

C-2-3

Water Absorption into ALD- Al_2O_3 Films as revealed by Physical Analysis and Electrical Characterization

Masaru Kadoshima¹, Masayasu Nishizawa², Tetsuji Yasuda², Toshihide Nabatame¹ and Akira Toriumi^{2,3}

¹MIRAI Project, Association of Super-Advanced Electronics Technologies (ASET), AIST Tsukuba West 7, 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan, Phone: +81-298-49-1558 Fax: +81-298-49-1529 e-mail: m-kadoshima@mirai.aist.go.jp

²MIRAI Project, Advanced Semiconductor Research Center (ASRC), National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-0046, Japan

³Department of Materials Science School of Engineering, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan

1. Introduction

Al_2O_3 is one of promising candidates for the high-k gate insulators in sub-100nm MOSFETs. It has some advantages such as a high barrier height and a good thermal stability with respect to Si. However, the water absorption is a big concern because aluminum hydroxides are reported to be more stable than its oxide in high humidity [1]. In this paper, we have investigated the water absorption into Al_2O_3 and its influence on the electrical properties.

2. Experimental

140nm- Al_2O_3 films were deposited by an atomic layer deposition (ALD) method on HF-last p-type silicon substrates, and they were annealed at 800 °C in N_2 . $\text{Al}(\text{CH}_3)_3$ and $\text{H}_2\text{O}(^{18}\text{O})$ were used as the ALD sources.

Water including 95% ^{18}O isotope ($\text{H}_2\text{O}(^{18}\text{O})$) was used in the experiment in order to distinguish the water used in the ALD process from that absorbed from moisture. The water absorption experiment was done in a saturated $\text{H}_2\text{O}(^{18}\text{O})$ moisture at 40 °C for a week. After a top Au electrode was deposited by vacuum evaporation, we attempted to dehydrate the samples by means of annealing as temperatures between 200 and 400 °C in N_2 .

3. Results and Discussion

Figure 1 shows the infrared absorption spectrum of Al_2O_3 after water absorption. The absorption peak from 3200 to 3700 cm^{-1} is assigned to the stretching mode of the hydroxyl groups. Furthermore, SIMS depth profiles show ^{18}O is located in about 5nm depth from the surface (Fig. 2).

Figure 3 shows the TDS spectra after water absorption. Two main desorption peaks for $\text{H}_2\text{O}(^{18}\text{O})$ are observed. The peak at 280 °C is considered to be derived from the physically absorbed $\text{H}_2\text{O}(^{18}\text{O})$ from the moisture, because the peaks due to the other gases are not simultaneously found. The peak at 375 °C can be reasonably assigned to hydrated (or chemisorbed) $\text{H}_2\text{O}(^{18}\text{O})$ because aluminum hydroxides start to dehydrate around 300 °C [2][3]. Therefore, it can be concluded that the water absorption substantially induces the hydration reactions in Al_2O_3 .

The hysteresis width of C-V characteristics increases

after water absorption (Fig. 4). This hysteresis indicates the existence of the positive mobile charges rather than the carrier injection [4]. On the other hand, by the dehydration annealing above 300 °C, the hysteresis width significantly decreases as shown in Fig. 5. Namely the apparent positive mobile charge densities decrease with dehydration temperature (Fig. 6). Note that this temperature range is consistent with the hydrated $\text{H}_2\text{O}(^{18}\text{O})$ desorption range as shown in Fig. 3. Therefore, it is considered that the positive mobile charges are protons or oxonium ions (H_3O^+) released from the acidic hydroxyl groups ($\text{Al}-\text{OH}$). However, I-V characteristics cannot be recovered to the initial level by the dehydration process as shown in Fig. 7. This is explained in terms that the vacancies of protons or hydroxyl groups are formed by desorption of hydrated H_2O (Fig. 8).

Figure 9 shows the equilibrium H_2O pressure ($P_{\text{H}_2\text{O}}$) for the reaction of $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{AlOOH}$. We calculated $P_{\text{H}_2\text{O}}$ using the relationship $\Delta G^0 = RT \ln P_{\text{H}_2\text{O}}$ and used thermodynamic data in Ref. 5. Here, ΔG^0 , R and T are the standard Gibbs' free energy of this reaction, the gas constant and absolute temperature, respectively. A typical hydration reaction, $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlOOH}$, is thermodynamically favored when the H_2O pressure is higher than $P_{\text{H}_2\text{O}}$ of this reaction (solid line in Fig. 9). The experimental results in this study show that hydration of Al_2O_3 is a relatively slow process at 40 °C. However, in order to eliminate any harmful effects of hydration, it is desirable to minimize exposure to the humid environment in the Al_2O_3 gate stack fabrication steps.

4. Conclusions

We have investigated the water absorption into Al_2O_3 by physical analysis and electrical characterization. It should be pointed out that the hydration reaction proceeds by water absorption, followed by the introduction of the positive mobile charges. On the other hand, the dehydration annealing can reduce those charges, but the leakage current density is significantly degraded. Thus, in order to obtain reliable MOSFETs using Al_2O_3 as a gate insulator, a special care should be paid between the dielectric deposition and

gate electrode formation processes.

Acknowledgments

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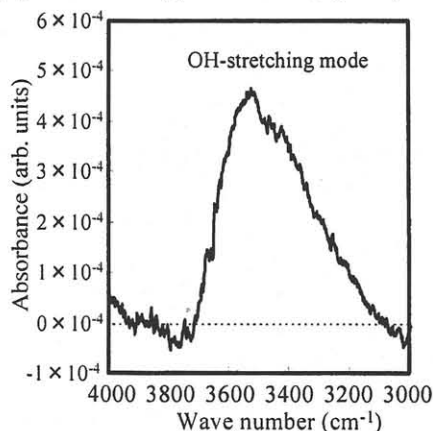


Fig. 1 Infrared absorption spectrum of Al_2O_3 after water absorption at 40°C for a week. $\text{H}_2\text{O}^{(16)\text{O}}$ moisture was used for peak assignment.

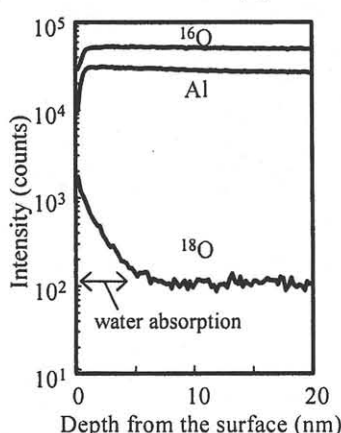


Fig. 2 SIMS depth profile of Al_2O_3 after water absorption. ^{18}O in the absorbed water is located in about 5nm depth. In the depth deeper than 5nm, we cannot distinguish ^{18}O in the absorbed water from that naturally exists in water of the ALD source.

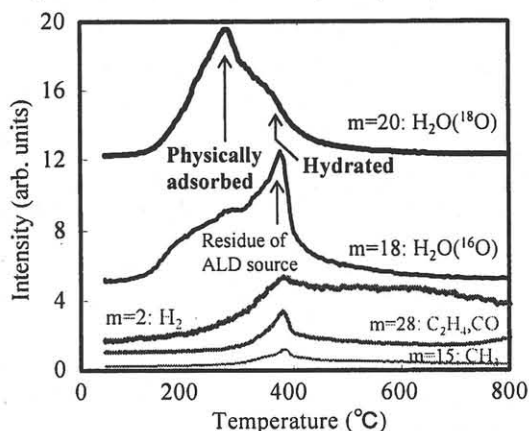


Fig. 3 TDS spectra of Al_2O_3 after water absorption. Each curve is offset for clarity. $\text{H}_2\text{O}^{(18)\text{O}}$ is absorbed from the moisture into Al_2O_3 . The desorption peak of $\text{H}_2\text{O}^{(18)\text{O}}$ at 375°C indicates the hydration of Al_2O_3 .

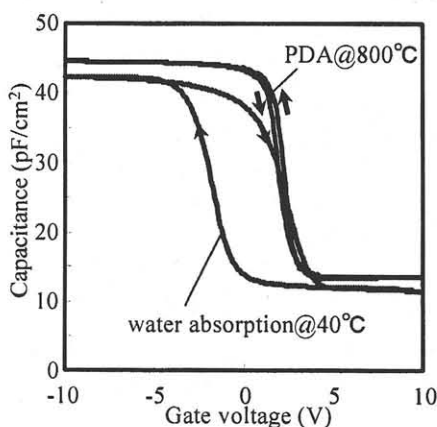


Fig. 4 Change of C-V characteristics after water absorption at 40°C for a week.

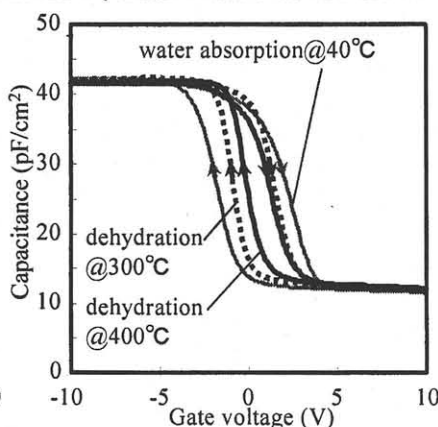


Fig. 5 Change of C-V characteristics after dehydration.

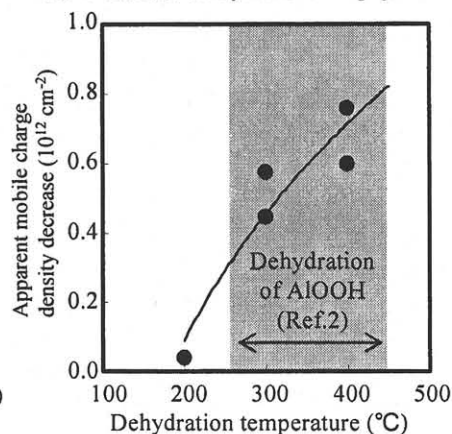


Fig. 6 Decrease of the apparent positive mobile charge densities by the dehydration annealing. The shadow region means the temperature where AlOOH was dehydrated (Ref.2).

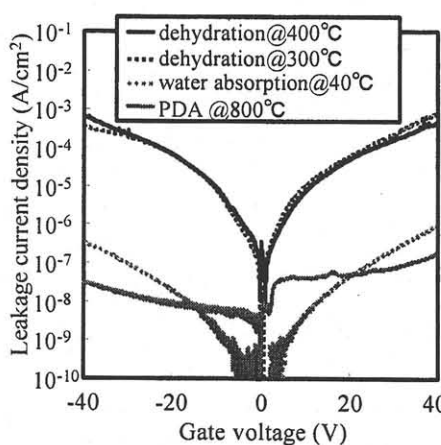


Fig. 7 I-V characteristics of Al_2O_3 films. Leakage current density is increased by the dehydration annealing.

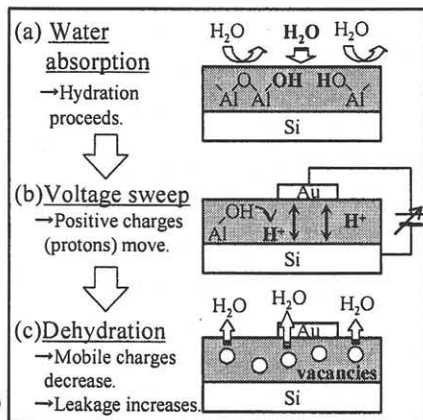


Fig. 8 A degradation model by water absorption and dehydration. (a) hydroxyl groups are introduced by the hydration reaction. (b) Mobile charges (H^+) are released from hydroxyl groups during voltage sweeps. (c) Vacancies of H^+ or OH^- are created by water desorption during dehydration.

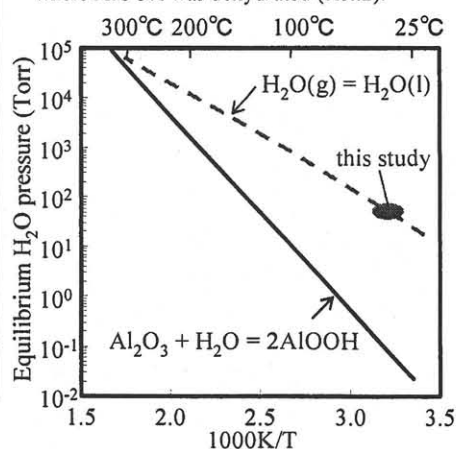


Fig. 9 Equilibrium H_2O pressure for aluminum oxide and its hydroxide. The dashed line is the saturated vapor pressure of water. The typical hydration reaction, $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlOOH}$, is thermodynamically favored above the solid line.