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ELECTRICAL PROPERTIES OF Al_2O_3 INCORPOLATED CeO_2 THIN FILMS DEPOSITED BY RF MAGNETRON SPUTTERING

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CeO_2 films incorporated with Al_2O_3 oxide (Al_2O_3 molar fraction of 0.0 ~ 0.6) were deposited on p-type Si (1-10 Ωcm) substrate by RF magnetron sputtering using CeO_2 and Al_2O_3 targets in the Ar ambient with 10 % O_2 introduction. The deposition was carried out using the combinatorial mask system. The annealing was performed in N_2 or O_2 at 500°C for 30 minutes. For the N_2 annealed sample with the Al_2O_3 molar fraction of 0.2, the minimum leakage current density of 1.6×10^{-8} A/cm^2 was obtained at the electric field of 1 MV/cm, which was much lower than that of the film without the Al_2O_3 incorporation by two orders of magnitude. The variation of the flat band voltage as a function of the incorporated Al_2O_3 molar fraction suggests the fixed positive charge generation. The generation was caused by the formation of lower Ce oxide in the film and/or the lower oxide of Si diffused from the substrate into the film.

I. Introduction

With the scaling down of MOS devices, the gate dielectrics thickness were getting thinner down giving rise to increase of leakage current density through the gate dioxide. Due to this increase, conventional silicon dioxide (SiO_2) gate electric limits the reliance of MOS devices. The demand for high-k (high dielectric constant) materials has increased in order to keep the insulator oxide thickness without reduction of the gate capacitance for advanced MOS devices (1-5).

In order to solve this problem, we replaced SiO_2 gate dielectric with CeO_2 as a high-k gate dielectric material. CeO_2 has the following merits for silicon device application: high dielectric constant of 26, chemical stability, the compatibility with Si regarding crystal structure and lattice mismatch of 0.35%.

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Even in the deposition by the sputtering, however, CeO_2 has a strong tendency to crystallize at room temperature. The grain boundary in the crystallized gate oxide give rise to increase in the gate leakage density as well as difficulty in the micro patterning in the course of LSI production (6-10). In our previous study, we tried the mixing of crystals with different structures to suppress CeO_2 film crystallization (11). We found that 10% Al_2O_3 incorporation into the CeO_2 thin film kept samples amorphous after annealing at 500°C in N_2.

In this work, we prepare the Al_2O_3 incorporated CeO_2 thin films (Al_2O_3 molar fraction of 0.0 ~ 0.6) and evaluate the electrical properties of the samples as a function of the Al_2O_3 composition and optimal value of Al_2O_3 molar fraction.

II. Experimental

Using the RF magnetron sputtering with the combinatorial mask system, we prepared the Al_2O_3 incorporated CeO_2 thin films. The Al_2O_3 molar fraction ranged from 0.0 to 0.6 against CeO_2 in the samples. Figure 1 illustrates the process of preparing the combinatorial thin films with the moving mask system. At the first step, the CeO_2 sheet layer with 0.16nm thick was deposited. At the second step, by the moving mask a wedge shaped CeO_2 layer with 0 to 0.24 nm thick was deposited. At the third step, a wedge shaped Al_2O_3 layer deposition with 0 to 0.24 nm thick by the mask moving to the counter direction. Through these Step.1 to 3, as 1 cycle, 0.4 nm thick film was formed. The process was repeated 80 times, resulting in the total film thickness of 32 nm. The deposition conditions are summarized in TABLE I.

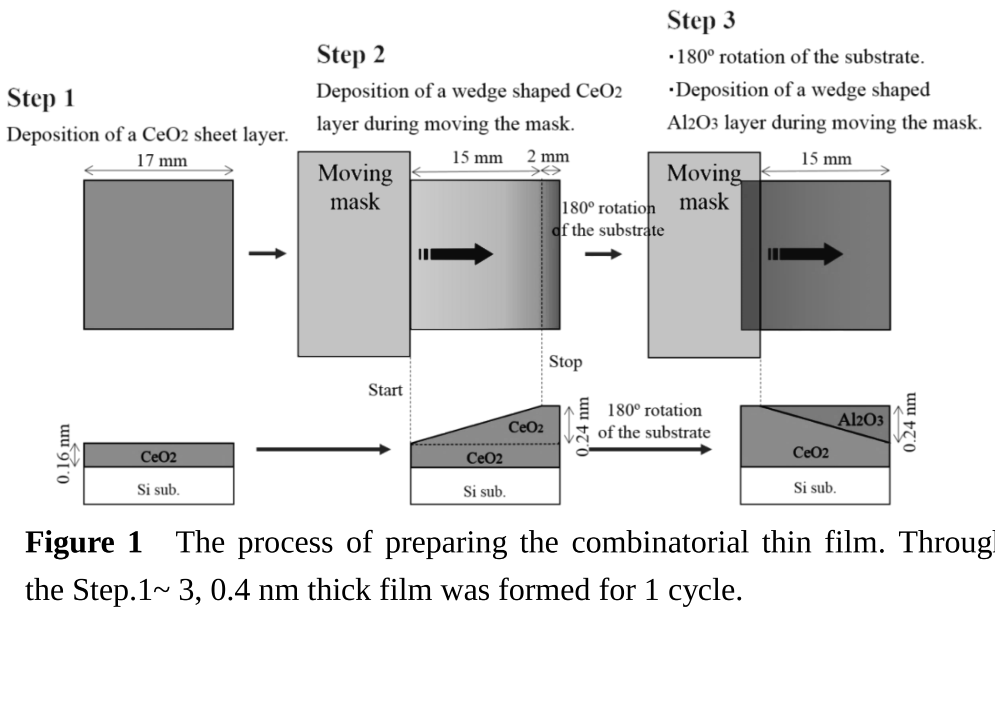

Figure 1 The process of preparing the combinatorial thin film. Through the Step.1~ 3, 0.4 nm thick film was formed for 1 cycle.

TABLE I Deposition conditions

Target	Al_2O_3 （50.8 mm Φ × 1 mm t）
	CeO_2 （50.8 mm Φ × 4 mm t）
Substrate	p-Si (1-10 Ωcm)
Background pressure	< 2 ×10-5 Pa
Sputtering pressure	0.5 Pa
Gas flow	Ar 45 sccm (90 %)
	O_2 5 sccm (10 %)
RF power/Deposition rate	Al_2O_3： RF 200 W / 0.00216 nm / s
	CeO_2：RF 150 W / 0.00631 nm / s
Temperature	R.T.

The prepared sample was divided into two pieces. One was annealed in N_2 and the other in O_2. Both two samples were annealed at 500 °C for 30 minutes. After annealing, Pt dot electrodes were formed on the surface of the sample by sputtering using the metal mask with openings of the 100 μm in diameter. The electrical properties were characterized from I-V and C-V measurements.

III. Results and Discussion

Figure 2 (a) (b) shows the I-V characteristics of the N_2 annealed sample as a function of the Al_2O_3 molar fraction. The ranges of Al_2O_3 molar fraction are 0.0 ~ 0.1 (a), and 0.2 ~ 0.6 (b), respectively.

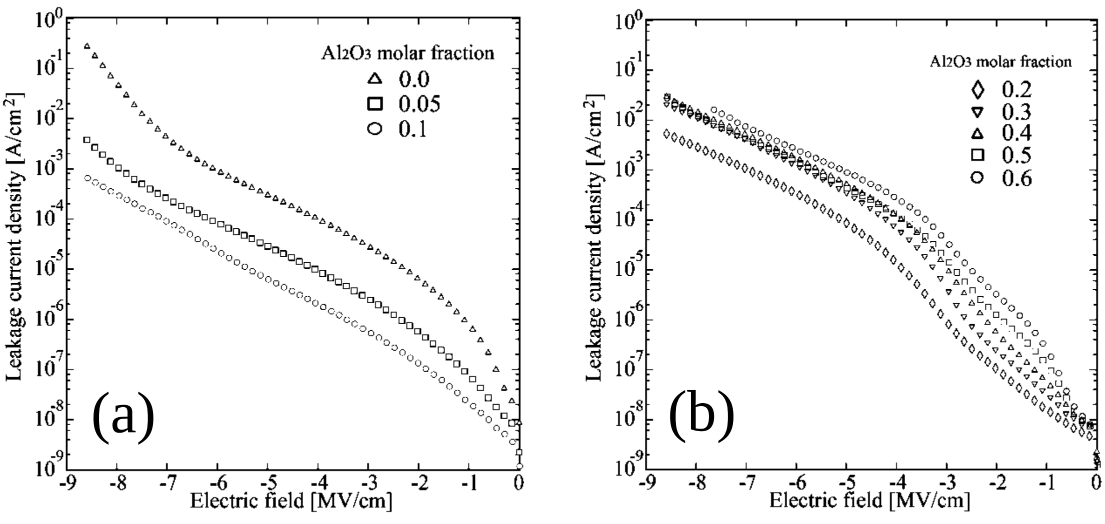

Figure 2 I-V characteristics of the N_2 annealed sample as a function of the Al_2O_3 molar fraction between 0.0 and 0.1 (a), and 0.2 and 0.6 (b).

With the increase in the Al_2O_3 molar fraction, the leakage current density for the Al_2O_3 molar fraction below 0.1 was decreased, while that for the Al_2O_3 molar fraction above 0.2 was increased. The increase for the Al_2O_3 molar fraction above 0.2 was probably due to the increase of the defects in the film with a large content of Al_2O_3.

The bending point appeared around -4 ~ -3 MV/cm and -3 ~ -2 MV/cm for the Al_2O_3 molar fraction above 0.2, and furthermore, the additional bending point appeared near -1MV/cm for the Al_2O_3 molar fraction of 0.5 and 0.6.

Figure 3 shows the leakage current density for the samples annealed in N_2 and O_2 at the applied electric field of -1 MV/cm (gate voltage = 3.2 V) as a function of the Al_2O_3 molar fraction. The leakage current densities of the samples annealed in N_2 and O_2 were once reduced to 1.6×10^{-8} and 9.1×10^{-8} A/cm^2, respectively. The former value was low compared with that of the films without Al_2O_3 incorporation by two orders of magnitude. At the Al_2O_3 molar fraction of 0, the leakage current densities of the sample annealed in O_2 were lower than that of the sample annealed in N_2, just as widely known behavior. On the other hand, for the Al_2O_3 molar fraction above 0.05, the leakage current densities of the sample annealed in O_2 were higher than that of the sample annealed in N_2. Further investigation is needed to explain these behaviors.

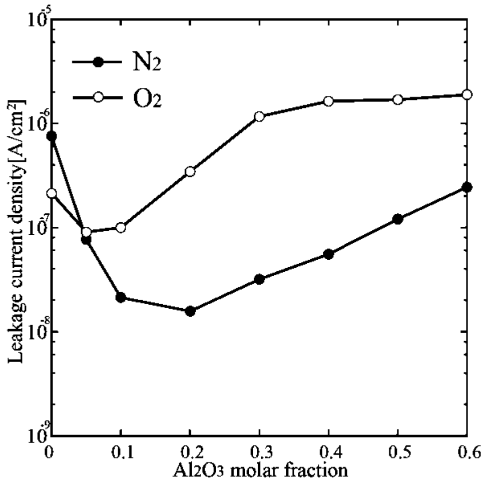

Figure 3 The leakage current density of the samples annealed in N_2 and O_2 at the applied electric field of -1 MV/cm as a function of the Al_2O_3 molar fraction.

Figure 4 shows the variation of (a) the dielectric constant, (b) the flat band voltage V_{fb}, (c) the fixed charge density Q_f, which are derived from the measured C-V data as a function of the molar fraction of Al_2O_3 incorporation.

As shown in Fig. 4 (a), during the increased Al_2O_3 molar fraction from 0.0 to 0.15, the dielectric constants of the sample annealed in O_2 quickly decreased from 16 to 6, but were almost independent of the Al_2O_3 molar fraction of 0.15.

Since the aluminum oxide is generally known gave rise to the negative charges in the films, the flat band voltage V_{fb} should have moved to the higher voltages with the increase of incorporated Al_2O_3 (12). However, Fig. 4 (b) shows that the V_{fb} shifted toward lower voltages on the whole with the Al_2O_3 incorporation. This variation toward lower voltages suggests the increase of the fixed positive charge in the films with the increase of the Al_2O_3 incorporation. The positive generation of the fixed positive charge is due to two causes: one is the generation of lower Ce oxide in the film and/or the other is the lower oxide of Si defused from the substrate into the films.

As shown in Fig. 4 (c), the fixed charge density Q_f was rapidly decreased to around 1.5×10^{12} cm^{-2} with the Al_2O_3 molar fraction up to 0.15, followed by the slight increase with the increase of Al_2O_3 incorporation. This variation was similar to that of the dielectric constants in Fig. 4 (a). For the sample annealed in O_2 the both Q_f and the flat band voltage V_{fb} in Fig. 4 (b) were low compared with those of the sample annealed in N_2. This behavior suggests that the amount of crystal defects was greater in the films annealed in O_2 than those annealed in a N_2.

It is considered that complicated variation in I-V and C-V characteristics of Al_2O_3 incorporated CeO_2 films was caused by the lower Ce oxide in the film or the lower oxide of Si defused from the substrate into the film.

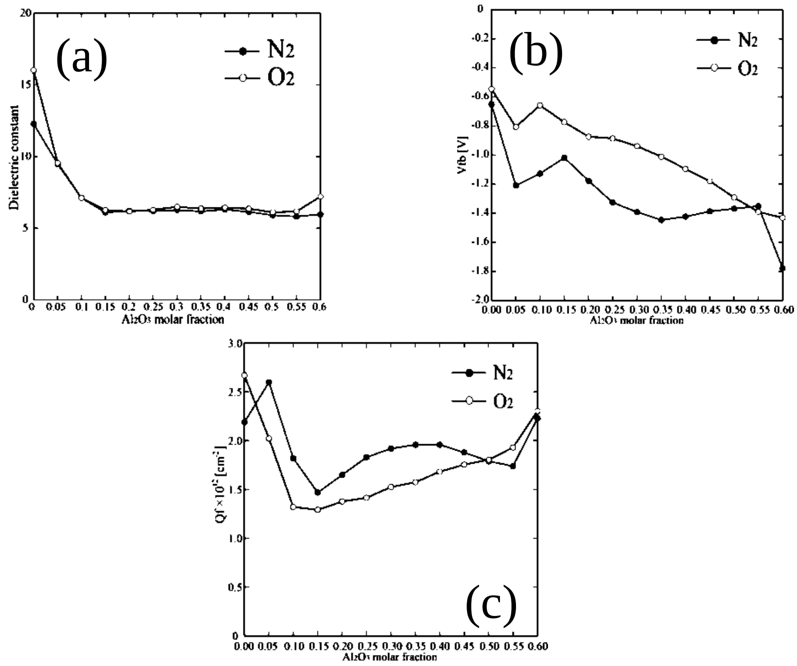

Figure 4 The variation of (a) the dielectric constant, (b) the flat band voltage V_{fb}, (c) the fixed charge density Q_f, derived from the measured C-V data as a function of the incorporated Al_2O_3 molar fraction and the annealing ambient.

IV. Summary

Using the combinatorial mask system, the Al_2O_3 incorporated CeO_2 thin films (Al_2O_3 molar fraction of 0.0 ~ 0.6) were prepared on p-type Si (1-10 Ωcm) substrate by means of the RF magnetron sputtering using CeO_2 and Al_2O_3 targets in Ar + 10% O_2.

For the samples annealed in the N_2 ambient with the Al_2O_3 molar fraction of 0.2, the leakage current density of 1.6×10^{-8} A/cm^2, obtained at the applied electric field of –1 MV/cm, was lower than that of the films without Al_2O_3 incorporation by two orders of magnitude. However, for the sample annealed in O_2 with the Al_2O_3 molar fraction of 0.05, the minimum leakage current density of 9.1×10^{-8} A/cm^2 was obtained.

The flat band voltage V_{fb} shifted toward lower voltages on the whole with the increase of incorporated Al_2O_3. This variation suggests the increase of the fixed positive charge in the films with the increase of the Al_2O_3 incorporation. The generation of the fixed positive charge was caused by the generation of lower Ce oxide in the film and/or the lower oxide of Si defused from the substrate into the films. It was found that the Al_2O_3 incorporation into CeO_2 film was effective in reducing the leakage current density, but this treatment caused complicated behavior in electrical properties.

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