

## On adsorption of aluminium and methyl groups on silica for TMA/H<sub>2</sub>O process in atomic layer deposition of aluminium oxide nano layers

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**Abstract.** A detailed chemisorption mechanism is proposed for the atomic layer deposition (ALD) of aluminium oxide nano layers using trimethyl aluminum (TMA) and water as precursors. Six possible chemisorption mechanisms, complete ligand exchange, partial ligand exchange, simple dissociation, complete dissociation via ligand exchange, complete dissociation and association, are proposed and related parameters like ligand to metal ratio (L/M), concentrations of metal atoms and methyl groups adsorbed are calculated and compared against reported values. The maximum number of methyl groups that can get attached on the surface is calculated in a different way which yields a more realistic value of 6.25 per nm<sup>2</sup> substrate area. The dependence of the number of metal atoms adsorbed on OH concentration is explained clearly. It is proposed that a combination of complete ligand exchange and complete dissociation is the most probable chemisorption mechanism taking place at various OH concentrations.

**Keywords.** ALD; chemisorption; aluminum oxide.

### 1. Introduction

The silicon–silicon dioxide MOSFET was invented in 1960 by Kahng and Attala (1960). By 1965 G E Moore was able to establish the famous trend known as Moore's law. Since then the main focus was on optimizing silicon dioxide as the gate oxide. This was due to the several key advantages of the thermally grown silicon dioxide offered (Wilk *et al* 2001). But the enhanced performance at a lower cost requires a higher density of transistors on a wafer (Baccarani *et al* 1984). This forced the feature sizes to be reduced, which in turn means a reduced thickness of the gate oxide. But as the gate oxide thickness is reduced below 2–3 nm, electron tunneling and high leakage currents occur in silicon dioxide which raises serious reliability issues (Wilk *et al* 2001; Jones *et al* 2004). This difficulty can be overcome if a thicker layer of a high- $k$  material is used as the gate oxide instead of the traditional silicon dioxide. Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) is one such high- $k$  material that is investigated by researchers for replacing SiO<sub>2</sub> as gate oxide in MOSFETs (Wilk *et al* 2001; Jones *et al* 2004; Lin *et al* 2005; Katemreddy *et al* 2006; Gao *et al* 2007). Among the several methods that have been used for the deposition of aluminium oxide films, atomic layer deposition (ALD) is found to be the most suitable technique for the formation of nano layers

of Al<sub>2</sub>O<sub>3</sub> (Dueñas *et al* 2006; Katemreddy *et al* 2006). ALD is a cyclic process with a sequence of self terminating process steps. ALD films grow on any substrate topology, with very good conformality and excellent uniformity (Pessa *et al* 1983; Goodman and Pessa 1986; Crowell 2003; Jones *et al* 2004; de Rouffignac and Gordon 2006). ALD is a process in which two precursors are introduced into a hot chamber one after the other with a purge of inert gas in between. Surface controlled reactions take place on the substrate on which a conformal pin hole free thin film is formed monolayer by monolayer.

Trimethyl aluminum (TMA)/H<sub>2</sub>O process is considered as most ideal for ALD of Al<sub>2</sub>O<sub>3</sub> nano layers (Ott *et al* 1996; Wank *et al* 2004; Gao *et al* 2007). This is because the precursors have very good reactivity, are thermally stable and the gaseous reaction product, methane, is rather inert.

When a precursor molecule makes contact with a solid surface, atoms or groups which are to be included in the film will be adsorbed on the surface and other atoms are removed as gaseous reaction byproducts. Non-reversible chemisorption is the mechanism taking place on the surface. Since the chemisorption involves making and breaking of bonds between the adsorbent and the surface, only a monolayer is adsorbed.

Chemisorption mechanism can be broadly divided into three types: (a) ligand exchange, (b) dissociation and (c) association, details of which are given elsewhere

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(Puurunen 2005b). We try to present here a more detailed surface reaction mechanism for the adsorption of metal and ligands and a different approach to calculate the maximum number of ligands which yields a more realistic value.

## 2. Model

Siimon and Aarik (1997) and Puurunen (2003) developed independently a model for calculating the maximum growth per cycle (GPC) of ALD grown layers. In this model, a theoretical maximum amount of precursor ligands adsorbed is calculated assuming a close packed monolayer of the ligands ( $L$ ), which is then divided by the ligand to metal ratio ( $L/M$ ) of the precursor to yield the information regarding the metal atoms ( $M$ ) adsorbed. This model is applied by Puurunen (2005b) to TMA/ $H_2O$  ALD process to calculate GPC. By taking the value of van der Waals radius (VDR) of methyl groups as 0.2 nm, he obtained a value for maximum amount of methyl groups adsorbed as 7.2 per  $nm^2$ .

### 2.1 OH concentration

Let us consider a substrate area (say, silicon covered with an oxide layer) of dimension  $1 \times 1$  nm. The surface of silica naturally has attached to it OH groups from various forms of silanols like free silanols, bridged silanols, geminal silanols and tertiary silanols in addition to siloxane bridges. This is generally due to the wafer cleaning procedures like RCA, Standard Clean-2, Piranha etc which leave a protective hydrous oxide film on the surface (Sparacin *et al* 2005). Considering the VDR of OH group as  $\sim 0.13$  nm (Pauling 1988), we can see that the maximum number of OH groups that can be accommodated in  $1$   $nm^2$  area is 14.79 or  $\sim 15$ . Here instead of considering a close packed system we have considered that each OH group effectively occupies an area of a square with sides equal to twice the VDR of OH group. The value obtained is comparable to the reported maximum value of 12 hydroxyl groups per  $nm^2$  (Stumm 1992; Okorn-Schmidt 1999). Here 15 is considered as the maximum number of OH groups which can be physically arranged on the surface of the substrate.

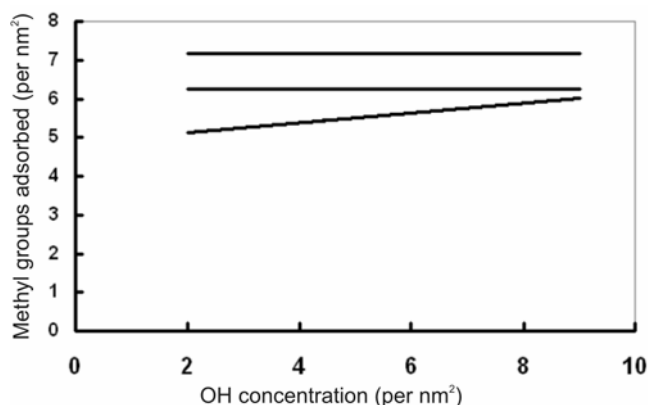
### 2.2 Methyl group concentration

Taking the VDR of methyl group as 0.2 nm, it can be shown that 6.25 methyl groups can be accommodated in  $1$   $nm^2$  area following the same reasoning as that for OH groups. This value is confirmed by experiments also (Uusitalo *et al* 2000). This also means that each methyl group effectively utilizes an area of a square with sides equal to twice the VDR of methyl group. Out of the maximum 15 OH sites in  $1$   $nm^2$  area, 8.75 are sterically

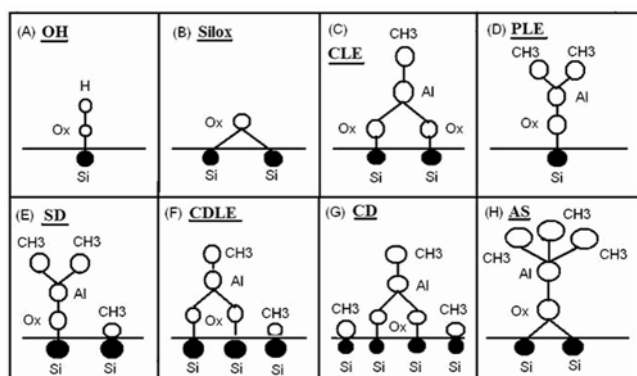
hindered (shielded) by methyl groups where other methyl groups cannot get attached. Hence a small variation of OH concentration will not affect the methyl group concentration on the substrate surface.

As the OH concentration decreases, the methyl group concentration need not decrease. This is because 15 is the maximum possible number of OH groups per  $nm^2$  substrate area. In practice, it will be a combination of OH groups and siloxane bridges which exist on the surface, i.e. surface need not contain the maximum number of OH groups (from free, geminal or [hydrogen] bridged silanols) at any time but some space can be occupied by the siloxane bridges also. This is especially true above a substrate temperature of 373 K, as above this temperature bridged silanols condense to form siloxane bridges (Alkan and Dogan 2006). As the OH concentration decreases (possibly at higher temperatures), siloxane bridges present on the silica surface start breaking and combine with the methyl groups and Al atoms of TMA. It is reported that (Si–O) behaves like a Lewis base (Okorn-Schmidt 1999) and hence this reaction is favoured by Si–O and TMA. This is the process which is called ‘dissociation’. Moreover ‘association’ also can take place with these siloxane bridges as illustrated in the same model. Partial ligand exchange also is a possibility at reduced OH concentrations in which one OH group adsorbs two methyl groups (explained in §2.3).

If the VDR of a siloxane bridge (Si–O–Si) is considered as  $\sim 0.26$  nm (Pauling 1988), 3.6 siloxane bridges maximum will be present in  $1$   $nm^2$  substrate area. Since maximum three methyl groups can be accommodated by one broken siloxane bridge (figure 2(E)), a maximum of  $\sim 11$  methyl groups can be accommodated in unit  $nm^2$  substrate area. But it has already been proved previously that maximum 6.25 methyl groups only can be accommodated per  $nm^2$  area, the methyl group concentration will



**Figure 1.** Methyl groups adsorbed per  $nm^2$  of the substrate surface. (Top line, predicted by Puurunen (2005b) (value 7.2), middle line, predicted by AP&KRRK (value 6.25), bottom line, observed methyl group adsorption (methyl group range  $\sim 5$ –6) (Puurunen 2005a, trend line with equation  $y = a + bx$ , where  $a = 4.9 \pm 0.2$  and  $b = 0.14 \pm 0.06$ )).



**Figure 2.** (A) & (B) Schematic of OH and siloxane bridge with oxygen atom on the surface (Puruunen 2005a), (C) complete ligand exchange [CLE] using two OH sites (Puruunen 2005b), (D) partial ligand exchange [PLE] using one OH site, (E) simple dissociation [SD] which uses one siloxane site, (F) complete dissociation via ligand exchange [CDLE] using one siloxane and one OH site, (G) complete dissociation [CD] which uses two siloxane sites and (H) association [AS] which uses one siloxane site (Puruunen 2005b).

again be 6.25 under this situation. At the lowest concentration of OH groups of 2 per nm<sup>2</sup> (Stumm 1992; Okorn-Schmidt 1999), i.e. when the surface is covered predominantly by siloxane, the adsorption process may proceed as depicted in figure 2(G) or (H), in which two siloxane bridges accommodate three methyl groups or one siloxane bridge accommodates three methyl groups, respectively (This is termed as ‘complete dissociation’ [CD] and ‘association’, respectively later in this article). In both cases it can be shown that the maximum methyl group concentration is 6.25 even at a lower concentration of OH on the surface of the substrate [figure 1 (middle line)]. This is closer to the observed value of 5–6 (bottom line) than 7.2 (top line) predicted earlier (Puruunen 2005a figure 22b; In fact a closer look at this figure reveals that except two points all other points are closer to the value 6).

It has to be noted that in this article we are not going into the reasons for the variation of OH sites on the substrate surface. It can be due to deposition temperature during ALD or substrate heat treatment before deposition (Puruunen 2005b; Alkan and Dogan 2006).

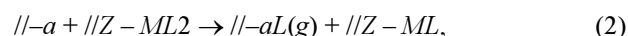
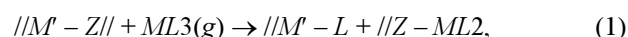
### 2.3 Detailed chemisorption mechanism

In the ligand exchange reaction, one methyl group of TMA combines with hydrogen of the surface hydroxyl group and escapes as methane. The remaining methyl groups and the aluminium atom get attached to the oxygen of the OH group (Puruunen *et al* 2000; Puruunen 2005b). If the reaction continues on the surface, we end up with one methyl group connected to the surface via an aluminum atom. Other two methyl groups combine with hydrogen

of the surface OH sites and escape as CH<sub>4</sub>. Thus the ligand to metal ratio (CH<sub>3</sub> is the ligand and aluminium is the metal in the case of TMA),  $L/M = 1$  for this case and this will result in adsorption of maximum metal atoms (Al) to the surface. This is called complete ligand exchange (CLE). But if the ligand exchange reaction stops at the first step, then two methyl groups will be attached to the surface OH site via an aluminium atom. Under this condition we will have  $L/M = 2$ . This is partial ligand exchange (PLE). For the usual simple dissociation (SD) and association (AS) (which are as described in Puruunen 2005b), we have three methyl groups for a single metal atom and hence the  $L/M = 3$  for them.

Simple dissociation is a phenomenon in which a surface siloxane bridge breaks and aluminium atom with two methyl groups of TMA gets attached to the oxygen of the siloxane bridge and the remaining methyl group attaches itself with the silicon atom on the surface. So in this case three methyl groups and one metal (Al) atom get attached to the substrate surface.

Consider a situation with less OH concentration but still with sufficient numbers to combine with methyl groups. Dissociation can proceed further on the surface, with a methyl group which is connected to aluminium atom, gets attached to the hydrogen atom of an OH site and escapes as methane. In this case called ‘complete dissociation via ligand exchange (CDLE)’, there are two methyl groups of the original TMA molecule attached to the silica; one attached to the siloxane bridge via aluminium atom and another directly connected to the silicon atom on the substrate, giving an  $L/M$  ratio of 2. Using the notations given in Puruunen (2005b) this can be represented for TMA as follows



where  $//M'$ ,  $//Z$  are siloxane surface sites and  $--a$  is OH site.  $M = \text{Al}$  and  $L_3 = \text{CH}_3$ .

Dissociation can proceed in one more way in the absence of sufficient OH sites. This is shown in figure 2. In this case from stage ‘E’, reaction proceeds to stage ‘G’ by breaking one more siloxane bridge. Note that in this case the  $L/M$  ratio is 3, which is the same as the simple dissociation. This is called ‘complete dissociation’.

So for dissociation mechanism, we have two  $L/M$  ratios, i.e. 2 and 3 corresponding to high and low OH concentrations on the surface.

### 2.4 Aluminium concentration

For the case of complete ligand exchange (CLE), we have one metal atom for one ligand. Therefore, the total number of metal atoms per nm<sup>2</sup> area is obtained by dividing 6.25 by the  $L/M$  ratio ( $= 1$  in this case), as 6.25. For each Al

atom adsorbed by CLE two OH sites should be used. Therefore, for 6.25 Al atoms adsorbed, 12.5 OH sites are required. For partial ligand exchange (PLE),  $L/M$  ratio = 2. Here we have one metal atom for two ligands. Therefore, the number of metal atoms adsorbed per  $\text{nm}^2$  area is equal to  $6.25/2$  equal to 3.125 and for 3.125 Al atoms adsorbed, OH sites required are 3.125. For simple dissociation and association the number of metal atoms per  $\text{nm}^2$  is obtained as 2.08 by considering one metal atom for three ligands. (Here we have to note that all the three methyl groups get attached to the surface either in association with the aluminium atom or two methyl groups with the aluminium atom and one methyl group alone on the surface site). Since for SD and AS, only siloxane sites are required, the number of siloxane sites used for 2.08 Al atoms is 2.08. For CDLE the number of metal atoms per  $\text{nm}^2$  area is  $6.25/2 = 3.125$ . Since for CDLE one siloxane bridge and one OH site are required for adsorption of one Al atom, for adsorption of 3.125 Al atom, 3.125 siloxane bridges and 3.125 OH sites are required. For complete dissociation (CD),  $L/M$  ratio is 3 and hence the number of Al adsorbed is  $6.25/3 = 2.08$ . But for CD two siloxane bridges are required for adsorption of one Al atom and hence for adsorption of 2.08 Al atoms  $2 \times 2.08 = 4.16$  siloxane bridges are required. But we know that only 3.6 siloxane bridges maximum can be accommodated in  $1 \text{ nm}^2$  area of the substrate. Therefore, the number of maximum Al atoms that can be accommodated by CD is only  $(2.08/4.16) \times 3.6 = 1.8$ . This is the minimum number of Al atoms accommodated on  $1 \text{ nm}^2$  area of the substrate when the surface is covered with only siloxane bridges and no OH groups present. The OH/siloxane sites which are not used in the case of each adsorption mechanism are sterically hindered by adsorbed methyl groups.

The  $L/M$  ratio, concentration of metal atoms, concentration of ligands and OH/siloxane sites used are given in table 1 for different chemisorption mechanisms.

It has to be noted that any of the chemisorption mechanisms or combination of them can be active at any time for any concentration of OH groups. Since CLE consumes more OH sites, this process can dominate only when more OH sites are available on the surface. On the contrary for SD, CD and AS no OH sites are required which make them dominant processes at low and very low OH concentrations.

From an investigation on the dependence of aluminum concentration on OH values we try to find out a model for the possible adsorption mechanisms which are active at different OH concentrations. For this we assume that CLE takes place on available OH sites and SD or CD takes place at the available siloxane sites. Further we assume that whenever possible a combination of these mechanisms occur on the surface with one or the other mechanism dominating.

From table 1, we can see that for an OH concentration of 12.5 the concentration of Al atoms is 6.25 per  $\text{nm}^2$ . Let us now take an OH concentration of 10 on the surface. (a) Number of Al atoms deposited per  $\text{nm}^2$  due to CLE is  $(6.25/12.5) \times 10 = 5$ , (b) area covered by 10 OH =  $(1/15) \times 10 = 0.67 \text{ nm}^2$ , (c) area covered by siloxane bridges =  $(1 - 0.67) = 0.33 \text{ nm}^2$ , (d) number of siloxanes in this area =  $(3.6/1) \times 0.33 = 1.19$ , (e) if we assume SD along with CLE the Al atoms that can be accommodated by SD = (no. of Al atoms adsorbed/no. of siloxane sites needed for this for SD)  $\times 1.19 = (2.08/2.08) \times 1.19 = 1.19$ , (f) therefore, total number of Al atoms on the surface due to CLE and SD =  $5 + 1.19 = 6.19$  and (g) if we assume CD along with CLE the Al atoms that can be accommodated by CD = (no. of Al atoms adsorbed/no. of siloxanes needed for this for CD)  $\times 1.19 = (1.8/3.6) \times 1.19 = 0.595$ .

Repeating these calculations for OH concentrations 8, 6, 4 and 2 we get the following results which are summarized in table 2. Table 2 also contains Al value for zero OH concentration (i.e. when there are 3.6 siloxane bridges on the surface so that no space left for OH groups) taken from table 1.

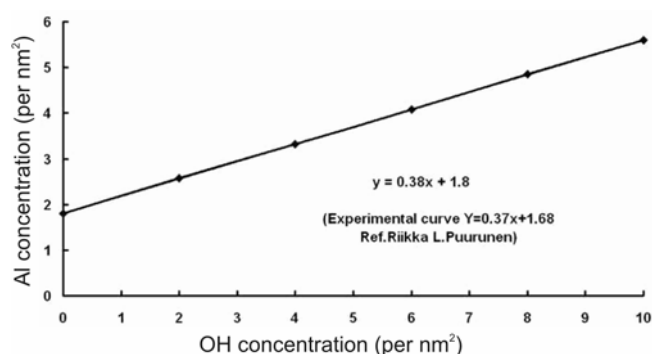
Figure 3 shows the number of aluminium atoms adsorbed per  $\text{nm}^2$  area of the substrate as a function of OH concentration on the surface. This plot is generated using data from the first and last columns of table 2. We have plotted all the data given in various columns of table 2 against OH concentrations and found that data in the last column fits exactly the experimental curve (figure 22a of Puruunen (2005b)). Equation for the experimental curve is given as  $Y = 0.37x + 1.68$ , whereas the present curve is  $Y = 0.38x + 1.8$ . This shows that there is a very good probability of the chemisorption mechanisms to be a combination of CLE and CD with CLE dominating at higher OH concentrations and CD at lower concentrations.

**Table 1.** Types of chemisorption mechanisms and related parameters.

Type of adsorption mechanism	$L/M$ ratio	No. of Al atoms adsorbed per $\text{nm}^2$	No. of methyl groups adsorbed per $\text{nm}^2$	No. of OH/siloxane sites used
Complete ligand exchange (CLE)	1	6.25	6.25	12.5 OH
Partial ligand exchange (PLE)	2	3.125	6.25	3.125 OH
CDLE	2	3.125	6.25	3.125 OH + 3.125 Silox.
Simple dissociation (SD)	3	2.08	6.25	2.08 Silox.
Complete dissociation (CD)	3	2.08 (max. possible 1.8)	6.25	4.16 Silox. (max. possible 3.6 only)
Association (AS)	3	2.08	6.25	2.08 Silox.

**Table 2.** Relationship between OH concentration per nm<sup>2</sup> area of the substrate and Al concentration for different chemisorption mechanisms.

OH concentration	Al due to CLE	Al due to SD	Al due to CD	Al due to CLE + SD	Al due to CLE + CD
10	5	1.19	0.595	6.19	5.595
8	4	1.69	0.845	5.69	4.85
6	3	2.16	1.08	5.16	4.08
4	2	2.63	1.315	4.63	3.32
2	1	3.13	1.57	4.13	2.57
0	0	3.6	1.8	3.6	1.8

**Figure 3.** Plot of OH concentration vs number of aluminium atoms adsorbed per nm<sup>2</sup> area of the substrate as given in the last column of table 2. This shows that the process most probably is a combination of CLE and CD.**Table 3.** Energies associated with various bonds.

Bond	Energy (eV)
Al–C	3.26
O–H	4.3
Al–O	4.62
C–H	4.4

As outlined earlier since any or a combination of the adsorption mechanisms can be active any time with differing contributions of each we may get different Al atom concentrations depending upon the experimental conditions. The present curve most probably shows one possibility of Al atom deposition that can be achieved at various OH concentrations on the substrate surface which satisfies the experimental data.

The transient pressure measurements during micro pulse dosing of TMA reported earlier by the team of Alan Weimer and George (McCormik *et al* 2007) have shown that TMA reacts with AlOH surface groups and liberate two CH<sub>4</sub> molecules, which supports the proposed dominant CLE surface reaction mechanism, over PLE.

Also if the total reaction energy is expressed in terms of bond energy (for example, as given in Xu and Musgrave 2004) for CLE and PLE we have for CLE,  $\Delta E = 2E$  (Al–C in TMA) +  $2E$  (O–H in surface group) –  $2E$  (Al–O in product) –  $2E$  (C–H in product CH<sub>4</sub>) = –2.92 eV and

for PLE,  $\Delta E = E$  (Al–C in TMA) +  $E$  (O–H in surface group) –  $E$  (Al–O in product) –  $E$  (C–H in product CH<sub>4</sub>) = –1.46 eV; (bond energies are given in table 3). This shows that CLE and PLE are exothermic processes and CLE is the more possible process.

These facts clearly show that at higher OH concentrations, CLE is the dominant chemisorption mechanism. We have already seen in §2.3 that at very low OH concentrations CD is the more probable chemisorption mechanism.

The present model is in agreement with the ‘adsorbate inhibition model’ in which the methyl termination inhibits the adsorption of excess TMA gas (Nishizawa and Kurabayashi 1988). This is evident from the fact that Al concentration never exceeds the methyl group concentration on the surface of the substrate.

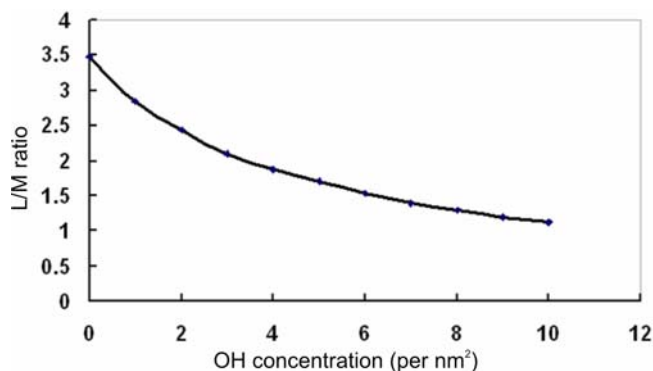
Figure 4 shows the  $L/M$  ratio as a function of surface OH concentration. The points on the graph are generated using the constant methyl group concentration (6.25, from figure 1) and concentration of aluminium atoms adsorbed (from figure 3). There is a reasonable agreement with the  $L/M$  ratios given by figure 22c of Puruunen (2005b) which are calculated using experimental values.

For each adsorbed methyl group, a carbon atom is present in the deposit. Hence for a maximum methyl group adsorption of 6.25 per nm<sup>2</sup> we have an equal concentration of carbon content per nm<sup>2</sup>. The observed maximum carbon content is 6 per nm<sup>2</sup> (Puruunen 2000) which agrees reasonably well with 6.25 predicted here.

### 3. Conclusions

A detailed chemisorption mechanism is proposed for the adsorption of methyl groups and aluminium atoms on the silica surface in the ALD of aluminium oxide using TMA/H<sub>2</sub>O precursors. Important conclusions are given below.

(I) Maximum number of methyl groups that can be accommodated on unit nm<sup>2</sup> area of the surface is 6.25. This was proved by considering the VDR of OH groups and siloxane bridges and assuming that they occupy the area of circumscribed square whose one side is equal to twice the VDR of the respective group. It is also assumed that only on these sites methyl groups get attached and not on any available space on the substrate surface.



**Figure 4.**  $L/M$  ratios plotted against OH concentrations. Values of  $L/M$  are generated by dividing the maximum methyl group concentration (6.25 per nm<sup>2</sup>) by Al concentration at different values of OH concentration (from figure 3). The curve agrees well with the experimental  $L/M$  ratio curve (Puruunen 2005b).

(II) The chemisorption process consists of six different mechanisms: complete ligand exchange, partial ligand exchange, and simple dissociation, complete dissociation via ligand exchange, complete dissociation, and association.

(III) Dependence of the number of metal atoms adsorbed on OH concentration is explained clearly by giving a theoretical explanation for the connection between OH, methyl and Al concentrations. The predicted Al concentration for different OH values agrees very well with reported experimental data.

(IV) It is proposed that Al concentration on the substrate surface is due to a combination of two types of chemisorption mechanisms: complete ligand exchange and complete dissociation. For high OH concentrations, CLE dominates the process while for low OH concentrations CD dominates. Domination of CLE over PLE is established by a simple bond energy calculation.

(V)  $L/M$  ratios are calculated. These are plotted against surface OH concentrations and compared against observed values and are found to agree well.

The carbon content deposited on the substrate surface is predicted which matches with the observed value.

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