A Comparative Study of GDOES, SIMS and XPS Depth Profiling of Thin Layers on Metallic Materials

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Glow discharge optical emission spectrometry (GDOES), which is an optical emission spectrometry using glow discharge plasma, gives the quantitative depth distribution of elements in a thin surface film formed on a metallic material. This paper describes GDOES depth profiling of surface films formed on two metallic materials. The samples were an anodized oxide film on aluminum and a chromium coating on tin free steel. The quantitative depth profiles give information of the layered structure of constituent elements in these surface films. The GDOES depth profiles were compared with depth profiles obtained by secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). On the basis of these results, characteristic features, such as advantages and disadvantages, of these surface analytical methods are discussed.

INTRODUCTION

Information on the chemical compositions of thin films and local areas in advanced materials is becoming important for the control of their properties, since their properties are strongly dominated by chemical characters in microscopic or nanoscopic regions. Thus, chemical analytical methods for evaluating microscopic regions are required to be established. However, it is sometimes difficult to quantitatively evaluate data measured by these analytical methods, because most materials are composed of inhomogeneous microstructures. Although there are still such remaining problems in chemical analysis of microscopic regions, some surface analytical methods have been established to evaluate the average depth distribution of elements in a surface film formed on materials. For instances, the usefulness of depth profiling by the glow discharge optical emission spectrometry (GDOES) has been well recognized through the international standardization of surface chemical analytical methods [1,2].

GDOES is often used to analyze surface films and coatings formed on a metallic material [2,3], since depth profiling by GDOES enables to analyze the quantitative composition and thickness of coatings. GDOES has several advantages: simple sample preparation, short measuring time, relatively high sensitivity and so on. Depth profiling by GDOES are obtained by measuring emission intensities during glow discharging without ultra-high vacuum.

The aim of this paper is to present two GDOES depth profiles for surface films formed on practical materials, and to discuss the usefulness of GDOES by comparing these depth profiles with obtained by the other methods. Analyzed samples are an anodized oxide film on aluminum and a chromium coating on tin free steel. Thickness of these surface films is very thin, being less than one micrometer. The other surface analytical methods used were secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS), which are often employed for analyzing thin surface films formed on materials. In order to understand characteristic features of these surface analytical methods, depth profiles obtained by SIMS and XPS were compared with those by GDOES.

EXPERIMENTAL

Two samples covered with different surface films were prepared for depth profiling measurements. One was an aluminum sheet covered with a 350 nm thick anodized oxide film. In the oxide film, a very thin chromium layer was embedded in 50 nm depth. Another sample was steel coated with an about 30 nm thick chromium layer, being tin free steel. The surface of the steel samples was relatively rough due to rolling of the sample, while the aluminum surface was flat. Thus, an influence of the roughness on depth profiling should be taken into account, when compositional depth profiles of a thin surface film are discussed.

GDOES apparatus used was Horiba JY-5000RF, by which depth profiles were obtained by measuring emission intensities for constituent elements as a function of sputtering time. The quantitative relationship between the composition and thickness were estimated according to a standard procedure [2]. SIMS and XPS depth profiling were also conducted for the same samples as measured by GDOES. Apparatus and measuring conditions for SIMS and XPS depth profiling were described elsewhere [4,5].

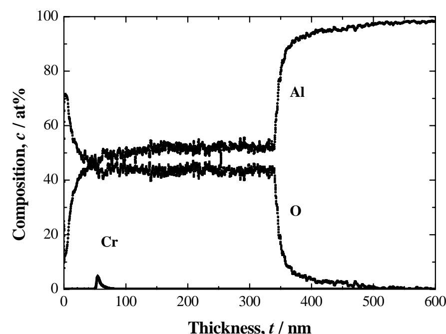

Fig.1 GDOES depth profile for an aluminum sheet covered with an anodized oxide layer.

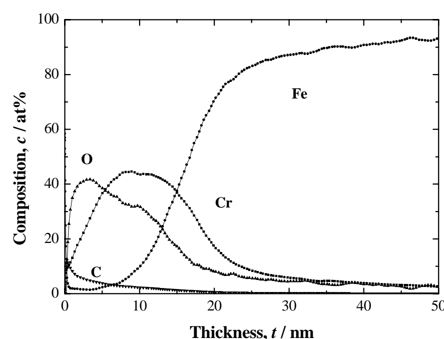

Fig.2 GDOES depth profile for a tin free sheet covered with a chromium layer.

RESULTS AND DISCUSSION

GDOES depth profiles

Figure 1 shows GDOES depth profiles of aluminum, oxygen and chromium in the aluminum sheet covered with an anodized oxide film. The depth profiles show that the measured thickness of the oxide film is in agreement with the real thickness, 350 nm, but the composition of the film is deviated from that for Al_2O_3. The deviation seems to arise from the fact that an emission yield of oxygen is not available for a non-conductive aluminum oxide, but obtained from data for an iron oxide. The very thin chromium layer embedded in the oxide layer was clearly detected in this GDOES profile.

GDOES depth profile of iron, chromium and oxygen for a tin free sheet coated with a chromium film is shown in Fig.2. The depth profiles of chromium and oxygen are broad. The broadness comes from the surface roughness of the sample. Nevertheless, the surface film on the sample sheet is shown to consist of chromium oxide and metallic chromium layers. In addition, clear carbon signal, which originates from hydrocarbon absorbed on the sample surface, appears to be significant in the depth profiles. This indicates that the adsorption of hydrocarbon considerably influences quantitative depth profiling of a very thin film, which was exposed to air.

SIMS DEPTH PROFILES

Small amount of elements are detectable in SIMS depth profiles, as secondary ions sputtered from a sample are measured. Figure 3 shows SIMS depth profiles of $CsAl^+$, CsO^+, $CsCr^+$, B^+, CsB^+ and CsH^+ from the aluminum sheet covered with an anodized oxide layer. The beam current of primary ions was 100nA. Aluminum, oxygen, chromium and hydrogen were detected using cesium cluster ions, to

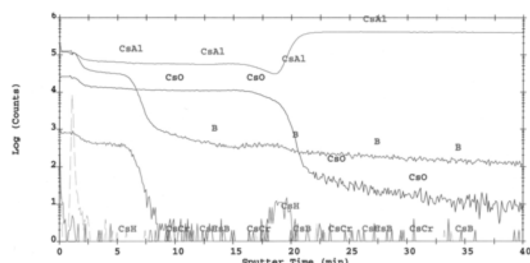

Fig.3 SIMS depth profile for an aluminum sheet covered with an anodized oxide layer.

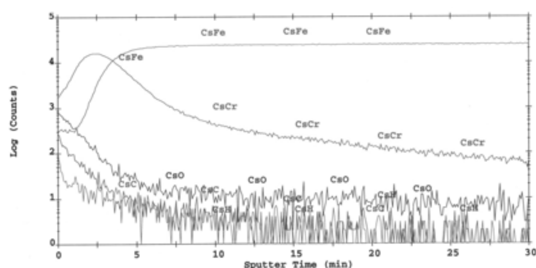

Fig.4 SIMS depth profile for a tin free sheet covered with a chromium layer.

measure adequately ion counts. B^+, CsB^+ and CsH^+ originate from residual elements in the oxide film. As it is hard to obtain reference samples and a calibration method for these SIMS depth profiles, quantitative analytical values of the composition and thickness were not obtained. Nevertheless, the characteristic distributions of boron and hydrogen in the surface film were detected owing to the high sensitivity of SIMS analysis.

Figures 4 shows SIMS depth profiles of $CsFe^+$, $CsCr^+$, CsO^+, CsC^+ and CsH^+ of tin free sheet covered with a chromium layer. As the thickness of the surface film was very thin, primary ion beam current was reduced to 5 nA. These depth profiles are again broad because of an influence of the surface roughness of the sample. A peak in the $CsCr^+$ profile was observed on the surface side of the tin free sheet. These qualitative results are consistent with the quantitative data obtained by GDOES.

XPS DEPTH PROFILES

XPS spectra give information of the chemical composition and state on the sample surface. A series of C 1s, O 1s, B 1s, Al 2p and Cr 2p XPS spectra from the aluminum sheet covered with an anodized oxide layer by argon ion sputtering are shown in Fig.5. The XPS spectra indicate the different chemical composition and state of these elements in-depth. For instance, changes in the chemical composition and state are observed in Cr 2p XPS spectra at an intermediate step. If the sputtering step is very fine, the chromium layer may be clearly detected. Then, it takes tremendously long time to measure suchXPS depth profiles. Thus, compositional depth profiles obtained by GDOES appear to be superior to XPS depth profiles, although information of the chemical state of elements is available by XPS only.

Figure 6 shows sequential XPS spectra of C 1s, O 1s, Cr 2p and Fe 2p XPS spectra were obtained from a tin free sheet covered with a chromium layer. An adsorbed carbon, a thin oxide layer and clear chromium layer are observed in these spectra. In

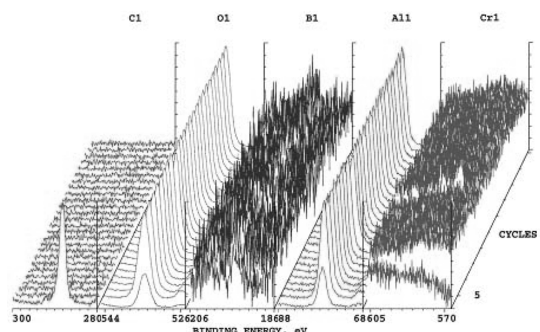

Fig.5 Sequential XPS spectra obtained by sputtering an aluminum sheet covered with an anodized oxide layer.

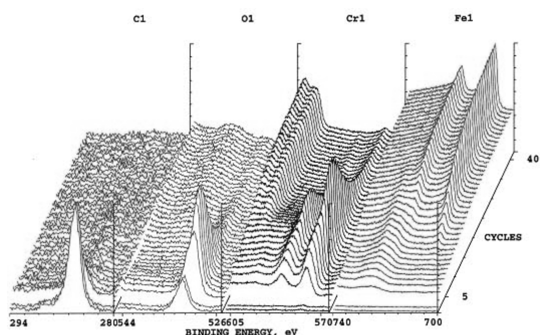

Fig.6 Sequential XPS spectra obtained by sputtering a tin free sheet covered with a chromium layer.

Tabel 1 Capabilities for depth profiling by GDOES, SIMS and XPS.

Method	Analyzed depth	Analyzed area	Measuring time
GDOES	1 nm – 100 μm	2 mm – 10 mm	ca.10 s for 1 μm
SIMS	1 nm – 10 μm	1 μm – 100 μm	ca.100 s for 1 μm
XPS	1 nm – 1 μm	10 μm – 1 mm	ca.1000 s for 1 μm

addition, chemical changes of iron and chromium in-depth are found in these XPS spectra. Although the sensitivity in the XPS spectra is not always sufficient, the XPS spectra reveal the chemical state of elements, which is not available in GDOES depth profiles.

COMPARISON OF CHARACTERISTIC OF DIFFERENT DEPTH PROFILES

Capabilities for depth profiling by GDOES, SIMS and XPS are summarized as shown in **Table 1**. The analyzed area in GDOES is relatively large, typically 4 mm in diameter, but GDOES can be applied to depth profiling up to about 100 micrometers. The depth resolution in depth profiling by these analytical techniques is practically dominated by the roughness of the sample surface. An advantage in depth profiling by GDOES is short measuring time, which is the reason why this method is adequate for analysis of industrial materials. Furthermore, the quantitative composition and thickness in a surface film can be obtained in depth profiling by GDOES. If a radio-frequency power supply is utilized as glow discharge source, a non-conductive surface film can also be analyzed in-depth.

Although some advantages in GDOES depth profiling are stressed here, important information of the sample surface is available by the other methods. SIMS is applied to detect a small amount of elements from a small area in a surface film, as shown in Figs.3 and 4. XPS spectra are very useful to study the chemical state of elements in a surface film, as shown in Figs.5 and 6. As a result, adequate combination of these surface analytical methods gives us information of realistic chemical features of a surface film formed on a material.

SUMMARY

Quantitative GDOES depth profiles have been shown for thin surface films formed on metallic materials.They are fundamentally consistent with the data obtained by SIMS and XPS, although different information is also obtained in SIMS and XPS depth profiles. Nevertheless, GDOES is superior for its rapid measurement and simple sample preparation required. The present comparative study shows that GDOES is very effective to chemical analysis of surface films on many practical metals.

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