Semiconductor Surface Analysis by Total Reflection X-ray Photoelectron Spectroscopy

Yoshitoki Iijima, Kousuke Miyoshi* and Shuichi Saito*

Application and Research Center, Electron Optics Division, JEOL Ltd., 3-1-2 Musashino, Akishima-shi, Tokyo 196-8558, Japan

*Crystal Technology Development Laboratory, ULSI Device Development Laboratories, NEC Co., 1120, Shimokuzawa, Sagamihara-shi, Kanagawa 229-1198, Japan

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Total reflection x-ray photoelectron spectroscopy (TRXPS) has been applied to measure contamination elements on Si wafers using an x-ray photoelectron spectrometer. The samples used are Si wafers contaminated with Fe and Cu. The spectral profiles have drastically changed backgrounds with using the incidence angle below the critical angle. The background intensity was reduced to less than 1/5 compared with that of the normal-type XPS, but the photoelectron peak intensity does not decrease remarkably. The detection limit of TRXPS was found to be 9×10^{10} atoms/cm^2 for Fe and Cu contaminated on Si wafers. As a result, the detection limit of TRXPS has been improved to more than 100 times better than that with that of normal type XPS. Accordingly, it can be said that TRXPS is a very effective method for the analysis of the contamination on an Si wafer.

1.Introduction

X-ray photoelectron spectroscopy (XPS) is a meaningful analytical technique for the chemical characterization of surfaces, and it has been used for the analysis of compositions, chemical bonding state, and depth profile. The detection limit of XPS is, however, inferior to that of the other methods of analysis, such as time-of-flight secondary ion mass spectrometry (TOF-SIMS) and total reflection x-ray fluorescence spectroscopy (TXRF) [1]. On the other hand, for the advance in ultralarge scale integrated (ULSI) manufacture technology, the preparation of ultraclean wafer surfaces has become essential [2]. Evaluation of the contamination on the Si wafer has been getting importance in the semiconductor industry for preparation of ultraclean wafer surfaces. In the analysis of impurities on the Si wafer surface, the necessary sensitivity is 1×10^{10} atoms/cm^2, but normal type XPS has a sensitivity of only 1×10^{13} to 1×10^{14} atoms/cm^2. In general, TXRF is a very useful analysis method for the high sensitivity measurement of impurities on the Si wafer [3-6]. However, TXRF cannot detect organic compounds and light element such as nitrogen and carbon. In addition, TXRF cannot measure the chemical bonding state of detected elements because of its low energy resolution.

The improvement method in XPS for higher sensitivity is the following two methods. One is to improve the energy analyzer (electrostatic lens and photoelectron detector), and the other is to improve the P/B (peak to background intensity ratio) of spectrum. The large P/B of the spectrum can improve the

sensitivity remarkably, but the former improves the detection limit only by about several times.

Pulse counting is used as the detection method in XPS and Auger electron spectroscopy(AES), and the detection limit (DL) is given by the following equation[7-9]:

$$DL = k \times (B)^{1/2}/S \quad (1)$$

where S and B are, respectively, the photoelectron peak intensity and the background intensity, and k is a constant. In the latter measurement method, the penetration depth of the x-rays irradiating the sample is made shallow, and so the P/B ratio can be improved by reducing inelastic electron scattering in sample. Thus, the demand for a large P/B ratio is satisfied by the photoelectron spectroscopy using the total reflection of x-rays, i.e., total reflection XPS (TRXPS)[10-15].

In this study, we examined the applicability of TRXPS using a commercial type XPS to the analysis of surface contamination on Si wafers.

2.Experimental

A schematic illustration of the present experimental spectrometer (JPS-9000MC, JEOL Ltd.) is given in Fig.1. The measurement principle of TRXPS is the same as that of TXRF. The x-ray beam size on the sample surface is restricted to 10 mm (vertical) and 3 mm (horizontal) by a slit placed in front of the x-ray anode and the crystal. The sample stage can be tilted by a stepping motor.

The samples were prepared by the following method. Si wafers were first cleaned by the RCA cleaning method. Then, the wafer surfaces were contaminated quantitatively with Fe and Cu using the dip method. The solutions used for the contamination were prepared by adding standard chemical analysis solutions (Fe HNO_3 0.2mol/l, Cu HNO_3 0.2mol/l) to the RCA cleaning solution. The amount of contamination on the Si wafers was regulated to $1 \times 10^{10} \sim 1 \times 10^{13}$ atoms/cm^2. After that, the samples were analyzed by TRXPS and TXRF.

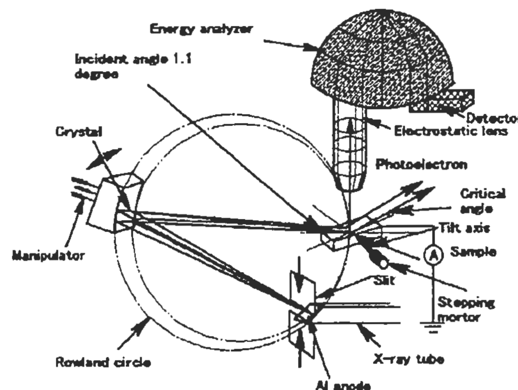

Figure 1. Schematic illustration of the experimental set up. Arrangement of x-ray source, crystal and sample stage in JPS-9000MC. The sample was tilted by a stepping motor.

TRXPS spectra were recorded using AlKα x-rays of energy 1486.6 eV. The x-ray power used for producing x-rays were 300 W (10 kV, 30 mA). The critical angle (θc) is computed by the following equation (2)[5].

$$\theta c = (5.4 \times 10^{10} \cdot (Z \rho / A) \cdot \lambda^2)^{1/2} \quad (2)$$

where Z, ρ, A and λ are, respectively, atomic number of reflective material, density of reflective material, mass number of reflective material and wavelength of incident x-ray. The critical angle of an Si for AlKα is 1.15° . In this experimental, the granzing angle of x-rays is 1.10° , which is smaller than the critical angle for Si surface, and

satisfies for the total reflection condition.

TXRF measurements were performed using a TREX 610 instrument (TECHNOS Ltd.). TXRF spectra were recorded using a W anode. The producing x-rays were 6 kW. The grazing angle was 0.05° and the acquisition time was 500 s for each sample.

3. Results and Discussions

The effective analysis depth of TRXPS, d, is given by [16]

$$1/d = \cos\theta/\lambda + 1/L \quad (3)$$

where λ is the inelastic photoelectron mean free path, L the x-ray penetration length in the solid, and θ the photoelectron detection angle. . L is calculated by the equation (4).

$$L=1/\{\sqrt{2}k([(\theta c^2-\theta^2)^2+4\beta^2]^{1/2}+\theta c^2-\theta^2)^{1/2}\} \quad (4)$$

Where β is the linear absorption coefficient and k is the wave vector.

For Si, λ is 2.4 nm [17]. L is 5.38 nm from a calculation taking account of absorption and reflectivity, and θ is 88.9° . This gives d=5.22nm. A wide scan spectrum for an Fe contaminated Si wafer is shown in Fig. 2. The Fe $2p_{3/2}$ spectrum is detected in spite of low intensity as shown in the insertion of Fig. 2.

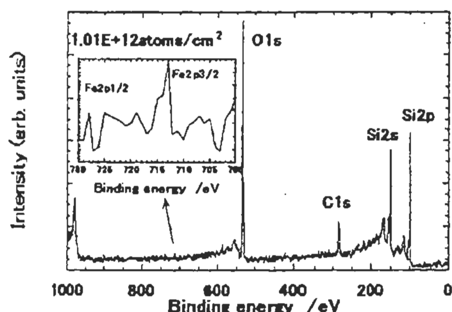

Figure 2. TRXPS wide scan spectrum. The amount of Fe contamination is 1.01E+12 atoms cm^{-2}.

Figure 3 shows superimposed Fe $2p_{3/2}$ spectra for samples with four different amounts of Fe contamination. In case the amount of contamination is 1.44×10^{10} atoms/cm^2, the Fe $2p_{3/2}$ spectrum does not give information on contamination, since the spectrum signal is almost equal to the random noise level with standard deviation (1 σ). However, in case the amount of contamination is 3.42×10^{12} or 1.26×10^{11} atoms/cm^2, the Fe $2p_{3/2}$ peak intensity gives an intensity high enough to analyze the chemical bonding state. The Fe $2p_{3/2}$ spectra for the samples with different amounts of contamination were almost identical in their shape, and did not show any change in their peak positions.

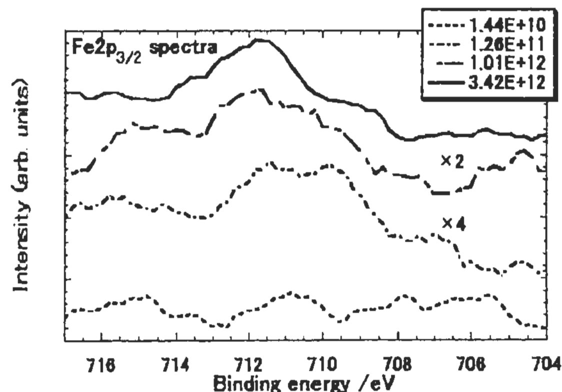

Figure 3. Fe$2p_{3/2}$ narrow scan spectra of TRXPS for different Fe concentration.

Figure 4 represents superimposed Cu $2p_{3/2}$ spectra for contaminated samples. Each Cu $2p_{3/2}$ peak intensity is high enough to analyze the chemical bonding state, though the photoelectron intensity for the sample with the minimum contamination is as small as the random noise level.

Figure 5 represents the calibration curve obtained from Figs. 4 and 5. As can be seen in

the figure, the calibration curve shows a good linearity against the Fe and Cu concentration in the logarithmic scale. This gives the detection limit of TRXPS to about 9×10^{10} atoms/cm^2 for Fe and Cu. Therefore, the experimental detection limit of TRXPS is improved to 100 times that of the normal type XPS. TRXPS is a very effective method for analyzing the contamination on Si wafers.

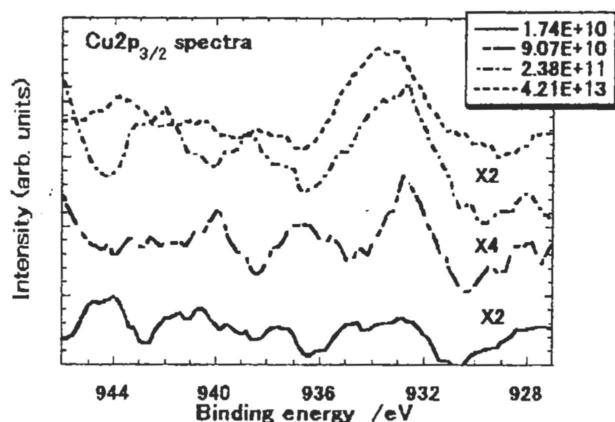

Figure 4. $Cu2p_{3/2}$ narrow scan spectra of TRXPS for different Cu concentrations.

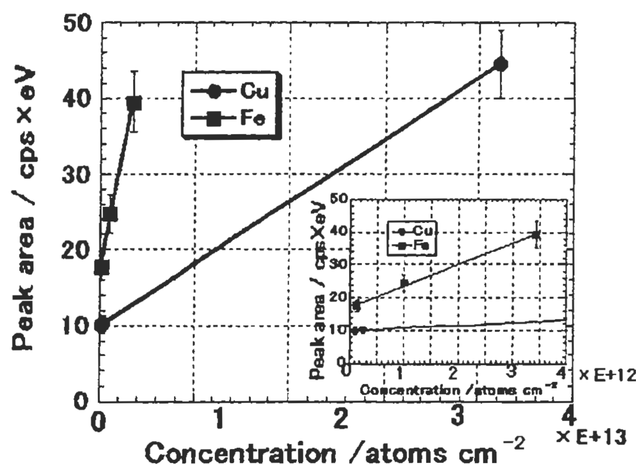

Figure 5. Calibration curves for Fe and Cu.

4. References

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