Sputter-induced cross-contamination in analytical AES and XPS instrumentation: utilization of the effect for the in situ deposition of ultrathin functional layers

Uwe Scheithauer

Abstract Cross-contamination is observed on sample surfaces by Auger electron spectroscopy and X-ray photoelectron spectroscopy if multiple samples are mounted on one sample holder and a neighbouring sample was sputter depth profiling. During sputter depth profiling, sputtered material is deposited on inner surfaces of the instrument. In a secondary sputter process, which is due to species leaving the primary sputter target with higher kinetic energy, the previously deposited material is transported from the inner surfaces to the other samples mounted on the sample holder. This reflective sputtering is utilized to deposit ultrathin layers on sample surfaces for X-ray photoelectron spectroscopy binding energy referencing purposes and to build up ultrathin conductive layers to make possible Auger electron spectroscopy measurements on insulating samples.

Keywords Sputtering · Ion bombardment · Cross-contamination · Auger electron spectroscopy · PHI 680 · X-ray photoelectron spectroscopy · Electron spectroscopy for chemical analysis · Quantum 2000 · Reflective sputtering · Ultrathin metal layer deposition · Auger electron spectroscopy measurements on insulating samples · X-ray photoelectron spectroscopy binding energy referencing

Introduction

Sputter-induced cross-contamination, also denoted as a memory effect, has been discussed in the context of secondary ion mass spectrometry depth profile measurements [1, 2]. This article reports on sputter-induced cross-contamination observed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Since the elemental detection limits of AES and XPS are approximately 0.1 at% in favourable cases and the secondary ion mass spectrometry detection limits are below the 1-ppm level, it is not expected to see a memory effect in AES or XPS depth profile measurements. But if in modern equipment multiple samples are mounted at the same time on a sample holder, cross-contamination is observed on sample surfaces if other, neighbouring samples were sputter depth profiling before. This cross-contamination effect is investigated and simulated by an experiment. The experiment explains that the effect is a result of material deposited on inner instrument surfaces, which is sputtered by high-energy particles emitted by the primary sputter depth profiling. But this effect of reflective sputtering is not only troublesome in producing misleading analysis results. It is shown how it is converted into a powerful tool to deposit ultrathin conductive layers which make possible AES measurements on insulating samples or make it possible to deposit ultrathin metal layers on samples for XPS binding energy referencing purposes.

Experimental

For the measurements presented here, a PHI 680 AES microprobe and a Quantum 2000 XPS microprobe were
used, respectively. Both instruments are manufactured by Physical Electronics.

The PHI 680 Auger microprobe, an instrument with a Schottky thermal field emitter, has a lateral resolution of approximately 15–30 nm under optimum conditions [3]. The Auger microprobe is equipped with a differentially pumped Ar⁺ ion sputter gun. If a 30° sample holder tilt is used as here, the primary electron beam hits the surface of a flat sample under an angle of 30° relative to the surface normal. The Ar⁺ ion impact angle is approximately 45° relative to the surface normal in that case.

The Quantum 2000 is an XPS instrument with a focused primary X-ray beam. The spatial resolution of a Quantum 2000 XPS microprobe is achieved by the combination of a fine-focused electron beam generating the X-rays on a water-cooled Al anode and an elliptical mirror quartz monochromator, which monochromatizes the X-rays and refocuses them on the sample surface [4–6]. By scanning the electron beam electrostatically across the Al anode, the X-ray beam scans across the sample. Using a rastered X-ray beam, sample features are localized by X-ray-beam-induced secondary electron (SE) images. The best focused X-ray beam has a diameter of approximately 10 μm. Beam diameters up to 200 μm are selectable. Details of the quantitative lateral resolution are discussed elsewhere [7]. For flat-mounted samples as used here in a Quantum 2000, the incoming X-rays are parallel to the surface normal. In this geometrical situation, the mean geometrical energy analyser take-off axis and the differentially pumped Ar⁺ ion gun, which is used for charge neutralization, sputter cleaning and depth profiling of the samples, are oriented at approximately 45° relative to the sample surface normal.

The differentially pumped Ar⁺ ion guns of both systems have an identical design. To avoid neutral Ar atoms hitting the sample surface, it has an electrostatic beam deflection of approximately 5°. The ion gun has a floating column so that it can supply Ar⁺ ions with a kinetic energy of a few electronvolts and a current high enough to provide effective compensation of sample charging in XPS and to make possible AES measurements on electrically conductive features in insulating surroundings, respectively [8].

The PHI software program Multipak 6.1 was used for the AES and XPS data evaluation. In the case of quantification of measured peak intensities, it uses a simplified model where all detected elements are distributed homogeneously within the volume analysed. This volume is defined by the analysis area and the information depth of electron spectroscopies, which is derived from the mean free path of electrons [9]. With use of this quantification approach, one monolayer on top of a sample quantifies to approximately 10–30 at% depending on the sample details.

Sputter-induced cross-contamination

Sputter-induced cross-contamination became evident from unexpected measurement results. One of these unexpected results was from the analysis of a Si wafer surface. It is discussed and the effect is investigated systematically.

Unexpected XPS analysis results of a Si wafer surface

The aim of the analysis was to inspect the Si wafer surface after a cleaning process at the beginning of the front-end wafer processing. Pieces of a Si wafer were analysed by XPS. A small Au signal was detected at the Si wafer surface ‘as received’ (Fig. 1). Using tabulated sensitivity factors, one can estimate the amount of Au to be a few per cent of an atomic monolayer. Under usual circumstances, metal contamination in this early stage of front-end wafer processing is not present or expected. Therefore, this result has to be checked very carefully regarding any measurement artefact.

In Fig. 1 the insert shows the Quantum 2000 sample holder with all samples mounted. Besides two pieces of the cleaned Si wafer (light grey), two pieces of fully processed wafers (dark grey) with an Au (350 nm)/Ti (700 nm)/Al (approximately 400–500 nm) back-side metallization are mounted. For different reasons, depth profiles of the two back-side metallizations were measured first before analysing the cleaned Si wafer surfaces. When the analysis of the cleaned Si wafer surface was repeated on new pieces of the same cleaned Si wafers, Au was no longer detected. So it was proven that the Au signal measured on the surface of the cleaned Si wafer before was cross-contamination due to the sputter depth profiling of the Au/Ti/Al metallizations.

Fig. 1 X-ray photoelectron spectroscopy (XPS) survey scan of a Si wafer surface after a cleaning process. Unexpectedly, Au was detected. It is due to redeposition during sputter depth profiling of another sample mounted on the sample holder (see the insert).
Even though the sputter depth profiling of the back-side metallization was done through the whole Au/Ti/Al metallization layer stack, only Au was detected on the surface of the cleaned Si wafer. This is explained by the relative ionization cross-sections, which are 0.537, 7.91 and 17.12 for Al\(^{2+}\), Ti\(^{3+}\) and Au\(^{4+}\), respectively [10]. These values correspond to the overall sensitivity factors of the Quantum 2000 X-ray microprobe used by the data evaluation software program Multipak 6.1, which are approximately 0.26, 2.1 and 6.8 for Al\(^{2+}\), Ti\(^{3+}\) and Au\(^{4+}\). Hence Au is detected more effectively and the other elements are not detected in the measured spectrum (Fig. 1).

Systematic investigation of the sputter-induced cross-contamination in a Quantum 2000 XPS microprobe

Figure 2 summarizes the result of a systematic investigation of the sputter-induced cross-contamination. As the sputter target again the Au/Ti/Al back-side metallization was used. On both sides, pieces of a clean Si wafer were mounted. The metallization stack was sputtered by 2-kV Ar\(^+\) ions with an impact angle of approximately 45° relative to the surface normal. The sputtering was interrupted after 5, 10 and 30 min and ended after 130 min. After 130 min, the whole metallization system was sputtered away. At each interruption of sputtering and at the end, the Au cross-contamination on the Si pieces was measured as a function of the relative position with regard to the sputter crater. After a sputter time of 130 min, Ti was detected too. Figure 2 shows that the Au coverage on the Si increases with increasing sputter time. Furthermore, it shows that relative to the incoming Ar\(^+\) ions, the coverage in the forward direction is higher than that in the backward direction.

Analysis of inner surfaces of the instrument

During sputter depth profiling the sputter material is emitted into the half-sphere above the sample and is deposited everywhere on the inner surfaces of the instrument. The drawing in the upper part of Fig. 3 shows the geometrical situation in a Quantum 2000 XPS microprobe. In the half-sphere above the sample a lot of mechanical instrument components are present. These devices are the Al foil window of the X-ray source and its mechanical mounting, parts...
of the Ar⁺ ion gun and the electron energy analyser entrance. Together with the electron neutralizer, these devices are fixed to a solid metal block. The Al foil window has to be replaced from time to time owing to a decrease in X-ray intensity. This way one has easy access to the inner surface of the instrument, which is located very close to the sample. The lower part of Fig. 3 shows a used Al foil. In the exposed area the colour has changed. Figure 4 shows the results of an XPS depth profile measurement of the material deposited on the foil. As depicted, a lot of elements are detected in the contamination layer. These elements and their depth distribution record the history of past sputter depth profile measurements. With the ion dose used to remove the contamination layer, approximately 35 nm of the SiO₂ reference material could be removed. Since the sputter rates of metals are higher than the SiO₂ sputter rate [11, 12], presumably the geometrical thickness of the layer is greater. And of course, this deposited material explains the primary X-ray intensity decrease.

Principle of reflective sputtering

A reflective sputtering experiment was designed on basis of previous results. Figure 5 shows the principle of the experiment. On the sample holder we have the primary sputter target and a piece of clean Si wafer. Above both a Si reflector, again a piece of clean Si wafer, is mounted at a distance of a few millimetres. The primary target is sputtered by Ar⁺ ions, i.e. sputtered material is deposited on the Si reflector. This material, which was deposited previously on the reflector, is sputtered by primary Ar⁺ ions, which are reflected, and by sputtered species of higher kinetic energy, which are emitted from the primary target [13, 14]. Some of this secondarily sputtered material from the reflector is deposited on the piece of Si wafer. In summary, this way material is transported from the primary target to the piece of Si wafer by reflective sputtering.

The reflective sputtering experiment was done using a PHI 680 Auger microprobe. In a first sputter step, a primary Ag target was sputtered with 2-kV Ar⁺ ions for sputter time \( t_0 \). Then the primary target was replaced by Au and a clean piece of Si wafer was mounted below the Si reflector. In a second sputter step, the Au target was sputtered too, for the same time \( t_0 \).

The surface coverage with Ag and Au deposited on the Si reflector and the Si wafer was measured with a Quantum 2000 XPS microprobe because the detection sensitivity for both elements is higher using XPS instead of AES. The results are presented in Fig. 6. The measured Ag and Au XPS signal intensities are plotted as a function of the distance from the forward edge of the Si reflector and Si wafer, respectively. On both samples, the Ag and Au intensity decreases with the distance from the edge. On the Si reflector, signal intensities higher by a factor of approximately 5 were detected. The metal layer thickness is estimated to be approximately two to three monolayers on the reflector and approximately half a monolayer on the Si wafer at maximum.

These results show that Ag from a precoated Si reflector and Au are deposited on the Si wafer during the reflective sputtering of Au. In summary, this experiment is a perfect simulation of the observed sputter-induced cross-contamination process.

Application of reflective sputtering

In daily analytical work misleading results which are due to sputter-induced cross-contamination are avoidable. Therefore, on a sample holder with multiple samples, all surfaces ‘as received’ must be measured before any sputter depth profiling is done. But reflective sputtering is not only a cumbersome concomitant phenomenon of
sputter depth profiling. It rather can be converted into a powerful tool which introduces new approaches to electron spectroscopy measurements.

Use of an ultrathin conductive layer for AES measurements of an insulating sample

A recent article summarizes the approaches for how to analyse insulators with AES [15]. Using reflective sputtering adds a new method to solve this problem. The basic concept is the same one as is commonly used in electron microscopy. On top of a non-conductive sample a thin conductive layer is deposited. The thickness of the ultrathin conductive layer on top is restricted to a few monolayers only, since roughly only the topmost ten monolayers contribute to the signal of an Auger measurement and the contribution of each monolayer decreases exponentially with the depth [9, 16].

To demonstrate this approach, on the Auger instrument sample holder a Cu foil was mounted beside an Al₂O₃ ceramic sample. Then the Cu foil was sputtered by Ar⁺ ions. Using the inner surfaces of the Auger instrument as a reflector, in situ we deposited an ultrathin Cu layer on the surface of the ceramic sample. As defined by the incoming Ar⁺ ion beam, the Al₂O₃ ceramic sample was mounted in the forward direction relative to the Cu foil. As seen earlier, this gives higher deposition rates.

Figure 7 shows a comparison of the uncoated Al₂O₃ ceramic sample in the upper part with a coated sample in the lower part. The SE image of the uncoated sample depicts the typical behaviour of sample charging. Drastic changes of SE intensity are observed from the left to the right and from line to line according to the raster scan directions of the SE image. The Auger spectrum is completely distorted and cannot be interpreted. The SE image of the coated sample is fine and has submicrometre resolution. The Auger spectrum shows no serious distortions. Only between 145 and 195 eV does the spectrum show some distortions. Besides Cu, the elements C, O, Al and Si are detected. This result is comparable to an XPS measurement of the same sample. Using quantification as described earlier, one can estimate the Cu layer thickness to be approximately one to two monolayers.

First, from the measurement we see that ultrathin conductive metal layers make Auger measurements of insulators possible. But the measurement on insulating samples is something which modern XPS equipment does without any effort. So, second, it has to be pointed out that the metallization technique using reflective sputtering makes possible measurements on insulating samples with the much higher lateral resolution of an Auger instrument.
This approach of in situ metal deposition may fail depending on the interaction of the insulator surface with the deposited metal. If, for instance, the deposited metal atoms are mobile on the insulator surface, they may form three-dimensional clusters rather than a conductive film. In detail, such processes are dependent on the insulator bulk material, the insulator surface contamination, the kind of metal used and the operating temperature. In experiments using a thick insulating SiO2 layer, the deposition of several monolayers of Cu at room temperature did not result in the formation of a conductive layer, for instance. In any case, besides some unsuccessful attempts, reflective sputter deposition is a useful approach to measure insulators using the lateral resolution of Auger instrumentation.

Ultrathin metal layers for energy-referencing purposes in XPS measurements

For the energy-scale calibration of XPS instruments with a monochromatic Al Kα X-ray source, the Au 4f7/2, Ag 3d5/2 and Cu 2p3/2 peaks are used as binding energy references [17]. Reflective sputtering was utilized for this experiment with a Quantum 2000 XPS microprobe to deposit Cu and Au on the surface of an Al2O3 ceramic sample for energy-referencing purposes. The insert and the optical image in Fig. 8 illustrate the experimental set-up. Pure Cu and Au foils are mounted close together on the sample holder by a mechanical clamp. Both foils are sputtered simultaneously with a rastered Ar+ ion beam. This way Cu and Au are deposited on the surface of the Al2O3 ceramic sample via reflective sputtering. By the quantification routines of the Multipak software program, the amount of material deposited on the Al2O3 ceramic sample surface was estimated to be 1.2 at% Au and 0.5 at% Cu. So, on top of the sample we have metal layers within a submonolayer thickness range.

Figure 8 shows some peaks of a high-energy resolution measurement. Table 1 summarizes the results. The measured binding energy difference between Cu 3p3/2 and Au 4f7/2 is 0.118 eV smaller than the value given in ISO 15472 [17]. The results shown in the left binding energy column in Table 1 are the measured values shifted by 3.199 eV. For the results shown in the right column, a linear function was used, setting the Cu2p3/2 and Au 4f7/2 binding energies to the reference values of 932.62 and 83.96 eV, respectively [17]. The XPS microprobe used here is operated with a calibrated energy scale [18]. Over long periods a precision of ±0.3 eV is achieved on conductive specimens. From the elaborate effort done within the framework of energy-scale calibration, it is known that the precision of a single binding energy measurement is estimated to be approximately ±0.12 eV. Taking this precision into account, we find both energy-scale corrections are valid.

In the past, many attempts were made to deposit materials on XPS samples for reference purposes. For instance, Au was evaporated in a vacuum onto different materials and Au 4f7/2 was used for energy-scale adjustment [19]. With increasing amount of Au, slight binding energy changes are observed. For the system of Au on Ni, a lowering of the Au 4f7/2 binding energy of approximately 0.3 eV for a coverage below one monolayer has reported, for instance [20]. To avoid these energy shifts, which may be explained by a surface having only single Au atoms or small Au nanoparticles built from a few atoms on top, colloidal noble metal particles dispersed in a high-purity liquid matrix were used in an ex situ deposition process [21].

![Fig. 8](image_url) Some peaks of a high-energy resolution XPS measurement of an Al2O3 sample. The sample is coated with Cu and Au in the submonolayer range for energy-referencing purposes. The experimental set-up is shown in the insert. The position of the measurement area is marked.

| Table 1 | Peak binding energies after energy-scale correction |
|---------|--------------------------------------------------|
| Binding energy (eV) | Content (at%) |
| Al2p     | 74.12     | 74.06     | 6.7 |
| Au4f7/2  | 84.02     | 83.96     | 0.48 |
| Au4f5/2  | 87.69     | 87.64     |     |
| Si2p     | 102.51    | 102.46    | 0.7 |
| S2p      | 168.73    | 168.68    | 0.65 |
| Cl2p     | 199.13    | 199.09    | 0.49 |
| C1s, C–C | 284.78    | 284.75    | 69.8 |
| O1s      | 531.63    | 531.64    | 18.9 |
| Cu2p3/2  | 932.56    | 932.62    | 1.2 |
| Na1s     | 1,071.79  | 1,071.87  | 1   |
In summary and with regard to the achievable precision of a binding energy measurement, every deposition of the reference materials Cu, Ag and Au represents an improvement of peak binding energy estimation. Reflective sputtering has the main advantage that for this approach the hardware needed, a sputter ion gun, is already available in typical analytical XPS instrumentation. Since it is an in situ technique, binding energies can be recalibrated after sputter erosion of a sample simply by reflective sputter depositioning of reference materials on this surface.

**Summary**

Sputter-induced cross-contamination on sample surfaces is observed with the electron spectroscopy methods AES and XPS. This contamination is due to prior sputter depth profiling of other samples mounted at the same time on the same sample holder. In detail, this cross-contamination is described by two processes. Sputtered material from the primary sputter depth profiling is deposited on the surface of mechanical devices which are positioned near the sample. As sputtering continues, in a secondary sputter process previously deposited material is removed from these inner surfaces. The secondary sputter process is attributed to reflected primary sputter ions and sputtered material, provided that both species have high enough kinetic energy. In summary, the reflective sputtering deposits material on surfaces of other samples mounted on the sample holder during sputter depth profiling of one sample. To avoid misleading results in analytical AES and XPS work, all surfaces ‘as received’ must be measured first before any depth profiling is done.

But reflective sputtering is not only a cumbersome process. It can be converted into a powerful tool. With Auger instrumentation, ultrathin conductive layers can be deposited on insulating samples in order to make possible measurements of insulator surfaces with the lateral resolution of an electron beam. With XPS instrumentation reflective sputtering may be utilized to deposit ultrathin metal layers on sample surfaces for binding energy referencing purposes. Both applications are easily realizable by using the depth profile sputter gun and metal foils mounted near the sample.

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