



The effect of glow discharge sputtering on the analysis of metal oxide films

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ABSTRACT

The potential of radiofrequency glow discharge optical emission spectrometry (rf-GD-OES) for the quantification and the solid-state speciation of metal oxide films has been investigated in this work. Two types of oxide coatings, an iron oxide film deposited on silicon and a chromate conversion coating (CCC), were studied at 700 Pa of pressure and 30 W of forward power. The metal to oxygen ratios in the quantitative depth profiles (Fe/O and Cr/O, respectively) were used to evaluate the oxidation states of iron and chromium in the oxide films, demonstrating the capability of GD-OES technique for depth-resolved solid-state speciation. Furthermore, the effect of glow discharge sputtering on the samples surface in terms of modifications in the surface morphology and species transformations, were investigated by using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The iron and chromium oxidation states were carefully studied by XPS at the original samples surface and at the bottom of GD craters, and a systematic reduction of metal elements was observed after rf-GD-OES analysis. In the case of thin oxide films, preferential sputtering can be considered as a critical factor since oxygen atoms can be preferentially sputtered, leaving a metal-enriched surface and, therefore, promoting the reduction of metal elements. In the present study preferential sputtering was found to be sample dependent, changing the proportion of the metal reduction in the oxide film with its composition. Additionally, alternative sputter-depth-profiling techniques such as secondary ion mass spectrometry (SIMS), femtosecond laser ablation (fs-LA), and XPS ion gun were used for the analysis of the CCC in order to evaluate the reduction of Cr⁶⁺ to Cr³⁺ depending on the sputtering mechanism.

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1. Introduction

The chemical form of a given element determines its actual toxicity, bioavailability, absorption to a living organism and its biogeochemical cycling in the environment, so the knowledge of the oxidation state is necessary to evaluate the toxicity of environmental pollutants. Due to the good corrosion resistance of chromate coatings, hexavalent chromium (Cr⁶⁺) compounds are widely used in the chemical and automotive industry for different applications such as pigments, metal plating, or leather tanning. As a result, Cr⁶⁺, which is a known carcinogenic, is released into the environment and can be available to humans. In order to limit and regulate the presence of Cr⁶⁺ in the environment, the European Union has recently promoted several directives that restrict the use of hexavalent chromium in the automotive industry and in electrical and electronic equipments (2000/53/EC and 2002/95/EC, respectively) [1,2]. Traditional methods of speciation analysis are based on the determination of the chemical forms of the element of interest

after wet extraction [3,4]. Although these methods provide a satisfactory level of accuracy and precision, the binding state of the element can change during the extraction stages. Furthermore, the required dissolution procedures are often the most time-consuming step of the analysis, may be associated with the risk of sample contamination and analyte loss, and any space-resolved information is most certainly lost.

Nowadays, there are different solid-state speciation techniques such as X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure spectroscopy (XANES), or secondary ion mass spectrometry (SIMS), which are successfully used to obtain detailed information of the surface stoichiometry in a broad range of applications [5–8]. Solid-state techniques may provide information of binding states of the elements at an atomic level as well as semi or quantitative depth-resolved analyses with an excellent spatial resolution [9]. In addition, some of these techniques allow non-destructive analyses, minimizing the conversion of the redox form of elements. However, the low depth reached in the analysis (for example, the XPS technique only supplies information of the first 5 nm of the sample surface) represents one of their main drawbacks in order to achieve depth-resolved solid-state speciation in coatings or multilayer systems of several tens of nanometers in thickness.

Thin film analysis by sputter-depth-profiling techniques is based on the erosion of surfaces as a result of energetic particle bombardment

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(mostly ions), with matter being removed continuously as a function of bombardment time. These analytical techniques can be divided in two main groups: removed-matter and remaining surface techniques [10]. In the so-called *removed-matter techniques* [e.g., secondary ion mass spectrometry (SIMS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), glow discharge optical emission spectrometry (GD-OES), and mass spectrometry (GD-MS)], the analysis of the sputtered matter as a function of the sputtering time allows the determination of the compositional distribution of a thin film *versus* the distance from the original surface. In the *remaining surface techniques* group [e.g., Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS)], the surface remaining after sputtering is analyzed. For both type of techniques, the incident particles for the sputtering process can be supplied by different sources such as an ion source, an X-ray source, a plasma, an accelerator, or by a radioactive material emitting alpha particles and, therefore, their analytical performances (e.g. maximum analysis depth, lateral and depth resolution, limits of detection, etc.) can significantly change (see Table 1).

According to its unique features, glow discharges (GDs) coupled to optical emission spectrometry (OES) and mass spectrometry (MS) are used in a wide variety of applications as a powerful analytical technique for the direct analysis of solid samples [11,12]. Advantages of GD sources include ease of use, fast sputtering rate, high depth resolution, excellent sensitivity, multielement capability, good quantification and high sample throughput. The main limitation of glow discharges resides in the inaccurate measurement of the radio-frequency (rf) GD parameters, especially for non-conducting films, and the lack of certified reference materials (CRMs) containing large amounts of light elements such as hydrogen, nitrogen, or oxygen. Nevertheless, in recent years, rf-GD-OES has proven to be a useful technique to perform compositional depth profiling studies on thin (<100 nm) and ultra-thin (<10 nm) films with high spatial resolution in an accurate and fast way [13]. Furthermore, although the determination of light elements in solid samples is complicated by the presence of these elements in the atmosphere, the use of high quality vacuum conditions has demonstrated the ability of rf-GD-OES to analyze light elements in both metals and non-metals [14].

We have investigated the potential of glow discharges to determine the different oxidation states of metals in oxide [15]. However, it should be highlighted that during ion bombardment several changes related to the composition and morphology of the sample surface may occur, and these effects have to be carefully evaluated and taken into account for chemical speciation studies. Although glow discharges have been widely employed for the analysis of many different types of samples, to our knowledge the influence of GD sputtering on the samples composition and morphology has not been investigated so far. Therefore, the main aim of the present work is to investigate the effect of glow discharge sputtering on the analysis

of metal oxide films in terms of morphological modifications and, mainly, species transformations by using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. The metal oxidation states were carefully investigated by XPS both at the original samples surface and at the bottom of GD craters, whereas AFM measurements were carried out to evaluate the morphological changes produced by GD sputtering into the samples surface. Two different types of oxide coatings, an iron oxide film deposited on silicon and a chromate conversion coating (CCC) deposited on zinc, were selected for the study. As a first stage, in order to obtain the compositional depth profiles of the oxide films and evaluate the capability of rf-GD-OES technique to achieve depth-resolved solid-state speciation, a multimatrix calibration (using both bulk CRMs and well-characterized coated calibration samples) associated with a dc bias voltage correction were employed in the quantification process. Additionally, alternative sputter-depth-profiling techniques such as SIMS, femtosecond LA, and XPS ion gun were used to analyze the chromate conversion coating and, thus, to investigate the influence of the different sputtering mechanisms on the species transformations.

2. Experimental

2.1. Samples and sample preparation

Two coated samples of high practical interest, a chromate conversion coating (CCC) and an iron oxide film, were selected to investigate the possibilities of space-resolved solid-state speciation using rf-GD-OES as well as to evaluate the effect of GD sputtering on the metal oxide films surface. First, a galvanized steel sheet, with a zinc layer of 10 μm thickness, was used as a substrate. The chromate conversion coating (in the order of 250–350 nm) was applied in a bath containing 200 g L^{-1} $\text{Na}_2\text{Cr}_2\text{O}_7 + 10 \text{ g L}^{-1}$ H_2SO_4 (pH 1.1–1.3) for 60 s at room temperature. After this chromating, the samples were rinsed in deionized water and the wet chromated samples were first dried using a hair dryer and then heated in an oven at 60 $^\circ\text{C}$ for 30 min. More detailed information on the sample preparation of the CCC is presented elsewhere [16].

On the other hand, the iron oxide film was deposited on a pure silicon wafer, and the sample was prepared using a Sputron (Balzers) experimental apparatus based on low-voltage plasma beam sputtering. During sputtering the iron target was subjected to a voltage of 1700 V and the current was kept constant at 0.6 A (current density $\sim 20 \text{ mA cm}^{-2}$). The target made from pure iron (60 mm in diameter) was sputtered in an atmosphere of argon and oxygen at a temperature below 120 $^\circ\text{C}$. The composition of the deposited iron oxide film ($1.82 \pm 0.05 \mu\text{m Fe}_3\text{O}_4$) depends on the partial pressure of oxygen and, in our case, the argon pressure was 2×10^{-1} Pa whereas the partial pressure of oxygen was in the range of $0.1\text{--}1.5 \times 10^{-1}$ Pa. Further details of the iron oxide film preparation are described elsewhere [17].

The thickness of the oxide layers was previously determined by scanning electron microscopy (SEM) on cross-sectioned witness samples, and a wide range of analytical techniques such as Auger electron spectroscopy (AES), X-ray diffraction (XRD) and atomic force microscopy (AFM) was used to check the samples composition, homogeneity and morphology. Additionally, the original samples and the samples analyzed by rf-GD-OES were kept under the same clean conditions in order to prevent, as much as possible, the effect of external contamination (e.g., air, light, or humidity) and, therefore, to ensure an appropriate comparison between the original samples surface and the bottom of GD craters.

2.2. Instrumentation

2.2.1. Glow discharge optical emission spectroscopy

GD-OES analysis was performed with a GD-Profiler 2TM instrument manufactured by HORIBA Jobin Yvon (Longjumeau Cedex, France). This instrument is equipped with a radiofrequency generator, a standard HJY

Table 1

Comparison of physical and analytical performances of several sputter-depth-profiling techniques

	GD-OES/MS	SIMS (dynamic)	XPS (Argon etching)
Particle bombardment	Ar^+	Ar^+ , Cs	Ar^+
Working pressure (mbar)	4–10	$10^{-10}\text{--}10^{-8}$	10^{-8}
Current density (mA cm^{-2})	50–500	<10	1–5
Incident angle ($^\circ$)	90	0–90	15–90
Ion energy (keV)	<0.3	1–30 (Ar^+)	1–5
Sputtering rates ($\mu\text{m min}^{-1}$)	1–10	<2	$5 \cdot 10^{-4}\text{--}5 \cdot 10^{-2}$
Max. analysis area (mm^2)	3–40	$3 \cdot 10^{-4}\text{--}1$	1–4
Max. analysis depth (μm)	100	1	<0.05
Lateral resolution (nm)	10^6	10^3	10^2
Depth resolution (nm)	<0.5	0.5–1.5	0.5–2.5
Limit of detection ($\mu\text{g g}^{-1}$)	$10^{-3}\text{--}1$	$10^{-3}\text{--}1$	10^3

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