Study of Capacitor Material for Advanced Memory Devices using Surface Analysis

Makoto Nakamura*and Masaaki Nakabayashi[1]
Fujitsu Analysis Laboratory Limited.; [1] *Technology Development Div. Fujitsu Limited.*
4-1-1 Kamikodanaka Nakanara-ku, Kawasaki, 211-8588, JAPAN

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High dielectric constant materials have received much attention for use as gate dielectric films and capacitor dielectric films of advanced devices. We plan to use Ta_2O_5 for capacitor dielectric films and Ru or RuO_2 for both top and bottom electrodes because Ta_2O_5/Ru (RuO_2) show excellent performance with the dielectric constant rising to about 70,*i.e.* an SiO_2-equivalent thickness of 0.7nm at a Ta_2O_5 thickness of 10nm. [1] We have adopted XPS (X-ray photoelectron spectroscopy) for one part of the capacitor evaluation. XPS is used not only for analysis of components and chemical states but also to depict the energy-band diagram from fine structure of the spectrum. This paper discusses part of our evaluation techniques for using XPS to study capacitor materials of advanced memory devices.

Introduction

New materials are being used in advanced ultra-large-scale integration (ULSI) devices because the properties of conventional materials have reached their physical limits. For example, copper has been adopted for wiring instead of aluminum alloy, organic compounds have been used for insulators, and high-dielectric-constant materials are planned for use as gate and capacitor dielectric films. We have scheduled the adoption of Ta_2O_5/Ru (RuO_2) system, which is a promising candidate for the production of 0.10-μm dynamic random access memory (DRAM) and beyond. [1] Compared to silicon oxide (SiO_2), the dielectric constant of Ta_xO_y is generally five times greater. However, materials with a high dielectric constant usually tend to have a small barrier height for electrons. [2] The use of Ta_xO_y/Ru (RuO_z) systems for capacitor dielectric films has been investigated using XPS. We have derived not only the components and chemical state from XPS spectrum, but also the energy band structure. A few papers have already reported on a band diagram using photoelectron spectra for gate dielectric films [3][4], but no paper has reported on application to capacitor dielectric films.

Experiments

The procedure of sample preparation is summarized in the flowchart in Fig. 1. We used three references to consider the chemical state and depict the energy band diagram of Ta_xO_y/Ru (RuO_z) systems. The Ti and TiN layers are deposited so as

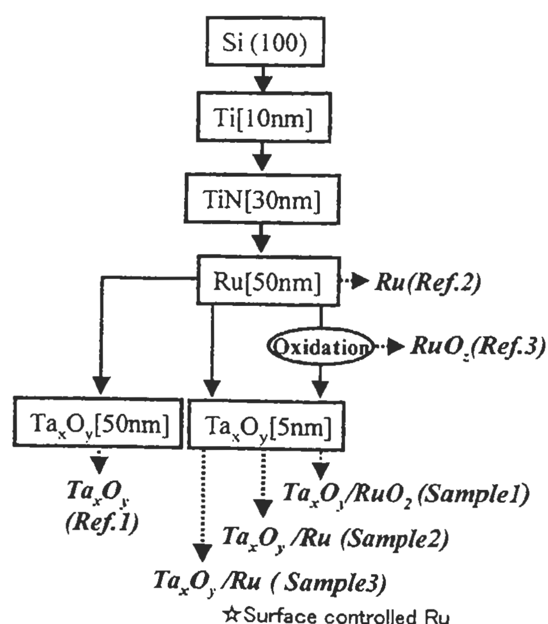

Fig. 1 Sample preparation process in our examination. We prepared three samples and three reference samples(Ta_xO_y, Ru. RuO_z)

to act as an adhesion layer of Ru (RuO_2) and SiO_2. The Ru, RuO_z and Ta_xO_y layers are deposited by chemical vapor deposition (CVD) using $Ru(C_2H_5C_5H_4)_2$ and $Ta(OC_2H_5)_5$ respectively. RuO_x is made by the oxidation of Ru. The high-resolution XPS measurements are performed with an ESCA-5400 MC (Physical Electronics Inc.), using monochromatic *Al-Kα (1486.6 eV)* radiation. Details of the conditions of the XPS analysis are given in Table 1. To prevent sample charge up, all the samples except the analysis area were wrapped with indium foils. The energy axes of all XPS spectra were corrected by Cu2p3/2*(932.67 eV)* and Cu3p*(75.14 eV)* peak position. In addition, all XPS data of the Ta_xO_y sample were compensated for using Ta4f7/2 peak *(26.70 eV)*.

The energy band diagrams are depicted using Itokawa's methods [3]. Thus, the energy band gap was determined from the O1s energy loss spectrum, and the valence band offset was determined from the valence band spectrum. The principle diagram used to estimate band gap is shown in Fig. 2. Several photoelectrons suffer inelastic loss due to plasmon and the band-to-band excitation, as shown in Fig. 2. The onset of the electron excitation from the valence to conduction bands can also be observed at an energy separated by the band-gap energy from the core level peaks. The band-gap energy corresponds to the threshold energy of the onset of energy loss. The principle diagram to determine band offset of the Ta_xO_y and Ru (RuO_z) interface is shown in Fig. 3. The valence band spectrum is composed of the density of states (DOS) for the Ta_2O_5 and Ru (RuO_z) spectra. To determine band offset, the valence band spectra of the standard samples (Ru and RuO_z) are subtracted from the sample spectra and compared to the spectrum of the standard Ta_xO_y sample.

Table 1 Analysis condition of XPS measurement.

XPS equipment	Physical Electronics Inc. 5400MC
Exitation	Al-Kα[monochro]-600W[15kV, 40mA]
Take off Angle	65 °
Analysis Area	1.1mmφ
Acceptance Angle	±5°
Pass Energy	17.9 eV[FWHM : 0.62 eV (Ag3d5/2)]
Acquisition Energy Step	0.05 eV/step
Base Pressur	<9.0E-9 Torr

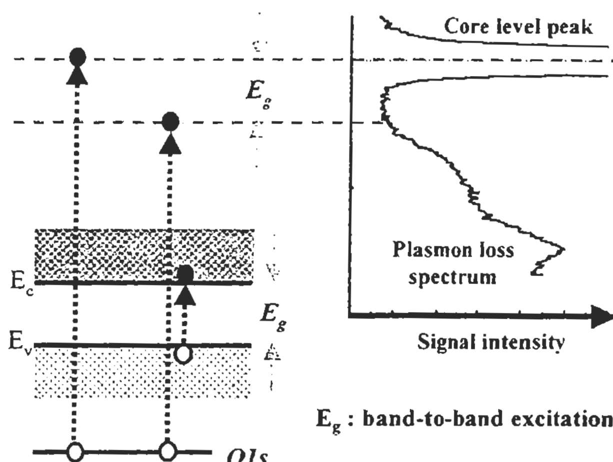

Fig. 2 Principle for determining energy band gap for dielectric materials using O1s photoelectron spectra.

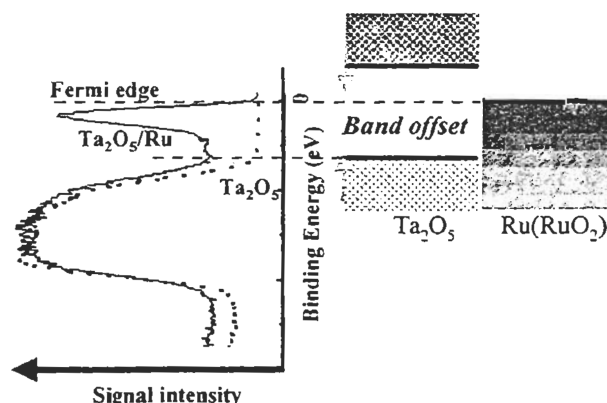

Fig. 3 Principle for determining band offset from valence band spectrum for Ta_2O_5/Ru systems.

Results and discussion

The XPS spectra of Ta_xO_y/Ru (RuO_z) samples and references are shown in Fig. 4. There are clear differences among the valence band, Ru3d and O1s spectra. The estimated results of the chemical state are also shown in figure 4. The differences in the Ru3d5/2 spectra primarily result from the presence of Ru and RuO_z. (The C1s spectrum of hydrocarbon adsorbed in the air overlaps the Ru3d3/2 spectrum.) From the Ru3d5/2 spectra, we found that the RuO_x phase existing in the Ta_xO_y/Ru system could not be observed in surface controlled Ru sample. (We confirmed that the RuO_x phase only exists in the Ta_xO_y/Ru interface and the phase appears crystalline

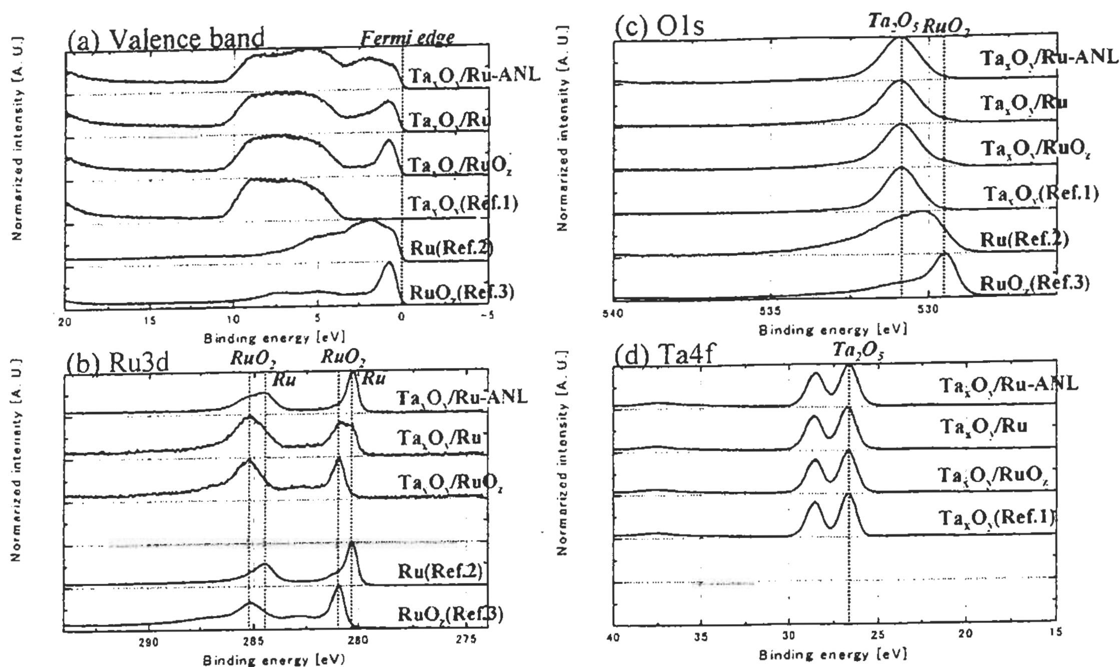

Fig. 4 XPS high resolution spectra of all samples. (a)Valence band spectra, (b) Ru3d spectra, (c) O1s spectra and (d) Ta4f spectra

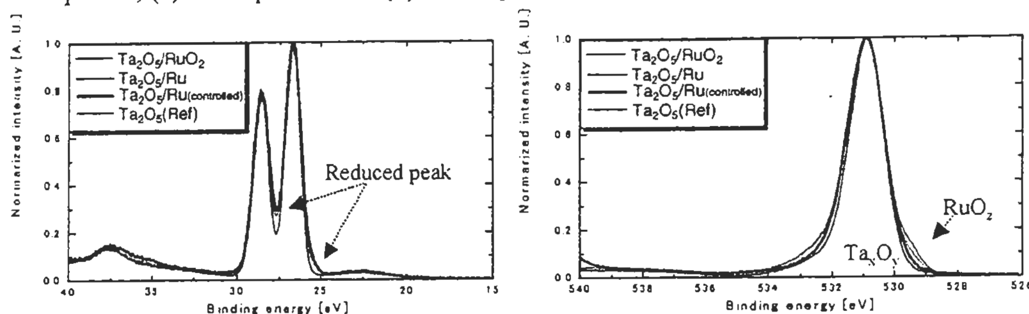

Fig. 5 Stacked Ta4f and O1s spectra of three samples and thick Ta_2O_5 reference.

using transmission electron microscopy (TEM).)

Figure 5 shows the stacked Ta4f and O1s spectra to distinguish the small difference because we are not able to see such small difference in Fig. 4. The small differences observed in Ta4f spectrum are caused by reduction of Ta_2O_5 or the stress of the lattice distortion in the interface as observed in O1s spectrum because of the presence of RuO_z.

To determine the band gap of the Ta_xO_y/Ru (RuO_z) systems, smoothed (seven-point Savitzky-Golay smoothing) and magnified O1s spectra are shown in figure 6. The estimated results of the energy gaps indicate that they differ from each other.

To determine band offset, valence band spectra were fitted using the reference spectra of Ta_xO_y, Ru and RuO_z. For the curve-fitting process of the valence band spectra, we are forced to apply a slight negative shift to the Ta_xO_y reference spectra for

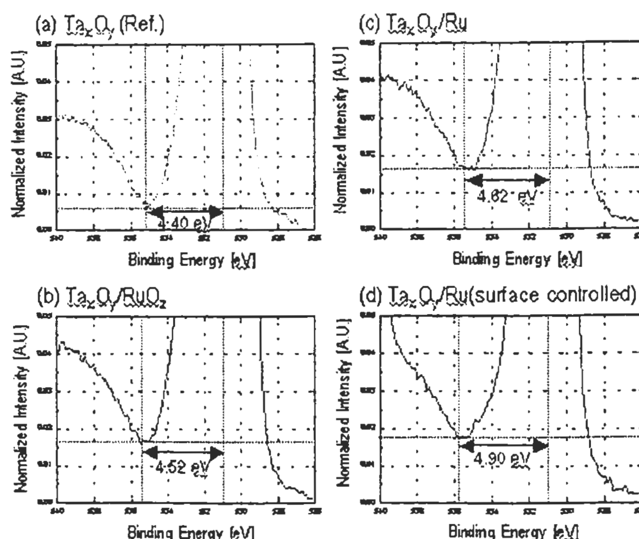

Fig. 6 Magnified O1s spectra to estimate band gap. All spectra were processed for smoothing.

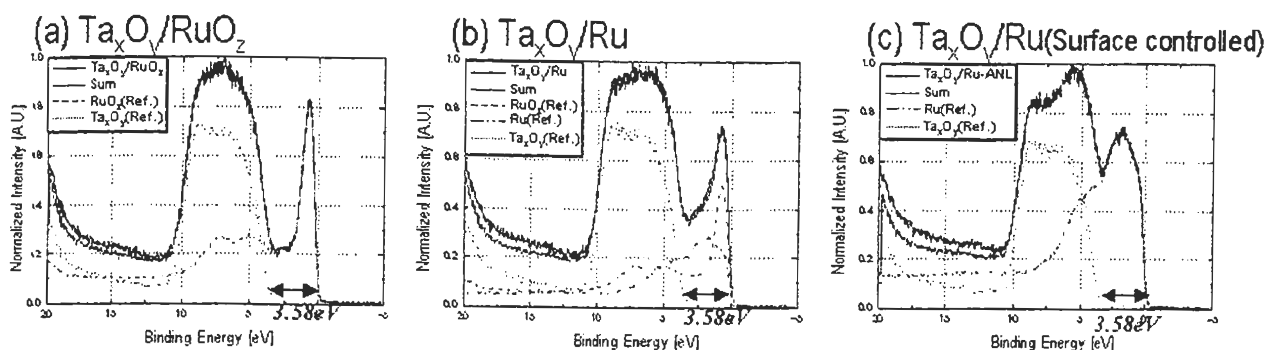

Fig. 7 Deconvoluted valence band spectra using reference sample's spectra. Ta_2O_5 reference spectrum was shifted 0.4eV to 0.35eV.

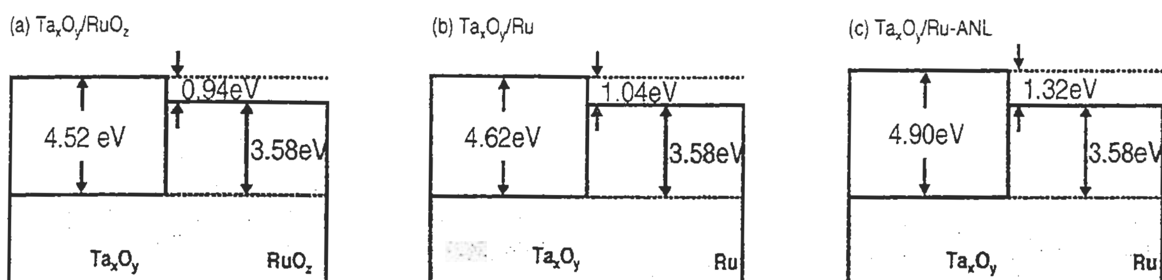

Fig. 8 Energy band diagram for the Ta_xO_y/Ru (RuO_z) systems using photoelectron data.

good agreement. To sum up, valence band top energy of the thin Ta_xO_y films deposited on Ru (RuO_z) is slightly higher than that of the thicker one. We think the reason for the energy difference originates in the reduction of Ta or interface stress. The curve-fitting results of valence band spectra are shown in Fig. 7. From the energy difference between the valence band tops of Ta_xO_y and Ru (RuO_z), the band alignment was determined to be 3.58 eV.

The band diagrams based on the previous procedure are illustrated in Fig. 8. The small differences originating from the energy band gap depend on difference in the electrodes.

Based on the Ta_xO_y band gap of 4.52 eV, 4.62 eV and 4.90 eV, the hight of the electron barrier for the Ta_xO_y/Ru (RuO_z) system is estimated to be 0.94 eV, 1.04 eV and 1.32 eV respectively. In this study, the measurement error seems ± 0.05 eV. Realization of a high electron barrier at the interface of the Ta_xO_y/Ru system requires establishment of a RuO_z-free process at the interface.

Conclusion

We used XPS to investigate the use of Ta_xO_y/Ru (RuO_z) systems for advanced memory devices. From the XPS spectra, we evaluated the difference of properties depending on the surface controlled process and succeeded in drawing energy band diagrams of the Ta_xO_y/Ru (RuO_z) systems. The existence of the RuO_z phase in the interface of Ta_xO_y/Ru system decreases the height of the electron barrier. We believe that the band diagram depicted by the XPS spectra is useful for evaluating new capacitor systems in the search for new dielectric materials.

Acknowledgement

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