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

Zenji Yatabe¹, Koshi Nishiyama¹, Kazuki Nishimura¹ and Yusui Nakamura^{1,2}

¹ Kumamoto Univ. 2-39-1, Kurokami, Chuo-ku, Kumamoto 860-8555, Japan E-mail: yatabe@cs.kumamoto-u.ac.jp ² Kumamoto Phoenics 3-11-38, Higashi-machi, Higashi-ku, Kumamoto 862-0901, Japan

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 ($E_{\rm G}$) 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 $E_{\rm G}$ and κ is using aluminum titanium oxide with intermediate properties of ${\rm Al}_2{\rm O}_3$ and ${\rm TiO}_2$. In fact, high-quality ${\rm Al}_{1-x}{\rm Ti}_x{\rm O}_y$ gate insulator deposited by ALD method for GaN-based devices [1,2]. One alternative approach to deposit ${\rm Al}_{1-x}{\rm Ti}_x{\rm O}_y$ films is the atmospheric pressure solution-processed mist-CVD technique. In this study, we report on the deposition of ${\rm Al}_{1-x}{\rm Ti}_x{\rm O}_y$ 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 °C 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 asdeposited mist-CVD of $Al_{1-x}Ti_xO_y$ films. **Figure 2** shows the

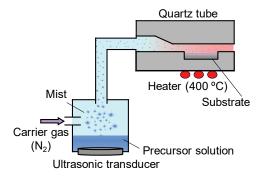


Fig. 1 Schematic illustration of the mist-CVD system.

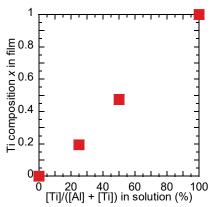


Fig. 2 Relation between Ti/(Al + Ti) in solution and the film.

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.

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 Al₂O₃ and Al_{1-x}Ti_xO_y films deposited at 400 °C has amorphous-phase structure. On the other hand, mist-CVD TiO₂ films deposited at 400 °C has anatase-phase structure because of its lower crystallization temperature than that of the Al₂O₃. 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 Al₂O₃ film causes a marked increase in the leakage current of the Al₂O₃/GaN MOS diode structure, which can be problematic especially at high voltage operations. The grain boundaries in the microcrystallized Al₂O₃ layer can serve as leakage paths and can lead to premature device breakdown.

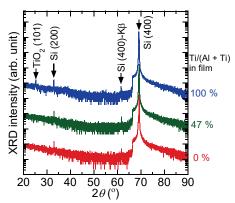


Fig. 3 XRD profiles of mist- $Al_{1-x}Ti_xO_y$ films on Si substrate.

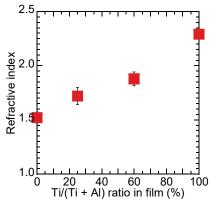


Fig.4 Refractive index of of mist- Al_{1-x}Ti_xO_y films.

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-Al₂O₃ film is more than 6 eV, rendering Tauc's formula [7] unsuitable in this situation. Accordingly, the bandgap of the mist-CVD Al₂O₃ with a nominal thickness of 38 nm was estimated from the energy-loss peak in the O 1s 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 Al₂O₃ [5,8] and TiO₂ [6,9] films are all comparable to those reported for high-quality Al₂O₃ and TiO₂ 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.

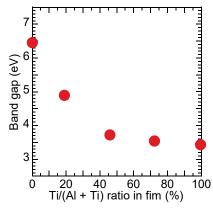


Fig. 5 XRD profiles of mist- $Al_{1-x}Ti_xO_y$ films on Si substrate.

3. Conclusions

An attractive high- κ dielectric material, aluminium titanium oxide (Al_{1-x}Ti_xO_y, an alloy of Al₂O₃ and TiO₂), 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 Al₂O₃ and TiO₂ films are all comparable to those reported for Al₂O₃ and TiO₂ 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.

Acknowledgements

One of the authors (ZY) sincerely thank Professors Tamotsu Hashizume and Masamichi Akazawa of the Research Center for Integrated Quantum Electronics (RCIQE), Hokkaido University and Professor Joel T. Asubar of the Graduate School of Engineering, University of Fukui for their valuable support. This work was supported by JSPS KAKENHI Grant Number JP19K04473.

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.