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Effects of the wet air on the properties of the lanthanum oxide and lanthanum aluminate thin films

Jin Hyung Jun, Doo Jin Choi *

Department of Ceramic Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, South Korea

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Abstract

Lanthanum oxide and lanthanum aluminate thin films were deposited on Si substrates. The as-grown films were stored in wet ambient and dry ambient for days and annealed after storage and also the structural and the electrical properties of the films were investigated. As the storage time increased, the La_2O_3 films stored in wet ambient showed rapid reaction with moisture and the properties degraded. In case of the LAO films, although the thickness of the film also increased during hydration, the properties of the film did not so much changed due to the role of the incorporated aluminum. The LAO films showed better hydration resistance characteristics and so more suitable for conventional wet cleaning process in semiconductor fabrication.

Keywords: Lanthanum oxide; Lanthanum aluminate; Structural and electrical properties; Hydration

1. Introduction

High dielectric-constant materials have attracted much attention for several years in silicon-based semiconductor technology since the scaling of semiconductor devices requires a gate dielectric with an equivalent oxide thickness (EOT) of less than 1.5 nm [1]. For this reason, some binary metal oxides such as ZrO_2 and HfO_2 [2] have been widely studied for use as gate dielectrics. In addition, it has been reported that the rare earth metal oxides such as La_2O_3 [3] and Y_2O_3 should be studied for use as next generation high dielectric constant gate dielectrics [4]. However, it is known that the La_2O_3 degraded by the absorption of moisture [5]. From this reason, when the La_2O_3 is used as gate dielectric, only dry cleaning process can be used for semiconductor fabrication instead of the conventional wet cleaning process. In a previous study [6], it is reported that the Al_2O_3 incorporated ZrO_2 showed improved hydration resistance. Accordingly, the study on the aluminum-incorporated La_2O_3 would be worth for use as a gate dielectric with conventional wet cleaning process. In addition, since the lanthanum aluminate ($La_xAl_{1-x}O_y$; LAO) is known as one of the most promising materials for use as next generation gate dielectric [4], the importance of the study on the hydration behavior of the LAO film is again emphasized.

In this paper, we deposited both the La_2O_3 and the LAO films by using metal organic chemical vapor deposition (MOCVD) method and stored the films in moisture ambient and dry ambient for days. After the films were stored in two different ambient, we compared the structural properties and the electrical properties of the films in order to investigate the effects of moisture on the properties of the films.

2. Experimental

The La_2O_3 films and the LAO films were deposited on p-type (100) Si wafers by using 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 La and Al metal. Nitrogen and oxygen were used as the carrier gas and the oxidizing gas, respectively. Substrate temperature was maintained at 350 °C during deposition and the working pressure was 2 Torr for both films. X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 220*i*-XL) analysis reveals that the atomic percen-

* Corresponding author. Tel.: +82 2 2123 2852; fax: +82 2 365 5882.
E-mail address: drchoidj@yonsei.ac.kr (D.J. Choi).

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tages of the Al and La metal in the LAO film were 17% and 28%, respectively. In order to examine the hydration effect on the properties of the film, the as-grown films were stored in wet and dry ambient for days. The ambient was made by using two desiccators which had a bowl containing de-ionized (DI) water and silica gels, respectively. The humidity of the wet ambient was maintained as about 80% and well-dried silica gels were frequently replenished in order to keep dry ambient.

The thicknesses of the films were measured by utilizing an ellipsometer (Gaertner, L117, λ=632.8 nm). The stored films were annealed at 600 °C for 90 s in N_2 ambient by using rapid thermal process (RTP). Atomic force microscopy (AFM) was used to calculate the root-mean-square (RMS) surface roughness. We also fabricated metal/oxide/silicon (MOS, Pt/LAO/Si) capacitor structures to examine the electrical properties. 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(a) shows the ratios of thickness changes as a function of exposure time after the La_2O_3 and LAO films were exposed to wet and dry ambient and Fig. 1(b) shows the ratios of thickness changes after the exposed (hydrated) films were annealed. The original thicknesses in both Fig. 1(a) and (b) mean that the thicknesses of the as-grown films were about 12 nm thick. In addition, the stored days have different meaning in Fig. 1(b), that is, the data points of 4 days mean the ratios of changed thickness of annealed films are already exposed to specific ambient for 4 days, for example. Since it is well known that the rare earth metal oxides are very sensitive to moisture and form hydroxyl group on their surface when they meet moisture [7], both the La_2O_3 films exposed to wet ambient (hereafter called wet-La_2O_3) and the LAO films exposed to wet ambient (hereafter called wet-LAO) showed more increase in thickness than dry-La_2O_3 and dry-LAO films did. In addition, between the two wet films, the thickness increase of the wet-La_2O_3 film is larger than that of the wet-LAO film and it seems that this is because the incorporated aluminum in the LAO films does not interact with moisture as much as lanthanum does. The thickness increase of the dry-La_2O_3 film seems to be caused by residual moisture in the desiccator which is frequently opened for the experiment.

The role of the incorporated aluminum was evidently revealed after annealing as shown in Fig. 1(b). Our previous works [8,9] showed that the thickness of the oxide films on Si substrate decreases after annealing process due to the densification of the film with or without interfacial layer growth and showed that the incorporated aluminum in the LAO film suppressed interfacial layer growth during annealing process. In these manners, the thickness of all films in this study decreased after annealing. There were, however, some differences between the La_2O_3 film and the LAO film and between wet film and dry film. The wet-La_2O_3 film showed the smallest thickness decreases which seemed to be the evidence of

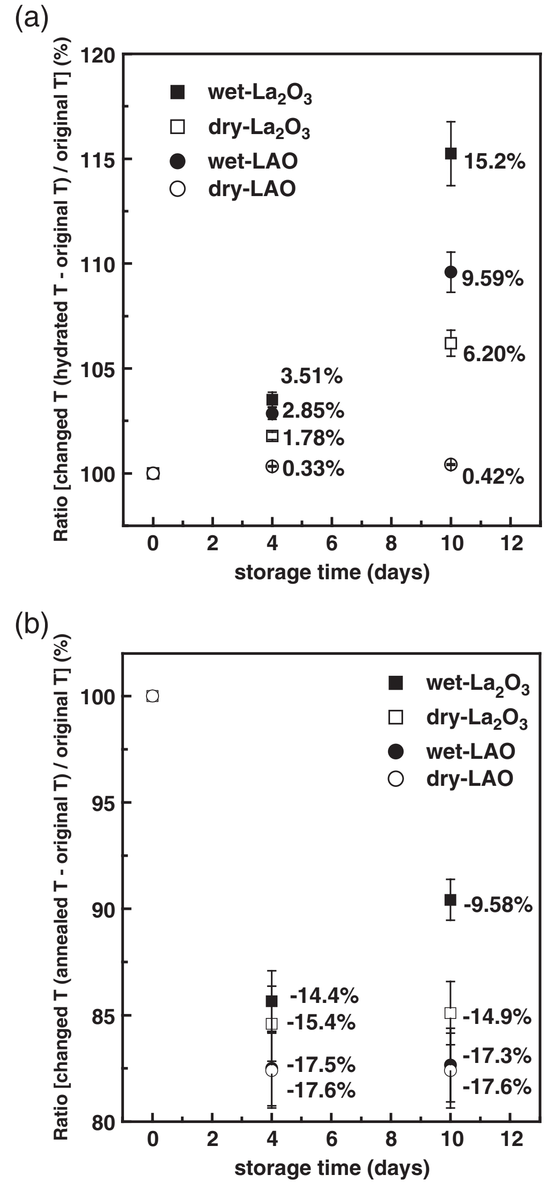

Fig. 1. The ratios of thickness changes (a) as a function of exposure time after the films were exposed to wet and dry ambient and (b) after the exposed films were annealed.

interfacial layer growth during annealing process. It is reported [10] that the surface hydroxyl group and/or absorbed moisture in rare earth oxide film diffused very rapidly into the film and toward film/silicon interface and reacted with silicon producing interfacial layer during annealing process. The same course seemed to be done in the case of the wet-La_2O_3 films. This assumption is reasonable when comparing 10 days stored wet-La_2O_3 film with 4 days stored wet-La_2O_3 film. The difference of decreasing percentage between the two films represents the difference of hydration degree of the films. In case of the wet-LAO film, the film showed drastic decrease in thickness as much as the dry-LAO film. This seems to be caused by the so-called aluminum-blocking effect. That is, the incorporated aluminum in the LAO film prohibits the diffusion of OH groups on the surface or in the film toward film/silicon interface and so the interfacial layer did not grow.