ULVAC PHI PHI5000 VersaProbe Part 1 Measurement Manual

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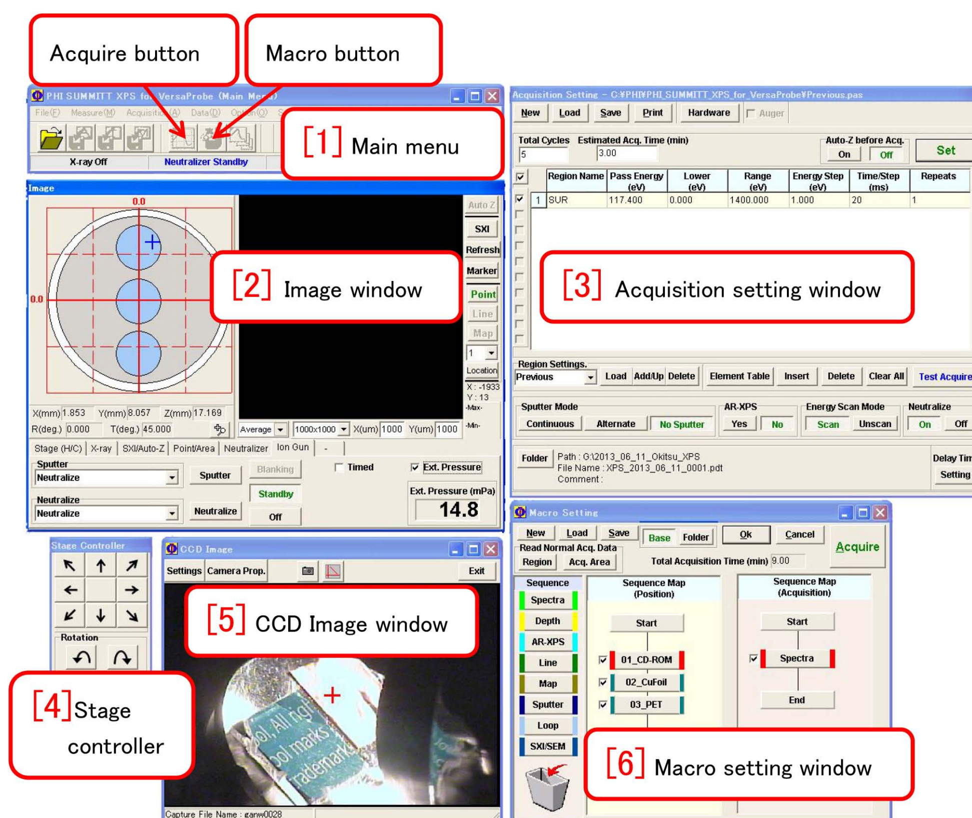


Figure 0: Measurement windows of macro mode

X-ray photoelectron spectroscopy can be done by using the measurement program 'Phi Summitt'. This manual describes the usage of 'Phi Summitt'. Since the use of the data-analyzing program 'MiltiPak' is also necessary during the measurement, the its usage is partially described.

The above windows have been opened by clicking 'Macro' button on '[1] Main Menu'. However, '[5] CCD Image window has been opened separately by clicking 'CCD Image' icon.

When 'Acquire' button on '[1] Main Menu' has been clicked, however, '[6] Macro setting' window does not open. In the normal (but not Macro) measurement mode, the measuring positions can be named and registered. After clicking the 'Close' button on the upper right corner of '[3] Acquisition setting' window (it does not appear on the above figure), an automatic measurement can be set by clicking the 'Macro' button. **The procedure just before the registration of positions described in §1.1.6 [p.3] and that just before starting the macro measurement described in §2.2 [p.10], should necessarily be done.**

During the measurement, 'Ext.Pressure' check box that appears by clicking 'Ion Gun' tab on '[2] Image window', should be unchecked. After finishing the experiment, it should be confirmed by letting the extractor pressure be displayed with 'Standby' button being green, that the value of it reaches $\sim$ 15 mPa within a few minutes after checking 'Ext.Pressure' check box, please.

Appendix A describes the usage of Mg&Zr X-ray sources.

Version 2020.07.28E. 2020/07/28.

Contents

1 Fundamental settings and position adjusting **1**
1.1 Fundamental settings . . . 1
1.1.1 Ion Gun tab . . . 1
1.1.2 Neutralizer tab . . . 2
1.1.3 Point/Area tab . . . 2
1.1.4 SXI/Auto-Z tab . . . 2
1.1.5 X-ray tab . . . 3
1.1.6 Stage(H/C) tab . . . 3
1.2 Auto-Z . . . 3
1.3 SXI . . . 4

2 Measurement of spectra **5**
2.1 Normal measurement (not using macro mode) . . . 5
2.1.1 Setting for survey spectrum measurement . . . 5
2.1.2 Measurement of a survey spectrum . . . 6
2.1.3 Analysis of the survey spectrum . . . 7
2.1.3.1 Reading data . . . 7
2.1.3.2 Assignment of peaks . . . 7
2.1.4 Setting window for measuring narrow spectra . . . 9
2.1.5 Measurement of narrow spectra . . . 9
2.1.6 Analysis of the narrow spectra . . . 9
2.1.6.1 Reading data . . . 9
2.1.6.2 Analysis of data . . . 9
2.1.6.3 Quantitative analysis . . . 9
2.2 Spectra measurement using the macro mode . . . 10
2.2.1 Setting before starting the macro mode . . . 10
2.2.2 Start of the macro mode and initial setting . . . 11
2.2.3 Position setting . . . 11
2.2.4 Selection of the registered position . . . 11
2.2.5 Selection of measurement menu . . . 11
2.2.6 Setting the measuring condition . . . 12
2.2.7 Completing the macro setting and starting the measurement . . . 12
2.2.8 Analysis of the survey spectrum measured by the macro mode . . . 13
2.2.9 Setting of measurement of narrow spectra by the macro mode . . . 13
2.2.10 Analysis of the narrow spectra measured by the macro mode . . . 13

3 Measurement of spectra with alternative sputtering **14**
3.1 Abstract of sputtering measurement . . . 14
3.2 Normal (not using macro) measurement of spectra with alternative sputtering . . 14
3.2.1 Set of the sputtering voltage . . . 14

3.2.2 Other settings on the image window 15
3.2.3 Setting the sputtering conditions on the acquisition setting window 15
3.2.4 Start and end of spettering measurement 15
3.2.5 Data analysis 15
3.3 Sputtering spectra measurement using macro mode 16
3.3.1 Finishing the normal mode and start up the macro mode 16
3.3.2 Reset of an old macro and set of a new macro 16
3.3.3 Set of a sputtering spectrum measurement 16
3.3.4 Set of acceleration voltage in the image window 16
3.3.5 Other settings in the image window 16
3.3.6 Settings in the acquisition setting window 16
3.3.7 Start and end of the sputtering measurement 17
3.3.8 Data analysis 17

4 Mapping measurement 18
4.1 Abstract of mapping measurement 18
4.2 Normal (not using macro) mapping measurement 18
4.2.1 Conformation of photoelectron spectrum 18
4.2.2 Settings in the image window 19
4.2.3 Settings in the acquisition setting window 19
4.2.4 Start of mapping measurement 20
4.2.5 Simultaneous mapping for plural peaks 21
4.3 mapping measurement using the macro mode 22

5 Angle-resolved spectrum measurement (AR-XPS) 23
5.1 Abstract of angle-resolved spectrum measurement (AR-XPS) 23
5.2 Sample holders that can be used for AR-XPS 23
5.3 AR-XPS measurement not using the macro mode 24
5.4 Angle-resolved measurement (AR-XPS) with the macro mode 24

A Spectroscopy with Mg&Zr X-ray sources 26
A.1 Concerning the experiment using Mg&Zr X-ray sources 26
A.2 Abstract the spectroscopy with Mg&Zr X-ray source 26
A.3 Selection of X-ray source 27
A.4 Automatic adjustment of the sample stage height (Auto-Z) 27
A.5 Setting spectral measurements 27
A.6 An example of measurement using the Mg X-ray source 28
A.7 An example measured with the Zr X-ray source 29
A.8 Several point to take care when using the Mg&Zr X-ray sources 29
A.9 Finishing the experiment with Mg&Zr X-ray source 30

List of Figures

0 Measurement windows of macro mode i

1.1 Settings before starting the measurement 1
1.2 Registration of the sample stage position 2
1.3 Auto-Z executing chart 2
1.4 SXI window 3
2.1 Settings of a survey scan (#1) 5

2.2 Settings of a survey scan (#2) 5
2.3 Window displaying a survey spectrum 6
2.4 File selection window of the 'MultiPak' 6
2.5 File selection window of the 'MultiPak' 7
2.6 An energy region can be selected by left-click&dragging the mouse. 7
2.7 Candidates of the peak can be displayed by right-click&dragging the mouse. . . . 8
2.8 Setting window for measuring narrow spectra (#1) 8
2.9 Setting window for measuring narrow spectra (#2) 8
2.10 Windows displaying the measurement of narrow spectra 8
2.11 Narrow spectra have been read. 9
2.12 A narrow spectrum has been enlarged. 10
2.13 Initial window of Macro setting 10
2.14 Macro setting window (Position Setting #1) 11
2.15 Macro setting window (Position Setting #2) 11
2.16 Setting of the next position 11
2.17 Acquisition setting window 12
2.18 Macro setting window (setting of the measurement) 12
2.19 Setting of the macro measurement has been completed. 12

3.1 Image Window. 'Ion Gun' tab has been opened. 14
3.2 Acquisition Setting Window. 'Alternative' button has been clicked. 14
3.3 A window displayed during the sputtering measurement 15
3.4 Macro Setting Window. A spectrum measurement has been set for registered position '01' 16
3.5 Macro Setting Window. A sputtering spectrum measurement has been set for position '01' 16
3.6 Macro Setting Window. A macro has been finished to set. 17

4.1 Si2p spectrum. Left: SiO_2, Right: Elemental Si 18
4.2 MAP mode has been selected in the image window. 18
4.3 Settings in acquisition setting window. 19
4.4 Distribution map of elemental silicon (image viewer). 20
4.5 Photoelectron spectrum of elemental silicon (spectral viewer). 20
4.6 Distribution map of SiO_2 (image viewer). 20

4.7 Photoelectron spectrum of SiO_2 (spectral viewer). 20
4.8 Settings in the acquisition setting window. 21
4.9 Distribution maps of elemental silicon and SiO_2 (Image Viewer). 21
4.10 Photoelectron spectrum of elemental silicon (Spectral Viewer). 21
4.11 Setting of a mapping measurement in the macro mode 21

5.1 Spectrum of Si2p. Left: SiO_2, Right: Elemental silicon. 23
5.2 'Position' has been drag&dropped. 24
5.3 'Position' has been right-clicked. 24
5.4 Stage setting window 24
5.5 'AR-XPS' has been drag&dropped. 24

A.1 Mg&Zr X-ray source has been slid in 26
A.2 Mg&Zr X-ray source has been slid in. 26
A.3 X-ray tab in the image window has been opened. (a) monochromatized Al $K\alpha$ (1486.6 eV), (b) Mg $K\alpha$ (1253.4 eV) and (c) Zr $L\alpha$ (2042.4 eV) X-ray source has been selected. 27
A.4 In the main menu window indicating that Mg $K\alpha$ X-ray source has been ON. . . 27
A.5 (a) dark main chamber comes to be (b) bright by being illuminated by the filament when the Mg&Zr X-ray source is ON. 27
A.6 A photoelectron spectrum measured with the Mg X-ray source for an SiO_2 sample. 28
A.7 Main menu. Zr X-ray source has been ON. 28
A.8 A photoelectron spectrum measured with the Zr X-ray source for an SiO_2 sample. 28
A.9 After finishing an experiment with the Mg&Zr X-ray source used with the situation shown in Fig. A.1 should be returned to be as shown in this figure. 28

Chapter 1

Fundamental settings and position adjusting

1.1 Fundamental settings

1.1.1 Ion Gun tab

In Fig. 1.1(a), 'Ion Gun' menu has been opened by clicking 'Ion Gun' tab. If the setting of the ion gun has been finished, 'Neutralize' should be selected from pull-down menus of both 'Sputter' and 'Neutralize'. Further, 'Standby' button in Fig. 1.1(a) should be clicked to be green.

In the case of insulator samples, the measuring point is charged up to be positive since the electrons are lost due to photoemission. the incidence position of X-rays should be neutralized such that the photoelectron peak positions do not shift to the left (high-energy side).

The use of not only low-energy electrons but also low-energy Ar ions with positive charge for neutralizing the surface of the sample, is one of the remarkable features of 'PHI5000 VersaProbe'. If only low-energy electrons were used for neutralizing, ring-shaped region with negative charge would be made since the low-energy electron beam is larger than the X-ray beam size ($<100\mu$m). These positive and negative charges can be simultaneously neutralized by using both the electron and Ar ion guns.

During the measurement, 'Ext.Pressure' check box in Fig. 1.1 (a) should be unchecked. After finishing the experiment, it should be confirmed by letting the extractor pressure be displayed with 'Standby' button being green that the value of it reaches $\sim$ 15 mPa within a few minutes after checking 'Ext.Pressure' check box, please. If the Ext.Pressure comes to be extremely smaller than 15 mPa, contact the manager (K. Okitsu; 27470, 090-2203-8789), please.

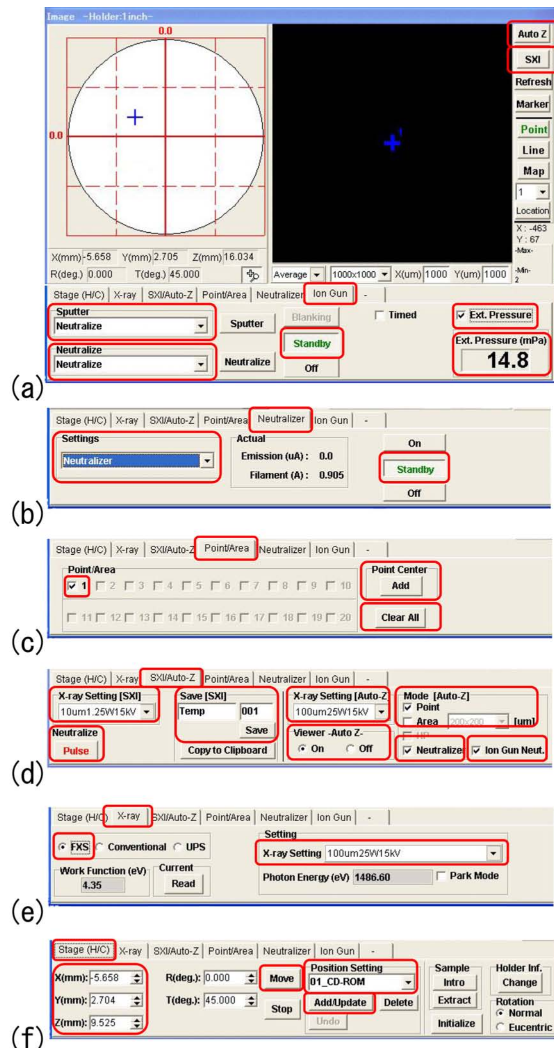


Figure 1.1: Settings before starting the measurement

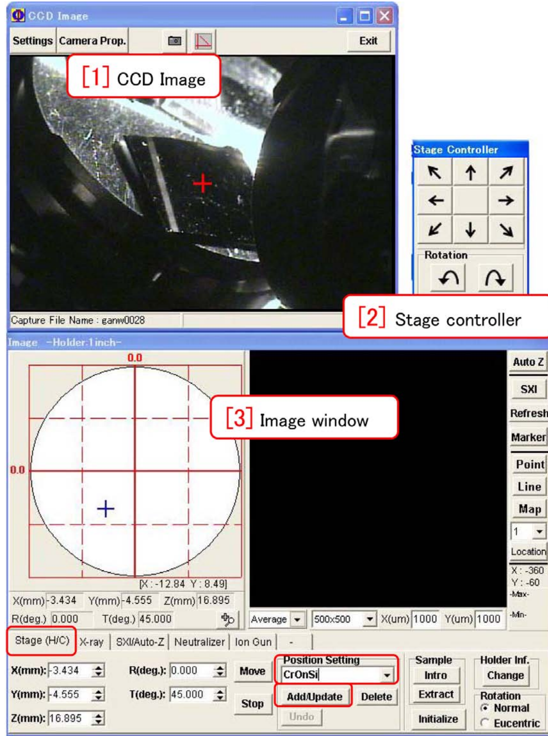


Figure 1.2: Registration of the sample stage position

1.1.2 Neutralizer tab

In Fig. 1.1(b) [p.1], 'Neutralizer' tab has been clicked to be opened in the 'Image Window'. Conditions of low-energy electron neutralizer can be set here. 'Neutralizer' should be selected from 'Settings' pull-down menu. 'Standby' button on the lower right corner of Fig. 1.1(b) [p.1] should be clicked to be green.

1.1.3 Point/Area tab

In Fig. 1.1(c) [p.1], 'Point/Area' tab has been clicked to be opened. Click 'Clear All' button, please, such that only '1' check box is checked. With this setting, only a position of the blue cross mark with a character '1' at the center of the black window in Fig. 1.1(a) [p.1], is measured. 'Point Center Add' button on the right of Fig. 1.1(c) [p.1], can also be clicked to add another cross mark to central position. This new cross mark can be moved by click&dragging the mouse. In such a way, plural points can be set to be measured.

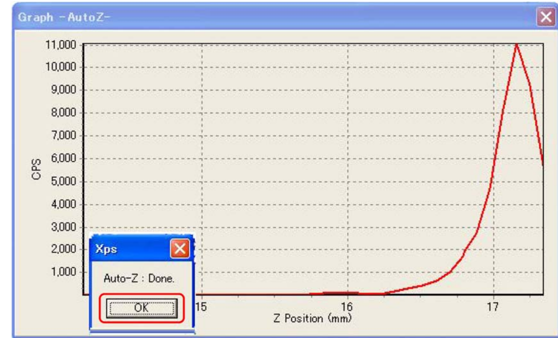


Figure 1.3: Auto-Z executing chart

1.1.4 SXI/Auto-Z tab

In Fig. 1.1(d) [p.1], 'SXI/Auto-Z' tab has been clicked to be opened. SXI (Scanning X-ray Imaging) is an imaging mode to obtain a photoelectron image with electrons whose biding energy is about 1400 eV. 'Auto-Z' is an automatic height (Z) adjusting mode of the sample stage with electrons whose binding energy is about 500 eV. 'Auto-Z' button and 'SXI' button are on the upper right corner of Fig. 1.1(a) [p.1].

In the left and right halves of Fig. 1.1(d) [p.1], conditions for 'SXI' and 'Auto-Z' can be set, respectively. Items in Fig. 1.1(d) [p.1] are describes from the left as follows.

Focus size of the incident X-rays can be selected from 'X-ray Setting [SXI]' pull-down menu. Small focus sizes of 10 $\sim$ 20μm can be selected for high spatial resolution. 'Neutralize' button should be clicked such that red characters 'Pulse' are displayed for neutralizing the sample when doing the 'SXI'. The 'SXI' image can be named and numbered to be saved by clicking 'Save' button. Take care, please, that it is not automatically saved.

Focus size of X-rays when doing 'Auto-Z' can be selected from 'X-ray Setting [Auto-Z]' pull-down menu. The largest focus size '100um25W15kV' is usually recommended. 'HP-100um100W20kV' is not recommended since it sometimes causes a trouble. 'On' is recommended to be checked for 'Viewer Auto-Z radio button' such that a chart is displayed during the 'Auto-Z'. 'Point' should be usually checked for the 'Auto-Z'. Check boxes of both 'Neutralizer' and 'Ion Gun Neut.' should be usually checked for neutralizing.

1.1.5 X-ray tab

In Fig. 1.1(e) [p.1], ‘X-ray’ tab has been clicked to be opened to set conditions of X-rays for measurement. ‘FXS’ radio button should necessarily be checked to select ‘Focused X-ray Scanning’ by using Al Kα radiation (1486.6eV). Focus size of X-rays for main measurement can be selected from ‘X-ray Setting’ pull-down menu. The largest focus size ‘100um25W15kV’ is generally recommended. Do not select ‘HP-100um100W20kV’ because it sometimes causes a trouble.

‘Point’ mode button has been usually clicked to be green on the right side in Fig. 1.1(a) [p.1]. In this mode, normal photoelectron spectra can be taken for one or plural point(s). However, mapping and line modes can also be selected on the right side in Fig. 1.1(a) [p.1]. For these modes that require high spatial resolution, small focus size e.g. $10 \sim 20\mu$m is recommended.

1.1.6 Stage(H/C) tab

In Fig. 1.1(f) [p.1], ‘Stage(H/C)’ tab has been clicked to be opened.

After inputting values in ‘X,Y,Z(mm)’ text box, the sample stage can be moved to the indicated position by clicking ‘Move’ button.

The stage position can be registered with an arbitrary name that can be typed in ‘Position setting’ pull-down menu by clicking ‘Add/Update’ button. Position names registered by the previous user are recommended to be erased by clicking ‘Delete’ button.

In Fig. 1.2, **after setting the value of ‘[7] T(deg.)’ to be 45.0 and clicking ‘[8] Move’, it should be confirmed that ‘[7] T(deg.)’ is 45.0±0.1. When ‘[7] T(deg.)’ is displayed as gray and no number can be typed, ‘[2] Tilt’ should be clicked such that ‘[7] T(deg.)’ is 45.0±0.1. Until finishing the experiment, ‘[2] Tilt’ should not be clicked.**

1.2 Auto-Z

Auto-Z is a function automatically to adjust the height (Z) of the sample stage.

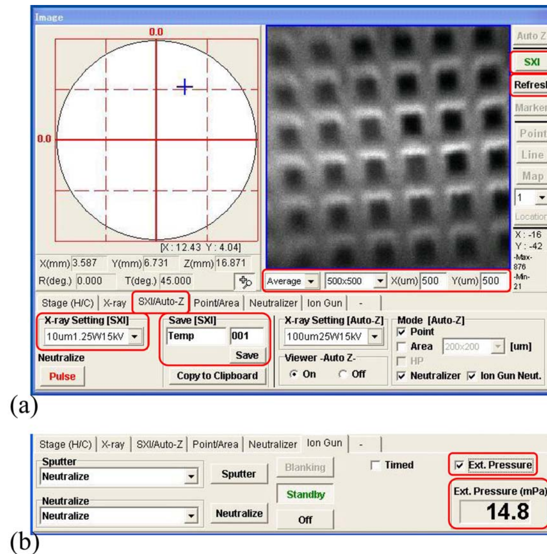


Figure 1.4: SXI window

For detail when setting the condition, refer to the description in §1.1.4 and the right half of Fig. 1.1(d) [p.1], please.

A chart as shown in Fig. 1.3 is displayed after clicking the ‘Auto-Z ’button on the upper right corner of Fig. 1.1(a) [p.1].

At first, move the sample stage upward by clicking ‘Move’ button on the lower center of Fig. 1.2, please, after setting a value $\sim (14.5 - t)$mm in ‘Z(mm)’ text box on the lower left of Fig. 1.2. Here, t (mm) is the thickness of the sample. Next, the sample stage should be moved by clicking ‘arrow buttons’ in ‘[2] Stage controller’ of Fig. 1.2 such that the red cross mark at the center of ‘[1] CCD Image’ of Fig. 1.2 comes to the position of the sample surface whose thickness is t mm. Then, click the ‘Auto-Z’ button on the upper right of ‘[3] Image window’, please, to adjust the height of the sample stage.

After doing the ‘Auto-Z’, the red cross mark at the center of ‘[1] CCD Image’ in Fig. 1.2 indicates the incidence position of X-rays. After adjusting X, Y position by clicking arrow buttons in ‘[2] Stage controller’ in Fig. 1.2. the ‘Auto-Z’ should be done again.

Here, this sample position should be registered with an arbitrary name as described in §1.1.6.

1.3 SXI

SXI (Scanning X-ray Imaging) is a mode to obtain an image of the surface of the sample with electrons whose binding energy is about 1400 eV.

For detail when setting the condition of SXI, please refer to the left half of Fig. 1.1(d) [p.1] and the description in §1.1.4 [p.2].

An SXI (Scanning X-ray Image) in Fig. 1.4 [p.3] is obtained for a copper mesh sample. It is not automatically saved. To save it, 'Save' button can be clicked after typing the prefix and number of the file name in the red frame of Save[SXI] on the lower center of Fig. 1.4 [p.3]. Before that, the folder into which the SXI is saved, should be set by clicking 'Folder' button on the lower left of '[3] Acquisition Setting window' in Fig. 0 on the cover of this manual.

There are pull-down menus of 'Average' and '500 × 500' and text boxes of 'X(um)' and 'Y(um)' in a red frame below the display window of Fig. 1.4 [p.3].

'Average' is a mode to integrate the photoelectron image. If it is changed to be 'Fast' or 'Slow', the image is refreshed every one second or two seconds, respectively.

The values of '500 × 500' in the pull-down menu should coincide with those of 'X(um)' and 'Y(um)'. If not, the setting should be selected again from the pull-down menu. This is the field size of SXI.

By clicking 'Refresh' button below the 'SXI' button after clicking any position in the SXI, the sample stage can be moved such that the clicked position is the center of the SXI.

When a field size of $1400 \times 1400(\mu\text{m})$ is selected, an image of which the upper and lower regions are dark is obtained. An SiO_2 bent crystal is used to focus and monochromatize the X-rays. The plane of incidence (scattering plane) of this monochromator is parallel to the vertical (Y) direction of Fig. 1.4 [p.3]. Bragg reflection angle of the X-rays that focuses on an upper (+Y) position in Fig. 1.4 [p.3] is larger than that for Al Kα radiation (1486.6eV). In the lower position in Fig. 1.4 [p.3], the situation is contrary. The intensity of X-rays whose photon energy is larger or smaller than the Al Kα radiation, is smaller than that of the Al Kα radiation. This is the reason for that the upper and lower regions are dark in the case of the field size of $1400 \times 1400(\mu\text{m})$. Take care that this dark contrast is not essential signal but due to 'chromatic aberration', please.

Chapter 2

Measurement of spectra

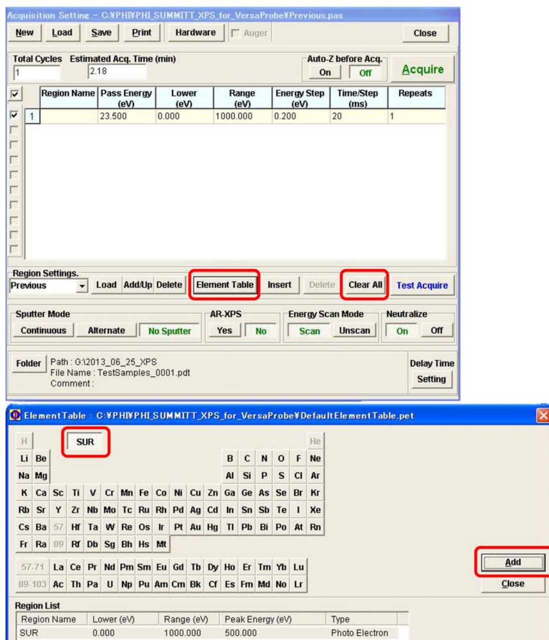


Figure 2.1: Settings of a survey scan (#1)

2.1 Normal measurement (not using macro mode)

2.1.1 Setting for survey spectrum measurement

Fig. 2.1 shows settings when a wide-range photoelectron spectrum (survey scan) is measured. At first, 'Clear All' button on the central right field of Fig. 2.1 should be clicked to clear the previous setting. Next, click central 'Element Table' button, please, to open the periodic table of the elements in the bottom half of Fig. 2.1. 'SUR' button (Survey button) has been pushed as default. Click 'Add' button and 'Close' button in this order to set a survey scan and close the periodic table, please.

In Fig. 2.2, values surrounded by red frames

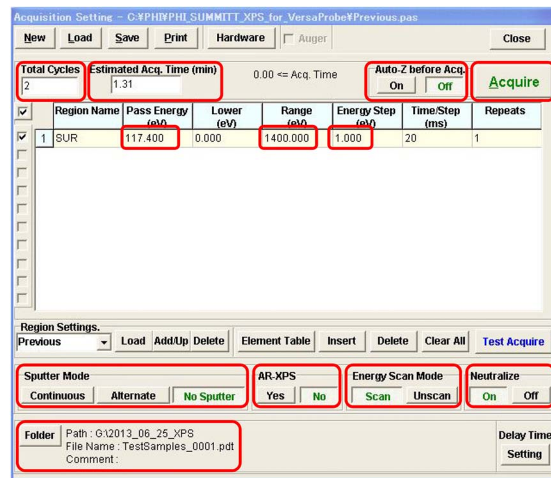


Figure 2.2: Settings of a survey scan (#2)

have been changed from default as the following description from upper left items.

'Total Cycles' set to be '2' means that the measurement is repeated two times. 'Estimated Acq. Time(min)' estimated to be 1.31 means that the two-time measurement takes 1.31 min. 'Auto-Z before Acq.' set to be 'No' means that 'Auto-Z' is not done before the measurement. 'Acquire' button can be clicked to start the measurement.

'Pass Energy' is the velocity energy of electrons that fly the central trajectory between the plus and minus spherical double electrodes of the electron analyzer. 117.4(eV) is a recommended value for survey scan. 'Range(eV)' is a scanning energy range and default for survey scan is 1000eV. However, 'Range(eV)' has been changed to be 1400 eV that is effective since this value is less than the photon energy of Al Kα radiation (1486.6 eV). 'Energy Step' has been changed from default (0.2 eV) to be 1.0 eV that is recommended to be $\sim$ 'Pass Energy' / 100.

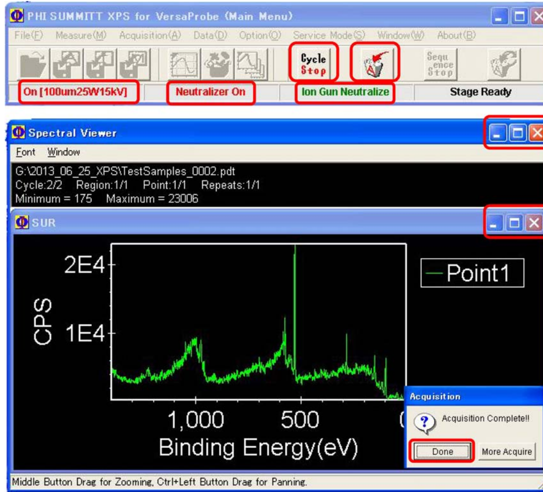


Figure 2.3: Window displaying a survey spectrum

‘Sputter Mode’ on the lower left of Fig. 2.2 [p.5] has been set to be ‘No Sputter’ such that the sample is measured without sputtering. ‘AR-XPS’ (qualitative measurement of depth profile by changing the tilt angle of the sample stage) has been set to be ‘No’. ‘Energy Scan Mode’ has been selected to be ‘Scan’ such that the electric field decelerating electrons before entering the spherical double electrode, is scanned. ‘Neutralize’ has been set to be ‘On’ such that the charge on the surface of sample is neutralized by using the low-energy electron and Ar ion guns. When the sample is an insulator, the measured photoelectron peaks shift to the left (high-energy side) if not using the neutralizer. Even in the case of metal sample, when not neutralizing, photoelectron peaks sometimes shift to the left due to oxide film covering the sample. When spectra measurement for metal samples without neutralizing are recommended to do after verifying that the spectra measured without neutralizing have peaks at the same positions as those obtained with neutralizing.

‘Folder’ button on the lower left of Fig. 2.2 [p.5] should be clicked to set prefix and initial number of file name and the folder in which the data files are saved. When a USB memory is set to the computer, it is recognized as G: partition. The users are recommended to save their data files in the USB memory. The file number automatically increases.

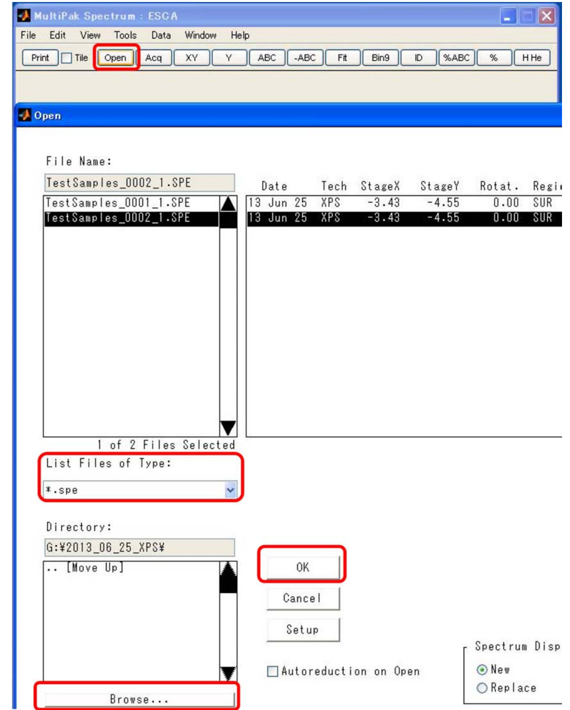


Figure 2.4: File selection window of the ‘MultiPak’

2.1.2 Measurement of a survey spectrum

The survey scan can be started by clicking ‘Acquire’ button on the upper right corner of Fig. 2.2 [p.5]. During the measurement, Fig. 2.3 is displayed. The upper is ‘Main Menu’ and the lower is ‘Spectral Viewer’. The items surrounded by red frames are explained as follows.

‘Cycle Stop’ button can be clicked to stop the measurement after finishing and saving the data of the present cycle. However, ‘A’ button (Abort button) can be clicked to stop the measurement soon without saving the data.

‘On [100um25W15kV]’ shows that the measurement is being done with X-rays whose focus size, power and voltage are 100μm, 25W and 15kV, respectively. ‘Neutralizer On’ and ‘Ion Gun Neutralize’ mean that the neutralizing with electron and Ar ion guns is being done.

Buttons on the right upper corner of the ‘Spectral Viewer’ can be clicked to minimize or maximize this window. However, this window cannot be closed by clicking ‘×’ button.

After the measurement is finished, a small window on the right lower corner of Fig. 2.3

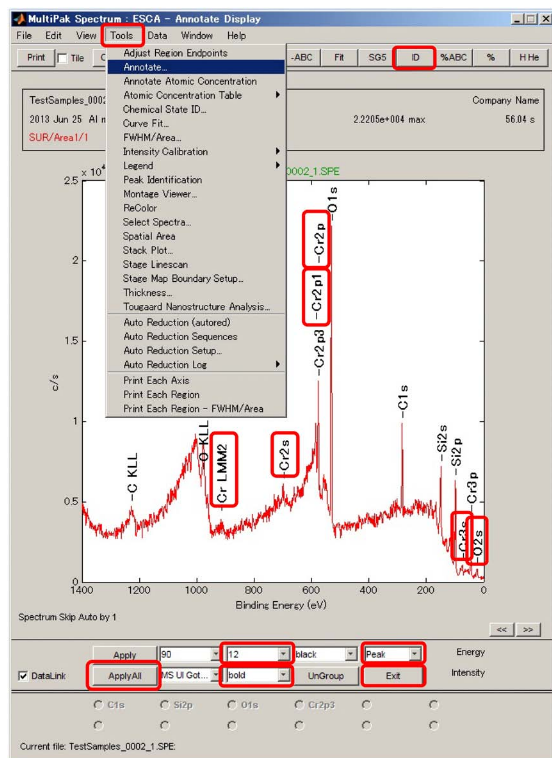


Figure 2.5: File selection window of the ‘MultiPak’

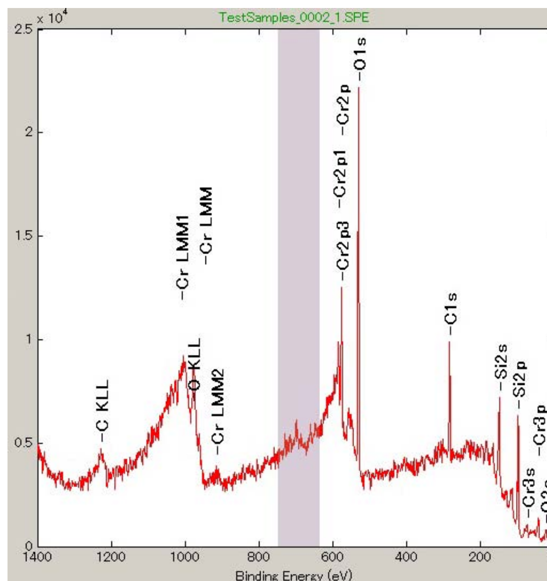


Figure 2.6: An energy region can be selected by left-click&dragging the mouse.

appears. ‘Done’ button should be clicked to go to the next step.

2.1.3 Analysis of the survey spectrum

2.1.3.1 Reading data

The measured survey spectrum can be analyzed soon by using the ‘MultiPak’. ‘Spectral Window’ as shown in Fig. 2.5 and ‘Element Table Window’ can be opened by double-clicking the ‘MultiPak’ icon. Fig. 2.4 is a file selection window that has been opened by clicking ‘Open’ button in the upper left region of the ‘Spectral Window’ of ‘MultiPak’ as shown in Fig. 2.5.

‘∗.spe’ (spectral data) is displayed as default in ‘List Files of Type’ pull-down menu around the center of Fig. 2.4. Other than ‘∗.spe’, ‘∗.pro’(Sputtering data), ‘∗.map’(Mapping data), ‘∗.lin’(line profile data), ‘∗.sxi’(SXI data), etc. can also be selected from the pull-down menu.

‘Browse’ button on the lower left of Fig. 2.4 can be clicked to open the explorer. Then, a data folder in which the data files have been saved should be opened.

After selecting the data file name, ‘OK’ button should be clicked to open it. Pressing [Shift] or [Ctrl] key allows also plural data files to be opened.

2.1.3.2 Assignment of peaks

The data file obtained by the survey scan has been opened in Fig. 2.5. The photoelectron peaks can automatically be assigned by clicking ‘ID’ button (Identification button) on the upper right of Fig. 2.5.

‘Annotate’ submenu in ‘Tools’ menu on the menu bar of Fig. 2.5 can be clicked to change the size and style of font with which characters are displayed in the spectral window. ‘Peak’ has been selected from a pull-down menu on the lower right of Fig. 2.5 to change properties of characters with which the peak names are displayed. As on the lower center of Fig. 2.5, 12 pt bold character has been selected. Then, ‘Apply All’ button can be clicked to apply the above setting. Finally, ‘Exit’ button should be clicked to go to the next operation.

The peaks surrounded by red frames in Fig. 2.5 are those that have not been assigned only by clicking the ‘ID’ button. To assign them, do the following procedure, please.

A periodic table window is displayed separately on the right of Fig. 2.5. Symbols of ele-

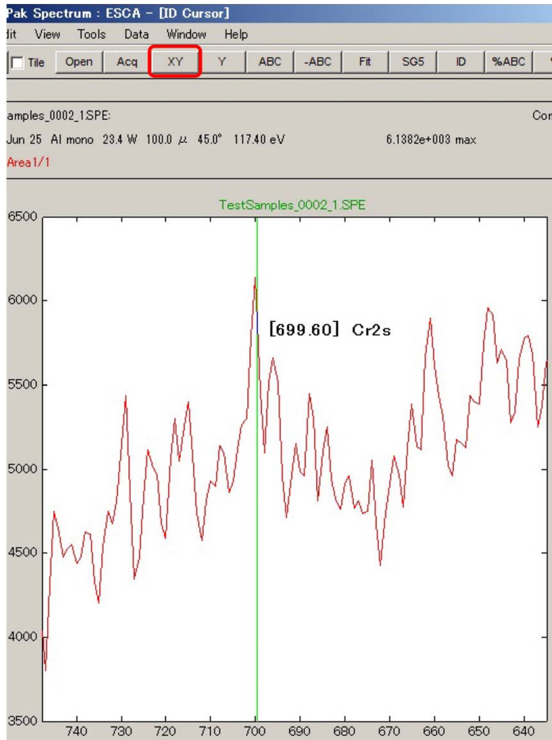


Figure 2.7: Candidates of the peak can be displayed by right-click&dragging the mouse.

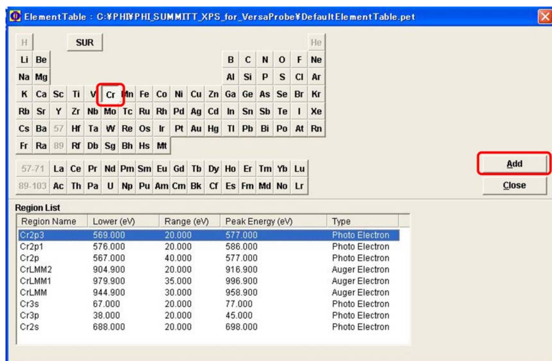


Figure 2.8: Setting window for measuring narrow spectra (#1)

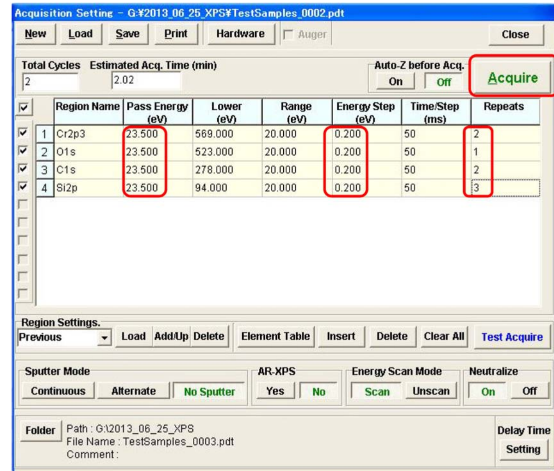


Figure 2.9: Setting window for measuring narrow spectra (#2)

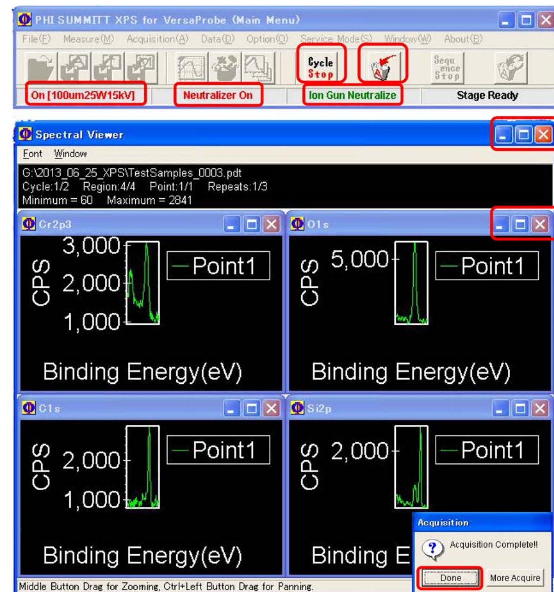


Figure 2.10: Windows displaying the measurement of narrow spectra

ments whose peaks have already been assigned are displayed to be green. Other peaks of those can sometimes be assigned by clicking the symbol twice. At first, the above procedure should be applied to all elements that have been assigned by clicking 'ID' button.

If there are unknown peaks even after doing the above procedure, try the following method of assignment, please.

In Fig. 2.6 [p.7], a spectral region in the vicinity of 700 eV has been selected by click&dragging horizontally around the center of the survey spectrum. Then, Fig. 2.7 is an enlargement of the selected region. Next, right-click&drag horizontally around the unknown peak, please, such that candidates of peak name are shown next to next. Cr2s peak has been found at 699.6eV. 'XY' button in the upper region of Fig. 2.7 can be clicked to restore the scale and show again Fig. 2.5 [p.7].

The latter method for manually assigning unknown peaks by right-click&dragging the mouse is recommended to experienced users of the 'MultiPak'.

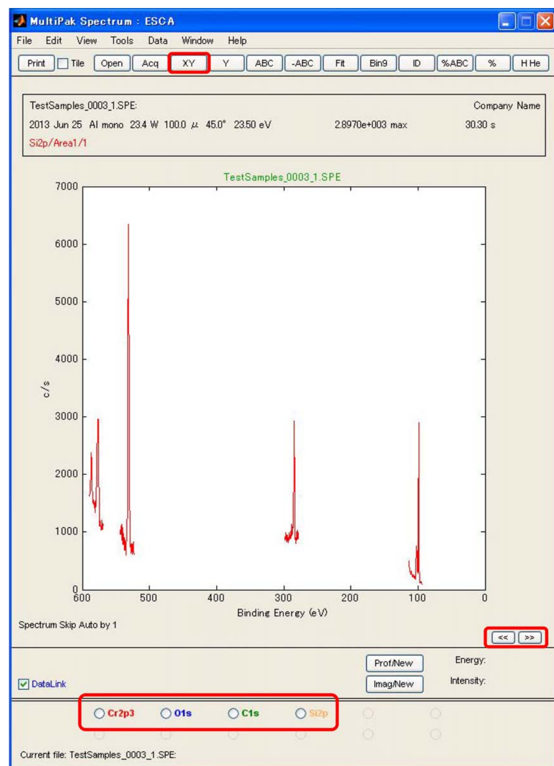


Figure 2.11: Narrow spectra have been read.

2.1.4 Setting window for measuring narrow spectra

The measurement of narrow spectra should be scheduled referring to the survey spectrum as shown in Fig. 2.5 [p.7]. At first, 'Element Table' button at the center of Fig. 2.1 [p.5] should be clicked to display the element table as shown in Fig. 2.8. A button of element can be clicked to display a list of photoelectron and Auger electron. Select only one spectral region from the list and then click 'Add' button, please. After repeating the above procedure for each spectral region to be measured, 'Close' button should be clicked to close the element table window.

Fig. 2.9 shows the schedule set for measuring narrow spectra. 'Pass Energy' has been set to be 23.5 eV that is less than the value when taking the survey spectrum (117.4 eV). 'Energy Step' has been set to be 0.2 eV (default) that is approximately equal to the recommended value ($\sim$ 'Pass Energy' /100)

When the position on which the photoelectrons emitted from the sample are focused, is defined as the 'North pole' of the double spherical electrodes, 16 channel electron detectors are arranged around the 'South pole' in the direction of the 'polar axis'. This is the direction of energy spread of the electron beam. The energy spread ΔE of detected electron beam is proportional to the value of the 'Pass Energy'. Therefore, the number of detected electrons and the energy resolution are in a trade-off relation. Larger or smaller values of the pass energy can be selected from the 'Pass Energy' pull-down menu for large number of counted electron or high energy resolution, respectively.

Numbers of 'Repeat' in Fig. 2.9 have been changed from the default (1) referring to the peak heights observed in the survey spectrum.

2.1.5 Measurement of narrow spectra

'Acquire' button on the upper right corner of Fig. 2.9 can be clicked to start the measurement such that Fig. 2.10 is displayed. The items surrounded by red frames in Fig. 2.10 are similar to those in Fig. 2.3 [p.6] and then should be referred to §2.1.2 [p.6].

2.1.6 Analysis of the narrow spectra

2.1.6.1 Reading data

The data should be read in an identical manner to that for Fig. 2.4 [p.6] referring to §2.1.3.1 [p.7]

2.1.6.2 Analysis of data

In Fig. 2.11, the narrow spectra have been read. When plural data files have been read, '[<<]' button or '[>>]' button on the lower right of Fig. 2.11 can be clicked to display previous or next data file.

Each spectral region can be enlarged by clicking the corresponding radio buttons on the lower part of Fig. 2.11. In Fig. 2.12 [p.10], an enlarged spectrum in the vicinity of Cr2p3 peak has been displayed. 'XY' button can be clicked to display the all spectra in the original scale as shown in Fig. 2.11.

2.1.6.3 Quantitative analysis

Vertical lines 'Left bar' and 'Right bar' can be found in the spectral window of Fig. 2.12. The

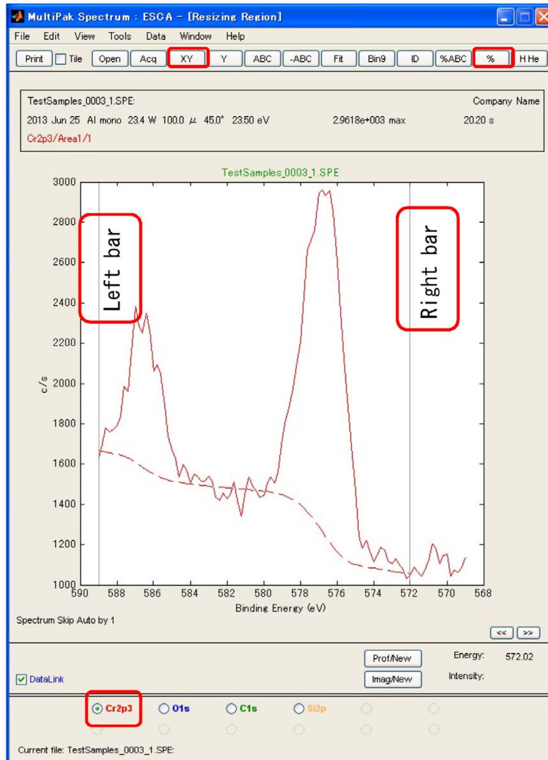


Figure 2.12: A narrow spectrum has been enlarged.

background shown as a red broken curve can be adjusted by click&dragging these bars.

After adjusting also the backgrounds of the spectra in the vicinity of O1s, C1s and Si2p, '%' button on the upper right corner of Fig. 2.12 can be clicked to display molar ratios of Cr, O, C and Si on the text editor. '%ABC' button on the left of '%' button can be clicked to display them in the spectral region of the window. Characters displayed in the spectral region can be erased by click&dragging them to outside the frame.

However, XPS measurement is not necessarily good at such a quantitative analysis. Quantitative analysis should be done taking into account that an error about $1 : 2(\pm 0.1)$ is included when a molar ratio of $1 : 2$ is obtained. The XPS is the most effective to estimate the chemical state of element from the horizontal shift of peak of photoelectrons that are emitted from the atoms whose depth from the surface are less than 10 nm.

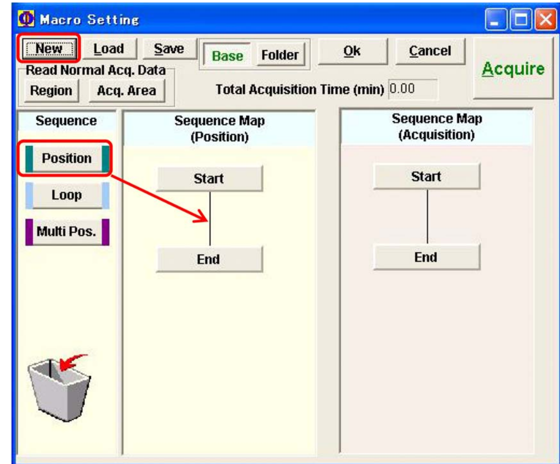


Figure 2.13: Initial window of Macro setting

2.2 Spectra measurement using the macro mode

'Phi Summitt' that controls PHI 5000 VersaProbe has the macro function that enables automatic measurement for many points registered by users.

The macro measurement should be set and done to obtain survey spectra by 3 ∼ 5 cycles for all positions that have been registered. One of the purpose of this measurement is to confirm that the all positions have been correctly registered, which should be verified by viewing the sample stage on the CCD image.

2.2.1 Setting before starting the macro mode

All the measurement positions should be registered with the normal (not macro) mode referring to Fig. 1.2 [p.2] and the description in §1.1.6 [p.3]. Also in the '[2] Image window' shown in Fig. 0, positions can be registered. However, registration of position in the macro mode should be avoided or the position is not correctly registered.

Before starting the macro mode, the normal mode windows should be closed by clicking 'Close' button above 'Acquire' button on the upper right corner of Fig. 2.2 [p.5]. By clicking it, '[2] Image window', '[3] Acquisition setting window' and '[4] Stage controller' of the normal mode similar to those in Fig. 0 on the cover

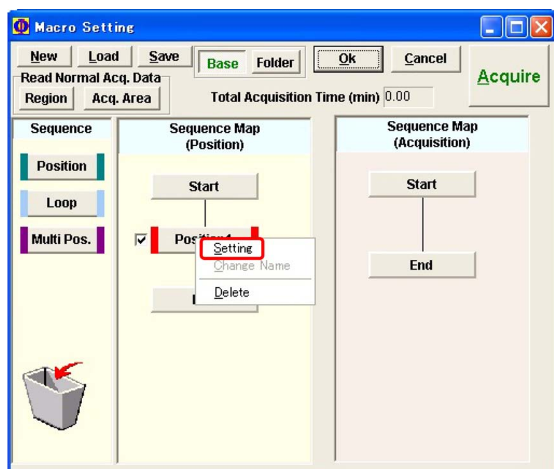


Figure 2.14: Macro setting window (Position Setting #1)

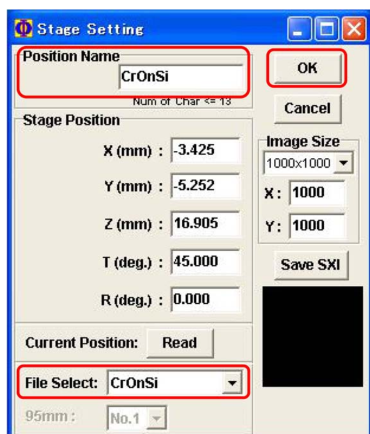


Figure 2.15: Macro setting window (Position Setting #2)

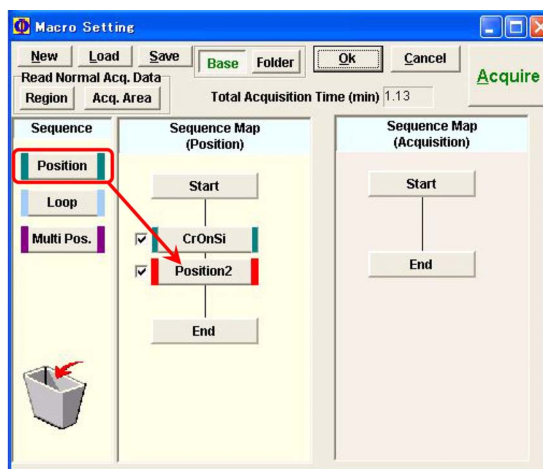


Figure 2.16: Setting of the next position

of this manual can simultaneously be closed.

2.2.2 Start of the macro mode and initial setting

'Macro' button of '[1] Main menu' on the upper left of Fig. 0 on the cover of this manual, has been clicked to start the macro mode. In '[6] Macro setting window' of Fig. 0, previous user's settings are shown in many cases. At first, 'New' button on the upper left of Fig. 2.13 should be clicked to clear them such that no items can be found between 'Start' and 'End' in both 'Sequence Map(Position)' region and 'Sequence Map(Acquisition)' region.

2.2.3 Position setting

Next, 'Position' button in 'Sequence' region on the left of Fig. 2.14 should be drag&dropped on 'Sequence Map(Position)' region. Then, follow the discription in §2.2.4, please, referring to Figs. 2.14 and 2.15.

From the second position onward, 'Position' button should be drag&dropped between the 'last position name button' and 'End' in the 'Sequence Map(Position)' region, as shown in Fig. 2.16

2.2.4 Selection of the registered position

The 'Position' button in Fig. 2.14 dropped in the 'Sequence Map(Position)' region should be right-clicked to open a menu. From the menu, 'Setting' should be left-clicked to display Fig. 2.15.

From 'File Select' pull-down menu in the lower part of Fig. 2.15, a position name should be selected. After verifying that the same position name as in the 'File Select' pull-down menu is displayed in 'Position name' text box, please click 'OK' button.

2.2.5 Selection of measurement menu

Any position between 'Start' and 'End' in the 'Sequence Map(Acquisition)' region in Fig. 2.14 can be clicked such that 'Spectra' etc. are displayed in the left 'Sequence' region. 'Spec-

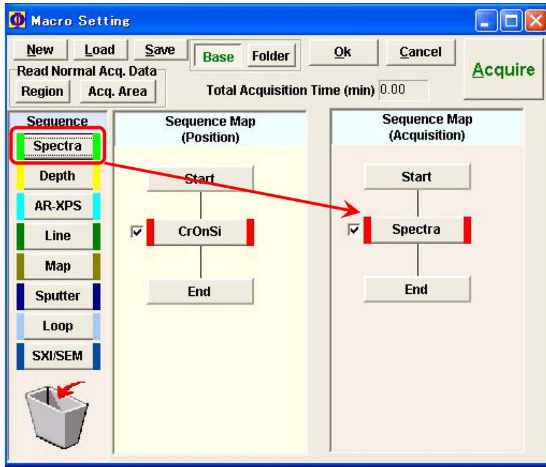


Figure 2.17: Acquisition setting window

tra' can be drag&dropped in the 'Sequence Map(Acquisition)' region as shown in Fig. 2.17.

2.2.6 Setting the measuring condition

The dropped 'Spectra' button in Fig. 2.17 should be left-clicked to set conditions for measurement. The response of this button is delayed by a few seconds. Next, items in '[2] Image window' and then '[3] Acquisition setting window' of Fig. 0 on the cover of this manual should be set.

Items of the '[2] Image window' in Fig. 0 should be set in the same manner as described in §1.1 [p.1] referring to Fig. 1.1 [p.1]. However, setting in the 'Position Setting' pull-down menu in Fig. 1.1 (f) [p.1] does not have to be changed since the position is already set following the description in §2.2.4 [p.11].

In '[3] Acquisition setting window' of Fig. 0 on the cover of this manual, settings should be done referring to Fig. 2.18 such that a survey scan is set.

At first, 'Folder' button on the lower left corner of Fig. 2.18 should be clicked such that the explorer is opened. After selecting or making a folder in the explorer, prefix and initial number of the file name should be set. Then, clear previous user's settings, please. After that, 'Element Table' button should be clicked to open the 'Element Table' window. 'SUR' button (Survey button) has been clicked as default. Click 'Add' button and then 'Close' button, please, to set a survey scan. In Fig. 2.18, 'Range' has been

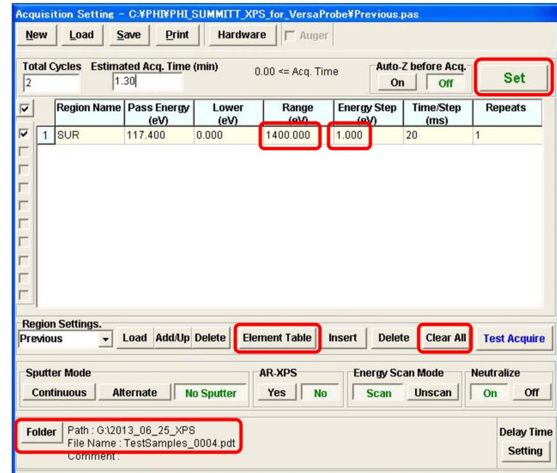


Figure 2.18: Macro setting window (setting of the measurement)

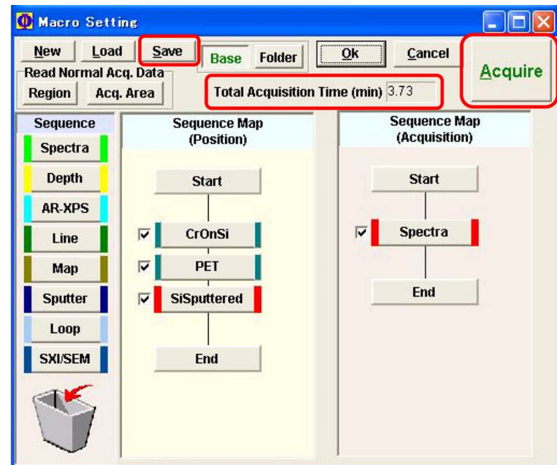


Figure 2.19: Setting of the macro measurement has been completed.

changed to be 1400 eV from 1000 eV (default). A value less than the photon energy of Al Kα radiation (1486.6 eV) can be set as 'Range'. 'Energy Step' has been changed to be a recommended value (1.0 eV), 'Pass Energy' / 100 from 0.2 eV (default).

2.2.7 Completing the macro setting and starting the measurement

The procedure described from §2.2.3 [p.11] to §2.2.6 should be repeated for all positions to be measured. From the second position onward, setting items in '[2] Image window' and '[3] Acquisition setting window' of Fig. 0 on the cover of this manual do not change in many cases. Then, the 'Set' button on the upper right cor-

ner of Fig. 2.18 can be clicked to set the survey scan with the same settings.

In Fig. 2.19, a macro measurement for three positions has been set. This setting can be saved by clicking 'Save' button and be loaded again by clicking 'Load' button.

On the upper part of Fig. 2.19 'Total Acquisition Time(min)' for complete measurement is displayed. 'Acquire' button on the upper right corner of Fig. 2.19 can be clicked to start the macro measurement.

2.2.8 Analysis of the survey spectrum measured by the macro mode

The measured survey spectra can be analyzed by using the 'MultiPak' in the same manner as described in §2.1.3 [p.7]. After assigning the spectral peaks, the strategy for measuring narrow spectra can be built.

2.2.9 Setting of measurement of narrow spectra by the macro mode

The settings of narrow scan can be made by revising the macro settings for the survey scan.

For example, 'CrOnSi' button in Fig. 2.19 can be left-clicked such that the both sides of this button come to be red. Next, the 'Spectra' button in the 'Sequence Map(Acquisition)' region can be left-clicked such that the schedule for taking narrow spectra can be set referring to the description in §2.1.4 [p.9].

With the same procedure, the schedule for taking narrow spectra can be set also for positions of 'PET' and 'SiSputtered'.

Since the narrow scan is the main measurement to take important data for each user, the schedule should be set carefully comparing the time remaining and the 'Total Acquisition Time(min)'.

2.2.10 Analysis of the narrow spectra measured by the macro mode

The narrow spectra can be analyzed in the same manner described in §2.1.6 [p.9].

For more details concerning the 'MultiPak', please refer to Part 2 manual.

Chapter 3

Measurement of spectra with alternative sputtering

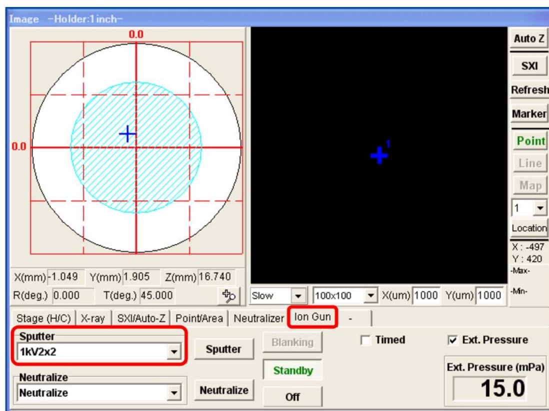


Figure 3.1: Image Window. ‘Ion Gun’ tab has been opened.

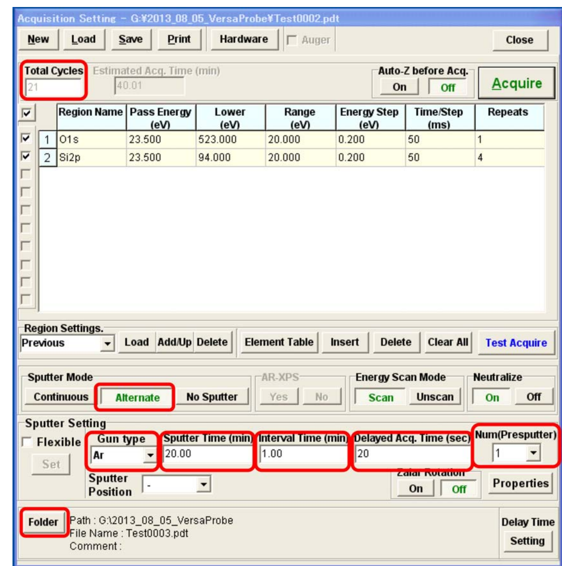


Figure 3.2: Acquisition Setting Window. ‘Alternative’ button has been clicked.

3.1 Abstract of sputtering measurement

PHI5000 VersaProbe has a function of sputtering with Ar ion. The surface of sample is etched with Ar ion. Then it is a destructive measurement. There are two purposes: one is measuring molar-ratio dependence of elements on the depth and the other is estimating chemical-state dependence of a particular element on the depth.

Sputtering rate of 1kV2×2 mode for SiO_2 is about 2nm / min. It is approximately proportional to the sputtering voltage and depends on the kind of material.

3.2 Normal (not using macro) measurement of spectra with alternative sputtering

3.2.1 Set of the sputtering voltage

In Fig. 3.1, ‘Ion Gun’ tab has been opened in the image window to select 1kV2×2 mode from the pull-down menu. (When not sputtering, ‘Neutralize’ should be selected).

The sputtering mode should be selected from 500V2×2, 1kV2×2, 2kV2×2, 3kV2×2 and 4kV2×2.

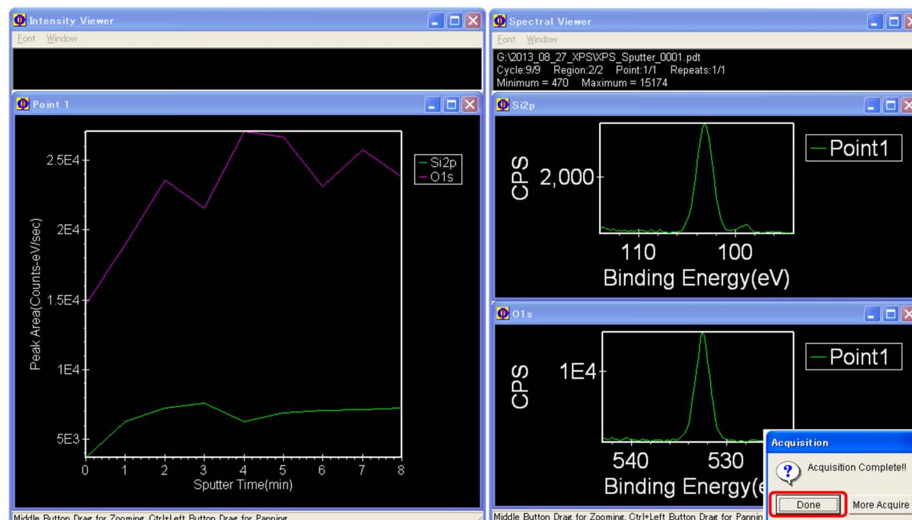


Figure 3.3: A window displayed during the sputtering measurement

3.2.2 Other settings on the image window

For setting other parameters on the image window, refer to the description in §1.1 [p.1].

3.2.3 Setting the sputtering conditions on the acquisition setting window

In Fig. 3.2, 'Alternative' button has been clicked in 'Sputtering Mode' on the lower left of the Acquisition Setting window. Below it, 'Sputter Setting' menu that does not appear when 'No Sputter' button has been clicked, has appeared. In 'Gun type' menu, only 'Ar' can be selected. In text boxes of 'Sputter Time (min)', 'Interval Time (min)' and 'Delayed Acq. Time (sec)', total sputtering time, sputtering time for every sputtering and delay time before starting spectral measurement after finishing every sputtering, have been shown. From 'Num(Presputter)' pull-down menu on the lower right of Fig. 3.2, time of spectral measurement before the first sputtering, can be selected from '0', '1' or '2'. '1' should usually be selected.

Because 1.00 as 'Interval Time (min)' and 20.00 as 'Sputter Time (min)' have been set in Fig. 3.2, sputtering is repeated 20 times. However, in 'Total Cycles' text box 21 is displayed because the spectral measurement before starting the first sputtering has been counted. Any number cannot be directly typed into 'Total Cycles' text box on the upper left of Fig. 3.2. The time of sputtering should be set by typing to change the value in 'Sputter Time (min)' text box.

3.2.4 Start and end of spettering measurement

'Acquire' button on the upper right of Fig. 3.2 can be clicked to start the measurement. During the measurement, A window as shown in Fig. 3.3 is displayed. Measured spectra are displayed in the right region of Fig. 3.3. Here, spectra of O1s and C1s are shown. On the left of the figure, integrated intensities of O1s and C1s are shown as a function of sputtering time.

Measured data are save in files '*.pro' in a folder set by clicking 'Folder' button on the lower left of Fig. 3.2.

When the measurement finished, 'Acquisition Complete' message is displayed as shown on the lower right corner of Fig. 3.3. 'OK' button can be clicked to do the next operation.

3.2.5 Data analysis

For analyzing the measured data, refer to the description in chapter 2 in Part 2 manual, please.

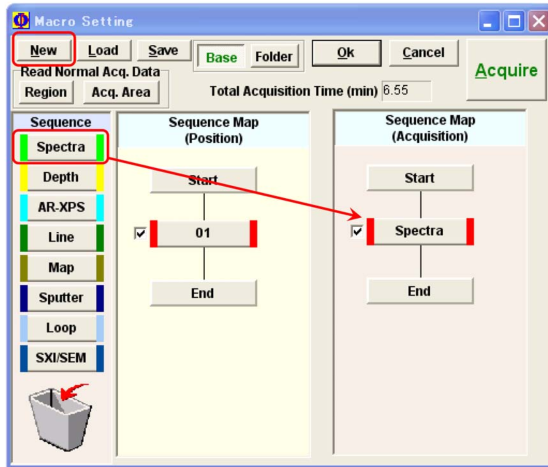


Figure 3.4: Macro Setting Window. A spectrum measurement has been set for registered position '01'

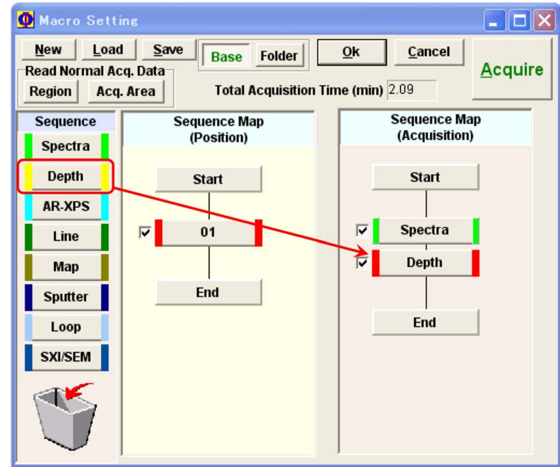


Figure 3.5: Macro Setting Window. A sputtering spectrum measurement has been set for position '01'

3.3 Sputtering spectra measurement using macro mode

3.3.1 Finishing the normal mode and start up the macro mode

By clicking 'Close' button on the lower right of Fig. 3.2, image window, acquisition setting window and stage controller can be closed. After that, by clicking 'Macro' button on the upper left of Fig. 0 on the cover of this manual, '[2] Image window', '[3] Acquisition setting window', '[4] Stage controller' and '[6] Macro setting window' can be opened as shown in Fig. 0 on the cover.

3.3.2 Reset of an old macro and set of a new macro

'New' button can be clicked to reset an old macro made by a previous user for setting a new macro. Figure 3.4 shows a situation that a spectrum measurement has been set for position '01' about which please refer to the description in §2.2 [p.10].

3.3.3 Set of a sputtering spectrum measurement

Figure 3.5 shows a situation that 'Depth' button has been drag&dropped from from sequence field in sequence map (acquisition) field. By left-clicking the dropped 'Depth' button (the response is delayed by 2 $\sim$ 3 seconds), conditions for a sputtering spectrum measurement can be set.

3.3.4 Set of acceleration voltage in the image window

While Fig. 3.1 [p.14] shows the image window for normal measurement, an identical window opens also in the case of macro measurement. 'Ion Gun' tab has been clicked to open in Fig. 3.1 [p.14]. Whereas 'Neutralize' should be selected for a normal (without sputtering) measurement from 'Sputter' pull-down menu, an acceleration voltage should be selected from it for sputtering measurement, about which refer to the description in §3.2.1 [p.14], please.

3.3.5 Other settings in the image window

Set other parameters in the image window, please, referring to the description in §1.1 [p.1].

3.3.6 Settings in the acquisition setting window

Set parameters in the acquisition setting window similarly to the case without using the

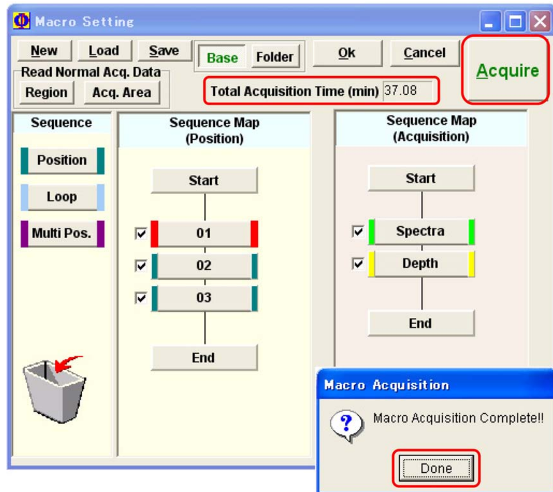


Figure 3.6: Macro Setting Window. A macro has been finished to set.

macro mode, please. Refer to the description in §3.2.3 [p.15].

3.3.7 Start and end of the sputtering measurement

Figure 3.6 shows a situation that a macro of sputtering measurement has been finished to set for positions '01', '02' and '03'. At the upper central position in Fig. 3.6, the estimated total measuring time is shown. Check boxes on the left of buttons of positions '01', '02' and '03' and/or them of measurement 'Spectra' and 'Depth' can be unchecked to let them not to be measured

The macro measurement can be started by clicking 'Acquire' button on the upper right corner of Fig. 3.6.

During the measurement, both sides of buttons of positions '01', '02' and '03' and/or them of measurement 'Spectra' and 'Depth' of which the measurement is being done, are displayed to be red.

When the total measurement has been finished, a message as shown on the lower right of Fig. 3.6 is displayed. 'Done' button can be clicked to continue.

3.3.8 Data analysis

Measured data can be analyzed by referring to the description in §2.1 of Part 2 manual.

Chapter 4

Mapping measurement

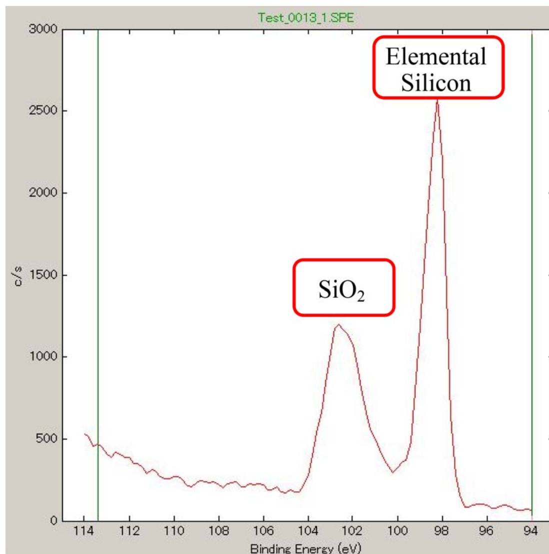


Figure 4.1: Si2p spectrum. Left: SiO_2, Right: Elemental Si

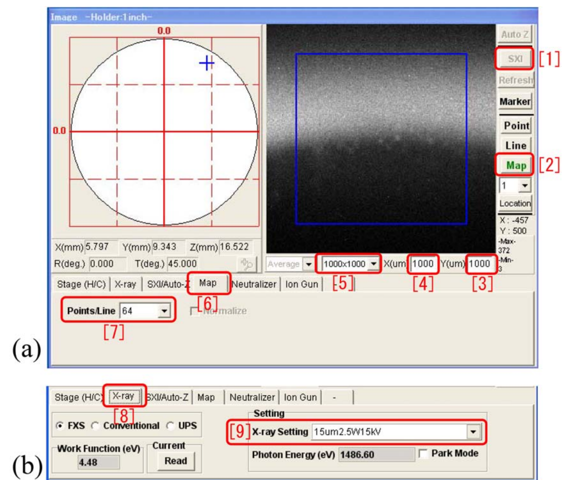


Figure 4.2: MAP mode has been selected in the image window.

4.1 Abstract of mapping measurement

PHI5000 VersaProbe has a function of mapping measurement. Mapping is a measurement mode to obtain a two-dimensional distribution map of element with a chemical state emitting photo electrons whose energy is in a set range.

SXI (Scanning X-ray Imaging) is a function to get an image of emitted electron whose binding energy is in a wide range about 1400 eV detecting electrons whose velocity energy is almost zero with a large value of pass energy.

Therefore, the image can be obtained with a relatively high refreshing rate (0.5 ∼ 1 Hz) in the SXI. However, the MAP is obtained with a speed far lower than SXI since it detects photoelectrons in a narrow energy range using a smaller pass energy.

4.2 Normal (not using macro) mapping measurement

4.2.1 Conformation of photoelectron spectrum

Figure 4.1 shows a photoelectron spectrum of Si2p obtained with a pass energy of 23.5 eV. The sample surface was prepared by partly removing SiO_2 layer of oxidized silicon wafer by Ar-sputtering. The peaks of SiO_2 (left) and that of elemental silicon (right) are found. In §4.2.2- §4.2.4 [p.20], a method to obtain maps of photoelectrons emitted from SiO_2 and elemental silicon, separately, is described. In §4.2.5 [p.21], a method simultaneously to obtain them is described.

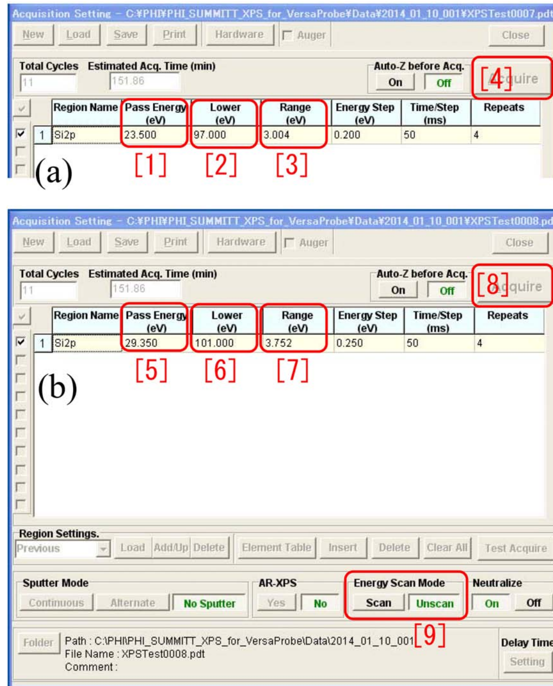


Figure 4.3: Settings in acquisition setting window.

4.2.2 Settings in the image window

In Fig. 4.2 (a), '[2] MAP' button has been clicked after clicking '[1] SXI' button to stop the SXI. '[3]', '[4]' and '[5]' are sizes of viewing field of SXI. The values of '[3]' and '[4]' should coincide with the values of '[5]'. If they do not coincide, SXI should be done again after selecting a field size from '[5]:' pull-down menu such that the sizes shown in '[3]', '[4]' and '[5]' coincide with each other. The SXI image shown in Fig. 4.2 (a) has been obtained in the vicinity of border line between not sputtered and sputtered to remove the oxidized layer of the silicon wafer.

The blue frame in the image field of Fig. 4.2 (a) can be right-clicked to set the size of mapping region.

'[6]MAP' tab can be clicked to display '[7]Points/Line' pull-down menu from which number of pixels of the map can be selected. The maximum number of pixels is 256. In the case of Fig. 4.2 (a), the map is obtained with a spatial resolution of 64 × 64.

In Fig. 4.2 (b), '[8] X-ray' tab has been clicked to open. Here, a sufficiently small focus size of X-rays ($e.g.$10 $\sim$ 20μm) has to be selected from '[9] X-ray Setting' pull-down menu.

4.2.3 Settings in the acquisition setting window

Figure 4.3 shows settings to obtain a map in the acquisition setting window. (a) and (b) are settings for obtaining maps with photoelectron emitted from elemental silicon and SiO_2, respectively. 'Unscan' has been clicked to select as '[9] Energy Scan Mode' on the lower right of ig. 4.3.

Here, motion of an electron flying between the spherical electrodes is discussed to clarify the rationality of the spherical shape of the electron analyzer in the following three paragraphs.

An electric field is applied to the electrons emitted from the sample such that the velocity energies of them are decelerated to be around the pass energy. The electrons condensed with electronic lenses at the entrance position of the analyzer. Hereafter this entrance position is referred to as the 'north pole' of the analyzer. The 16-channel electron detectors are arranged in the direction of the 'polar axis' of the analyzer around the 'south pole'. While an electron whose velocity energy is larger than the pass energy is detected by a channel of the detector outside the 'south pole'. an electron with a smaller velocity energy is detected inside the 'south pole'. Therefore, there is an energy spread of ΔE in the velocity energy of detected electron.

Incidentally, it is relatively easy to describe the motion of an electron flying between the 'double spherical electrodes'. Since the direction of electric field applied by the spherical electrodes is radial from the center of the sphere. Therefore, the motion of an electron can be described in the same way as that of a planet orbiting around the sun and then follows Kepler's law. Large and small pass energies mean heavy and light 'sun' around which a planet orbits rapidly or slowly, respectively. Based on this consideration, it can be derived that ΔE is proportional to the pass energy.

Further, the electrons condensed at the 'north pole' flies along any longitude to reach to the 'south pole', from which the rationality of the spherical shape of the electron analyzer can be understood.

But to return to the settings for mapping, the

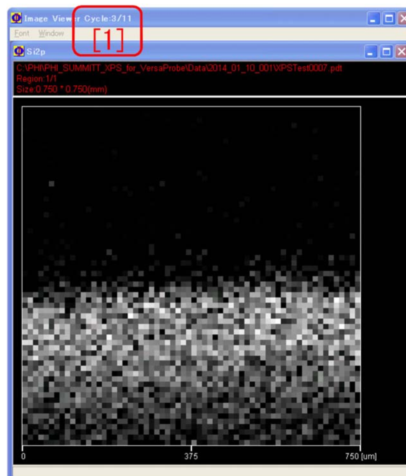


Figure 4.4: Distribution map of elemental silicon (image viewer).

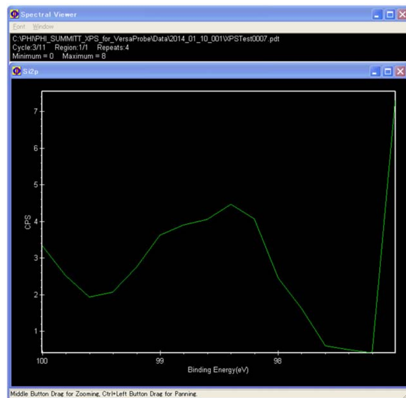


Figure 4.5: Photoelectron spectrum of elemental silicon (spectral viewer).

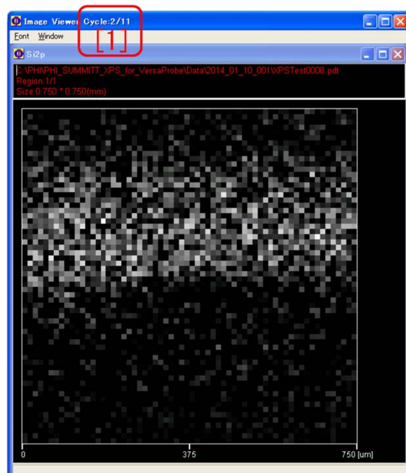


Figure 4.6: Distribution map of SiO_2 (image viewer).

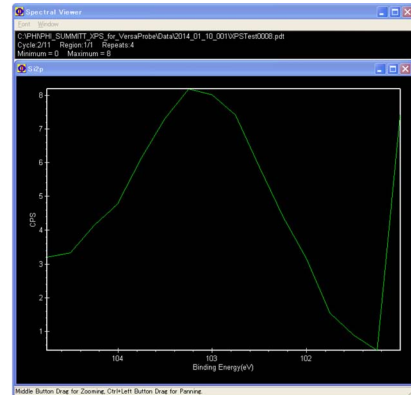


Figure 4.7: Photoelectron spectrum of SiO_2 (spectral viewer).

decelerating electric field is fixed in the ‘Unscan’ mode such that the spectrum can be measured only by using 16 channels of the electron detector whereas the decelerating electric field is changed for spectroscopy such that the binding energy of electrons detected with the electron detector changes in the ‘Scan’ mode.

In the case of ‘Unscan’ mode, ‘Lower(eV)’ of ‘[2]’ and ‘[6]’ can be changed by typing values and ‘Range(eV)’ of ‘[3]’ and ‘[7]’ can be set by selecting ‘Pass Energy (eV)’ of ‘[1]’ and ‘[5]’ from the pull-down menu in Fig. 4.3 [p.19]. Note that the energy ranges set in Figs. 4.3 (a) and 4.3 (b) [p.19] cover the ranges of peaks of elemental silicon and SiO_2 as shown in Fig. 4.1 [p.18], please.

4.2.4 Start of mapping measurement

‘Acquire’ button of ‘[4]’ or ‘[8]’ on the upper right of Fig. 4.3 [p.19] can be clicked to start the measurement.

Figs. 4.4 and 4.5 are shown during the measurement with settings of Fig. 4.3 (a) [p.19]. Figure 4.4 shows a distribution map of elemental silicon obtained by repeating horizontal scan from up to down. ‘Cycle 3/11 [1]’ on the upper left of Fig. 4.4 shows that third cycle of measurement is being done while total 11 cycle measurement has been set. Fig. 4.5 shows a spectrum taken with the 16 channel electron detector. While a large value of counted electron is found at the right edge, this is caused by adjustment of the detector and not an essential signal.

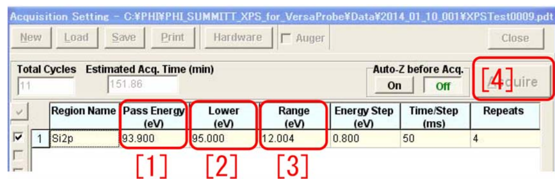


Figure 4.8: Settings in the acquisition setting window.

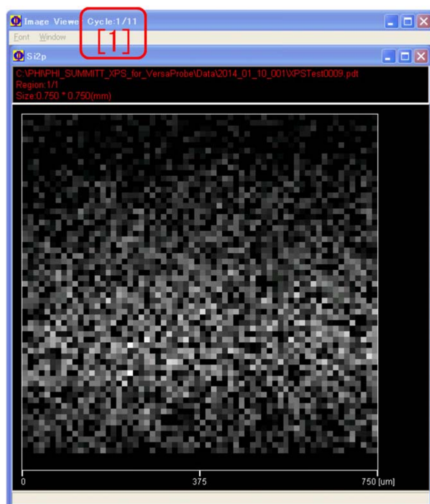


Figure 4.9: Distribution maps of elemental silicon and SiO_2 (Image Viewer).

Similarly, Figs. 4.6 and 4.7 are displayed during the measurement with settings of Fig. 4.3 (b) [p.19] Contrary contrasts can be found in Figs. 4.4 and 4.6. 'Cycle 2/11 [1]' means that the second cycle of measurement is being done while total 11 cycle measurement has been set.

In the lower part of Fig. 4.4 and upper part of 4.6, dark regions are found. However, these are due to chromatic aberration of the monochromator and not essential signals. Concerning the aberration, please refer to §1.3 [p.4].

For analyzing and processing the measured data, refer to Part 2 manual, please.

4.2.5 Simultaneous mapping for plural peaks

In Fig. 4.8, simultaneous mapping measurement for both spectral peaks of SiO_2 and elemental silicon found in Fig. 4.1 [p.18] has been set. Setting on the lower half is the same as Fig. 4.3 (b) [p.19]. '[1]', '[2]' and '[3]' can be set in the same

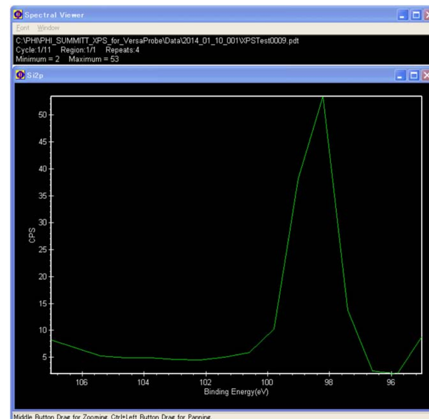


Figure 4.10: Photoelectron spectrum of elemental silicon (Spectral Viewer).

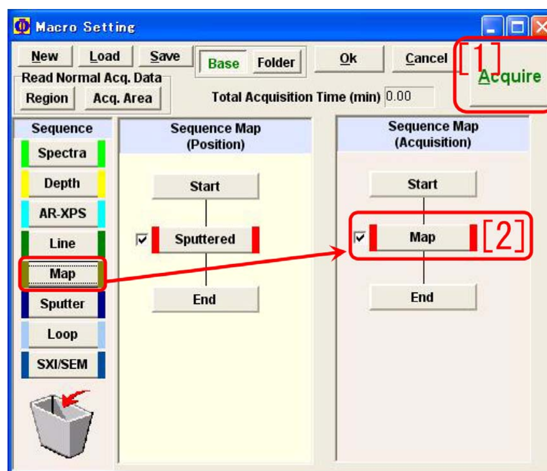


Figure 4.11: Setting of a mapping measurement in the macro mode

way as Fig. 4.3 [p.19]. Refer to the description in §4.2.3 [p.19], please.

'[4] Acquire' button in Fig. 4.8 can be clicked to start the measurement. During the measurement, Figs. 4.9 and 4.10 are shown. Any clear contrast cannot be found since electrons emitted from both elemental silicon and SiO_2 are counted. In Fig. 4.10, only a peak of elemental silicon is found since the lower region are being measured in Fig. 4.9.

Maps of elemental silicon and SiO_2 can be extracted separately from the data obtained in this way by using 'MultiPak'. Refer to Part 2 manual, please.

4.3 mapping measurement using the macro mode

Macro mode can be started in the same way as measurement of spectra. Refer to the description in §2.2.7 [p.12].

In Fig. 4.11 [p.21], a mapping measurement has been set for position 'Sputtered' that has been registered in the normal (not macro) mode. Position names should necessarily registered in the normal mode.

'[2] Map' button can be left-clicked to set the measurement. The response is delayed for $2 \sim 3$ seconds. Similarly to the normal mode, 'Image window' and 'Acquisition setting window' are displayed also in the macro mode.

Settings in the 'Image window' should be done as shown in Fig. 4.2 [p.18]. In Fig. 4.2 (b) [p.18], do not forget to select a sufficiently small focus size (*e.g.* $10 \sim 20\mu$m) from '[9] X-ray Setting' pull-down menu, please.

Settings in 'Acquisition setting window' should be done referring to the description in §4.2.3 [p.19], please.

'[1] Acquire' button can be left-clicked to start the measurement.

Chapter 5

Angle-resolved spectrum measurement (AR-XPS)

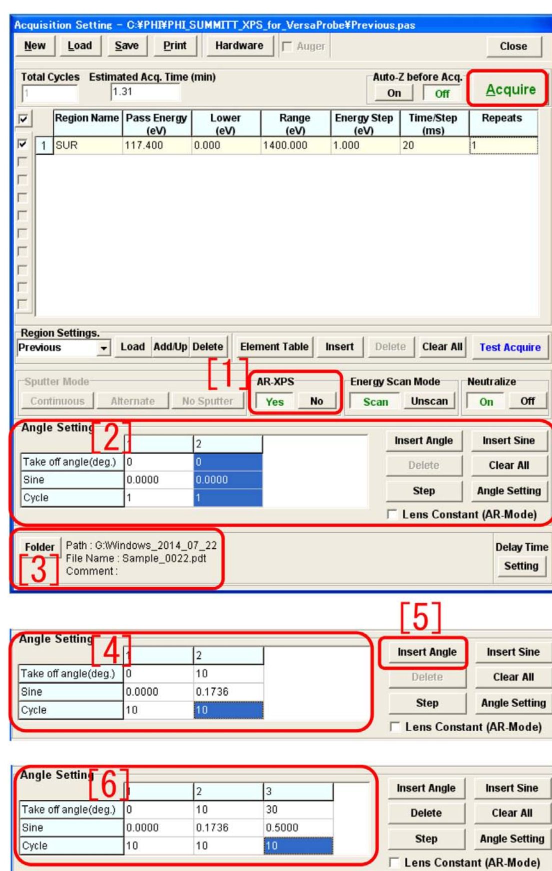


Figure 5.1: Spectrum of Si2p. Left: SiO_2, Right: Elemental silicon.

5.1 Abstract of angle-resolved spectrum measurement (AR-XPS)

PHI5000 VersaProbe has a function of angle-resolved XPS (AR-XPS). AR-XPS is a spectrum measuring mode with which spectra are measured by changing tilt angle of the sample stage.

The entrance aperture of electron analyzer is inclined by 45° from the horizontal surface of the sample stage. Relative angle of electrons taking-off from the sample surface and entering the electron analyzer (takeoff angle) can be changed by tilting the sample stage. When the takeoff angle is small, electrons emitted from atoms at an arbitrary depth have to fly a large distance in the sample before reaching the surface. When an electron can freely fly a distance l in the sample, electrons emitted from atoms at a depth of $l\sin(\theta_{to})$ can reach the sample surface. Here, θ_{to} is the takeoff angle. Photoelectron signal obtained even when θ_{to} is small is that emitted from atoms whose depth is small. AR-XPS is a measuring mode that is nondestructive and can give qualitative information about depth distribution of elements and/or chemical states.

5.2 Sample holders that can be used for AR-XPS

Sample holders that can be used for AR-XPS are AR-XPS holder and 1-inch holder. **When using an AR-XPS holder, absolutely follow its usage described in Appendix A of Part 0 manual, please.** In the case of 1-inch sample holder, AR-XPS can be done at a position whose Y coordinate is $-4.0 < Y < -2.0$. The value of Y can be seen as shown on the lower left of Fig. 1.2 [p.2] by clicking 'Stage(H/C)' tab to open.

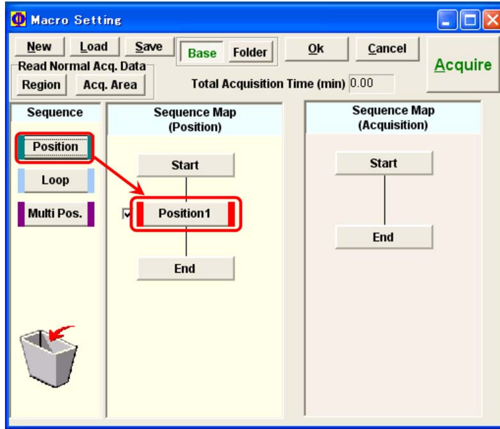


Figure 5.2: 'Position' has been drag&dropped.

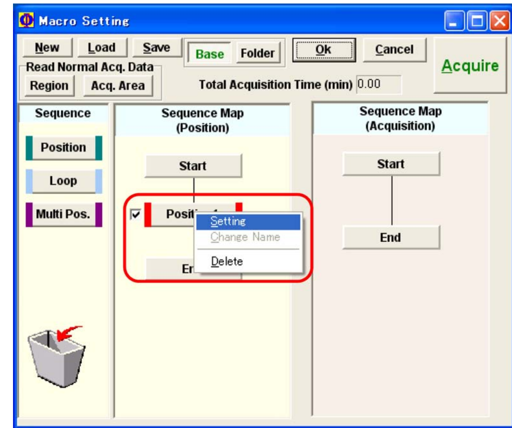


Figure 5.3: 'Position' has been right-clicked.

5.3 AR-XPS measurement not using the macro mode

Figure. 5.1 [p.23] shows settings in 'Acquisition setting window' for an AR-XPS measurement.

'Yes' in '[1] AR-XPS 'button can be clicked to open 'Angle Setting [2]' window. Just when this window is opened, only initial two angles can be input in 'Angle Setting [2]'. Here, '[3] Folder' button has to be clicked to set folder and file name.

In Fig. 5.1 [p.23], the values of 'Take off angle' and 'Cycle' in 'Angle Setting [4]' can be double-clicked to type or select. 'Sine' is value of $\sin(\theta_{to})$ and automatically calculated. When the second column of the table is blue as shown in Fig. 5.1 [p.23], '[5] Insert Angle' button can be clicked to insert the third column into which the third values can be input. After setting parameters repeating the above procedure, 'Acquire' button on the upper right of Fig. 5.1 [p.23] can be clicked to start the measurement. The measured data are saved in a data file '∗.ang'.

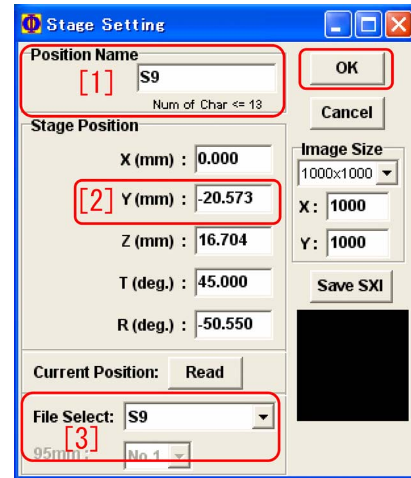


Figure 5.4: Stage setting window

5.4 Angle-resolved measurement (AR-XPS) with the macro mode

A macro measurement can fundamentally be set in the same way as spectrum measurement and/or sputtering spectrum measurement. Positions have to be registered in the normal

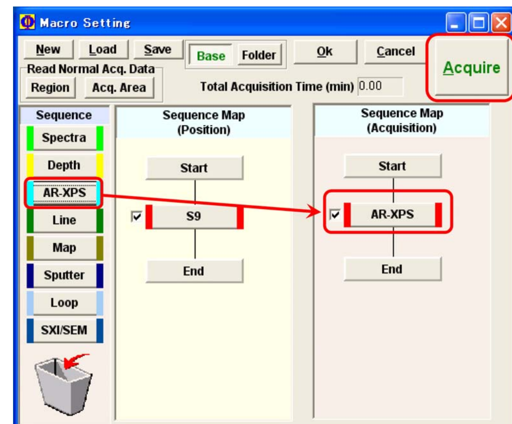


Figure 5.5: 'AR-XPS' has been drag&dropped.

mode. Registration of positions in the macro mode causes positioning error. The 'Close' button above the 'Acquire' button on the upper right of Fig. 5.1 [p.23] can be clicked to finish the macro mode. The normal or macro mode can be started up by clicking 'Acquire' button or 'Macro' button in Fig. 0 on the cover of this manual can be clicked to start up the normal or macro mode, respectively.

In Fig. 5.2, 'Position' button has been drag&dropped into between 'Start' and 'End' of the central 'Sequence Map (Position)' field from the left 'Sequence' field in the macro setting window.

The dropped 'Position 1' can be right-clicked to display Fig. 5.3. Here, 'Setting' should be clicked to display Fig. 5.4. Select a position name from '[3] File Select' pull-down menu, please. '[1] Position Name' in Fig. 5.4 should be the same as the position name selected from the pull-down menu. When a 1-inch sample holder has been used, the value of '[2] Y(mm)' should be in a range $-0.4 < Y < -0.2$. 'OK' button should be clicked to confirm the position.

Click anywhere between 'Start' and 'End' in the right 'Sequence Map (Acquisition)' field, please, such that the left 'Sequence' field changes as shown in Fig. 5.5. 'AR-XPS' should be drag&dropped between 'Start' and 'End' as shown in this figure.

The dropped 'AR-XPS' should be left-clicked to set measurement parameters. The response for this clicking is delayed by a few seconds. Settings in the image window as shown in Fig. 1.1 [p.1] should be confirmed at first. Then, set a schedule as shown in Fig. 5.1 [p.23] referring to the description in §5.3, please. 'Acquire' button in the macro setting window can be clicked to start the measurement.

Appendix A

Spectroscopy with Mg&Zr X-ray sources

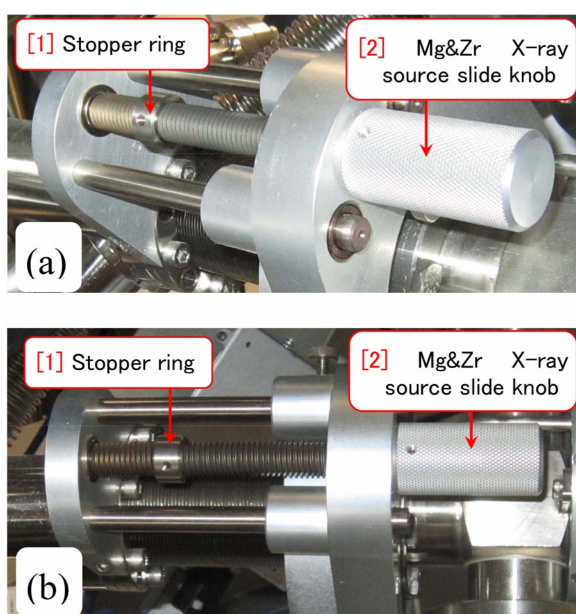


Figure A.1: Mg&Zr X-ray source has been slid in

A.1 Concerning the experiment using Mg&Zr X-ray sources

For preparing Mg&Zr X-ray sources, descriptions in Appendix F of Part 0 manual should thoroughly read. Before doing procedures described in this chapter, please verify the situation as shown in Fig. A.1 behind PHI5000 VersaProbe and Fig. A.2 viewed from the side window of the main chamber. Only a 1-inch sample holder can be used.

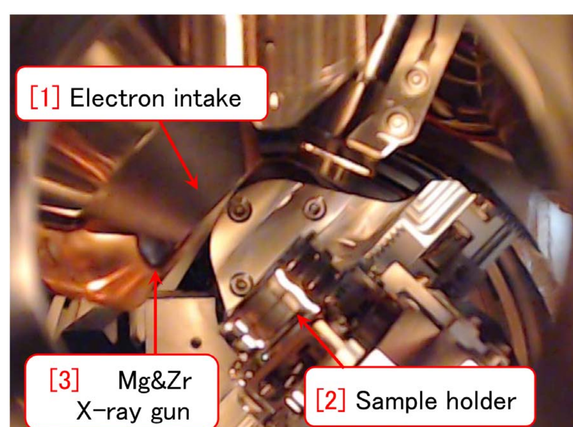


Figure A.2: Mg&Zr X-ray source has been slid in.

A.2 Abstract the spectroscopy with Mg&Zr X-ray source

In addition to the monochromatized Al $K\alpha$ (1486.6 eV) X-ray source, PHI5000 VersaProbe is equipped with Mg $K\alpha$ (1253.4 eV) and Zr $L\alpha$ (2042.4 eV) X-ray sources without monochromator. Only spectroscopy can be done with the Mg&Zr X-ray source.

For a sample including many elements, many photoelectron and Auger electron peaks are found in which a photoelectron peak sometimes overlaps with another Auger electron peak. The Mg&Zr X-ray source is prepared in order to avoid such an overlap of photoelectron and Auger electron peaks.

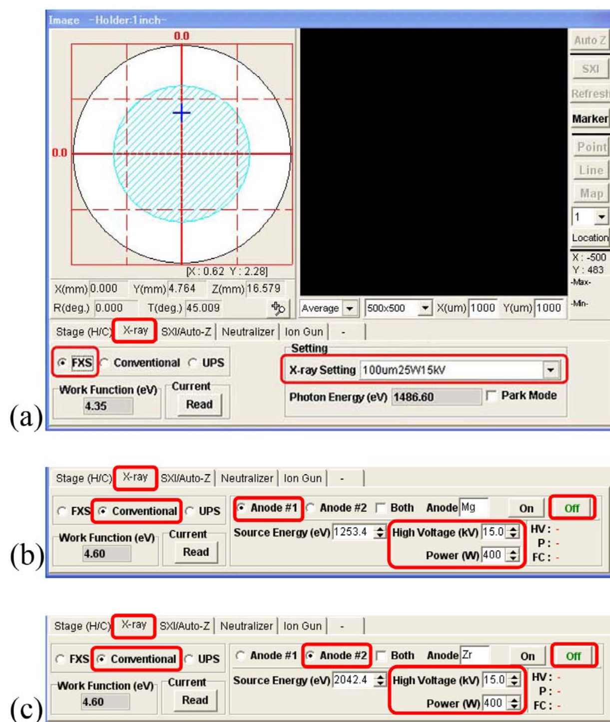


Figure A.3: X-ray tab in the image window has been opened. (a) monochromatized Al $K\alpha$ (1486.6 eV), (b) Mg $K\alpha$ (1253.4 eV) and (c) Zr $L\alpha$ (2042.4 eV) X-ray source has been selected.

Figure A.5: (a) dark main chamber comes to be (b) bright by being illuminated by the filament when the Mg&Zr X-ray source is ON.

Figure A.4: In the main menu window indicating that Mg $K\alpha$ X-ray source has been ON.

A.3 Selection of X-ray source

In Fig. A.3, X-ray tab has been opened in the image window. While the monochromatized Al $K\alpha$ X-ray source has been selected in Fig. A.3 (a) with 'FXS radio button' being checked, Anode#1(Mg) and Anode#2(Zr) X-ray source has been selected in Fig. A.3 (b) and Fig. A.3 (c), respectively, with 'Conventional radio button' being checked. Both Mg and Zr X-ray sources should be used necessarily with 15kV, 400W. With 'Off button' being green on the right of Figs. A.3 (b) and A.3 (c) spectral measurements can be set.

A.4 Automatic adjustment of the sample stage height (Auto-Z)

The height of the sample stage can be adjusted with the focused Al X-ray source similarly to the case using the Al X-ray source. It can be done by clicking 'Auto-Z button' on the upper right corner of the image window in Fig. A.3. After verifying the settings described in §1.1.4 [p.2], do the procedures referring to §1.2 [p.3], please.

A.5 Setting spectral measurements

Spectral measurements can be set fundamentally in the same way as the case using the Al X-ray source, for manual mode by referring to §2.1 [p.5] and for macro mode by referring to §2.2 [p.10].

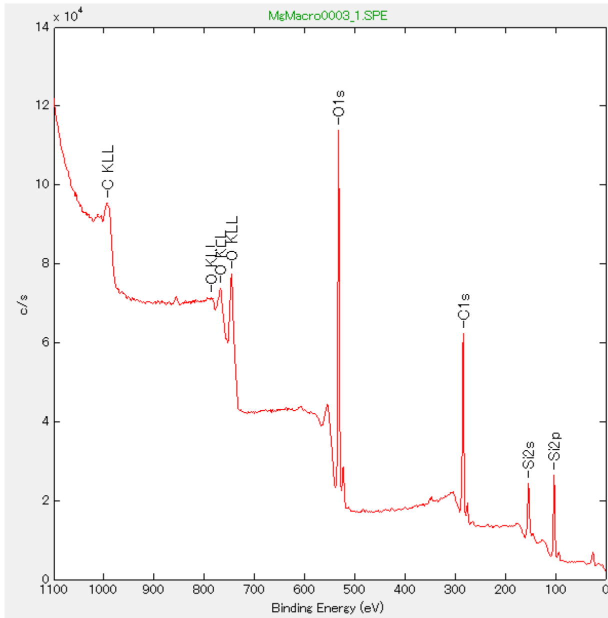


Figure A.6: A photoelectron spectrum measured with the Mg X-ray source for an SiO_2 sample.

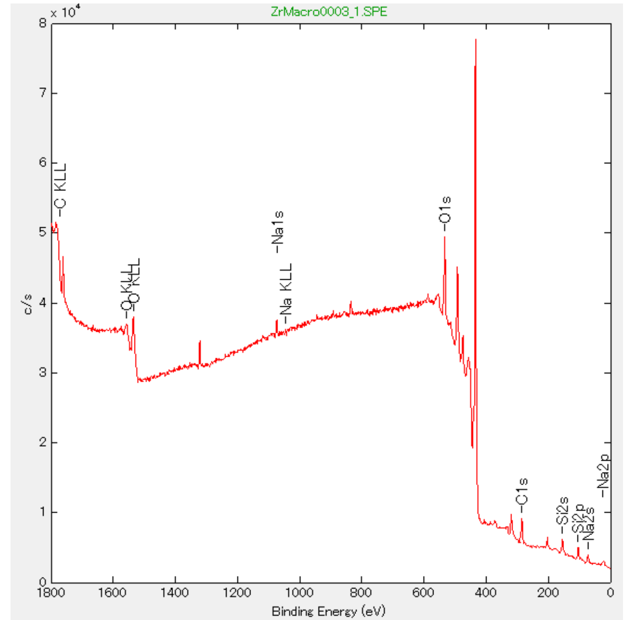
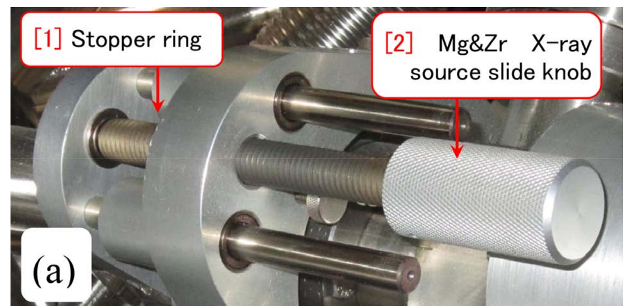


Figure A.8: A photoelectron spectrum measured with the Zr X-ray source for an SiO_2 sample.

Figure A.7: Main menu. Zr X-ray source has been ON.



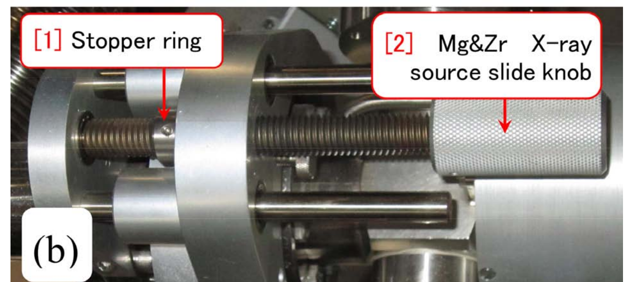


Figure A.9: After finishing an experiment with the Mg&Zr X-ray source used with the situation shown in Fig. A.1 should be returned to be as shown in this figure.

A.6 An example of measurement using the Mg X-ray source

Figure A.4 [p.27] shows the main menu after starting a spectral measurement by using the Mg X-ray source. As shown on the left of Fig. A.4 [p.27], the Mg X-ray source has been shown to be ON. The CCD image through the back window comes to be bright as shown in Figs. A.5 (a) [p.27] and A.5(b) [p.27] being illuminated by the filament.

Figure A.6 shows a survey (wide) spectrum measured with the Mg X-ray source for a silicon wafer whose surface has a 25 nm SiO_2 layer.

A.7 An example measured with the Zr X-ray source

Figure A.7 show the main menu after starting a spectral measurement with the Zr X-ray source. On the left of Fig. A.7, the Zr X-ray source has been indicated to be ON. Fig. A.5(a) [p.27] and Fig. A.5 (b) [p.27] show the CCD image before and after starting the spectral measurement. Fig. A.5 (b) [p.27] is bright illuminated by the filament similarly with the case using the Mg X-ray source.

Figure A.8 shows a survey spectrum measured with the Zr X-ray source for a silicon wafer whose surface has a 25 nm SiO_2 layer. Please note the difference between spectral positions of O KLL and C KLL Auger peaks for the Mg (Fig. A.6) and the Zr (Fig. A.8) X-ray sources. The binding energy (E_B) of photoelectron can be estimate by the equation $E_B = h\nu - E_V$. Here, $h\nu$ is the photon energy of X-rays and E_V is the measured velocity energy of the photoelectron. By applying the above equation also to Auger electron, 'superficial binding energy' is estimated. For example, a KLL Auger electron is emitted from an L electron that receives directly a K-L energy difference when another L electron transits to K level from which a photoelectron has been emitted. Therefore, the velocity energy of Auger electron is always identical not depending on the photon energy of the incident X-rays. Then, the 'superficial binding energy' plotted on a photoelectron spectrum is different depending on the photon energy of the incident X-rays.

When using the Zr X-ray source, please take care concerning the following several points.

Energy range for a survey scan is recommended to be 1800eV$\sim$0eV for the Zr X-ray source. However, such an energy range cannot be set sometimes with a message of 'Range Error'. In such a case, change the X-ray source to be Mg once please as shown in Fig. A.3 (b) [p.27]. Then, set the default survey scan range at first. Next, set the X-ray source to be Zr, please, as shown in Fig. A.3 (c) [p.27] successfully to set parameters etc. the energy range.

Furthermore, when attempting to set a narrow scan less (righter) than 450 eV, it sometimes fails.

In Fig. A.8, a large peak that has not been assigned is found. This is a silicon KLL Auger peak. Whereas Si K electron cannot be excited by Al $K\alpha$ (1486.7 eV) or Mg $K\alpha$ (1253.4 eV) X-rays, it can be excited by using Zr $L\alpha$ (2042.4 eV) X-rays. Then, Si KLL Auger peak can be observed when using the Zr X-ray source. There are some report that peak shift of Si KLL is more sensitive for chemical state of silicon. Also Al KLL Auger peak is sometimes observed when using Zr X-ray source. Such Auger peaks should be assigned referring to e.g. database of NIST (see Appendix C of Part 2 manual).

Since the database in the software 'MultiPak' for analysis of XPS data is not sufficient for Zr $L\alpha$ (2042.4 eV) X-ray source, Analysis of data taken by using Zr X-ray source is not so easy. However, it may be an attractive X-ray source for some users who want to do pioneering works in the field of XPS.

A.8 Several point to take care when using the Mg&Zr X-ray sources

There are several point to take care when analyzing data taken by using the Mg&Zr X-ray source since PHI5000 VersaProbe is not equipped with the monochromator for the Mg&Zr X-ray source.

At first, even when having selected the Zr X-ray source, Also Mg $K\alpha$ X-rays are slightly incident on the sample, photoelectron peaks excited by the Mg $K\alpha$ X-rays are sometimes observed. In general, XPS sensitivity for Mg $K\alpha$ X-rays is almost ten times as large as for Zr $L\alpha$. Since the energy difference between Mg $K\alpha$ (1253.4 eV) and Zr $L\alpha$ (2042.4 eV) X-rays is 789 eV, when a small peak whose energy is 789 eV larger than the main peak, it may be a ghost peak due to Mg $K\alpha$.

Further, since photon energy of Zr $L\beta$ X-rays is 82 eV higher than Zr $L\alpha$ X-rays, a sub peak due to Zr $L\beta$ is found at 82 eV lower (righter) than the main peak.

Also when selecting the Mg $K\alpha$ (1253.4 eV) X-rays, Zr $L\alpha$ (2042.4 eV) X-rays are slightly incident on the sample. However, photoelectron sensitivity for Zr $L\alpha$ X-rays is ten times as small as for Mg $K\alpha$ X-rays. Then, a ghost peak due

to Zr $L\alpha$ X-rays is rarely found.

A.9 Finishing the experiment with Mg&Zr X-ray source

After finishing the experiment using the Mg&Zr X-ray source, '[2] Mg&Zr X-ray source slide knob' in Fig. A.9 [p.28] should be rotated clockwise neccesarily to return to be as shown in Fig. A.9 [p.28].

End of the document

Index

Symbols

ΔE 9
∗.ang 24
∗.lin 7
∗.map 7
∗.pro 7
∗.spe 7
∗.sxi 7
%ABC button 10

INdexSample 1

A

Abort button 6
Acceleration voltage 16
Acquire button 9, 10, 13, 15
Acquisition complete 15
Acquisition Setting Window 15
Acquisition setting window i, 10, 12, 16, 18
Add button 5, 9
Al Kα radiation (1486.6 eV) 12
Alternative button 15
Annotate submenu 7
Apply all button 7
Ar ion 14
Ar ion gun 6
AR-XPS 6, 23, 24
Assignment of peaks 7
Auto-Z 5
Auto-Z before Acq. 5

B

Background 9
Browse button 7

C

CCD Image i
Charge up 6
Clear all button 5
Close button 5, 9, 10, 16
Cycle Stop button 6

D

Delayed Acq. Time (sec) 15
Depth button 16
Done button 7

E

Element Table button 9, 12
Element table button 5
Element Table window 12
Elemental Si peak 18
Energy scan mode 6
Energy step 9, 12
Estimated Acq. Time(min) 5
Ext.Pressure i

F

File select pull-down menu 11
File selection window 7
Folder button 6, 15

G

Gun type menu 15

I

ID button 7
Image window i, 10, 15, 16, 18, 23, 24
Index1 5
Interval time (min) 15
Ion Gun Neutralize 6
Ion gun tab i, 14, 16

L

List Files of Type pull-down menu 7
Load button 13

M

Macro button i, 16
Macro mode i, 11, 13, 16
Macro setting window i, 11, 16
Main Menu i
Main menu i, 6
MAP 18
Mapping 18
Mapping mode 18
Mgr X-ray source 26
Mg&Zr X-ray sources 26
Molar ratio 10

MultiPak i, 6–8, 13

N

Narrow spectra 8, 9
Neutralize 6, 14, 16
Neutralizer On 6
No sputter button 15
Normal (but not Macro) mode i, 5
Num(Presputter) pull-down menu 15

P

Part 2 manual 13, 15, 17
Pass energy 5, 9, 12, 18
Pass energy pull-down menu 9
Phi Summitt i, 10
Position button 11
Position name text box 11
Position setting pull-down menu 12

Q

Quantitative analysis 9

R

Range 12

S

Save button 13
Scan 6
Sequence Map(Acquisition) 11
Sequence Map(Position) 11
Sequence region 11
Set button 13
Si2p spectrum 18
SiO_2 peak 18
Spectral Viewer 6
Spectral window 7
Spherical double electrode 6
Sputter mode 6
Sputter pull-down menu 16
Sputter setting menu 15
Sputter time (min) 15
Sputter time (min) text box 15
Sputtering 14–16
Sputtering mode 15
Sputtering voltage 14
Stage controller 10, 16
Stage setting window 24
SUR button 5, 12
Survey scan 5, 6
SXI 7, 18

T

Tools menu 7
Total Acquisition Time(min) 13
Total cycles 5
Total cycles text box 15

U

USB memory 6

X

XY button 8, 9

Z

Zr X-ray source 26