Preliminary investigation of high-*k* materials Ti doped Ta_2O_5 Films by remote plasma ALD

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Introduction

Driven by the shrinking of microelectronic devices there is a strong demand for novel ultra high-*k* dielectrics (UHK) and electrode materials. It has been reported that the dielectric constant of $(TiO_2)_x(Ta_2O_5)_{1-x}$ bulk materials (x=0.08) is over 120[1]. Recently, atomic layer deposition technology is widely used for both of materials researches and coating extreme geometries of devices. The process details of $(TiO_2)_x(Ta_2O_5)_{1-x}$ (x is up to 0.45) films by remote plasma ALD will be reported in this work. The growth-rates of the ALD films measured by ellipsometer are in a range of 0.8 - 1.06 Å/cycle at a deposition temperature of 300°C, depending on Ti/(Ti+Ta) ratio. In order to evaluate the high-*k* materials of Ti-doped Ta_2O_5 films, EDX and AES were used for determining the composition of the films. The thickness and optical properties of the films were measured by a spectral ellipsometer and CV-measurement was applied for testing the electrical property of the film. Furthermore, the effects of thermal anneal and in-situ O_2-oxidation on thickness, refractive index and electrical property of $(TiO_2)_x$-$(Ta_2O_5)_{1-x}$ films are also discussed.

$(TiO_2)_x(Ta_2O_5)_{1-x}$ polycrystalline[1]

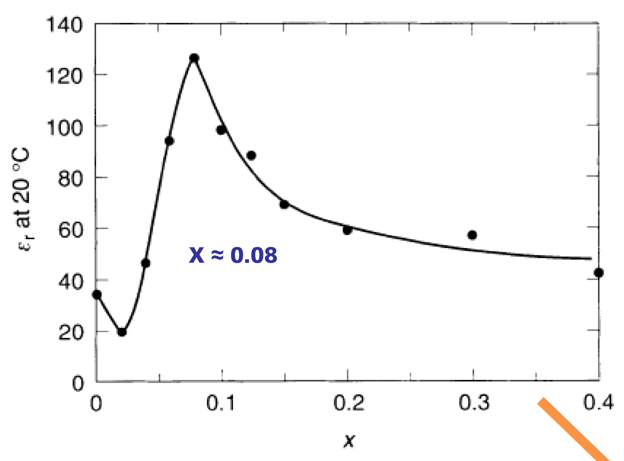

***Figure.1** Dielectric constant in $(TiO_2)_x(Ta_2O_5)_{1-x}$ Bulk materials at 20°C as a function of composition.*

$(TiO_2)_x(Ta_2O_5)_{1-x}$ Thin films

- RF Sputtering
- MOCVD
- UV-CVD
- The best thin film result of dielectric constant of **50** for 8%Ti doped Ta_2O_5 from UV-CVD was achieved [2].

Challenges and problems:

- Poor composition controlling
- Poor process reproductivity
- Need suitable annealing

Could the advantages of ALD overcome the problems?

a) Laminate structure or co-deposition of TiO_2 and Ta_2O_5
b) Optimise ALD process
c) Fine composition control
d) In-situ and ex-situ anneal processes available

Experimental

The process of $(TiO_2)_x(Ta_2O_5)_{1-x}$ (x is up to 0.40) films carried out by remote plasma ALD, using t-butylimido tris(dimethylamido) tantalum (TBTMET) and titanium isopropoxide (TIIP) as Ta and Ti source, respectively. The thickness and the refractive index were measured using a J.A. Woollam M2000V spectroscopic ellipsometer (370nm-1000nm wavelengths). EDX and AES were used for determining the composition of the films. CV-measurement was applied for testing the electrical property of the films.

Results and discussion

Pure Ta_2O_5

Ta_2O_5 films were deposited firstly by using t-butylimido tris(dimethylamido)Tantalum, also known as TBTMET, and O_2 plasma. The results show in (Fig. 2-4):

1) Growth rate (GR) is around 1.10 Å/cycle, refractive index (RI) of ALD Ta_2O_5 is 2.150 at 300°C.
2) AES of 33nm Ta2O5 on Si/SiO2, Ta : O ≈ 1 : 2.5 , no carbon in bulk and detected only on the surface.

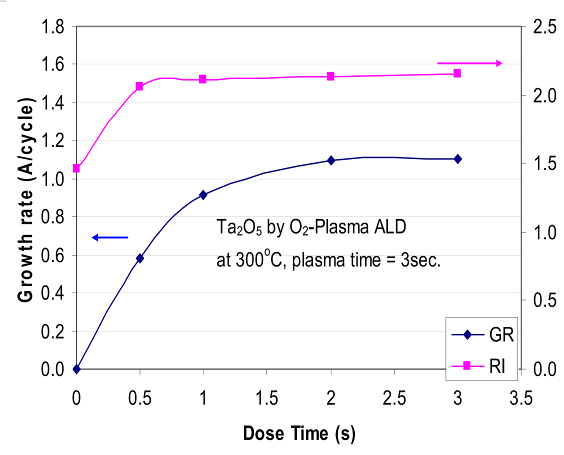

Figure-2, GR & RI of Ta_2O_5 vs dose-time

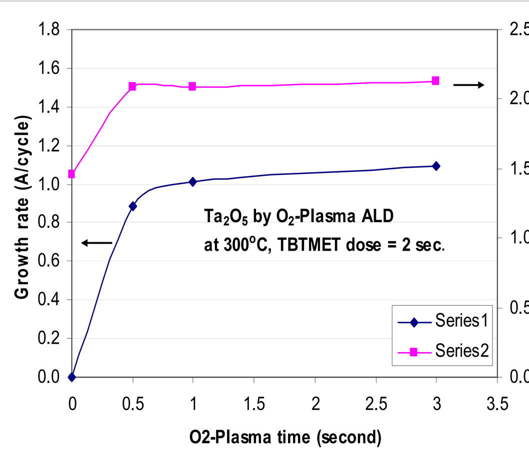

Figure-3, GR & RI of Ta_2O_5 vs O_2-plasma time

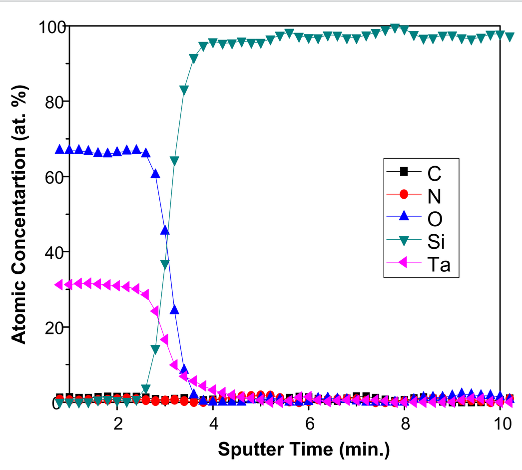

Figure-4, AES of Ta_2O_5 by plasma-ALD

TiO_2 doped Ta_2O_5

TiO_2 doped Ta_2O_5 ($TiTaO_y$) films were deposited on Si with TiO_2 mol% from 2% to 45%, which confirmed by EDX and AES measurement, in laminate structures. The results show in (Fig. 5-6):

1)The growth-rate of the ALD films are in a range of 0.8 - 1.15 Å/cycle at 300°C, depending on Ti/(Ti+Ta) ratio. Growth rate (GR) decreases, while refractive index (RI) decreases with increasing TiO_2 ratio at 300°C. It is noted that the relationship of RI and TiO_2-composition is not linear in the range of 7%-12%, which implied that there are some micro-structural changing in the laminate material.
2) AES of 8%TiO_2 doped Ta_2O_5 on Si/SiO_2, no carbon in bulk and in-set shows interface state of the film and substrate.

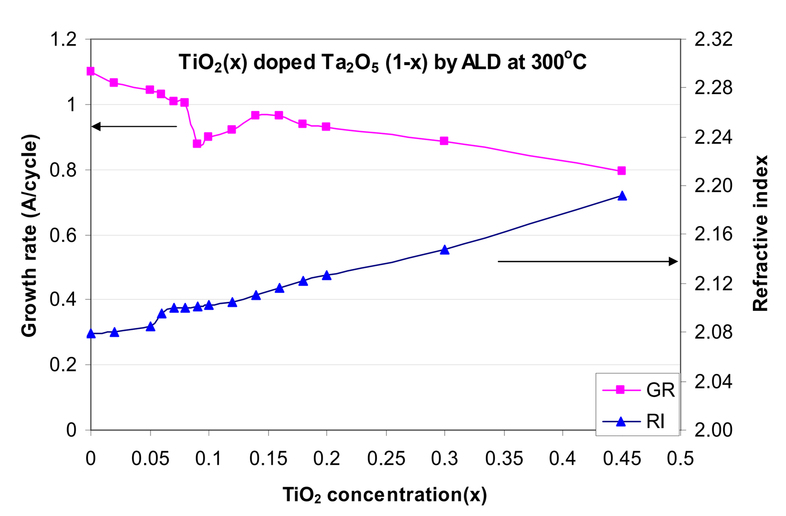

Figure-5, GR & RI of $(TiO_2)_x(Ta_2O_5)_{1-x}$ vs TiO_2-composition in the films

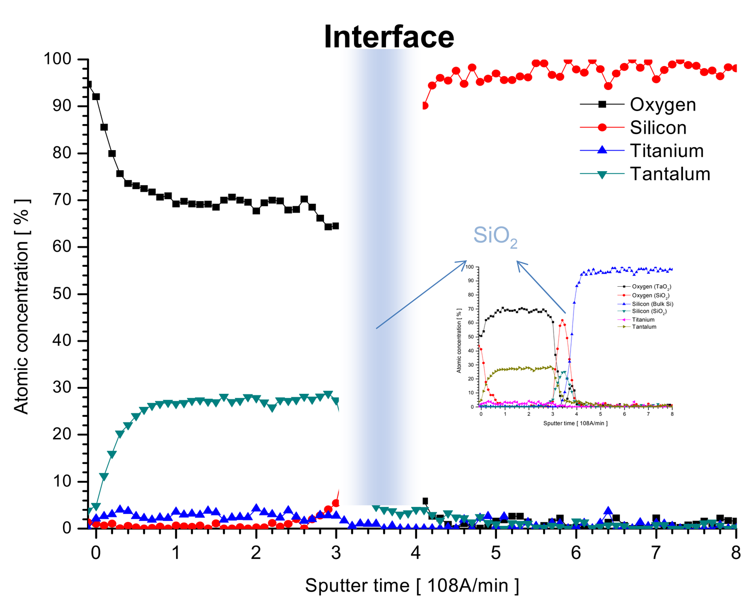

Figure-6, AES of (TiO2)x(Ta2O5)1-x (x=0.08) by plasma-ALD

References

[1] R.F. Cava, W.F. Peck & J.J. Krajewski, ***Nature*** 377, 215-217 (1995).

[2] Never Kaliwoh, Jun-Ying Zhang, Ian W. Boyd, *Applied Surface Science*, ***168***, Issues 1-4, Pages 13-16,(2000)

[3] S.B.S. Heil, J.L. van Hemmen, C.J. Hodson, N. Singh, J.H. Klootwijk, F. Roozeboom, M.C.M. van de Sanden and W.M.M. Kessels, J. Vac. Sci. Technol. A, 1357, (2007).

Experimental set-up

The Oxford Instruments FlexAL® remote plasma ALD reactor, described in detail in Ref [3], was used for this work. A schematic and photograph of the reactor are included below in figures 1 and 2.

- Remote plasma and thermal ALD capabilities within a single system
- Enables low temperature ALD processes by using plasma
- Maximum flexibility in the choice of materials and precursors
- Ability to handle small wafer pieces up to 200 mm wafers
- Built in ports for in-situ diagnostics e.g. ellipsometry, RGA, etc

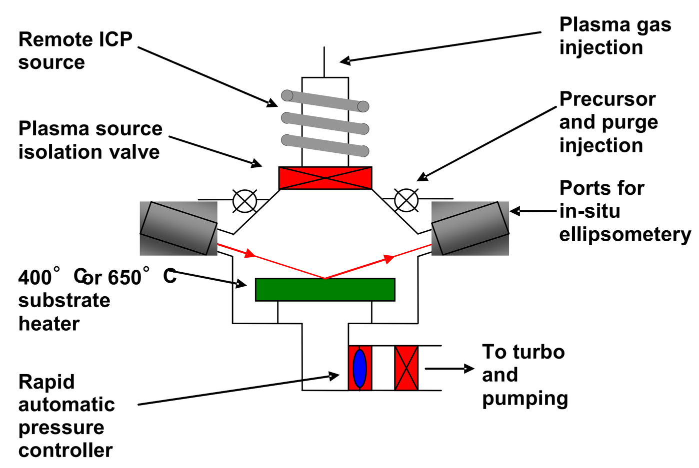

Figure 1 (left), schematic of the FlexAL® reactor.

Figure 2 (right), photograph of the FlexAL® reactor

In-situ oxidation and thermal annealing of TiO_2 doped Ta_2O_5

To investigate the effect of annealing on material properties,TiO_2 doped Ta_2O_5 ($TiTaO_y$) films were applied for both in-situ O_2-plasma oxidation and thermal annealing (in air for 30min). The results show in (Fig. 7-8):

1) In-situ oxidation Fig.7 shows that thickness of $TiTaO_y$ film reduced fast in in-situ oxidation at the first minute then it goes flat, while refractive index of $TiTaO_y$ increases with O_2-plasma oxidation time.
This result tells that there are some micro-structural changing during a short-time of in-situ oxidation.
2) Thermal annealing Fig.8 shows that thickness of $TiTaO_y$ film reduced with anneal temperature, there is a turning point change starting at 450°C.

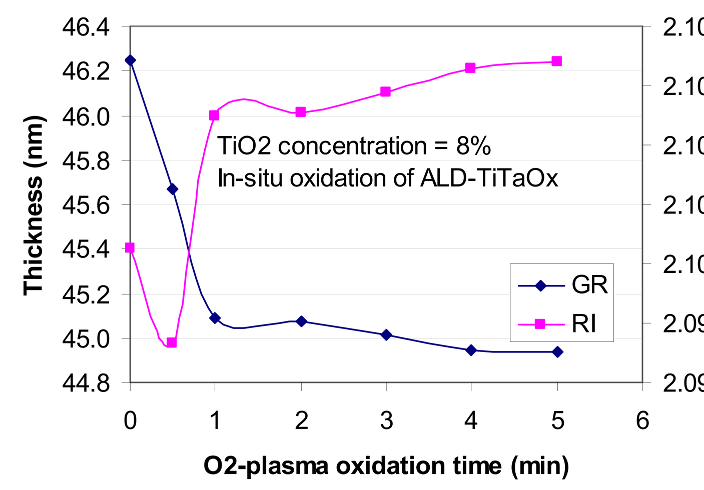

Figure-7, thickness & RI changing of TiO_2 doped Ta_2O_5 (x=8%) films vs in-situ O_2-plasma oxidation time at 300°C.

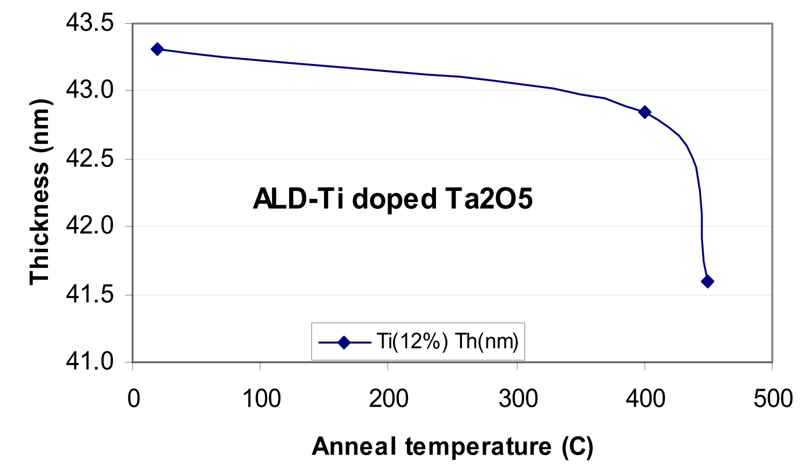

Figure-8, thickness changing of TiO_2 doped Ta_2O_5 (x=12%) films vs thermal annealing time (in air for 30min).

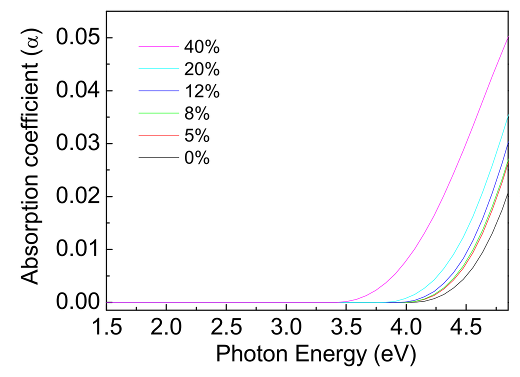

Figure 9, the absorption coefficient of the $TiTaO_y$ films with different Ti-incorporation content.

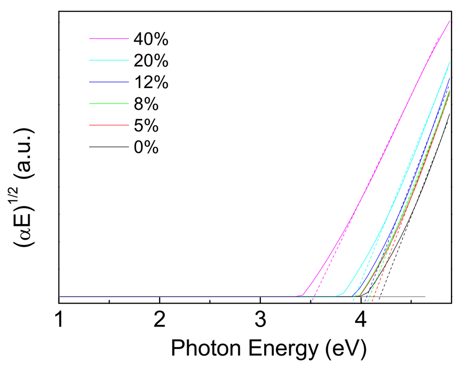

Fig.10, the optical band gap which is determined by the energy dependence characteristic of the indirect allowed transition as illustrated by the $(\alpha h\nu)^{1/2}$ vs the photon energy ($h\nu$).

Table-1 Optical band gap with thermal annealing

Ti content (atom%)	Annealing temp (°C)	Thickness (nm)	Eg (eV)
0	0	46.416	4.038
	400	45.627	4.047
	550	44.860	4.057
5	0	50.317	3.985
8	0	47.740	3.983
	400	47.700	3.983
	550	46.293	3.988
12	0	43.308	3.933
	400	41.601	3.939
	550	42.841	3.945
20	0	44.122	3.802
40	0	35.11	3.412
	400	35.07	3.434
	550	34.38	3.457

Table-2

Electrical and physical properties of TiO_2-dope Ta_2O_5 (TiTaOx)

(1) as-deposited by plasma ALD and
(2) after annealing by in-situ oxidation and thermal annealing.
(3) Annealing can increase film density, capacitance, and dielectric constant.
(4) In-situ O_2-plasma oxidation is comparable with thermal annealing, but it needs only very short time.
(5) The highest K-value of 27 @ 1MHZ (39 @ 100HZ) shows the Laminate structure by ALD is not good integration of both Ti and Ta composites.

Samples	TiO_2 (x %)	Annealing	Thickness (nm)	Refrac-tive index	Capacitance (pF) @1MHz	Capacitance (pF) @100Hz	Dielectric constant *k* @ 1MHz	Dielectric constant *k* @ 100Hz
A-03	5	As-deposited	45.74	2.0949	183	224	20	22
P-03	5	In-situ oxidation (4min)	45.04	2.1018	231	305	21	25
A-06	8	As-deposited	40.69	2.1014	228	275	21	23
P-06	8	In-situ oxidation (4min)	40.17	2.2062	250	351	27	35
A-08	12	As-deposited	40.92	2.1055	202	251	20	22
P-08	12	In-situ oxidation (4min)	40.14	2.1106	261	298	26	39
A-07	10	As-deposited	42.01	2.1044	210	252	20	23
P-07	10	Thermal anneal (700C for 30min)	41.46	2.1143	223	277	23	30

Conclusions

- Uniform and composition accurately controlled $(TiO_2)_x(Ta_2O_5)_{1-x}$ laminate films have been deposited on Si substrates by using remote plasma ALD technology. The growth-rate of the ALD films are in a range of 0.8 - 1.06 Å/cycle at 300°C, depending on Ti/(Ti+Ta) ratio.
- AES profile measurements of TiO_2 doped Ta_2O_5 show the composition of the films can be well control and no carbon is in bulk. Annealing process can increase the density, capacitance, and dielectric constant of the films. In-situ O_2-plasma oxidation is comparable with thermal annealing, but it needs only very short time.
- This preliminary results of TiO_2 doped Ta_2O_5 films shows the laminate structure by ALD is not good integration of Ti and Ta composites. Co-deposition by ALD and improved annealing the films are planed for next approach to increase the dielectric constant.

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