High-resolution secondary ion mass spectrometry depth profiling of nanolayers

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RATIONALE: Although the fundamental physical limits for depth resolution of secondary ion mass spectrometry are well understood in theory, the experimental work to achieve and demonstrate them is still ongoing. We report results of high-resolution TOF SIMS (time-of-flight secondary ion mass spectrometry) depth profiling experiments on a nanolayered structure, a stack of 16 alternating MgO and ZnO ~5.5 nm layers grown on a Si substrate by atomic layer deposition.

METHODS: The measurements were performed using a newly developed approach implementing a low-energy direct current normally incident Ar+ ion beam for ion milling (250 eV and 500 eV energy), in combination with a pulsed 5 keV Ar+ ion beam at 60° incidence for TOF SIMS analysis. By this optimized arrangement, a noticeably improved version of the dual-beam (DB) approach to TOF SIMS depth profiling is introduced, which can be dubbed gentleDB.

RESULTS: The mixing-roughness-information model was applied to detailed analysis of experimental results. It revealed that the gentleDB approach allows ultimate depth resolution by confining the ion beam mixing length to about two monolayers. This corresponds to the escape depth of secondary ions, the fundamental depth resolution limitation in SIMS. Other parameters deduced from the measured depth profiles indicated that a single layer thickness is equal to 6 nm so that the ‘flat’ layer thickness d is 3 nm and the interfacial roughness σ is 1.5 nm, thus yielding d + 2σ ~ 6 nm.

CONCLUSIONS: We have demonstrated that gentleDB TOF SIMS depth profiling with noble gas ion beams is capable of revealing the structural features of a stack of nanolayers, resolving its original surface and estimating the roughness of interlayer interfaces, information which is difficult to obtain by traditional approaches. Copyright © 2012 John Wiley & Sons, Ltd.
Dual-beam (DB) depth profiling\cite{17} was introduced in time-of-flight (TOF) SIMS instruments to decouple the depth resolution of the direct current (dc) ion milling beam from the lateral resolution of the pulsed analysis ion beam. In the DB approach, the sputtering/milling and analysis cycles are independent, and the depth resolution is controlled only by the ion milling beam parameters as long as a parameter $\alpha < 1$. We introduce here the parameter $\alpha$ for accurate comparison of ion sources with different operating currents, beam energies, and primary species types $\alpha = E_{t}/E_{b}$. The parameter $E$ can be called here the effective erosion efficiency ($E^2$) of an ion source (in at/cm$^2$) at a specific current density $j$ and sputtering yield $Y_{A}(E_{b})$, that depends on the sputtering species and their energy $E_{b}$, and incidence angle, where $A$ denotes the element or material under sputtering $E = \frac{Y_{A}(E_{b})}{j}$, where $e$ is the elementary charge and $t$ is the time interval when an ion gun is on during a single milling or analysis cycle. One can compare this strict parameter $\alpha$ with simple ratio of current densities $\frac{j_{analyzing}}{j_{milling}}$ proposed by Iltgen et al.\cite{17} In order to fully realize the potential of the DB sputter depth profiling approach, we further improved it by implementing a normally incident sputtering/milling ion beam, which is extracted from the ion source at a nominal energy of a few keV and delivered with the same energy into the target region, where the target potential can decelerate it so that the impact energy does not exceed a few hundred eV. This permits direct adjustment of the ion milling beam energy (down to the sputtering threshold) without losses of the ion beam current and degradation of the beam spot quality. An important benefit of the normal incidence sputtering/milling is the significant reduction in roughening of the surface induced by the ion beam.\cite{19} Moreover, the lower the impact energy, the lower are the ion-mixing effects. The low-energy normally incident sputtering/milling ion beam maximizes the benefits of the DB sputter depth profiling and allows us to create a versatile instrument, suitable both for ultra-trace surface analysis\cite{18,20} and for applications in materials, and thus to address current problems in the successful application of nanodevices discussed by Richman and Hutchison.\cite{21}

We apply here a gentleDB approach to better understand the chemistry and structure of ultra-thin films produced by atomic layer deposition (ALD). The ALD technique is widely used for a layer-by-layer materials synthesis and has great application potential in many areas due to its ability to coat high-aspect-ratio substrates by conformal layered structures with precisely predefined compositional profiles.\cite{22,23} One such important application area is the functionalization of material surfaces for use in novel detectors and sensors. Our effort here is a contribution to the Large Area Picosecond Photo-Detector collaboration,\cite{24} which is focused on fast particle detectors with large areas functionalized by ALD. It is known that thin films of metal oxides can serve as very efficient emitters of secondary electrons and be used for improving detector performance. Moreover, it has recently been shown that such ALD-grown films of several nm thickness enable independent tailoring of the electrical resistance and the secondary electron emission yield.\cite{25} A functionalization of a detector based on a large area (tens square centimeters) microchannel plate means that surfaces of the vast amount of microchannel plate pores must be coated by thin films with predefined characteristics. This task is the perfect match to the unique capabilities of ALD. At the same time, understanding and controlling the coating uniformity (thickness fluctuation, etc.) and the condition of interfaces between resistive and emitting layers as well as between those and the substrate are extremely important for improving the materials’ performance and functionality.

With this goal in mind, we have characterized in this work a stack of 16 alternating ~5.5-nm MgO and ZnO layers (8 of each) using our gentleDB SIMS depth profiling approach with normally incident 250 eV and 500 eV Ar$^+$ ion beams for sputtering/milling and a pulsed 5 keV Ar$^+$ beam (pointed at 60° from the target normal) for analysis. The chosen stack of 8 pairs MgO/ZnO, being one of the proposed functionalization systems, serves two purposes. The first one is to create a planar (unfolded) model of an actual microchannel plate pore surface coating with complex geometry in order to reveal the layer-to-layer reproducibility of the ALD process starting from the substrate, along with the layers’ uniformity and the conditions of interlayer interfaces. The other purpose is to test the depth profiling capabilities of the gentleDB approach. Furthermore, multilayer nanostructures and devices are at the forefront of materials science. Giant magnetoresistance multilayer films\cite{26} or superlattices of transition metal oxides\cite{27} are striking examples of this. The desired performance of such structures strongly depends on the interfacial roughness, interdiffusion between layers, layer-to-layer consistency, and also layer conformity. Thus, we aim to demonstrate in this work the unique synergy of the combination of low-energy sputtering/milling with inert gas ions and the normal incidence angle, which makes the gentleDB depth profiling approach superior to many others, especially when applied to characterization of nanolayers. In this case, the capability of sputter depth profiling without alteration of the sample chemical composition and modification of its surface and interface morphology does minimize instrumental artifacts and experimental/procedural assumptions and thus helps to elucidate the relationship between these parameters and advance materials synthesis approaches. We will support these statements by demonstrating accurate depth profiling on the nanometer scale and determining key characterization parameters such as the ion beam mixing length, and the decay $\lambda_{d}$ and leading $\lambda_{up}$ lengths, which effectively characterize the resolution of an instrument and can be compared with those of other approaches/setups in the field. The proposed characterization approach becomes even more important if one imagines that less-than-nm depth resolution is achieved laterally over the area of ~1 mm$^2$ (in general, this area can be varied between ~100 x 100 $\mu$m$^2$ and several $\text{mm}^2$).

**EXPERIMENTAL**

**Samples by ALD**

A layered structure 15.5 nm MgO/5.5 nm ZnO $\times 8$ was grown by the ALD technique on a Si substrate and characterized by X-ray diffraction and ellipsometry. The standard calibration and characterization procedures of ALD can be found in the literature.\cite{23,28-30} The structural data obtained from these measurements indicated that MgO layers are amorphous and ZnO layers are polycrystalline in the wurtzite phase. Although
the surface roughness of the MgO/ZnO sample was not measured, Al2O3/ZnO multilayers prepared under similar conditions had a surface roughness of 0.9–1.5 nm. The roughness of the Si substrate was ~0.3 nm. The initial layer-to-layer mixing due to thermal diffusion during growth at T = 473 K was expected to be extremely low.

**gentleDB TOF SIMS depth profiling**

The depth profiling of the layered structure described above was performed using a custom-made SARISA (Surface Analysis by Resonance Ionization of Sputtered Atoms) instrument operated in SIMS mode (instead of its primary mode of secondary neutral mass spectrometry with laser post-ionization). The SARISA TOF mass spectrometer was designed to operate in multiple modes using the same set of ion optics. With post-ionization lasers switched off, the instrument operation corresponds to that of TOF SIMS with long primary ion pulses (~0.2–1 µs) and delayed extraction of secondary ions. For the experiments described below, the SARISA instrument’s ion optics either delivered the primary milling Ar+ ion beam to the sample assuring its orthogonal impact onto sample surface and controlling its impact energy, or extracted secondary ions generated by a pulsed analytical Ar+ ion beam and performed their TOF MS analysis. Fast switching between these regimes was performed electronically by changing the potentials of the optics electrodes.

The low-energy ion beam is formed by injecting a keV ion beam produced by a VG EX05 gun (formerly VG Microtech, East Grinstead, UK, presently Thermo Fisher Scientific Inc.) into the TOF spectrometer ion optics, by delivering and focusing the beam at normal incidence to the sample and by decelerating the ions to the desired low impact energy by biasing the target with an appropriate voltage (see Fig. 1). The beam defocusing, which accompanies this deceleration, is compensated for by changing the voltage of the outlet electrostatic lens, called Lens1. The impact energy of this milling beam was set in this study to either 250 or 500 eV, and the ion current was ~1 µA. This beam was raster scanned over the sample surface by engaging an octupole deflector present in the TOF system ion path (the Shaping Octupole in Fig. 1), so that a square crater of ~1.5 × 1.5 mm² (shown in Fig. 1 as a blue

Figure 1. (a) Diagram of the dual-beam system. The primary Ar+ beam comes from the VG low-energy column and is deflected into the front TOF column by the Bending System optics. The ion beam is tightly focused with front end Lens1, impinging at normal incidence with respect to the sample surface. The beam is raster scanned by the Shaping Octupole. The separate Atomika ion gun is pointed at the target at 60° from its normal and equipped with a pulsing and raster scanning plates. The electron gun images the surface topography. (b) White light interferometry image of a high-energy Atomika Raster crater positioned in the center of a low-energy VG Raster crater, showing very good superimposing of sputtering/milling and analysis ion beams to perform correct dual-beam depth profiling. The Atomika Raster crater was dc sputtered just after the completion of the gentleDB SIMS measurements in order to reveal the place where the analysis was carried out, since the pulsed analytical beam does not produce any visible bowl under conditions satisfying |x| < 1.
Depth profiling of nanolayers by high-resolution SIMS

square) was eroded. The exact size of the crater depends on the deceleration potential of the target, which also deflects the beam when it is raster scanned. For example, the ratio of the crater sides between \( \eta_1 = 250 \text{ eV} \) and \( \eta_2 = 3 \text{ keV} \) is 1.3, this value was proved both by crater imaging and by SIMION 3D\(^{[33]}\) simulation.

The analytical ion beam, used to probe the sample at various depths, comes from an Atomika WF421 gun (formerly Atomika Instruments GmbH, Oberschleißheim, Munich, Germany, presently CAMECA, part of AMETEK Materials Analysis Division\(^{[34]}\)) pointed at 60° incidence with respect to the target normal (Fig. 1). This ion beam can be independently tuned, raster scanned, and pulsed. The primary Ar\(^{+} \) ion energy was always 5 keV, and the pulse duration used in the analysis in all the experiments was 200 ns, since mass resolution under these conditions was sufficient. The raster scan size of this ion beam in all the experiments described here was set to \( 500 \times 500 \mu \text{m}^2 \) (the smaller green square in Fig. 1). During the TOF MS analysis cycle, the deceleration potential on the target is switched off. In the gentleDB depth profiling regime, the Atomika ion beam was only used for analysis. By choosing an appropriate aperture, the primary ion current was set to 30 nA, in order to attenuate the secondary ion signal so that the TOF MS detector is not saturated. For the two ion beams used in these experiments, the parameter \( \alpha = E_{\text{Atomika}}/E_{\text{low energy}} \) was \( 10^{-5} \).

In order to perform the gentleDB depth profiling, the analysis beam raster was fitted into the center of the low-energy milling beam raster. To achieve this pre-alignment, a Faraday cup was used for ion beam collection which took advantage of available crater imaging capabilities. Crater imaging was carried out \textit{in situ} by an optical Schwarzschild-type microscope\(^{[18]} \) and scanning electron microscopy\(^{[18,35]} \) or by \textit{ex situ} optical white light interferometry\(^{[36]} \) (Fig. 1(b)).

**RESULTS AND DISCUSSION**

Figure 2 demonstrates normalized depth profiles obtained by the gentleDB approach at ion milling beam energies of 250 and 500 eV. The 24\(^{Mg} \) and 64\(^{Zn} \) depth profiles are very similar and feature high contrast and high stability of the signal all the way through the multilayer structure. The model structure of the 24\(^{Mg} \) distribution based on ellipsometry measurements is shown in Fig. 2 as a black dotted line. The end of the last layer depth profile is marked by a 28\(^{Si} \) signal spike from the substrate. The variation in the 28\(^{Si} \) SIMS signal is due to variation in the Si secondary ion yield \( \gamma \) from SiO\(_2\), and its subsequent drop and stabilization are observed at a 100-fold lower level than the spike magnitude, which coincides with the known ratio \( \frac{\gamma_{\text{SiO}_2}}{\gamma_{\text{Si}}} \approx 100 \). The first peak in the 24\(^{Mg} \) profile has an asymmetrical shape (cotangent-like) starting at the surface from the highest SIMS intensities converting directly into the trailing edge (no actual peak), while the 64\(^{Zn} \) profile starts approximately at the zero level; both profiles then have a steady sine-like shape. Table 1 shows the leading and decay lengths extracted from the depth profiles. The definition for the leading \( \lambda_{\text{up}} \) or decay \( \lambda_{\text{d}} \) length is the inverse of the first order coefficient for the linear approximation of the leading or trailing edges of a peak represented in semi-log scale, \( \ln \) (Intensity) vs. depth.\(^{[37]} \) Here, both \( \lambda_{\text{up}} \) and \( \lambda_{\text{d}} \) are \( \approx 5 \) nm for 24\(^{Mg} \), \( \approx 2 \) nm for 64\(^{Zn} \), and \( \lambda_{\text{up}} = 0.4 \) nm for 28\(^{Si} \). The measured leading and decay lengths were of the same order or better than published to-date corresponding data obtained with commercial state-of-the-art SIMS instrumentation using cluster/molecular or low energy O\(_2^+\)/Cs\(^+\) ion sources, or with laser-assisted atom probe tomography\(^{[9,10,12,13,17,38,39]} \)

As mentioned above, the first 24\(^{Mg} \) peak of the stack was not resolved from the surface constituent, which caps the structure. In order to resolve in the depth profile the 24\(^{Mg} \) peak corresponding to the topmost ALD layer from the surface contamination, we decreased the duration of the individual ion milling cycles and proportionally increased their number. Figure 3 shows the depth profile of a few top layers performed with more data points per depth increment to distinguish between the peak from the mass 24 capping layer and the first 24\(^{Mg} \) peak in the depth.

**Table 1.** Leading and decay lengths for \( ^{24}\text{Mg} \), \( ^{64}\text{Zn} \), and \( ^{28}\text{Si} \) extracted from low-energy dual-beam depth profiles

|            | \( ^{24}\text{Mg} \) | \( ^{64}\text{Zn} \) | \( ^{28}\text{Si} \) |
|------------|---------------------|---------------------|---------------------|
| \( \lambda_{\text{up}} \) (nm) | 5.6                 | 2.1                 | –                    |
| \( \lambda_{\text{d}} \) (nm) | 5.1                 | 2.1                 | –                    |
| \( \lambda_{\text{d}} \) at Si interface (nm) | 1.3                 | 1.1                 | 0.4                  |
| \( \lambda_{\text{up}} \) (nm) | –                   | –                   | 0.4                  |
profile attributed to the first MgO layer. The green solid line here corresponds to the \(^{24}\)Mg depth profile with fewer depth increments, shown in Fig. 2. This emphasizes the potential for further enhancement of the resolving power by fine tuning of the gentleDB protocol. The distance between subsequent depth points in Fig. 3 is ~0.2 nm, which precisely correlates with half of the average lattice parameter of 3.9 Å for wurtzite MgO\(^{40}\) and half of the cubical unit cell size of crystalline MgO with a lattice parameter of 4.2 Å\(^{41}\).

The ratios of \(^{25}\)Mg/\(^{24}\)Mg and \(^{26}\)Mg/\(^{24}\)Mg proved that the mass 24 peak appears to be from Mg with correct terrestrial isotopic ratio values. Such stoichiometry enrichment may be mostly by the cascade mixing and roughness.

These experimental results clearly demonstrate the remarkable resolving power of the gentleDB approach to depth profiling. In this regard, as normal incidence should not noticeably affect the native sample roughness\(^{19}\), let us qualify what the definition 'gentle' means. For this, we apply the MRI (mixing-roughness-information) model\(^{42,43}\) to simulate the \(^{64}\)Zn peak in the 500 eV high-resolution gentleDB depth profiles using the model parameters \(w\) (cascade mixing length), \(\sigma\) (r.m.s., root mean square, roughness), and \(\lambda\) (information depth, or escape depth, ~1–2 monolayers in the case of SIMS).

A summary of the MRI model for the SIMS experiment is shown below. Note that the preferential sputtering effect is not taken into account here, since there is no such effect for MgO and ZnO. As a starting point, the ion mixing is modeled first by the differential Eqn. (1) for an ideal, flat layer of thickness \(d\), with the boundary conditions (2) and (3):

\[
\frac{dc_m(z)}{dz} + \frac{1}{w}c_m(z) = \frac{1}{w}c_{act}(z + w)
\]

\[
\begin{align*}
C_M^{up}(z) &= A \left(1 - \exp\left(-\frac{z}{w}\right)\right) \\
C_M^{up}|_{z = w} &= 0 \\
\Rightarrow C_M^{up}(z) &= 1 - \exp\left(-\frac{z - z_1 + w}{w}\right)
\end{align*}
\]

(1)

(2)

(3)

where \(c_M(z)\) and \(c_{act}(z + w)\) are apparent (at any depth \(z\)) and actual (at \(w\) deeper relative to \(z\)) concentrations of an element, respectively; \(w\) is the ion mixing length; \(z_1\) and \(z_2\) are the flat boundaries of the arbitrary layer of interest, so that \(z_2 - z_1 = d\) equals the flat layer thickness, \(d\). \(C_M^{up}\) and \(C_M^{cd}\) are the leading and trailing edges of the depth profile peak, respectively. Thus, due to the cascade mixing, the solution yields:

\[
C_M(z) = \begin{cases} 
1 - \exp\left(-\frac{z - z_1 + w}{w}\right), & z \in [z_1 - w; z_2 - w] \\
1 - \exp\left(-\frac{z_2 - z_1}{w}\right) \exp\left(-\frac{z - z_2 + w}{w}\right), & z > z_2 - w 
\end{cases}
\]

(4)

If the surface roughness (either inherent, or induced, or both) is taken into account, the profile broadens as:

\[
C_{MR}(z) = \frac{1}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} C_M(t) \exp\left(-\frac{(t - z)^2}{2\sigma^2}\right) dt,
\]

(5)

where the mixing is convolved with the Gaussian function that takes the r.m.s. roughness \(\sigma\) as the standard deviation.

Finally, when both the \(C_{MR}(z)\) parameter and the effective depth contributing to the signal are considered, the depth profile shape can be expressed as:

\[
C_{MRI}(z) = \frac{1}{\lambda} \int_{-\infty}^{\infty} C_{MR}(x) \exp\left(-\frac{z - x}{\lambda}\right) dx,
\]

(6)

where \(\lambda\) is the information depth or ion escape depth, by conventional definition. Generally speaking, in the case of SIMS, the value of \(\lambda\) makes a negligible contribution to the elemental peak dependence on the depth \(C_{MRI}(z)\), defined mostly by the cascade mixing and roughness.
We found that the best matching between the measured and modeled profiles occurred when the MRI parameters \( w \) and \( \sigma \) were set as: \( w = 0.4 \text{ nm} \), \( \sigma = 1.5 \text{ nm} \), and the parameter \( \lambda \) was fixed at value 0.2 nm corresponding to one monolayer. The nominal thickness (flat thickness) of the layer, \( d \), had to be 3 nm to get the best peak fit in Fig. 4. The thickness \( d \) is not a free parameter of the MRI model. Nevertheless, being unknown \textit{a priori}, it had to be varied in order to define the boundary conditions (2) and (3). The effective thickness of a single ZnO layer, i.e., \( 2\sigma + d \), is then equal to 6 nm. This value obtained by MRI agrees well with those estimated for a single ALD layer by ellipsometry and the quartz crystal microbalance technique except that the real material layer is not ideally flat; it can be represented by a structure made of a flat inner layer squeezed between comparable-in-thickness additions on both sides representing wavy interfaces. Thus, under gentleDB conditions, the value \( \sigma = 1.5 \text{ nm} \) calculated for the first \( ^{64}\text{Zn} \) peak can be accepted as the native roughness of the sample inner interfaces (see Fig. 4). In agreement with the MRI model results, this roughness causes symmetrical peak broadening in sputter depth profiling experiments.

It is interesting that some previous studies, e.g., Bartok et al.,\cite{44} concluded that the attenuation of the signal intensity of each subsequent layer in laminate/multilayer structures, by approximately \( \sin(\chi) \cdot \exp(-\chi \cdot \lambda) \) law, occurs only due to the native interface roughness of layered structures. However, the results of the gentleDB depth profiling on a sample of exceedingly disturbed grown interfaces suggest that the native roughness is not the dominant factor in the degradation and smearing of depth profiles in SIMS. To prove this, we applied the conventional single-beam TOF SIMS depth profiling approach to the same sample, using 5 keV Ar\(^+\) ions with 60\(^\circ\) incidence angle (generated by the Atomika WF421 ion gun) – for both ion milling and TOF MS analysis. The comparison between the single-beam and gentleDB approaches (to be published elsewhere) revealed dramatic differences: the ion beam mixing length \( w \) increased from 0.4 nm to 3 to 4 nm,\cite{45} which is of the order of the entire ALD layer thickness. Moreover, we observed with the single-beam approach the periodical sine signal with exponential attenuation mentioned above as well as smearing of the peak shapes for deeper layers. To summarize, ion beam mixing appears to be the most important phenomenon to account for depth profiling experiments on nanolayered structures. Reducing the ion mixing length \( w \) by a proper choice of the analytical procedure can produce depth profiles such as the ones shown in Fig. 2 that reveal much more information about the samples than about the measurement artifacts and distortions.

**CONCLUSIONS**

We have outlined herein an approach to characterization of nanoscopic layered structures by application of TOF SIMS. Our gentle variant of the dual-beam sputter depth profiling (gentleDB) applied to characterization of nanolayered materials has been described and the sub-nanometer depth resolution of this method has been demonstrated. This approach combines a normally incident low-energy (down to sputtering threshold) Ar\(^+\) ion beam for milling with a several keV pulsed Ar\(^+\) ion beam (60\(^\circ\) incidence angle) for analysis. The shallow penetration depth of these milling primary ions results in an ultra-short range crystal lattice disturbance of about 0.4 nm thus enabling measurements of structural parameters (flat thickness and roughness) of a stack of 16 alternating MgO and ZnO nanolayers (8 of each, with thickness of ~5.5 nm) grown by ALD on a Si substrate. The interfacial roughness as small as 1.5 nm estimated by the gentleDB sputter depth profiling agrees well with measurements obtained by other techniques: the surface roughness of individual ZnO layers (~0.5 nm) determined by atomic force microscopy\cite{30} and the roughness of the multilayer structure (~0.9–1.5 nm) determined by X-ray reflectivity and atomic force microscopy for comparable ALD-grown Al\(_2\)O\(_3\)/ZnO multilayers.\cite{23,30}

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**REFERENCES**

[1] O. Ingolfsson, A. M. Wodtke. Bridging the cluster-to-bulk divide: electron attachment time-of-flight mass spectrometry reveals geometrical shell closings in (SF\(_6\))\(_n\) clusters \((n = 2–550)\). Phys. Rev. Lett. \textbf{2001}, \textit{87}, 183401.

[2] R. J. H. Morris, M. G. Dowsett. Ion yields and erosion rates for Si\(_{1–x}\) Ge\(_x\) \( (0 < x < 1) \) ultralow energy O\(_2\) secondary ion mass spectrometry in the energy range of 0.25–1 keV. \textit{J. Appl. Phys.} \textbf{2009}, \textit{105}, 114316.

[3] N. Vanhove, P. Lievens, W. Vandervorst. Particle emission from chemically enhanced electron-beam-induced etching.
of Si. An approach for zero-energy secondary-ion mass spectrometry. Phys. Rev. B 2009, 79, 035305.

[4] H. Oechsner, R. Getto, M. Kopnarski. Quantitative characterization of solid state phases by secondary neutral mass spectrometry. J. Appl. Phys. 2009, 105, 063525.

[5] A. Lakatos, G. A. Langer, A. Csik, C. Cserháti, M. Kis-Varga, L. Daroczi, G. L. Katona, Z. Erdélyi, G. Erdélyi, K. Vad, D. L. Beke. Nanoscale investigations of shift of individual interfaces in temperature induced processes of Ni–Si system by secondary neutral mass spectrometry. Appl. Phys. Lett. 2010, 97, 233103.

[6] M. P. Seah, C. P. A. Mulcahy, S. Biswas. Nonlinearities in depth profiling nanometer layers. J. Vac. Sci. Technol. B 2010, 28, 1215.

[7] G. Betz, G. K. Wehner. Sputtering of multicomponent materials. Topics Appl. Phys. 1983, 52, 11.

[8] M. Nastasi, J. W. Mayer. Ion beam mixing in metallic and semiconductor materials. Mater. Sci. Eng.: R. Reports 1994, 12, 1.

[9] S. Koelling, M. Gilbert, J. Goossens, A. Hikavyy, O. Richard, W. Vandervorst. High depth resolution analysis of Si/SiGe multilayers with the atom probe. Appl. Phys. Lett. 2009, 95, 144106.

[10] Y. Shimizu, Y. Kawamura, M. Uematsu, M. Tomita, T. Kinno, N. Okada, M. Kato, H. Uchida, M. Takahashi, H. Ito, H. Ishikawa, Y. Ohji, H. Takamizawa, Y. Nagai, K. M. Itoh. Depth and lateral resolution of laser-assisted atom probe microscopy of silicon revealed by isotopic heterostructures. J. Appl. Phys. 2011, 109, 036102.

[11] M. G. Dowsett, N. S. Smith, R. Bridgeland, D. Richards, A. C. Lovejoy, P. Pedrick, in Secondary Ion Mass Spectrometry SIMS X: Proceedings of the 10th International Conference on Secondary Ion Mass Spectrometry, (Eds: A. Benninghoven, B. Hagenhoff, H. W. Werner), John Wiley, Chichester, 1997, p. 367.

[12] A. Chanbasha, A. Wei. Ultralow-energy SIMS for shallow semiconductor depth profiling. Appl. Surf. Sci. 2008, 255, 1307.

[13] K. Itgten, A. Benninghoven, E. Niehuis, in Secondary Ion Mass Spectrometry SIMS XI: Proceedings of the 11th International Conference on Secondary Ion Mass Spectrometry, (Eds: G. Gillen, R. Lareau, J. Bennett, F. Stevie), John Wiley, Chichester, 1998, p.367.

[14] N. Winograd. The magic of cluster SIMS. Anal. Chem. 2005, 77, A142.

[15] D. Touboul, F. Kollmer, E. Niehuis, A. Brunelle, O. Laprévote. Improvement of biological time-of-flight-secondary ion mass spectrometry imaging with a bismuth cluster ion source. J. Am. Soc. Mass Spectrom. 2005, 16, 1608.

[16] I. Yamada, J. Matsuo, N. Toyoda, A. Kirkpatrick. Materials processing by gas cluster ion beams. Mater. Sci. Eng.: R. Reports 2001, 34, 231.

[17] K. Itgten, C. Bendel, A. Benninghoven, E. Niehuis. Optimized time-of-flight secondary ion mass spectrometry depth profiling with a dual beam technique. J. Vac. Sci. Technol. A 1997, 15, 460.

[18] I. Veryovkin, C. E. Tripa, M. Pellin. Efficient multiple beam ion optics for quantitative surface analysis: from simulations to a fully operational instrument. Phys. Procedia 2008, 1, 379.

[19] T. J. Ormsby, D. P. Chu, M. G. Dowsett, G. A. Cooke, S. B. Patel. The advantages of normal incidence ultra-low energy secondary ion mass spectrometry depth profiling. Appl. Surf. Sci. 1999, 144/145, 292.

[20] I. V. Veryovkin, C. E. Tripa, A. V. Zinovev, S. V. Baryshev, M. J. Pellin, D. S. Burnett. Multielement RIMS analysis of genesis solar wind collectors – Recent progress towards better accuracy, in Proceedings 42nd Lunar and Planetary Science Conference, 2011, Abstract #2308.

[21] E. K. Richman, J. E. Hutchison. The nanomaterial characterization bottleneck. ACS Nano 2009, 3, 2441.

[22] E. Thimsen, Q. Peng, A. B. F. Martinson, M. J. Pellin, J. W. Elam. Ion exchange in ultrathin films of CuZn and ZnS under atomic layer deposition conditions. Chem. Mater. 2011, 23, 4411.

[23] J. M. Jensen, A. B. Oelkers, T. Toivola, D. C. Johnson, J. W. Elam, S. M. George. X-ray reflectivity characterization of ZnO/Al2O3 multilayers prepared by atomic layer deposition. Chem. Mater. 2002, 14, 2276.

[24] Available: http://psec.uchicago.edu/.

[25] A. U. Mane, Q. Peng, M. J. Wetstein, R. G. Wagner, H. J. Frisch, O. H. W. Siegmund, M. J. Minot, B. W. Adams, M. C. Chollet, J. W. Elam. A novel atomic layer deposition method to fabricate economical and robust large area microchannel plates. Proc. SPIE 2011, 8031, 80312 H.

[26] I. Bakonyi, L. Péter. Electrodeposited multilayer films with giant magnetoresistance (GMR): Progress and problems. Prog. Mater. Sci. 2010, 55, 107.

[27] J. M. Rondinelli, N. A. Spaldin. Structure and properties of functional oxide thin films: insights from electronic-structure calculations. Advanced Mater. 2011, 23, 3363.

[28] V. Lujala, J. Skarp, M. Tammenmaa, T. Suntola. Atomic layer epitaxy growth of doped zinc oxide thin films from organometals. Appl. Surf. Sci. 1994, 82–83, 34.

[29] M. Putkonen, T. Sajavaara, L. Niinistö. Enhanced growth rate in atomic layer epitaxy deposition of magnesium oxide thin films. J. Mater. Chem. 2000, 10, 1857.

[30] J. W. Elam, Z. A. Schrist, S. M. George. ZrO2/Al2O3 nanolaminates fabricated by atomic layer deposition: growth and surface roughness measurements. Thin Solid Films 2002, 414, 43.

[31] I. Veryovkin, W. Calaway, M. Pellin. Ion optics of a new time-of-flight mass spectrometer for quantitative surface analysis. Nucl. Instrum. Methods Phys. Res. Section A 2004, 519, 353.

[32] https://www.thermo.com/eThermo/CMA/PDFs/Product/productPDF_56795.PDF

[33] SIMION software. Scientific Instrument Services, Inc. Available: http://www.simion.com/.

[34] http://www.cameca.com.

[35] S. V. Baryshev, A. V. Zinovev, C. E. Tripa, M. J. Pellin, D. S. Burnett, I. V. Veryovkin. Fine structure of near-surface solar wind depth profile by SNMS/SEM imaging, in Proceedings 43rd Lunar and Planetary Science Conference, 2012, Abstract #2909.

[36] S. V. Baryshev, A. V. Zinovev, C. E. Tripa, R. A. Erck, I. V. Veryovkin. White light interferometry for quantitative surface characterization in ion sputtering experiments. Appl. Surf. Sci. 2012, 258, 9693.

[37] K. Wittmaack. Impact-energy dependence of atomic mixing and selective sputtering of light impurities in cesium-bombarded silicon. Nucl. Instrum. Methods Phys. Res. 1983, 209/210, 191.

[38] M. J. P. Hopstaken, M. S. Gordon, D. Pfeiffer, D. K. Sadana, T. Topuria, P. M. Rice, C. Gerl, M. Richter, T. Marchiori. Sputtering behavior and evolution of depth resolution upon low energy ion irradiation of GaAs. J. Vac. Sci. Technol. B 2010, 28, 1287.

[39] M. G. Dowsett, D. P. Chu. Quantification of secondary-ion-mass spectrometry depth profiles using maximum entropy deconvolution with a sample independent response function. J. Vac. Sci. Technol. B 1998, 16, 377.

[40] H. Sowa, H. Alsfahls. High-pressure X-ray investigation of zincate ZnO single crystals using diamond anvils with an improved shape. J. Appl. Crystallogr. 2006, 39, 169.

[41] W.-Y. Hsu, R. Raj. MgO epitaxial thin films on (100) GaAs as a substrate for the growth of oriented PbTiO3. Appl. Phys. Lett. 1992, 60, 3105.

[42] S. Hofmann. Cascade mixing limitations in sputter profiling. J. Vac. Sci. Technol. B 1992, 10, 316.

[43] S. Hofmann. Atomic mixing, surface roughness and information depth in high-resolution AES depth profiling of a GaAs/AlAs superlattice structure. Surf. Interface Anal. 1994, 21, 673.

[44] A. Bartok, A. Csillag, K. Vad, G. Molnar, E. Toth-Kadar, L. Pinter. Application of surface roughness data for the evaluation of depth profile measurements of nanoscale multilayers. J. Electrochem. Soc. 2009, 156, D253.

[45] S. Hofmann. Sputter depth profile analysis of interfaces. Reports Prog. Phys. 1998, 61, 827.