Sputter depth profiling by secondary ion mass spectrometry coupled with sample current measurements

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Abstract

Ion-induced secondary electron emission determined via sample current measurements (SCM) was employed as a useful adjunct to conventional secondary ion mass spectrometry (SIMS). This paper reports on the results of 3–6 keV O2+ SIMS–SCM sputter depth profiling through CrN/AlN multilayer coatings on nickel alloy, titanium dioxide films deposited on stainless steel, and corrosion layers formed onto surface of magnesium alloy after long-term interaction with an ionic liquid. For Au/AlNO/Ta films on silicon, in addition to SIMS–SCM profiles, the signal of mass–energy separated backscattered Ne+ ions was monitored as a function of the depth sputtered as well. The results presented here indicate that secondary electron yields are less affected by “matrix effect” than secondary ion yields, and at the same time, more sensitive to work function variations and surface charging effects. SCM depth profiling, with suppression of “the crater effect” by electronic gating of the registration system is capable of monitoring interfaces in the multilayer structure, particularly, metal–dielectric boundaries. In contrast to SIMS, SCM data are not influenced by the angle and energy windows of an analyser. However, the sample current measurements provide lower dynamic range of the signal registration than SIMS, and SCM is applicable only to the structures with different secondary electron emission properties and/or different conductivity of the layers. To increase the efficiency, SCM should be accompanied by SIMS measurements or predetermined by proper calibration using other elemental-sensitive techniques.

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1. Introduction

Electron emission is an important process occurring under ion-beam bombardment of a solid surface (see, e.g. [1–4]). The energy distribution of the emitted electrons and their angular ejection pattern are widely used as sources of basic information about particle-solid interactions and for samples characterization. Less attention is paid to the total electron yields determined via sample (target) current measurements. Till now, there is no generally accepted name of this method. Wittmaack carried out target current measurements as a means of studying electron emission and ion reflection from Mg, Al and Si [5], and for investigation of energy- and angular-dependent compositional changes of Si under oxygen and nitrogen ion-beam bombardment [6,7]. Karolewski and Cavell referred to this technique as measurements of the ion-induced crystal current [8]. They combined it with static secondary ion mass spectrometry (SIMS) for monitoring adsorption processes on In and Cu [8,9] and for the characterization of the metal overlayer growth on oxygen-predosed Ni surface [10]. Milne et al. [11] were the first to employ simultaneous collection of ion-induced electron spectra while sputter profiling Nb/Al2O3/Al/Nb multilayered structure. They found similarities between the in-depth variations of some specific electron yields and secondary ion yields that facilitated interpretation of SIMS depth profiles complicated with matrix effects. The monitoring of the ion-induced secondary electron yield is presently a common method of end-point detection for focused ion-beam milling operations and other complex processes in micro and nanotechnology. There are some commercial focused ion-beam instruments operating in end-point detection mode, for instance LEO 1500XB and FIB 200 SIMS III by FEI, in which a total stage current (primary ion-beam plus secondary electron currents) is traced as a function of the depth milled [12].

Since the early 1990s, we have been employing a method named by us sample current measurements (SCM) along with dynamic SIMS and low-energy mass-resolved ion scattering spectrometry (MARISS) [13–17] for routine depth characterization of thin films and multilayer coatings [18–24]. In the present work, we discuss the principles, pros and cons of the SCM technique, and summarize our experience in its application for sputter depth profiling of the structures with different secondary electron emission properties and conductivity of the layers.

2. Experimental

The measurements described here were performed using a multifunctional custom-built installation [15,16,25]. For SIMS a duoplasmatron ion gun (model DP50B by VG Fison) generated mass-filtered 16O2+ primary ions with a bombarding energy of 1.5–3 keV/atom, and for MARISS 1–5 keV inert gas ions, mainly Ne+, were produced by an electron-impact ionisation source IQE 12/38 by SPECS. The secondary and scattered ion species were measured by a Hiden EQS 1000 Mass Energy Analyser, which combines an electrostatic energy analyser and a 1–1000 m/z quadrupole mass spectrometer. The depth of sputter craters, surface roughness and topography were determined with a Tencor Stylus Profiler P-10.

2.1. Method

Generally, sample current is measured by an amperemeter interposed between a sample and ground. We used a wideband preamplifier connected with a free ADC input channel of the Hiden control unit allowing faster current registration. The sample potential was biased in our experiments (Fig. 1). For the positive primary ion beam, the value of the sample current \( I_s \) can be defined as

\[
I_s = I_0 + I_e - I_+ + I_- \quad (1)
\]

where \( I_0 \) is the primary ion current, \( I_e \) is the current of secondary electrons, \( I_+ \) is the sum of the currents due to positive secondary ion emission and ion reflection (scattering), and \( I_- \) is the current of negative secondary ions plus contribution of recharged scattered ions.

We carried out two successive sample current measurements: (i) with a negative sample bias \( U_b = -100 \) V relative to ground) and a positive potential applied to the extractor and other surrounding electrodes (\( U_a = +300 \) V), and (ii) vice versa, i.e. with a positive sample potential and negatively biased surroundings. In the first case, the most part of positive ion emission was suppressed, and the sample current
could be expressed as

\[ I_1 \approx I_0 + I_e + I_0^{-} \]  \hspace{1cm} (2)

In the latter case, we measured

\[ I_2 \approx I_0 - I_1^{+} \]  \hspace{1cm} (3)

The resulting sample current monitored in our experiments was calculated as

\[ I_s = I_1 - I_2 = I_e + I_1^{+} + I_0^{-} = I_0(\gamma_e + \gamma_1^{+} + \gamma_0^{-}) \]  \hspace{1cm} (4)

where \( \gamma_e \) and \( \gamma_i^{\pm} \) are the coefficients of secondary electron and net positive (negative) ion emission, respectively. Typically, \( \gamma_i^{\pm} \) can be neglected in comparison with \( \gamma_e \), in which case \( I_s \) variations reflect changes in the ion-induced secondary electron yield. However, for bombardment-induced SiO\(_2\) formation on Si the total yield of positive and negative secondary ions might amount to 5–10% [26] and could not be ignored if the electron yield was of similar magnitude. For glancing beam incidence, reflection of primary ions was able to disturb the measurements as well, particularly in the case of Ne\(^{+}\) projectiles [5].

To use the sample current measurements for sputter depth profiling, we took into account possible variations in the value of \( I_0 \) since the experiments could last some hours. Our experimental procedure provided for continual monitoring of the primary ion current by means of measuring the \( I_2 \) current followed by the calculation of the \( I_s \) value.

During sputter depth profiling, the sample current was recorded in a quasi-parallel manner with the intensities of selected secondary and scattered ions under appropriate adjustment of the apparatus for each mode. The primary beam was raster-scanned, and the analysed zone of the crater eroded was limited by means of electronic gating of the registration systems for all signals including \( I_s \). As far as we know, there are no references in the literature about application of the electronic gating for ion-induced electron yield measurements.

2.2. Samples

The selection of the samples for the present work is linked to our scientific and technological interest, mainly addressed to development and characterization of the various coatings and thin layers. The following samples were measured:

1. The PVD multilayer CrN/AlN coatings on a Nimonic-75 superalloy developed by Teer Coatings [27] for application as abrasive materials for tipping turbine blades. We studied the high-temperature oxidation of these coatings by SIMS, SCM, XPS and MARISS (for details, see ref. [24]). Here our focus is on the 3 keV O\(_2^+\) SIMS–SCM depth profiles of as-received samples consisted of 14 (7 + 7) alternating layers of CrN and AlN with nominal layer widths of 0.3 and 0.1 \( \mu \)m, respectively.

2. Titanium dioxide films, 0.3–0.5 \( \mu \)m thick, deposited on stainless steel by Vacuum Surtec [28] using PVD technique. Due to the high photocatalytic activity, titania films, particularly in the anatase phase, are widely used for water and air purification [29], and in other fields [30]. We monitored 6 keV O\(_2^+\) SIMS–SCM depth profiles and measured thickness of the films to optimise the method of their manufacture.

3. Corrosion layer formed onto the surface of AZ91 alloy (wt.%, Al 8.0–9.5, Zn 0.3–1.0, Mn 0.1–0.3, Mg balance) after long-term interaction with ionic liquids (ILs). Magnesium and its alloys are
considered in automotive industry amongst promising materials for ultra-light gearbox fabrication. However, they are very sensitive to corrosion due to their high chemical and electrochemical activities. Ionic liquids are non-toxic room temperature molten salts composed of many combinations of organic and/or inorganic ions. ILs are used as solvents for clean synthesis and catalytic processes, as working fluids in batteries and capacitors, and as lubricant materials [31]. We investigated the corrosion behaviour of AZ91 alloy immersed in an ionic liquid composed by 1-ethyl-3-methyl-imidazolium and bis(trifluoromethanesulfonyl)imide ([C4mim][Tf2N]). The immersion test was performed in a Carbolite furnace (model CWF 13/5) at 225 °C for 20 days. The detailed study on the interaction between ionic liquids and different metal alloys will be published elsewhere [32]; here we present 3 keV O2+ SIMS–SCM data only.

4. The Au/AlNO/Ta films on Si(1 0 0) wafer manufactured by INESC-MN [33] using ion-beam deposition and oxidation. In this paper we report on 1 keV Ne+ SIMS–MARİSS–SCM profiles measured for the ultra-thin (about 2 nm) superficial gold and buried tantalum layers. It is known [34] that such metal-oxide sandwich layers are rather complicated objects with regard to the correct interpretation of their sputter depth profiles, notably when using inert gas primary ions. Here our attention is focused only on analysis of the superficial Au and buried Ta films, which were considered as special marker metal layers. Round robin investigations of these samples organized by the International Atomic Energy Agency were described in ref. [35]; the detailed results of our measurements were published in ref. [22].

3. Results and discussion

3.1. CrN/AlN multilayer coatings

Fig. 2 depicts the results of SIMS–SCM depth profiling through the CrN/AlN multilayer coatings deposited on a Nimonic-75 superalloy. In the figure, we show the in-depth distributions of 43(AlO)+ and 120(Cr2O)+ molecular ions selected as characteristic ions for the coating materials. The profiles including SCM data are scaled to the maximum intensity of the corresponding signals. The intensities related to the first (superficial) layers are not considered since they could be greatly raised due to the enhancement of the secondary ion (electron) yields caused by oxidation and contamination of the sample surface.

The data presented in Fig. 2 are affected to a certain extent by different artefacts associated with ion-beam sputtering. These are well-documented physical and apparatus problems [36–38], mainly beam-induced interlayer mixing, resulting in the progressive decay of the signals oscillations with increasing eroded depth. We could compare SIMS and SCM profiles measured simultaneously, in the same experimental conditions. For that, we calculated the modulation factor $K = \frac{I_{\text{max}}}{I_{\text{min}}}$ for SIMS AlO+ and for SCM peaks at the beginning and at the end of their in-depth distributions (labelled by numbers 2 and 7 in Fig. 2). $I_{\text{min}}$ was estimated as an arithmetic average of the valleys intensities at the right and left sides of the peaks. The results are presented in Table 1. The ratio $K_2/K_7$ specifying degradation of the profiles versus eroded depth is bigger for the SIMS data, namely 3.4 against 1.3 calculated for the SCM profile. These results show that in the same experimental conditions ion yield is more sensitive to the “matrix effect” than ion-induced secondary electron emission.
Note that of the secondary ion species, Cr$_2$O$^+$ and AlO$^+$, representing the coating layers of different composition, the sample current variations follow specifically the AlO$^+$ oscillations (Fig. 2). To explain such selectivity, we should consider relevant factors, which determine the emission properties of the layers. Employing O$_2^+$ bombardment brings about loading of the sample surface with implanted oxygen, and retention of oxygen in a matrix can be high enough [39]. Respectively, modification of the surface chemical state occurs. The stationary surface concentration of implanted oxygen in the AlN layer is expected to be larger than in CrN, because of a lower sputtering yield [24]. As a consequence, strong metal–oxygen bonds and even small oxide particles can be formed on the surface. Oxidation of Al results in a decrease of work function and in an increase of the ion induced electron yield, $\gamma_e$, which may be assumed proportional to the concentration of oxygen in the oxide layer [40]. On the contrary, oxidation of Cr is accompanied by a work function increase [41] that would suppress ion–electron emission. One more factor can enhance ion–electron emission from the Al–O/Al–N layers as compared to Cr–O/Cr–N. Both theoretical and experimental works established the direct proportionality of $\gamma_e$ to the electronic stopping power $S_e(x, E_i)$ of bombarding ions in the target [42]. At low energies of projectiles that are used in the present work the influence of the nuclear stopping power, $S_n$, should also be taken into account [42]. The calculations performed by using SRIM-2003 program [43] show that the electronic stopping power of 1.5 keV O$^+$ ions in both AlN (5.8 eV/Å) and Al$_2$O$_3$ (6.1 eV/Å) is larger than that in respective layers of CrN (4.1 eV/Å) and Cr$_2$O$_3$ (4.9 eV/Å), and the same is valid for the nuclear stopping $S_n$.

Besides, ion-induced oxidation of the coating gives increase of an abundant emission of various oxygen-containing secondary ions such as Al$_m$O$_m^+$, Cr$_m$O$_m^+$, CrAlO$_m^+$ [24]. Under O$_2^+$ bombardment, positive secondary ion yield of Al, $\gamma_{Al}^+$, rises greatly and is known to be about 5.6 times that of Cr [44]; for Al, also a higher negative secondary ion yield, $\gamma_{Al}^-$, is expected [45]. Thus, for AlN(+O), all the parameters ($\gamma_e, \gamma_e^+, \gamma_e^-$) entering into Eq. (4) are expected to be significantly larger than those for CrN(+O) so that the registered variations of the sample current $I_s$ will be associated with the AlN layers due to their predominant emission properties. Note that surface charging of the coating under ion-beam bombardment was found in our experiments [24] to be negligible despite the AlN film is an insulator. An efficient charge leakage through the coating appears to be associated with metallic-type electrical properties of thick Cr$_x$N layers [46] or conductivity in the Cr$_x$Al$_{1-x}$N structure [47].

3.2. Titanium dioxide on stainless steel

SIMS–SCM depth profiles for the TiO$_2$ films on stainless steel are presented in Fig. 3. The data in Fig. 3a are shown on the logarithmic scale for Cr$^+$, Ti$^+$ and TiO$^+$ secondary ions and on the linear scale for $I_s$. Fig. 3b depicts the normalized in-depth distributions, where the corresponding values of the minimal signals are subtracted.

The SCM and SIMS TiO$^+$ depth profiles coincide in each detail (Fig. 3b). The modulations, observed at the depth of 100–300 nm, are similar for both curves. However, in the near-surface region they exhibit opposite character. It is likely that the TiO$^+$ ion yield is considerably enhanced in this region, while the secondary electron emission is to a lesser degree subjected to the influence of the “matrix effect”. At the boundary between the TiO$_2$ film and a stainless steel the depth profile of the atomic Ti$^+$ secondary ions looks similar to the SCM and SIMS TiO$^+$ data, except modulations mentioned above. These modulations are less pronounced for the Ti$^+$ in-depth distribution. We can roughly estimate the secondary electron yield as $\gamma_e = I_e/I_s$. For the TiO$_2$ film, this ratio amounts to 1.8–2 (6 keV $^{16}$O$_2^+$ projectiles, 60° incident angle with respect to the sample surface).

3.3. Corrosion layer on the surface of AZ 91 alloy

The elemental and chemical composition of the corrosion layer formed onto surface of the AZ91 alloy after long-term interaction with an ionic liquid is
found to be very complex. According to our XPS and SIMS measurements [32], the products of the IL decomposition, such as –CF₃ and C=N groups, are the main components of the corrosion layer. The metals (Mg, Al, Zn and Mn) were detected only in oxidized forms (oxides, hydroxides and/or carbonates). The layer thickness was estimated to be within the range of 0.8–1.2 μm. The average surface roughness exhibited a five-fold increase after the immersion test in comparison with the initial state.

Fig. 4 shows the surface mapping of the AZ91 alloy measured by a stylus profiler in the different points after ending of the ion-beam sputtering. The surface topography is encoded by a colour wedge presented on the right side of the panels. The corrosion layer is inhomogeneous: the nonuniform part with corroded pits and cavities is shown in Fig. 4b, while Fig. 4a depicts the region with relatively uniform corrosion.

The results of SIMS–SCM depth profiling performed in these areas are shown in Fig. 5. We measured the intensity of the C⁻, F⁻ and C₂H₂⁻ ions for the corrosion layer and of AlO₂⁻ clusters for the AZ91 alloy. All profiles including SCM data are scaled to the maximum intensity of the corresponding signals. The thickness of the corrosion layer, calculated as that corresponding to the maximum of the fluorine in-depth distribution is different for the uniform and nonuniform parts, being 1 and 1.2 μm, respectively. The SIMS signals at the near-surface zone are reduced due to the surface charging, and the width of this zone depends on the thickness of the corrosion layer. In contrast to the titania films on stainless steel described above, the sample current increased during the sputtering of the corrosion layer, and the ion-induced secondary electron yield finally reached a value of 4. The SCM profile is shifted towards the surface with respect to the SIMS AlO₂⁻ in-depth distribution, and this shift is more pronounced for the uniform part of the corrosion layer.

It is known [6,10] that secondary electron yield is strongly influenced by work function variations, to a greater extent than secondary ion yield. Most likely, the shift of the SCM profiles mirrors modifications occurring in the energy band structure of the corrosion layer, mainly in the band gap. In the nonuniform part, the corrosion proceeded more rapidly, so the layer formed is supposed to be thicker than that in the uniform part of the sample. Such a difference results in a stronger surface charging under ion-beam bombardment and in the suppression of the SIMS signals for the nonuniform part as against the uniform one.

3.4. Au/AlNO/Ta films on silicon

The superimposed SIMS–MARISS–SCM depth profiling data are presented in Fig. 6. At the initial stage, the sample surface was covered by residual gas molecules and by some other contaminations resulting from the remaining protecting photoresist. None of the techniques used showed a 100% Au content (Fig. 6a). The maximum of the SIMS Au⁺ profile is shifted from the surface into the volume of the sample, presumably
Fig. 4. Surface mapping of the AZ91 alloy measured by a stylus profiler after termination of sputter profiling: (a) a region of uniform corrosion, and (b) a region with corrosion-produced pits and cavities.
due to a strong enhancement \cite{34} of the Au$^+$ secondary ion yield from the gold partly relocated into the oxynitride film. On the other hand, this relocation does not affect greatly the Ne$^+$ scattering ion yield, and the MARISS Ne$^+$/Au profile more correctly depicts the “true” elemental depth distribution. The sample current steadily grows during the sputtering of the gold layer and culminates when the corresponding SIMS and MARISS curves are at about half maximum level. The subsequent abrupt drop of the SCM signal corresponds to reaching the Au–oxynitride layer interface; it is accompanied by charging of the sample surface and, as a result, by suppression of secondary electron emission.

The depth profiles of the buried Ta layer are presented in Fig. 6b. The maxima of the sputtered and scattered ion signals, specifying depth position of the Ta layer, practically coincide with each other. However, the SIMS Ta$^+$ profile is broader than corresponding MARISS Ne$^+$/Ta curve because of the rise of the tantalum secondary ion yield from AINO layer due to “matrix effect”, like in the case of
aforesaid Au⁺-yield enhancement. Upon reaching the conductive Ta layer the SCM signal peaks and then falls down because of decreasing secondary electron yield in the bulk tantalum.

4. Summary

We studied in detail the analytical applications of ion-induced secondary electron emission determined via sample current measurements. As examples, different thin-film structures, including PVD multilayer coatings on a nickel alloy and corrosion layers formed onto the surface of a magnesium alloy after long-term interaction with an ionic liquid were considered. The results presented here indicate that SCM may be employed as a useful complement to conventional SIMS (MARISS) depth profiling.

For all the samples, the secondary electron yields are found to be less affected by “matrix effect” than the secondary ion yields and at the same time, more sensitive to work function variations and surface charging effects. SCM depth profiling, with suppression of the “crater effect” by electronic gating of the registration system is capable of monitoring interfaces in the multilayer structures, in particular, metal–dielectric boundaries. In contrast to SIMS, SCM data are not influenced by angle and energy windows of an analyser. However, the sample current measurements provide lower dynamic range of the signal registration than SIMS, and SCM is applicable only to the structures with different secondary electron emission properties and/or different conductivity of the layers. To increase the efficiency SCM should be accompanied by SIMS measurements or predetermined by proper calibration using other elemental-sensitive techniques.

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