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Effect of hydration on the properties of lanthanum oxide and lanthanum aluminate thin films

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Abstract

The properties of lanthanum oxide films and lanthanum aluminate films were investigated after dipping the films in DI-water. The La_2O_3 film showed rapid dissolution in DI-water and a swift decrease in thickness resulting in an increased leakage current density. The LAO film showed almost no changes in thickness due to the formation of a layer, preventing dissolution. It was revealed that the changes in the films' oxygen contents during the hydration process affected the films' dielectric constants. The LAO films showed better hydration resistance characteristics, which are typically more suitable for conventional semiconductor manufacturing processes.

Keywords: C. Dielectric properties; Hydration; High-k material; Gate oxide

1. Introduction

High dielectric constant materials have attracted much attention in recent years since the scaling of semiconductor devices requires a gate dielectric that 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 gate 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 gate dielectric materials [6]. However, since it is known that rare earth metal oxides are degraded by the adsorption of moisture and hydration reactions [7], the conventional wet cleaning process which contains water (H_2O) species within the cleaning solution are not appropriate when La_2O_3 is used as a gate dielectric material. In the previous study [8], it has been reported that Al_2O_3-incorporated ZrO_2 showed improved hydration resistance. Consequently, it may be beneficial to study the compatibility of the aluminum-incorporated La_2O_3, that is, lanthanum aluminate ($La_xAl_{1-x}O_y$; LAO), with a conventional wet cleaning process. Furthermore, since LAO is known as one of the most promising next-generation gate dielectric materials [6], the importance of studying the hydration behavior of the LAO film is reemphasized.

In this study, both La_2O_3 and LAO films were deposited using a metal organic chemical vapor deposition (MOCVD) method. The films were dipped in de-ionized (DI) water for up to 2 h. Although the hydration reaction of the films in high humidity ambient was previously reported [9], this type of study is more valuable because this work more closely duplicates the semiconductor manufacturing process. After dipping the films in DI-water, the physical properties of the films were compared in order to investigate the effects of the hydration reaction on the properties of the films.

2. Experimental procedure

La_2O_3 films and LAO films with a thickness of about 12 nm were deposited on p-type (1 0 0) Si wafers using the MOCVD method. The wafers were degreased in organic solvents and then treated with a 10% hydrofluoric (HF) solution to remove the native oxide. $La(tmhd)_3$-tetraglyme adduct [$La(C_{11}H_{19}O_2)_3 \cdot CH_3(OCH_2CH_2)_4OCH_3$, Strem Chemical Inc., USA] and Al-acetylacetonate [$Al(CH_3COCH)$, Aldrich Chemical Company Inc., USA] were used as precursors for the La and Al metals. Nitrogen and oxygen were used as the carrier gas and the oxidizing gas, respectively. The substrate temperature was

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maintained at 350 °C during deposition and the working pressure was 2 Torr for both films. In order to examine the effect of the hydration reactions on the properties of the film, the as-grown films were dipped in DI-water for up to 2 h using an ultrasonic vibrator.

Film thicknesses were measured using an ellipsometer (Gaertner, L117, $\lambda = 632.8$ nm). Surface compositions of the films were analyzed by X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700 ESCA spectrometer) with a Mg Kα ($h\nu = 1253.6$ eV) X-ray source. Metal/oxide/silicon (MOS, Pt/oxide/Si) capacitor structures were fabricated to examine the electrical properties. The circular Pt electrode of the MOS capacitor with a thickness of 150 nm was deposited using magnetron sputtering and shadow masks. The capacitor area was 9.25×10^{-4} cm^2 for all samples. High-frequency (1 MHz) capacitance–voltage (*C–V*) characteristics were measured with an HP4284 precision LCR meter and leakage current density–voltage (*J–V*) curves were obtained by an HP4145B semiconductor parameter analyzer.

3. Results and discussion

Fig. 1 shows the ratios of thickness changes of the La_2O_3 films and the LAO films as a function of time dipped in DI-water. Two films showed different hydration characteristics; the thickness of the La_2O_3 film gradually decreased as dipping time increased, while the LAO film showed almost no change or a slight increase in thickness. These behaviors seem to be caused by chemical and structural differences. When the La_2O_3 contacts H_2O, a hydration reaction changes La_2O_3 into $La(OH)_3$ (lanthanum hydroxide), as has been already reported by other researchers [10]. Then, the formed $La(OH)_3$ easily dissolves in water which decreases the thickness of the La_2O_3 film. Additionally, in the absence of ultrasonic vibration, the La_2O_3 film showed somewhat of a decrease in thickness under water. In the case of the LAO film, surface La_2O_3 (La–O bonds near the film surface) seemed to change into $La(OH)_3$ and dissolve in DI-water; however, the thickness of the LAO film changed very little. This could be explained by the previous work of other researchers [11]. In the case of hydration experiments on an Al_2O_3 film, through a series of steps, the adsorbed water layer converts the surface Al_2O_3 layer to an amorphous aluminum oxyhydroxide (aluminum hydroxylate) of several nanometers-in thickness [11]. It would seem that this formation of an aluminum oxyhydroxide layer acts as barrier layer which prevents additional dissolution of the film and results in a slight increase rather than a decrease of the LAO film thickness.

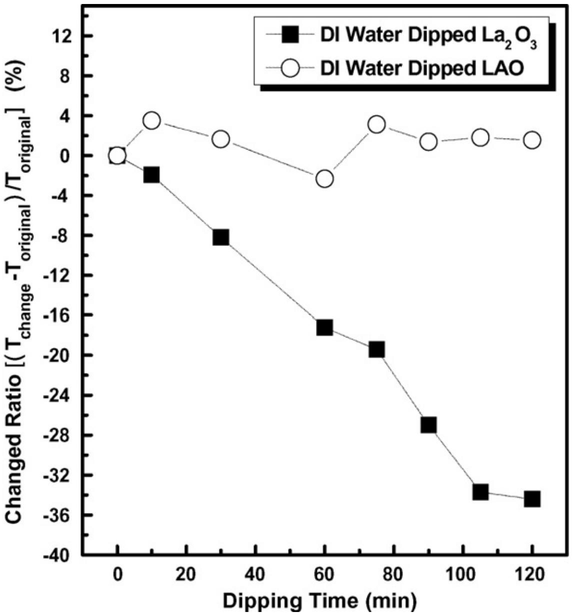

Fig. 1. The ratios of changes of film thickness as a function of dipping time in DI-water.

Fig. 2 shows the atomic concentration of the La_2O_3 and LAO films as a function of dipping time. The oxygen contents of the films increased as dipping time increased. It is known [12] that surface La, which originally has one oxygen atom, comes to have two oxygen atoms during the hydration process. The composition of lanthanum oxide film which originally had an oxygen deficient nature nearly approached a stoichiometric composition after the film was dipped in DI-water for 30 and 60 min. It seems that the hydroxyl group, which diffuses into the film during hydration and dissolution, slightly increases the oxygen composition of the film. The LAO film which originally showed oxygen sufficient nature, also showed a continuous increase of oxygen content with a large reduction of the lanthanum content to aluminum content after hydration for 30 min. The reduction of the lanthanum content resulted from the fast dissolution of surface lanthanum oxide that turned into $La(OH)_3$ before the formation of an aluminum oxyhydroxide layer at the film surface. After dipping for 60 min, the lanthanum and aluminum contents slightly decreased in proportion to a slight increase of the oxygen content.

Fig. 3 shows the changes of the dielectric constant of the La_2O_3 and LAO films as a function of dipping time. The dielectric constant of the La_2O_3 film gradually increased for the first 30 min and then decreased after dipping for 60 min. The increase of the dielectric constant seems to be related to the composition of the film which can then change the electrical properties of the film [13]. That is, the fact that the film composition approached stoichiometric ratios after dipping for 30 min, as discussed above, affected the increase of the dielectric constant of the film. On the other hand, the dielectric constant of the film that was dipped for 60 min decreased in spite of stoichiometric ratios within the film. There are two plausible reasons for this behavior. One reason could be the dielectric constant of the $La(OH)_3$. It was reported in a previous moisture adsorption experiment of a La_2O_3 film [14] that the dielectric constant of the $La(OH)_3$ film was estimated to be as low as 10. This could be inaccurate, however, since the value is not a measured value but an estimated value. Another reason could be the thickness of the film. As shown in Fig. 2(a), the thickness of the La_2O_3 film decreased about 20% after dipping in DI-water for 60 min. This severe reduction of film thickness

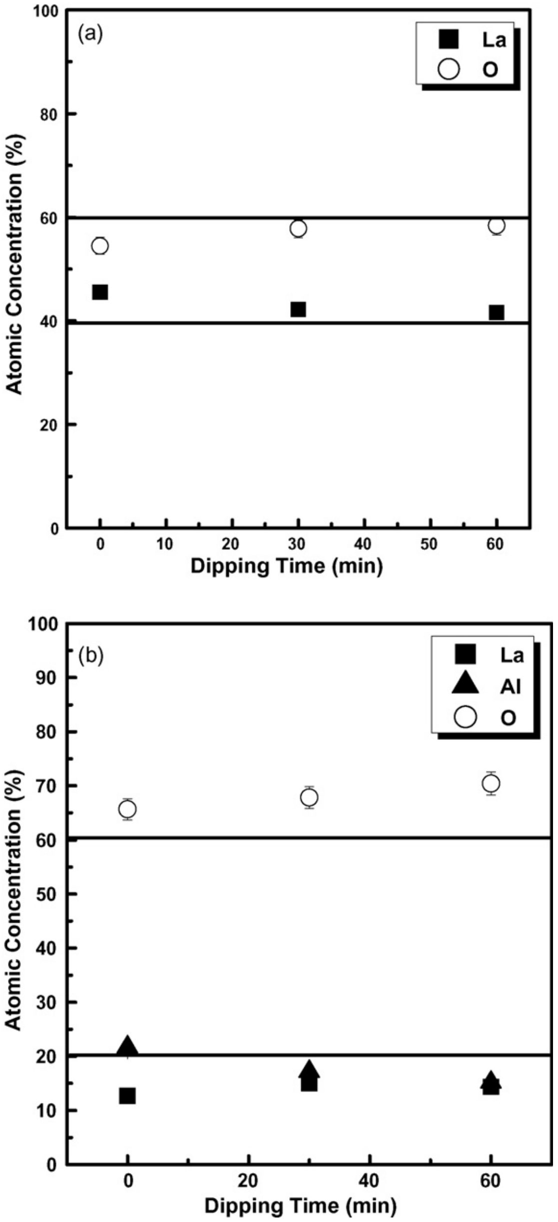

Fig. 2. The atomic concentration of (a) the La_2O_3 and (b) the LAO films as a function of dipping time in DI-water.

enhanced the tunneling current through the film, which degraded the dielectric property of the film. Between these two explanations, because the formed $La(OH)_3$ rapidly dissolved in DI-water, the latter is the more plausible explanation. In the case of the LAO film, the dielectric constant decreased after dipping for 30 min. This seems to be caused by rapid dissolution of La–O bonds within the film as demonstrated by XPS analysis. After the film was dipped for 60 min, the capacitance slightly increased with respect to the capacitance of the film dipped for 30 min. The reason for the increase of the dielectric constant is currently under investigation.

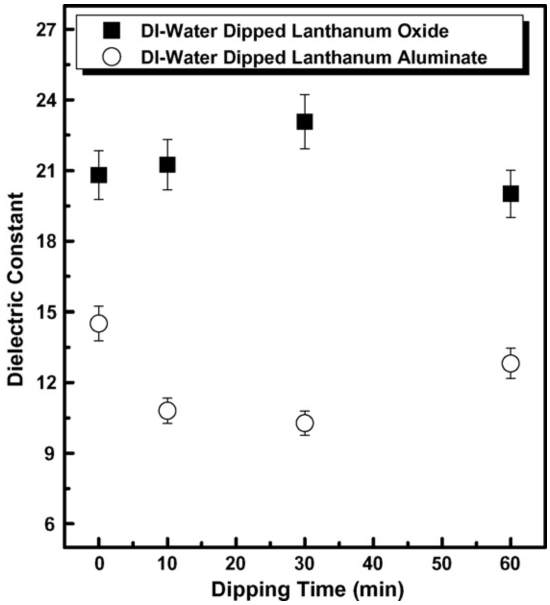

Fig. 3. The changes of dielectric constant of the La_2O_3 and the LAO films as a function of dipping time in DI-water.

Fig. 4 shows changes of the leakage current densities of the films measured at the voltage of $V_{fb} - V_g = -1$ V as a function of dipping time. For as-grown films, the leakage current density of the LAO film (about 10^{-2} A/cm^2) was about one order of magnitude lower than that of the La_2O_3 film (about 10^{-1} A/cm^2). After dipping the films in DI-water, the leakage current density increased as dipping time increased in the case of the lanthanum oxide film while the density was essentially unchanged in the case of the lanthanum aluminate film. The increase of the leakage current density of the lanthanum oxide film was caused by a decrease in the physical thickness during the hydration process. Since the physical thickness of the lanthanum aluminate films was nearly the same for all dipping times, the leakage current density of the lanthanum aluminate films showed no distinct changes.

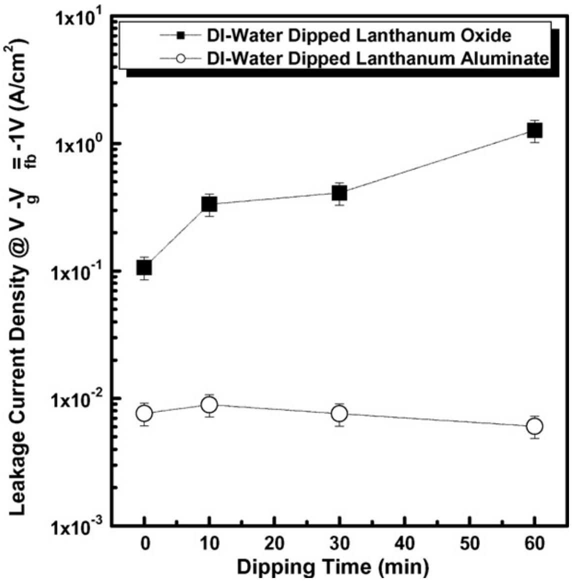

Fig. 4. The changes of leakage current densities of the films measured at the voltage of $V_{fb} - V_g = -1$ V as a function of dipping time in DI-water.

4. Conclusions

Changes of the structural and electrical properties of the La_2O_3 and LAO films after dipping in DI-water were investigated and compared. The La_2O_3 films were rapidly dissolved in DI-water through the formation of lanthanum hydroxide and after dipping for 2 h, the thickness of the film decreased about 35% with respect to the original thickness. In the case of the LAO films, however, there were no distinct changes in film thickness since an aluminum oxyhydroxide layer was formed and prevented film dissolution. As dipping time increased, the stoichiometry of the La_2O_3 film was improved, and this affected the increase of dielectric constant of the film after dipping. In the case of the LAO films, the oxygen concentration also increased with a decrease in lanthanum concentration due to the rapid dissolution of surface lanthanum oxide. The dielectric constant of the La_2O_3 film increased for the first 30 min and then decreased after dipping for 60 min while that of the LAO film decreased for the first 30 min and then again increased after dipping for 60 min. The leakage current density of the La_2O_3 film increased slightly after dipping for 30 min and increased as much as two orders of magnitude after dipping for 60 min. The current density of the LAO film was essentially the same, regardless of dipping time. It was confirmed that the hydration resistance of the LAO films was better and more applicable to conventional CMOS manufacturing processes.

Acknowledgement

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