Combination of High-Resolution RBS and Angle-Resolved XPS: Accurate Depth Profiling of Chemical States

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A new method for the combination analysis of high-resolution Rutherford backscattering spectroscopy (HRBS) and angle-resolved X-ray photoelectron spectroscopy (AR-XPS) is proposed for accurate depth profiling of chemical states. In this method, attenuation lengths (ALs) for the photoelectrons are first determined so that the AR-XPS result is consistent with the HRBS result. Depth profiling of the chemical states are then performed in the AR-XPS analysis using the compositional depth profiles obtained by HRBS as constrained conditions. This method is successfully applied to a hafnium-based gate stack structure demonstrating its feasibility.

1. Introduction

The accurate analysis of ultrathin films is of great importance in many research fields and industries, especially in the microelectronics industry. High-resolution Rutherford backscattering spectroscopy (HRBS) is one of the most reliable techniques for this purpose. It allows quantitative compositional analysis with a depth resolution of sub-nm [1]. The simple Rutherford cross section guarantees high accuracy of HRBS in composition analysis. The depth information can be derived from the HRBS spectra using the stopping cross sections for the probe ion. The precision of the tabulated stopping cross sections [2] is believed to be better than a few % for sub-MeV He ions, which are commonly used in HRBS. In addition, HRBS is a nondestructive technique and does not require any specific sample preparation. There are, of course, some drawbacks and its major drawback is the insensitivity to chemical states. In this respect, angle-resolved X-ray photoelectron spectroscopy (AR-XPS) can be a good complement to HRBS [3]. The recent development of the data-analysis technique using maximum entropy method makes AR-XPS more reliable, but it is still difficult to derive accurate depth profiles only from the AR-XPS data without prior information of the sample. In this work, we propose a new method for the combination analysis of HRBS and AR-XPS. Both HRBS and AR-XPS measurements are performed with the same sample. The attenuation lengths (ALs) for the photoelectrons are first determined so that the compositional depth profiles obtained by HRBS reproduce the AR-XPS result. Depth profiling of the chemical states is then performed by employing a standard data-analysis procedure of AR-XPS using the HRBS profiles as constrained conditions. This method is applied to the analysis of a hafnium-based gate stack structure to examine its feasibility.

2. Experimental

A gate stack structure, HfO2/SiON/Si(001), was prepared as the sample. A 2.5-nm-thick HfO2 layer was deposited using atomic layer deposition (ALD) at 300°C on a thin SiON layer (nominal thickness ~1.6 nm), which was grown by a direct plasma nitridation on a cleaned Si(001) surface. This sample was measured by HRBS using a 400 keV He+ ion beam [1]. The beam size and the typical beam current were ~2 × 2 mm² and ~50 nA, respectively. Energy spectra of He+ ions scattered at 50° were measured by a 90° sector magnetic spectrometer, which was equipped with a one-dimensional position-sensitive detector (100 mm in length) consisting of microchannel plates and a resistive anode. The energy window of the spectrometer was 25% of the central energy and the energy resolution was 0.1%. A HRBS spectrum was measured at an incident angle θi = 50.2° with respect to the surface normal. During the measurement, the sample was rotated around the axis of surface normal to avoid the channeling/blocking effects. In addition to this so-called random spectrum, the [111] axial channeling spectrum was also measured to reduce the Si substrate signal. The reduction of Si signal allows precise measurements of light elements (oxygen and nitrogen).

AR-XPS measurements of HfO2/SiON/Si(001)
were performed on a Thermo instrument equipped with an Al Kα (1486.6 eV) source. This instrument allows us to collect AR-XPS data in parallel without tilting the sample. Photoelectron spectra of Hf 4f, Si 2p, O 1s and N 1s were measured at emission angles, θ_e, from 20° to 80° with respect to the surface normal. Shirley background subtraction and peak fitting were used when extracting photoelectron yields.

3. Results and discussion

Examples of the observed HRBS spectra for HfO2/SiON/Si(001) are shown in Fig. 1. There are several peaks in the channeling spectrum. The large peak at ~390 keV corresponds to Hf in the HfO2 layer. A peak seen at ~350 keV is the Si signal from both the interface SiON layer and the substrate Si in the interface region. Owing to the channeling effect, the substrate Si signal is reduced as compared to the random spectrum. As the result, the oxygen (~330 keV) and nitrogen (~315 keV) signals can be clearly seen. Compositional depth profiles were obtained after a simulation of HRBS spectra. Figure 2 shows the obtained profiles, which are consistent with the designed sample structure.

The same sample was measured by AR-XPS with Al Kα X-ray. The observed photoelectron yields of Hf 4f, O 1s and N 1s normalized to the Si 2p yield (including both oxidized and bulk Si) are shown as a function of θ_e in Fig. 3. As the first step of the combination analysis of HRBS and AR-XPS, the photoelectron yields were calculated with the compositional depth profiles (Fig. 2) obtained by HRBS using the inelastic mean free paths (IMFPs) as the ALs of the photoelectrons. In the calculation, the TPP-2M formula [4,5] was employed to estimate the composition-dependent IMFPs. The details of the calculation are described elsewhere [6].

The calculated results (dashed lines) are compared with the observed ratios of signal intensities in the AR-XPS measurements in Fig. 3. There is a large discrepancy (30% or larger) between the calculated and observed results. This discrepancy may be ascribed to the effect of elastic scattering of photoelectrons in the sample. Because the actual path length is longer than the straight line due to elastic scattering, effective ALs should be smaller than the IMFPs (Fig. 4(a)). If we reduce the ALs by 15%, better agreement between the calculated and observed results can be obtained at θ_e < 55°, as shown by the solid lines. The remaining discrepancy at larger θ_e is also ascribed to the effect of elastic scattering because the photoelectrons may escape from the surface by a shortcut when θ_e is...
We have to modify the simple exponential decay function of photoelectron yields if further agreement is required [6].

We now proceed to the next step, namely, the depth profiling of the chemical states. Si 2p photoelectron spectra were divided into two components, i.e. the oxidized Si and bulk Si. The observed photoelectron yields of Hf 4f, Si 2p (bulk), O 1s and N 1s normalized to the oxidized Si 2p yield were shown in Fig. 5. The Si profile derived by HRBS was also divided into two profiles, i.e. the profiles of the oxidized Si and bulk Si, so that the calculated photoelectron yields reproduce the observed results. In the calculation, the above-obtained ALs (85% of the IMFPs) were used. Figure 5 shows the best-fit results (solid lines). The obtained depth profiles of the oxidized Si and bulk Si are shown by the short and long dashed lines, respectively in Fig. 6. The oxidized Si is localized at the interface between the HfO₂ film and the substrate Si, indicating that the present analysis provides reasonable profiles of the chemical states.

4. Conclusion

A new method of the combination analysis of AR-XPS and HRBS was proposed. The method was applied to the analysis of a hafnium-based gate stack structures. The ALs for the photoelectrons were first determined by the comparison between the observed AR-XPS results and the XPS yields calculated with the HRBS profiles. The obtained ALs were about 15% smaller than the IMFPs estimated by the TPP-2M formula. Depth profiling of the chemical states of Si were then performed using the compositional depth profiles derived by HRBS as constrained conditions. Reasonable depth profiles were obtained by this procedure, demonstrating the feasibility of the present method. It was also shown that the applicability of the simple exponential decay function of the photoelectron yields is limited to $\theta_e < 55^\circ$ for the standard laboratory XPS with Al Kα X-ray in the present case.

5. References