Analysis of Ultra-Thin HfO$_2$/SiON/Si(001): Comparison of Three Different Techniques

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Composition depth profiling of HfO$_2$ (2.5 nm)/SiON (1.6 nm)/Si(001) was performed by three diffetent analytical techniques: high-resolution Rutherford backscattering spectroscopy (HRBS), angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and high-resolution elastic recoil detection (HR-ERD). By comparing these results we found the following: (1) HRBS generally provides accurate depth profiles. However, care must be taken in backgroud subtraction for depth profiling of light elements. (2) In the standard AR-XPS analysis, a simple exponential formula is often used to calculate the photoelectron escape probability. This simple formula, however, cannot be used for the precise depth profiling. (2) Although HR-ERD is the most reliable technique for the depth profiling of light elements, it may suffer from multiple scattering, which deteriorates the depth resolution, and also may cause a large background.

Introduction

The analysis of ultrathin films becomes important across a variety of research fields and industries, especially in the micro-electronics industry. The thicknesses of films used in the microelectronics devices are now a few nm, or even thinner. The quantitative analysis of such thin films is a big challenge. High-resolution Rutherford backscattering spectroscopy (HRBS) is one of the most promising techniques for this purpose. It allows quantitative analysis with a depth resolution of sub-nm level.[1] The quantification of HRBS relies on the simple Rutherford cross section. This guarantees high accuracy in composition analysis. Depth information can be derived from the HRBS spectra using the stopping power of the probe ion. The precision of the tabulated stopping power[2] is generally better than a few % for sub-MeV He ions, which are commonly used in HRBS. In addition, HRBS is a nondestructive technique and no special pretreatment of the sample is required.

There are, of course, some drawbacks of HRBS, and a major one is low sensitivity to light elements because the Rutherford cross section is proportional to the square of the atomic number. In addition, the signals of light elements often overlap with strong signals of heavy matrices. In such a case, the extraction of signals of light elements from the observed HRBS spectrum is rather difficult. In this respect, elastic recoil detection (ERD) is a powerful technique for depth profiling of light elements.[3] Although the depth resolution of the standard ERD (typically ~10 nm) is not good enough for the analysis of ultrathin films, the depth resolution can be improved up to the sub-nm level

using a sophisticated magnetic spectrograph.[4,5] This technique, called high-resolution ERD (HR-ERD), allows for the quantitative analysis of light elements with a sub-nm depth resolution. HR-ERD, however, requires a rather big facility, for example, a 14-MV tandem accelerator and a huge magnetic spectrometer. Another potential candidate for the analysis of ultrathin films is angle-resolved X-ray photoelectron spectroscopy (AR-XPS). However, it is generally difficult to derive accurate depth profiles from only AR-XPS data. If appropriate information on the sample is available in advance, accurate depth profiling can be performed by AR-XPS.[6]

In the present work, a typical high-k gate stack structure, HfO$_2$ (2.5 nm)/SiON (1.6 nm)/Si(001), was analyzed by HRBS, HR-ERD and AR-XPS. By comparing with these results, the advantages and drawbacks of these techniques were considered with particular emphasis placed on the feasibility of nitrogen depth profiling.

Experimental

A typical gate stack structure, HfO$_2$/SiON/Si(001), was prepared by the following procedures. A thin SiON layer (nominal thickness ~1.6 nm) was grown by direct plasma nitridation on a cleaned 200 mm Si(001) wafer. A 2.5-nm-thick HfO$_2$ layer was deposited on SiON/Si(001) at 300°C using atomic layer deposition (ALD). The thickness uniformity of the prepared layer was examined by ellipsometry. The measured standard deviation of the thickness was ~ 2%. The prepared Si wafer was divided into small pieces, which were measured by HRBS, HR-ERD and AR-XPS.

HRBS measurements were performed at Kyoto University. The sample was irradiated by a beam of 400 keV He$^+$. The beam

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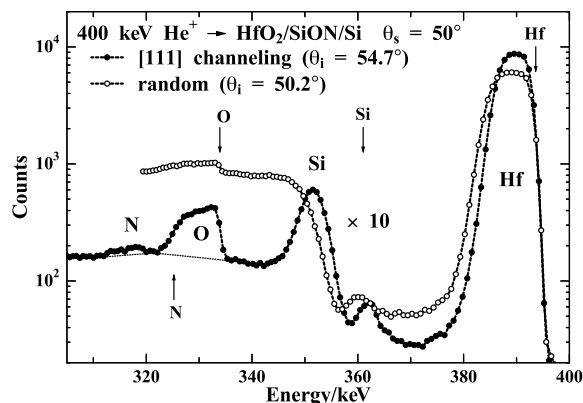E-mail: kimura@kues.kyoto-u.ac.jp

Fig. 1 Random (open circles) and [111] channeling (solid circles) spectra of HfO₂/SiON/Si(001). The arrows show the energies of He ions scattered from constituent atoms (Hf, Si, O, and N) located at the surface. The dashed lines show the estimated Si background for the channeling spectrum.

Fig. 2 Composition depth profiles of HfO₂/SiON/Si(001) derived by the HRBS analysis (thick lines). The result for the standard AR-XPS analysis using IMFP is also shown by thin lines.

size and the typical beam current were ~2 × 2 mm² and ~50 nA, respectively. The 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 micro-channel plates and a resistive anode. The energy window of the spectrometer was 25% of the central energy and the energy resolution was 0.1%. During the measurements, the sample was rotated around the axis of the surface normal to avoid any 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. A reduction of the Si signal allows precise measurements of light elements (oxygen and nitrogen in the present case).

HR-ERD measurements were performed at the 14-MV tandem accelerator at Munich Technical University. A beam of 40 MeV Au ions was incident on the sample at an incident angle of 10° with respect to the surface plane. Such a heavy incident ion can recoil target atoms in the forward direction. These recoiled ions were momentum analyzed by a Q3D magnetic spectrograph and detected by a gas ionization chamber. The energy resolution of the spectrograph was 0.05% at an acceptance angle of 5 mrad. This excellent energy resolution guarantees a depth resolution of better than 1 nm.

AR-XPS measurements were performed using a Theta Probe (Thermo Fisher Scientific Inc.) equipped with an Al K$_\alpha$ source at IMEC. This instrument allowed 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 the photoelectron intensity.

Results and Discussion

HRBS

The observed random spectrum for HfO₂/SiON/Si(001) is shown by open circles in Fig. 1 (the incident angle was 50.2° with respect to the surface normal and the scattering angle was 50°). The arrows show the energies of He ions scattered from the constituent atoms (Hf, Si, O, and N) located at the surface.
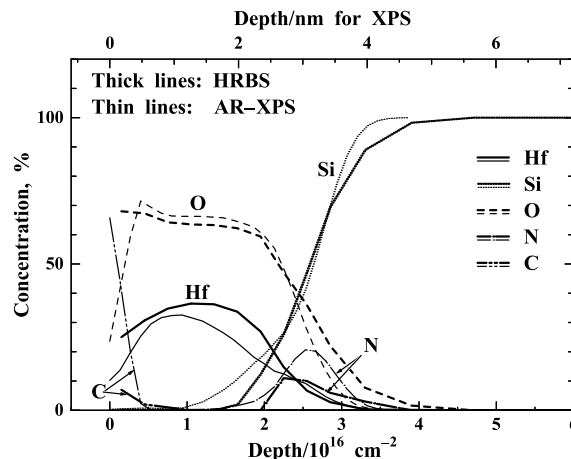
A large peak seen at ~390 keV corresponds to Hf in the HfO₂ layer. There is a small peak at ~360 keV, which coincides with the energy of the surface Si. The origin of this small peak is discussed later. A plateau-like spectrum is seen at energies lower than ~350 keV, which corresponds to the substrate Si. The signal of oxygen is seen on top of the Si signal at ~330 keV. Due to this overlapping, extracting the oxygen signal is rather difficult.

In order to reduce this difficulty, the incident He⁺ beam was aligned to the [111] channeling direction (incident angle of 54.7°). The observed [111] channeling spectrum is shown by the filled circles in Fig. 1. Compared to the random spectrum, the Si signal is significantly reduced and the oxygen peak is clearly seen at ~330 keV. There is an additional small broad peak at ~315 keV, which corresponds to nitrogen in the SiON layer. From this channeling spectrum, the oxygen and nitrogen signals were extracted by subtracting the Si background (the estimated Si background is shown by a dotted line in Fig. 1). In passing, we note that the small peak appearing at ~361 keV cannot be attributed to the surface Si, because the peak energy changes when the incident angle is changed from 50.2° to 54.7°. This small peak is assigned to chlorine contamination (~ 2 × 10¹⁴ atoms/cm²) at the HfO₂/SiON interface, which originates from HfCl₄ used in ALD as the source gas.

The composition depth profiles were derived from these spectra through a spectrum simulation. The derived composition depth profiles are shown by thick lines in Fig. 2. It should be noted that HRBS provides the depth scale in units of areal density (atoms/cm²), as shown in Fig. 2. This depth scale was converted into nm using the atomic density of HfO₂ (8.3 × 10²² atoms/cm³), and is shown in the upper abscissa as a guide.

AR-XPS

Another piece of the same sample was measured by AR-XPS with Al K$_\alpha$ X-rays. The observed photoelectron intensities were normalized by the cross section, and the effect of the asymmetric parameter was also corrected. The ratios of the corrected photoelectron intensities, Si2p/Hf4f, O1s/Hf4f and N1s/Hf4f, are shown as a function of the emission angle, θ_e, in Fig. 3.

The angular dependence of the photoelectron intensity can be calculated using the composition depth profiles derived by an HRBS analysis. In this calculation, the escape probabilities of
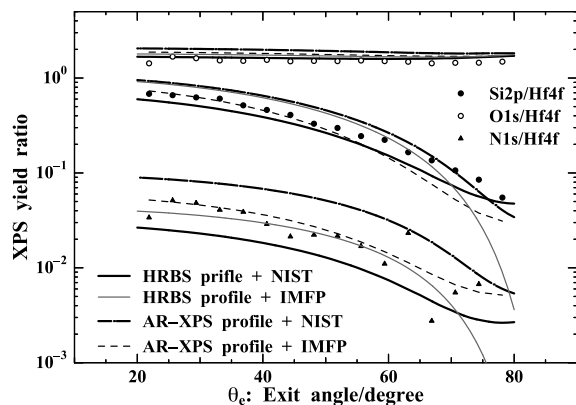
Fig. 3 Comparison between experimental (symbols) and calculated (lines) θ_e-dependences of XPS intensities for HfO$_2$/SiON/Si(001). The intensity ratios Si2p/Hf4f, O1s/Hf4f and N1s/Hf4f are shown. The intensity ratios calculated with the HRBS profiles and IMFP (thin solid lines), HRBS profiles and NIST database (thick solid lines), AR-XPS profiles and IMFP (dashed lines) and AR-XPS and NIST database (dot-dashed lines) are shown.

Fig. 4 Composition depth profiles of HfO$_2$/SiON/Si(001) derived by the HR-ERD analysis (thin lines). The result of HRBS is also shown for a comparison (thick lines).

photoelectrons emitted at a depth x, which is usually called the depth distribution function (DDF), was calculated with a simple exponential formula,

$$P(x) = \exp\left(-\frac{x}{\lambda \cos\theta_e}\right).$$ (1)

In the calculation, the inelastic mean free path (IMFP) calculated by the TPP-2M formula[7,8] was used as the attenuation length, λ. The thin solid lines show the calculated result. The agreement between the observed and calculated results is roughly good, but there is a rather large discrepancy in the Si2p/Hf4f ratio.

The composition depth profiles can be derived from the observed AR-XPS result by a standard AR-XPS analysis, *i.e.* by the least-squares fitting. The best-fit result is shown by the dashed lines in Fig. 3. The derived depth profiles are shown by the thin lines in Fig. 2. The obtained AR-XPS profiles are roughly in good agreement with the HRBS profiles. Looking at the profiles more closely, however, the HRBS profiles indicate steeper interfaces at both HfO$_2$/SiON and SiON/SiO$_2$. In addition, AR-XPS profiles show a larger nitrogen peak than HRBS. By integrating the nitrogen profile, the amount of nitrogen was estimated to be 2×10^{15} atoms/cm^2, which is twice larger than the HRBS result (1×10^{15} atoms/cm^2).

From Fig. 3, it is clear that the best-fit result of the AR-XPS analysis (dashed lines) agrees with the observed result much better than that calculated from the HRBS profiles (thin solid lines). This, however, does not directly mean that the AR-XPS provides more accurate depth profiles than HRBS, because Eq. (1) does not take into account the elastic scattering of photoelectrons, which may cause a large error.[9] Actually, the best-fit result for Si2p/Hf4f deviates from the observed one at θ_e larger than ~50°. This deviation cannot be removed using any realistic depth profiles, showing the limitations of the standard AR-XPS analysis using Eq. (1). This is because the elastic scattering seriously affects the intensity of the photoelectrons emitted from deeper regions at larger θ_e.[9] The effective attenuation length under such conditions is much larger than the IMFP due to the effects of elastic scattering. In the present sample, Si exists in the deepest position among other elements.
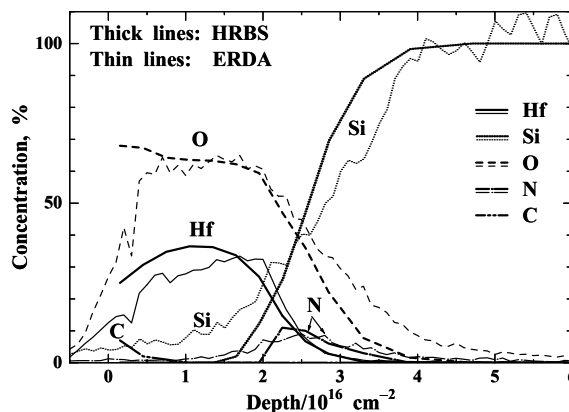
Accordingly, the Si2p signal observed at large θ_e is larger than the result calculated with Eq. (1). This is the reason why the data observed at large θ_e are often neglected in the standard AR-XPS analysis, although these data are important for a precise XPS analysis.[10]

There is a database published by the National Institute of Standards and Technology (NIST) that provides DDFs.[11] The database is based on a solution of the kinetic Boltzmann equation within the so-called transport approximation, which includes the effects of elastic scattering.[12] We have recently demonstrated that the DDFs calculated by the NIST database are reliable for a wide range of θ_e.[13] We found that the angular dependence of the photoelectron intensity calculated with the DDFs given by the NIST database reproduces the observed AR-XPS result fairly well.[12] This means that the AR-XPS data observed at large θ_e can be precisely analyzed using the NIST database.

Using the NIST database and the composition depth profiles derived by the standard AR-XPS analysis (thin lines in Fig. 2), the photoelectron intensities were calculated. The result is shown by dot-dashed lines in Fig. 3. Compared to the previous result (dashed lines in Fig. 3) the agreement with the observed result becomes worse, especially for N1s/Hf4f. The calculated N1s/Hf4f ratio is about twice larger than the observed one, indicating that the standard AR-XPS analysis overestimates the nitrogen concentration in the present case.

In order to see the accuracy of the HRBS result, the photoelectron intensities were calculated using the HRBS profiles and the NIST database. The calculated result, shown by thick solid lines in Fig. 3, is in good agreement with the observed one, although the intensity ratio of N1s/Hf4f is slightly smaller than the observed one. This suggests that HRBS slightly underestimates the nitrogen concentration. A possible origin of this underestimation is an error in the background subtraction procedure from the channeling spectrum.

HR-ERD

Another piece of the same sample was measured by HR-ERD. Figure 4 shows the composition depth profiles measured by HR-ERD (thin lines) together with the HRBS result (thick lines). The agreement between the HRBS and HR-ERD results looks good. By integrating the nitrogen profile measured by HR-ERD, the amount of nitrogen was estimated to be 1.6×10^{15} atoms/cm^2, which is about 60% larger than the HRBS result

$(1 \times 10^{15}$ atoms/cm^2). This confirms that HRBS underestimates the nitrogen concentration due to the error in the background subtraction. The error can be reduced by choosing an appropriate geometry (scattering angle and/or incident angle), so that the separation between the nitrogen and the oxygen peaks is large enough for a more accurate estimation of the Si background.

Looking at the profiles more closely, there are small differences. The main difference between the HRBS and HR-ERD profiles is the interface slope. The HR-ERD profiles indicate broader interfaces. The Si profile unrealistically extends into the HfO$_2$ film, in particular. Because both the primary Au ion and the recoiled ions are rather heavy, they suffer from strong multiple scattering in the HR-ERD measurement. This multiple scattering deteriorates the depth resolution. It should be noted that using primary ions with higher energies, the effect of multiple scattering can be reduced, and a better depth resolution can be achieved in HR-ERD.

Conclusion

Composition depth profiles in a typical gate stack structure, HfO$_2$/SiON/Si(001), were measured by three different techniques: HRBS, AR-XPS and HR-ERD. It was shown that the simple exponential formula for the escape probability of photoelectrons cannot be used for a precise AR-XPS analysis. The effects of elastic scattering should be taken into account. Accurate depth profiling of oxygen, silicon and hafnium can be performed by HRBS. However, care must be taken in background subtraction for nitrogen. Although HR-ERD is the most reliable technique for depth profiling of nitrogen, a rather big facility is required, and it often suffers from the effects of multiple scattering. These results indicate that there is no perfect technique. Combining these techniques must be the best solution for precise depth profiling including light elements.

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