

Effect of the hydration on the properties of an aluminum oxide film

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The properties of Al_2O_3 films were investigated after dipping the films in DI-water. The thickness of the films did not change due to formation of Al-hydroxide layer on their surfaces. After dipping in DI-water, the dielectric constant of the Al_2O_3 film increased and this seems to be caused by a structural change of the film surface. Using this phenomenon, the overall dielectric constant which includes an Al_2O_3 layer can be raised easily through a simple treatment.

Key words: Al_2O_3 , Al-hydroxide, dielectric constant, hydration, structural change

Introduction

High dielectric-constant materials have attracted much attention in recent years since the scaling of semiconductor devices requires a gate dielectric which has an equivalent oxide thickness (EOT) of less than 1.5 nm [1]. Some binary metal oxides such as ZrO_2 and HfO_2 and their aluminates have been widely researched for use as alternative dielectric materials [2-5]. In addition, rare earth metal oxides such as La_2O_3 and ternary oxides such as LaAlO_3 and SrTiO_3 have been proposed for use as next generation high dielectric constant dielectric materials [6]. However, since it is known that the rare earth metal oxides degrade by the adsorption of moisture and the hydration reaction [7], the conventional wet cleaning process which has water (H_2O) species in the mixed cleaning solution will not be able to be applied when the La_2O_3 is used as a dielectric material. Based on a previous study [8] which reported the improvement of hydration resistance of the Al_2O_3 by incorporating ZrO_2 , we studied the hydration characteristics of lanthanum aluminate ($\text{La}_x\text{Al}_{1-x}\text{O}_y$; LAO) film and reported [9,10] better hydration resistance of the LAO film than that of the La_2O_3 film. Additionally, in our studies, the LAO film showed a slight increase of its dielectric constant after hydration. However, the reason for the increase for the dielectric constant was not revealed in those studies.

In order to reveal the reason for the dielectric constant increase, in this study, we deposited the Al_2O_3 films using a metal organic chemical vapor deposition (MOCVD) method and dipped the films in de-ionized (DI) water for a time. After dipping the films in DI-water, we investigated the physical properties of the films in order to find out the effects of the hydration reaction on the properties of Al_2O_3 films.

Experimental procedure

The Al_2O_3 films with a thickness of about 20 nm were deposited on p-type (100) Si wafers by a MOCVD method. The wafers were degreased in organic solvents and then dipped in 10% hydrofluoric (HF) solution to remove the native oxide. Al-acetylacetone [$\text{Al}(\text{CH}_3\text{COCH})_3$, Aldrich Chemical Company, Inc., USA] was used as the precursor of the Al metal. Nitrogen was used as the carrier gas of the vaporized source and ozone gas generated from an ozone generator (Model Lab-I, Ozone Tech Co. Ltd., Korea) was used as the oxidizing gas. The substrate temperature was maintained at 335°C during deposition and the working pressure was 2 torr (266.6 Pa). Detailed deposition conditions are listed in table 1. After deposition, the films were dipped in de-ionized (DI) water in order to investigate the effect of the hydration reaction on the properties of the film.

The thicknesses of Al_2O_3 films were measured utilizing an ellipsometer (Gaertner, L117, $\lambda = 632.8$ nm) with a He-Ne laser. The surface compositions and chemical state changes of the films were analyzed by employing an X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700 ESCA spectrometer) with a Mg K α ($\text{h}\nu = 1253.6$ eV) X-ray source. In order to avoid the change of chemical state during sputtering, the surface of the films was not etched off

The metal/oxide/silicon (MOS) capacitor structures were fabricated in which platinum was employed as a

Table 1. Detailed experimental conditions for deposition of Al_2O_3 films.

Substrate temperature	335°C
Working pressure	2 torr (266.6 Pa)
Temperature of $\text{Al}(\text{acac})_3$	185°C
$\text{Al}(\text{acac})_3$ carrier gas flow rate	30 sccm
O_3 flow rate	100 sccm
Substrate	p-type (100) Si wafer

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top electrode with a thickness of about 150 nm. The ohmic contact of the bottom electrode was achieved using an indium (In) soldering method and the platinum top electrodes were deposited by a dc magnetron sputtering method. The size of the platinum dot was controlled as about 180 μm in diameter using a shadow mask. For the electrical characterization of the MOS capacitor, a light free probe station was used. The capacitance values were measured with a C-V method using a HP4280A 1 MHz C Meter/CV Plotter. EOT of the film has been calculated from the C-V data. The leakage current was measured with a I-V method using a HP4145B semiconductor parameter analyzer.

Results and Discussion

Figure 1 shows the ratios of thickness changes of Al_2O_3 films as a function of dipping time in DI-water. There was no distinct change in thickness of the films. This could be explained by the previous study [11]. In case of the hydration reaction on the Al_2O_3 film for anodic electrode applications, through the following steps, the adsorbed water layer turns the surface Al_2O_3 layer into an amorphous aluminum oxyhydroxide (aluminum hydroxylate) layer several nanometers-thick [11]. When the Al_2O_3 layer contacts with water, the adsorbed water layer causes Al-O bond breaking and localized dissolution of the layer at defect sites of the oxide layer. Then, hydroxylation occurs at the outer region of the oxide layer. With this reaction, an amorphous aluminum oxyhydroxide region is formed. It seems that this formation of an aluminum oxyhydroxide layer acts as a barrier layer which prevents additional dissolution of the film and this results in a slight increase rather than a decrease of the thickness of the lanthanum aluminate film.

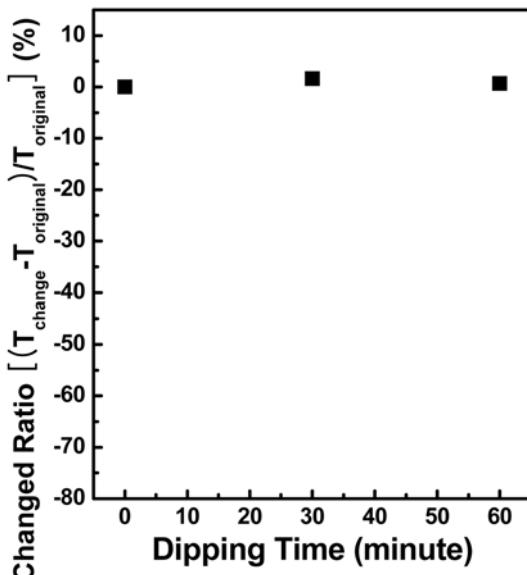


Fig. 1. The ratios of thickness changes of Al_2O_3 films as a function of dipping time in DI-water.

Figure 2 shows narrow scan XPS spectra of the Al 2p peaks of the Al_2O_3 films as a function of dipping time. The Al 2p peak of the as-grown Al_2O_3 film (Fig. 2(a)) is deconvoluted into two peaks such as the Al-O bond peak and the Al-carbonate peak. After dipping the Al_2O_3 film in DI-water for 30 minutes (Fig. 2(b)), a very small increase of the shoulder around a binding energy of 72.8 eV as indicated which resulted from the Al-hydroxide peak is shown. The Al-hydroxide peak area was about 0.4% of the whole peak area. As the dipping time increased to 60 minutes (Fig. 2(c)), the shoulder peak around 72.8 eV became distinguishable and the Al-ratio of the hydroxide peak area was about 2% to the total area of the peak. The formation of aluminum hydroxide is confirmed from the analysis of the chemical state changes. From this figure, it is thought that the hydroxyl group of water reacts with Al_2O_3 and forms Al-hydroxide bonds during the hydration process.

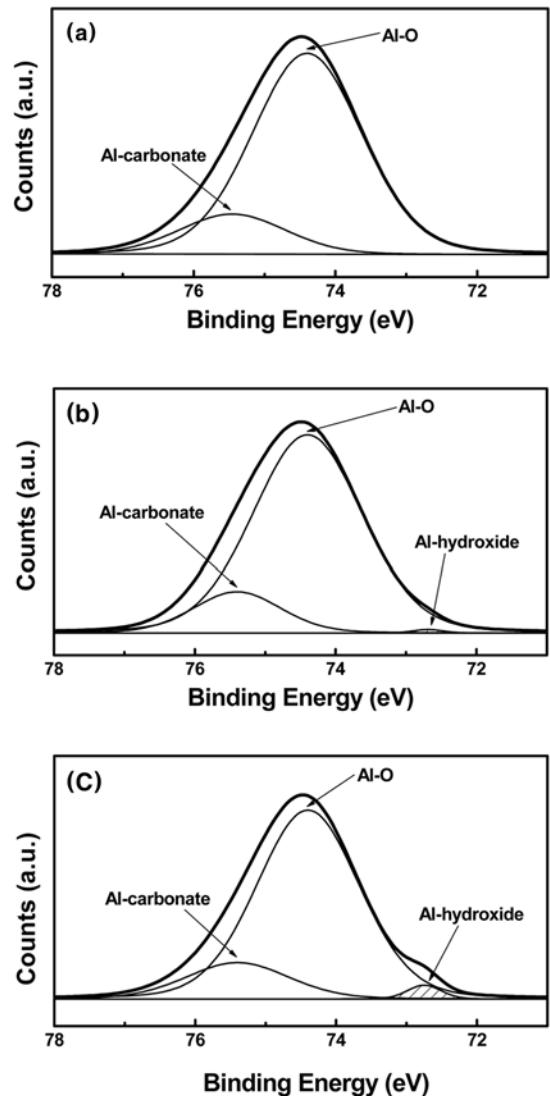


Fig. 2. Narrow scan XPS spectra of Al 2p peaks of Al_2O_3 films as a function of dipping time of (a) 0, (b) 30 and (c) 60 minutes.

Figure 3 shows the dielectric constant changes of the Al_2O_3 films as a function of dipping time. For the as-grown film, the dielectric constant was about 7.8, which is slightly lower than the generally known dielectric constant of a thin film aluminum oxide. Interestingly, after dipping, the dielectric constant of the Al_2O_3 film increased up to 11.5 with a dipping time increase which exceeded the ideal dielectric constant of crystalline Al_2O_3 . The reason could be found in the previous studies [12]. As already stated, the surface of an Al_2O_3 film turns into an aluminum oxyhydroxide layer when reacted with sufficient water. It is reported [12] that the hydroxide ions in the hydroxyl layer are shown to be present in boehmite-like configurations as well as in more amorphous

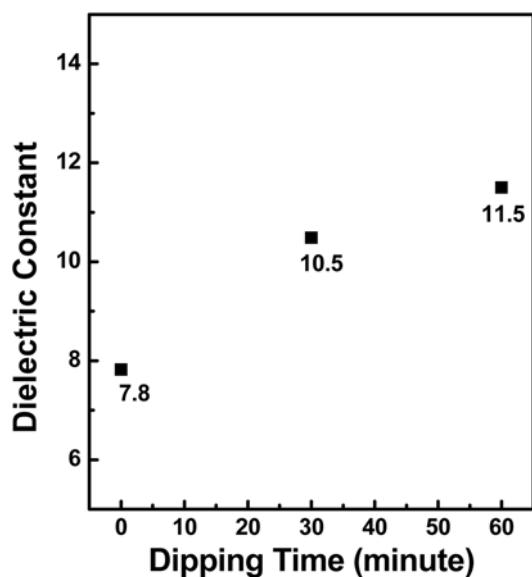


Fig. 3. The dielectric constant changes of Al_2O_3 films as a function of dipping time.

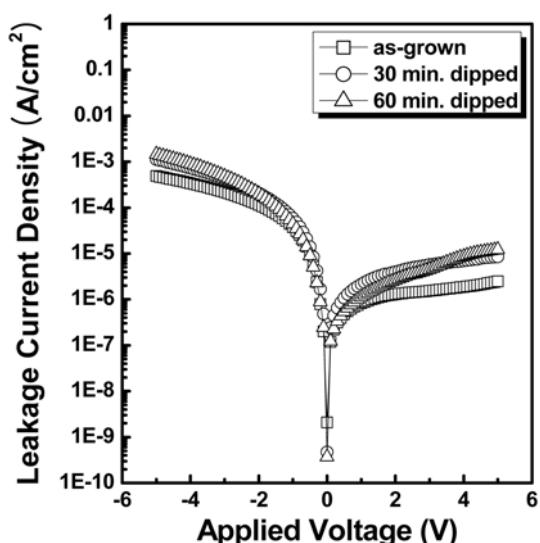


Fig. 4. The I-V curves of Al_2O_3 films with a variation of dipping time.

arrangements. All of the hydroxyl ions are within 3 nm of the surface, and hence the individual particles are probably platelets due to lack of flexible spaces. The material appears to be identical to "pseudo-boehmite" which is a meta-stable aluminum hydroxide formed in water above room temperature. Unlike the well-crystallized hydroxides such as bayerite or boehmite which are formed at a slow rate due to the slow dissolution and reprecipitation process, pseudo-boehmite forms rapidly. This pseudo-boehmite easily grows to extensive sheets of a structure similar to the single (010) layers in the boehmite structure. Subsequently, a few sheets join over small areas in much the same way as in boehmite. In addition, there are some reports about the dielectric constant of boehmite. Glemser reported that the dielectric constant of boehmite is 20.5 and that of Al_2O_3 is 10.6 [13]. Ebert and Langhammer also reported that the dielectric constant of boehmite is 3.2 and that of Al_2O_3 is 2.4 [14]. In the two reports, although the dielectric constant of Al_2O_3 is not in agreement with generally reported value, the dielectric constant of boehmite is at least 1.5 times and up to 2 times higher than that of aluminum oxide with the same measurement conditions. Hence, it can be concluded that the increase of dielectric constant of Al_2O_3 films after dipping in DI-water is resulted from the structural change from aluminum oxide to pseudo-boehmite of the film surface. The dielectric constant increases in the case of the wet-ambient stored LAO film [9] and the DI-water dipped LAO [10] could be explained in the same way.

Figure 4 shows the I-V curves of the Al_2O_3 films with a variation of dipping time. The as-grown Al_2O_3 showed a very low leakage current density of $3.8 \times 10^{-4} \text{ A/cm}^2$ at a voltage of $V_g - V_{fb} = -1 \text{ V}$. The leakage current densities increased to $5.9 \times 10^{-4} \text{ A/cm}^2$ after dipping for 30 minutes and $4.4 \times 10^{-4} \text{ A/cm}^2$ after dipping for 60 minutes. The increase of leakage current density seems to be caused by the increase in crystallinity of the film which is due to the formation of the pseudo-boehmite structure during hydration process.

Conclusions

The variation of the properties in Al_2O_3 films after dipping in DI-water has been investigated. Due to the formation of an aluminum oxyhydroxide layer on the surface of the films, the thickness of the Al_2O_3 films was not changed after dipping for one hour. From the XPS analysis, the formation of Al-hydroxide bonds was confirmed. Surprisingly, the dielectric constant of the Al_2O_3 film increased up to 11.5 which exceeded the ideal dielectric constant of crystalline Al_2O_3 after one hour's dipping in DI-water. It is assumed that the increase of the dielectric constant resulted from the formation of a pseudo-boehmite layer at the surface of the film. In addition, after hydration, the leakage current densities did not show much change.

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