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Moisture Absorption-Induced Permittivity Deterioration and Surface Roughness Enhancement of Lanthanum Oxide Films on Silicon

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1. Introduction

Lanthanum oxide (La_2O_3) is a promising material to substitute SiO_2 as the gate dielectric film because of its relatively high permittivity and a large band gap of 6eV[1]. However, concerning the permittivity of La_2O_3 there is not a widely accepted value. Both of very high[2] and low[3] permittivity La_2O_3 films were reported. Two possible reasons for low permittivity have been considered. One is the low density of amorphous La_2O_3 films, and the other is silicate formation at the interface of La_2O_3 film and silicon. On the other hand, it is well known that La_2O_3 films are hygroscopic, forming hydroxide[4] which creates charges in the gate dielectric and results in a large flat-band voltage shift[5]. However, effects of moisture absorption on the permittivity and surface morphology change of La_2O_3 film have not been investigated intensively. In this work, effects of the moisture absorption on the permittivity of La_2O_3 film to elucidate the reason for the unstable k-value of La_2O_3 and the surface roughness of La_2O_3 film have been investigated.

2. Experiments

La_2O_3 films were deposited on HF-last Si with RF sputtering method in argon ambient at room temperature and were annealed at 600 ºC in pure N_2 ambient for 30 seconds. **Fig.1** shows the sample preparation procedures. The physical thicknesses of La_2O_3 films were determined with the grazing incident x-ray reflectivity (GIXR) measurements.

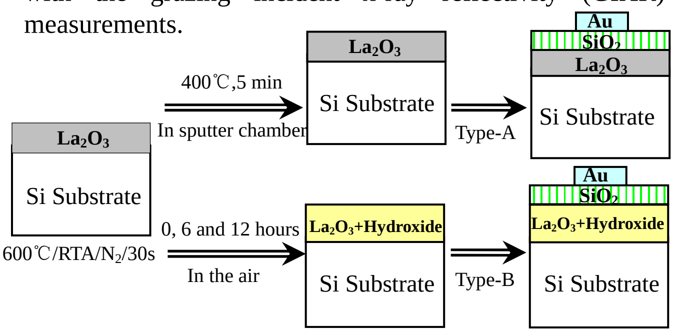

Fig.1. Illustration of two kinds of sample preparation procedures. One is the water desorbed La_2O_3 film (Type-A) which was annealed at 400℃ in sputter chamber to make lanthanum hydroxide decompose into lanthanum oxide and H_2O[6]. The other is the moisture absorbed sample (Type-B) which was exposed to the air with different time. Both samples were followed by 6nm SiO_2 layer deposition without any exposure to the air to prevent the moisture absorption.

3. Results and Discussion

The permittivity of Type-A La_2O_3 film in Fig.1 was investigated. Capacitance-Voltage (C-V) measurements were performed for Au/SiO_2/La_2O_3/Si/Al MIS capacitors with the frequency of 100 kHz. The CET has a good linear relationship with La_2O_3 film thickness as shown in **Fig.2**. The permittivity calculated from the slope is about 24.

Figure 3 shows the CET versus La_2O_3 film thickness plot for Type-B samples in Fig.1. Zero hour exposed to the air means that the sample was put in the sputter chamber for SiO_2 layer deposition as quickly as possible after annealing. Also the permittivity (k_{exp}) of the La_2O_3 film exposed to the air can be calculated from slopes of linear fitting curves. It can be observed that the permittivity of the film changes with the time exposure to the air. Therefore moisture absorption should be a very possible reason for the unstable k-value of La_2O_3 films in previous literatures.

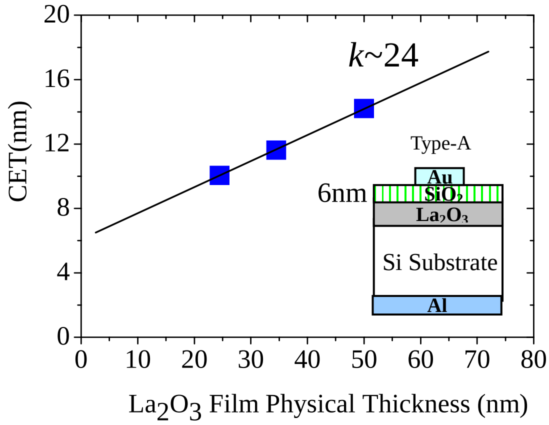

Fig.2. The relationship of CET to the La_2O_3 physical thickness for Au/SiO_2/ La_2O_3/Si/Al MIS capacitors.

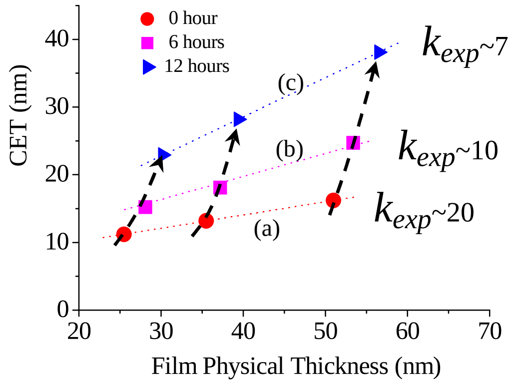

Fig.3. The relationship of CET to Type-B La_2O_3 physical thickness for Au/SiO_2/ La_2O_3/Si MIS capacitors. The sample was exposed to the air for (a) zero hour, (b) 6 hours and (c) 12 hours before SiO_2 layer deposition.

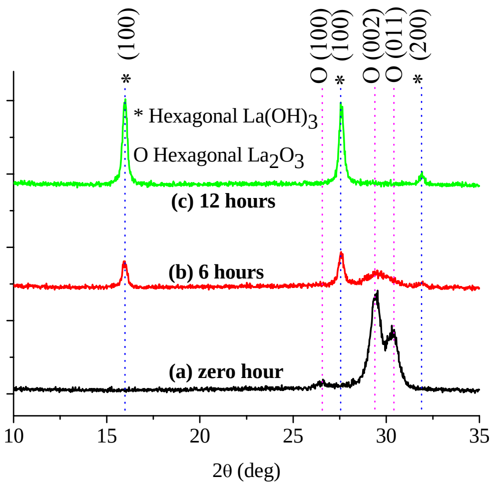

Fig.4. XRD patterns of La_2O_3 films on silicon after they were exposed to the air for (a) zero hour, (b) 6 hours, and (c) 12 hours.

From the XRD patterns of La_2O_3 films (**Fig.4**), zero hour exposed to the air La_2O_3 film is poly-crystallized in the hexagonal phase. After the exposure to the air for 6 hours, peaks attributed to $La(OH)_3$ appears, whereas the intensity of peaks attributed to the hexagonal La_2O_3 decreases. After the exposure to the air for 12 hours, strong $La(OH)_3$ phase peaks are found and peaks of hexagonal La_2O_3 disappear completely. Therefore we can conclude that the amount of hexagonal $La(OH)_3$ in the La_2O_3 film increased with the time exposed to the air. Although there is no report about the permittivity of hexagonal $La(OH)_3$, from Shannon's consideration[7] we can estimate the permittivity of hexagonal $La(OH)_3$ (k~10) on the basis of additivity rule of the polarizability. In fact, with the time exposed to the air Fig. 3 shows the degradation of k_{exp} (k-value obtained experimentally from the slope), though it is necessary to take account of an inhomogeneity of the film due to the partial reaction of the La_2O_3 with the moisture. We can also point the effect of moisture absorption on the permittivity of La_2O_3 film from the relationship of CET change to the time exposed the air. As shown in Fig.3, the CET of La_2O_3 film increases with the time exposed to the air, while only a slight change of the physical film thickness is observed. This fact implies that the CET increase should principally be caused by the permittivity deterioration of La_2O_3 film with the moisture absorption.

In addition, **Fig.5** shows the AFM images of La_2O_3 films which indicate the surface roughness increase in La_2O_3 films exposed to the air. One very possible cause of surface roughness enhancement is the nonuniform reaction of La_2O_3 and H_2O followed by the nonuniform volume expansion of the film due to moisture absorption. This observation should be another concern of hygroscopic La_2O_3 film properties.

Fig. 6 summarizes that all of CET, RMS and the amount of $La(OH)_3$ in La_2O_3 film increase with the time exposed to the air.

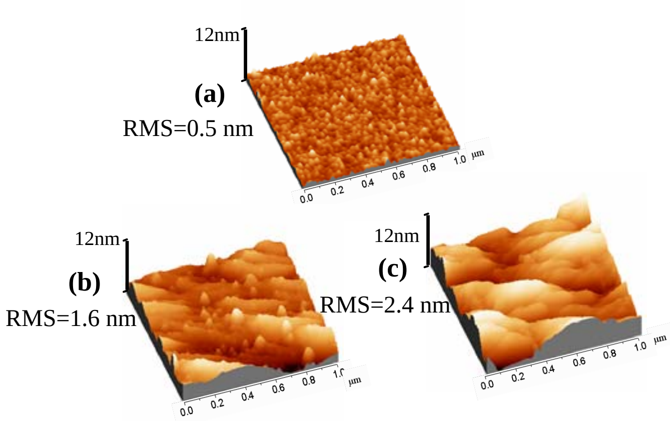

Fig.5. AFM images (1μm×1μm) of La_2O_3 film surfaces after the exposure to the air for (a) zero hour, (b) 6 hours, and (c) 12 hours.

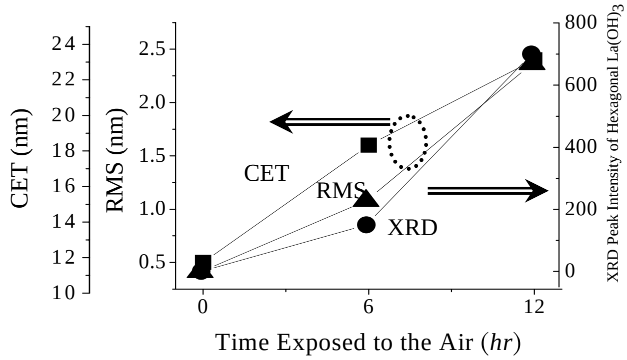

Fig.6. CET, RMS and hexagonal $La(OH)_3$ (100) XRD peak intensity as a function of the time exposed to the air of La_2O_3 film on silicon.

4. Conclusions

We found that the moisture absorption can degrade the permittivity of La_2O_3 film after the film was exposed to the air for several hours because of the formation of $La(OH)_3$ with a low permittivity. Thus it is concluded that the moisture absorption should be a possible reason for unstable k-value of La_2O_3 films. Furthermore AFM results indicate that the moisture absorption also increases the surface roughness of La_2O_3 films on silicon.

Acknowledgements

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