Formation of Alumina Nanoparticles in a Cold Wall Atomic Layer Deposition System and their Characterization

An explanation for the possible mechanism of formation of alumina nanoparticles in Atomic Layer Deposition process of alumina using Trimethyl Aluminum (TMA) and water in a cold wall ALD chamber based on the physisorption of TMA and surface energy of alumina thin films is presented here. Characterizations of synthesized particles are also presented.

7.1 Introduction

As outlined in the previous chapters Atomic Layer Deposition is a cyclic process with a sequence of self terminating process steps and films grow on any substrate topology [1-5]. The intrinsic surface control mechanism of ALD process is based on the saturation of an individual, sequentially-performed surface reaction between the substrate and precursor molecules. Most metal reactants used in ALD fulfill the criteria of self termination and adsorption in a monolayer. In the reaction of metal reactants (ML\textsubscript{n}) with a solid oxide material, however, MO\textsubscript{n/2} particles can form in a single saturating reaction of metal reactant [6-12] and so multilayer formation occurs. These unexplained formation of nanoparticles of metal oxides in the chamber during the ALD of binary oxides for high-k gate applications was occasionally reported in the literature[6,7]. Metal oxide particles were formed during the reaction of metal precursor with oxide substrate used for various applications. In this present work we report the formation of alumina nanoparticles at the cold walls of the ALD chamber during the deposition of alumina films by atomic layer deposition. Trimethyl aluminum (TMA) and water were used as precursors. Attempts were made to explain the reaction mechanism which controls the formation of alumina nano particles. Detailed characterizations of these alumina nano particles
were also done. Detailed description of chemisorption mechanisms involved during TMA exposure on the substrate in done at chapter 4.

7.2 Formation of metal oxide particles in atomic layer deposition: A brief review

The first report of MO\(_{n/2}\) particle formation during CVD was reported by Kooyman et al. in 1992 [6]. They observed TiO\(_2\) particles after the reaction of TiCl\(_4\) with silica crystals. The particles were 0.2-0.3\(\mu\)m in size and were chemically anchored to silicon substrate. In ALD investigations, MO\(_{n/2}\) particle formation during ALD was first reported by Haukke et al. in 1993 [7]. They also observed TiO\(_2\) particles after the chemisorption of TiCl\(_4\) on porous high surface area silica. Haukke et al. examined particle formation in detail and found that TiO\(_2\) particles were thin plate and with maximum dimensions of 2\(\mu\)m. These findings were in accord with the reports by Kooyman [6]. These authors concluded that TiO\(_2\) formation is saturating and limited by the number of hydroxyl groups on the silicon substrate, and found that size and crystallinity of particles depend on process conditions, like reaction temperature and nature of substrates. Ritala et al. also reported unexpected observation of particles when they investigated the growth of TiO\(_2\) on the flat oxide substrates by the TiCl\(_4\)/H\(_2\)O ALD process [13,14].

In 1996 Kytokivi et al. reported the formation of ZrO\(_2\) particles when they investigated the ZrCl\(_4\) chemisorption on porous high surface area silica and on alumina [9]. ZrO\(_2\) particles were considerably smaller, with dimensions in the order of 10 nm [10]. Kytokivi et al. suggested that the ZrO\(_2\) particles might be from the formation and decomposition of hydroxychloride Zr(OH)\(_{m}\)Cl\(_{4-m}\) or oxychloride ZrOCl\(_2\) intermediates. Kytokivi and Haukka showed by infrared measurements that TiO\(_2\) and ZrO\(_2\) particles are bonded to silica substrate through Si-O-Ti and Si-O-Zr bonds respectively [11].

In 2004 Elam et al. and Graugnard et al. again reported the formation of TiO\(_2\) [15-17]. In 2005 Rikka L. Puurunen published a review on the formation of Metal Oxide particles in Atomic Layer Deposition during the chemisorption of metal chlorides [9]. She reviewed the experimental
results and suggested a mechanism for metal oxide particle formation and proposed a new mechanism based on Ligand Exchange reaction typical for ALD with hydroxyl and chlorine groups as reactive sites. None of the mechanism suggested so far can fully account for the experimental observations of the metal oxide particle formation. In the present work we try to explain the possible mechanism of formation of alumina nanoparticles in the cold wall ALD chamber during the Atomic Layer Deposition, based on the physisorption of TMA and surface energy of alumina thin films [18].

7.3 Experimental

Alumina nano particles were observed to grow simultaneously along with the alumina films under certain experimental conditions in our home made Atomic Layer Deposition system. Later these particles were grown purposefully to study their formation conditions. They were also subjected to structural and morphological characterization. A detailed description of the experimental setup is given in chapter 3. TMA (Trimethylaluminum: Sigma-Aldrich, 2.0 M solution in Toluene) and water were used as precursors for aluminum oxide deposition. Initially the precursors were loaded in stainless steel bubblers in vacuum and were introduced alternately to the hot zone of the chamber with an inert carrier gas (Nitrogen, 99.999 %). Between each precursor exposure a purge gas was pulsed through the deposition chamber in order to remove unreacted precursors and reaction by products. The flow rates of precursors and purge gas were measured with Mass Flow Meters (Bronkhorst). The order and typical time of the cycles used in these experiments were (i) TMA-3 seconds (ii) purge-15 seconds, (iii) water-2 seconds and (iv) purge-15 seconds. Nitrogen was used as the carrier gas at a rate of 250 sccm. The experiment was repeated by varying the conditions like chamber pressures, temperature and exposure times. The chamber pressure was varied between 0.15 mbar to 0.45mbar. Temperature of the hot zone was varied from room temperature to 300°C. The chamber outer walls were water cooled. It was observed that the alumina powder gets deposited on the cooled surfaces of the chamber when the hot zone was at a higher
temperature and the deposition occurs everywhere inside the chamber when
the hot zone was at room temperature.

Structural characterizations of the as prepared and post annealed
\( \text{Al}_2\text{O}_3 \) samples were performed using X-ray diffraction (Bruker AXS D8
Advanced, Source: Cu- K\( \alpha \)- 1.5414Å). The powder morphology was studied
using Scanning Electron Microscopy (SEM- JEOL JSM6390LV) and
HRTEM (JEOL3010 operated at 200keV). The samples were also subjected
to Selective Area Electron Diffraction (SAED). The chemical compositions
of the as prepared samples were determined by Energy Dispersive Analysis
through X-ray spectroscopy (EDS -JEOL JED 2300). The FTIR spectra were
recorded on Thermo Nicolet Avatar 370. The samples were pelletized at
7x10\(^4\)N and the dielectric studies were carried out using an LCR bridge
(Fluke PM 6306).

7. 4 Results and discussion

There are two types of adsorption mechanisms- physical sorption
(physisorption) and chemical sorption (chemisorption). Physisorption is due
to weak Van der Waals forces (maximum value of heat of physisorption is
taken as, 8kcal/mol=0.347eV/molecule) with minimum changes in the
adsorbate, whereas chemisorption involves much more energy (heat of
chemisorption is up to 250 kcal/mol) [20,21] and making and breaking of
bonds. Hence only one layer is adsorbed in the case of chemisorption and the
adsorbate remains on the adsorbed site (site specific), where as in
physorption this restriction is not there. Physisorption generally occurs at
low temperature areas of the chamber since the energy involved in this
process is much smaller.

In ALD, the required adsorption mechanism is irreversible
chemisorption to satisfy the condition of self termination of reaction [22].
Therefore it is safe to believe that at the water cooled walls of the reaction
chamber (~300K) TMA is physisorbed rather than chemisorbed. This is
aided by the fact that stainless steel surface of the chamber walls lack the
OH surface species required for the easy chemisorption of TMA molecules.
Since the physisorption is a reversible mechanism, some of the TMA may be
reemitted during the subsequent pumping and purging. But it is possible that some are retained on the walls. These TMA molecules react with the water molecules which enter the chamber in the next pulse and form alumina molecules. The reaction by products is removed from the chamber in the subsequent argon purging. These newly formed aluminum acts as substrate for further cycles.

How nanoparticles are formed instead of a nano film? The surface formation energy of alumina has a comparatively high value of 16.23 - 17.48 eV/nm² [1,23, 24]. From Ref. [22] Figure 22 we can find out the maximum number of alumina molecules per nm² area of silica substrate as 4.8. Assuming that (i) in the present case also this is the maximum possible number and (ii) the heat of physisorption is same as the energy of physisorption [20], the total energy associated with physisorption of 4.8 molecules per nm² area is 0.347eV×4.8 = 1.67 eV/nm². We can see that this is much smaller than the surface formation energy of alumina. In other words, to form 1 nm² surface area of alumina film, it requires minimum 16.23 eV, where as physisorption can provide only 1.67 eV energy to hold the film to the substrate. Hence the newly forming film will try to reduce the surface area by coalescing and assuming spherical shape. This is aided by the mobility of physisorbed molecules on the surface of the substrate. The spherical particles so formed will act as substrates for the subsequent cycles of deposition. It has to be noted that at the hot zone, since chemisorption takes place, which involves energies up to 10eV per molecule and since chemisorbed molecules are bound to the point where they are adsorbed, this curling of the film does not happen. This explains the mechanism of nano particle or nano rod formation in the cold regions of ALD chamber.

It is important to note here that there are reports of alumina films prepared by ALD at a substrate temperature of 33°C [25] and absence of any effect of substrate temperature on ‘growth per cycle of alumina films [22]. But a literature survey reveals that most of the work in this field is done at a substrate temperature of 170°C or more to get good quality alumina films [26-32]. Our experiments also support this observation [Table 5.2]. The films which were prepared at 33°C show degradation in all its electrical and
optical properties. During deposition long purge and exposure time is also needed. We have repeated the experiment by simply switching off the heater, keeping all other experimental conditions same. It was observed that particles were formed everywhere inside the chamber which was at a temperature of 27°C, without forming any detectable film on the substrate. Particles were formed even with longer purge durations after water pulses. This eliminates the possibility of TMA reacting with residual water vapour which may be present in the chamber. From these it is clear that particle formation can occur in a cold wall ALD system even with optimized process parameters with sufficiently long deposition durations.

7.5 Characterization of Alumina particles

7.5.1 Structural characterization

Figure 7.1: X-ray diffraction patterns of Alumina powder samples-(a) as prepared, (b) 900°C and (c) 1200°C annealed.
The structural characterization of the powder was done using XRD. Figure 7.1 shows the XRD pattern of as prepared Al₂O₃ powder and annealed samples. Amorphous nature of the as prepared sample is evident from the pattern. The 900°C and 1200°C annealed samples show weak Bragg peaks of η-Al₂O₃ and α-Al₂O₃ respectively. The broad hump in 900°C annealed samples indicates that the powder is not completely crystalline. Comparison of these values with JCPDS files [33] clearly shows that the annealed samples are indeed η and α polymorphs of alumina. The α phase samples were the most stable phase of alumina. The crystal size calculated using Debye-Scherer formula for 900°C annealed samples is 19.5nm whereas that for samples annealed at 1200°C is between 34.2nm to 43.07nm.

### 7.5.2 Compositional analysis

Chemical compositions of the prepared powder samples were identified using EDS measurement. From Table 7.1 it is clear that the O/Al ratio of the annealed samples is less than that of as prepared samples which is in amorphous state.

| Table 1: Comparison of EDS data of as prepared and annealed Al₂O₃ |
|-----------------|--------|--------|--------|
| Element         | Wt%   | At%    | O/Al   |
| Alumina powder as prepared |       |        |        |
| O               | 43.93 | 56.92  | 1.32   |
| Al              | 56.07 | 43.08  |        |
| Alumina powder annealed at 900°C |       |        |        |
| O               | 42.39 | 55.38  | 1.24   |
| Al              | 57.61 | 44.62  |        |
| Alumina powder annealed at 1200°C |       |        |        |
| O               | 36.25 | 48.95  | 0.96   |
| Al              | 63.75 | 51.05  |        |
7.5.3 Surface morphology

Powder morphology of the samples was analyzed using SEM. Figure 7.2 shows the SEM photograph of as prepared, 900°C and 1200°C annealed alumina powders. As the sample is annealed, the powder agglomerates. Further increase in annealing temperature showed an enhancement in the cluster formation.

Figure 7.2: SEM images of the alumina powder: (a) as prepared (b) as prepared sample at higher magnification.

Figure 7.2: SEM images of the alumina powder: (a) 900°C annealed (b) 900°C annealed at higher magnification.
Surface morphology of the prepared samples were analyzed using HRTEM. Figure 7.3 shows the HRTEM images of the as prepared and 1200°C annealed samples. It is evident from various HRTEM images of as prepared and annealed samples that most of the annealed particles are in the range ~35-45 nm in size whereas as prepared samples are smaller.

Figure 7.3: HRTEM images of alumina Nanoparticles (a) as prepared sample (50nm scale) (b) as prepared sample (20nm scale).
Figure 7.3: HRTEM images of alumina nanoparticles; (c) annealed at 1200 °C (50nm scale), (d) annealed at 1200°C (10nm scale), (e) annealed at 1200°C (5nm scale) shows crystal planes, (f) SAED of 1200°C annealed sample.

This increase in particle size is due to the agglomeration of particles at higher temperature. Figure 3(f) shows SAED pattern of sample annealed at 1200°C. The more or less circular pattern instead of clear cut points in SAED, confirms the nano crystalline nature of the samples [1]. The d values and planes calculated from this is tabulated in Table 7.2 which match well with results from the powder XRD. The good agreement between the reported and experimental ‘d’ values is a conclusive proof that the nano
particles formed are indeed α-alumina. This result in agreement with x-ray diffraction studies of 1200°C samples in the above section.

Table 7.2: Comparison of reported and experimental ‘d’ values and planes from SAED data. (*From JCPDS 1998)

<table>
<thead>
<tr>
<th>‘d’ reported*</th>
<th>‘d’ expt.</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5520</td>
<td>2.556</td>
<td>104</td>
</tr>
<tr>
<td>2.0850</td>
<td>2.084</td>
<td>113</td>
</tr>
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<td>1.4044</td>
<td>1.461</td>
<td>---</td>
</tr>
<tr>
<td>1.1898</td>
<td>1.189</td>
<td>220</td>
</tr>
<tr>
<td>1.0988</td>
<td>1.095</td>
<td>0210</td>
</tr>
</tbody>
</table>

The as prepared alumina nano powder was pelletized at 7x10^4 N and annealed at 200°C for 3 hours. The diameter and thickness of the pellets were 6mm and 2mm respectively. Aluminum electrodes were vacuum deposited onto both flat sides of the pellets and were subjected to dielectric measurements. The dielectric constant obtained was 9.08 at 1 MHz and was found to be in agreement with the reported values [34-36].

**7.5.4 FTIR Analysis**

Figure 7.4 (a) and (b) show the FTIR spectra of as prepared and annealed Al₂O₃ powder material. Amorphous nano alumina powder shows a broad peak in the range of 500-900 cm⁻¹. This is due to Al-O stretching mode (750-850 cm⁻¹) and O-Al-O bending mode (650-700 cm⁻¹) [37]. There is a broad peak between 3000 cm⁻¹ and 3700 cm⁻¹ which indicates OH stretching region. The peak at 1633.01 which can be considered as the H-O-H scissor mode [38] are the peak at 3438.15 can be due to water molecule. Annealed sample has multiple peaks in the range 500-900 cm⁻¹, which confirms the crystalline nature [39].
Figure 7.4: FTIR spectra of Alumina powder material. (a) As prepared sample. (b) Sample annealed at 1200°C.

Stretching vibrations of Al-O and OH are observed at 582.25 cm\(^{-1}\) and 3415.66 cm\(^{-1}\) respectively. The lack of H-O-H scissor mode in annealed
sample indicates that OH stretching mode at 3415.66 cm\(^{-1}\) corresponds to hydroxyl species. CH bending vibrations of CH\(_3\) are present at 1388.88 cm\(^{-1}\) in the annealed sample.

7.6 Conclusions

Nano alumina particles of size ranging from 20-45nm were observed at the cold walls of our home made cold wall type Atomic Layer Deposition system during the deposition of alumina thin films using TMA and Water as precursors. An explanation is given for this phenomena based on the physisorption of TMA on the cold walls of the ALD chamber. It was shown here that since the surface energy of alumina is larger than the physisorption energy, the newly forming film will try to reduce the surface area and assume spherical shape whenever physisorption take place. Structural characterization of as prepared and annealed particles were done by various characterization tools. In prepared state the particles are amorphous in nature and become crystalline after annealing. Crystal size as calculated using Debye-Scherrer formula was 19-44nm range and that found from HRTEM images was in the range 20-45 nm. The dielectric constant of the pelletized sample was found to be 9.08 at 1MHz which matches well with the reported values.

References

1. Anu Philip, Subin Thomas and K. Rajeev Kumar, Vacuum 85, 368 (2010).