Mist CVD as a Green Fabrication Process for Insulating Oxide Thin Films

T. Kawaharamura[1], J. Piao[2],
T. Uchida[1], T. Toda[1], M. Furuta[1], C. Li[1],
S. Katori[2], T. Hirao[2], S. Fujita[2]

[1]Institute for Nanotechnology, Kochi University of Technology
[2]Department of Electronic Engineering and Science, Kyoto University

高知工科大学
KOCHI UNIVERSITY OF TECHNOLOGY

京都大学
KYOTO UNIVERSITY

AA9.01

– Motivations –

Recently, numerous high-dielectric constant (high-*k*) oxides, such as aluminium oxide (Al_2O_3), hafnium oxide (HfO_2), zirconium oxide (ZrO_2), lanthanum oxide (La_2O_3), and yttrium oxide (Y_2O_3), have received considerable attention to reduce a driving voltage of metal-oxide-semiconductor (MOS) based devices.1-5) The physical properties of each material (which are reported with bulk materials or in other reviews) are summarized in Table 1.5-8) There are a lot of reports of thermal stability about such materials since it is very important for device fabrication. For example, in La_2O_3 and HfO_2, crystal is easily formed at low temperature9,10) and, in HfO_2 and ZrO_2, silicate is easily formed for higher reactivity with Si.9,11) The crystal phase transition and the silicate formation cause a volume change and a roughness increment on the film surface. Therefore, there are lot of researches about stabilizations of thin film state, such as a post annealing process after thin film deposition or a mixture alloy with Si, Al, and Y.4,9,11-16) Ultimately, SiO and Al_2O_3 has wide band gap, high breakdown field, and high thermal stability. Also, SiO and Al_2O_3 thin films are used for a passivation owing to low permeability of water and ambient air. Thus, SiO and Al_2O_3 are promising materials for both a high-*stability* gate insulator and a passivation of electronic devices.

The physical properties of high-k dielectrics

	Band gap *Eg* (eV)	Dielectric constant ε_r (-)	Lattice energy $\Delta H_L^\circ/n$ (kJ/mol)	Bond strength (eV)	Crystallization (°C) (blow 1000°C)	Contact stability with Si (kJ/mol)	Silicate (°C)
SiO_2	9	3.9	6520	8.29	–	–	–
Al_2O_3	7.4–9	9.34	5060	5.3	–	265.3	> 900
HfO_2	5.8	22–25	5510	8.3	< 400	199.4	727
ZrO_2	4.7–5.8	11–25	5450	8.03	Monoclic	177.1	≈ 500
La_2O_3	–6	25–30	4050	8.30	< 600	412.0	≈ 1000
Y_2O_3	–6	15	4300	7.45	–	488.8	≈ 1000

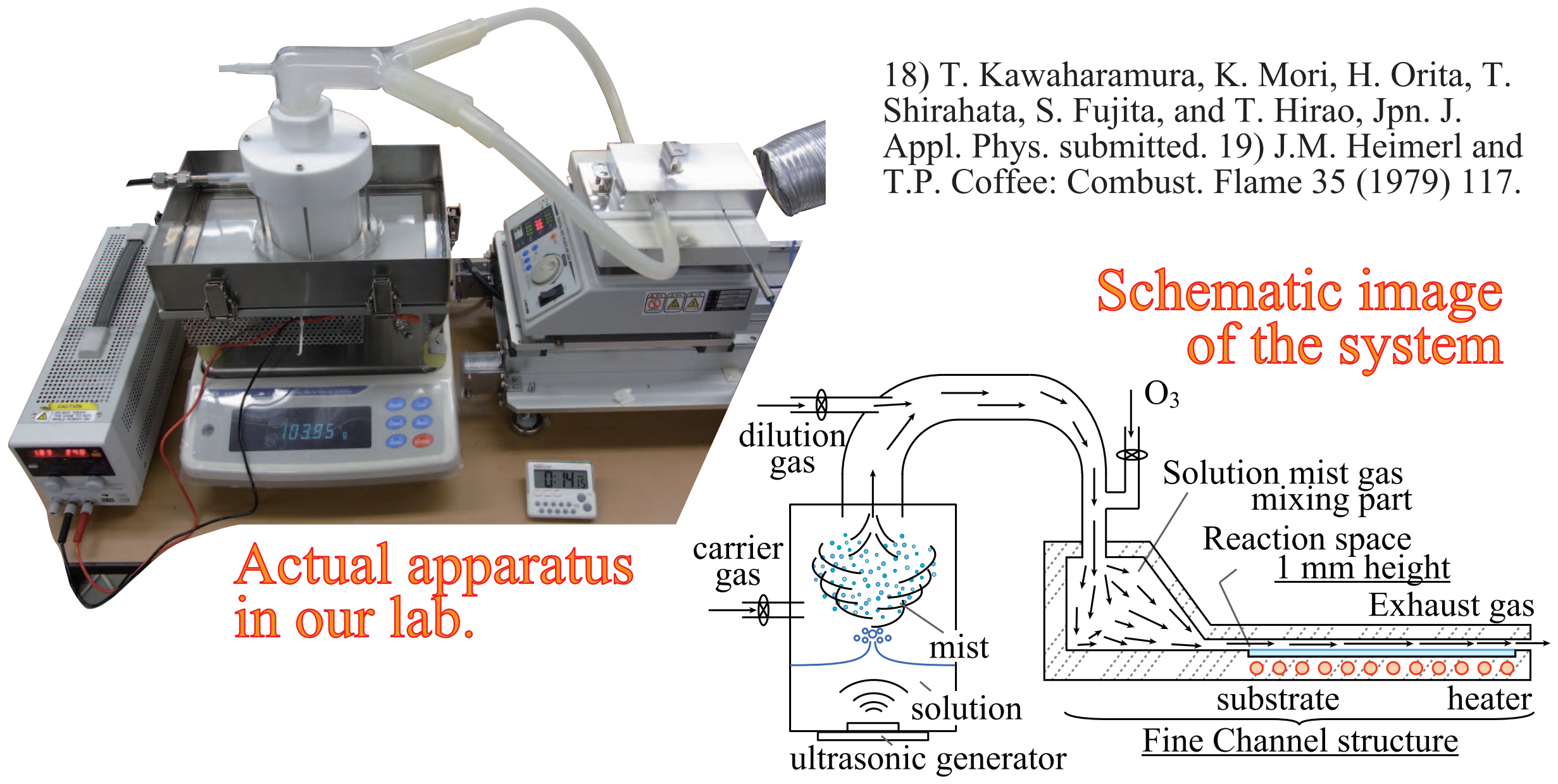
1) M.-H. Cho, D.-H. Ko, Y.G. Choi, K. Jeong, I.W. Lyo, D.Y. Noh, H.J. Kim, and C.N. Whang: J. Vac. Sci. Technol. A, 19 (2001) 192. 2) E.P. Gusev, M.Copel, E. Cartier, I.J.R. Baumvol, C. Krug, and M.A. Gribelyuk: Appl. Phys. Lett., 76 (2000) 176. 3) H.J. Quah, K.Y. Cheong, Z. Hassan, Z. Lockman, F.A. Jasni, and W.F. Lim: J. Electrochem. Soc., 157 (2010) H6. 4) A.I. Kingon, J.-P. Maria, and S.K. Streiffer: Nature, 406 (2008) 1032. 5) A. Chin, Y.H. Wu, S.B. Chen, C.C. Liao, and W.J. Chen: Symp. on VLSI Tech. Dig. Tech. Papar, 2000, p.16. 6) K.J. Hubbard and D.G. Schlom: J. Mater. Res., 11 (1996) 2757. 7) Y.-H. Li: A Compendium of Geochemistry. From Solar Nebula to the Human Brain (Princeton University Press, Princeton, N.J, 2000) Chap.1. 8) J. Robertson: Eur. Phys. J. Appl. Phys., 28 (2004) 265. 9) W.J. Zhu, T. Tamagawa, M. Gibson, T. Furukawa, and T.P. Ma: IEEE Electron Device Letters, 23 (2002) 649. 10) Y. Yamamoto, K. Kita, K. Kyuno, and A. Toriumi: Appl. Phys. Lett., 89 (2006) 032903. 11) G.D. Wilk, R.M. Wallace, and J.M. Anthony: J. Appl. Phys., 87 (2000) 484. 12) H.Y. Yu, M.F. Li, B.J. Cho, C.C. Yeo, M.S. Joo, D.L. Kwong, J.S. Oan, C.H. Ang, J.Z. Zheng, and S. Ramanathan: Appl. Phys. Lett., 81 (2002) 376. 13) K. Akimoto, N. Terasawa, V. Wolfgang, T. Takahashi: PF News, 28 (2010) 20 [in Japanese]. 14) R.J. Ackermann, S.P.Grag, and E.G. Scott: J. Solid. State. Chem. Soc., 61 (1978) 275. 15) T. Nishide, S. Honda, M. Matsuura, Y. Ito, T. Takase: Jpn. J. Appl. Phys., 39 (2000) 237. 16) J.-H. Kim, V.A. Ignatova, M. Weisheit: Microelectron. Eng., 86 (2009) 357.

– Mist Chemical Vapour deposition (Mist CVD) –

A technique promising as an atmospheric pressure process!

Fine channel type Mist CVD system

The FC structure, which is a depo. space of 1 mm-in-height, gives the thin films grown under a strong oxidation and high reaction efficiency due to high pressure in the local area [17].



Actual apparatus in our lab.

Schematic image of the system

18) T. Kawaharamura, K. Mori, H. Orita, T. Shirahata, S. Fujita, and T. Hirao, Jpn. J. Appl. Phys. submitted. 19) J.M. Heimerl and T.P. Coffee: Combust. Flame 35 (1979) 117.

Please refer [17]
"Study on mist CVD and its application to the growth of ZnO thin films"
T. Kawaharamura,, Ph.D. Thesis, Faculty of Engineering, Kyoto-Univ., 2008 [in Japanese]
http://repository.kulib.kyoto-u.ac.jp/dspace/bitstream/2433/57270/1/26041.pdf

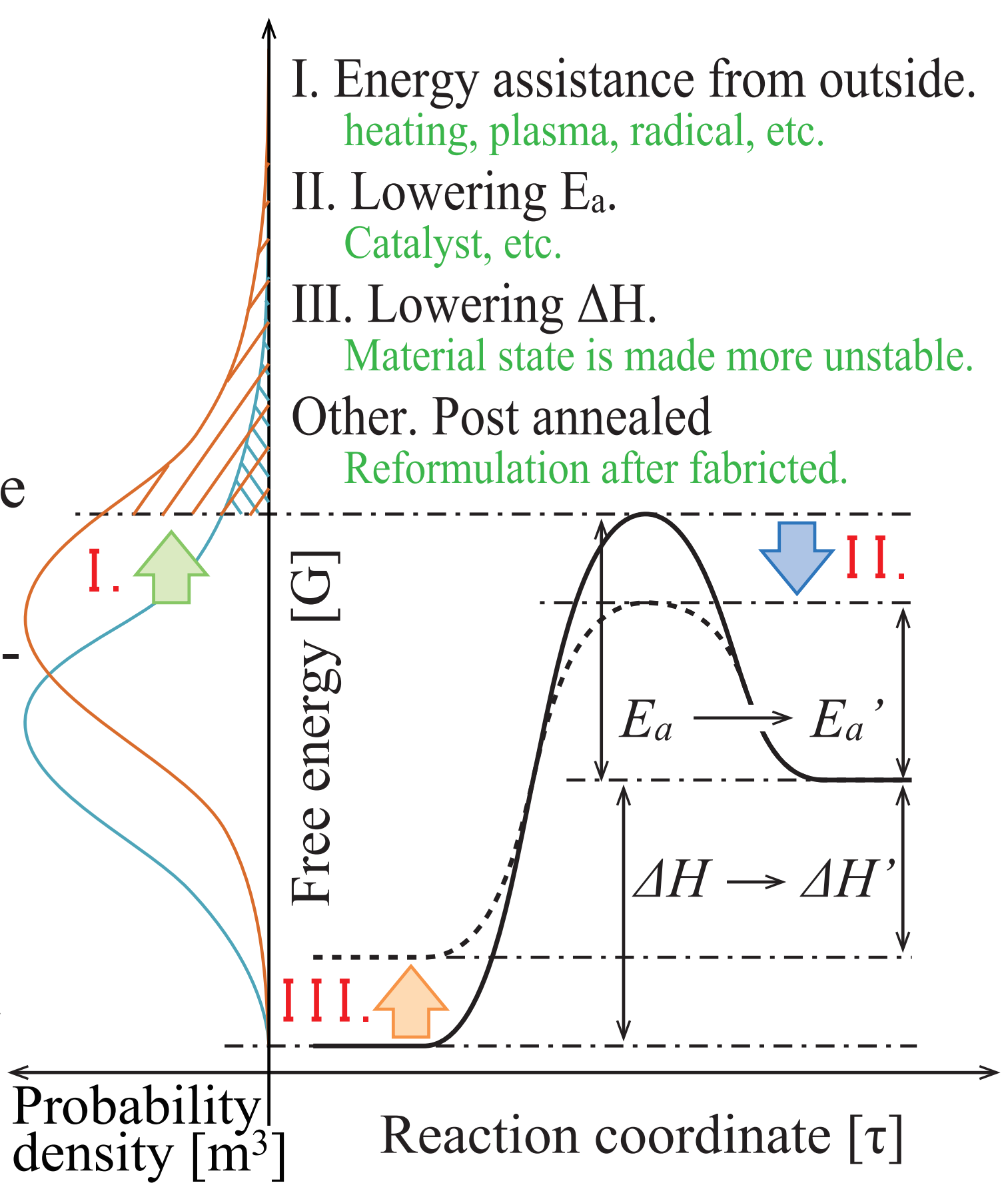
It was verified that, when MgO thin films are prepared by the mist CVD, the assistance of O_3 is effective to lower the substrate temperature from 450°C to 400°C [18]. It is presumed that the decrease of growth temperature by the assistance of O_3 is mainly caused by its active force. And oxygen radical (O·) generated from O_3 by thermal decomposition [19], viz.

$$O_3 \longleftrightarrow O_2 + O\cdot$$

The precursor materials are attached and decomposed by the activated oxygen sources such as O_3 and O·. And the lowering of growth temperature is due to the active force of the oxygen sources.

And, in this time, fabrications of SiO_x and AlO_x thin films at low temperature with assistance of O_3 were carried out.

A means to promote a reaction

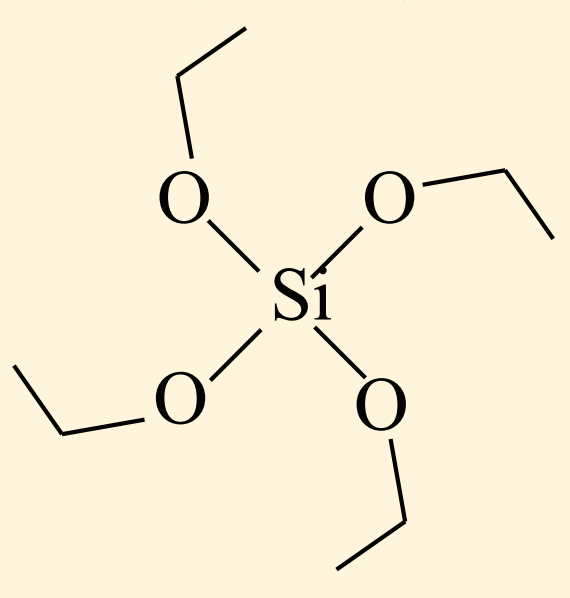


I. Energy assistance from outside.
heating, plasma, radical, etc.
II. Lowering E_a.
Catalyst, etc.
III. Lowering ΔH.
Material state is made more unstable.
Other. Post annealed
Reformulation after fabricted.

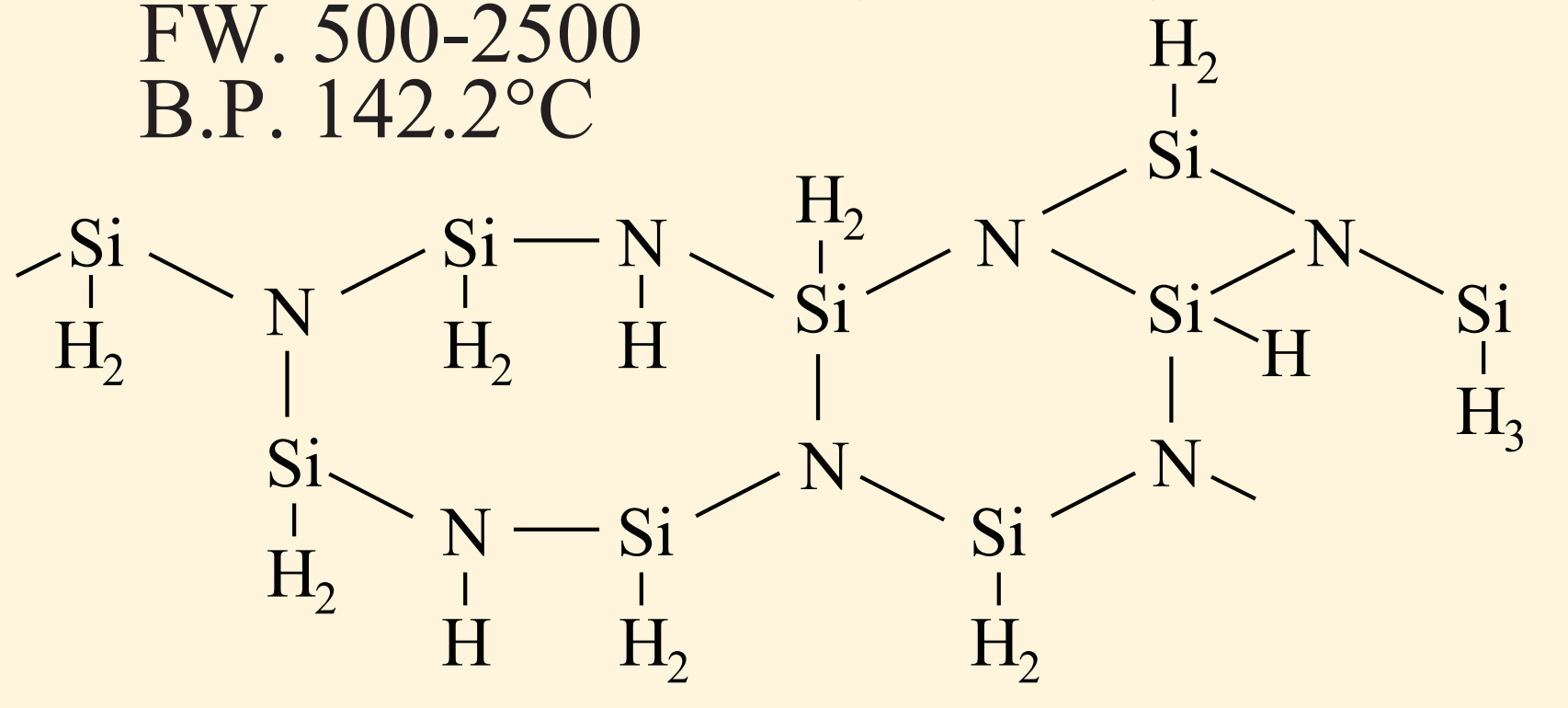
I wish the result gave the industrial world an immeasurable impact.

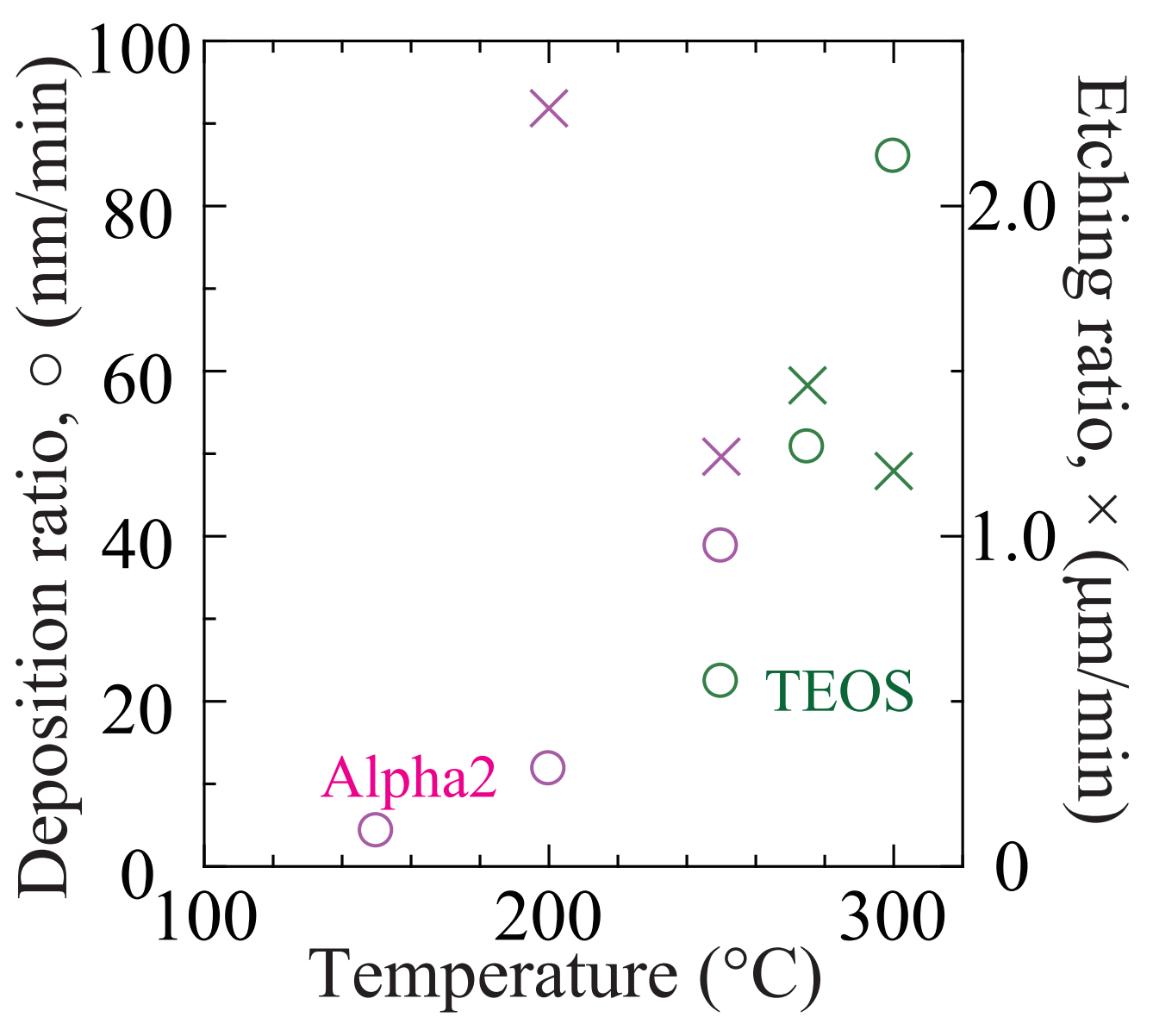
– Fabrication & Properties of SiOx thin films grown by the mist CVD –

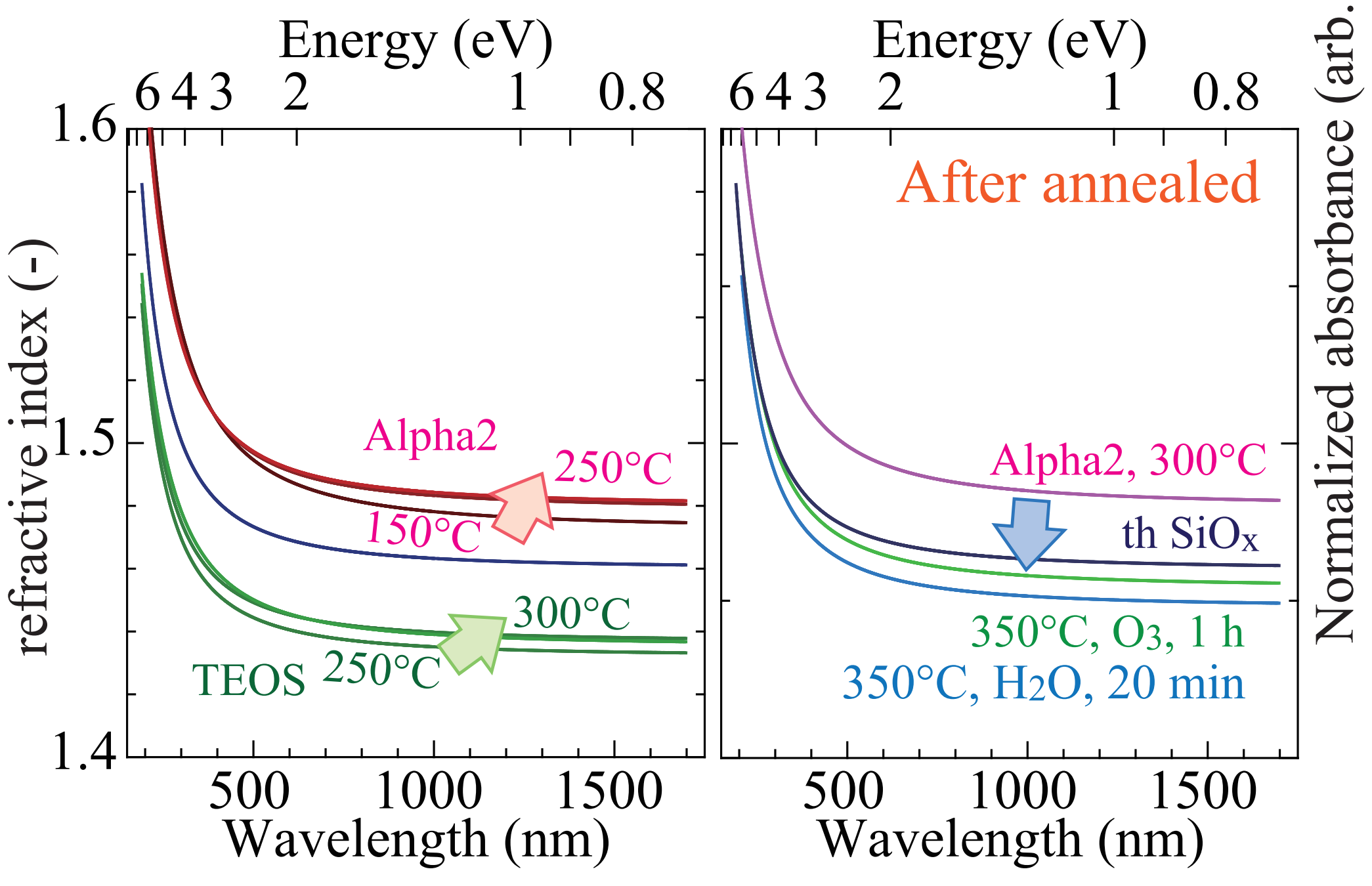
TEOS (Tetraethylortho Silicate)
Chemical Formula $C_8H_{20}O_4Si$
FW. 208.33
VP. 200Pa (20°C)



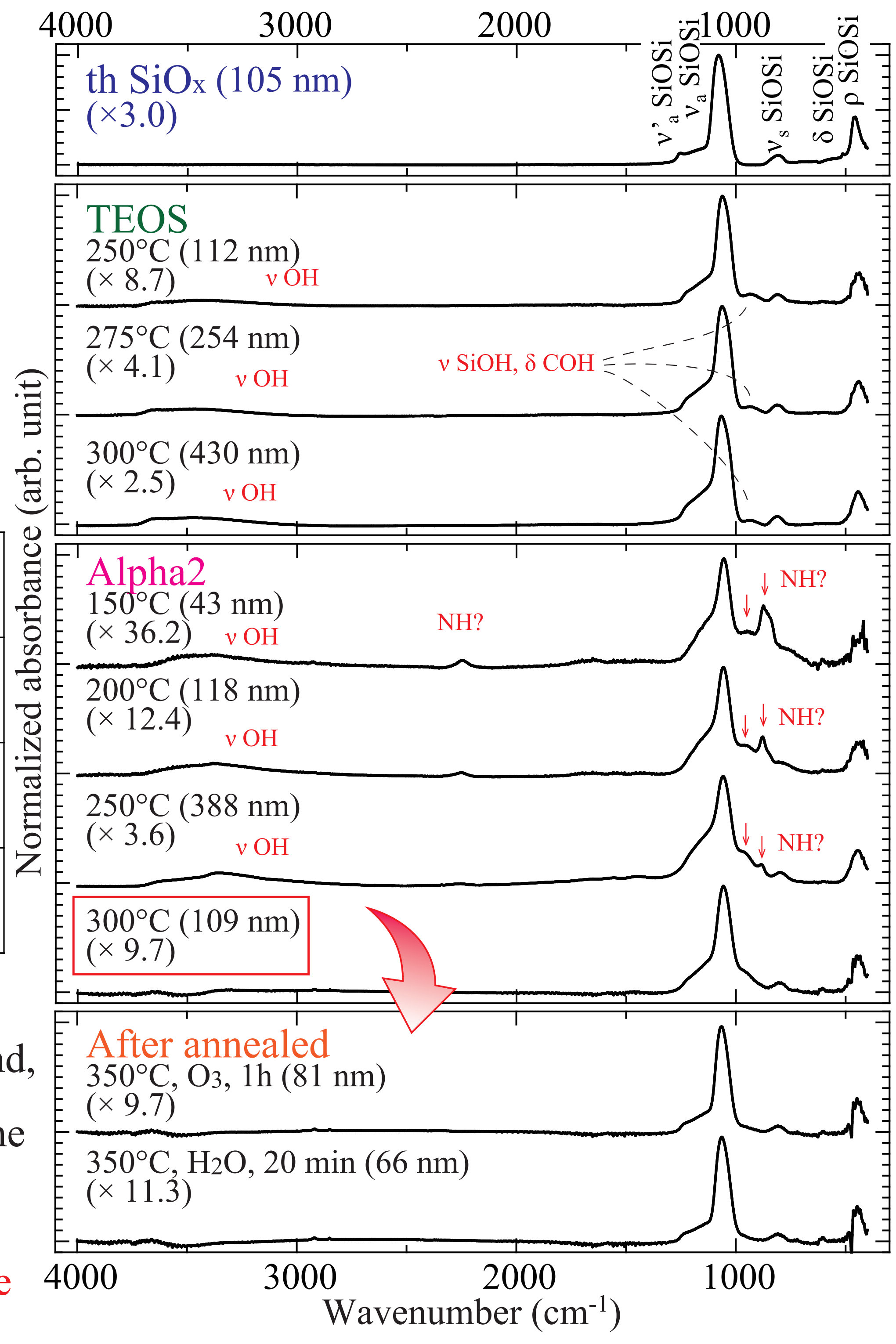
PHPS (Polysilazane) - alpha2
Chemical Formula -(SiH_3NH)-
FW. 500-2500
B.P. 142.2°C





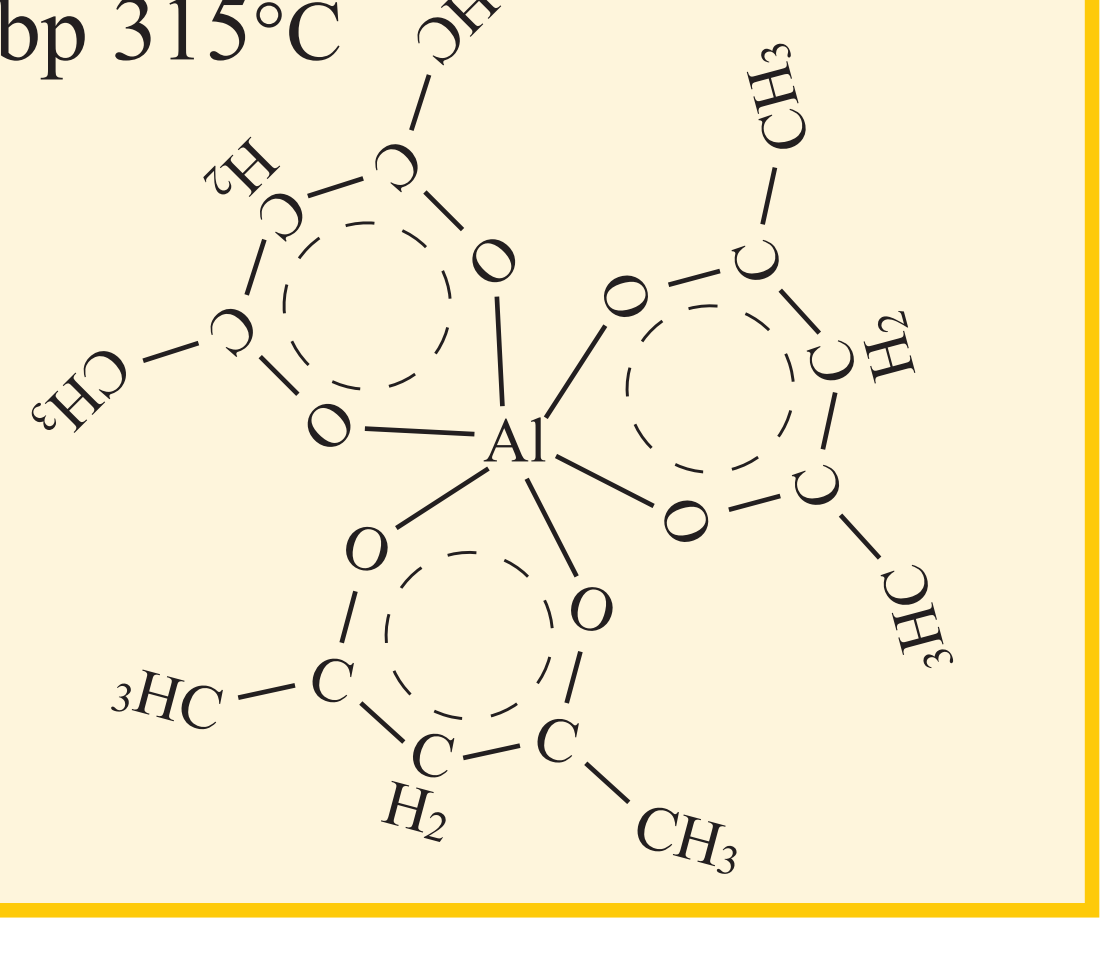


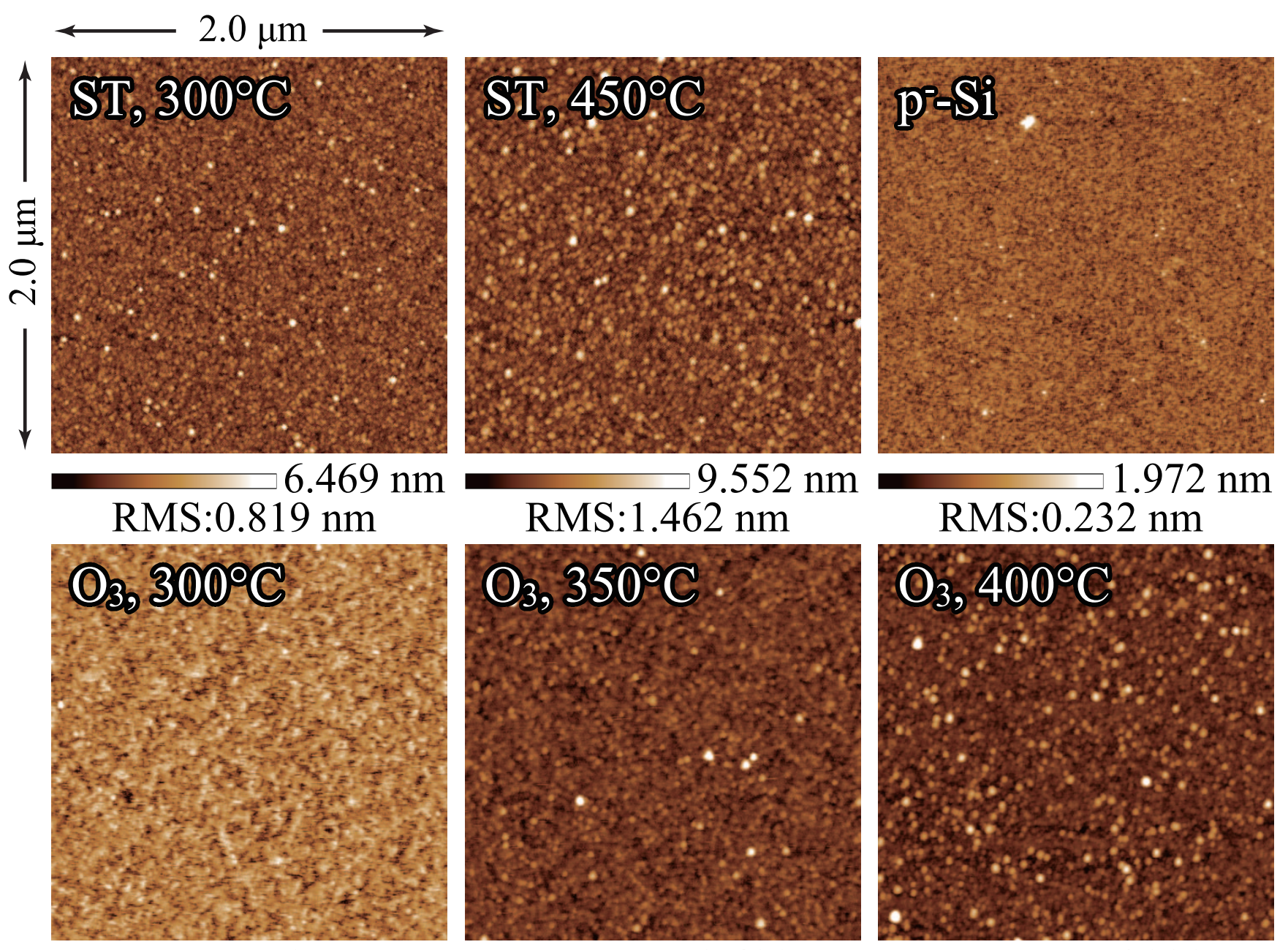
SiO_x thin films were able to be grown from the liquid source, such as TEOS, HMDS, and, HMDSO, by the mist CVD at temperature above 250°C. On the other hand, SiO_x thin films were grown from polysilazane (alpha2), which is a relatively stable material, by the mist CVD at temperatures of 150-300°C with a reasonable growth rate of 12 nm/min at 200°C. However, the residuals in the SiO_x thin films were observed. Then the SiO_x thin films were heat-treated with O_3 or H_2O. As a result, the SiO_x thin films were improved dramatically. The resistivity was changed from 10^{13}Ωcm to 10^{16}Ωcm. And the refractive index was changed to 1.45-1.46, which is nearly same as refractive index of SiO_2.

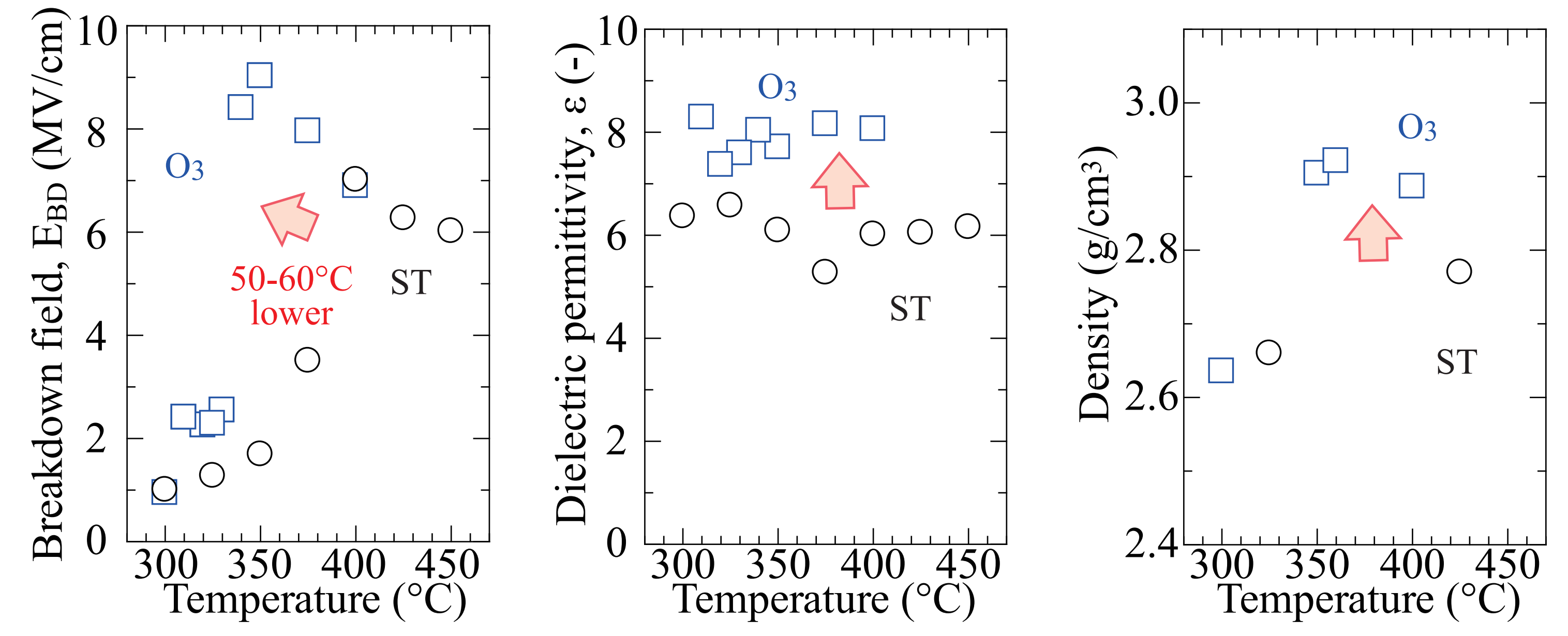


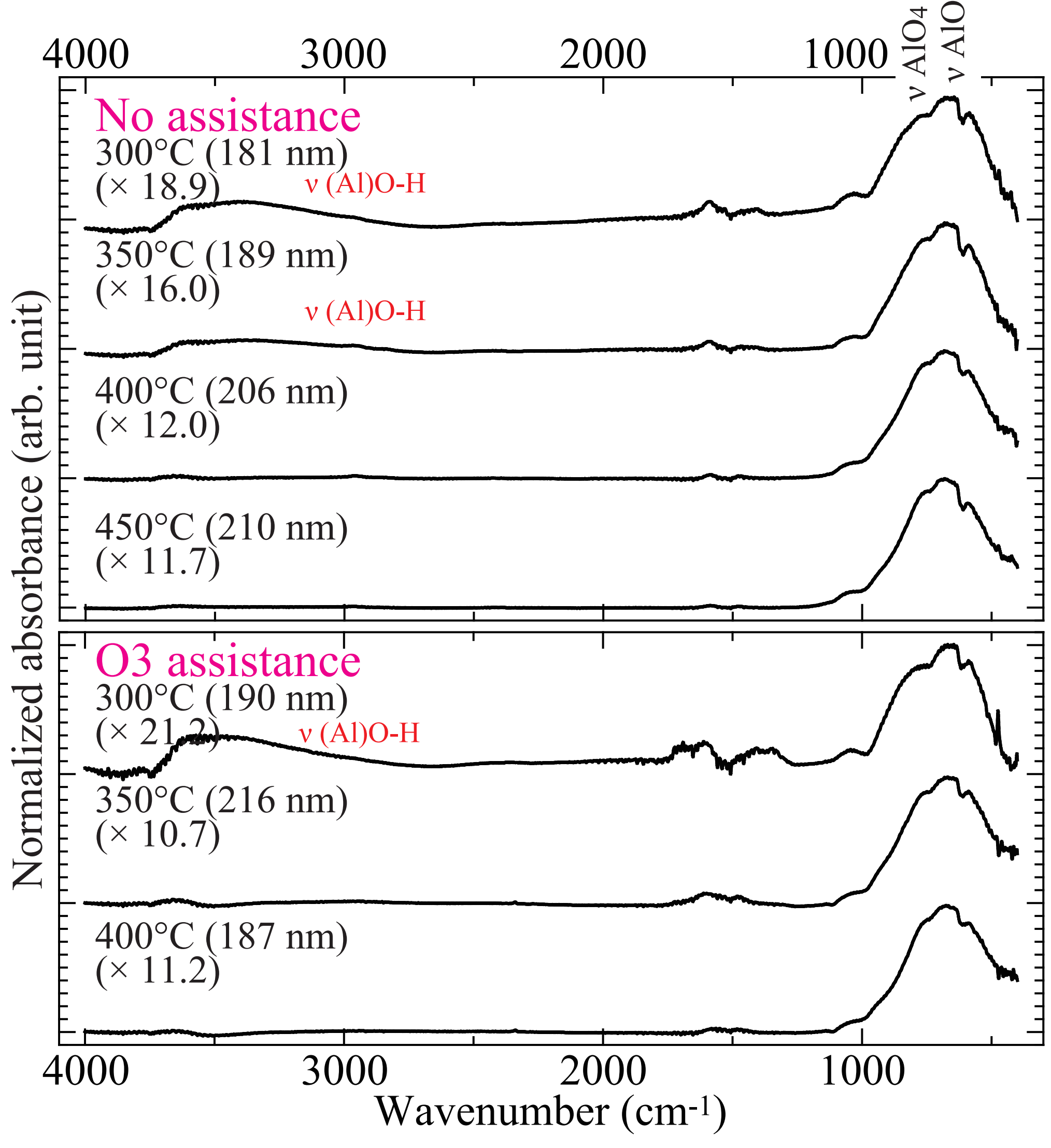
– Fabrication & Properties of AlOx thin films grown by the mist CVD –

$Al(acac)_3$ (Aluminum acetylacetonate)
FW. 324.31
bp 315°C









From our previous reports, it is suggested that the residual including OH bonding in the AlO_x thin film at the low temperature, which effects the density decrease and/or ion conduction, causes the degradation of breakdown field (E_{BD}). With assistance of O_3, the residual OH bonding in the AlOx thin film is not seen even at lower temperature. And the E_{BD}, dielectric permittivity, and density were improved. Ultimately, when the AlO_x thin films are fabricated by the mist CVD, the assistance of O_3 is effective to lower the substrate temperature from 400°C to 360°C.

In the mist CVD, the oxide thin films were grown at lower temperature, thanks to the assistance of O_3, which is the active oxygen sources.

Contact me!

Affiliation: Institute for Nanotechnology,
Kochi University of Technology
Address: 185 Miyanokuti Tosayamada-chou
Kami-city, Kochi, 782-8502, Japan
Tel., Fax.: +81-887-57-2747, +81-887-57-2714
E-mail: kawaharamura.toshiyuki@kochi-tech.ac.jp
Web page http://www.nano.kochi-tech.ac.jp/tosiyuki/index.html