

Practical Technique for Restraining Differential Charging in X-ray Photoelectron Spectroscopy: Os Coating

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Differential charging was observed in composite materials consisting of a metal and an insulator with electrical conduction between the specimen and the spectrometer in X-ray photoelectron spectroscopy (XPS). Gold evaporation was not suitable for the composite materials, although gold is the standard reference material for the binding energy, because its uniform evaporation on the rough surface was impossible. In contrast, as a result of using an Os coating formed by Plasma Chemical Vapor Deposition (PCVD) carried out to a 1nm target thickness to achieve electrical contact between the metallic and insulated materials, and thus measurements under a stable surface potential while restraining the charging and the differential charging of insulated materials became possible. We concluded that applying an Os coating is an effective method for achieving charge compensation of composite materials in XPS.

INTRODUCTION

The chemical state of the sample surface, which should ideally be homogeneous, is important in XPS. In the development of materials science, practical surface analysis has revealed that there are a number of composite materials, electric components and circuit patterns that consist of both insulating and conductive materials. They are heterogeneous in terms of microstructure and chemical composition. Generally, the reference binding energy for conductive and semi conductive surfaces is the Fermi edge, and the charging reference for insulated materials is an internal standard, adventitious carbon and evaporated gold. However, the reference binding energy for composite materials is not apparent.

In composite materials consisting of insulated and conductive materials, the electronic conductivity is usually not uniform, and this causes differential charging in the insulating parts of composite materials, for example, a material with a surface configuration such as that of an electronics circuit pattern or component [1-3], or a native oxide thin film on a metallic material [4-6]. Also, in mineral substances [7] and on ceramic surfaces [8], differential charging occurs because they have

variable surface compositions or surface roughness.

There are two causes to be considered. The first is the conduction between the specimen and spectrometer, and the second is the secondary emission characteristics from the surface due to the composition or surface roughness. Regarding the first cause, it is necessary to perform measurements to check the insulation of specimens for the spectrometer in order to avoid differential charging [1-6,9]. However, regarding the second one, the serious problem is how to restrain the differential charging with the insulation of specimens for the spectrometer, because of the secondary emission characteristic from the surface. Accurate measurement of the composite materials in XPS is very difficult. Therefore, it is of great importance to study the charging and the differential charging with a third material, namely, a nanocoating coated onto the rough composite materials in order to form an electrical contact between the metal and insulated materials.

In this study, first, gold evaporation was investigated because gold is the standard reference material for the binding energy, and second; the new technique of Os coating by means of plasma-CVD on

the rough surface of the composite materials was applied in XPS.

EXPERIMENTAL DETAIL

A ZrO₂-Pt cermet on polycrystal ZrO₂ ceramics, used as an oxygen sensor having a heterogeneous microstructure, was analyzed using an XPS instrument. ZrO₂ particles of various sizes were dispersed in/on the Pt matrix, and the electrode surface was porous, rough and heterogeneous in terms of the chemical composition and microstructure.

A gold coating was applied by using an *in situ* evaporation system in UHV (ULVAC-PHI). The deposition temperature was 850°C, and the thickness was controlled by the coating time (30, 60, 90s). An Os coating (*ex situ*) was formed using NL-OPC40 (Nippon Laser and Electronics Lab.). The ZrO₂/Pt cermet was set on a negative electrode, thereby it will be insulated from the electrode. The deposition system was evacuated to a background pressure of 0.8Pa and subsequently an OsO₄ gas introduced to the working pressure of 5Pa by heating a powdered OsO₄. Os coating was carried out under DC glow discharge between parallel plates, in which the voltage was 1.2kV and the discharge current was 1mA. The plasma-induced chemical reaction (OsO₄(g) Os(s)+2O₂(g)) occurred in the negative sheath region. As a result, an Os thin film was formed on the rough surface of the composite materials. By TEM observation, this Os film of 5nm thickness was confirmed to be amorphous in structure and uniform in thickness (Fig.1). For this XPS study of the chemical state and charging of the composite materials, over-coating of Os was controlled to be a thickness of approximately 1nm by the coating time, while considering the escape depth of photoelectrons.

The specimen was mounted on a sample holder with a Mo mask (Φ6mm), and then it was introduced into the XPS instrument. XPS was carried out using ESCA-5700ci (Physical Electronics, Inc.) with a non-monochromatic Mg *ka* line at 1253.6eV (14kV, 400W). All spectra were measured at an interval of 0.1eV and the pass energy of 23.5eV. The binding energies of the peaks were evaluated on the basis of the median method of the peak (ISO/TC201/SC7 N23

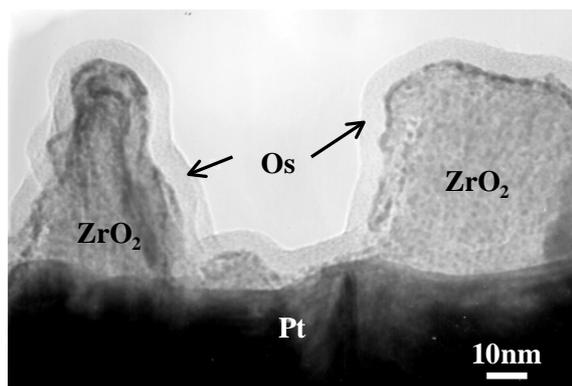


Fig.1 TEM image of 5nm Os coating.

P10 (a)). By comparing the full widths at half maximum (FWHMs) and the binding energies of Pt 4f_{7/2}, Zr 3d_{5/2} and C 1s with reference spectra, the charging was estimated in detail, with and without electrical conduction between the specimen and the spectrometer (i.e., in the grounding and the floating modes, respectively).

RESULTS AND DISCUSSION

Charging of composite materials after applying gold evaporation

Figure 2 (a)-(b) shows the Pt 4f, Au 4f and Zr 3d spectra, for which different thicknesses of gold were deposited (as-received, 30s, 60s, 90s) in the grounding mode. With respect to this result, the first remarkable point is that the Au 4f peaks were separated, and each peak was assigned to either the gold on the ZrO₂ particle or that on the Pt matrix. This means that charging of the ZrO₂ particle with gold coating occurred. The next remarkable point was that the FWHMs of the Zr3d and Y 3d peaks degenerated, indicating that differential charging of the ZrO₂ particles had occurred. SEM image obtained after gold evaporation (90s), for which the sample was tilted at 60°, is shown in Fig.3. In the dark area of this image, the charging occurred in the shadows of the gold evaporated ZrO₂ particles, namely, in the contact area with the Pt matrix. There was no gold in the shadows. This image confirms that achieving uniformity of the gold evaporation on the rough surface is impossible.

In the floating mode, the FWHMs of the Zr 3d and Y 3d peaks were improved as compared with

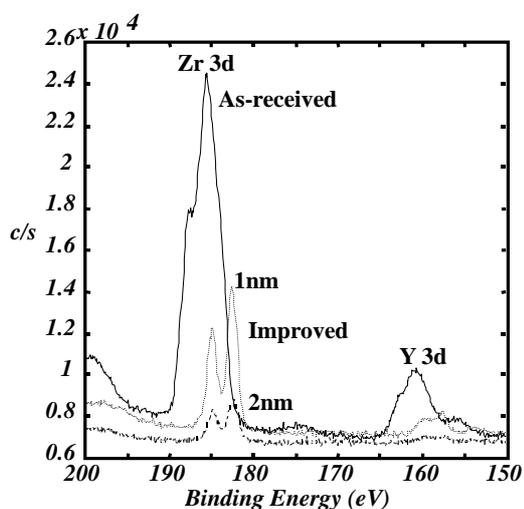
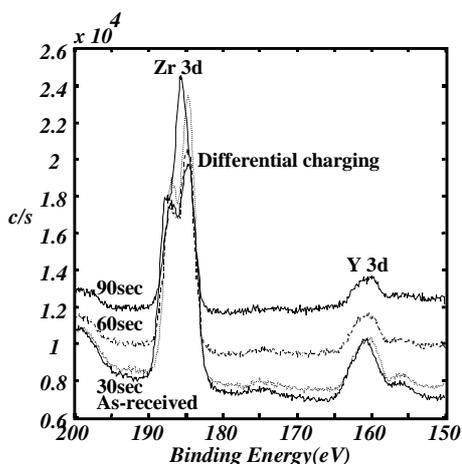
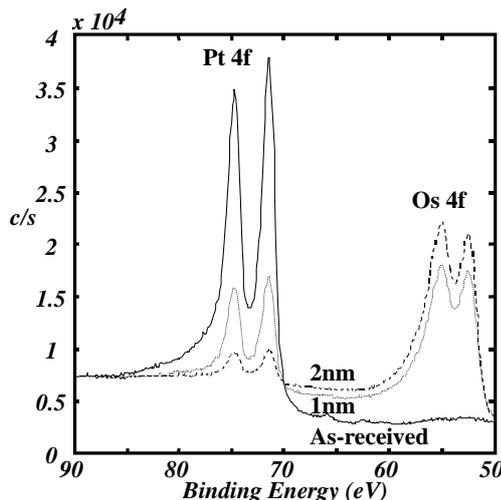
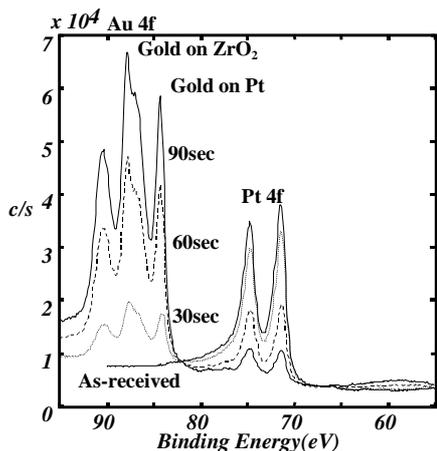


Fig.2 Spectra of Pt 4f, Au 4f, Zr 3d and Y 3d with gold deposition in the grounding mode.

Fig.4 Spectra of Pt 4f, Au 4f, Zr 3d and Y 3d with the Os coating in the grounding mode.

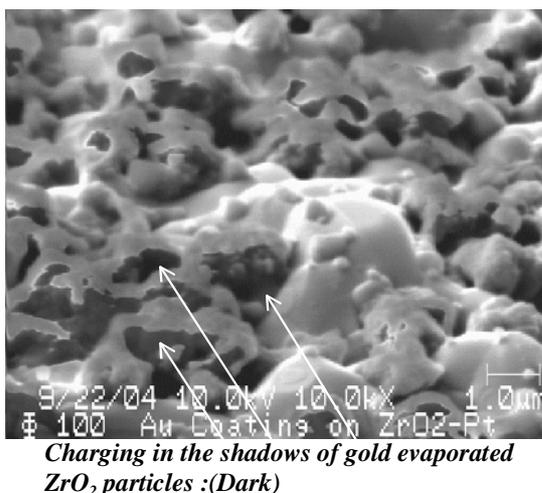


Fig.3 SEM image of evaporated gold coating on the insulator.

those in the grounding mode. However, the Au 4f peaks remained separated, and each peak was assigned to either the gold on the ZrO₂ particle or that on the Pt matrix. Data obtained after the gold evaporation is listed in Table 1. The peak-to-peak distance between Zr3d_{5/2} and Pt4f_{7/2}, which restrain the differential charging of the ZrO₂ particle in the floating mode, differed from the standard value (Zr3d_{5/2}-Pt4f_{7/2}:111.0eV) by 1.7eV. This means that the charging of ZrO₂ particles with gold coating had occurred due to the secondary emission characteristics dependent on the surface roughness, and the reference binding energies of the peaks between Pt and ZrO₂ for the various gold coating and

the modes of grounding and floating differed. Thus, the two reference binding energies were found to coexist in one spectrum. As a consequence, gold evaporation was not suitable for composite materials of rough surface.

Charging and chemical state of composite materials with Os coating

Figures 4 (a) and (b) show the co-line spectra of Pt 4f, Au 4f and Zr 3d, which obtained from the samples deposited with different Os coating thicknesses (as-received, and target thicknesses 1nm and 2nm) in the grounding mode. The intensity of the Pt 4f and Zr 3d peaks with 1nm Os thickness decreased to 1/3 from the as-received surface, due to the thickness of the Os overcoat. XPS observation after applying the Os coating indicated that the Zr3d peak shifted to the lower energies, and the Zr3d_{5/2} and Zr3d_{3/2} peaks separated (the FWHM of Zr3d was improved to be the intrinsic one), without any neutralizing electrons. Also, as a result, the binding energies and FWHMs of Zr 3d_{5/2}, Pt 4f_{7/2} and C 1s were kept almost constant with increasing neutralizing electrons. Moreover, the charging and differential charging were restrained by the

application of the Os coating. Thus, we confirmed that the electrical contact among Pt, ZrO₂ and Os coating was sufficient enough to neutralize the sample surface of insulators.

Data obtained after application of the Os coating is listed in Table 1. Remarkably, the peak-to-peak distance between Zr3d_{5/2} and Pt4f_{7/2} and the binding energy of Zr3d_{5/2} agreed with the standard values (Zr3d_{5/2}: 182.2eV, Pt4f_{7/2}: 71.2eV, Zr3d_{5/2}-Pt4f_{7/2}: 111.0eV) for restrained differential charging without any aids of neutralizing electrons. Thus, since the charging is restrained by applying the Os coating, ZrO₂ and Pt could be measured with an accuracy of ±0.1eV.

In this study, we confirmed that forming an Os coating using PCVD can enable the measurement of heterogeneous materials on a rough surface and this would provide a method of charge compensation in XPS. However, there remains a problem concerning about the peak intensity, which became 1/3 weaker of the intrinsic one after application of the 1nm thick Os coating. In the future, we will investigate the dependence of charging on the Os coatings thickness less than 1nm and this may improve the peak intensities.

Table 1 Data obtained after applying coating. (DC: differential charging)

		Binding Energy [eV] FWHM in parentheses				Difference in Binding Energy [eV]
		Pt 4f _{7/2}	Au 4f _{7/2}	Zr 3d _{5/2}	C 1s	Zr 3d _{5/2} -Pt 4f _{7/2}
Gold evaporation Grounding mode	0sec	71.2 (1.48)	-	185.4* (4.45)DC	284.3, 287.2 DC	114.2
	30sec	71.1 (1.42)	83.9, 87.4 DC	184.5* (4.11) DC	285.0, 286.9 DC	113.4
	60sec	71.1 (1.42)	84.1, 87.6 DC	184.6* (4.15)DC	285.2, 287.1 DC	113.5
Gold evaporation Floating mode	0sec	80.2 (1.46)	-	192.0 (1.42)	293.3 (1.7)	111.8
	60sec	80.4 (1.40)	93.4, 94.8 DC	193.1 (1.54)	294.9 (2.88) DC	112.7
Os coating Grounding mode	1nm	71.2 (1.50)	52.2 (Os 4f _{7/2})	182.2 (1.37)	284.6 (1.65)	111.0
	2nm	71.2 (1.53)	52.2 (Os 4f _{7/2})	182.2 (1.44)	284.6 (1.56)	111.0
Standard value [11]		71.2	84.0	182.2	-	111.0

* The Zr3d peak is indicated because the Zr3d_{5/2} and Zr3d_{3/2} peaks were not separated.

-Standard value of binding energy. Pt 4f_{7/2}: 71.2eV(Pt); Zr 3d_{5/2}: 182.2eV(ZrO₂); Au 4f_{7/2}: 84.0V(Au) [11]

-Reference value of measured spectrometer (ESCA5700ci) : Cu 2p_{3/2} :932.70eV, Cu 3p :75.15eV

(Standard : Cu 2p_{3/2}:932.66eV,Cu 3p :75.13eV) [12]

CONCLUSION

Differential charging was observed in composite materials consisting of a metal and an insulator with electrical conduction between the specimen and the spectrometer in XPS. As a result of using an Os coating formed by PCVD carried out to a 1nm target thickness to achieve electrical contact between the metallic and insulated materials, measurements under a stable surface potential while restraining the differential charging of insulated materials became possible. Thus, either the metal or insulator can be measured with an accuracy of $\pm 0.1\text{eV}$. We concluded that applying an Os overcoat by PCVD is an effective method for achieving charge compensation of composite materials in XPS.

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