Applications of Micro-Area Analysis Using JPS-9200 X-ray Photoelectron Spectrometer

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Introduction
Recently, with advances in the development of nanotechnology, the analysis materials, such as semiconductor device, are increasingly thinner and smaller. Moreover, without obtaining precise information on the chemical bonding on the surfaces of these newly developed materials, the progress of research and development of newly developed materials or products might be seriously affected.

The X-ray Photoelectron Spectrometer (XPS) is very useful for surface analysis method since XPS provides the chemical bonding state information for the material surface analysis method. However, because the photoelectron intensity obtained by micro analysis for an analysis region less than 100 µm in diameter is very weak, the objective analysis positions are difficult to identify, or other reasons, the micro XPS analysis has seen little demand until a few years ago. As the technology has progressed recently, these problems are being solved, and micro XPS has now become widely used for practical purposes. Unfortunately, because the various measurement data in the micro XPS are exclusively used for troubleshooting analyses, useful analysis examples or data on materials showing the effectiveness of the micro XPS are not widely known except for a few measurements by limited number of researchers. So, many researchers are asking themselves, “What can we do by using the micro XPS?”

JEOL Ltd., has dedicated great efforts to research and development of the micro XPS for many years, and beginning in fiscal year 2000, we have started to deliver the JPS-9200, which is a micro XPS instrument for researchers and those who engage in the material analysis. In this paper, some application examples of micro analysis measured by the JPS-9200 are introduced. We hope that these application data will contribute to the progress of the application research of XPS using the micro XPS from now on.

Purpose of micro-area analysis using XPS
The purposes of micro-area analysis by using XPS are as follows;

1) Analysis of the composition and/or chemical bonding state of faintly discolored or abnormal parts
2) Analysis area is small less than several hundred µm square.

In general, the above reasons, micro-area surface measurement are done by using micro-area analysis XPS. However, some XPS analyses require also analyzing the changes in the local chemical state on the surface of a polymer or segregation of a compound. Actually, such sample analyses are frequently carried out in the XPS. In many cases, those samples have the same color for the main body and the chemically changed parts. These situations allow conducting only a macro analysis for a region few µm in diameter, because it is usually not possible to locate the position to analyze. In some cases, however, it is not enough to analyze the surface chemical changes with macro analysis. Chemical bonding information of microscopic region must be obtained.

Figure 1 shows a wide scan spectrum of a fuel cell electrode measured in macro-area analysis (6 mm in diameter). As shown in the figure, the only elements detected are F and C, which are constituents of the Teflon-family high-polymer and carbon black, the materials of the electrode. Figure 2 is the photograph of fuel cell electrode observed using optical microscope. In this photograph, no chemical changes (such as discoloration or segregation) can be observed. Consequently, micro analysis of such a sample is not allowed, but macro analysis of a region a few mm in diameter yields average information on the sample surface.

Figure 3 shows the concentration ratios of C-F bonding, whose peak is caused by the Teflon-family polymer, and C, whose peak is caused by the carbon black, measured at analysis areas of 6 mm, 1 mm, 200 µm and 30 µm in diameter. As shown in the Fig. 3, the concentration ratio is found to increase as the analysis size decreases. From this result, it is supposed that the Teflon-family polymer is localized on the surface of the sample.

Figures 4, 5 and 6 show the photoelectron images by the photoelectron peak of C-F bonding in the regions of 6 mm × 6 mm, 2 mm × 2 mm and 400 µm × 400 µm, respectively. In the photoelectron image shown in Fig. 4, the distribution of C-F bonding state on the fuel cell electrode can hardly be observed. On the other hand, the distribution of C-F bond

Fig. 1. Wide scan spectrum on the surface of an electrode. Analyzing area: 6 mm in diameter.

Fig. 2. Photograph of the central of the electrode observed using the optical microscope (The surface color is black and the shape changes are not observed).

Fig. 3. Component ratio for C-F bonding state and carbon black in C 1s spectrum for each analysis region.
bonding begins to be observed in the 2 mm × 2 mm region, and it is clearly observed for the 400 µm × 400 µm region. These results proved that the distribution of the Teflon polymer, which cannot be observed using an optical microscope, is segregated on the surface of the electrode.

These results suggested that the micro analysis gives us different chemical bonding information on the surface for a substance whose chemical bonding information has so far been obtained only by the macro analysis. Therefore, micro analysis can also be effective for even a substance whose segregation positions cannot be identified by using an optical microscope or a similar apparatus as described above.

Summarizing the above discussions, the micro-area analysis using XPS can be useful not only for analyzing a tiny discolored part or troubleshooting of products, but also for properly grasping the segregation of a surface that appears to be uniform, and developing new materials.

**Application of micro-area analysis using by XPS, JPS-9200**

**Example of corrosion analysis**

The micro XPS analysis is mainly carried out for troubleshooting of a product. **Figure 7** shows an optical photomicrograph of Cu alloy lead frame. In this photograph, it is found that the surface is discolored. This sample, which is Ag plated on Cu, has become discolored due to some cause. This discoloration is different from position to position on the sample, and analysis of the causes is requested for XPS. **Figure 8** shows a wide energy spectrum measured at Point A with a region 200 µm in diameter. The elements detected in the region 200 µm in diameter are Ag, Cu, O, S and C. As the analysis region at Point A occupies 2 mm × 1 mm, an analysis diameter of 200 µm is good enough for ordinary analysis. **Figures** 9, 10 and 11 show wide scan spectra measured for analysis regions 50 µm in diameter at Point B. **Figure 10** shows a wide scan spectrum measured with analysis region 50 µm in diameter at Point B. **Figure 11** shows a wide scan spectrum measured with analysis region 50 µm in diameter at Point C.
Points A, B, and C, respectively. The measurement conditions for these photoelectron spectra are as follows: x-ray used is MgKα, x-ray radiation power is 300 W, and analyzer pass energies are 50 eV and 10 eV for wide scan spectrum and narrow scan spectrum (energy resolutions are 1.8 eV and 0.9 eV), respectively.

The detected elements from each point are as follows:

Measurement point  Detected elements
A  Ag, Cu, O, C
B  Ag, O, C, S
C  Ag, O, C, S

From the above results, the element S, which is detected in Fig. 8 (200 µm in diameter), is only detected at Points B and C, and not detected at Point A, in the analysis region 50 µm in diameter. These results are caused by the difference of element distribution near point A observed in the visual field of the optical microscope, and suggest that the analysis researchers must be carried out in a region as small as possible for such samples.

Furthermore, in Figs. 10 and 11, the amounts S detected at Points A and B are different from each other. The amount of S at Point B is found to be slightly larger than that at Point C. Figure 12 shows the curve-fitting spectrum of S2p spectrum at point B. The S_2p3/2 peak position is 161.9 eV, and Ag_3d5/2 peak position is 368.3 eV from the narrow scan spectrum. Hence, the chemical bonding state of S at Point A is assigned to be Ag-S. Based on this result as well as the measured wide scan spectrum at each point, the photoelectron images at the Ag_3d5/2 peak and S_2p(the energy position is adjusted to the peak belonging to Ag-S) are shown in Figs. 13 and 14, respectively. These imaging results indicate that Ag is abundant in the same discolored region that contains Point B. Similarly, S is also abundant in the same discolored region that contains Point B. Moreover, it is also found from these imaging results that the region that contains Point B consists of Ag-S.

For the reason stated above, the chemical bonding information on the discolored part can be properly obtained by measuring with the analysis region as small as possible.

### Example of surface analysis discolored part on polymer

Polymers are among the most frequently measured samples in XPS. Generally, XPS analysis for the surface of a polymer is useful for clarifying the differences in wetting ability, causes of discoloration, and other phenomena. In some cases, however, it is useful for clarifying the chemical changes in the surface bonding state after irradiated with laser light or an ion beam.

![Figure 12: S_2p curve-fitting spectrum measured at Point B. S_2p3/2 peak position is 161.9 eV.](image)

We made the sample by sputtering Ar ion randomly on the surface of PET (polyethylene terephthalate) film, and investigated how to find the sputtered position and analyze the sample using XPS. Figure 15 shows the O_1s photoelectron image on the 7 mm × 7 mm region around the position on which the Ar ions seem to have been sputtered. The analysis region is 30 µm in diameter for each position. Generally, when Ar ions are sputtered on the surface of a PET-like polymer, it releases oxygen from the C-O or COO bond, which is present in the constituent functional group. Hence, a photoelectron spectrum with reduced oxygen intensity can be observed. In Fig. 15, it is shown that the position with reduced oxygen intensity corresponds to the position sputtered by the Ar ion beam.

Figure 16 shows line spectra (C_1s and O_1s spectra) between the two points, a and b, indicated in Fig. 15. In this figure, the bottom and top lines correspond to the points a and b, respectively. Although the CH peak position is observed at 285.0 eV, it shifts to 284.0 eV as the measuring position moves to point b. Also, C-O and COO groups intensities decrease markedly as the measuring position moves from point a to point b. Similar phenomena are also observed for O_1s spectra.

Figure 17 shows the concentration distributions of O and C (in atomic%) when these line scans are carried out. As shown in the figure,
conspicuous decrease in the oxygen amount and accompanying increase in the carbon amount can be observed at the measuring positions 2 mm or farther from the point a indicated in Fig. 15.

For the sample mentioned above, it is found that the region sputtered by the Ar ion beam is 3 to 4 mm in the direction of the X-axis (wide) and 6 mm in the direction of the Y-axis (long), and that the most strongly sputtered position is at 3.5 mm from point a on the a-b line.

Thus, in the micro analysis of a sample whose analysis position is difficult to identify, it is possible to carry out the measurement at a precise analysis position by identifying the appropriate analysis position using macro-area imaging measurement as well as line measurement or other similar ones, and finally making the photoelectron spectrum measurement at the goal.

Example of electrode surface analysis

Although fuel cell have been developed since several decades ago, interest in them has increased recently due to environmental problems. The fuel cell is a direct power-generation system with ideal energy transformation efficiency of nearly 100%, and classified as follows by the kind of fuel, electrolyte and method.

- Hydrogen-oxygen fuel cell: fuel
- Solid electrolyte fuel cell: electrolyte
- Gas-diffusion fuel cell: method

Fuel cells are used mainly for space projects such as space shuttle, submarine operation boat, electric automobiles, and central power stations.

One of the most serious problems in using fuel cells is deterioration, or lifetime of the electrode. Since the fuel cell makes chemical reactions that occur on the surface of the electrode, material changes on the electrode cannot be avoided. Hence, it is possible to enhance the performance of the fuel cell by analyzing in detail how the surface of the electrode changes with chemical reactions (discharges). For this purpose, electrode are widely evaluated and analyzed by using various analytical instruments.

Figure 18 shows the electrode part of the gas-diffusion fuel cell, which is used for the present measurement. The surface structure of the electrode is diagrammed schematically in Fig. 19. The Teflon-family polymer used in this measurement has no CF3 bonding at the ends, but has abundant CF bonding at the side chains. Therefore, unlike ordinary Teflon, it is a high polymer with peaks in the spectrum indicating the presence of CF2 and CHF bonding. Such a Teflon-family polymer mixed with carbon black constitutes the substance of the electrode.

The purpose of analyzing such an electrode surface by using XPS is to analyze the changes (clarifying deterioration mechanism) of the Teflon-family polymer before and after the chemical reaction as well as the changes of added catalyst. By considering the photograph of Fig. 2 and the surface structure of the electrode shown in Fig. 19, the analysis region generally takes up a wide area a few mm in diameter from which the average information is obtained. However, as described in previous section, the Teflon-family polymer is evidently segregated on the surface. Consequently, by analyzing the chemical bonding state of the segregated Teflon-family polymer, information on the state changes of the electrode accompanying its reaction (after discharge) can be obtained.

The electrode shown in Fig. 18 is made by mixing the Teflon-family polymer and carbon black first, putting it between Al plates, and then pressing it at high temperature (380°C). Three electrode samples were used in the present micro analyses: (1) after mixing, (2) after pressing, and (3) after discharging. Figures 20, 21 and 22 show the results of imaging measurement of the CF bonding (F1s photoelectron) in the 400 µm × 400 µm region on these electrode surfaces. The distribution of F on the electrode sample surface after mixing extends over the whole sample surface. After
pressing at high temperature, segregation in regions less than or equal to 100 µm in diameter can be observed. After discharging, however, the distribution of F begins to spread similarly like after mixing (1). In order to investigate the chemical bonding states in these distributions of F, the C1s spectrum measurement was carried out at every point shown in the Fig. 23. The analysis diameter at each point was 30 µm.

Figure 23 shows the result at the electrode (point α) after mixing. As shown in the Fig. 24, a strong peak at 284.0 eV caused by carbon black is observed, and other peaks related to the C-F bonding are found to be minor. By using spectrum curve fitting, the observed peaks caused by the Teflon-family polymer are identified as CF2-CF2, CF2-CHF, CF2-CH2 and CHF-CH2. From the peak intensities of these peaks obtained by the spectrum curve fitting, the main component is found to be CF2-CHF bonding state, whose peak corresponds to the side-chain functional group in the Teflon-family polymer.

Figure 24 shows the analysis of C1s spectrum of the electrode surface after pressing at high temperature. At the position with lower F concentration (point β), the CHF-CF2 bonding is observed to be the major component. Conversely, at the position with higher F concentration (point γ), both CHF-CF2 and CF2-CF2 are observed to be the main components (Fig. 25). These two bonding components are considered to be the main components constituting the Teflon-family polymer. Hence, it is found that pressing at high temperature after mixing localizes the Teflon-family polymer on the electrode surface.

Figure 26 shows the analysis of C1s spectrum of the electrode surface (point δ) after discharging. As shown in the Fig. 26, both CHF-CF2 and CF2-CF2 are observed to be the major components as observed at point γ after pressing at high temperature. Of these two components, the amount of the CF2-CF2 bonding is observed to be higher than that of CHF-CF2. Moreover, the amounts of the components caused by the Teflon-family polymer are conspicuously lower compared with those of the point γ after pressing at high temperature, and the surface distributions of these components are spread more widely than after pressing at high temperature.

Iijima, et al. reported that the side-chain components in the Teflon-family polymer decompose and change to CF2-CF2 bonding after discharging [1,2]. Moreover, from SEM observation of the electrode after discharge, it is reported that fibers are produced locally by the decomposition of the Teflon-family polymer [1,2].

The above results suggest that after discharging, the Teflon-family polymer decomposes and distributes on the surface a compound with CF2-CF2 bonding as the main component.

Conclusions

In the present investigation, various materials have been analyzed by using micro-area analysis XPS. The results obtained are different from the macro-area analysis results that had been obtained so far. For XPS analysis of materials, in particular, such as an electrode, whose analysis position cannot be identified by surface shape or a difference of color using optical microscopy, the micro-area XPS analysis can clearly show the difference of the chemical-bonding state in their images or spectra.

The JPS-9200 can carry out imaging measurements at scales ranging from macro area to micro area, and thus enables us to make proper XPS analyses for surface segregation, difference of chemical-bonding states between parts having the same color, and so forth.

From now on, with the progress of application research for various materials by micro-area analysis XPS, we hope that more useful chemical information about the local surface can be obtained.

References