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Characterization of Ultra-Thin Capacitors Fabricated Using RTN Treatment Prior to CVD Ta_2O_5 Film Formation

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This paper describes the electrical and physical characterization of highly reliable ultra-thin Ta_2O_5 capacitor dielectric layers, fabricated using rapid thermal nitridation (RTN) of poly-silicon, prior to CVD Ta_2O_5 film formation. The RTN treatment allows a reduction of the SiO_2 equivalent thickness (t_{eq}), as well as superior leakage and TDDB characteristics. Densification of the CVD Ta_2O_5 by dry O_2 annealing is an indispensable process to form highly reliable ultra-thin capacitors. During densification, desorption of CH_4 and H_2O from the as-grown CVD Ta_2O_5 film occurs, and the ultra-thin Ta_2O_5 film is crystallized above 700°C with an orthorhombic structure.

INTRODUCTION

Highly integrated memory devices require a very thin dielectric film for three-dimensional stacked or trenched capacitor structures[1,2]. CVD Ta_2O_5 is a potential material, because of its high dielectric constant (εr=25), and its excellent step coverage characteristics. Therefore, many workers have studied CVD Ta_2O_5 method[3-6] and the capacitor process associated with it[7,8].

This paper describes the characterization of highly reliable ultra-thin Ta_2O_5 capacitors (t_{eq}<3nm), fabricated using RTN treatment of the stacked polysilicon surface prior to CVD Ta_2O_5 film formation. The merits of using the RTN treatment are : (1) A reduction of the SiO_2 equivalent thickness, because the nitrided polysilicon surface prevents the polysilicon from being oxidized during Ta_2O_5 deposition and the annealing treatments following Ta_2O_5 deposition, (2) Superior leakage characteristics for the ultra-thin capacitors with RTN treatment, than for those with no-RTN treatment, (3) An extension by about 50 times of the TDDB stress time of 50% cumulative failure for the ultra-thin capacitors with RTN treatment compared to those with no-RTN treatment.

EXPERIMENTAL PROCEDURE

RTN treatments were carried out at temperatures ranging from 800 to 1100°C for 60 sec in NH_3, just after cleaning the stacked polysilicon surface by a diluted HF treatment (DHF). Ta_2O_5 films were deposited at 470°C by LPCVD using $Ta(OC_2H_5)_5$ and oxygen. Ta_2O_5 films were annealed in a furnace at temperatures ranging from 600 to 900°C, in dry O_2 or N_2 atmosphere. Then, TiN plate electrodes were deposited on Ta_2O_5 by reactive sputtering, because the leakage characteristics of the ultra-thin capacitors with TiN electrodes are far superior than those with W electrodes[8]. The electrical characteristics of the ultra-thin capacitors were investigated by measuring C-V, I-V and TDDB. Further, in order to characterize the Ta_2O_5 films, thermal desorption spectroscopy (TDS), X-ray diffraction (XRD), and transmission electron microscopy (TEM) analyses were carried out.

RESULTS and DISCUSSION

The RTN treatment of the stacked polysilicon surface before Ta_2O_5 deposition, and dry O_2 annealing following Ta_2O_5 deposition are indispensable processes to form highly reliable ultra-thin Ta_2O_5 capacitors.

The variation of t_{eq} with the annealing temperature is shown in Fig.1, where (a) and (b) are for furnace annealing in dry O_2 and N_2 atmospheres, respectively. In this figure, the results for RTN and no-RTN samples are shown for comparison. As shown in this figure, the RTN treatment remarkably reduces the SiO_2 equivalent thickness, because the nitrided polysilicon surface prevents the polysilicon from being oxidized during Ta_2O_5 deposition and the annealing treatments following Ta_2O_5 deposition.

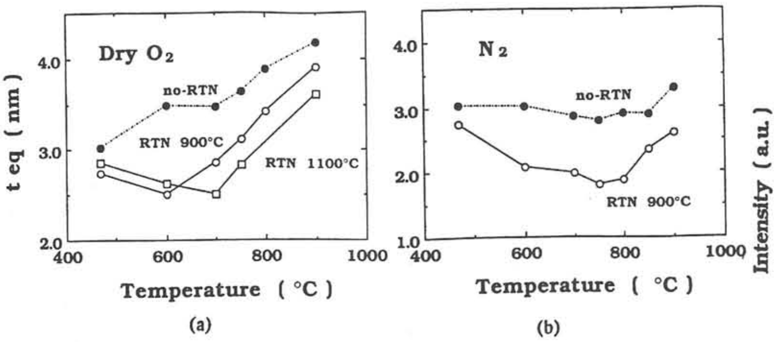

Fig.1 Variation of the SiO_2 equivalent thickness (t_{eq}) with the annealing temperature : (a) dry O_2 and (b) N_2.

TDS results of the as-grown CVD Ta_2O_5 films, are shown in Fig.2. TDS measurements were carried out from room temperature (R.T.) to 1000°C with a temperature increase rate of 100°C/minute. As shown in this figure, CH_4 (m/z=13,14,15,16), and H_2O (m/z=17,18) gases diffuse out at about 600°C. As a result, the thickness of Ta_2O_5 films densified at 700° in N_2 atmosphere is decreased by about 10%, in comparison with the as-grown films.

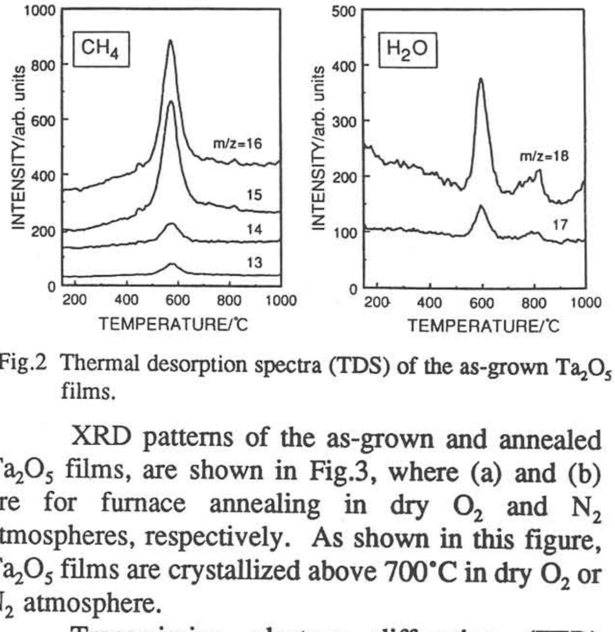

Fig.2 Thermal desorption spectra (TDS) of the as-grown Ta_2O_5 films.

XRD patterns of the as-grown and annealed Ta_2O_5 films, are shown in Fig.3, where (a) and (b) are for furnace annealing in dry O_2 and N_2 atmospheres, respectively. As shown in this figure, Ta_2O_5 films are crystallized above 700°C in dry O_2 or N_2 atmosphere.

Transmission electron diffraction (TED) results of the ultra-thin Ta_2O_5 films, are shown in Fig.4, where (a) and (b) are for the as-grown and annealed Ta_2O_5 at 750°C in dry O_2 atmosphere, respectively. As shown in Fig.4(a), the as-grown of the ultra-thin Ta_2O_5 film is amorphous, because a halo pattern is observed in TED. Further, as shown in Fig.4(b), the annealed of the ultra-thin Ta_2O_5 film is crystallized, because a sharp ring pattern is observed in TED. The net-plane spacings corresponding to the sharp ring pattern of the annealed Ta_2O_5 film are shown in Table I. It is compared with previous X-ray data for orthorhombic Ta_2O_5 (β-Ta_2O_5)[9]. From this table, it is found that most of the rings of the crystallized ultra-thin Ta_2O_5 film agree with the X-ray data for orthorhombic Ta_2O_5.

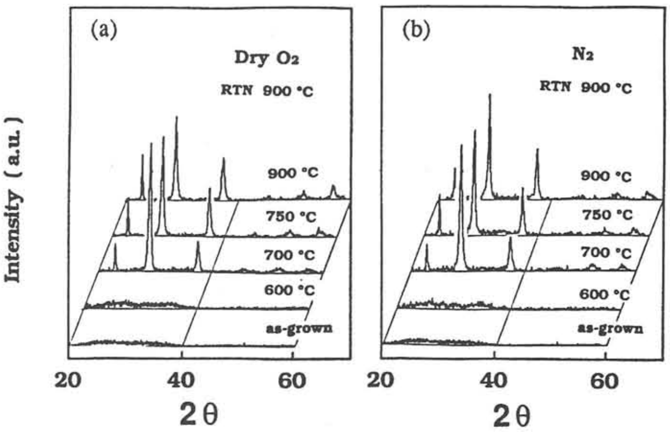

Fig.3 X-ray diffraction pattern dependence on the annealing temperature of the Ta_2O_5 films : (a) dry O_2 and (b) N_2.

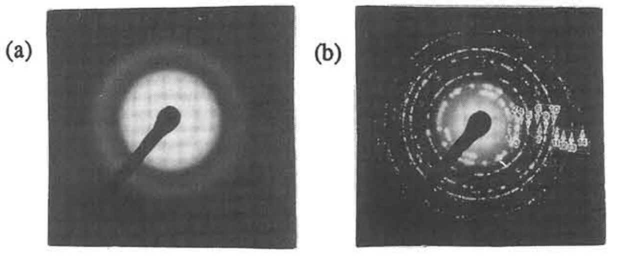

Fig.4 Transmission electron diffraction of the ultra-thin Ta_2O_5 films : (a) as-grown and (b) annealed at 750 °C in dry O_2.

No.	d (hkl) observed	observed intensity	d (hkl) theoritical	theoritical intensity (%)	plane (hkl)
1	3.89	VS	3.88	85	0 0 1
2	3.40	W	3.377	5	1 10 0
3	3.15	VS	3.152	100	1 0 0
			3.098	40	2 0 0
4	2.87	W	2.876	2	0 14 0
5	2.45	S	2.449	75	1 11 1
			2.423	35	2 0 1
6	2.11	W	2.105	3	1 18 0
7	2.01	W	2.007	4	1 19 0
8	1.94	S	1.944	25	0 0 2
9	1.83	S	1.832	17	0 22 0
			1.799	18	3 11 0
10	1.65	S	1.656	30	0 22 1
			1.655	35	1 11 2
			1.647	15	2 0 2
			1.633	12	3 11 1
11	1.58	M	1.576	9	2 22 0
12	1.46	M	1.461	10	2 22 1
13	1.33	S	1.333	6	0 22 2

(VS : Very Strong, S : Strong, M : Medium, W : Weak)

Table I Net-plane spacings corresponding to the sharp ring pattern observed for the annealed ultra-thin Ta_2O_5 film, and comparison with previous X-ray data for orthorhombic Ta_2O_5 (β-Ta_2O_5).

I-V characteristics of the ultra-thin Ta_2O_5 capacitors are shown in Fig.5. In this figure, the solid and dashed lines show the results for RTN and no-RTN treatments, respectively. These results show that superior leakage characteristics are obtained for the ultra-thin capacitors with RTN treatment, than for those with no-RTN treatment. The leakage current of the ultra-thin capacitors (t_{eq}<3nm), with RTN treatment and densification at 750°C in dry O_2 atmosphere, is significantly reduced to a value of 10^{-8} A/cm^2, at 4.3MV/cm for positive bias. Further, the leakage characteristics of the same sample are much better in the case of negative bias, with a value of 10^{-8} A/cm^2 at 8.6MV/cm.

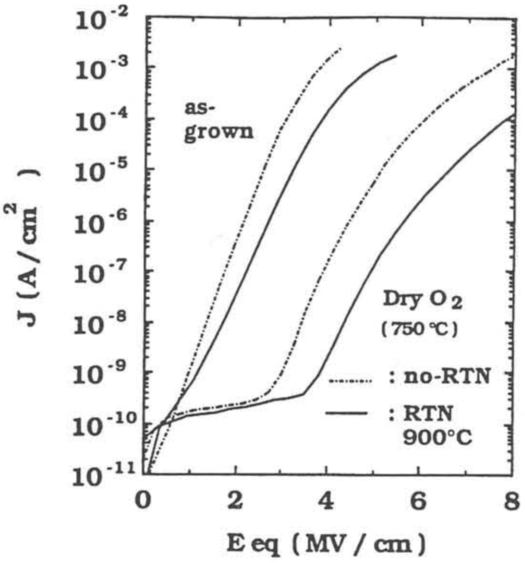

Fig.5 Leakage current characteristics of the ultra-thin Ta_2O_5 capacitors. (Positive bias)

TDDB stress time dependence of cumulative failure for the ultra-thin Ta_2O_5 capacitors is shown in Fig.6, where the stress conditions are positive bias, SiO_2 equivalent field E_{eq}=15MV/cm (with E_{eq} = V (applied voltage) / t_{eq}), and a 100°C temperature. As shown in this figure, the plotted points follow straight lines for no-RTN and RTN treatments (900,1100°C), and random failure modes are not observed. These results show an extension by about 50 times of the TDDB stress time of 50% cumulative failure for the ultra-thin capacitor with RTN treatment compared to those with no-RTN treatment. Further, TDDB reliability tests showed that the reliability of these ultra-thin capacitors is significantly much higher than 10 years for half V_{cc}=1.25V, and 100°C operating conditions.

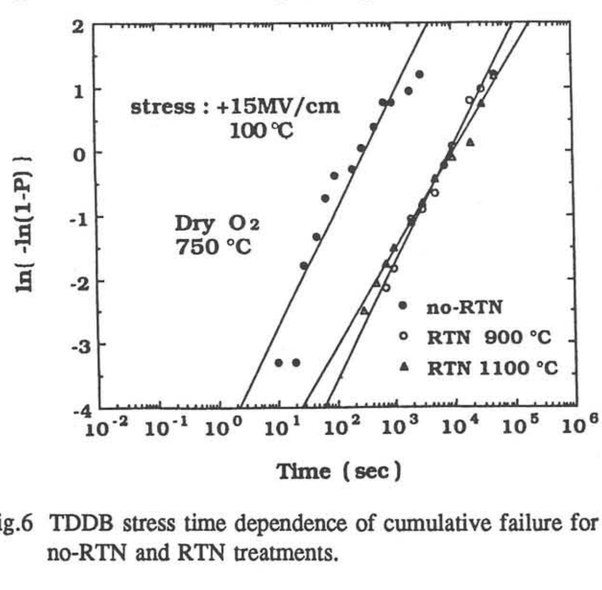

Fig.6 TDDB stress time dependence of cumulative failure for no-RTN and RTN treatments.

CONCLUSION

This study shows that highly reliable ultra-thin Ta_2O_5 capacitor dielectric layers can be fabricated by using RTN treatment of the stacked polysilicon surface prior to CVD Ta_2O_5 film formation. The merits of using RTN treatment are a reduction of the SiO_2 equivalent thickness, superior leakage characteristics, and an extension by about 50 times of the TDDB stress time of 50% cumulative failure for the ultra-thin capacitor with RTN treatment compared to those with no-RTN treatment. Densification of the CVD Ta_2O_5 by dry O_2 annealing is an indispensable process to form highly reliable ultra-thin capacitors. During densification, desorption of CH_4 and H_2O from the as-grown CVD Ta_2O_5 film occurs, and the ultra-thin Ta_2O_5 film is crystallized above 700°C with an orthorhombic structure. TDDB reliability tests showed that the reliability of these ultra-thin capacitors is significantly much higher than 10 years for half V_{cc}=1.25V, and 100°C operating conditions. As a result, highly reliable ultra-thin Ta_2O_5 capacitors fabricated using RTN process technology reported here are suitable for use in future high density DRAMs.

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