Surface Microanalysis by Low-Energy Ion Scattering

T. Grehl,* E. Niehuis, and H. H. Brongersma
ION-TOF GmbH, Heisenbergstr. 15, 48149 Münster, Germany
* thomas.grehl@iontof.com

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Introduction

Low-energy ion scattering (LEIS) has gained new capabilities and now provides high-end instrumentation for real-world surface analytical applications [1]. Although the technique has been available for some decades, recent developments in instrumentation make the unique capabilities of LEIS accessible for everyday applications. Special ion energy analyzer designs allow LEIS to be used for non-destructive quantitative analysis of the elemental composition of the outermost atomic layer with high sensitivity and high mass resolution. At the same time, the composition of the first 10 nm of sub-surface material is also assessed. Applications are very broad, ranging from catalysts to various thin films to polymers.

Instrumentation and Methods

Low-energy ion scattering is based on the scattering of noble gas ions that are directed at the surface with a kinetic energy of 1–8 keV. In a binary collision, some of the ions are scattered back from an atom in the surface and can be detected by an energy analyzer. In the collision event, the ions exhibit a characteristic energy loss that is measured and used to determine the mass of the surface atom that acted as the scattering partner. In contrast to non-dedicated instruments, which often utilize hemispherical energy analyzers, the sensitivity of the Qtac analyzer (Figure 1) is high enough to work under "static" conditions, where all required information of a given area is detected before the surface is noticeably modified by the ion bombardment. With the Qtac analyzer design, good energy resolution and a specific scattering geometry allow the separation of signals for virtually any pair of elements, even with overlapping isotopes [2]. By using a pulsed primary beam and taking the time-of-flight of the detected ions into account, the scattered ions can even be separated from sputtered ions to further increase the sensitivity, especially for light elements [3].

In addition to quantitative elemental composition analysis of the first atomic layer, LEIS spectra contain information about deeper layers. As in higher-energy ion scattering spectroscopy (MEIS, RBS), scattering may also take place in layers beneath the surface. In addition to the element-specific energy loss due to the scattering event, the ions exhibit a depth-proportional energy loss on their way into the sample and back to the surface. In the energy spectrum, these ions appear at a lower energy than the ions scattered by atoms of the same element at the surface (Figure 2). Because noble gas ions are used for the primary beam, the ions are effectively neutralized while traveling within the sample. They can be detected by the electrostatic analyzer only if they are re-ionized when leaving the surface. This results in a lower intensity of the ions scattered in deeper layers compared to those scattered at the surface by the same element. Thus, all peaks in the spectra can be attributed to scattering from atoms on the outermost surface, whereas intensities at energies below these peaks correspond to the in-depth distribution of the same element. Because the energy loss in a given material can be calculated or measured, the width of the distribution can be converted into a layer thickness. Conversely, if no surface peak is detected but a signal from deeper layers is observed, the energy shift of this

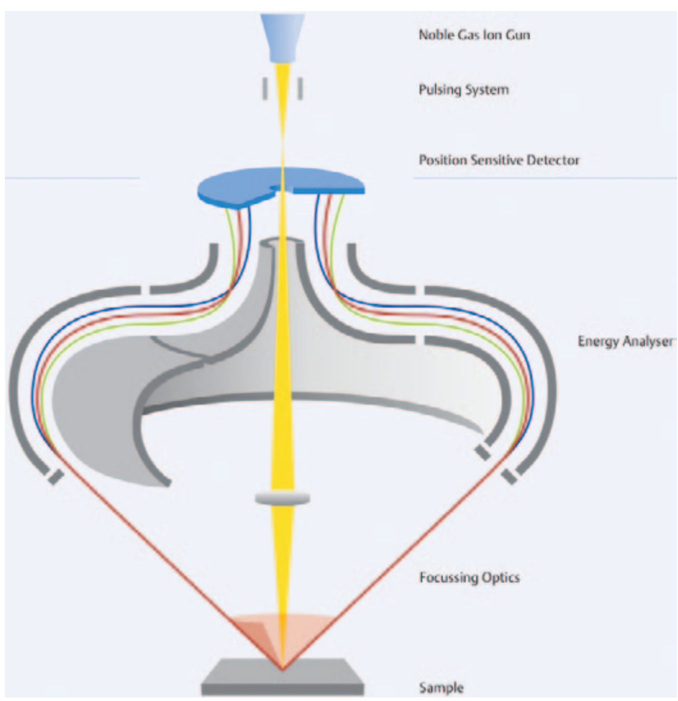


Figure 1: Schematics of the Qtac analyzer design. The primary ion beam (normal incidence) is directed through the analyzer toward the sample. Scattered ions are detected over all azimuths and analyzed with respect to their energy in the electrostatic analyzer. Ions in a range of energies are detected in parallel on the position sensitive detector.

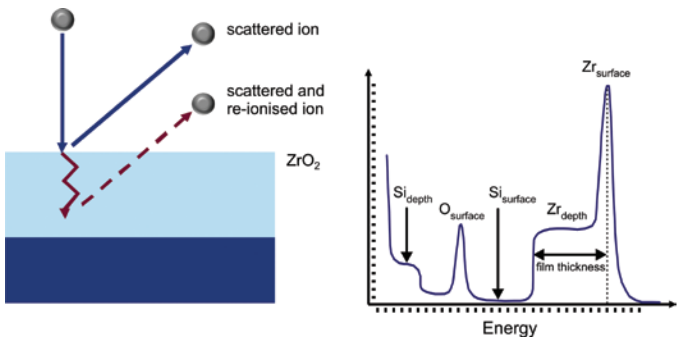
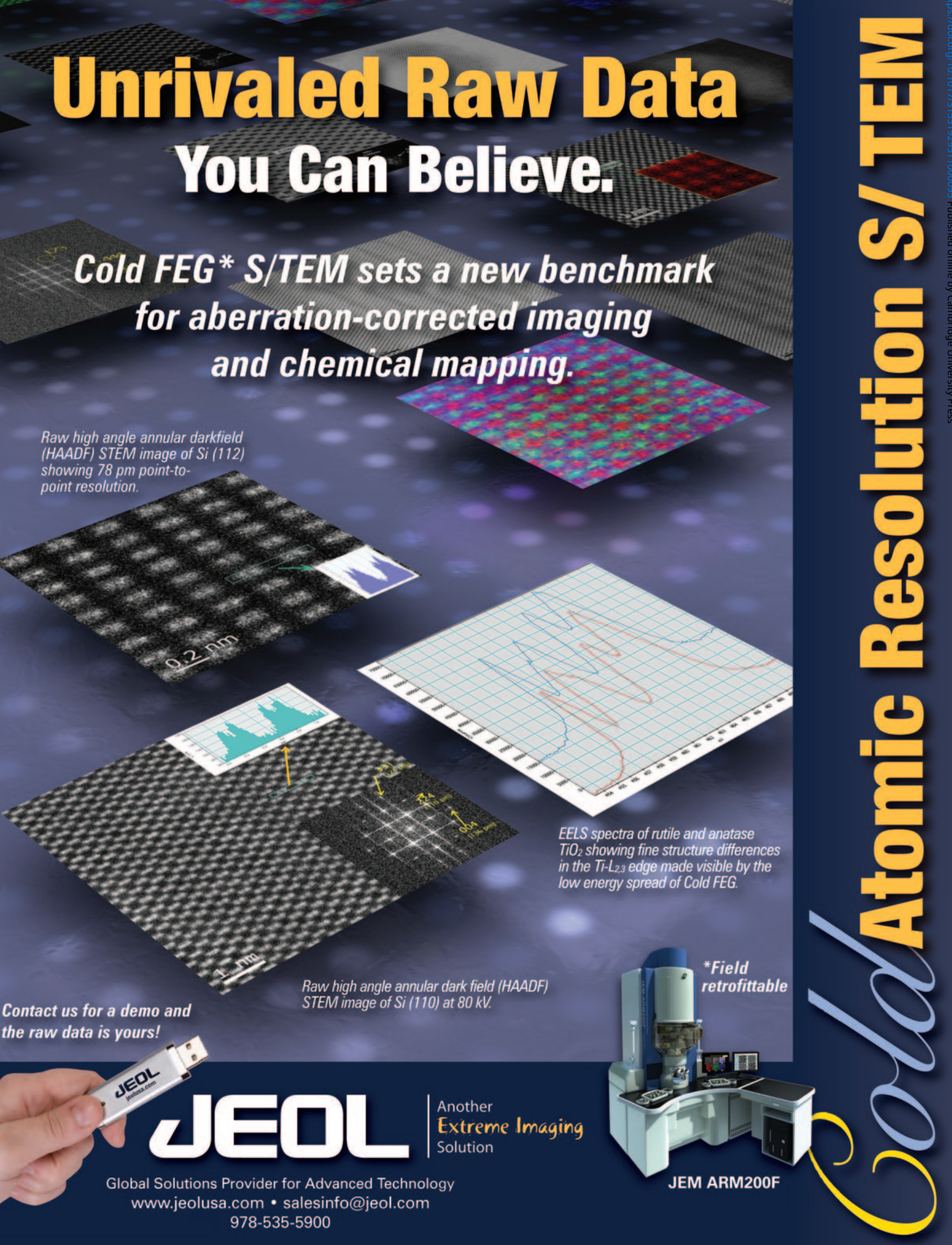


Figure 2: Ions may be scattered at the surface or in deeper layers. Peaks correspond to elements present at the surface. Other ions scatter at atoms deeper in the solid. On their way into the material and back to the surface they exhibit an additional energy loss, resulting in signals at lower energies corresponding to the in-depth distribution. Thickness information is obtained from the shift in energy.



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signal relative to the surface peak position can be converted into a thickness of the covering layer.

Because of the extremely high surface specificity and sensitivity of LEIS, surface contamination plays an important role in a typical analysis. Several applications relate to detection and identification of surface contaminations. Different sample preparation and cleaning techniques are applied while the sample is in the ultra-high vacuum of the instrument. In addition, depending on the kind of sample and the analytical task, *in-situ* sample preparation is possible. This includes DC-sputter cleaning, cleavage, film deposition, and high-temperature treatment in reactive atmospheres, for example, to activate a catalyst. After cooling the sample to room temperature, the surface state may be maintained for the time of the analysis.

Applications

Applications of LEIS range from fundamental research to industrial materials, especially in the field of thin films and catalysis. LEIS has been used to analyze nanoparticles [4], self-assembled monolayers [5], and polymers [6]; LEIS also has been used to study diffusion within the first few nanometers below the surface [7, 8] or an event taking place at the surface [9].

Catalysis. Top-atomic-layer surface sensitivity and the ability to analyze extremely rough and insulating samples make LEIS an ideal technique for catalysis applications where the activity and selectivity of the catalyst is localized at the outer surface [10]. Also, the concentrations of the active phase and promoters on the support may be very low. With detection limits in the range of a few atomic percent for light elements down to 10 ppm for heavy elements—as a fraction of the outermost atomic layer—modern LEIS does not need model systems with higher concentrations of the active phase or flat surfaces; high-sensitivity LEIS works directly on industrial catalysts.

On these samples, LEIS can determine the amount of the active phase on the support that is at the surface and available for the catalysis. Furthermore, when comparing catalysts before and after use, changes in the amount of specific elements at the surface can be observed, which may indicate sintering of the active phase or poisoning. The location of poisons can be determined by the change in surface coverage of the different elements during operation of the catalyst.

A very common application is the analysis of coke and coke formation [11]. These carbon-rich phases are deposited during operation of the catalyst and often limit the lifetime of the material. Avoiding the nucleation of coke can significantly increase the operation time of the reactor and is therefore of great importance. Although many analytical techniques can detect the coke, the decrease of elemental peaks in LEIS indicates which elements are covered by coke and thus which phase of the catalyst is responsible for coke nucleation. This may be the active phase, which is hard to modify without loss of catalytic performance, or the binder, or the support. Similarly, probe molecules that are specific to certain structures (for example, active sites) on the sample can be adsorbed on the surface. By measuring the differences in the LEIS spectra, the number of the probe molecules on the surface, and therefore the density of respective sites, can be determined [12].

For smaller nanoclusters, even the (average) size of a high surface area catalyst has been determined with a non-imaging methodology [13, 14]. This technique does not suffer from size discrimination and statistical errors caused by the limited field of view of imaging techniques that basically rely on particle counting. In LEIS, the absolute surface area of the metal is measured. The surface area of the support can be measured by gas adsorption (BET method). Taking both surface areas into account, the average particle size can be determined assuming a certain average shape of the particles, for example, spherical. This value is averaged over the whole analysis area of up to 2×2 mm. For a given amount of material, the surface area and therefore the LEIS signal increases for smaller particles. Thus, this technique is especially powerful with particles of 1–10 nm in size, where imaging techniques tend to discriminate against the smaller particles, especially on rough and complex support materials, and need a limited field of view for the detection. The latter additionally imposes the risk of sampling non-representative areas of the sample.

Thin films. In thin-film technology, the extreme surface sensitivity of LEIS is used to study growth modes and nucleation behavior in the early stages of film formation. In combination with the high-detection sensitivity, it is possible to determine how much material is deposited in each deposition cycle and how the deposition rate changes with the amount of deposited material. The increase in surface coverage can be observed in detail before the layer is closed. By this method, the minimum thickness required for closure of the film can be determined, which is often an important quality measure for the deposition process.

In addition to the surface coverage of the relevant elements, LEIS also provides very valuable in-depth information. Even before a complete monolayer is formed (the layer is closed), island formation and diffusion can be observed. Figure 3 shows

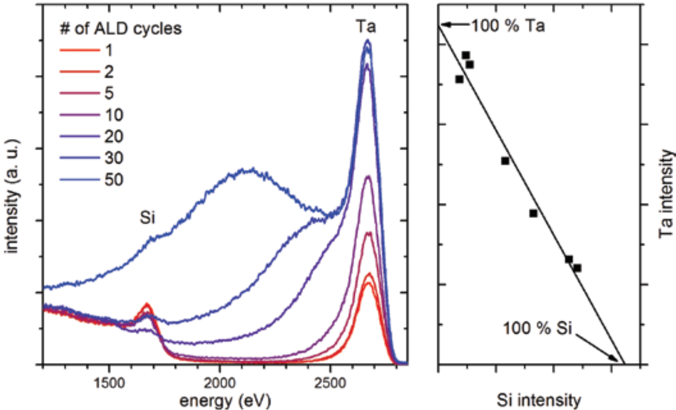

Figure 3: LEIS spectra of Ta(SiN) layers (left) and peak intensity of Ta vs. Si (right). The spectra show increasing surface coverage with increasing number of atomic layer deposition (ALD) cycles. This is determined from the growing intensity of the Ta surface peak and decreasing intensity of the Si surface peak. From 5 cycles onward, a depth distribution can also be observed, as the Ta peak becomes asymmetric and a low-energy tail develops. Under these conditions, a width of this tail of 160 eV relates to a film thickness of 1 nm. After 30 cycles the layer is closed. After 50 cycles the thickness has grown without change in coverage. The graph on the right shows the linear relationship between Ta and Si peak intensity (i.e., surface coverage), allowing straightforward quantification of the surface composition.

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an example of Ta(SiN) grown by atomic layer deposition (ALD) [15] on Si. The spectra show samples after different numbers of growth cycles. During the first 30 cycles, the surface coverage of Ta increases whereas the Si coverage decreases. As the film gets closed, the surface coverage stabilizes, which is the case after 50 cycles. The low-energy tails of the Ta surface peak, developing after 5 cycles, indicate multilayer growth even in this early phase of the deposition process and long before the layer is closed. The in-depth signal after 50 cycles represents a closed layer with a thickness of several nm. The spectrum after 30 cycles shows 100 percent Ta concentration close to the surface and then a decline of the Ta concentration in greater depth. The energy at which the two spectra separate (2500 eV or about 150 eV lower than the surface peak) can be converted into a depth of about 1 nm, based on ion energy loss calculations in this material. This is the minimum thickness of the 30-cycles layer, with some parts of the layer having a thickness of approximately 5 nm, which can be estimated from the extension of the tail to about 1700 eV. This thickness may be due to island growth or diffusion into the substrate, which cannot be distinguished by ion scattering.

For thicker films, the depth range of 5–10 nm that is covered by the in-depth information of the static (non-destructive) spectra is not sufficient. It is now possible to combine LEIS with sputter-depth profiling to cover a depth range of up to a few microns, with good sensitivity and easy quantification. Here, as in other surface analytical techniques (XPS, AES, ToF-SIMS), the sample is eroded with a low-energy sputter ion beam, while the surface composition at the center of the sputter crater is analyzed. The small information depth of LEIS provides good depth resolution, while the straightforward quantification makes the data analysis relatively simple. The first results [16] of this new mode show interesting complementarities with more established depth-profiling techniques like ToF-SIMS. The latter offers significantly better detection limits but lacks the ease of quantification especially close to the surface and at interfaces.

One of the first examples of these capabilities is shown in Figure 4. A stack of nominally 3-nm Al_2O_3/2-nm HfO_2/3-nm Al_2O_3/10-nm HfO_2 on Si substrate [17] was sputtered by 1 keV Ar ions at an angle of incidence of 59° to the surface normal and analyzed with 3-keV He ion scattering. The dose of the higher-energy He ions is low enough that the sputtering is dominated by the low-energy Ar beam. The depth profile acquired in this mode shows that the layer structure can be quantified very easily. Sensitivity factors for the metals are calculated based on the assumption of pure stoichiometric oxides in the first Al_2O_3 and the thick HfO_2 film. The oxygen concentration can also be calibrated based on the first Al_2O_3 film. This results in the correct stoichiometry for the other oxide layers as well; the quantification is consistent. The data show an increase in the oxygen content very close to the Si substrate, which was confirmed by ToF-SIMS profiles of the same film. However, in ToF-SIMS this higher oxygen content results in a higher Hf signal, which is due to the matrix effect that hinders quantification in this case.

In addition to the concentration profile, the LEIS data give more information about the film by showing the in-depth signal in the spectra that were acquired at each depth. Figure 4 shows four representative spectra acquired while sputtering through the first Al_2O_3 film. When comparing the onset of the in-depth signal of the buried Hf with the spectrum of the virgin surface, a shift toward higher energies is observed. As the covering film on top of the first HfO_2 film is sputtered away, the ions undergo a lower depth-dependent energy loss with increasing sputter dose density. By converting this shift in energy to a depth, based on the calculated energy loss of He in alumina [18], the crater depth can be plotted as a function of the sputter dose density, allowing a quasi-continuous measurement of the sputter rate. This methodology allows the analyst to correct for potential sputter artifacts and to determine a reliable depth scale even in complex film structures with changing sputter rates.

Conclusion

LEIS is the most surface-sensitive characterization technique for elemental composition; it can be used in all applications requiring analysis of the outermost surface. With the instrumentation available today and the available knowledge about sample pre-treatment and preparation, LEIS can be applied on a routine basis in materials science and surface science. In catalysis and thin films research, its

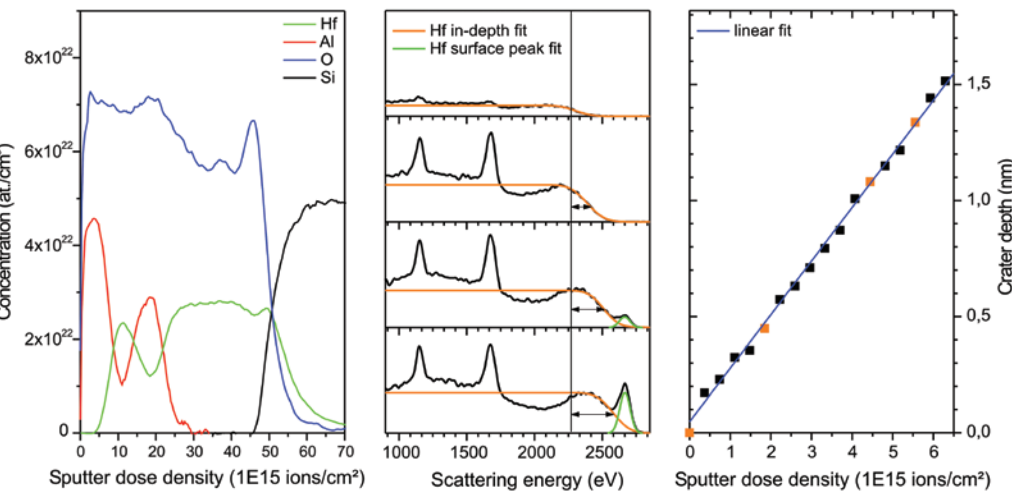

Figure 4: LEIS sputter depth profile of an Al_2O_3/HfO_2 multilayer on Si (left). Besides the straightforward quantification based on nominal atomic concentrations of the metals in the respective films and of the oxygen in the first Al_2O_3 layer, the oxygen concentration is consistent in the other films. Close to the Si layer, there is a higher oxygen content. The LEIS spectra taken at different depths in the first Al_2O_3 film (middle) can be used to determine the actual crater depth at each point. The energy shift of the Hf in depth signal can be converted to a change in depth, which may be plotted versus the sputter dose density (right). This allows determination of changes in sputter rate with angstrom resolution. Here the sputter rate becomes constant after sputtering to about 0.2 nm (2 Å).

potential has already been demonstrated. Other applications are currently being developed.

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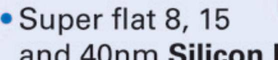

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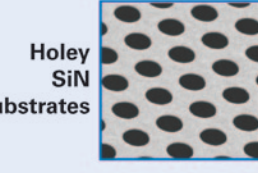

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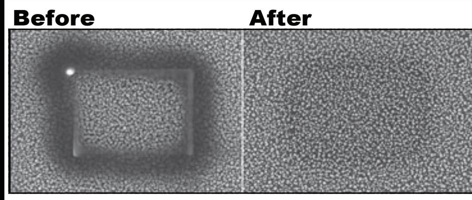

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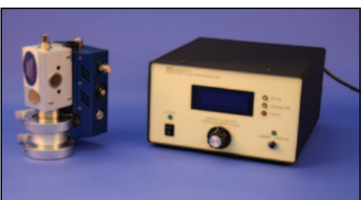

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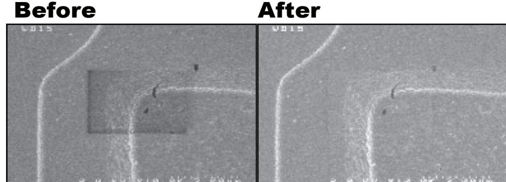

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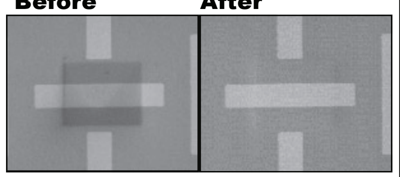

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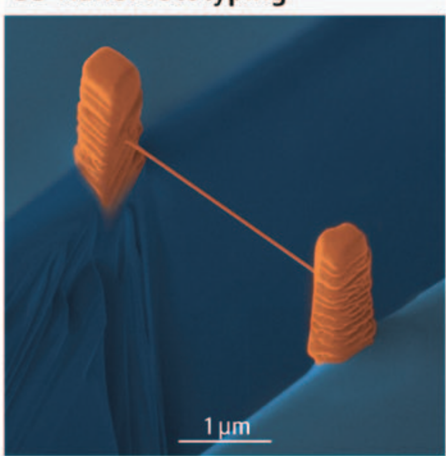
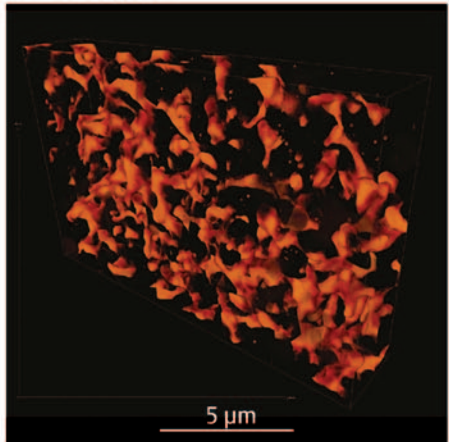


Platinum nanowire deposited and milled to about 50 nm diameter for use as a gas sensor

Courtesy of Peter Heard, Bristol University, United Kingdom
Image is coloured for artistic impression

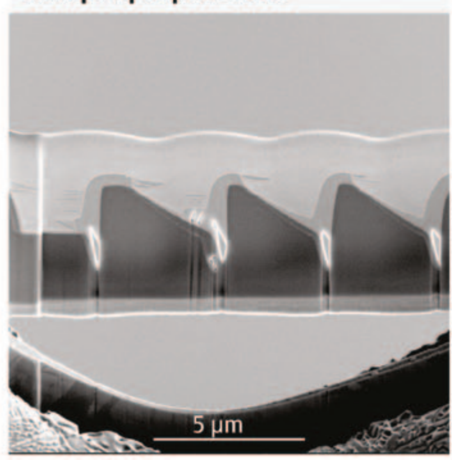
3D Analysis



Voltex visualization of porosities in a fuel cell electrode

Courtesy of Sabanci University, Turkey

Sample preparation



TEM lamella created to measure the amorphous damage created during FIB sample preparation

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