A-6-2

Design Methodology for La₂O₃-Based Ternally Higher-κ Dielectrics

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1. Introduction

The high-κ ternally composite oxides are reported to be promising in terms of permittivity (κ) [1-2], and high crystallization temperature (T_c) [3]. However, it has not been clarified how to choose the component oxides and adjust the composition, to meet the three requirements ; high κ, high T_c, and large bandgap (E_g). The intimacy with Si is another important issue, but it has been already discussed in detail elsewhere [4]. In this study, we propose a design methodology of ternally oxides and demonstrate a κ.enhancement by appropriate choice of component oxides and their composition.

2. Concept of design methodology

We introduce a classification of the component oxides in three groups by their roles in the composite oxides ; "V_m-modulator," which modulates the molar volume (V_m) by helping structural ordering and stabilizing a closely-packed structure, "polarizer," which has extremely high molar polarizability (α_m) and enhances α_m of the composites, and "amorphousizer," which disturbs the structural ordering and restrains the composites from the crystallization. The last group increases T_c while the first two groups will modify the κ value, which is understandable from the Clausius-Mossotti (C-M) relationship $\kappa=(1+8\pi\alpha_m/3V_m)/(1-4\pi\alpha_m/3V_m)$. This equation indicates that the larger (α_m/V_m) gives higher κ value, i.e. increasing α_m or decreasing V_m will result in κ enhancement. The V_m-modulator can change the structural ordering and crystal phase of the composite oxides, which strongly affects the V_m. We have already reported that Y₂O₃ works as a V_m-modulator for HfO₂ by inducing a phase transformation from loosely-packed phase (monoclinic) to closely-packed phase (cubic), and increases k of HfO₂ significantly [1]. On the other hand, the polarizer increases α_m, because the α_m of composite oxides is often approximated by the molar fractional average of the α_m for each component [5], although the polarizer might degrade

the E_g of the composite films at the same time, since high-α_m oxide always shows small E_g [6].

To obtain amorphous ternally oxides, we have to start with the oxide classified into the amorphousizer. La₂O₃ is an attractive amorphousizer, because of its higher κ value than other typical oxides categorized into this group, SiO₂ and Al₂O₃. Its character as the amorphousizer probably comes from the fact that La³⁺ ion has a large ionic radius and disturbs the formation of common structures of the ternally compounds with other oxides. As a matter of fact, it is reported that the addition of La₂O₃ to HfO₂ resulted in the increase of T_c [7]. In this study, we select La₂O₃ as the starting material and fabricate the ternally oxides by the addition of the V_m-modulator or the polarizer into La₂O₃. The examples of the oxides classified to those three groups are listed in **Table 1**. Y₂O₃ will work as the stabilizer for La₂O₃, whereas TiO₂ is a typical polarizer. **Fig.1** is the schematic image of the concept of designing ternally oxides based on the role-classification of the components, in the case of selecting La₂O₃ as the starting material.

3. Sample Fabrication

In order to evaluate the permittivity of the ternally composite oxide films, MIM (metal-insulator-metal) capacitors were fabricated. The ternally oxide films (15-20 nm thick) were deposited by RF co-sputtering of the oxide targets (La₂O₃, Y₂O₃, and TiO₂) in Ar ambient, on 100 nm-thick Pt films, which were previously deposited on thermally grown oxide on Si wafers. The films were annealed in N₂ or 0.1%-O₂+N₂ ambient at 400-800ºC, followed by Au electrodes deposition. The thickness and the composition of the films were determined by the glazing incident x-ray reflectivity and the x-ray photoelectron spectroscopy measurement, respectively.

4. Results and Discussions

As the content of the V_m-modulator (Y₂O₃) increases, La₂O₃-Y₂O₃ composite films come to crystallize at 600ºC as shown in **Fig.2-(a)**, while they remain amorphous at

Table 1. The properties of the component oxides and their classification into three groups. The α_m and V_m for Y₂O₃ and La₂O₃ are described with the form of (α_m/2)×2 and (V_m/2)×2, respectively, just for the comparison with other oxides.

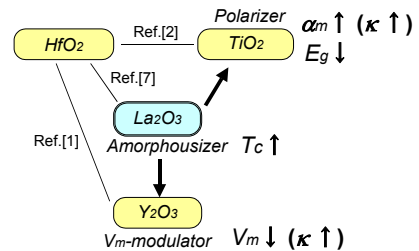|	La₂O₃	Y₂O₃	TiO₂	HfO₂
Classification	Amorphsizer,	V_m-modulator	Polarizer	-
α_m (Å³)	12 ×2 [5]	6.9 ×2 [5]	15.6 [5]	(not reported)
V_m (Å³)	41.2 ×2 (hexagonal)	37.3 ×2 (cubic)	34.5 (anatase) / 31.1 (rutile)	34.4 (mono.) / 33.4 (cubic)
Metal ion radius (Å)	1.04 (La³⁺)	0.97 (Y³⁺)	0.68 (Ti⁴⁺)	0.82 (Hf⁴⁺)
E_g (eV)	6 [6]	6 [6]	3.5	5.8 [6]
Electron configuration	$5d6s^2$	$4d5s^2$	$3d^24s^2$	$5d^26s^2$

Fig. 1 Schematic of our concept to design the ternally oxides, in the case of selecting La₂O₃ as the starting material. The component oxides are classified into three groups by their roles in the composite oxides, "amorphousizer," "V_m-modulator," and "polarizer." The κ, T_c, and E_g can be designed by the selection of the components and their compositions.
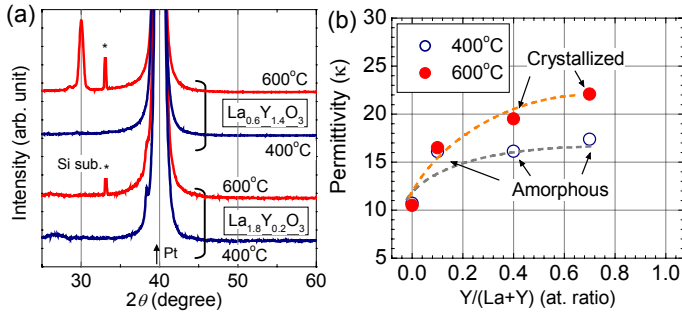
Fig. 2 (a) XRD spectra of La_2O_3-Y_2O_3 composite films. The Y-rich film crystallizes at 600ºC, while La-rich film remains amorphous. The peak at around 30º is attributed to orthorhombic $LaYO_3$ or hexagonal La_2O_3. The peaks at 33º and 40º (strong) are caused by Si-substrate and Pt electrode, respectively. (b) The κ of La_2O_3-Y_2O_3 composite films. The addition of Y_2O_3 increases κ value, but only the crystallized films show a significant κ enhancement.

400ºC. The observed sharp peak at $2\theta\sim30º$ can be attributed to orthorhombic $LaYO_3$ or hexagonal La_2O_3. The κ of La_2O_3-Y_2O_3 composite films are shown in **Fig.2-(b)**. The κ enhancement by Y_2O_3 addition is clearly observed, however, it is not significant while the films are in amorphous phase. These results show that Y_2O_3 stabilizes the $LaYO_3$ or La_2O_3 crystal structure, and shrinks the V_m of the composite films. Thus it is suggested that the V_m-*modulator* cannot fully contribute to the κ enhancement until the film crystallizes, probably because the shrinkage of V_m does not proceed efficiently in amorphous phase.

Then, in order to design higher-κ composite films without crystallization, the modification of the other parameter of the *C-M* relationship, *i.e.* increasing α_m, is required. Thus we examined the effect of the addition of *polarizer* (TiO_2) into amorphous La_2O_3 films. As the results, the T_c beyond 800ºC is attained as shown in **Fig.3**, as long as Ti/(La+Ti) is below 50at.%. The κ values of La_2O_3-TiO_2 composite films are shown in **Fig.4**. The κ increases significantly and approaches 30, even in amorphous phase, as the content of *polarizer* increases. However, there is a concern that the *polarizer* might decrease E_g of the composite films. **Fig.5** shows the extinction coefficient of the La_2O_3-TiO_2 composite films observed by the spectroscopic ellipsometry. The optical bandgap significantly decreases with the TiO_2 addition, which will cause a conduction band-offset degradation at oxide/Si interface seriously. $Hf_xTi_{1-x}O_2$ film is also reported to have a small conduction band-offset [8]. These facts indicate that controlling the content of *polarizer* is indispensable, to balance the high κ value with the large E_g. The alternative solution might be the choice of another *polarizer* which has moderate α_m value, or the formation of the higher-κ film stacking on a large-E_g oxide layer [9].

5. Conclusions

Designing of amorphous higher-k composite oxides was demonstrated by alloying La_2O_3 with other oxides. The κ enhancement was clearly observed by both decreasing V_m with the addition of V_m-*modulator* (Y_2O_3)*,* and increasing α_m with the addition of *polarizer* (TiO_2). The *polarizer* effectively worked even in amorphous films, but the effect of the V_m-*modulator* was not apparent without
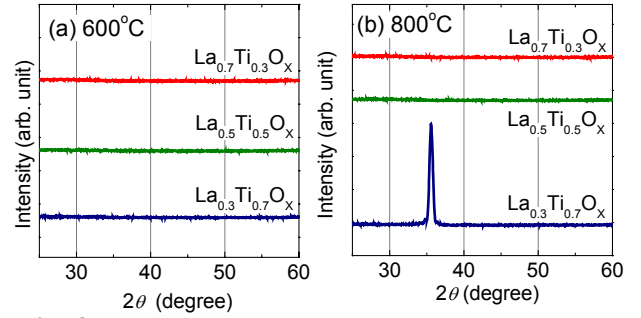

Fig. 3 XRD spectra of the La_2O_3-TiO_2 composite films deposited on Si substrate (without Pt electrode) and annealed at (a) 600ºC and (b) 800ºC. No peaks are detected even at 800ºC, except for the Ti-rich film ($La_{0.3}Ti_{0.7}O_x$), which shows a peak probably attributable to rutile-TiO_2.
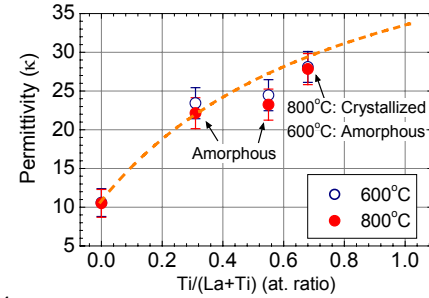

Fig. 4 Permittivity of La_2O_3-TiO_2 composite films. The high α_m value of TiO_2 can increase κ significantly even in the amorphous phase. The κ of Ti-rich film is approaching ~30.
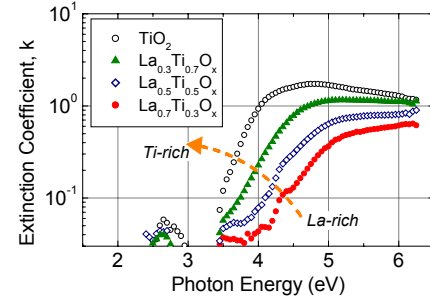

Fig. 5 Extinction coefficient of La_2O_3-TiO_2 composite films evaluated with the spectroscopic elliprometry. The refractive indices were extracted from Ψ-Δ data by point-by-point calculations. The optical bandgap degrades seriously by Ti addition. The main gap seems to be ~5eV for $La_{0.7}Ti_{0.3}O_x$ film, whereas ~4.5eV for $La_{0.3}Ti_{i0.7}O_x$ film.

crystallization. However, the content of the *polarizer* would be limited to prevent the degradation of E_g. These considerations will give a guideline for the design of the ternally higher-κ oxides for the advanced gate dielectrics.

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