

Characteristics of an Al₂O₃ Thin Film Deposited by a Plasma Enhanced Atomic Layer Deposition Method Using N₂O Plasma

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Several properties of ultra thin aluminum oxide films deposited by a plasma enhanced atomic layer deposition (PEALD) method were studied. The Al₂O₃ films were deposited on an HF cleaned Si (100) substrate using Trimethylaluminum (TMA)-Al(CH₃)₃ as an Al source and N₂O plasma as an oxidant. High resolution transmission electron microscope (TEM) images showed the existence of an interfacial layer between the Si substrate and the Al₂O₃ film. Depth profiles obtained by Auger electron spectroscopy (AES) indicated that a small amount of nitrogen was incorporated into the film and that it had accumulated slightly at the interface of the Si/Al₂O₃. X-ray photoelectron spectroscopy (XPS) data revealed that the as-deposited film showed noise-like weak nitrogen bonding, while the 800°C annealed film showed Si₃N₄ bonding. Film density was also measured by X-ray reflectometry (XRR).

Key words: ALD, Al₂O₃, N₂O, plasma

1. INTRODUCTION

Al₂O₃ films have been studied for applications such as insulators in III-V MIS structures^[1], high-k gate dielectrics^[2,3] and tunnel barriers in spin-electronic devices^[4], due to their large band gap (8.7 eV) relative to SiO₂, large conduction band offset (2.8 eV) to Si, and low leakage current^[5]. Since these applications require an ultra thin, uniform Al₂O₃ film, the relatively thick films deposited by sputtering and oxidation of MBE-grown Al are generally unsatisfactory. The atomic layer deposition (ALD) method is a new deposition technique that allows control of the film thickness at a monolayer scale. The advantages of ALD are that it is a low temperature process, has no gas-phase reaction, and offers good step coverage. However, the ALD process with a metal-organic (MO) precursor normally yields a relatively high impurity level in the film. A previous investigation showed that films deposited by the plasma enhanced ALD method have fewer impurities than those deposited via thermal ALD using an MO precursor^[6].

Although N₂O is a highly reactive oxidant, thermally activated and plasma enhanced N₂O can be used to incorporate nitrogen into the oxide film. N₂O has been reported to decompose in two steps as follows: (1) N₂O → N₂ + O and (2) N₂O + O → 2NO^[7]. The former reaction is believed to be related to oxidation and the latter is thought to be responsible for nitridation. Since the above two reactions occur dur-

ing the plasma process, it is expected that they lead to incorporation of nitrogen into the oxide film. The incorporated nitrogen was reported to not only exist in the oxide layer, but also to form a slightly nitrogen-rich layer at the interface between the silicon substrate and oxide layer^[8]. Nitrogen incorporation into the oxide film reportedly offers several advantages in gate dielectric and capacitor devices. Nitrogen contributes to the achievement of a low capacitance equivalent thickness (CET), and is a good reaction barrier between the dielectric and silicon substrate. Indeed, nitrogen is also reported to improve the current drive and break-down properties and to reduce electron traps^[2]. For this reason, in the present study, we demonstrate ALD growth of an Al₂O₃ film using N₂O plasma, and discuss the physical properties of the Al₂O₃ film based on the results of AES, XPS, XRR, and TEM.

2. EXPERIMENTAL

The Al₂O₃ films were grown on p-type silicon (100) substrates using TMA and N₂O plasma in a traveling wave type ALD reactor. The silicon substrate was cleaned by dipping it in a piranha solution (H₂SO₄:H₂O₂=4:1) for 10 min and then in a diluted HF solution (HF:H₂O=1:100) for 2 min to remove organic impurities and native oxide, respectively. The TMA precursor was kept below 17°C and vaporized from the liquid and then introduced into the ALD chamber with an Ar carrier gas. The direct plasma of N₂O was used as an oxidant in this experiment. The direct plasma was an RF type of 13.56 MHz and 100 W. Ar purge gas was introduced

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in order to ensure complete separation of the source and reactant gases. From various experiments conducted to identify an ALD process window, we employed the following process parameters: a substrate temperature of 180°C, a process pressure of 1 torr, and each pulse time was set to TMA (1 sec)-Ar purge (2 sec)-N₂O direct plasma (2 sec)-Ar purge (2 sec). After deposition, the as-deposited film underwent rapid thermal annealing at 800°C for 10 sec under a pure N₂ ambient atmosphere. The physical and chemical characteristics of the Al₂O₃ film were analyzed by Auger electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS). The film thickness and interface were examined with a high resolution cross sectional transmission electron microscope (HRTEM). X-Ray Reflectivity (XRR) was used to measure the density and thickness of the Al₂O₃ film.

3. RESULTS AND DISCUSSION

The ALD process window of the Al₂O₃ film deposited by

TMA and the N₂O plasma is shown in Fig 1. Figure 1(a) shows the saturated growth rate at a given temperature for the Al₂O₃ film. A constant growth rate appeared in a temperature range of 140°C to 220°C, which constitutes the stable process window for the ALD process. Figure 1(b) shows the Al₂O₃ thin film growth rate as a function of the TMA precursor exposure time at 180°C. Saturation of the growth rate was observed at an exposure time of 1 sec. Figure 1(c) shows the Al₂O₃ film growth rate in accordance with the N₂O plasma time at a substrate temperature of 180°C. The saturated growth rate was observed after 1.5 s of N₂O plasma time. This saturation indicated that Al₂O₃ film growth using TMA and the N₂O plasma reached a self-limiting mode in the ALD process without a gas phase reaction. To determine the film growth rate, we prepared Al₂O₃ films deposited under 20, 50, 100, 200, 400, 600, and 1000 cycles and measured the thickness with TEM and ellipsometry, as shown in Fig. 1(d). The average film growth rate of the Al₂O₃ film was about 1.3 Å/cycle.

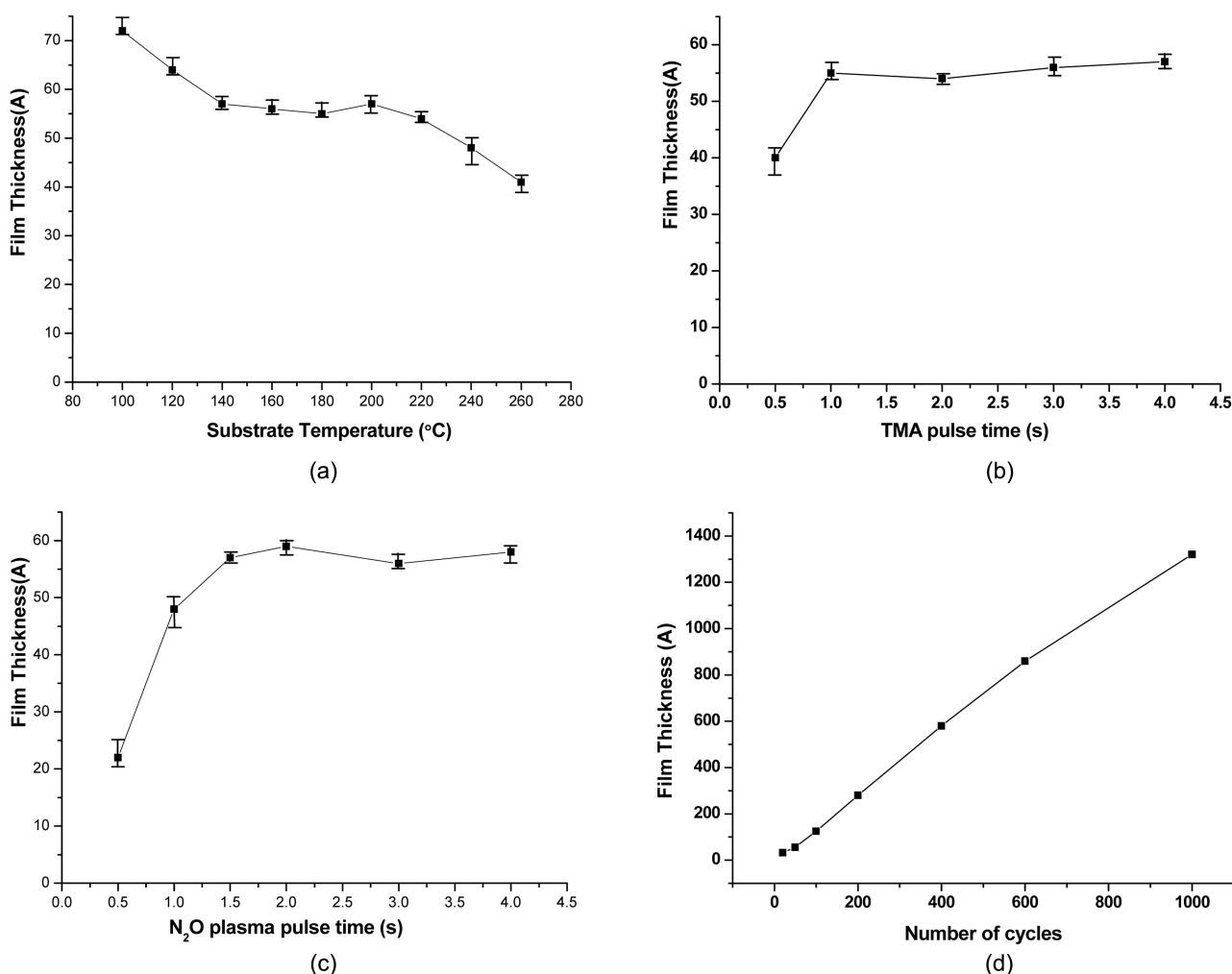


Fig. 1. ALD process windows determination according to (a) substrate temperatures, (b) TMA precursor flow time (sec), and (c) N₂O plasma time (sec); and (d) Al₂O₃ film growth rate depending on the number of ALD cycles.

The depth profiles of Auger electron spectrometry, as shown in Fig. 2, show evidence of aluminum, oxygen, silicon, and nitrogen content in the film. Al₂O₃ films deposited by the PEALD method showed an extremely low carbon content, below 1 at %, which is close to the detection limit for the AES analysis. It is clearly seen that a small amount of nitrogen was incorporated in the film and nitrogen accumulated slightly at the Si/Al₂O₃ interface. This agrees well with the results of the high temperature thermal N₂O oxidation process and electron cyclotron resonance (ECR) N₂O plasma oxidation process^[9,12]. When the Si substrate was thermally oxidized with N₂O gas at 950 °C, about 0.8% N was incorporated in the film^[12]. Lee *et al.*^[9] investigated the nitrogen concentration of SiO₂ film deposited by ECR N₂O plasma with secondary ion mass spectroscopy (SIMS) and showed that 4~5 at. % nitrogen accumulated at the Si/SiO₂ interface. This surface nitridation can be explained by the following two mechanisms. First, the incorporated N substitutes the defects at the Si/oxide layer such as silicon dangling bonds, non-

bridging oxygen, and oxygen vacancies, most of which are localized near the Si/oxide layer interface owing to a lattice mismatch. Second, since the strain at the SiO₂/Si interface is much higher than that of Si₃N₄/Si, incorporated N can reduce the interfacial strain and break weak bonds such as Si-O and Si-H bonds^[7]. Hence, the incorporated N can accumulate and bond with the Si substrate at the interface between Si and the Al₂O₃ film.

Figure 3(a) shows XPS data for Al₂O₃ and indicates the XPS N 1s peak, which reveals noise-like N bonding in the as-deposited films. However, when the film is annealed at 800 °C, the weak N 1s peaks disappeared and a relatively intensive N 1s peak from Si₃N₄ bonding (397 eV-398 eV) was observed. This result can be explained by previous studies. Kim *et al.*, investigated SiON films and studied changes in N bonding as a function of annealing temperature^[13]. They reported that nitrogen-oxygen bonds such as Si-O-N located at the silicon substrate are easily converted to silicon-nitrogen bonds during the annealing treatment. The narrow scan

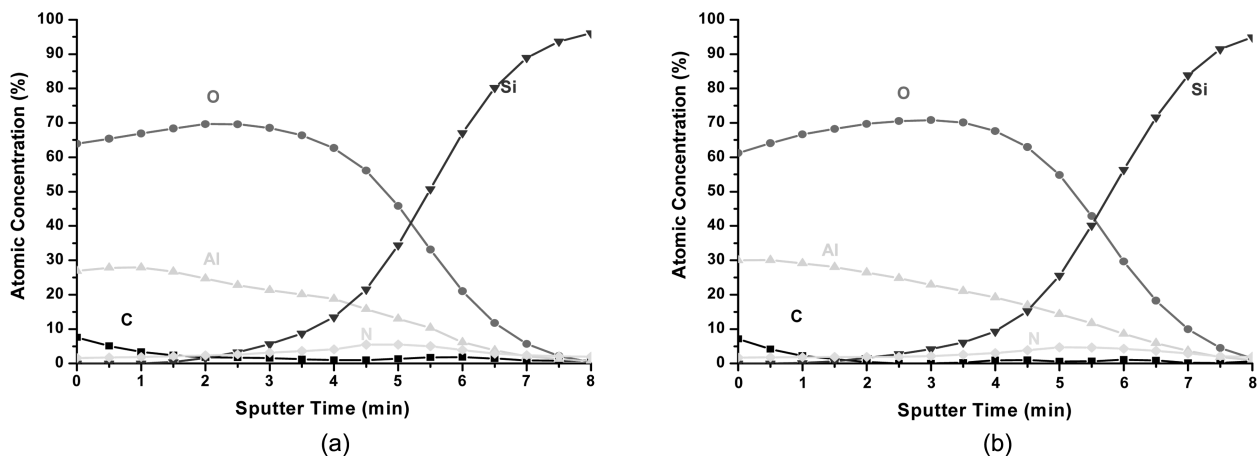


Fig. 2. AES depth profile of the Al₂O₃ deposited with 50 cycles; (a) as-deposited sample and (b) 800 °C annealed sample.

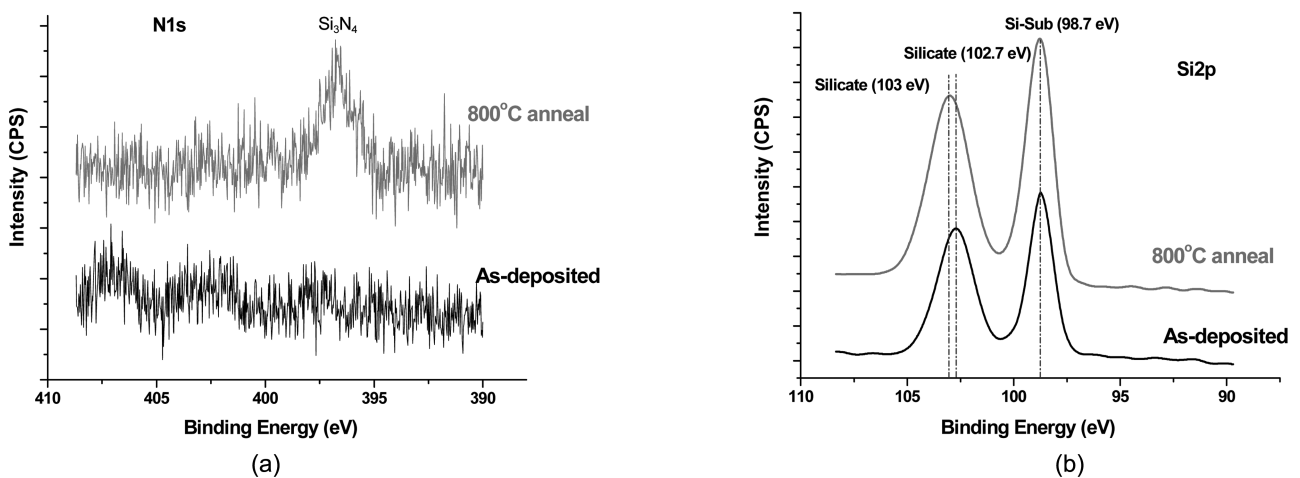
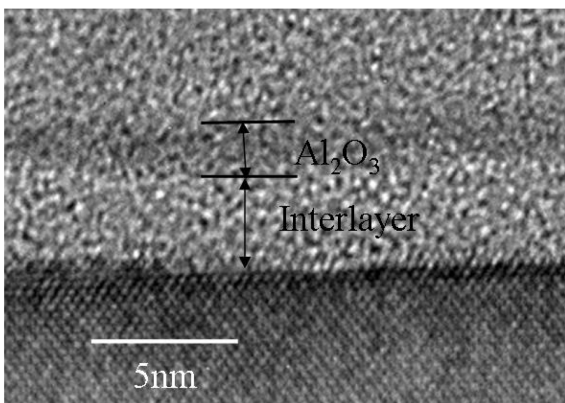


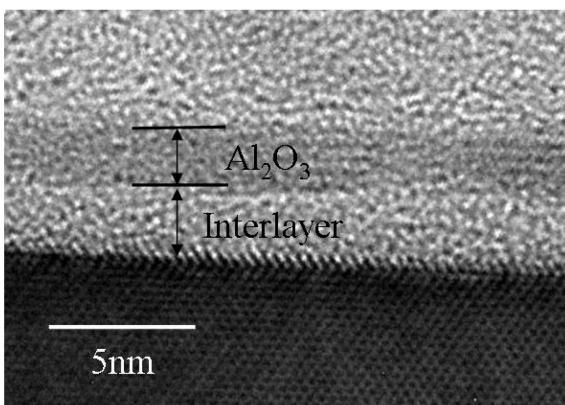
Fig. 3. XPS narrow scan data of Al₂O₃ films of (a) N 1s peak and (b) Si 2p peak.

spectra of Si 2*p* of the Al₂O₃ films are shown in Fig. 3(b). The binding energy at around 98.7 eV is directly related with the Si 2*p* spectra from the silicon substrate, and the binding energy at approximately 102.7 eV is from the interfacial layer, which is believed to be silicate. The annealing of the sample at 800 °C showed a silicate peak at 103 eV, which is a slightly higher binding energy for the silicate peak than that of the as-deposited sample. This is likely due to the 800 °C annealing process, which might increase the oxygen content in the silicate layer. As the oxygen content was increased in the film, a the Si-O bonding was also increased. Since the bonding energy of SiO₂ is higher than that of silicate, the silicate peak can be moved to high binding energy after the annealing process. The formation of a silicate layer in the Al₂O₃ film was not observed in thermally grown Al₂O₃ film. Our previous study regarding Al₂O₃ films deposited by a thermal ALD method revealed that there is no significant evidence of a silicate layer. However, the Al₂O₃ film created by the plasma enhanced ALD process with N₂O exhibited a thick interlayer of Al₂O₃, as shown in Fig. 4.

The HRTEM images presented in Fig. 4 are additional evi-



(a)

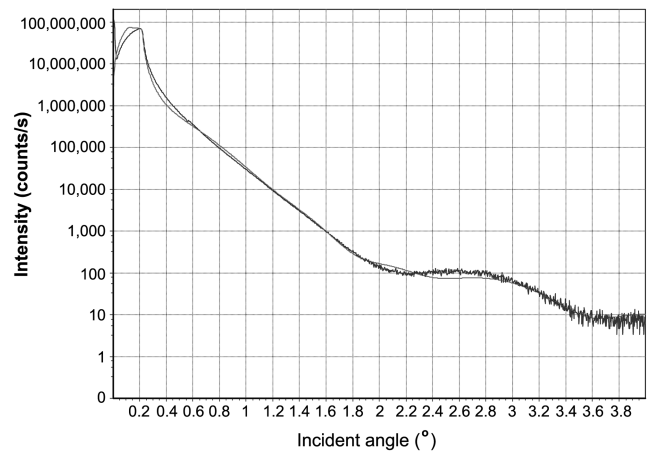


(b)

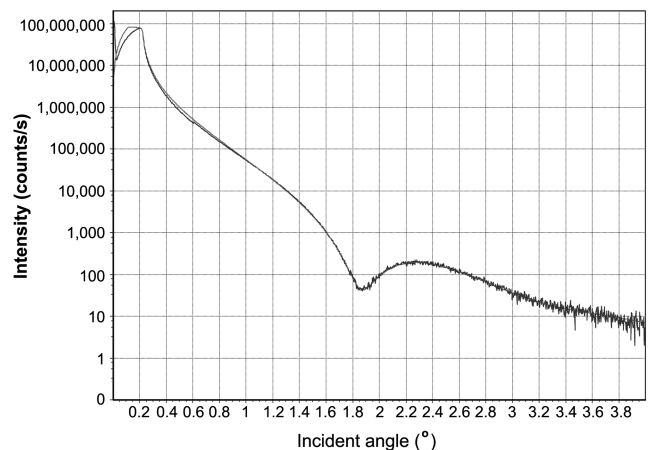
Fig. 4. High resolution cross sectional TEM image of Al₂O₃ films deposited with 50 cycles (a) as-deposited sample and (b) 800 °C annealed sample.

dence of the formation of an interlayer, as shown previously by XPS. The HRTEM images of Figs. 4(a) and (b) show the existence of an interlayer, and its thickness changes after post deposition annealing. The total thickness of the as-deposited sample was roughly 50-52 Å, and that of the 800 °C annealed sample was about 44-46 Å in thickness. The interlayer thickness of the as-deposited sample is about 35 Å, while the 800 °C annealed sample was about 25 Å thick. Comparing Figs. 4(a) and (b), the interlayer thickness decreased after the 800 °C annealing process while the upper Al₂O₃ layer retained its thickness.

To investigate this change, we attempted to determine the film density of each layer. Film density was analyzed by an XRR instrument and the results are shown in Fig. 5. The density of the as-deposited Al₂O₃ sample was 2.2 g/cm³ for



(a)



(b)

Fig. 5. X-Ray Reflectometry data of Al₂O₃ sample; (a) For the as-deposited sample, the film densities are 2.2 g/cm³ for the interlayer and 3.8 g/cm³ for the Al₂O₃ layer. The film thicknesses of the two layers are 3.7 nm for the interlayer and 2.2 nm for the Al₂O₃ layer. (b) In the case of the 800 °C annealed sample, the film densities are 2.5 g/cm³ for the interlayer and 3.9 g/cm³ of Al₂O₃ layer. The film thicknesses are 2.2 nm for the interlayer and 2.3 nm for the Al₂O₃ layer.

the interlayer and 3.8 g/cm³ for the Al₂O₃ layer. The densities of the 800 °C annealed Al₂O₃ sample were 2.5 g/cm³ and 3.9 g/cm³, respectively. The densities of Al₂O₃ layer of both the as-deposited and 800 °C annealed samples agreed well with values typically reported for an amorphous Al₂O₃, the density of which is 3.8 g/cm³[14]. However, the densities of the interlayer from both the as-deposited and 800 °C annealed samples were significantly lower than the reported value of 3.8 g/cm³. Indeed, the interlayer density of the as-deposited sample was densified after the annealing process. This film density change that occurs along with the film thickness change indicates that the thickness of the interlayer was slightly thinned and densified by the annealing process.

4. CONCLUSIONS

In summary, the physical properties of Al₂O₃ film prepared by the PEALD method using TMA and N₂O plasma have been investigated. We found that a small amount of N was incorporated in the Al₂O₃ film and nitrogen slightly accumulated at the Si/Al₂O₃ interface, as shown in the AES data. From the XPS analysis, N was found to have noise-like bondings in the as-deposited film, but after the annealing process, this was converted to Si₃N₄ bonding, which is thermally stable. The XPS data also showed a binding energy peak of the interfacial layer at 102.7 eV for the as-deposited film. When the film was annealed at 800 °C, the binding energy peak of the interlayer was shifted to 103 eV. This is likely due to increased oxygen content in the interlayer. TEM images also revealed the existence of an interfacial layer and demonstrated that the thickness of the interlayer was decreased after the annealing process. XRR analysis indicated that the interlayer was slightly densified after the annealing process.

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