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Nucleation and growth of platinum films on high-*k*/metal gate materials by remote plasma and thermal ALD

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Introduction

Ultrathin metallic layers such as Pt, Ru, Pd and Cu deposited onto oxide structural surfaces have wide applications in microelectronics, catalysis, photonics and chemical sensing [1-3]. Atomic layer deposition (ALD) as an outstanding technique of self-limiting and thickness accurately controlling, is used to fabricate ultrathin and conformal thin film structures for many semiconductor and thin film device applications. In this work, we report that platinum films were deposited by both remote plasma and thermal atomic layers deposition using $MeCpPtMe_3$ and O_2 as precursors on oxide materials including SiO_2, Al_2O_3 and high-*k* dielectric HfO_2. The nucleation and growth of both thermal and plasma ALD Pt films on oxide substrates were also investigated.

Experimental Results and Discussion

Platinum films were deposited by both remote plasma and thermal ALD using methyl-cyclopentadienyl-trimethyl platinum ($MeCpPtMe_3$) and O_2 as precursors on oxide materials including SiO_2 (10nm, ALD), Al_2O_3 (18nm, ALD) and high-*k* dielectric HfO_2 (10nm, ALD). The Pt films with a thickness range up to 100 nm have been grown. The ALD Pt-films were homogeneous and resulted in a low resistivity down to 4.6 μΩ.cm.

Growth rate and resistivity of Pt films by thermal-ALD

Platinum films were grown using thermal-ALD at 300°C. The growth rate of 0.45-0.47 Å/cycle was obtained (Fig. 3). The nucleation process in thermal ALD was found at about 50 cycles. The resistivity of the Pt layer on Si was found to be reduced with increasing Pt thickness, the lowest resistivity of 4.6 μΩ.cm were measured with a Pt thickness of 100nm on Si substracte. (Fig. 4).

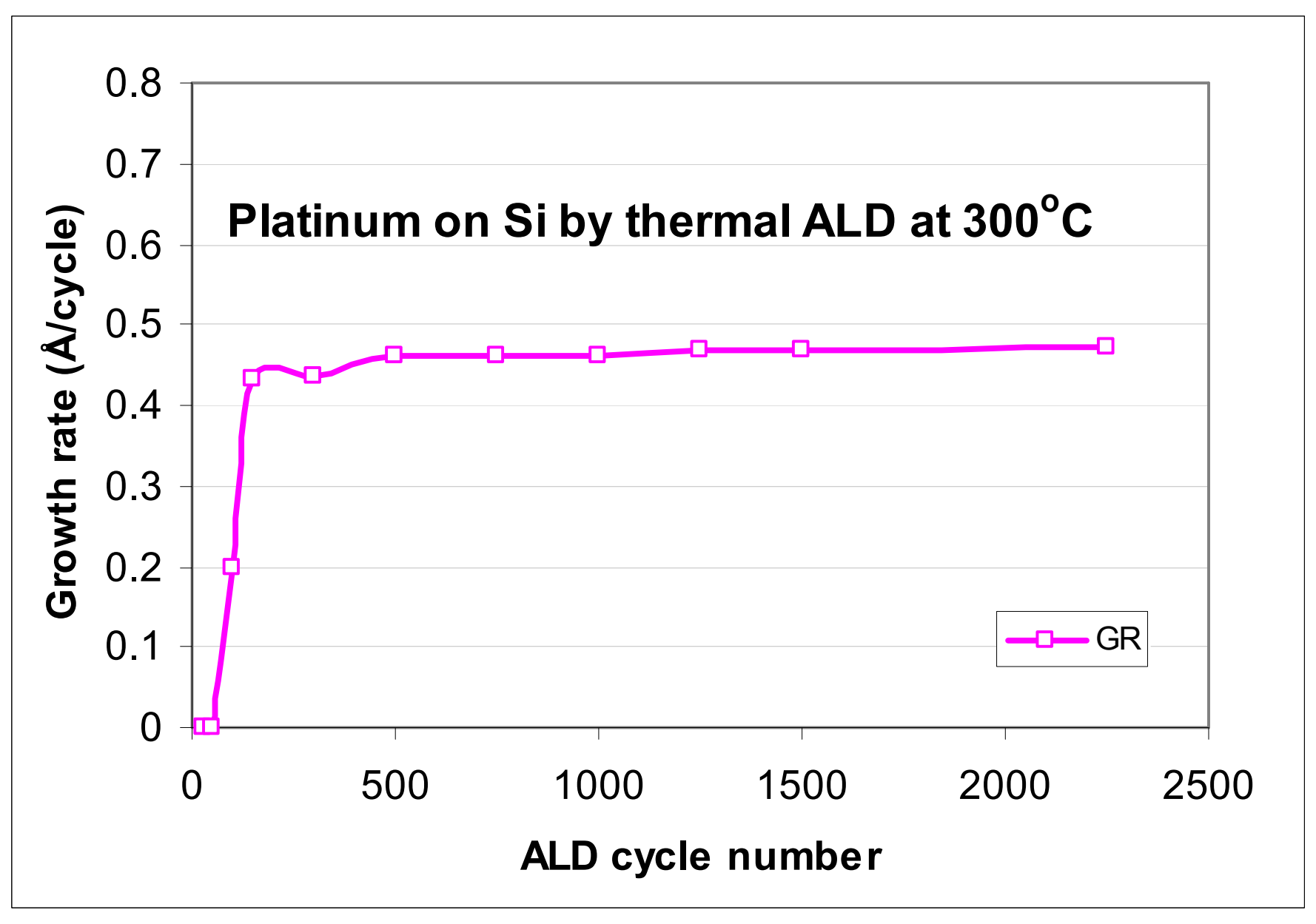

***Figure 3**, growth rate of thermal ALD Pt films/Si vs cycle numbers*

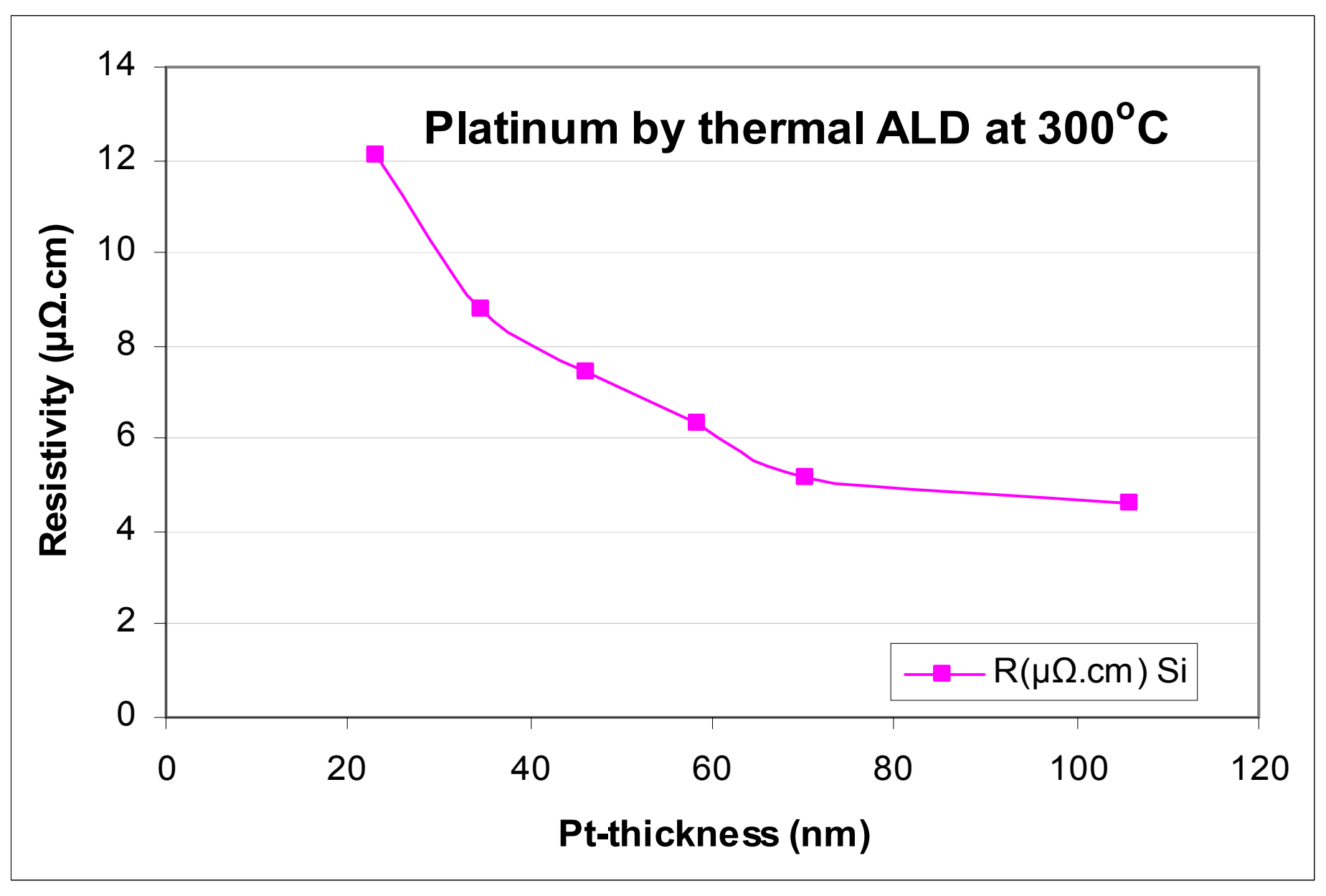

***Figure 4**, resistivity of thermal ALD Pt films/Si vs thickness*

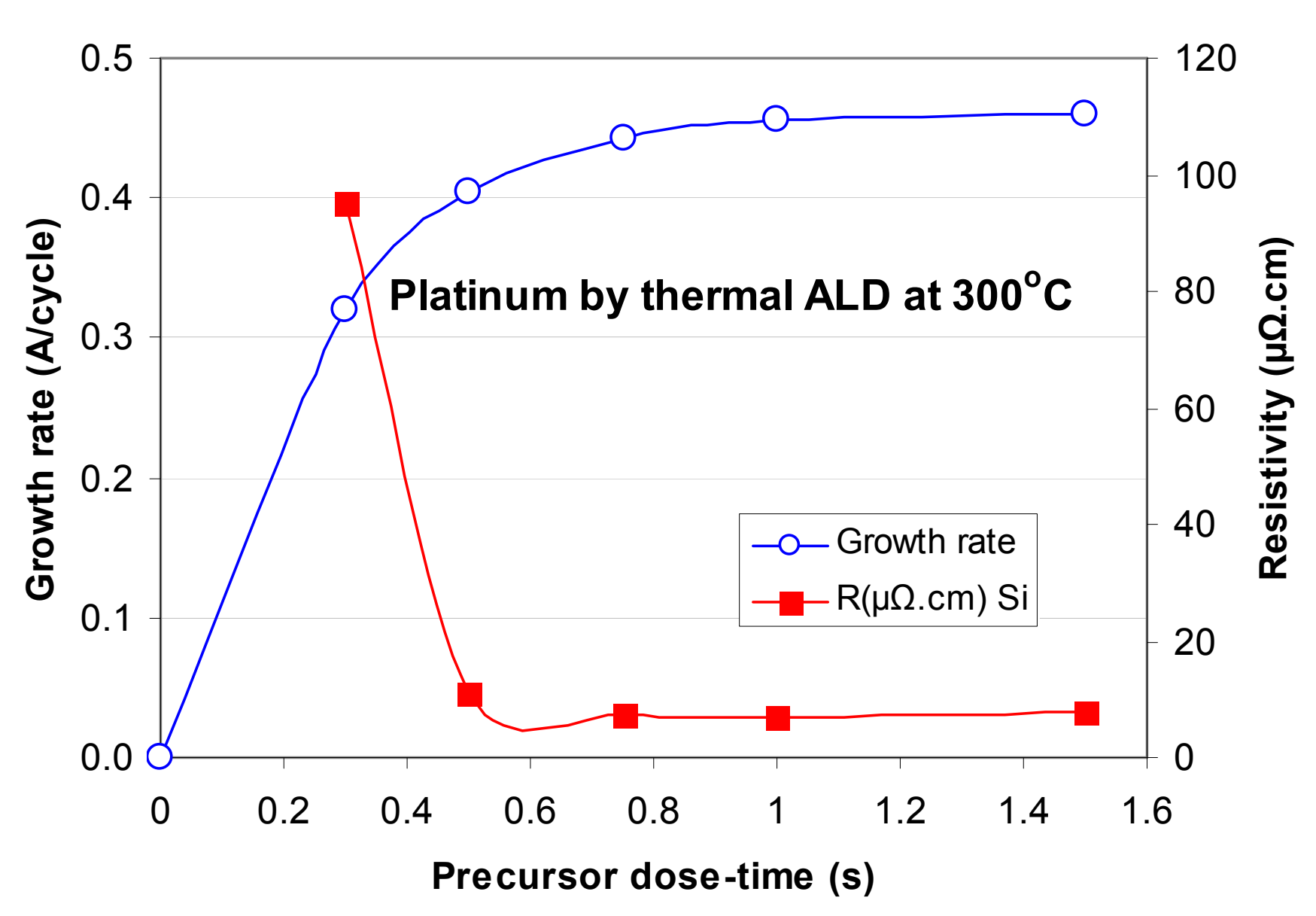

***Figure 5**, growth rate and resistivity of thermal ALD Pt films vs precursor dose-time.*

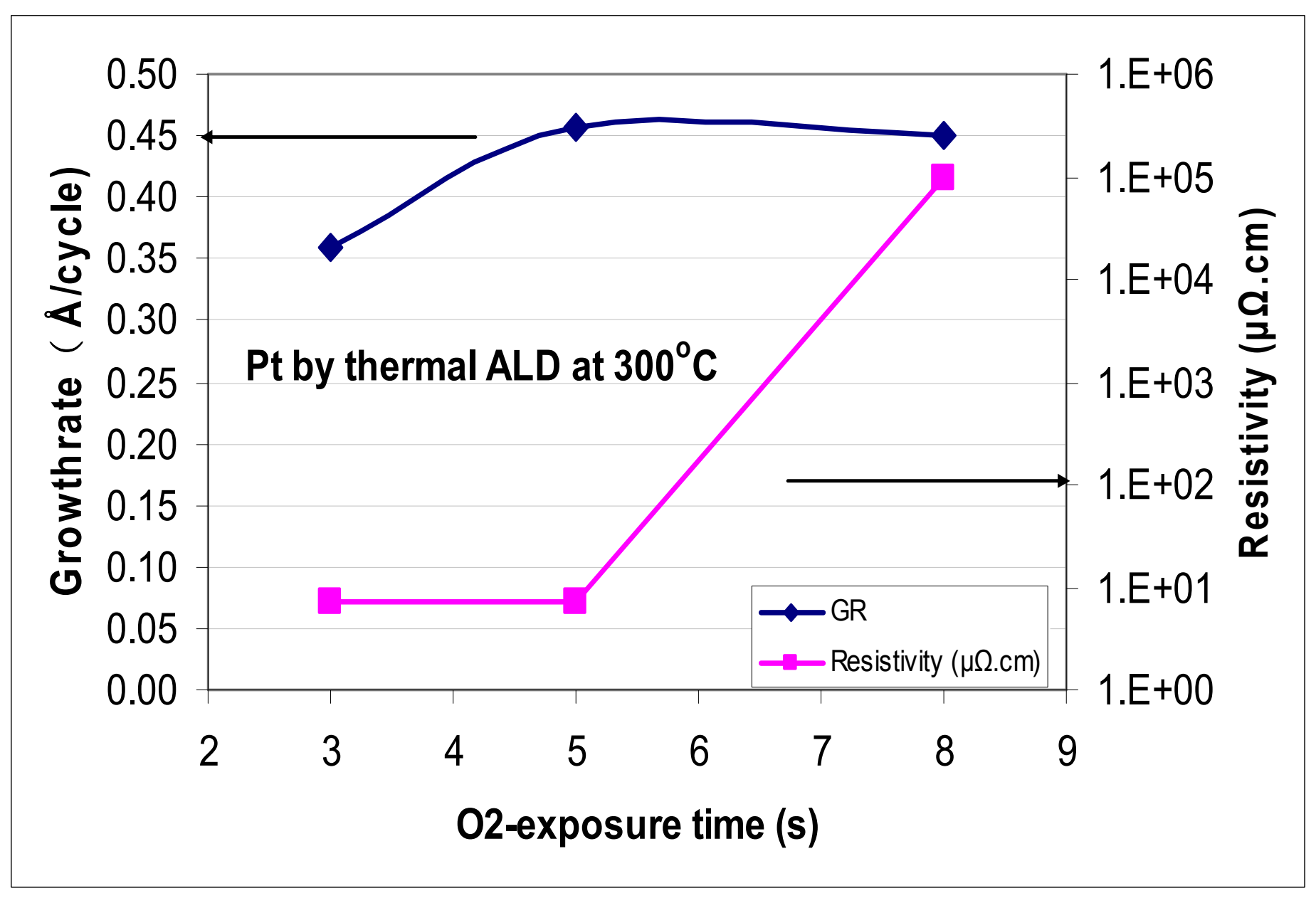

***Figure 6**, growth rate and resistivity of thermal ALD Pt films vs oxygen exposure-time.*

The self-limited growth rate of 0.45 Å/cycle with low resistivity was obtained (Fig. 5). The growth rate goes flat as oxygen exposure-time of 5 seconds and increase the oxygen exposure-time, then the resistivity increases, as shown in Fig. 6. It is believed that increasing oxygen exposure time forms PtO.

Growth rate and resistivity of Pt films by plasma-ALD

Platinum films were grown using plasma-ALD at 300°C. The growth rates of 0.43-0.45 Å/cycle were obtained (Fig. 7), which is comparable to that of thermal ALD. The resistivity of the Pt layers was found to be reduced with increasing precursor dose up to 1.5s and the lowest resitivity of Pt was found on HfO_2, as shown in Fig. 8.

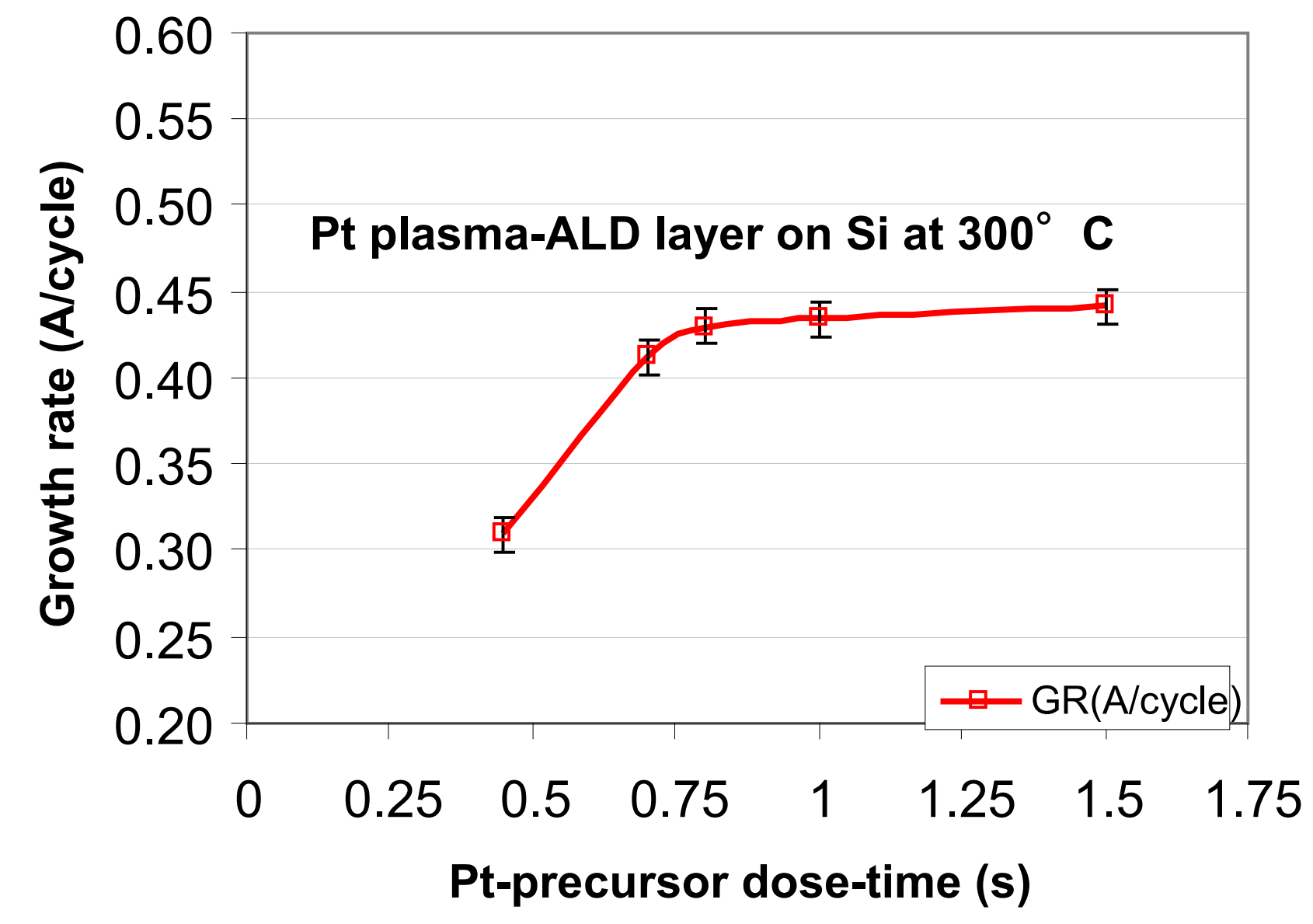

***Figure 7**, growth rate of plasma ALD Pt films/Si vs dose-time*

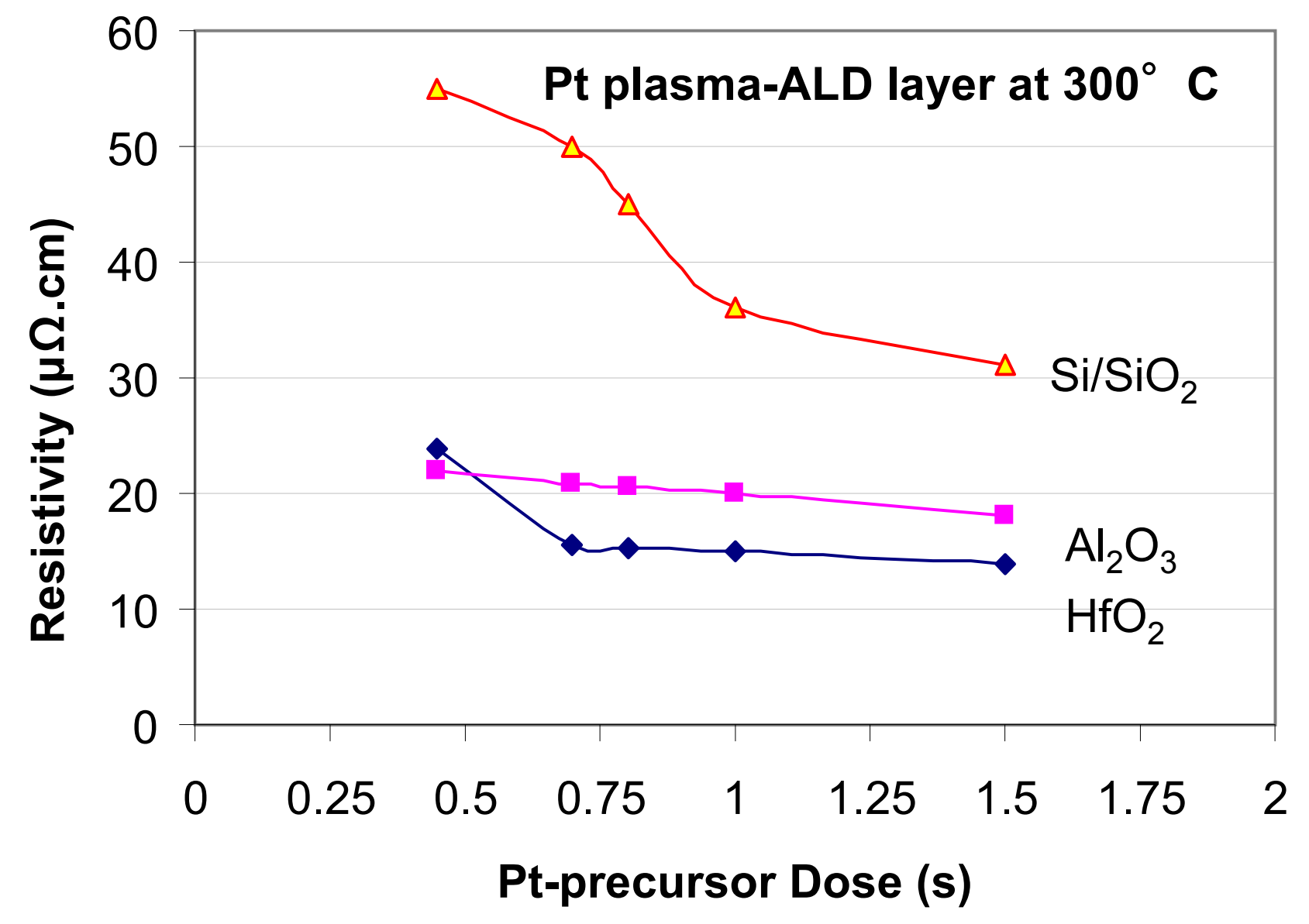

***Figure 8**, resistivity of plasma ALD Pt films/oxides vs dose-time*

Table 1, the four types of substrates used: Si wafers, ALD films of oxides including SiO_2, Al_2O_3 and high-*k* dielectric HfO_2 on Si substrates.

Substrate	ALD-oxide process	ALD oxide film thickness (nm)	ALD process temperature (ºC)	ALD precursors
Si(100)	/	/	/	/
SiO_2/Si	Plasma-ALD	10	200	TRDMAS
Al_2O_3/Si	Plasma-ALD	18	200	TMA
HfO_2/Si	Plasma-ALD	10	290	TEMAH

Experimental set-up

The Oxford Instruments FlexAL® remote plasma ALD reactor, described in detail in Ref [4], was used for this work. A schematic and photograph of the reactor is shown in Fig. 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

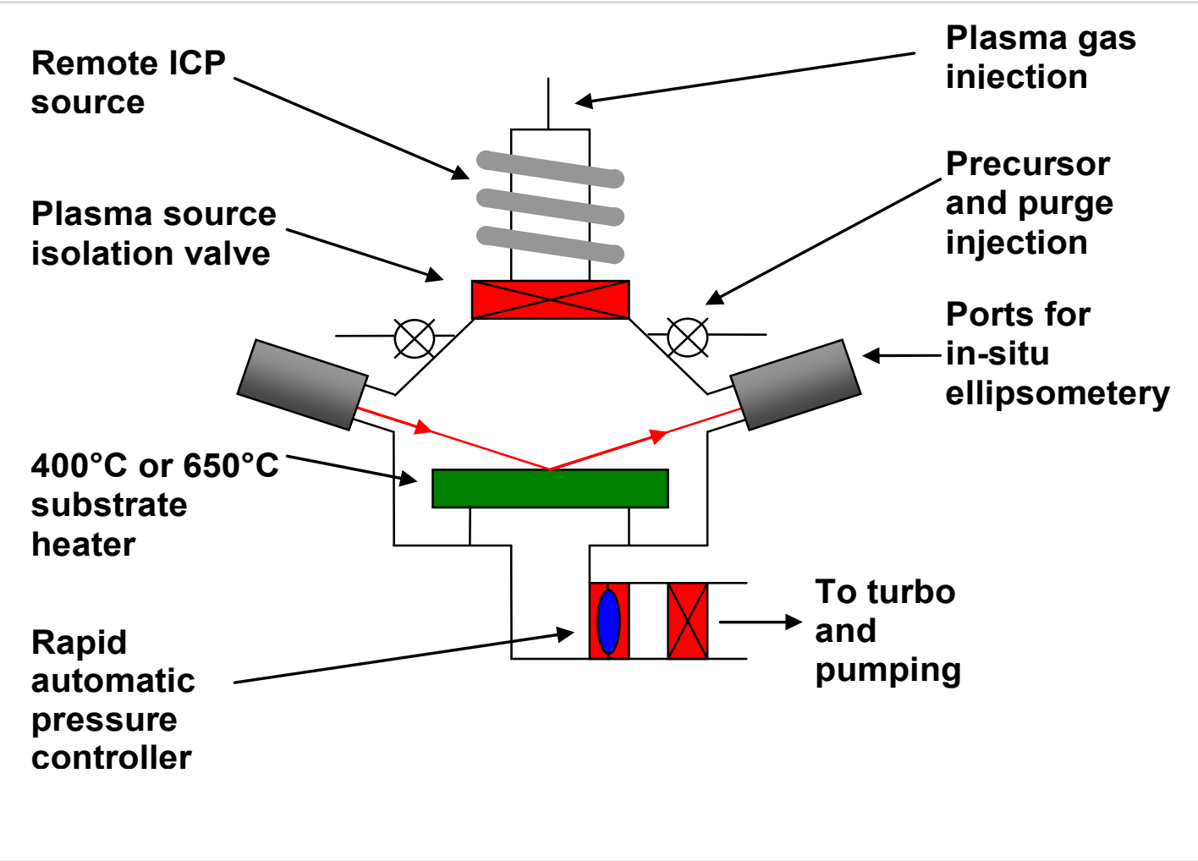

***Figure 1** (left), schematic of the FlexAL® reactor.*

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

Measurement and analysis of Pt films by ALD

SEM and EDX were used to investigate Pt nucleation and growth in ALD processes and AES was applied for the elemental analysis in the film and interfaces. AES studies revealed high quality Pt films deposited by both thermal and plasma ALD with carbon impurity less than 1.5% and oxygen found only in the interface (Fig.9).

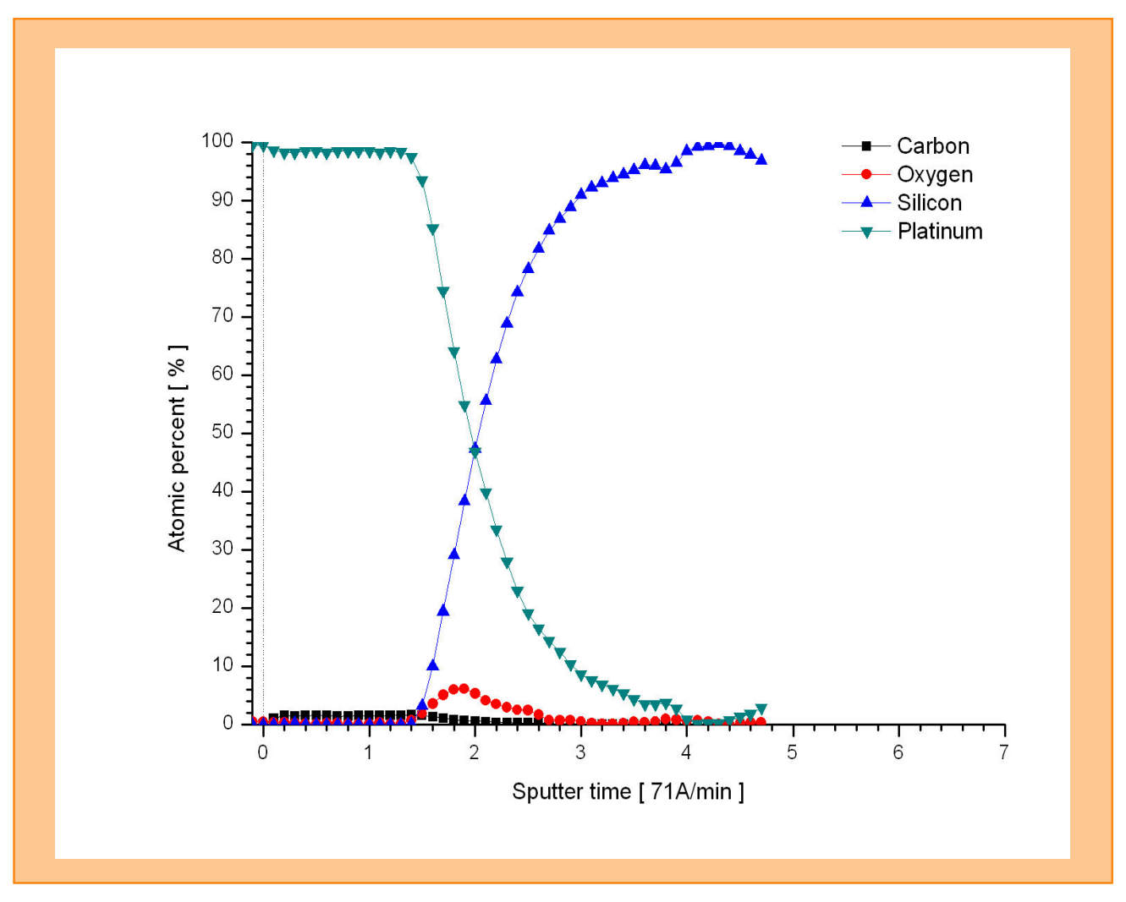

***Figure 9**, AES of 30nm Pt-ALD film on Si.*

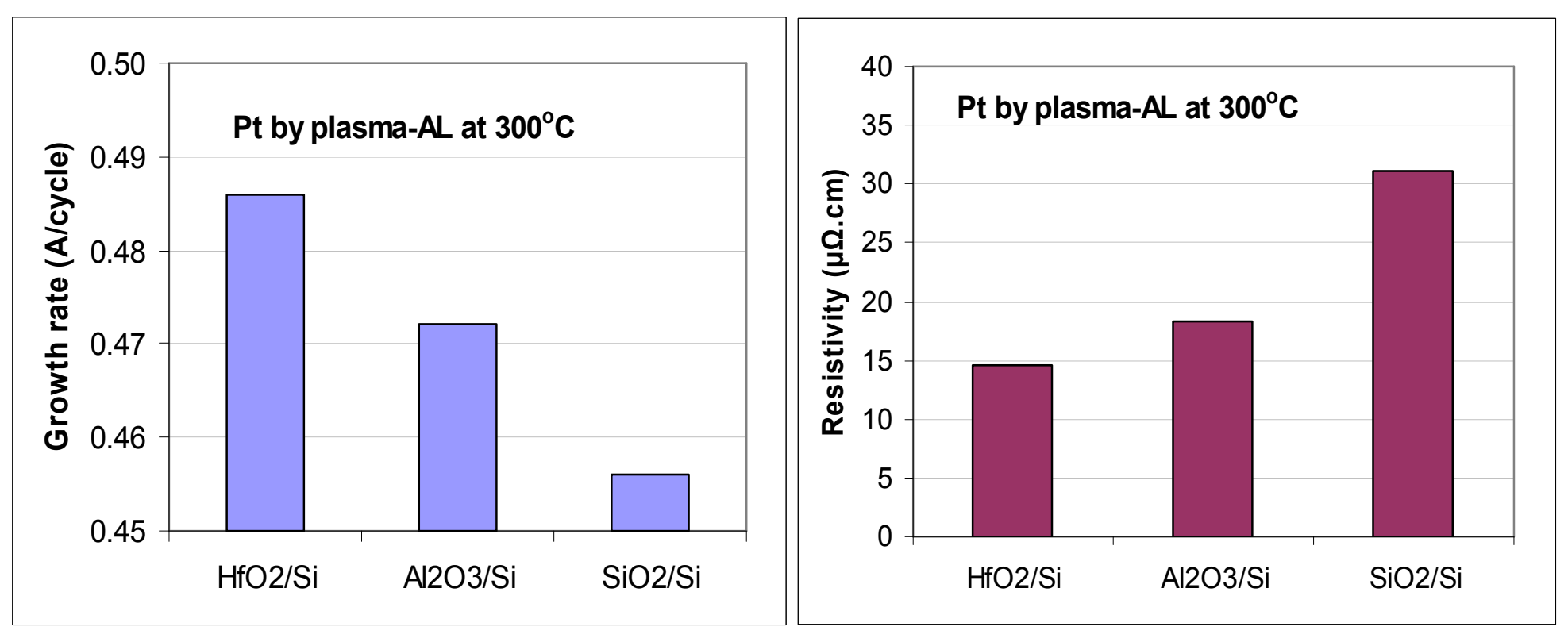

***Figure 10**, growth rate and resistivity of Pt-ALD layers on various oxides. HfO_2 is shown the highest growth rate and Lowest resistivity. It is believed that surface functionazation by plasma-ALD and rich-absorbed oxygen on HfO_2 surface are the reasons.*

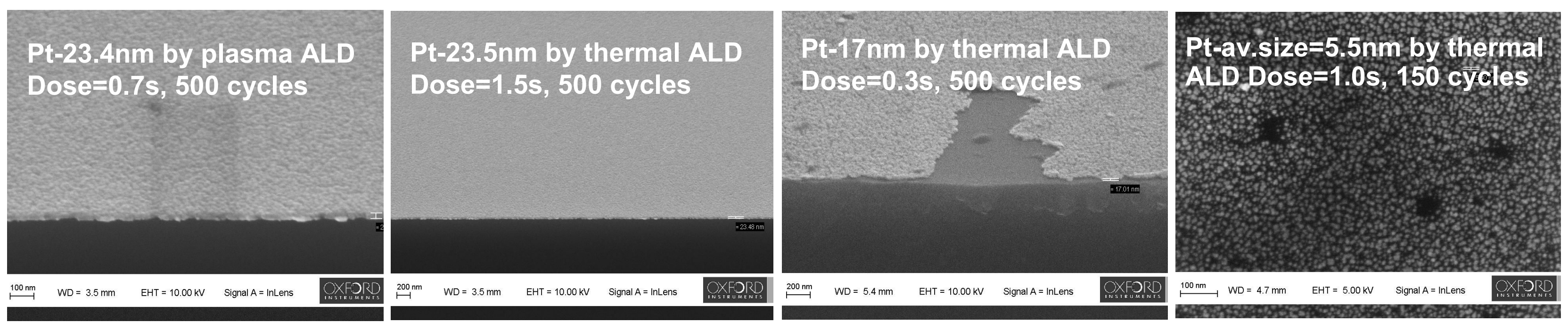

***Figure 11**, SEM of Pt-ALD films (cross-section of thickness and particle-size measurement).*

Table 2.
The process data of Pt films on the surface of Si, SiO_2, Al_2O_3 and HfO_2 deposited at 300° C by thermal and remote plasma ALD using $MeCpPtMe_3$ and O_2 gas or O_2 plasma (500 cycles)

Pt-sample runs	ALD process	Substrate	Particle size at 50 cycles	Particle size at 100 cycles	Growth rate (Å/cycle)	Resistivity (μΩ-cm)
1	Thermal-ALD	Si/native SiO_2(~1nm)	1.6 ±0.2	2.1 ±0.2	0.44 ±0.01	12.1 ±0.2
2	Plasma-ALD	Si/native SiO_2(~1nm)	2.0 ±0.2	3.2 ±0.2	0.45 ±0.01	12.5 ±0.2
3	Thermal-ALD	Si/SiO_2(10nm ALD)	2.2 ±0.2	2.6 ±0.2	0.43 ±0.01	15.1 ±0.2
4	Plasma-ALD	Si/SiO_2(10nm ALD)	2.5 ±0.2	3.6 ±0.2	0.44 ±0.01	31.2 ±0.5
5	Thermal-ALD	Si/Al_2O_3(18nm ALD)	/	/	0.46 ±0.01	25.2 ±0.5
6	Plasma-ALD	Si/Al_2O_3(18nm ALD)	/	/	0.47 ±0.02	18.3 ±0.3
7	Plasma-ALD	Si/HfO_2 (10nm ALD)	3.7 ±0.3	5.6 ±0.5	0.49 ±0.02	14.0 ±0.5

Conclusions

- Platinum films were deposited by both remote plasma and thermal atomic layer deposition (ALD) using methyl-cyclopentadienyl-trimethyl platinum (MeCpPtMe3) and O_2 as precursors on oxide materials.
- The ALD Pt-films deposited were homogeneous and resulted in a low resistivity of 4.6 μΩ-cm.

1. AES studies revealed high quality Pt films deposited by both thermal and plasma ALD with carbon impurity less than 1.5% and oxygen found only in the interface.
2. SEM and EDX were used to investigate Pt nucleation and growth in ALD processes. The plasma ALD can form bigger size Pt particles in the early stage and reduce the nucleation delay. In the O_2 plasma, O radicals are created, leading to two effects on the Pt-growth by reduce the nucleation delay: 1) providing active atomic O to the surface and increasing oxidation with the ligands of the chemisorbed precursor on the surface, 2) increasing Pt nucleation by extra plasma energy.

References
[1] H. C. M. Knoops, A. J. M. Mackus, M. E. Donders, M. C. M. van de Sanden, P. H. L. Notten and W. M. M. Kesselsb, *Electrochemical and Solid-State Letters,* **12** (7) G34-G36 (2009).
[2] M. Armand and J. M. Tarascon, *Nature (London)*, **451**, 652 (2008).
[3] R. R. Hoover and Y. V. Tolmachev, *J. Electrochem. Soc.*, **156**, A37 (2009).
[4] 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).

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