

# LOW ENERGY ION SCATTERING (LEIS) – INTRODUCTION TO THEORY AND PRACTICAL APPLICATION

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## INTRODUCTION

In heterogeneous model catalysis, electronic, geometric and chemical properties of metallic surfaces decide whether certain chemical reactions take place or not. Over decades, many different characterisation methods were developed which are based on the interaction of sample surfaces with either probe particles (photons, electrons, ions, atoms) or applied fields under ultrahigh vacuum (UHV). Though, the most significant obstacle is the surface sensitivity and only very few techniques describe the topmost atomic layers exclusively. One of these techniques is LEIS and it features a series of advantages over other eligible methods.

## THEORY AND EXPERIMENTAL

Theoretical aspects of LEIS are presented in analogy to a game of billiard. In doing so, fundamentals that should facilitate interpretation of spectra for users are discussed, as well as the origin of the method's ultimate surface sensitivity. The focus is on determining the chemical composition of the utmost atomic layer of solid surfaces, in particular that of metallic alloys or intermetallic compounds, which are important substrates for growing model catalysts. Preserving the chemical and structural integrity of the topmost atomic layer during analysis poses a great challenge. However, scattering of low-energetic  $\text{He}^+$ -ions keeps the investigated surface intact and also offers utmost surface sensitivity, which is a unique combination in surface analytics.

As an example for the practical application of LEIS, a new  $\text{Pt}_3\text{Zr}(0001)$  single crystal was used, which provides the opportunity to grow an ultrathin  $\text{ZrO}_2$  film.  $\text{ZrO}_2$  is a material of highest interest, especially concerning current research on solid oxide fuel cells (SOFC) and related catalytic properties. The synthesis of a  $\text{ZrO}_2$  film through deposition of Zr under UHV by common techniques (e.g. electron beam evaporation) is difficult because Zr has a high melting point and a low vapour pressure at the melting point.<sup>[1]</sup>

Nevertheless, it has been reported in literature, that oxidation at elevated temperatures liberates the Zr from the top atomic layers and a thin  $\text{ZrO}_2$  film is formed.<sup>[2]</sup> In this way, continuous  $\text{ZrO}_2$  thin films are accessible with uniform surface structure, and with a high reproducibility. However, this only works if the surface of the single crystal is clean and has the correct stoichiometry. Up to now,

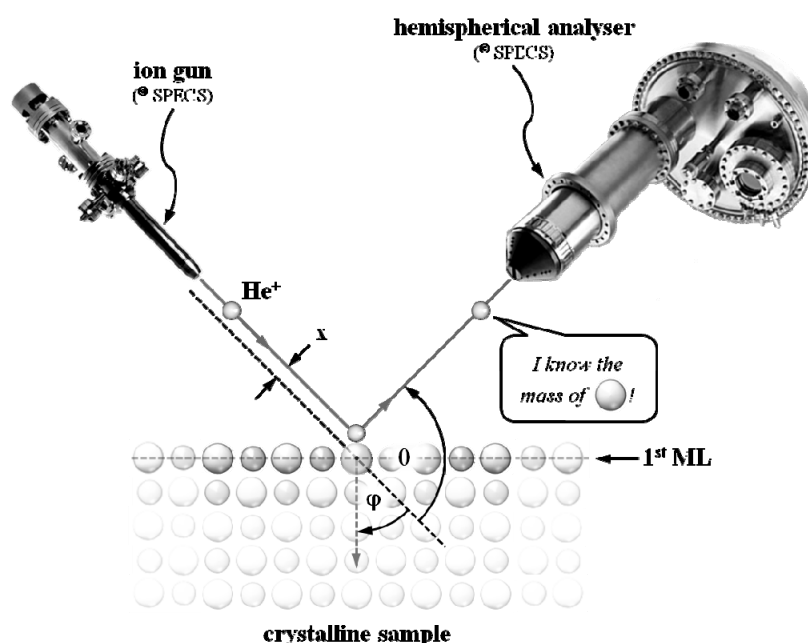


Figure 1: Sketch of the experimental setup

scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) have been applied to study the surface structure of alloy and oxide film.<sup>[3]</sup> LEIS experiments complement chemical information on the surface of this model system. In addition, LEIS may also shed light on the thermal stability of metal nanoparticles (e.g. Ni), deposited onto the ZrO<sub>2</sub> film. These represent catalytically active centres of SOFC anodes.

The implementation of LEIS requires an accurate geometric arrangement of the ion source, the sample and ion detector inside the respective UHV setup. This means that the ion beam, being invisible to the human eye, must be focussed onto the sample. Therefore, a Au/Cu-target was designed to adjust the sample position and spot size of the ion beam, aiming for the strongest possible Au-response. Optimum settings of the manipulator and ion gun yielded an accuracy of roughly 83.3 at-% of Au.

## RESULTS AND DISCUSSION

In order to determine the chemical composition of the topmost atomic layer of Pt<sub>3</sub>Zr(0001), quantification was carried out by employing polycrystalline metal foils (Pt, Zr) as elemental standards. Also, a polycrystalline Ni foil was measured, enabling the quantification of Ni nanoparticles on ZrO<sub>2</sub>/Pt<sub>3</sub>Zr(0001). After performing extensive cleaning procedures, LEIS and X-ray photoelectron spectroscopy (XPS) survey spectra were obtained. It was obvious that during cleaning bulk impurities present in the foils at a ppm-level continuously segregated to the surface.

Due to a significant contamination of Pt<sub>3</sub>Zr(0001) by graphitic carbon, an ultrathin ZrO<sub>2</sub> film could not be grown – despite multiple attempts and optimisation. LEIS results obtained after short sputtering demonstrated a modified surface stoichiometry (Pt/Zr  $\approx$  5:1 instead of 3:1). Depth profile analysis by angle-resolved XPS, performed after two different pre-treatments, indicated that the desired stoichiometry was only present in the bulk. Upon annealing, carbon, most likely located at interstitials, segregated to the surface. It is assumed that the origin of the carbon impurity within the single crystal is related to its synthesis.

## CONCLUSION

Experimental results demonstrate the outstanding surface sensitivity of LEIS, especially in comparison to XPS which is also known for its high sensitivity. Furthermore, it is shown that LEIS is a suitable tool for observing the segregation of bulk impurities which has a significant impact on sample preparation and catalytic activity. The implementation of LEIS in our UHV setup was successful. Yet, there is still room for improvement which will be part of further studies.

## ACKNOWLEDGMENTS

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