# EXAFS STUDIES OF THE DIFFERENCE IN LOCAL STRUCTURE OF VARIOUS TANTALUM OXIDE CAPACITOR FILMS

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## ABSTRACT

The extended x-ray absorption fine structure (EXAFS) above the Ta $L_3$-edge on tantalum oxide capacitor films has been measured. Four kinds of tantalum oxide films were studied: as-deposited (amorphous), dry $O_2$ annealed (crystalline) , $O_2$-plasma annealed (amorphous) and 2-step ($O_2$-plasma + dry $O_2$) annealed (crystalline). From EXAFS analysis, differences in the local structures of tantalum oxide capacitor films, in terms of oxygen deficiency around Ta, were observed in the various annealed films. The leakage current characteristics of tantalum oxide capacitors correspond with the differences in the local structures around Ta. The discussion looks at the relationship between the leakage current characteristics and the local structures around Ta.

## INTRODUCTION

In highly integrated memory devices, such as 256 mega-bit dynamic random access memories (DRAMs), the thickness of the storage dielectrics must be reduced below the effective $SiO_2$ film thickness of 5nm for three-dimensional stacked or trenched capacitor structures.[1] Conventional films such as $Si_3N_4/SiO_2$ film on polycrystalline silicon have reached their physical limits (~5nm) of thinning.[2] This is because the direct tunneling current greatly increases below an effective $SiO_2$ film thickness of 5nm.

On the other hand, CVD tantalum oxide is a potential film material, because of its high dielectric constant[3] and its excellent step coverage characteristics.[4] Unfortunately, however, tantalum oxide capacitors with sufficient leakage current characteristics have not yet been fabricated, even with as good characteristics as conventional silicon nitride capacitors.

There have been many studies on the structure of crystallized tantalum oxide films to elucidate the relation to the leakage current characteristics.[5-8] Shinriki et al.[5] reported that oxygen addition and crystallization, which is a hexagonal phase, are key points for good

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insulating properties. On the other hand, Oehrlein et al.[6] concluded that polycrystalline $Ta_2O_5$ films on Si, formed by thermal oxidation of deposited Ta, have worse dc conduction properties and lower dielectric breakdown strength than comparable amorphous $Ta_2O_5$ films.

Thus the leakage current characteristics seemed to have no simple relationship to crystal structure based on the long-range order. In our previous studies we found that the leakage current characteristics for the $O_2$-plasma annealed film was markedly improved in comparison with any other films reported so far.[10,11] We found that the oxygen contents around Ta atom in $O_2$-plasma annealed film, which is amorphous, is the most among as-deposited (amorphous), dry $O_2$ annealed (crystalline) and $O_2$-plasma annealed films. As a result, we revealed that this characteristics depend on the oxygen contents around Ta atom, not on the long-range ordered crystal structure.[10,11] In order to use the tantalum oxide capacitor films for memory devices, the crystalline film is believed to be better because of the stability. Then, 2-step ($O_2$-plasma + dry $O_2$) annealing method was adopted to make a crystalline film with filling vacancies in as-deposited film with oxygen. On the contrary, however, the leakage current was found to deteriorate to almost the same level as that for dry $O_2$ annealing.[10] In this paper, we will show the EXAFS results of 2-step annealed tantalum oxide capacitor film together with as-deposited, dry $O_2$ annealed and $O_2$-plasma annealed films and show by EXAFS experiments that the relationship between the leakage current characteristics and the degree of deficiency of oxygen atoms adjacent to the tantalum atoms still hold.

## EXPERIMENTAL

Tantalum oxide films of 100Å thickness were deposited on a nitrided polycrystalline-silicon surface using a pentaethoxy-tantalum $Ta(OC_2H_5)_5$ and oxygen gas mixture at 400℃.[9] After deposition, one of the following annealing conditions was performed on the as-deposited films: (1) in $O_2$-plasma atmosphere at 400℃ for 10 minutes ($O_2$-plasma annealing), (2) in dry $O_2$ at 750℃ for 10 minutes (dry $O_2$ annealing) and (3) dry $O_2$ annealing after $O_2$-plasma annealing (2-step annealing).

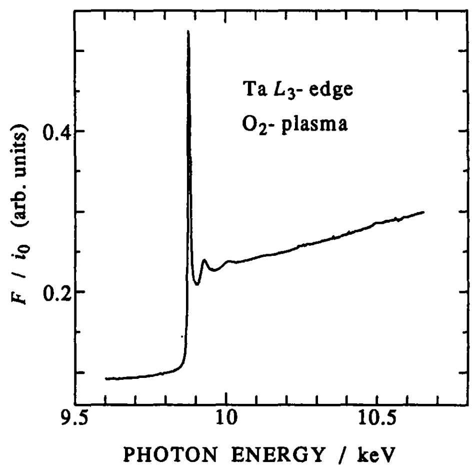


Fig. 1. EXAFS spectrum around Ta $L_3$-edge of $O_2$-plasma annealed tantalum oxide film, taken at room temperature.

EXAFS measurements were carried out with a Si(111) double crystal monochromator at BL-9C of the Photon Factory in the National Laboratory for High Energy Physics (KEK, Tsukuba, Japan). The measurements were done on the Ta $L_3$-edge at room temperature in the fluorescent mode using an ion chamber with nitrogen fill gas and a Lytle detector with argon fill gas. The photon energy $E$ was calibrated with a Cu foil by assigning 8.9788keV to the pre-edge peak of absorption.

The energy step size was 0.5eV for XANES (x-ray absorption near edge structure) scans and 2.0 to 3.0eV for EXAFS scans.

Leakage current measurements for each film were also carried out using the dc step method.

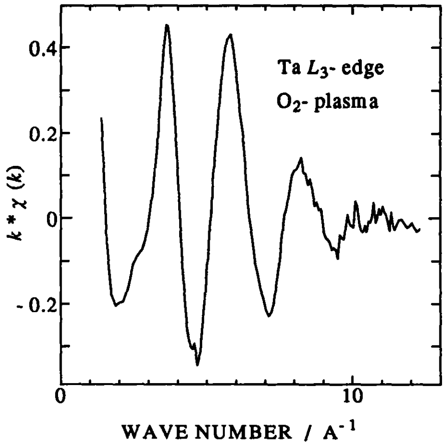


Fig. 2. EXAFS oscillations, $k^* \chi(k)$ vs. $k(Å^{-1})$, background-subtracted from Fig. 1.

## DATA ANALYSIS

A typical fluorescent EXAFS spectrum near the Ta $L_3$-edge of tantalum oxide is shown in Fig. 1 for a $O_2$-plasma annealed film. The EXAFS oscillations in $k$-space extracted from the EXAFS spectrum are shown in Fig. 2. In the EXAFS analysis to determine local structure parameters, the standard procedure was adopted.[12] The magnitude of the Fourier transform of the EXAFS oscillations gives the radial structure function around the absorbing atoms. Figure 3 shows this radial structure functions around Ta atoms of the measured annealed tantalum oxide films. Several sharp peaks observed in this figure are shifted to smaller

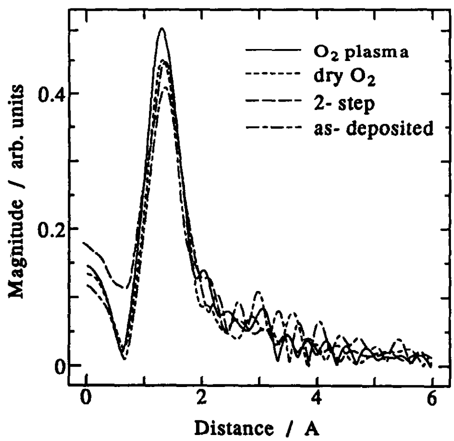


Fig. 3. Magnitude of the Fourier transform of the EXAFS oscillations using data range 2.5<k< 12 $Å^{-1}$ of various tantalum oxide films.

values by a few tenths of an angstrom from their crystallographic distance due to the phase shift effect. The single-shell fitting was carried out for the Ta-O bond in the tantalum oxide based on the harmonic lattice vibration model. The local structure parameters, such as interatomic distance, coordination number and Debye-Waller factor, were allowed to best fit the Fourier filtered Ta-O EXAFS oscillations.

## RESULTS AND DISCUSSION

As shown in Fig. 4, the leakage current characteristics through the dry $O_2$ annealed tantalum oxide film that were improved in comparison with those of as-deposited films. Furthermore, for $O_2$-plasma annealed films, the leakage current was greatly reduced compared with that of the dry $O_2$ annealed films. However, for 2-step annealed films, the leakage current increased to almost the same level as that of the $O_2$-plasma annealed films.

Prior to these EXAFS experiments, the crystal structures based on the long-range order of tantalum oxide films were characterized by x-ray diffraction and transmission electron microscopy.[7] It was observed that the as-deposited and $O_2$-plasma annealed films are amorphous, and the dry $O_2$ annealed and 2-step annealed films are crystallized orthorhombic phase, which agree with our previous studies.[10]

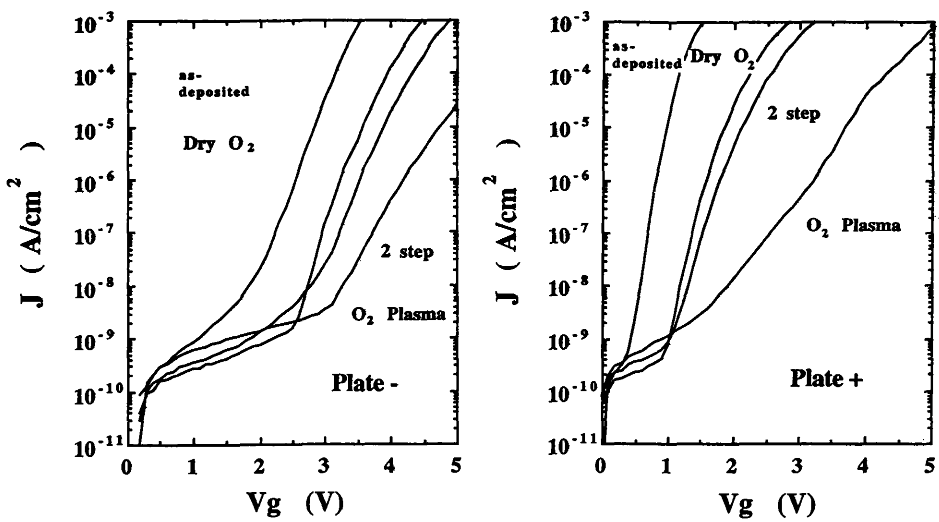


Fig. 4. The dependence of the leakage current characteristics for ultrathin tantalum oxide capacitors on annealing treatment: (left) the plate electrode is negatively biased, and (right) the plate electrode is positively biased.

In Fig. 3, the peak positions of the nearest Ta-O interatomic distances are almost independent of the annealing treatments. However, the peak intensity for the $O_2$-plasma annealed film is the highest among the films studied. As expected from the I-V measurements, shown in Fig. 4, what we found was that the oxygen contents were reduced by the crystallization treatment. These results contrast to the report by Shinriki et al.,[5] in which the crystallization process necessary to stabilize added oxygen in the film decreases oxygen vacancy.

The best-fit results of the EXAFS analysis are tabulated in Table I. The sequence of the films from the worst in terms of oxygen deficiency is; as-deposited film; dry $O_2$ annealed film or 2-step annealed film; and $O_2$-plasma annealed film. This sequence corresponds with that of the leakage current characteristics. From these results, It can be said that the oxygen deficiency around a Ta atom produces the path for the leakage current in the film.

Therefore, it can be concluded that differences in the leakage current characteristics of tantalum oxide capacitors that are treated by various processes are not due to differences in crystalline structure, but, to the degree of deficiency of oxygen atoms adjacent to the tantalum atoms.

## SUMMARY

The EXAFS of Ta $L_3$-edges have been measured for various annealed tantalum oxide capacitors. From these results, we found that all of the tantalum oxide capacitors had the same Ta-O interatomic distance, within our experimental resolution. On the other hand, the coordination number of oxygen atoms to tantalum atoms was different with different annealing treatments. The sequence of the oxygen deficiency almost corresponds with that of the leakage current characteristics. Therefore, we can conclude that the local structure around Ta plays an important role in the leakage current characteristics of tantalum oxide capacitor films.

TABLE I. Local structure parameters in tantalum oxide capacitor films at room temperature: the least-squares refined Ta-O interatomic distance and coordination number using Fourier filtered data range $5<k<11(\text{Å}^{-1})$.

| | $O_2$-plasma | 2-step | dry $O_2$ | as deposited |
|---|---|---|---|---|
| interatomic distance (Å) | 2.05 | 2.06 | 2.06 | 2.05 |
| | ±0.02 | ±0.02 | ±0.02 | ±0.02 |
| coordination number | 7.8 | 7.3 | 7.3 | 6.1 |
| | ±0.5 | ±0.5 | ±0.5 | ±0.5 |

In near future highly reliable ultrathin tantalum oxide capacitors could be produced by filling vacancies in as-deposited films with oxygen by methods such as $O_2$-plasma annealing.

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