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Effect of Oxygen Addition on Structure and Current Conduction Mechanism of Amorphous and Crystallized Extremely Thin CVD-Ta_2O_5 Films

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The improvement in the insulating properties of CVD-Ta_2O_5 film by 2-step annealing with UV-O_3 then dry-O_2, is explained by analyzing the structure using low glancing-angle X-rays, SR-EXAFS, and XPS. Oxygen addition by UV-O_3, corresponding to reducing number of oxygen vacancies, is confirmed by XPS. X-ray and EXAFS analysis show that shorter Ta-O bond length and higher oxygen coordination number as usual is formed in crystallized 10 nm-thick CVD-Ta_2O_5 film treated by the 2-step annealing.

Introduction

We have reported a new fabrication technique of extremely thin Ta_2O_5 film using LPCVD with $Ta(OC_2H_5)_5$ followed by 2-step annealing of UV-O_3 and dry O_2.(1) The film was applied as a storage dielectric to fabricate 1.5V-operated 64 Mbit DRAMs.(2) The insulating characteristics of the film, leakage current and defect density, were found to be improved dramatically by the 2-step annealing.

In this paper, new detailed explanations of the film structure and current conduction mechanism are given for every step of annealing. **Low glancing angle X-ray diffraction, SR-EXAFS, XPS,** and **electrical measurements** are used to determine the effect of oxygen addition on the structural and electrical properties of 10 nm-thick Ta_2O_5 films equivalent to 3 nm-thick SiO_2 film.

Experimental Procedure

Structures of Ta_2O_5 films after every step of annealing were estimated by low glancing angle X-ray diffraction, SR-EXAFS and XPS. In the low glancing angle X-ray measurement, a glancing angle was set at 1^o for obtaining sufficient signal intensity. In the EXAFS measuments, X-ray beam generated by SOR ring was used, which is effective for structural analysis of extremely thin film. The EXAFS spectra of thin Ta_2O_5 films on single crystal silicon were measured near the tantalum L(III) absorption edge. In capacitors for the electrical mesurement, Ta_2O_5 film was deposited on phosphorus-doped polycrystalline silicon and exposed to one of the following annealing processes: UV-O_3, DRY-O_2, or 2-step annealing. After that, W-gate was fabricated. The UV-O_3 annealing was took place in an ozone (9-percent volume)/oxygen mixture radiated by a mercury lamp at 300^oC. The dry-O_2 annealing was done in a dry oxygen atomosphere at 800^oC. The 2-step annealing involved the UV-O_3 followed by the dry-O_2.

Results and Discussions

Low glancing angle($\alpha=1^o$) X-ray diffraction spectra (Fig.1) show that the 10 nm-thick CVD-Ta_2O_5 film after UV-O_3 annealing is amorphous, and that the crystal phase of Ta_2O_5 appears after the subsequent dry-O_2

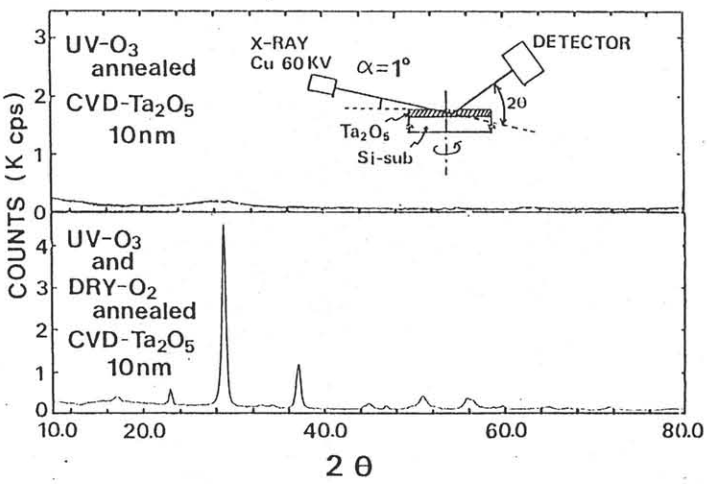

Fig.1 X-ray diffraction patterns of 10 nm-thick UV-O_3 annealed and 2-step annealed CVD-Ta_2O_5 film.

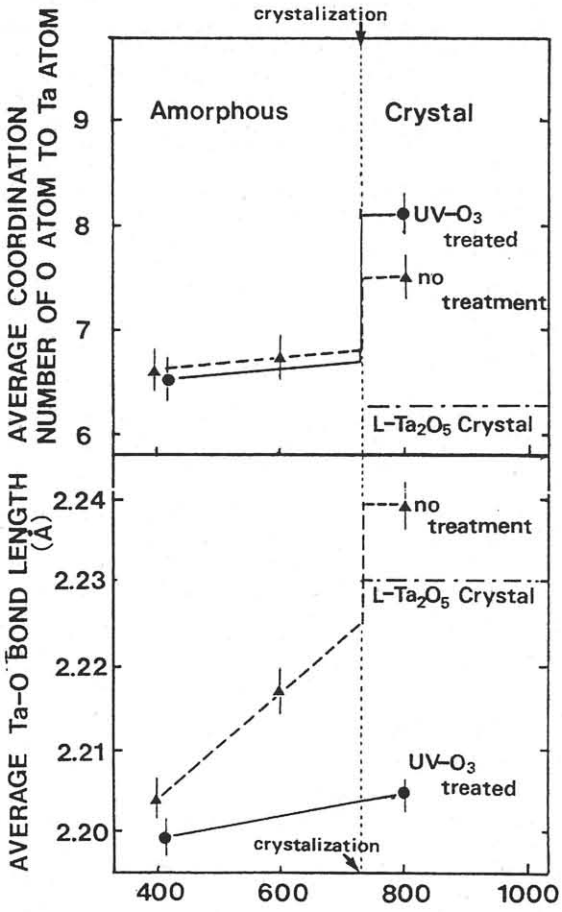

Fig.2 Dependence of average coordination number and average Ta-O bond length in 10 nm-thick Ta_2O_5 film on annealing temperature in dry-O_2 atomosphere with UV-O_3 pretreated or not pretreated film.

annealing. An assignment of this diffraction spectra was achieved by considering results of an EXAFS analysis. Figure 2 shows dependences of average Ta-O bond length and average coordination number of oxygen atom to Ta atom in 10 nm-thick Ta_2O_5 film on annealing temperature in dry-O_2 atmosphere. It is noted that much higher coordination number is observed in the 10 nm-thick crystallized film than that of L-Ta_2O_5 crystal form usually observed in bulk. Thus the crystal form seems to be peculiar to thin film region. Considering with the diffraction spectra and approximately 8 coordination number in UV-O_3 treated film, the crystal form seems to be δ-Ta_2O_5 (hexagonal) among tantalum oxide crystal forms still reported . Concerned with effect of UV-O_3 treatment for structure, UV-O_3 pre-treatment promote remarkable shortening of Ta-O bond length and increase in coordination number in the 2-step annealed film as shown in Fig.2. Thus, UV-O_3 treatement seems to form precusor in amorphous state for the growth of the crystal form having extremely tight chemical bonds by reparing oygen deficients.

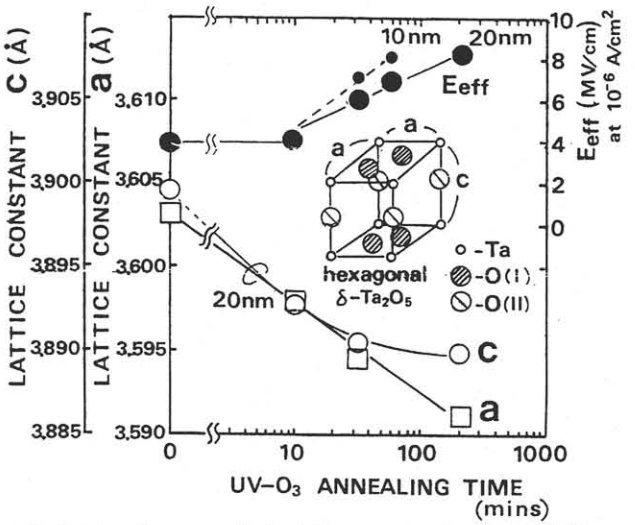

Fig.3 Dependence of lattice constant and E_{eff} of 10 nm and 20 nm-thick CVD-Ta_2O_5 film on UV-O_3 annealing time. (Inset:Structure of δ-Ta_2O_5 (hexagonal) unit cell)

Figure 3 shows changes in lattice constants and effective electric field E_{eff} of the 2-step annealed 10 and 20 nm-thick CVD-Ta_2O_5 films versus UV-O_3 annealing time. Lattice constants are estimated by assuming that crystal form is δ-Ta_2O_5 and unit cell consist of one molecule. For the 20 nm film, both **a** and **c** decrease with annealing time and the corresponding increase in E_{eff} was observed. Noted here that lattice constant **c** levels off after about 30 mins of annealing, although E_{eff} continues to increase. Thus, the increase in E_{eff} is mainly attributed to the shortening of lattice constant **a**. These relationships can be explained by the crystal structure of Ta_2O_5, especially by the oxygen chemical bonds. For oxygen bonds to Ta atoms, there are two types of oxygen position O(I) and O(II) in the cell (inset in Fig.2). Lattice constant **a** corresponds to the distance of Ta-Ta, which can be determined from the bond length Ta-O(I) or O(I)-O(I), and **c** corresponds to the Ta-O(II)-Ta chain length. A shorter lattice constant **a** implies that the bond length of either Ta-O(I) or O(I)-O(I) is shorter due to the stronger covalency. Oxygen vacancies, left in the amorphous film after the UV-O_3 treatment, show a tendency to take position at O(I) rather than O(II) during the crystallization. Thus, longer UV-O_3 treatment reduces the density of oxygen vacancies in the amorphous film, resulting in a higher filling probability of an oxygen atom at O(I) in the crystallized film. On the other hand, the filling probability of an oxygen atoms at O(II) is estimated to be very high initially and remain almost unchanged with increasing annealing time. Thus, the increase in E_{eff} is thought to be achieved by adding oxygen to the vacancies at O(I). The following results obtained by XPS support this model.

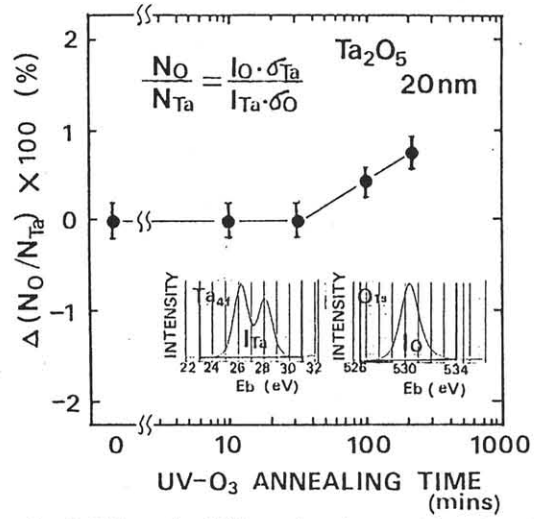

Fig.4 Shift of O/Ta atomic ratio in 20 nm-thick CVD-Ta_2O_5 film as a function of UV-O_3 annealing time.

Figure 4 shows the shift in O/Ta ratio in the film versus UV-O_3 annealing time; the ratio is derived from the ratio of Ta_{4f} peak intensity to O_{1s} peak intensity in XPS spectra. The amount of oxygen starts to increase after UV-O_3 for 30 mins and is 0.8% higher than the as-deposited film after 200 mins. Thus, activated oxygen atoms produced by the UV-O_3 are thought to diffuse into the Ta_2O_5 film and fill the vacancies.

Finally, the effects of the oxygen addition on the current conduction mechanism are described. In the amorphous film, the current conduction mechanism gradually changes from the modified Poole-Frenkel (a=2) to the normal Poole-Frenkel(a=1) as the number of oxygen vacancies decreases (Fig.5). The distribution of E_{eff} is very wide due to the wide distribution of oxygen vacancies in the film (Fig.6). In the crystallized film, current conduction is thought to be due to trap assisted tunneling because tunneling current is drastically reduced by adding oxygen(FIG.5). Noted that a sharp distribution of E_{eff} is obtained due to the oxygen vacancies moving to the O(I) positions during crystallization (Fig.6).

Conclusion

This study shows that an effective process for controlling oxygen vacancies in CVD-Ta_2O_5 films, such as oxygen addition and crystallization by 2-step annealing, gives good insulating properties.

Acknowledgment

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Three dimensional Poole-Frenkel process

$$I=\sigma_o \beta^2 (\beta E^{1/2} - 1)\exp.(\beta E^{1/2}/a)$$

σ_o :constant
β = 12.87 at room temperature

a=1 normal Pool-Frenkel process
a=2 modified Pool-Frenkel process

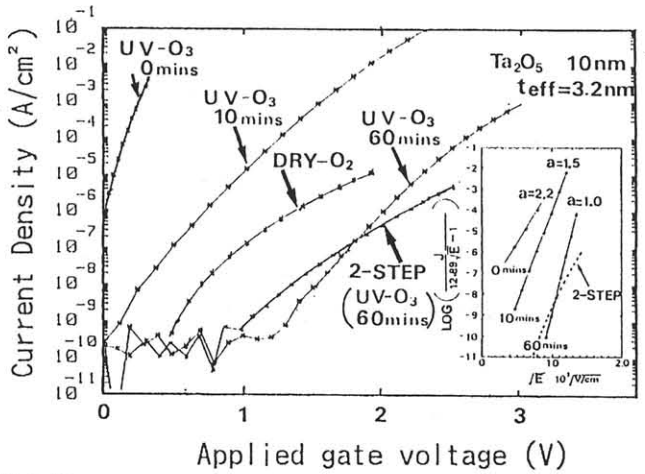

Fig.5
Leakage Current Characteristics of CVD-Ta_2O_5 film and the I-V relationship for three-dimensional Poole-Frenkel process. (inset:three dimensional Poole-Frenkel plot)

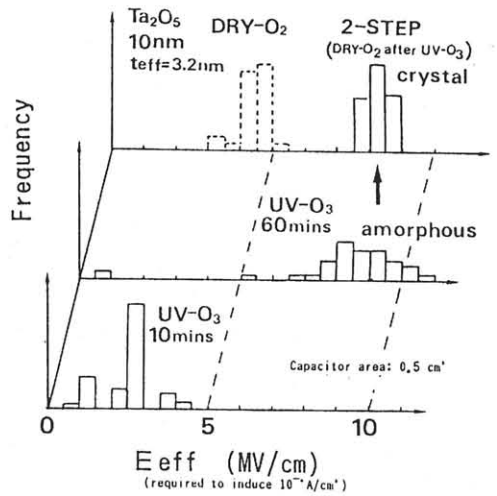

Fig.6
Histogram of E_{eff} required to induce 10^{-6} A/cm^2 for UV-O_3(10, 60mins),DRY-O_2 and 2-step annealed CVD-Ta_2O_5 film.

References

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(2) Y.Kawamoto, et al.,Tech. Dig of VLSI Symp., p13 (1990)