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Characterization of $Al_{1-x}Ti_xO_y$ thin films deposited by mist-CVD

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Abstract

An attractive high-κ dielectric material, aluminium titanium oxide ($Al_{1-x}Ti_xO_y$, an alloy of Al_2O_3 and TiO_2), were deposited by mist chemical vapor deposition (mist-CVD). Our results showed that the bandgap of the $Al_{1-x}Ti_xO_y$, films increases with increasing Al composition. Moreover, the obtained mass density, refractive index and bandgap of Al_2O_3 and TiO_2 films are all comparable to those reported for Al_2O_3 and TiO_2 films deposited by atomic layer deposition (ALD). This fact indicates that atmospheric pressure solution-processed mist-CVD technique is promising for depositing high-quality $Al_{1-x}Ti_xO_y$ gate insulator and surface passivation layer.

1. Introduction

One of the main challenges is finding a gate dielectric material possessing both wide bandgap (E_G) and high permittivity (κ) for realizing high-performance metal–oxide–semiconductor field–effect transistors (MOSFETs). However, there is a well-known trade-off between these two properties. One effective solution for balancing between E_G and κ is using aluminum titanium oxide with intermediate properties of Al_2O_3 and TiO_2. In fact, high-quality $Al_{1-x}Ti_xO_y$ gate insulator deposited by ALD method for GaN-based devices [1,2]. One alternative approach to deposit $Al_{1-x}Ti_xO_y$ films is the atmospheric pressure solution-processed mist-CVD technique. In this study, we report on the deposition of $Al_{1-x}Ti_xO_y$ films by mist-CVD technique, and subsequent investigation of the chemical properties, crystallinity, refractive index mass density and bandgap of the obtained films.

2. Experiment

$Al_{1-x}Ti_xO_y$ films were deposited using a homemade fine-channel-type mist-CVD system as shown **Fig. 1**. The homemade mist-CVD system was described in detail elsewhere [3,4] Aluminum acetylacetonate and titanium isopropoxide were used as the Al and Ti precursors, respectively. These Al and Ti precursors were dissolved in a mixture of methanol with acetylacetone. The $Al_{1-x}Ti_xO_y$ alloy films were deposited on Si substrates at 400 ºC with nitrogen carrier gas at a flow rate of 3 L/min. Note that all the characterizations were performed on as-deposited samples without undergoing any post-deposition annealing process.

3. Results & discussion

We initially characterized the chemical properties of as-deposited mist-CVD of $Al_{1-x}Ti_xO_y$ films. **Figure 2** shows the relation between the Ti/(Al + Ti) ratio in the precursor solution and the films x obtained by quantitative analysis of X-ray fluorescence (XRF) spectrum, showing good linear relationship. This results clearly indicated that the Ti/(Al + Ti) ratio in precursor solution enables the tuning of the x in the film.

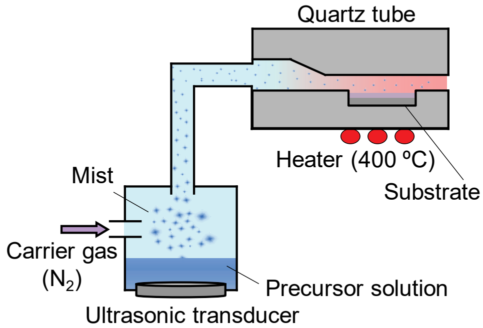

Fig. 1 Schematic illustration of the mist-CVD system.

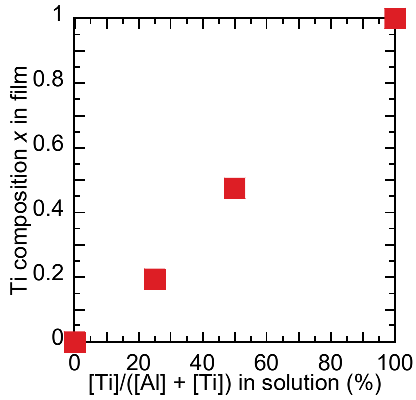

Fig. 2 Relation between Ti/(Al + Ti) in solution and the film.

Figure 3 shows the X-ray diffraction (XRD) patterns of the mist-CVD $Al_{1-x}Ti_xO_y$ films grown on Si substrate, which indicate that mist-CVD Al_2O_3 and $Al_{1-x}Ti_xO_y$ films deposited at 400 ºC has amorphous-phase structure. On the other hand, mist-CVD TiO_2 films deposited at 400 ºC has anatase-phase structure because of its lower crystallization temperature than that of the Al_2O_3. For the application of $Al_{1-x}Ti_xO_y$ as a gate dielectric, the amorphous-phase structure is a highly desirable and feasible. Hori et al. [5] showed that microcrystallized Al_2O_3 film causes a marked increase in the leakage current of the Al_2O_3/GaN MOS diode structure, which can be problematic especially at high voltage operations. The grain boundaries in the microcrystallized Al_2O_3 layer can serve as leakage paths and can lead to premature device breakdown.

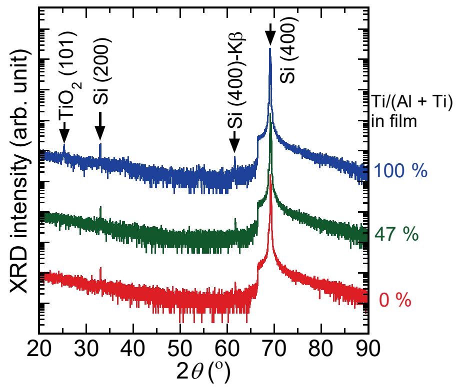

Fig. 3 XRD profiles of mist- $Al_{1-x}Ti_xO_y$ films on Si substrate.

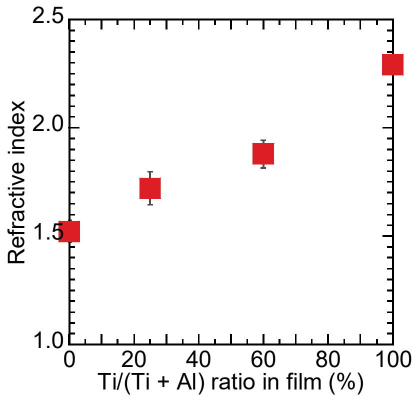

Fig.4 Refractive index of of mist- $Al_{1-x}Ti_xO_y$ films.

Figures 4 shows the relation between the Ti/(Al + Ti) ratio in the film and the refractive index obtained by ellipsometry, which increases with increase in the Ti composition. Note that the measured refractive index Al_2O_3 and TiO_2 films are comparable to those reported for high-quality Al_2O_3 and TiO_2 film deposited by ALD [5,6]. Since carbon impurities in the films and film porosity may affect the refractive index, the obtained mist-CVD of $Al_{1-x}Ti_xO_y$ films are likely dense as well as having low carbon impurity contamination.

Finally, bandgap of the $Al_{1-x}Ti_xO_y$ films was estimated from ultraviolet-visible spectroscopy. However, the bandgap of obtained mist-Al_2O_3 film is more than 6 eV, rendering Tauc's formula [7] unsuitable in this situation. Accordingly, the bandgap of the mist-CVD Al_2O_3 with a nominal thickness of 38 nm was estimated from the energy-loss peak in the O 1*s* XPS spectrum. As shown in **Fig. 5**, the bandgap is a monotonous decreasing behavior with increase in the Ti composition. It should be noted that the obtained refractive index, mass density (not shown here) and bandgap of Al_2O_3 [5,8] and TiO_2 [6,9] films are all comparable to those reported for high-quality Al_2O_3 and TiO_2 films deposited by ALD, thereby demonstrating the efficacy of using mist-CVD in synthesizing films having almost the same properties as those prepared by the more mature ALD.

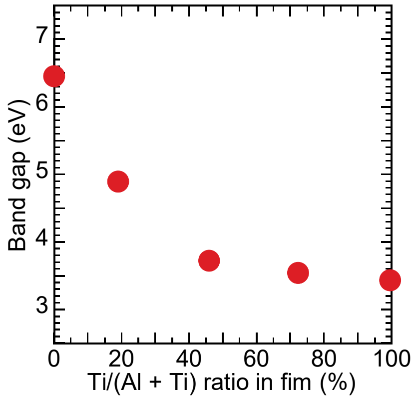

Fig. 5 XRD profiles of mist- $Al_{1-x}Ti_xO_y$ films on Si substrate.

3. Conclusions

An attractive high-κ dielectric material, aluminium titanium oxide ($Al_{1-x}Ti_xO_y$, an alloy of Al_2O_3 and TiO_2), were deposited by mist-CVD. Our results showed that the bandgap of the $Al_{1-x}Ti_xO_y$, films increases with increasing Al composition. Moreover, the obtained mass density, refractive index and bandgap of Al_2O_3 and TiO_2 films are all comparable to those reported for Al_2O_3 and TiO_2 films deposited by ALD. This fact indicates that atmospheric pressure solution-processed mist-CVD tech-nique is promising for depositing high-quality $Al_{1-x}Ti_xO_y$ gate insulator and surface passivation layer.

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References

[1] S. P. Le, T. Ui, T. Q. Nguyen, H.-A. Shih, and T. Suzuki, J. Appl. Phys. **119** (2016) 204503.
[2] S. P. Le, D. D. Nguyen, and T. Suzuki, J. Appl. Phys. **123** (2018) 034504.
[3] Z. Yatabe, T. Tsuda, J. Matsushita, T. Sato, T. Otabe, K. Sue, S. Nagaoka and Y. Nakamura, Phys. Status Solidi C, **14** (2017) 1600148.
[4] H. Tanoue, M. Takenouchi, T. Yamashita, S. Wada, Z. Yatabe, S. Nagaoka, Y. Naka, and Y. Nakamura, Phys. Status Solidi A **214** (2017) 1600603.
[5] Y. Hori, C. Mizue and T. Hashizume, Jpn. J. Appl. Phys., **49** (2010) 080201.
[6] J. Aarika, A. Aidlaa, A.-A. Kiislera, T. Uustarea, and V. Sammelselgb, Thin Solid Films **305** (1997) 270.
[7] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi A **15** (1996) 627.
[8] J. Yang, B. S. Eller, M. Kaur, R. J. Nemanich, J. Vac. Sci. Technol. A **32**, (2014) 021514.
[9] B. Abendroth, T. Moebus, S. Rentrop, R. Strohmeyer, M. Vinnichenko, T. Weling, H. Stöcker, and D. C.Meyer, Thin Solid Films **545** (2013) 176.