Application of ‘Storing Matter’ technique in SIMS depth profile analysis

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Abstract

Secondary ion mass spectrometry (SIMS) is a very useful technique for the analysis of layered systems. It is based on the primary ion beam sputtering of solids and mass analysis of the emitted secondary ions. A main limitation of this technique results from the direct quantitative analysis, since the ionization efficiency of a given atom is highly influenced by the neighbouring atoms at the surface. This phenomenon is known as the ‘matrix effect’.

This problem can be partially solved by separation of the sputtering and ionization processes. The ‘Storing Matter’ technique involves deposition of the sputtered matter onto a rotating collector. Subsequently, ionisation occurs during the ion beam bombardment of the stored matter.

In case of sputtering of a given layered structure, the stored matter deposit presents the sequence of the deposition process and the analysis of this deposit reflects the investigated structure.

We analyse a set of oxidized steel samples and oxidized steel covered by aluminium. These types of structures are known for strong matrix effects at the metal oxide interfaces. The results of the ‘Storing Matter’ analyses are compared with the results of the classical SIMS analysis.

1. Introduction

Secondary ion mass spectrometry (SIMS) is a very useful surface analytical technique which allows to analyze layered systems with a very high depth resolution. Apart from many advantages such as: very low detection limit, high signal/noise dynamics, the SIMS technique is burdened with so-called matrix effect (ME) [1]. In surface analysis matrix refers to the components of the surface other than the analyte of interest. In SIMS, typically less than 1% of the sputtered material is ionized [2] and the matrix has a considerable effect on ionisation efficiency.

Slodzian [3] suggested a way to limit the matrix effect in SIMS. He proposed to split the sputtering and ionization processes in SIMS analysis. According to his idea, the sample is sputtered and the sputtered material is stored onto the rotating substrate (collector). In this sense, the sputtering history of a given sample is recorded on the rotating collector as a surface deposit. Additionally, important condition has to be fulfilled, namely, the thickness of the deposit has to be in the submonolayer range, in order to limit interactions between the deposited atoms. As a result, the collector becomes to be an independent matrix for the deposited atoms.

We decided to perform SM analysis of oxidized stainless steel grade 304 due to the strong matrix effects observed in standard SIMS analysis of such type samples. Comparison of the standard SIMS results with SM results allowed us to determine the matrix effects in this case study.

2. Experimental

In our experiment we used the SIMS SAJW-05 apparatus [4], equipped with the Physical Electronics 06-350E ion gun, with 500nA, 45° incidence, Ar + ion beam of 200 μm diameter. As mass spectrometer we used Balzers QMA-410. quadrupole mass filter. The initial pressure in the analytical chamber of SIMS was of the order of 5 × 10⁻¹⁰ Tr. To introduce samples we use two-stage sample load-lock pumped by a system consisting of turbomolecular and ion-sorption pumps. Primary ion beam is digitally scanned over 1.6 mm × 1.6 mm area with 15% electronic gate.

Analysed samples were electrochemically polished 304 steel sheet (72% Fe, 18% Cr, 9% Ni). The oxidation of the steel samples was carried out in 500° C and 760° C in a furnace in air. The two temperatures were selected so that significant differences in the segregation behaviour of the 304 steel components could be compared. Selected part of the oxidized steel samples were also covered with a 50 nm layer of aluminium by vacuum evaporation (evaporation pressure was about 8 mTorr) using an Edwards E 3020 vacuum evaporator.
The SM procedure has been described extensively elsewhere[2,5]. It consists of sputtering the sample and deposition of the sputtered material through the diaphragm onto the rotating collector. In our design [5], the collector rotation is provided by a hand-watch mechanism that ensures the collector to rotate at a speed of 1 rev/h. The mechanism operates in dry conditions (without any grease). Between the analyzed sample and the rotating collector, a 0.1 mm × 2 mm rectangular diaphragm is positioned 2 mm above the sample and is oriented along the radius of the collector. The collector rotates 0.5 mm above the diaphragm. The rectangular diaphragm provides a higher resolution compared to the round one that was used earlier[5,6]. The schematic diagram of the SM measuring system is shown in Fig. 1.

The 5 keV Ar+ ion sputtering conditions were chosen so that 55 min of the sputtering process of the sample was sufficient to deposit roughly 250 nm thick structure onto the collector. The sputtering rate for 304 steel was approximately 4 nm/min. The Ar+ ion beam of the same parameters was used for the analysis of the collector, the only difference was that the beam was 2.5 mm line scanned (along the radius of the collector) instead of 1.6 mm × 1.6 mm raster scan used for sputter deposition process. Deposition of material onto collector was carried out using the same parameters of primary ion beam as in standard SIMS analysis.

The collectors used were 1 mm thick titanium discs with 10 mm internal diameter and 24.5 mm outer diameter. The discs were covered with molybdenum oxide, which was evaporated in an evaporation chamber at a pressure of about 1 × 10−4 mbar. Molybdenum oxide acts as an active matrix for SM analysis. In current study we investigate metals whose ionization efficiency can be increased in the presence of oxygen, the highly electronegative element of the MoOx compound. We have previously tried several other oxide coatings, but the best results for chromium were obtained for MoOx [6].

3. Results and discussion

Below we present a part of the results. Fig. 2 shows the results of SIMS analysis of non-oxidized, electropolished sample and two oxidized steel samples at 500 °C and 760 °C respectively. The sputtering rate during the SIMS analysis was 4 nm/min. We can see that the non-oxidized sample has a very thin oxide layer on top and no segregation of the alloy components is observed in this case. The analysis of the oxidized layers in 500 °C and 760 °C heated samples shows significant enhancement (above one order of magnitude) of emission of the main components with respect to the emission detected from the bulk of the steel. This is a typical ME. It happened due to the fact that strongly electronegative oxygen in the oxidised layer enhances the ionization of the positive secondary ions. Such enhancement of secondary ion emission is not observed in the case of SM measurement: see the raw data presented in Fig. 3. The artefact sinusoidal shape of the curves represents the secondary ionic signals at SM is caused by fluctuating distance of the rotating collector to the mass analyzer head.

The raw results presented in Figs. 2 and 3 have been normalised into ion currents with the use of selected sensitivity factors. Then conversion into ion ratio data was done by dividing the normalized currents by the sum of the normalized currents of the main components of steel. The result of this transformation is presented in Fig. 4. The sensitivity factors were chosen so that the ion ratio values measured at the end of the analysis (in the bulk) correspond to the actual value of particular component concentration of 304 steel. Results in Fig. 4 allow to compare the oxidized samples measured by standard SIMS (thin lines) and SM (thick lines). We see that SM analysis shows uniform distribution of components along the profile. There is no significant change in the concentration of Cr, Fe and Ni in the sample at 500 °C. However the standard SIMS analysis shows non uniform distributions. Local extrema of Cr and Fe curves can be explained by strong ME.

In the case of the sample baked at 760 °C, both analyses, standard SIMS and SM show not uniform distributions of Cr, Fe and Ni. Generally
samples covered by 50 nm of aluminum.

Fig. 5. Raw data of standard SIMS depth profile analysis of oxidized steel samples covered by 50 nm of aluminum.

we see chromium enrichment as well as iron and nickel depletion in the 200 nm depth range.

Considering the sputtering rate, it was assumed that it is approximately constant in time. In fact, the sputtering process strongly depends on the surface composition. The main limitation in precise determining of the depth is preferential sputtering. It is worth to note that in both analyses regular SIMS and SM sputtering parameters are the same, and as a result preferential sputtering is also the same, but conversion of sputtering time into depth is very difficult.

Chromium segregation to the surface is well known phenomenon in austenitic steels [7] and in the current study we use these compositional changes to quantify ME in SIMS. Fig. 5 shows the result of standard SIMS analysis of the same oxidized steel samples but coated with ~50 nm aluminium layer. Raw results of depth profile analysis show strong ME of Al signals at the surface and at Al/steel interface due to the oxidation effect. The data in Fig. 6 are the normalized results of the SIMS and SM depth profile analysis of these samples. SIMS Al profiles are burdened by ME, while SM Al profiles are free of ME. Also SIMS Cr and Fe profiles suffer from strong ME in SIMS (we observe local depletion of Fe at a depth of ~70 nm for both 500 °C and 760 °C samples), while SM analyses are free of it.

Fig. 7 shows the data for oxidized stainless steel samples and presents the results of calculation of the ME dependent of the Cr concentration [Cr]. Chromium ME_{Cr} is defined as:

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ME_{Cr} = \frac{[Cr]_{SIMS} - [Cr]_{SM}}{[Cr]_{SIMS}}
\]

where [Cr] is the chromium concentration resulted from SM and SIMS measurements. Thus, the value of ME directly comes from the comparison of the result of SM and SIMS. It is clear that the largest matrix effect is observed for the sample heated at a higher temperature. The highest value of ME_{Cr} is for Cr/Fe ratio approx. 1:1.

In our study a very important is sticking coefficient onto collector for different elements. In order to reduce this effect we used a collector covered with molybdenum oxide with high dielectric constant \( \varepsilon \sim 6.3 \). In case of high \( \varepsilon \) materials electronic forces between metal and oxide are relatively high resulting also in a high sticking coefficient [8].

In general, adhesion of various elements onto collector strongly depends on electronic properties of the surface [8,9]. Stoneham [8] writes that strong metal—support interaction of transition metal iridium is a function of a dielectric constant \( \varepsilon \) of given oxides. Moreover he says that the highest interaction is observed for TiO_2 (\( \varepsilon = 6.8 \)) while in case of \( \varepsilon < 5 \) oxides like HfO_2 (4.9), ZrO_2 (4.75), Al_2O_3 (2.9), SiO_2 (2.4) strong interaction is not observed. Dielectric constant \( \varepsilon \) for MoO_3 is 6.3 so we consider that molybdenum oxide gives strong metal-support interaction for transition metals which are the aim of our study.

We do not know the exact adhesion coefficients of Cr, Fe and Ni to molybdenum oxide support, however in our studies we assume linear correlation between amount of the sputtered component and its equivalent deposited onto this collector. With this assumption, after normalization of the secondary ion signals to the bulk values, the normalized signals present a semi-quantitative result and allow to calculate ME_{Cr}. In fact, the ME is a function of oxidation stage of the surface and variable concentration of the main components and dopants.

Fig. 7 presents ME dependence on chromium concentration.

4. Conclusions

The aim of this study was to investigate the usefulness of the SM technique in the study of oxidized metals. The other aim was calculation of chromium ME in oxidized austenitic steel 304. Results of this study show that, comparing to SIMS analysis, ME has been significantly reduced when SM technique is used. The signal levels of secondary ions emitted from the oxide layer are comparable in both analytical techniques (SIMS and SM) despite the very thin (sub nanometer) deposited layer in case of the SM technique. Signal levels of components from the bulk of steel samples are much higher in the SM technique than in standard SIMS due to increased ionization efficiency by MoO_3 collector.

The depth resolution parameter in case of SM technique is lower than in typical SIMS analysis. This parameter is lower mainly due to the size (100 μm) of the diaphragm located between the sample and the collector. Also the type of beam scanning during SM analysis is...
important. In our solution, we use 2.5 mm line scan along the direction of the collector radius, while the Ar⁺ beam diameter is about 200 μm. This means that the beam diameter is two times wider than the width of the diaphragm. Another limitation is the step between data points, which for a single mass is more than 10 s. In case of four “masses” detected in SM analysis the step reaches 1 min, which corresponds to 6° rotation of the collector and the sputter depth interval of 4 nm, since sputtering rate during deposition in SM is estimated to be 250 nm per hour.

Despite the number of limitations, the SM results allowed us to calculate the chromium ME for the oxidized samples of 304 steel. As it was expected, the highest ME is observed in the chromium enriched oxide layer, at a depth of about 35 nm.

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References: