

# Comparative X-ray Photoelectron Spectroscopy Study of Plasma Enhanced Chemical Vapor Deposition and Micro Pressure Chemical Vapor Deposition of Phosphorus Silicate Glass Layers after Rapid Thermal Annealing

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**Abstract.** In this paper the bonding state of Phosphorus Silicate Glass (PSG) layers obtained by two different technological approaches, *i.e.* in two types of reactors: Plasma Enhanced Chemical Vapor Deposition (PECVD) and Micro Pressure Chemical Vapor Deposition ( $\mu$ PCVD) are investigated employing XPS and AES. The PSG layers are deposited at 380°C and 420°C in corresponding reactors. XPS and AES analyses show that Si2p peak recorded from PECVD layers are not as expected at their position characteristics of silicon dioxide but instead they are at the characteristic of elemental silicon. Plasma enhancement during deposition leads to less oxidized and more inhomogeneous layer. After rapid thermal annealing the Si2p peak is situated at position characteristic of silicon dioxide.

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## 1 Introduction

Many authors [1-12] investigated various methods of deposition (APCVD, PECVD,  $\mu$ PCVD) and different methods for characterization (XPS, AES, SEM, I-V, C-V) of doped and undoped SiO<sub>2</sub> layers. PSG are used effectively as

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medium insulating layers in modern microelectronics. They are prepared in various types of reactors and processes – APCVD, PECVD, LCVD depending on the technology applied. Some authors investigate parameters of the layers obtained depending on technological conditions and effect of additional treatment on the electrical parameters, chemical composition, structure and morphology of the layers.

It is the aim of this paper using XPS and AES to make comparative investigations of the layers obtained in two different reactors.

## 2 Experimental

The PSG layers were obtained in industrial reactors of the type PECVD and  $\mu$ PCVD at conditions listed in Table 1.

Table 1. Technological conditions of deposition

Technological conditions	Type of reactor	
	PECVD	$\mu$ PCVD
Temperature [ $^{\circ}$ C]	380	420
pH <sub>3</sub> (100%) [sccm]	25	7
O <sub>2</sub> [sccm]	14	200
N <sub>2</sub> O [l/min]	1.76	—
RF	60 W	—
SiH <sub>4</sub> (100%)	260	80
V <sub>dep</sub> [A/min]	160	120

Layers of the type  $\mu$ PCVD were deposited at 0.25 Torr micropressure and temperature of deposition 420 $^{\circ}$ C. The only oxidizing agent was oxygen and N<sub>2</sub>O. Layers of the type PECVD were prepared at temperature of deposition 380 $^{\circ}$ C.

## 3 Results and Discussion

Composition of layers obtained by PECVD and  $\mu$ PCVD is listed in Table 2.

As can be seen from Table 2 oxygen content is larger in case of PECVD layers. Content of Si is also higher in this case.

Table 2. Composition of layers obtained of the types PECVD and  $\mu$ PCVD

	C1s	N1s	O1s	Si2p	P2p	Au4f
$\mu$ PCVD ( $T_d = 420^{\circ}$ C)	18.9	0.8	54.9	23.0	3.3	0.1
PECVD ( $T_d = 380^{\circ}$ C)	8.5	1.6	60.0	26.8	2.8	0.3

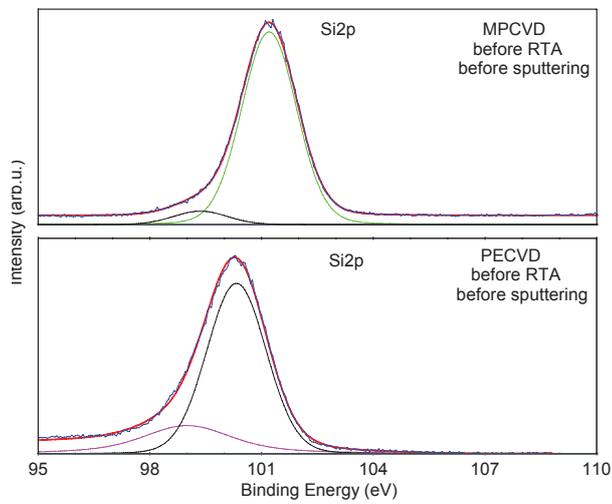


Figure 1. Si2p peaks from the same layers.

But if we compare Si2p peaks of the same layers in Figures 1a and b we can see that the peak from PECVD layer is shifted to lower energies corresponding to the position of silicon atoms in amorphous silicon [13]. This is because accelerated by the field silicon atoms are stuck in interstitial position not coinciding with apexes of polyhedral network of chemical bonds. These atoms are

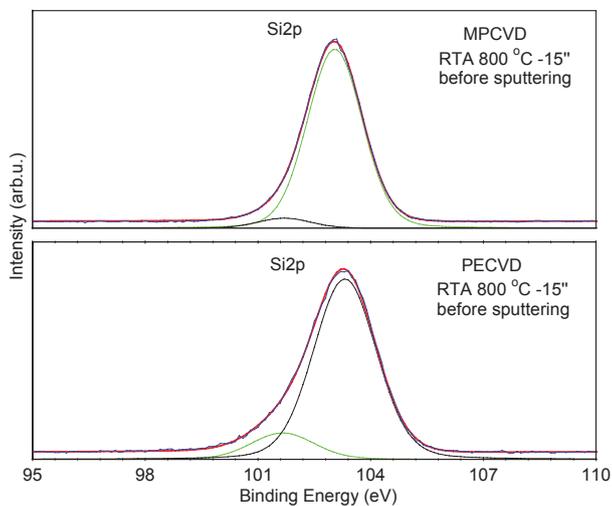


Figure 2. Comparison of Si2p peaks of the two types of expletive layers after RTA.

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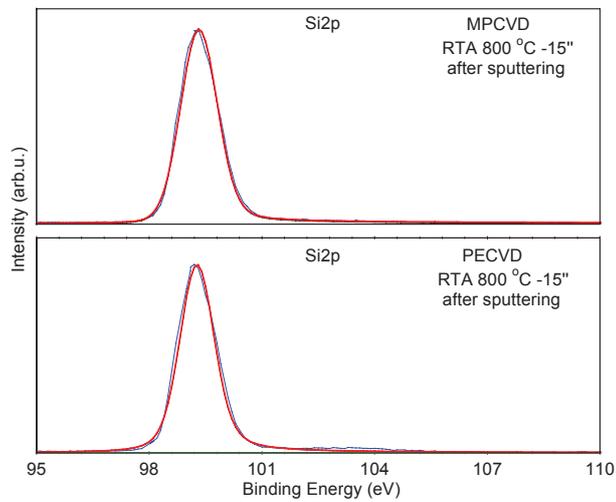


Figure 3. Si2p peaks recorded after RTA and sputtering with argon ions.

not chemically bonded yet. Due to action of two oxidizing agents (which have lower oxidation ability compared to  $O_2$  in  $\mu$ PCVD reactor) more oxygen is incorporated in the layer in interstitial positions. The feature at 101 eV is typical of SiC [14] and suggests presence of some Si-C bonds.

After rapid thermal annealing the Si2p peak is situated at a position of 103.20 eV characteristic of non stoichiometric ( $SiO_{1.8}$ ) silicon dioxide.

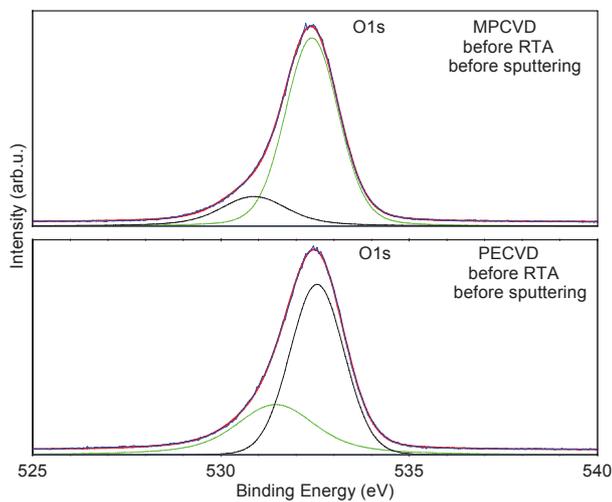


Figure 4. O1s peaks of both layers.

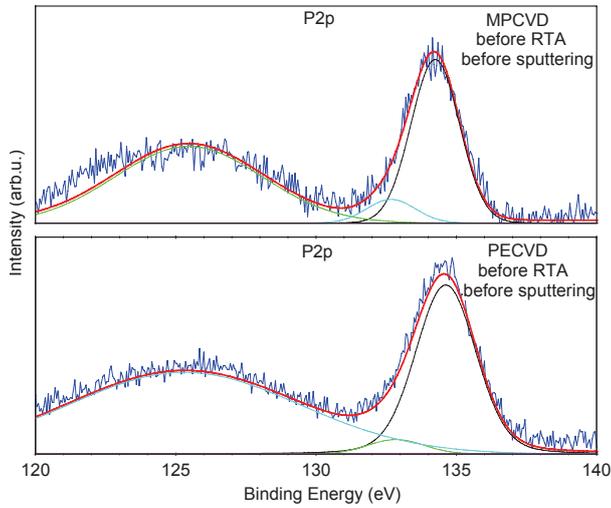


Figure 5. P2p peaks of the two layers.

In Figure 4 O1s peaks typical of both layers are illustrated. They are centered at 532.7 eV – energy characteristic of oxygen in SiO<sub>2</sub> or SiO<sub>2</sub>/(SiO<sub>2</sub>+SiC) [15]. O1s peak recorded from PECVD layer is broader suggesting more than one surroundings of oxygen atoms. One possible explanation of the peak at 530.8 eV obtained by deconvolution is interstitial position of oxygen atoms without chemical bonding to the nearest neighbor [16].

In Figure 5 the P2p peaks of the two corresponding layers are compared. The P2p peak of the PECVD film is broader and the content of phosphorus is higher in this case. Some more complex bonds using P atom as common in tetrahedral structure could be the reason for this. The peak position at 133 eV was identified by some authors [17] as due to P<sup>5+</sup> state resulting from PO<sub>4</sub><sup>3+</sup> atom group and the peak at 128.4 eV was assigned to P<sup>3+</sup> state.

As can be seen from Table 3 showing chemical composition after sputtering oxygen content is considerably decreased at expense of silicon. It is worth to note that sputtering removes all phosphorus from PECVD layer surface.

Table 3. Composition of the two layers spectra after sputtering with argon ions

	C1s	N1s	O1s	Si2p	P2p
μPCVD (after sputtering)	3.8	0.3	2.2	93.7	7.7
PECVD (after sputtering)	2.7	0.9	2.5	93.9	0

In Figure 6 Si2p spectra are shown recorded from the layers after sputtering. They are very similar centered 99.85 eV – energy which is characteristic of

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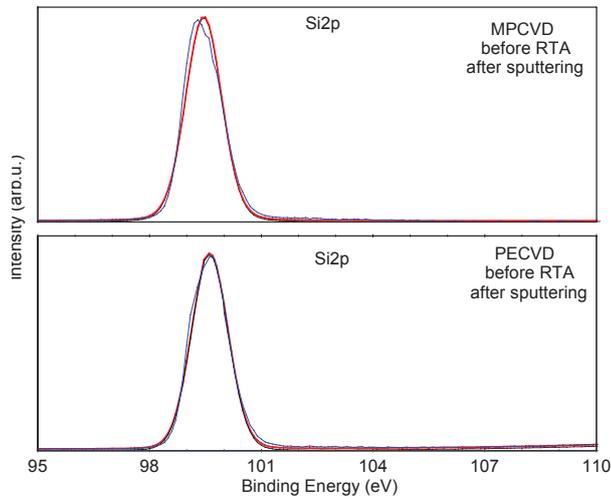


Figure 6. Si2p spectra recorded from the layers after sputtering.

elemental silicon [18]. This is obviously due to reducing effect of ion sputtering.

In Figures 7 and 8 O1s peaks of the two layers before and after sputtering are shown. In Figure 7 a peak centered at 532.7 eV characteristic of SiO<sub>2</sub>/(SiO<sub>2</sub>+SiC) [15] is visible. Sputtering leads to break of oxygen bonds and for that reason the peaks are shifted to lower energy positions and peaks are

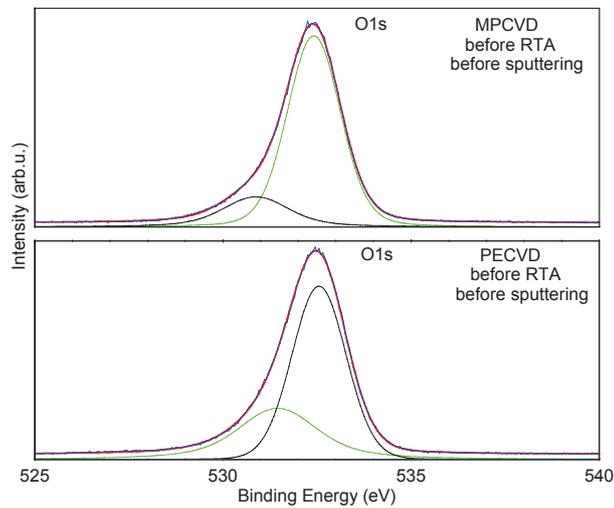


Figure 7. O1s peaks of the two layers before sputtering.

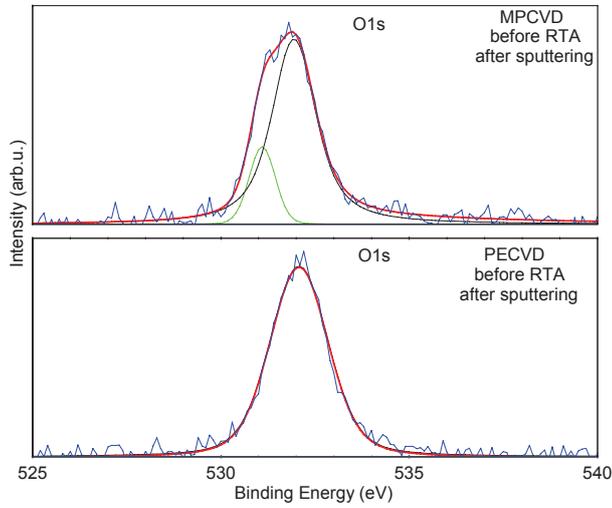


Figure 8. O1s peaks of the two layers and after sputtering.

sharper than before suggesting less complicated bonding after sputtering.

Figure 9 shows profile in depth of the  $\mu$ PCVD layer recorded using sputtering with Ar ions. We can recognize surface layer corresponding to stoichiometry of  $\text{SiO}_2$  with some phosphorus atoms incorporated in it. After about 40 min sputtering the O1s peak is very small and the layer in depth consists almost of pure silicon.

Figure 10 shows a profile in depth of the PECVD layer recorded using sputtering with Ar ions. Complicated shape of the graphs of Si and oxygen contents

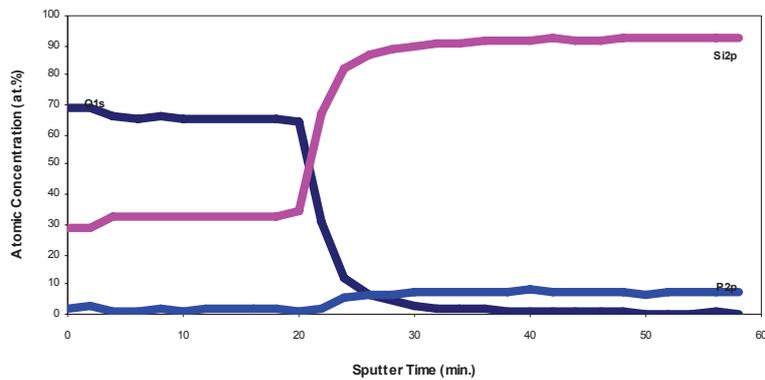


Figure 9. A profile in depth of the layer  $\mu$ PCVD recorded using sputtering with Ar ions.

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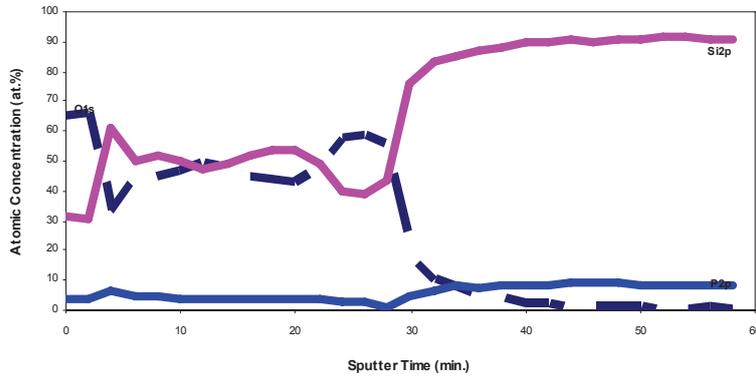


Figure 10. A profile in depth of the layer PECVD recorded using sputtering with Ar ions.

suggests that the layer is inhomogeneous but after about 40 min sputtering O1s peak also is very small and the layer in depth consists almost of pure silicon. Ripples on the graphs suggest inhomogeneity of the layer on nm scale.

AES investigations reveal that layers deposited in PECVD reactor contain Si which is not oxidized. This is due to lesser oxidizing ability of oxidizing gases used (namely diluted oxygen:  $N_2O + O_2$ ) compared to  $O_2$  used in PCVD reactor. Analyses of the data show that PECVD layers have stoichiometry  $SiO_{1.84}$  while layers deposited without plasma enhancement exhibit stoichiometry  $SiO_{1.98}$ . Characteristic of PECVD layers is the existence of surface (20 nm thick) layer of depleted oxygen content which is due to decrease of the power of plasma at the switching of the reactor. These layers are characterized also by lower etch rate in p-etcher ( $HF:NH_4F$  1:20) featuring  $V_{etch} = 5 \text{ \AA/s}$  while layers obtained by PCVD reactor have  $V_{etch} = 7 \text{ \AA/s}$ .

After additional thermal treatment at  $1000^\circ\text{C}$  for 30 min in oxygen atmosphere etch rate of PECVD layers increases and becomes equal to that of PCVD layers. This is one more evidence of full silicon oxidation.

These AES data correlate very well with the results from XPS analyses. Situation of the Si2p peak at 100 eV is due to interstitial positions of silicon atoms. This means that Si and P are not fully oxidized.

Formation of those layers is a result of deposition and chemical reactions leading to metastable compounds. Small amount of N is involved in rings as can be seen from the line N1s at 400 eV in wide scan spectra [20].

The P2p peak of PECVD is broader and content of phosphorus is higher in this layer. Due to relatively high reactivity of phosphorus at elevated temperatures exchange of parts through and reconstruction of bonds occur. Groups of  $PO_4$  (tetrahedral) connect through common O atoms and form complex structures. Basic groups  $PO_4$  consisting of one atom P and tetrahedral configuration of oxygen

atoms contain these additional electrons for every group needed to form closed valence shell. These additional electrons are due to instant participation of oxygen atoms in two tetrahedra or due to instant participation of Si atoms, or due to transition of electrons (depending on ionization of Si atom) [17]. The Si2p peak observed for PECVD layer is shifted to lower energies corresponding to silicon atoms in amorphous silicon. This is because accelerated by the field silicon atoms are stuck in interstitial position not coinciding with apexes of polyhedral network of chemical bonds. These atoms are not chemically bonded yet. After rapid thermal annealing Si2p peak is situated at position characteristic of silicon dioxide because chemical bonds are established.

#### 4 Conclusion

Due to peculiarities of plasma enhancement PSG layers deposited are depleted of Si due to lower oxidizing ability of  $N_2O+O_2$  and silicon is not fully oxidized compared to the process with  $O_2$  used in  $\mu$ PCVD reactor.

Plasma enhancement during deposition leads to less oxidized and more inhomogeneous layer with silicon atoms in interstitial positions which are not bonded by chemical bonds. After rapid thermal annealing chemical bonds characteristic of  $SiO_2$  are established.

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