various production processes.

In XPS the kinetic energy of photoelectrons is analyzed to identify the chemical composition of the first few nanometer of the sample. Photoelectrons are produced by irradiating the surface with X-rays to transfer energy to the inner shell electrons of atoms (typically K and L shell). They are emitted with a specific residual kinetic energy for the different elements. The energy analysis of these electrons is used to identify the chemical composition at the surface. For imaging XPS instruments, topographical steps at the edges of different materials disturb the lateral calibration of the measurement (Fig 1). This is mainly caused by two effects: First, the photoelectrons are emitted through the side of these edges, interfering with the electrons emitted from the surface. Secondly, at the edges electronic fields with high gradients are present, deflecting the electrons and hence leading to an erroneous lateral imaging.

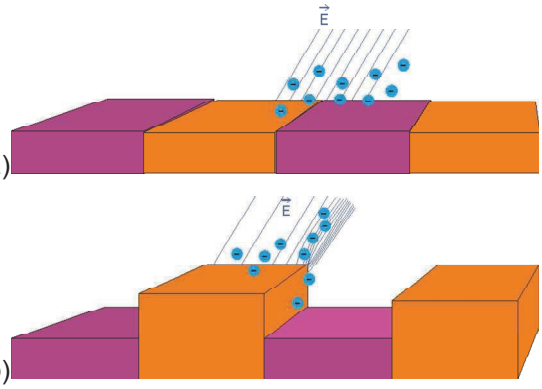

Fig. 1. a) Ideal structure (zero-topography) for reference material for imaging XPS. b) The image is disturbed by photoelectrons, which are emitted from the side walls and high gradients of the electric fields caused by edges

The same problems appear in imaging AES. Auger electrons are not only excited within the spot area of the electron beam but also in regions next to it caused by electron scattering and/or backscattering. This results in several distortion effects in AES mappings and line scans like the intensity enhancement at rims observed in Fig. 2.

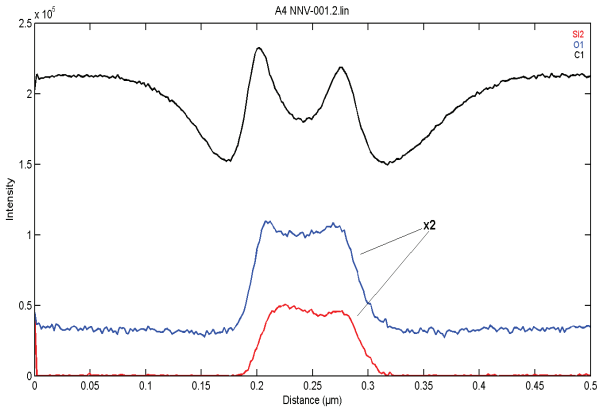

Fig. 2: AES line scans (C KLL (top), O KLL (middle) and Si KLL (bottom) across a nanoparticle (~ 80 nm diameter) deposited on a conventional TEM carbon coated copper grid.

The valleys of the carbon signal at the particle rims in Fig. 2 are caused by the particle which shields the carbon Auger electrons from the carbon film. The enhancement of the carbon signal at the projected particle rims cannot be attributed to higher carbon concentrations but to well-known edge and topographical effects [1, 2, 3]. This also holds true for the intensity enhancements of silicon and oxygen Auger emission at the projected particle rims.

To overcome these difficulties a new type of lateral resolution standard is required where the surface structure is without topography variations.

According to ISO 19319:2013 [4, 5] the ideal straight edge in chemical surface analysis is a sharp chemical gradient between two constant levels of concentration of a chemical constituent without height differences in the related topography. Currently no appropriate reference materials for imaging XPS are available, but highly demanded for its successful introduction to production. Therefore a new approach was undertaken at PTB to produce such a reference material.

Basic challenges of the fabrication process for zero-topography reference material

Basically thin films structured with lithography are well suited to produce test pattern for all kinds of resolution reference materials [6]. In Fig 3 the principle of the fabrication process for such a structure is depicted.

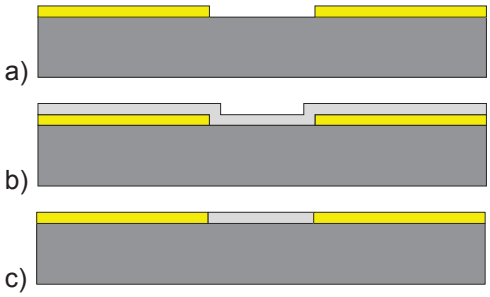

Fig. 3. Idealized fabrication process for a zero-topography reference material, a) deposition and structuring of the first material partner, b) applying of the second material partner, c) structuring of the second material partner

The first material partner is applied to the substrate and then structured using photo- (or e-beam) lithography and etching technologies. (Fig. 3 a). Then the second material partner is applied to the substrate and again is structured using the described technologies (Fig. 3 b/c). Two main issues occur with this process:

- Misalignment of the two film layers
- Varying film thicknesses

In reality it is impossible to adjust the two layers without any misalignment. The misalignment results in a step on the one side and a gap on the other of the structure (Fig 4) leading to the disturbing effects described earlier.

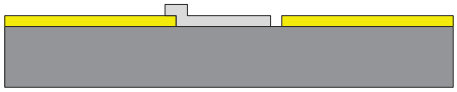

Fig. 4. Edges occur due to misalignment

The second issue occurring with this process is depicted in Fig 5. Due to different film thicknesses, which always occur using deposition processes, a step between the two materials results. Therefore a different approach has to be made for producing a zero-topography material contrast.

Fig. 5. Edges occur due to different film thicknesses

Initial fabrication process

The initial fabrication method is based on a two stage lift off process using photoresist as the first and aluminum as the second sacrificial layer. The process flow is described in Fig. 6. It resulted in the first prototypes for zero-topography reference material with lateral material contrast. The problem with this process is that the topography strongly depends on the layer thickness of two components (gold and

silver). The control of layer thickness is a critical point resulting in a low yield and makes this process not very robust and therefore unsuitable to produce this type of reference materials on an industrial scale. Therefore a different approach has been undertaken and resulted in a new robust process for the production of a zero-topography reference material.

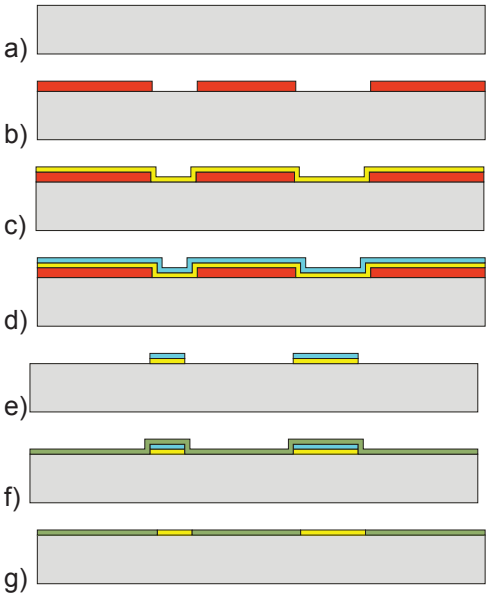

Fig. 6. Initial process flow for the production of a zero-topography reference material. a) base material is a <100> silicon wafer, b) spin on coating was used to apply photo-resist as sacrificial layer, c/d) Gold and Aluminum was applied by vacuum deposition, followed by a lift-off process (e). f) A silver layer with the same thickness like the gold layer was applied by vacuum deposition. g) As last step the Aluminum layer was etched resulting in a nearly zero-topography material contrast (max. 3-5 nm topography variations)

Advanced fabrication process

As base material a standard <100> silicon wafer with a silicon nitride layer was used. The first step was the application of the first composite of the material pair (chromium). This layer was structured using wet chemical etching techniques. Then the second part of the material composite was applied (aluminium). In an ongoing step a glass wafer (Pyrex) was attached to the Si wafer using anodic bonding. Anodic bonding is a well known fabrication process capable of attaching silicon oxide wafers to silicon wafers. It is a combination of a thermally and electrostatically induced wafer bond process [7]. During the bond process the wafer stack is exposed to a temperature of 300-400 °C. At this temperature the glass wafer starts softening which enables the material to level the topography caused by the underlying gold structures. As ongoing step the silicon wafer was removed using a wet chemical etching process (KOH). This etching process stops on the silicon nitride layer. As last step the silicon nitride layer was removed using a dry etch process. Since this process is equipped with end point detection the removal of the silicon nitride layer can be controlled very precisely. After the removal of the Nitride layer the structured material composite is freely accessible resulting in a material contrast with no topography variations.

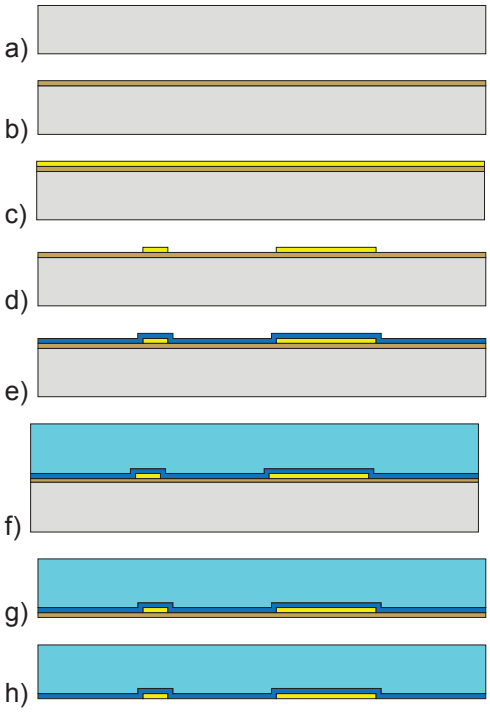

Fig. 7. Advanced process flow for the production of a zero-topography reference material. a) as substrate a standard <100> silicon wafer, polished on both sides was used, b) silicon nitride layer is applied as etch stop, c) chromium was applied as first part of the material composite by vaporization, d) the gold layer was structured using a lift off process, e) aluminum was applied as second part of the material composite, f) a glass wafer (Pyrex) was attached to the Si wafer by anodic bonding, g) the silicon wafer is removed by wet etching in KOH, i) the silicon nitride layer is removed using a dry etching process with end point detection

Fig 8 shows a microscopic image of the produced structure. Depicted is a Chromium structure with a width of 10 µm embedded in an aluminium matrix. It can be observed that the aluminium matrix is disturbed which is caused by the anodic bonding process. Nevertheless the transition region between the chromium and the aluminium is nearly defect free. For the future a defect free aluminium matrix is desirable.

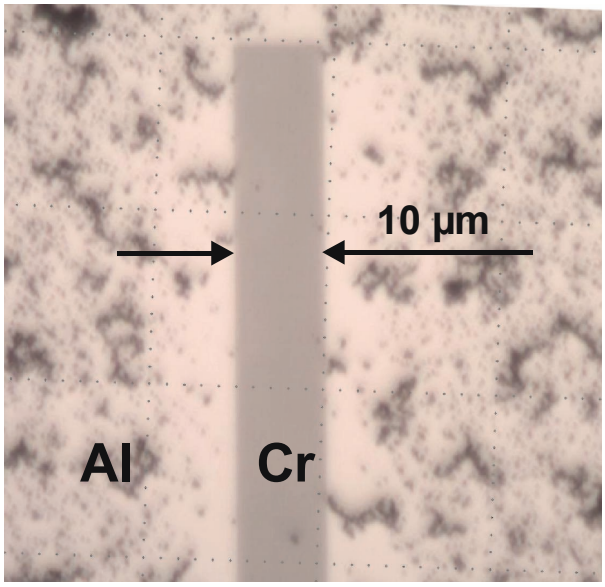

Fig. 8. microscopic image of the zero-topography reference material

AFM-measurements

As first test the structures were measured using an AFM (atomic force microscope) to characterize the topography of the transient region of the material contrast. Fig 9 shows the result.

A step of approximately 1.3 nm can be observed. The problem with AFM- as well as with the iXPS-measurements is that the sensor tip interacts with the atoms of the surface. Since the attracting forces vary with different materials, the observed step can also be caused by the different attracting force characteristics of tip and chromium compared to tip and aluminium. Also the gap of approximately 8 nm is probably caused by the phenomena described above. This shows another interesting potential of this type of reference material.

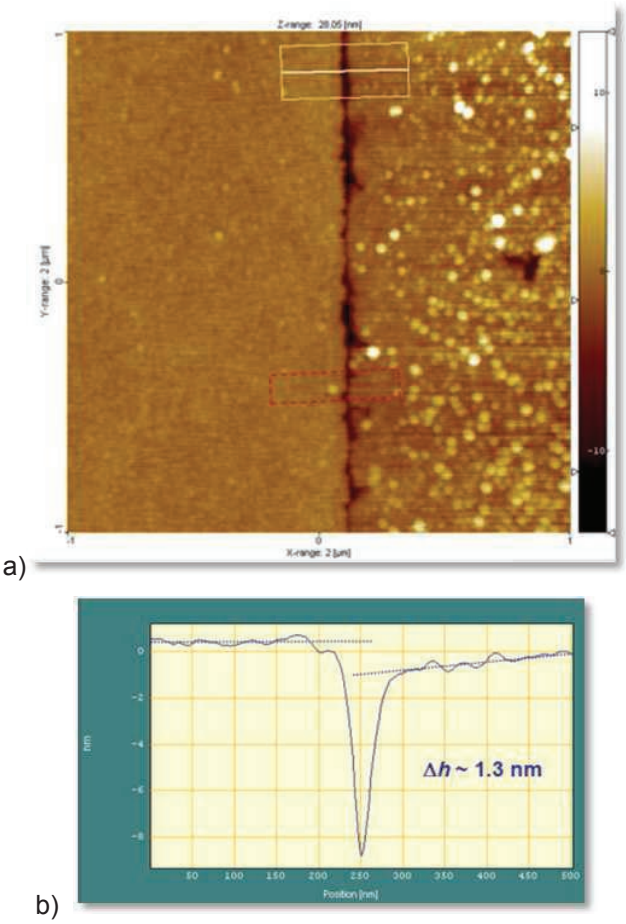

Fig. 9. AFM-measurement of the transient region between the aluminium and chromium areas. The observed step off approximately 1.3 nm may also be caused by the different attracting force characteristics of the materials causing a „virtual topography“

iXPS-measurements

XPS image measurements were carried out with an AXIS Ultra DLD electron spectrometer manufactured by Kratos Analytical, UK. XPS parallel images were recorded using monochromated Al Kα excitation at pass energies of 160 eV. The electron emission angle was 0 degree, and the source-to-analyzer angle was 60 degree. The binding energy scale of the instrument was calibrated following a Kratos Analytical procedure which uses ISO 15472 binding energy (BE) data. XPS Images were taken by setting the instrument to the imaging mode and the small area mode providing approximately a 330 µm×330 µm analysis area. Fig 10 shows an iXPS image of the produced structure. Depicted is a chromium structure with a width of 30 µm embedded in an aluminium matrix.

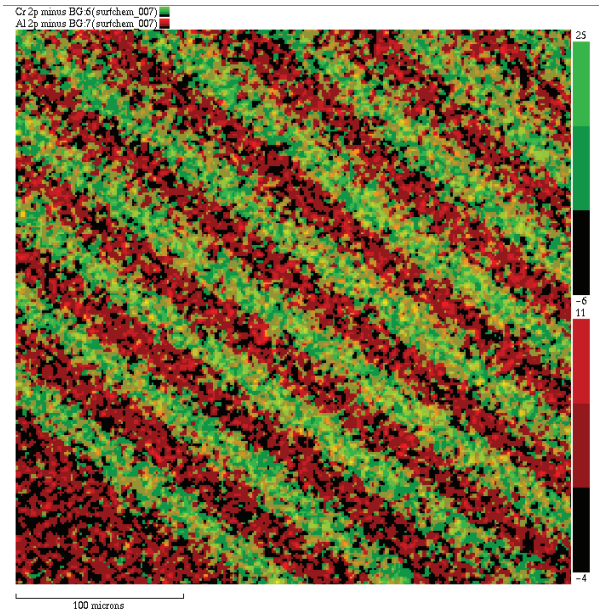

Fig. 10. XPS image of the produced structure

Conclusion

A new approach for the production of a zero-topography reference material for the characterization of imaging XPS- instruments was presented. The challenges of the production process are described and a robust fabrication process is reported. This new approach resulted in prototypes which were characterized using an atomic force microscope. The functionality of the produced prototype was validated through iXPS measurements.

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