La_2O_3 insulators prepared by ALD using $La(^iPrCp)_3$ source: self-limiting growth conditions and electrical properties

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Abstract

La_2O_3 insulators have been prepared by ALD using $La(^iPrCp)_3$ and H_2O as the source materials. We identified two necessary conditions to achieve the self-limiting growth: temperatures lower than 200 °C and extremely long purging after H_2O pulses. La_2O_3 insulators annealed at 500 °C showed good MOS properties with no hysteresis and small flat-band voltage shift. Comparisons to the La_2O_3 films prepared by electron-beam evaporation indicated that the ALD process needs further optimization especially to improve the *k* value (presently ~12) as well as the leakage suppression.

1. Introduction

La_2O_3 and its alloys with other metal oxides are promising insulators for the next-generation high-*k* gate insulators to achieve higher drivability as well as lower gate leakage [1]. There have been many studies to deposit La_2O_3 and related rare-earth oxides by physical vapor depositon such as electron-beam (EB) evaporaton and sputtering. Implementation of these materials to CMOS manufacturing needs more studies of the CVD or ALD processes. As for the La_2O_3 growth, β-diketonate and silylamide precursors were initially used as the La source [2,3]. Recently, cyclopentadienyls (Cp) and amidinates were often used because of their high vapor pressures and moderate reactivity. ALD of La_2O_3 using the Cp sources was investtigated by several groups in the temprature range of 260-450 °C [4-8]. However, there is no consensus regarding the optimal growth condition.

In this paper, we first identify the ALD conditions to realize a self-limiting growth using La iso-propyl cyclopentadienyl, $La(^iPrCp)_3$ and H_2O. We then evaluate the electrical properties of ALD-grown La_2O_3 and compare the results with those obtained by EB evaporation.

2. Experimental conditions

The gas-feed sequence of an ALD cycle is schematically shown in Fig.1. The $La(^iPrCp)_3$ and H_2O sources were kept at 135±2 °C and room temperature, respectively. The Ar flow rates during the $La(^iPrCp)_3/H_2O$ feed and purge periods were 100 and 300 sccm, respectively. Ar purge time after the La feed (t_{Ar1}) was 10 s whereas that after the H_2O feed (t_{Ar2}) was 100 s. The reason for extremely long t_{Ar2} is described later. La_2O_3 growth took place in a quarzt-tube reactor heated by an electrical furnace. Growth temperature (T_s) was changed from 135 °C to 250 °C. The gases were pumped by two turbomolecular pumps: one dedicated to the La source and the other to H_2O. Prior to each growth run, a Si(100) wafer was etched in a diluted HF solution and was introduced to the reactor through a loadlock chamber. For MOS capacitor evaluation, tungsten were deposited by RF sputtering and the electrodes were defined by plasma etching. Post-metallization anneal (PMA) was carried out in a 3% H_2 forming gas at 500°C for 30 min.

3. Results and discussion

A self-limiting growth is generally characterized by a constant growth rate per cycle with varying the feed time or pressure of the source gases. In addition, the self-limiting growth is only weakly dependent on T_s. Figures 2, 3, and 4 show, respectively, the effects of the La feed time (t_{La}), H_2O feed time (t_{H2O}), and T_s on the growth rate. In Fig. 2, the growth rate was almost constant for t_{La} of 2.5 – 10 s when T_s was below 200 °C. On the other hand, the growth rate increased with increasing t_{La} at T_s higher than 200 °C, These results indicate that T_s needs to be below 200 °C to achieve the self-limiting growth and that growth above 200 °C gives rise to the CVD-like mechanism. Figure 3 shows that the growth rate does not depend on t_{H2O} for both the low T_s (175 °C) and high T_s (250 °C) conditions. Figure 4 shows the Arrhenius plot of the growth rate in the T_s range from 135 to 250 °C. The growth rate is only weakly dependent on T_s, with an activation energy of 12 kJ/mol (0.12 eV). Figs. 2, 3, and 4 clearly show that La_2O_3 growth using $La(^iPrCp)_3$ and H_2O is self-limiting when the T_s is kept below 200°C. Refractive index of the

La_2O_3 film deposited at 175 °C was 1.74. As it agrees well with the reference data, the films were reasonably dense even though they were formed at relatively low T_s.

Thickness uniformity was greatly improved by adopting this self-limiting growth condition, as shown in Fig. 5. In this figure, the importance of the long t_{Ar2} is also shown. Thickness uniformity was improved by extending t_{Ar2} from 10 to 100 s.

Figure 6 showed the CVcharacteristics of a 13.4-nm-thick La_2O_3 layer deposited under the self-limiting condition at 175 °C. Although the as-deposited sample showed hysteresis, it disappeared by PMA at 500 °C. The *k* value is estimated to be 12. This value compares well with those reported for cubic La_2O_3 (k=11-14) [8]. Figure 7 compares the CV characteristics for a thinner ALD-La_2O_3 insulator (5.2 nm) to those for La_2O_3 prepared by EB evaporation (5.0 nm). The *k* value for La_2O_3 by EB evaporation was 15, which is higher than that for ALD-La_2O_3. However, the flat-band voltage (V_{fb}) was negatively shifted for the EB evaporation sample. ALD-La_2O_3 showed nearly ideal V_{fb} (+0.26 V), which indicates that the fixed charge density is as low as ~10^{11} cm^{-2}.

Figure 8 shows IV curves for ALD-La_2O_3. Thickness and ALD condition were the same as in Fig. 7. Leakage current was suppresed by 500 °C PMA. Figure 9 shows a benchmark plot of the leakage characteristics. The leakage current for annealed La_2O_3 under +1 V bias is ~1/100 lower than the ITRS requirements for the LOP devices and is close to those for the LSTP devices.

Electrical evaluation shown in Figs. 6, 7, and 8 indicate that the La_2O_3 ALD process needs to be improved to increase the *k* value to >20 as well as to suppress the leakage current. There are two factors to be addressed in this regard. First, since La_2O_3 is hygroscopic, La_2O_3 films must be capped by the electrode material immediately following proper annealing treatments. This was done for the EB evaporation sample in Fig. 7, but not for the ALD sample. Second, carbon impurities in the ALD samples presumably cause degradation in *k* and leakage characteristics. These issues are now under investigation in our research group.

4. Summary

We have shown that La_2O_3 growth using La(^{i}PrCp)$_3$ and H_2O becomes self-limiting at temperatures lower than 200 °C and with extremely long purging after H_2O feed. La_2O_3 insulators annealed at 500 °C showed good MOS properties with no hysteresis and small V_{fb} shift. Further optimization of the ALD and annealing/metallization processes is necessary to improve their *k* values and leakage characteristics.

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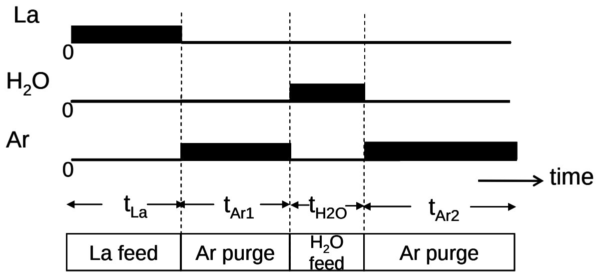

Figure 1. Flow sequence of ALD.

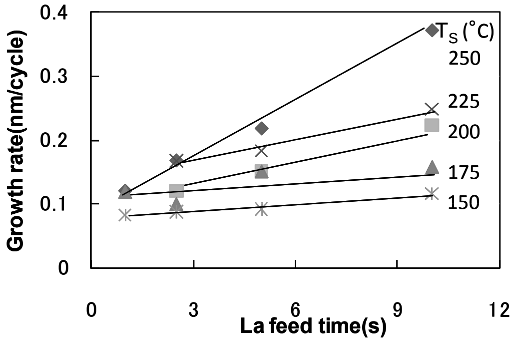

Figure 2. Dependence of growth rate on La feed time at various temperatures. H_2O feed time was 1s.

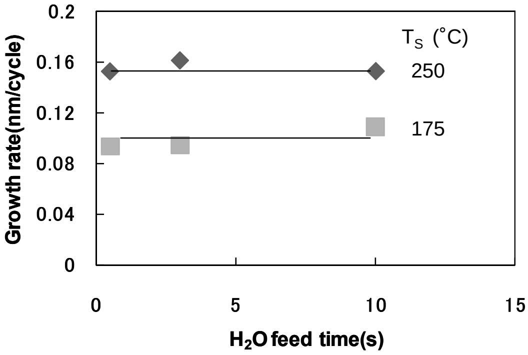

Figure 3. Dependence of growth rate on H_2O feed time at 175 and 250 °C. t_{La} was 2.5 s.

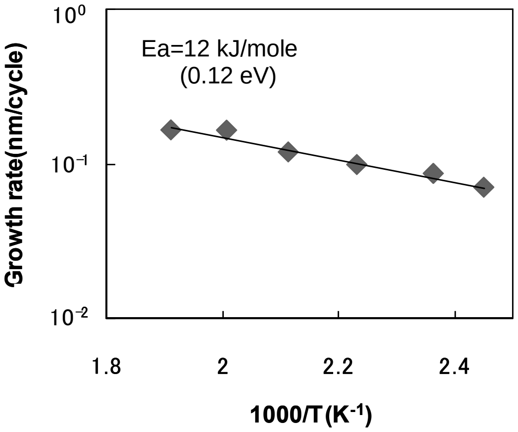

Figure 4. Arrhenius plot of the growth rate . t_{La} and t_{H2O} were 2.5 and 1 s, respectively.

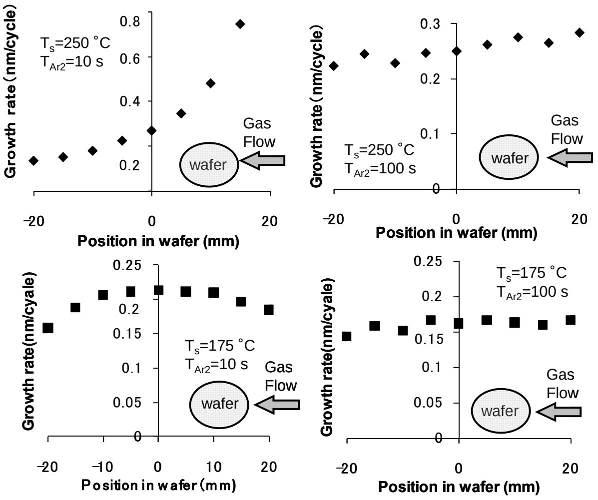

Figure 5. Thickness profiles of the La_2O_3 film along the gas-flow direction. Data for Ts of 175 and 250 °C and for t_{Ar2} of 100 s and 10 s are compared. tLa and t_{H2O} was 5 and 1 s, respectively.

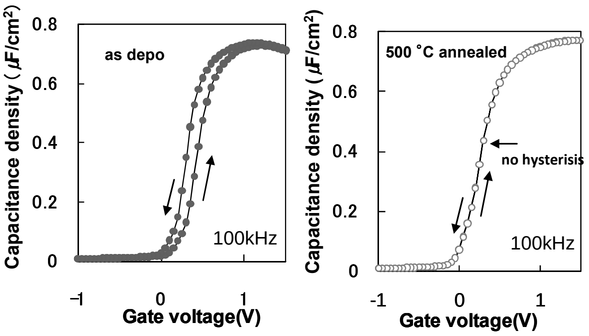

Figure 6. CVcharacteristics of the MOS capacitor with 13.4 nm La_2O_3 deposited at 175 °C. t_{La} and t_{H2O} were 2.5 and 1 s, respectively.

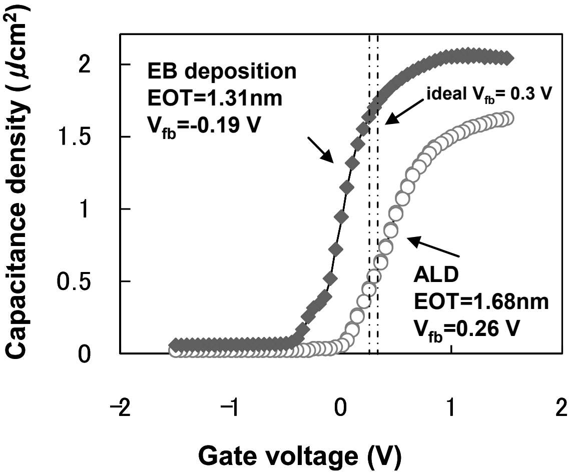

Figure 7. Comparison of the CV characteristics of La_2O_3 insulators prepared by ALD and EB deposition. La $_2O_3$ thickness was 5.2 and 5.0 nm for ALD and EB deposition respectively.Both films received PMA at 500 °C. ALD condition was the same as in Fig. 7. Ideal V_{fb} is +0.3 V.

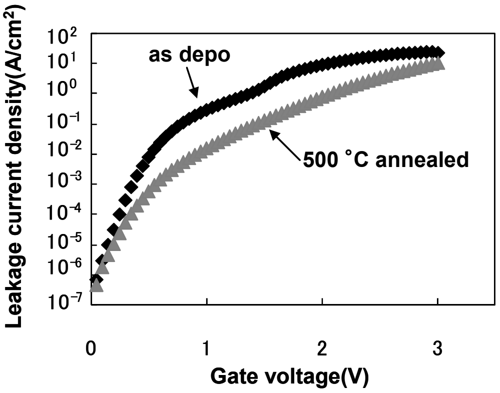

Figure 8. IV characteristic of the ALD La_2O_3 insulator. Thickness and ALD condition were the same as in Fig. 7.

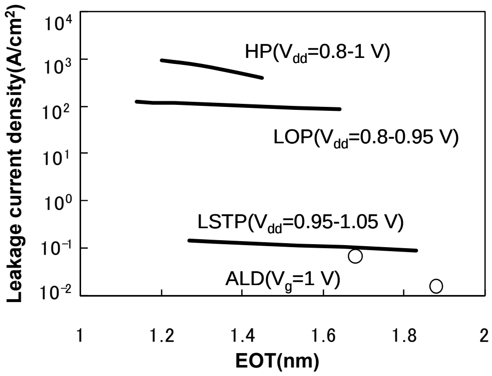

Figure 9. Bench mark plot of lekage current under +1 V with respect the ITRS requiments. Data for the 500 °C PMA sample are ploted.