APPLICATION OF TOF-LEIS AND XPS FOR SURFACE STUDIES

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ABSTRACT

In the contribution complementary experiments on analysis of solid surfaces using time-of-flight low energy ion scattering (TOF-LEIS) and X-ray photoelectron spectroscopy (XPS) are presented. The attention is paid both to analysis of surfaces and ultra-thin films (Si, Ag, Ga) modified or prepared in situ. The advantages of application of complementary in situ techniques to surface analysis are demonstrated.

INTRODUCTION

At the Institute of Brno University of Technology an UHV apparatus for ion beam-based deposition techniques has been developed. In addition to direct depositions of thin films by low energy ion beams, evaporation of ultra-thin films provided e.g. by an effusion cell under or without the assistance of low energy ion beams might be carried out.

A significant advantage of these UHV technological processes results from the fact that various in situ monitoring techniques can be applied and thus direct control over technological processes and properties of films improved. The apparatus possesses several analytical methods like low energy ion scattering (LEIS), secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning probe microscopy (STM/AFM). The presence of both technological and analytical techniques makes it possible to monitor sample parameters in situ. UHV conditions help to keep the surface contamination of samples at very low levels for time periods long enough to carry out a series of above mentioned surface analytical methods.

The apparatus produces focused ion beams of ultra low- and low energies (10^1 – 10^3 eV). Hence, the low energy ion beam can also be used for ion beam scattering experiments, generally known as LEIS. By this technique one can monitor in situ surface elemental composition and surface atomic structure of substrates and thin films. Due to the negligible penetration of low energy ions into a solid material, LEIS is considered an excellent surface analytical method giving us information about the *outermost surface layers* [1].

The interaction of the ion (called the projectile) with an energy equal to or higher than 10^2 eV, with a solid surface may be described within a significant accuracy as the sequence of the binary collisions between the projectile and the target atoms. Applying the energy and momentum conservation laws one is able to calculate the kinetic energy of the projectile after its collision with a target atom without any knowledge of the interaction potential. According to a simple formula this energy only depends on the masses of the projectile and target atom, the scattering angle and, of course, on the initial kinetic energy of the projectile [2]. Knowing the mass of the projectile, scattering angle and initial energy, and having measured the final projectile energy by means of an energy analyser (i.e. after projectile's collision), this formula makes it possible to find the mass of the individual surface atoms taking place in collisions. Hence, LEIS provides *qualitative elemental analysis* of surfaces.

For simplicity, inert ions, like He^+, Ne^+ and Ar^+, are applied in LEIS generally. From experiments it is known that nearly 100% of the scattered inert ions become neutralised during their collision with metallic targets [3]. This means that by measuring ion energy with an electrostatic energy analyser (e.g. hemispherical or cylindrical mirror analyser) almost all the scattered particles are lost for the LEIS technique. To avoid these signal losses, either electropositive alkali ions (where neutralisation is limited [4]), or Time-of-Flight technique (TOF) may be used to determine the particle energy [5].

To find the yields of individual atoms embedded on a surface, i.e. to carry out a quantitative surface analysis, one must know the differential scattering cross-section, which is fully determined by the interatomic potential between the projectile and the target atom [2]. Although different potential approximations (e.g. Molier and Biersack-Ziegler potentials [5], [6]) are applied in an ion energy range of 10^2 to 10^3 eV, it is difficult to determine surface concentrations of atoms. Two phenomena depending on surface concentration like neutralization of ions during scattering (lowering of detected ions) and geometrical screening are responsible for that. To estimate the yields of atoms on specific surfaces by LEIS, careful calibration taking into account matrix effects has to be carried out [7]. Therefore, LEIS is not generally considered a quantitative chemical surface analysis and it is advantageous to combine this technique with other, if possible, quantitative methods. In the contribution examples of complementary analysis of solid surfaces using time-of-flight low energy ion scattering (TOF-LEIS) and XPS are presented.

EXPERIMENTAL

Experiments were carried out in the technological and analytical UHV apparatus shown in Fig. 1. The LEIS experiments were run in a deposition chamber under an operational pressure in the order of 10^{-8} mb by the home-built TOF spectrometer. In this spectrometer the time of flight of scattered ions over a known distance is measured and consequently ion energy calculated. He ions with an energy of 1500 – 3000 eV were applied. The base pressure was about $5x10^{-9}$ mb. The substrates and layers were thermally treated by a small oven (resistance and electron bombardment heating of the rear part of the sample) built in into a sample manipulator. Native oxides on surfaces of silicon substrates (used exclusively) were in specified cases removed by thermal flashing over 1200° C. Evaporation of metals (Ga) was provided by an effusion cell (Omicron). XPS analysis was carried out in the analytical chamber I by a commercial XPS system (Omicron EA 125 U5) under similar pressure conditions to those in the deposition chamber. The transfer of samples between both chambers was provided by an UHV-tight magnetically driven bar without any exposure of samples to high pressure conditions. All samples were analysed by TOF-LEIS and XPS before and after each operation (thermal treatment, evaporation).

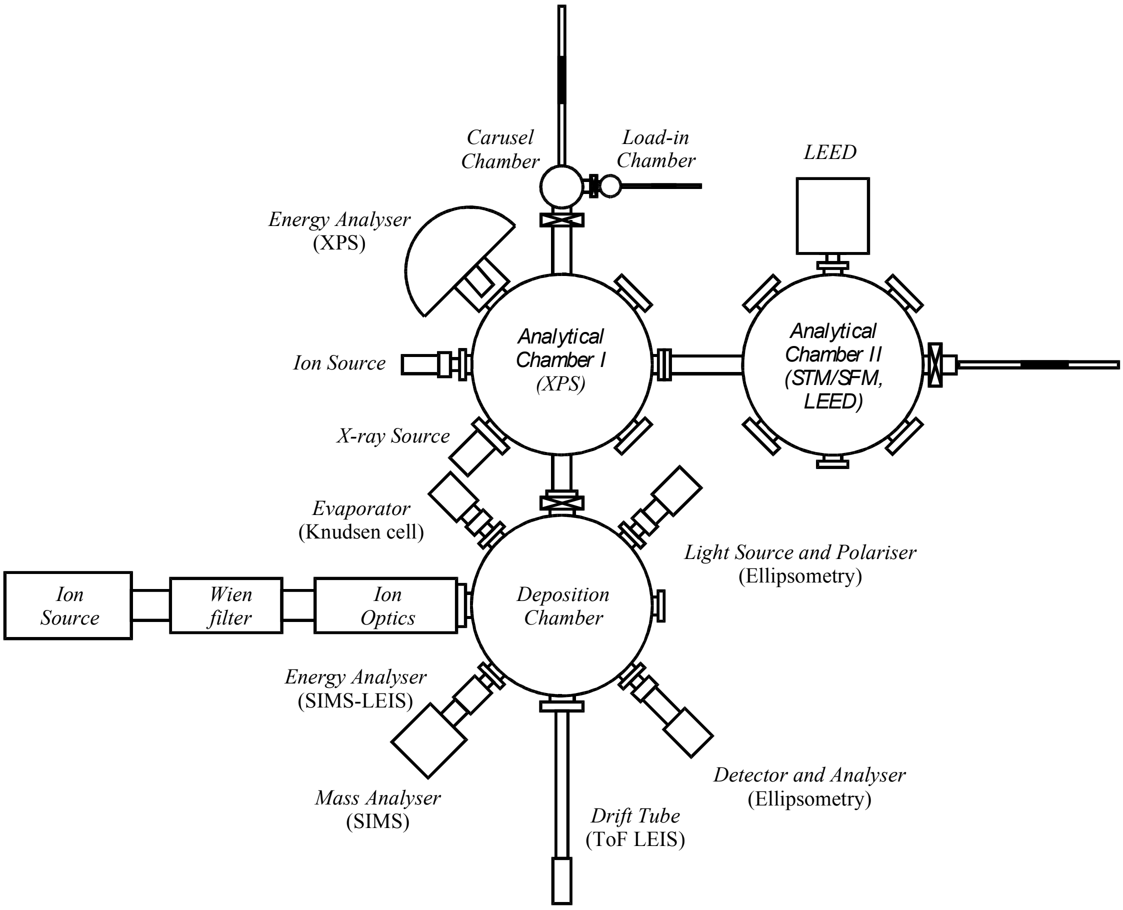

Fig.1. Schematic view of the UHV apparatus.

RESULTS AND DISCUSSION

In the following text selected examples of complementary analysis of solid surfaces carried out in situ under UHV conditions are demonstrated.

In Fig. 2. there is a TOF-LEIS spectrum of a Si (111) surface with a native oxide significantly reduced by thermal flashing over 1200 °C. The central part of the sample silicon was melted due to non-homogeneous electron bombardment. In addition to the highest peak of Si, there is a series of peaks corresponding to surface impurities like F, O, N and C. High concentrations of impurity elements result from relatively high pressure (in surface-science-point of view) in the deposition chamber ($\approx 10^{-8}$ mb). At this pressure, one monolayer of molecules of impurity gases is formed on the Si surface during hundreds of seconds. As the spectrum data collection lasts for the approximately same time, the impurity peaks are well developed. In this spectrum the presence of a separate peak in front of Si peak was the most surprising feature of the experiment. The position of the peak suggested should correspond to a heavier element like Cu, but it was difficult to identify the peak unambiguously. The sample was transferred into the analytical chamber I and analysed by XPS (Mg Kα). By comparison of the previous XPS spectrum, taken before flashing the sample, with that obtained after the thermal treatment it was obvious that the peak belongs to Cu (Fig. 3). The origin of Cu on the Si sample was unknown at the beginning. Later the source of copper was located – it was

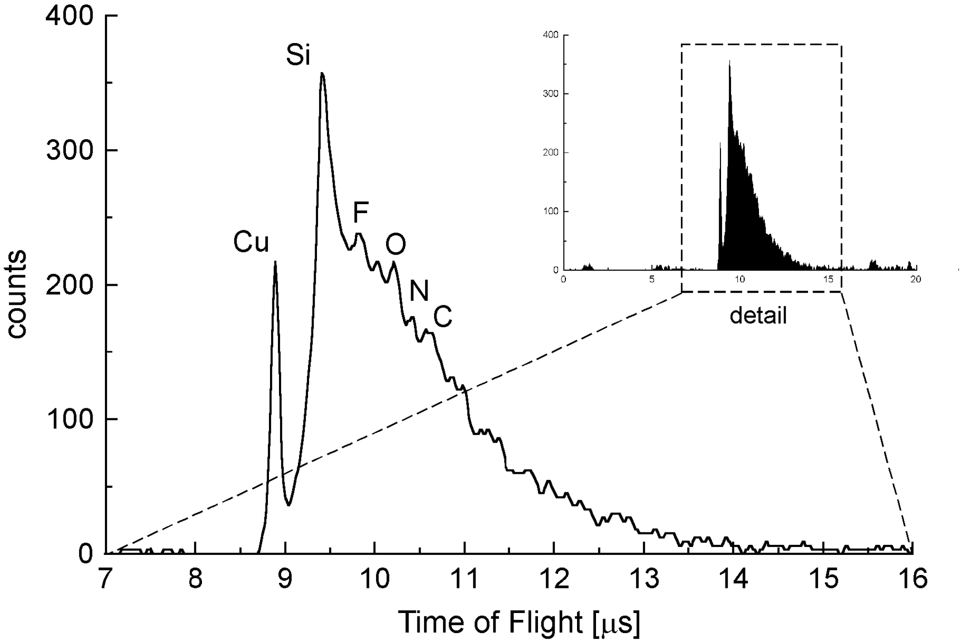

Fig. 2. TOF-LEIS spectrum of a Si (111) sample after flashing over 1200 °C (He^+ ions, 2000 eV).

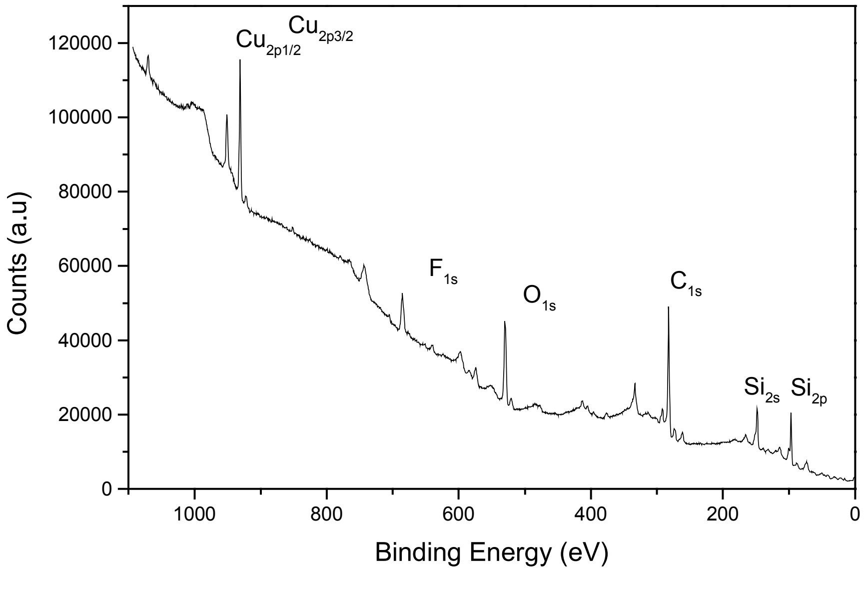

Fig.3. XPS spectrum of a Si (111) sample after flashing over 1200 °C (grazing angle).

a Cu lead overheated in the vicinity of the oven due to a loosen contact. Copper atoms were thus evaporated on the rear part of the silicon substrate and after that penetrated by means of diffusion through a melting silicon towards the front surface of the sample facing the analytical facilities.

In Fig. 4. TOF-LEIS spectra of a sample surface formed by an Au-ultrathin layer (≈ 10^1 nm)

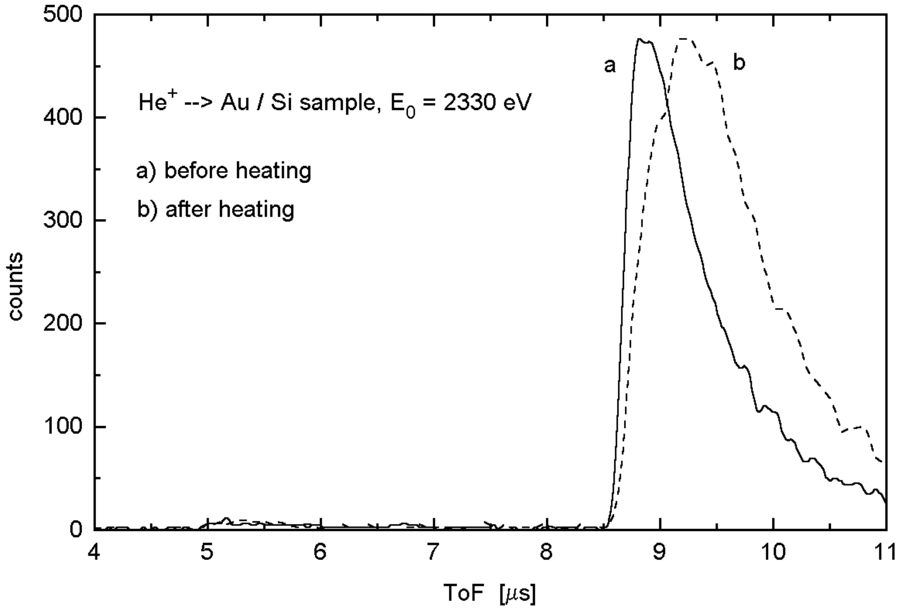

Fig. 4. TOF-LEIS spectrum of a Au/Si sample a) before and b) after annealing at 600 °C .

evaporated ex situ on a Si (111) substrate covered with a native oxide are shown. The spectrum marked as *a* was taken as deposited. On can see there a narrower peak with a steep front edge corresponding to Au. The tail of the peak is formed mostly by ions scattered on impurities. In the second spectrum *b,* which was taken after the annealing of the sample at 600° C, the peak is broader and has a less steeper onset due to a smaller Au sub-peak, which was obviously overgrown by a new one. However, the resolution of the spectrometer was too low to clearly determine its origin. Using the XPS analysis the process was identified. Whereas, the XPS spectrum taken before the annealing did not show up any presence of Si peaks, these peaks became available in the spectrum recorded after the annealing (Fig. 5). Hence, one can deduce that due to low eutectic temperature of the Au-Si system (363° C) and high solubility of Au in Si, gold dissolved into the silicon substrate.

Analysis of Ga surface prepared by in situ evaporation from an effusion cell on a Si (111) substrate covered with a native oxide is shown in Fig. 6. The substrate was kept at room temperature. The presence of a silicon peak in the spectrum and outermost layer selectivity of the method suggests that the surface was not fully covered by gallium. On the other hand, the appearance of a relatively high Ga peak in the corresponding XPS spectrum (Fig. 7) shows that on the silicon surface most likely Ga atoms form a 3D-island structure.

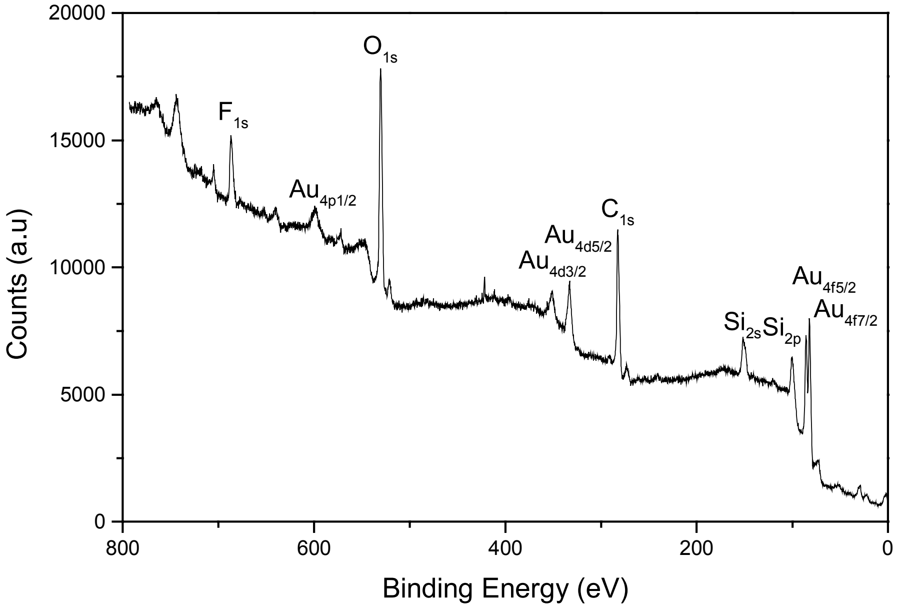

Fig. 5. XPS spectrum of a Au/Si sample after annealing at 600 °C .

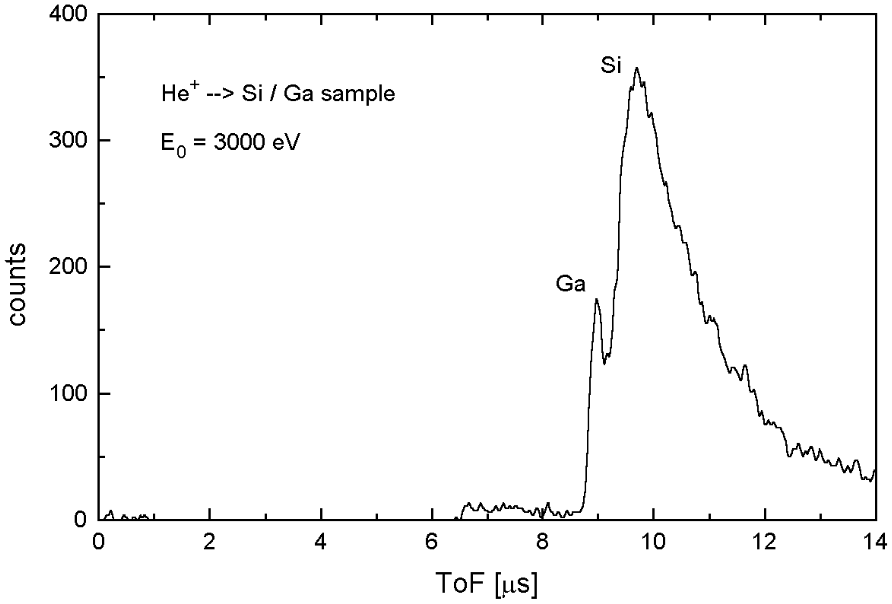

Fig. 6. TOF-LEIS spectrum of a Ga/Si sample prepared by Ga evaporation on a Si substrate.

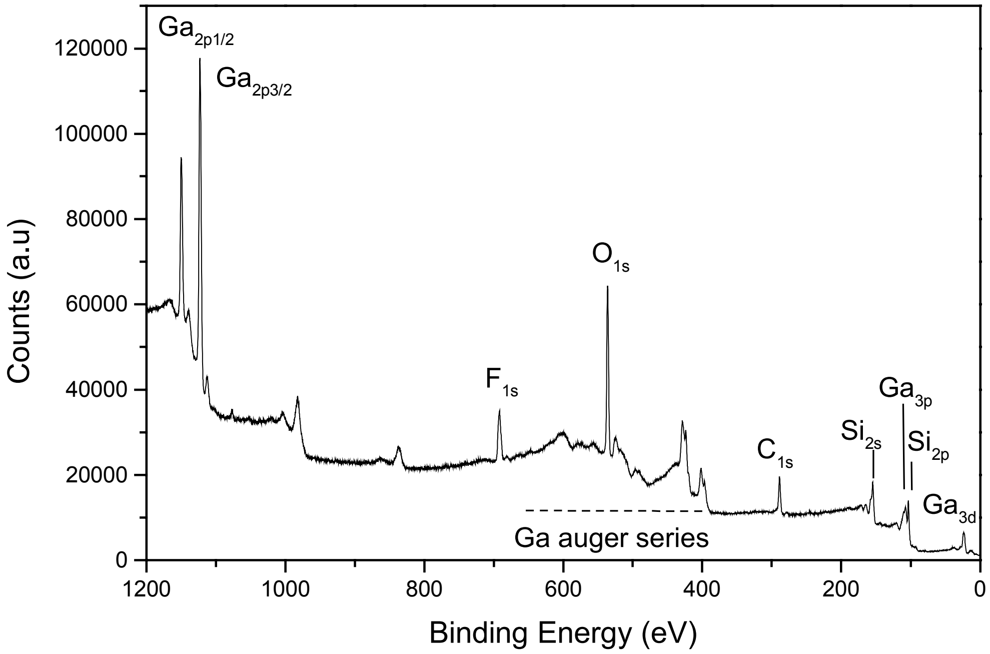

Fig. 7. TOF-LEIS spectrum of a Ga/Si sample prepared by Ga evaporation on a Si substrate.

CONCLUSIONS

The ability of the UHV apparatus to provide in situ complementary analytical experiments by means of TOF-LEIS- and XPS methods has been demonstrated. The methods were applied to monitor in situ modified solid surfaces. In addition, other in situ monitoring techniques like SIMS, AES, LEED, ellipsometry and STM/AFM are available in the apparatus. Hence, the more complex processes (e.g. epitaxial thin film growth) can be studied there in the near future by this experimental setup.

ACKNOWLEDGEMENT

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