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Insight in the outside: materials science at the atomic level using LEIS

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Abstract

Modern low energy ion scattering (LEIS) can provide new information on the atomic composition of both outermost surface and sub-surface layers. The wide scope of new possibilities is illustrated with results on ceramics, polymers and ultra-thin layers. Most of the results presented are difficult or even impossible to obtain otherwise. The combination of LEIS and isotopic oxygen exchange reactions was used to investigate the surface of yttria stabilised zirconia (YSZ) that is used in the solid oxide fuel cell. It is found that under working conditions the surface is covered by a monolayer of contamination, followed by an yttria segregated layer. The quantification of LEIS is demonstrated for fluorinated self-assembled monolayers, while also the conformation of the endgroups is determined. The use of LEIS to follow the growth of ultra-thin layers is discussed for a TiN barrier layer on silicon.

Keywords: Films; Fuel cells; Perovskites; Self-assembly; Surfaces

1. Introduction

In modern technology new subnanometer materials and preparation techniques are developed. Advancement heavily relies on the availability of analytic techniques that can validate the preparation. One of the analytic techniques is low-energy ion scattering (LEIS), which can be used to selectively determine the composition of the outermost atomic layer of all kinds of materials.[1–3] In LEIS a mono-energetic beam of low energy (0.5–5 keV) noble gas ions (He, Ne, Ar) is directed towards the surface. Ions that are (back)scattered over a certain angle (generally around 145°) enter an electrostatic analyser after which they will be detected. The obtained energy spectrum is easily converted into a mass spectrum of surface atoms using the laws on conservation of energy and momentum. LEIS obtains its monolayer sensitivity by the combination of a high neutralisation probability of noble gas ions and the use of an electrostatic analyser. Other surface analytic techniques, such as XPS, ToF-SIMS and Auger, probe much deeper. The surface elements to be quantified determine the choice of the incident energy and ion. In a LEIS spectrum the scattered ion energy increases with the atomic mass of the target atom. The energy separation of the peaks becomes poor for a large target atom to incident ion ratio. A heavier incident ion or higher incident energy can be used to improve the mass separation of the target atoms. The use of a heavier ion also has the consequence that the scattered ions have a lower energy. When the ratio of the masses of the target atom and incident ion is 2.5 or less, the final energy becomes so low that the sensitivity drops significantly. The background in the LEIS spectrum on which the peaks are situated is partly caused by ionised particles sputtered from the target, partly by incident ions, which are scattered from atoms lying below the surface. These ions are neutralized beyond the first atomic layer, scatter in the matrix and are re-ionized just before leaving the target surface causing them to be detected. This re-ionization process is matrix dependent. Information of the near surface can be obtained this way (down to 6 nm). Although a heavier ion can give better mass resolution, it also sputters the sample surface more effectively than lighter incident ions, thus providing another way to obtain a depth profile. In case only the surface composition is required, one should reduce the ion dose to such low values that sputter effects are negligible. An ion dose in the order of 10^{13} ions/cm^2 is already enough to measure the LEIS spectrum. Moreover, molecular

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dynamics simulations have shown that the back-scattered ions, that carry the valuable surface information, have already scattered back from the sample surface before any detectable damage can be done to it.

It is now possible to quantitatively determine the composition of the outermost atoms of almost any material at any temperature. Such studies have shown that the outer surface is very often completely different from what one expected. This is especially true for oxides and polymers. To illustrate this, LEIS investigations of the surfaces of the electrolyte of a solid oxide fuel cell (SOFC), of fluorinated polymers and of ultra-thin layers of TiN are discussed. Much of the information that has been obtained with LEIS is impossible (or very difficult) to obtain by any other analytic technique.

All measurements are done with the LEIS set up developed in Eindhoven. A new type of analyser using parallel detection has increased the sensitivity of LEIS by about three orders of magnitude, while better charge-compensating techniques now even enable quantitative studies of highly dispersed insulating targets.

2. LEIS on the solid oxide fuel cell electrolyte

The fuel cell may become an important energy conversion system in a sustainable future. The solid oxide fuel cell (SOFC) is one of many types of fuel cells. It operates at a temperature of around 1000 °C. However, to make the SOFC economically feasible the operating temperature has to be lowered by some 200–300 °C.

The rate-limiting factor in the performance of the SOFC is the oxygen exchange at the electrolyte surface. The surface composition will, therefore, play an important role in the process of converting the oxygen gas molecules to oxygen ions incorporated in the electrolyte matrix. Previously, mainly surface science techniques, such as XPS and AES have been used for this purpose. Due to the large probing depth these techniques only give average compositions of the surface region. Therefore, the surface segregation behaviour in electrolytes is still often very controversial.

Yttria stabilised zirconia (YSZ) is the preferred electrolyte for the SOFC, because of its high ionic conductivity and good chemical stability. In the following we will show with the use of LEIS that indeed the outermost surface layer of the YSZ electrolyte is quite different from that of the bulk. Furthermore, it will be shown that this difference influences the oxygen exchange dramatically.

2.1. *Time-of-Flight (ToF)-LEIS*

Quantification of LEIS signals is mainly done by comparing the signals from reference samples with those of the sample of interest. This method is not straightforward for YSZ. With the presently available LEIS equipment the Y and Zr peaks cannot be separated, because of their closeness in mass: Y has mass 89 amu and Zr, with its five natural isotopes, has an average mass of 91.2 amu. Quantification is further complicated by the increasing background on which the Y and Zr peaks are situated in the LEIS spectrum. Therefore, special YSZ samples have been prepared from Y_2O_3 and isotopically enriched zirconia ($^{94}ZrO_2$). ToF-LEIS is used to determine the different contributions of scattered and sputtered ions to the conventional LEIS spectrum. ToF-LEIS measurements only differ from conventional LEIS measurements in that the incoming ion beam is pulsed and only scattered (or sputtered) ions that pass the analyser within a certain time window are detected.

Fig. 1 shows a comparison between a conventional LEIS spectrum measured on a 10 mol% Y_2O_3 doped $^{94}ZrO_2$ sample and the results of the ToF-LEIS measurements on the same sample. The conventional LEIS spectrum is measured with 5 keV $^{40}Ar^+$ ions and an ion-beam current of 0.17 nA and is given by the solid curve in Fig. 1. The Y and Zr peaks can clearly be separated. The ion dose used to measure the spectrum equals 5×10^{12} ions/cm^2. The ToF-LEIS measurements are done with a 5 keV $^{40}Ar^+$ pulsed ion beam (pulse duration of 300 ns, repetition frequency of 110 kHz) and an ion beam current of 5 nA (during the pulse). The used dose to measure one ToF-LEIS spectrum is also

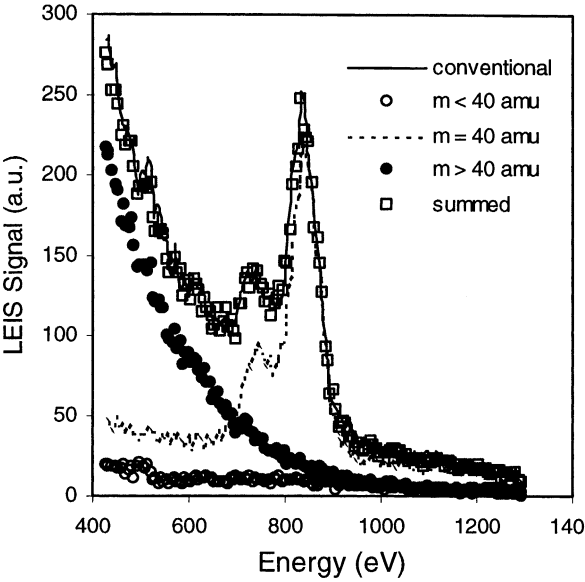

Fig. 1. Conventional and ToF-LEIS spectra (5 keV, $^{40}Ar^+$) of $^{94}ZrO_2$. The *solid curve* shows the conventional LEIS spectrum. The *open* and *closed circles* and the *broken curve* are spectra measured with the ToF option. The *open circles* represent the detected ions with mass lower than 40 amu, the *broken curve* represents the detected ions with mass 40 amu ($^{40}Ar^+$) and the *closed circles* represent the detected ions with mass higher than 40 amu. The *open squares* are a summation of the three contributions measured with ToF-LEIS.

5×10^{12} ions/cm^2 making a direct comparison between LEIS and ToF-LEIS spectra possible. The broken curve shows the ToF-LEIS spectrum for the scattered particles. The high intensity of the background at low energies is reduced considerably compared to that of the conventional LEIS spectrum. Therefore, sputtered particles from the sample surface make up a large part of the conventional LEIS spectrum. The remaining background is partly caused by a combination of ^{40}Ar, which is re-ionised at the surface after multiple scattering, and sputtered particles from the surface. The open circles in Fig. 1 show the spectrum obtained from particles with mass lower than 40 amu, while the closed circles show the spectrum obtained from particles with mass higher than 40 amu. It is clear that sputtered ions heavier than $^{40}Ar^+$ dominate the background. The open squares in Fig. 1 show the spectrum after summation of the signals from the three separate contributions (mass lower, equal and higher than 40 amu). This summed spectrum is practically identical to the conventional LEIS spectrum, confirming that there are no other significant contributions to that LEIS spectrum.

Similar results are obtained for Y_2O_3 and $^{94}ZrO_2$ samples. With the results from the ToF-LEIS an accurate correction for the background and fit of the peaks in the conventional YSZ LEIS spectrum can be made.

2.2. Sputter profiles

In order to determine the composition of the outermost surface layer and the changes with respect to the bulk of a 3 mol% Y_2O_3 doped $^{94}ZrO_2$ sample, sputter profiles are measured. First the sample is calcined in a tube oven for 5 h. After cooling down to room temperature the sample is transferred to the LEIS apparatus. The LEIS measurements are done with 5 keV $^{40}Ar^+$ ions. The ion dose used to measure one spectrum is about 5×10^{13} ions/cm^2. To prevent the samples from charging they are flooded with low-energy electrons. Because the sample surface is also sputtered as a consequence of the measurement, compositional information from "deeper" layers is obtained, hence making the sputter profile.

The results after calcining the sample for 5 h to 900 and 1050 °C, respectively are given in Fig. 2a and b. After calcination at 900 °C the Y sputter profile reveals an increased yttria content at the surface. Accordingly, the Zr yield is reduced at the surface. Sputtering restores the Y and Zr yields to their bulk values. For the profile after calcination at 1050 °C the Y signal first increases until about 7×10^{14} ions/cm^2 and subsequently decreases until about 4×10^{15} ions/cm^2 after which it stays constant. The increase is caused by the removal of impurity oxides, such as SiO_2 and CaO, from the surface, as confirmed by LEIS measurements with 3 keV $^4He^+$ (with Ar ions Si and Ca cannot be detected). The increase of the Y signal will continue until the impurities are removed from the surface and the Y signal becomes constant. However, the segregation of yttria to the subsurface results in a Y signal, which is higher than its bulk value. Continued sputtering, therefore, decreases the Y signal until it becomes equal to the bulk value. The Zr signal increases sharply with sputter dose until 2×10^{15} ions/cm^2 after which it increases only gradually until it stays constant for doses higher than 4×10^{15} ions/cm^2. The increase is caused both by the removal of impurities as well as the excess yttria in the enriched subsurface layer. Simulations are used to determine both the thickness of the impurity and yttria enriched layers as well as the extent of the yttria enrichment. In

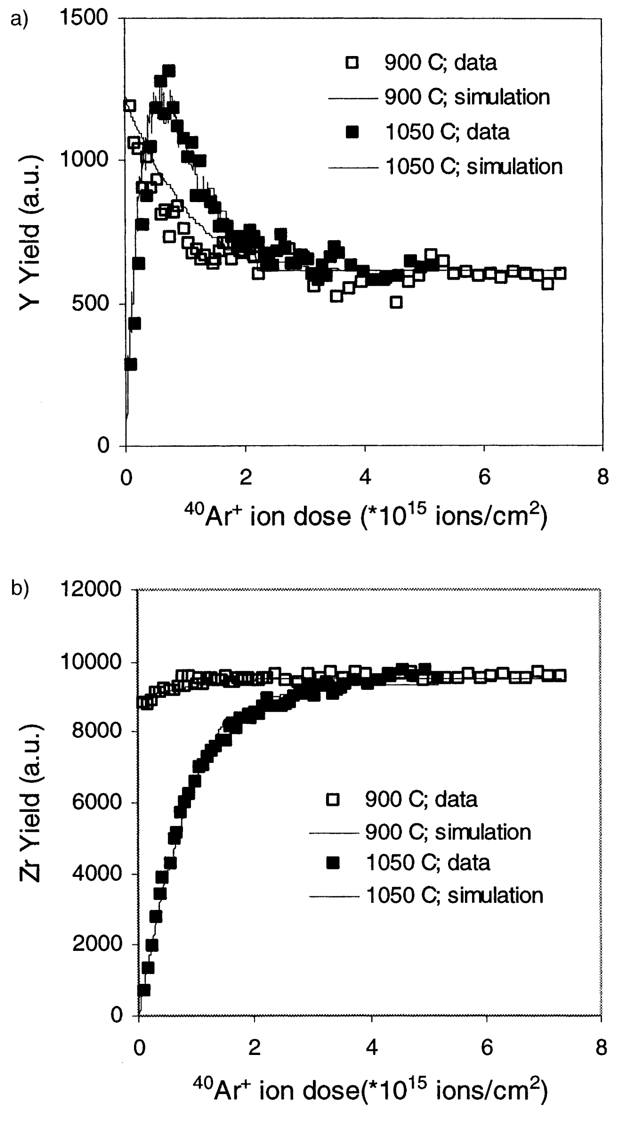

Fig. 2. Sputter profiles of (a) Y and (b) Zr, measured with 5 keV $^{40}Ar^+$ ions on 3 mol% Y_2O_3 doped $^{94}ZrO_2$ after calcination at 900 and 1050 °C. The *open squares* indicate the results after calcination to 900 °C, the *solid squares* indicate the results after calcination to 1050 °C. The solid curves are the simulated sputter profiles using a random sputter model.

the model the particles are sputtered at random from the various surface layers. The O concentration is taken the same for all layers. Preferential sputtering is neglected. No distinction is made between the different impurities. Typical results of the simulations for the Y and Zr sputter profiles are given by the solid curves in Fig. 2a and b.

From the simulations it follows that the impurity oxide and yttria enriched layers are only one monolayer thick. After calcination to 900 °C the yttria surface concentration is 6 mol%, which is a factor 2 higher than in the bulk. From the second layer on, the bulk composition of 3 mol% Y_2O_3 holds. After calcination to 1050 °C the subsurface enriched yttria layer is composed of 30 mol% $YO_{1.5}$ (=18 mol% Y_2O_3) and 70 mol% ZrO_2.

Thus, in contrast to literature, where it is suggested that the outermost surface is enriched in yttria after calcination to temperatures in excess of 1000 °C,[4] the excess Y is present in the subsurface layer. Also, the extent of the enriched layer thickness is much smaller than the values of 2–6 nm suggested previously.[5,6]

2.3. Oxygen exchange

The electrolyte is always calcined to temperatures in excess of 1000 °C in order to make it gas-tight. After calcination bulk impurities will have segregated to the external surface and will have covered it completely. However, for oxygen exchange the surface oxide has to pick up an extra oxygen and pass it on to the electrolyte matrix. The metal ion, therefore, has to be able to change its valence. The impurity oxides, SiO_2, CaO and Na_2O, are all very stable oxides and will hinder the oxygen exchange.

The extent to which an impurity oxide can influence the oxygen exchange has been demonstrated on an YSZ sample with different CaO coverages. The different CaO coverages are obtained by calcining the sample to different temperatures and for different times. After calcination the sample is annealed in $^{18}O_2$ for 10 min at 500 °C. The result is shown in Fig. 3. The LEIS spectra are measured with 3 keV $^4He^+$.

The isotopic fraction, which is defined as the ratio of ^{18}O to the total amount of oxygen present in the sample surface, decreases linearly with increasing CaO coverage. For an uncovered YSZ surface the isotopic fraction is about 0.52. This value is much higher than the 0.008 reported by Manning et al.[7] measured with SIMS on a 9.5 mol% YSZ single crystal (oxygen exchange at 500 °C for 2 h).The result of Manning should, therefore, be compared with a surface covered by impurity oxides. A YSZ surface completely covered by CaO does not show any sign of oxygen exchange (Fig. 3).

If oxygen exchange only takes place at the uncovered YSZ surface, the isotopic fractions given in Fig. 3 are underestimated as total ^{16}O and ^{18}O LEIS signals are used. When it is assumed that only the oxygen from YSZ and not the oxygen from CaO takes part in the oxygen exchange process, the isotopic fraction is constant. This suggests that the exchange mechanism does not change as a consequence of the CaO segregation to the surface. The presence of CaO only reduces the effective surface area for oxygen exchange.

3. Quantification of F in self-assembled monolayers and polymers

In coating systems, where water repellency, low friction and cleanability are required, fluorine containing polymers are increasingly used. Recently it was demonstrated that fluorinated polymers (PMMA) show a strong segregation of fluorine to the surface.[8,9] Also, when using LEIS, a direct relationship was found between the fluorine signal and the surface energy of the polymer. Other surface techniques, such as XPS, did not show this relationship. Since XPS probes several nm deep, this observation supports that the surface segregation is restricted to the outermost surface.

As there are generally no matrix effects in LEIS, this means that the sensitivities for the He^+ ions scattered by F atoms in different materials are identical, simple reference targets can be used for quantification. To quantify the atomic density of fluorine in the outermost atomic layer the fluorine LEIS signals for polytetrafluoroethylene (PTFE; trade name: Teflon), LiF (100) and a self-assembled monolayer of a fluorinated thiol on gold have been compared. Since the electronic structure of F in the polymer, in the organic monolayer and in the

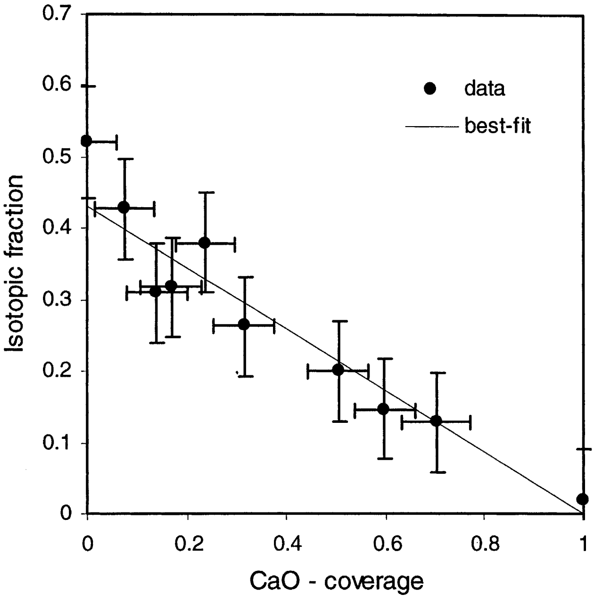

Fig. 3. Isotopic fraction of surface oxygen as a function of the CaO coverage. Results after 10 min. calcination at 500 °C in $^{18}O_2$.

inorganic ionic crystal will be very different, this is also a severe test for the calibration of fluorine with reference samples.

The LiF (100) surface was prepared by cleaving a single crystal just before insertion into the LEIS set-up. It is known from literature that such a surface stays atomically clean in air for prolonged times.[10] The surface density of F in the (100) surface has been calculated to be 1.23×10^{15} F atoms/cm^2.

The self-assembled monolayer was prepared by exposing a Au substrate to a solution of a fluorinated thiol [$HS–(CH_2)_2–(CF_2)_7–CF_3$] (F-8 thiol) in absolute ethanol. The strong interaction of Au with the thiol-groups, as well as the low surface energy of the fluorinated tails, lead to self-assembling and formation of a close-packed monolayer (Fig. 4).

The LEIS spectra for LiF (100), the self-assembled monolayer and PTFE are given in Fig. 5. The Li signal, which is very weak due to the low sensitivity for lithium, cannot be seen in this figure, since the peak is outside the energy range shown.

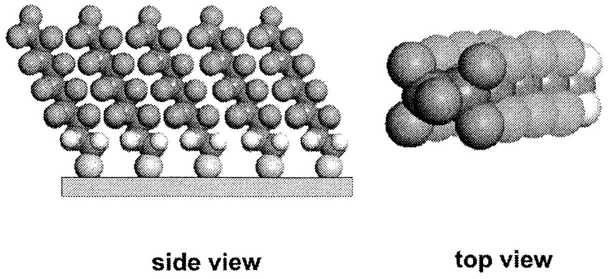

Fig. 4. Schematic drawing of an idealised packing of a self-assembled monolayer of F-8 thiol on Au(111): (a) side view, (b) top view.

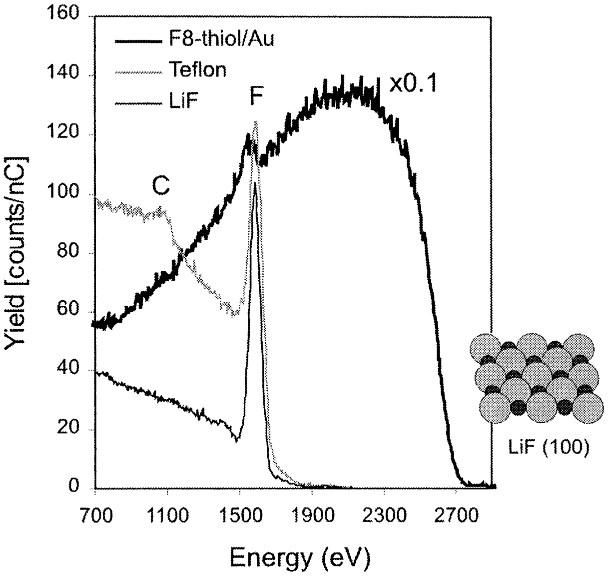

Fig. 5. 3 keV $^3He^+$ LEIS spectra of LiF (100), Teflon (PTFE) and a self-assembled monolayer of F-8 thiol on Au(111).

In the LEIS spectrum of the self-assembled thiol, no sulfur is visible, confirming the orientation of the molecules with the sulfur bonded to the gold (Fig. 4). The fluorine signal is on a high background which extends up to about 2700 eV. This signal is due to He^+ ions that straggled through the organic layer, suffered multiple scattering in the underlying Au substrate (while suffering various energy losses) and were finally scattered back into the analyser. The high-energy onset of the tail is thus characteristic for scattering by Au.

Since the analyser uses electrostatic deflection, only ionised particles are detected. However, upon penetration of the ions into the surface, most ions will have been neutralized. The tails in the spectra thus indicate that a significant fraction of the backscattered particles has been reionised upon leaving the surface. This is characteristic for these molecules. The background is especially high for the thiol on gold, since the backscattering depends on the atomic atomic of the substrate atoms and is thus very high for Au.

Notwithstanding the high background, the F-peak area can easily be quantified. In Table 1 the fluorine signals are given which have been quantified by calibration against the fluorine signal for the LiF (100) surface.

For the self-assembled monolayer 1.48×10^{15} F atoms/cm^2 are found. This value can be compared with the results of Liu et al.[11] who studied these fluorinated thiols with both atomic force microscopy (AFM) and grazing incidence X-ray diffraction. A coherent picture was obtained in which a hexagonal lattice is formed with a nearest neighbour distance of 5.7 (±0.2) Å. This implies a packing density of 3.5×10^{14} chains/cm^2. Since the surface peak in LEIS results from the outer atoms, one would expect that only the end group ($–CF_3$) contributes to the F signal. Based on the AFM results one would thus have expected 1.05×10^{15} F atoms/cm^2, which is significantly less than what is observed. The difference is also well beyond the experimental uncertainty. The high fluorine signal in LEIS (4.2 F atoms/chain) can be understood, however, if one assumes that not only the CF_3-endgroup, but also the two fluorine atoms of the CF_2-group below it are partially visible. To understand this, one has to realize that in the F8-thiol the chains make an angle of about 22° with the surface normal.[12] When the end groups of the thiol are rotated around the backbone, the full–CF_2–CF_3 comes parallel to the surface. With space filling models it can be shown

Table 1
The atomic densities of fluorine [10^{15} atoms /cm^2] determined by LEIS

Sample	LEIS
LiF (100)	1.23[a]
s.-a. monolayer	1.48±0.03
PTFE	1.24±0.03

[a] The atomic density of F on LiF (100) is used for calibration.

that for the 22° inclination the distances between the chains are (precisely) enough to allow for this rotation. Fig. 4 illustrates the rotated conformation of the –CF_2–CF_3.[9] In this configuration the F of the CF_3 group that is on top is 100% visible, while the four other F atoms are partially shielded.

Using the space-filling model it is easy to estimate that effectively 4.3 F atoms per chain are visible. This agrees well with the experimentally observed value of 4.2 F atoms/chain. The LEIS results thus confirm the results by Lui et al.[11] and also provide the surface conformation. Thermodynamically one can understand that this conformation is favoured, since a close-packed surface will produce the lowest surface energy.

For PTFE a value of 1.24×10^{15} F atoms/cm^2 is found. This value seems reasonable, since the backbone will expose CF_2- rather than CF_3-groups. Also, the PTFE backbone has only limited flexibility. These factors will reduce the F density in comparison to that in the self-assembled monolayer. The presence of carbon atoms is also clearly visible in the LEIS spectrum for PTFE (Fig. 5).

The results also confirm that under our experimental conditions the sensitivity for F atoms is the same for F atoms in PTFE, the F8-thiol and in LiF (100). Thus, there are no matrix effects in the LEIS signals for fluorine in these materials, which makes the LEIS quantification straightforward.

4. LEIS of ultra-thin TiN films

An interesting barrier film against Cu diffusion in interconnects of integrated circuits is TiN. Such a film should be ultra-thin to keep the advantage of low resistance. One of the challenges is to grow these films by atomic layer deposition (ALD), since the use of cycles of self-limiting reactions opens the potential to digital controllability. Satta et al.[13] have studied the deposition of TiN by ALD. They admitted $TiCl_4$ and NH_3 sequentially into the reactor. By using a pure nitrogen purge gas in between the pulses of the reactants, gas-phase reactions were excluded. The deposited layers were analyzed using techniques such as LEIS and RBS. In Fig. 6 the LEIS results for 3 keV He^+ scattering are shown for the layers after 1, 50, 100, 150 and 200 cycles. To eliminate the influence of the transport to the Calipso LEIS in Eindhoven, the samples were cleaned with atomic oxygen just before the analysis. Such a treatment will not only remove possible organic contamination due to the transport, but also replaces the nitrogen in the surface by oxygen. The Ti, Si and O peaks are around 2100, 1650 and 1100 eV. The spectra illustrate that after 50 cycles most of the surface is covered by titania (62%), while silica is clearly visible. Although the layer is far from complete, the strong asymmetry (low-energy tail) of the Ti peak indicates that part of the Ti is already present as multilayers. Similar to the background observed for the self-assembled monolayer in Section 3, the tail results from scattering in deeper layers. The incident ions that were neutralized at the surface, penetrated into the TiN layer where they lost some energy in multiple collisions, scattered back at some depth, lost more energy on the way out and were finally reionized just before leaving the surface. Atoms such as O, Si and Ti are known to be very effective in reionizing He atoms.[2,14]

The scattering processes are similar to those in high-energy ion scattering (also called RBS). The difference being that in LEIS the scattered particles have to be reionized to be detected. Also, the relatively higher energy loss in LEIS allows for a much better depth resolution.

A complete titania layer is obtained around 100 cycles. This means that from there on the Ti surface peak does not grow anymore, while the Si peak has disappeared completely.

The surface peaks in LEIS are only sensitive to the outermost atoms. Thus the peaks in the spectra don't change anymore during subsequent cycles. The width of the low-energy tail of the Ti peak, however, clearly increases with the number of cycles. Since the surface is now fully covered by TiN, the growth will everywhere be the same. The differences in layer thickness (islands), that were formed during the first 100 cycles, thus remain unaffected during further growth. This is clear from the spectra after 150 and 200 cycles. At energies above 1750 eV the spectra coincide, thus proving that the outer surfaces as well as the near-surface regions are the same.

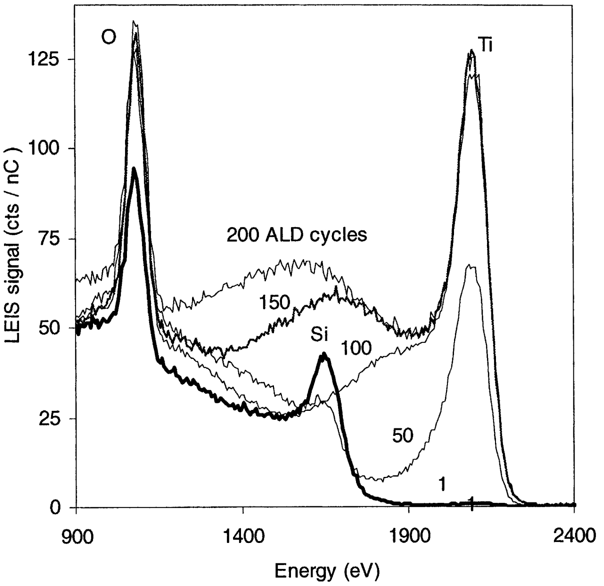

Fig. 6. LEIS spectra for a Si wafer with ALD grown TiN layers. Spectra are measured with 3 keV $^4He^+$ incident ions. Spectra after 1, 50, 100, 150 and 200 ALD cycles are given.

For lower energies the signals drop to the value for the sample after 50 cycles. Although these drops occur at different energies, due to the difference in layer thickness after 150 and 200 cycles, the rates of the decrease are very similar (same underlying structures). For the present experimental conditions a total energy loss of 1000 eV during the ingoing and outgoing trajectory in the layer is estimated to be due to a layer thickness of about 6 nm. Thus after completion of the surface coverage (100 cycles), an additional 3 nm was grown in the following 100 cycles.

As the above results illustrate for TiN layers, LEIS can be used to detect and quantify the total area of pinholes and also provides (non-destructively) the in-depth distribution. These features have proven very important information for the optimization of the experimental parameters in the growth of ultra-thin layers. Other surface techniques, such as XPS cannot provide this kind of information, since the much higher information depth makes it impossible to distinguish whether the signal from the substrate is due to pinholes or due to a somewhat thinner overlayer.

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