Exploring the Optimal Growth Parameters of Al₂O₃ Grown by Atomic Layer Deposition

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Abstract: High quality Al₂O₃ thin film is grown by atomic layer deposition (ALD). The influence of growth parameters such as growth temperature and purge time on the surface morphology, dielectric constant and so on have been investigated. It is found that Al₂O₃ thin film at a flow rate of 150 sccm, H₂O flow rate of 150 sccm, pulse time of 0.1 s, purge time of 6 s, cycle period of 450 times and growth temperature of 150°C, exhibits the optimal material quality with a growth rate of 0.79 Å /cycle, a root-square surface roughness (RMS) of 0.152 nm and a capacitance of 13.8 nF.

1. Introduction
Al₂O₃ thin film is considered to be the most promising candidate to traditional silicon dioxide gate dielectric materials due to the large band gap, high hardness, excellent electrical properties, chemical stability and thermal stability. In recent years, the research on the deposition technology of Al₂O₃ film has attracted numerous attentions. The methods of film deposition include physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition (ALD). Among them, the atomic layer deposition technology can precisely control the growth thickness (the thickness unit is accurate to the atomic level) and has a good step coverage ability due to its special reaction mechanism. It is widely used in the preparation of high-k dielectric films.

This paper introduces a method for preparing high mobility Al₂O₃ films by atomic layer deposition. The surface morphology, dielectric properties, etc. of alumina films prepared under different deposition temperatures and purge time are analyzed. The variation in characteristics is to obtain suitable parameters and conditions for depositing high-quality Al₂O₃ thin film.

2. Experiment
2.1. Experimental Principle
Atom layer deposition (ALD) is a vapor-phase technique for preparing dense and ultrathin films with precise growth control. In a typical ALD procedures for depositing a binary compound film, sequential alternating pluses of gas precursors are introduced into a reaction chamber with an inert purge step in between until the appropriate thickness is reached. Precursors are then absorbed onto the substrate and react with each other to form the desired film. The reaction between precursors and the substrates is crucial for depositing films. Trimethylaluminum and high-purity H₂O were used as precursors and the carrier gas was nitrogen (N₂).
2.2. Experimental Chemicals
Chemicals used in this paper included acetone (CH₃COCH₃), isopropyl alcohol ((CH₃)₂CHOH) and TMA and so on.

2.3. Experimental Equipments
Al₂O₃ thin film was grown on silicon substrates in an R-200 Advanced ALD system. Prior to the growth of Al₂O₃ thin film, substrates were pre-treated using ultrasonic cleaner to achieve better surface morphology. For material characterization, its thickness was measured by ellipsometer (M-2000DI J. A. Woollam). Atom force microscopy (AFM, Brucker Dimension ICON) was applied for surface inspection. Its electrical properties were evaluated by parameter analyzer (Keithley 4200). The specific models and manufacturers are shown in table 1.

| Experimental equipments                          | Model            | Manufacturer                           | Application                      |
|------------------------------------------------|------------------|----------------------------------------|----------------------------------|
| Ultrasonic cleaner                              | KQ-600E          | Kunshan Ultrasonic Instrument Co., Ltd.| Sample clean                     |
| Atomic layer deposition system                  | R-200 Advanced   | Picosun                                | Film deposition                   |
| Atomic force microscope                         | Burker           | Dimension ICON                         | Analysis of Surface morphology   |
| Spectral ellipsometer                           | M-2000DI         | J.A. Woollam                           | Thickness test                    |
| Semiconductor characteristic analysis system    | Keithley4200, Suss PM8 | Keithley, Suss                          | Electrical performance test       |

3. The Influence of Growth Temperature on the Properties of Al₂O₃ Thin Film
Three Al₂O₃ thin film samples were grown at 100°C, 120°C and 150°C to study the influence of growth temperature. The flow rate of TMA and H₂O were both set to be 150 sccm. The timing sequence (TMA exposure, purge, water exposure, purge) during these TMA/H₂O cycles was (0.1 s, 1 s, 0.1 s, 1 s).

3.1. The Influence of Deposition Temperatures on Surface Morphology
Fig. 1 shows the surface morphology of these Al₂O₃ thin film samples measured by AFM in contact mode and the root mean square (RMS) roughness for each sample grown in different temperatures were displayed in table 2.

![Figure 1](image-url)
Table 2. The film RMS at different deposition temperature

| Deposition temperature (°C) | RMS (nm) |
|-----------------------------|----------|
| 100                         | 0.189    |
| 120                         | 0.176    |
| 150                         | 0.152    |

The surface was shown to be smoother with evaluated growth temperature and the RMS roughness has reached to the smallest of 0.152 nm for the sample grown at 150°C. Weakened chemical reaction and decreased growth rate mainly account for the rougher surface at lower temperature. TMA may not fully decompose so that other substances might be incorporated into the film, leading to more uneven surface. Enhanced physical absorption at lower temperature is another reason for the rougher surface. In that case, multi-layers tend to form on the growing surface and then interfere the next cycle, resulting in the undulated surface condition.

3.2. The Influence of Deposition Temperatures on Growth Rate

In order to study the influence of different deposition temperatures on the growth rate of the film, the thickness of the film at different deposition temperatures were tested by ellipsometer. The results are shown in table 3.

Table 3. The growth rate of different deposition temperature

| Deposition temperature (°C) | Thickness (nm) | Growth rate (Å /cycle) |
|-----------------------------|----------------|------------------------|
| 100                         | 30.7           | 0.68                   |
| 120                         | 32.8           | 0.73                   |
| 150                         | 35.6           | 0.79                   |

As can be seen from the table 3, the deposition temperature has little influence on the growth rate. The growth rate of 100°C, 120°C, 150°C is 0.68 Å /cycle, 0.73 Å /cycle, 0.79 Å /cycle, respectively. The largest growth rate is achieved at 150°C.

3.3. The Influence of Deposition Temperatures on Dielectric Constant

The relationship between the dielectric constant and the capacitance of the film can be expressed by Equation 1-1, the dielectric constant of the film is proportional to the capacitance of the film.

\[
\varepsilon = \varepsilon_r \frac{A}{t_{ox}}
\]

Where \( C \) is gate capacitance, \( \varepsilon_r \) is relative permittivity, \( \varepsilon_0 \) is Vacuum dielectric constant, \( A \) is the area of Al₂O₃ thin film and \( t_{ox} \) is thickness of Al₂O₃ thin film.

In order to study the influence of different deposition temperatures on the dielectric constant, a semiconductor analysis system was used to measure the film capacitance obtained at different deposition temperatures. The test results are shown in table 4.

Table 4. The capacitance of different deposition temperature

| Deposition temperature (150 °C) | Thickness (nm) | Capacitance (nf) |
|---------------------------------|----------------|------------------|
| 100                             | 30.7           | 0.20             |
| 120                             | 32.8           | 0.25             |
| 150                             | 35.6           | 13.8             |
When the deposition temperature is changed from 100°C to 150°C, the thickness of the film is nonlinear with the film capacitance. The Al₂O₃ thin film prepared at the deposition temperature of 100°C and 120°C has a low capacitance and a low dielectric constant. When the deposition temperature reaches 150°C, the capacitance of the film changes significantly, increasing to 13.8 nF. The Al₂O₃ thin film prepared at the deposition temperature of 150°C has the highest capacitance and dielectric constant, and the dielectric properties of the film are the best.

4. The Influence of Purge Time on the Properties of Al₂O₃ Thin Film

The influence of purging time on the film quality of Al₂O₃ was studied. The experimental conditions were designed as follows: carrier gas flow rate TMA is 150 sccm, H₂O flow rate is 150 sccm, pulse time is set to 0.1 s, deposition temperature is 150°C, and cycle period is 450 times. The film preparation was carried out by setting the purge time to 3 s, 6 s, and 9 s, respectively.

4.1. The Influence of Purge Time on Surface Morphology

In order to study the influence of the purge time on the surface morphology of the Al₂O₃ thin film, the morphology of the film is obtained by AFM as shown in Fig. 2.

![Figure 2. The surface morphology of different purge time](image)

(a) 3 s  
(b) 6 s  
(c) 9 s

The RMS of the film measured under different purge time is shown in Table 5.

| Purge time (s) | RMS (nm) |
|---------------|----------|
| 3             | 0.326    |
| 6             | 0.152    |
| 9             | 0.398    |

The surface morphology of the film is significantly changed with different purge time. The RMS is 0.326 nm at a purge time of 3 s, a roughness of 0.152 nm at a purge time of 6 s, and a roughness of 0.398 nm at a purge time of 9 s. At the purge time of 6 s, the surface roughness is the lowest, which is 0.152 nm.

4.2. The Influence of Different Purge Time on Growth Rate

In order to study the influence of different purge time on film thickness, the growth rate of the film under different purge time was tested by ellipsometer as shown in Table 6.
Table 6. The growth rate of different purge time

| Purge time (s) | Thickness (nm) | Growth rate (Å/cycle) |
|---------------|----------------|-----------------------|
| 3             | 35.1           | 0.78                  |
| 6             | 35.6           | 0.79                  |
| 9             | 35.5           | 0.79                  |

It is known from the data that the influence of the purge time on the growth rate of Al$_2$O$_3$ thin film is not very significant, and the difference between the thicknesses caused by the different purge times is ignorable. However, it can be seen that after the purge time is more than 6 s, the thickness uniformity of the Al$_2$O$_3$ thin film is relatively better, and the rate of deposition of the film is relatively stable. Therefore, we choose the purge time of 6 s as the better growth condition when the pulse time of TMA is 0.1 s. The reason for the difference is mainly due to the fact that when the purge time is relatively short, the TMA entering the reaction chamber is not completely purged, and residual TMA will react with other substances in the chamber.

4.3. The Influence of Different Purge Time on Dielectric Constant

In order to study the influence of different purge time on the dielectric constant of the film, the capacitance of the prepared film was tested by a semiconductor analysis system. The test results are shown in table 7.

Table 7. The capacitance of different purge time

| Purge time (s) | Thickness (nm) | Capacitance (nf) |
|---------------|----------------|------------------|
| 3             | 35.1           | 8.2              |
| 6             | 35.6           | 13.8             |
| 9             | 35.5           | 3.0              |

With the increasing of purge time, the capacitance of the film does not change regularly. From table 7, at the purge time of 3 s, 6 s, 9 s, the capacitance is 8.2 nf, 13.8 nf, 3.0 nf, respectively. When the purge time is 6 s, the dielectric properties of the film are optimal compared to the capacitance and dielectric constant obtained at 3s and 9s.

5. Summary

In summary, we have studied the influence of deposition temperature and purge time on the surface morphology, film thickness, deposition rate and dielectric constant of the Al$_2$O$_3$ thin film which is deposited by ALD. By the optimization of growth parameters, we obtained a better Al$_2$O$_3$ thin film with growth rate of 0.79 Å/cycle, RMS of 0.512 nm, capacitance of 13.8 nf, which the flow rate of TMA is 150 sccm, the H$_2$O flow rate is 150 sccm, the pulse time is 0.1 s, purge time is 6 s and cycle period is 450 times.

6. Reference

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