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Nucleation mechanisms of atomic layer deposition of lanthanum oxide on Si

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Contents

- Properties of La_2O_3 as a potential high-k material
- *In-situ* transmission Fourier transform infrared spectroscopy (FTIR) performed during atomic layer deposition

  (Precursors : Lanthanum tris-N,N'-diisopropylacetamidinate, D_2O)

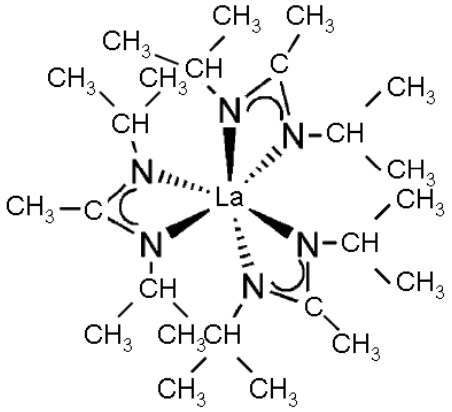
  $La(^{i}Pr_2amd)_3$ + N_2 purge + FTIR + D_2O + N_2 purge + FTIR + …
- Initial surface nucleation mechanisms and post deposition annealing effects
- Conclusion

La_2O_3 on Silicon & *in-situ* IR measurements

La_2O_3

→ *Potential material for high-κ gate dielectrics*

- Large permittivity (ε ~ 27)
- Thermal stability in contact with Si
- high electrical breakdown field strength
- Suitable band gap (E_g ~ 4.3 eV) and conduction band offset

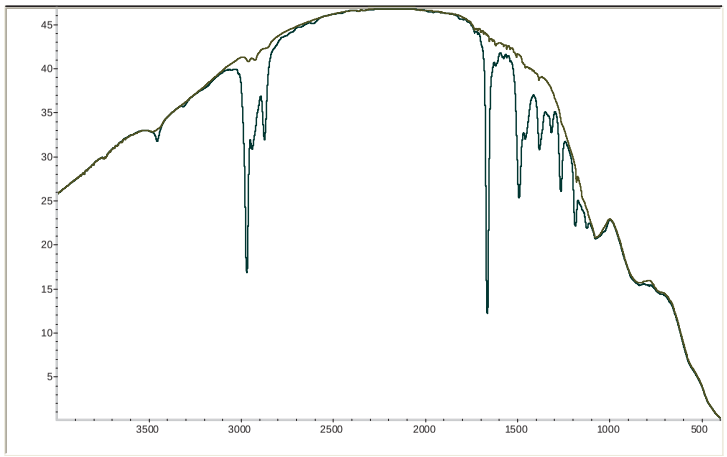


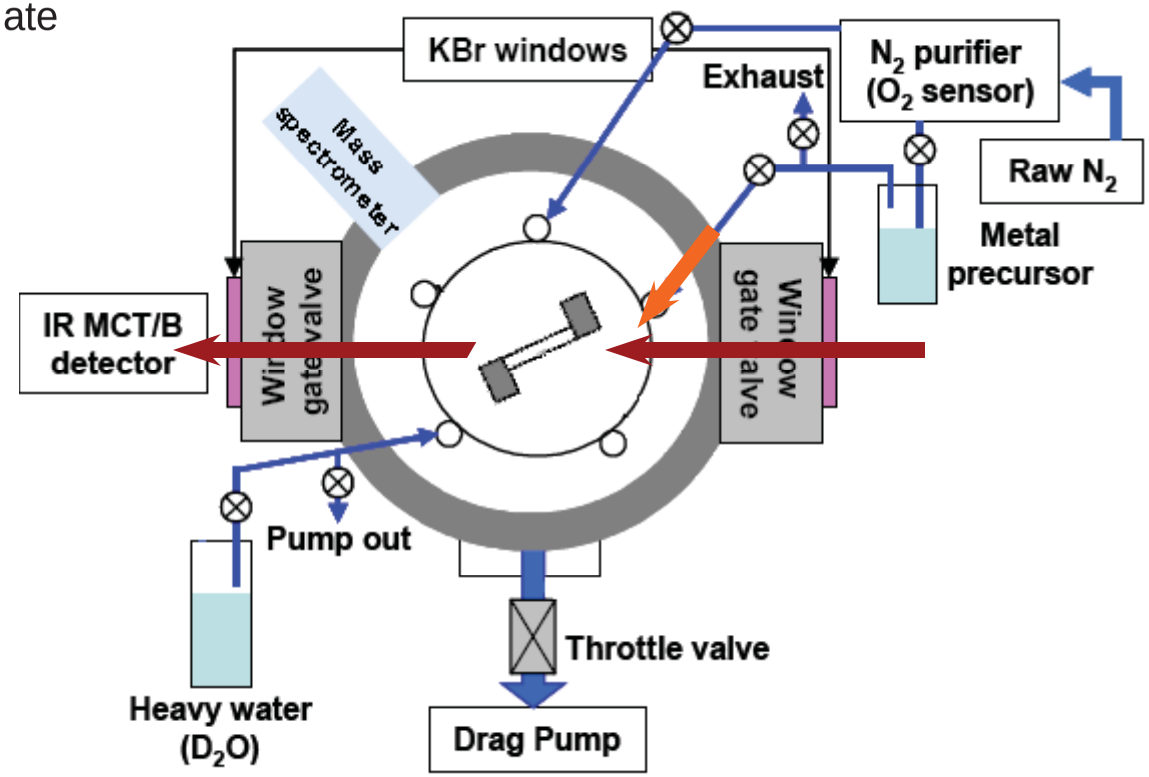
Precursors:

Lanthanum tris-N,N'-diisopropylacetamidinate

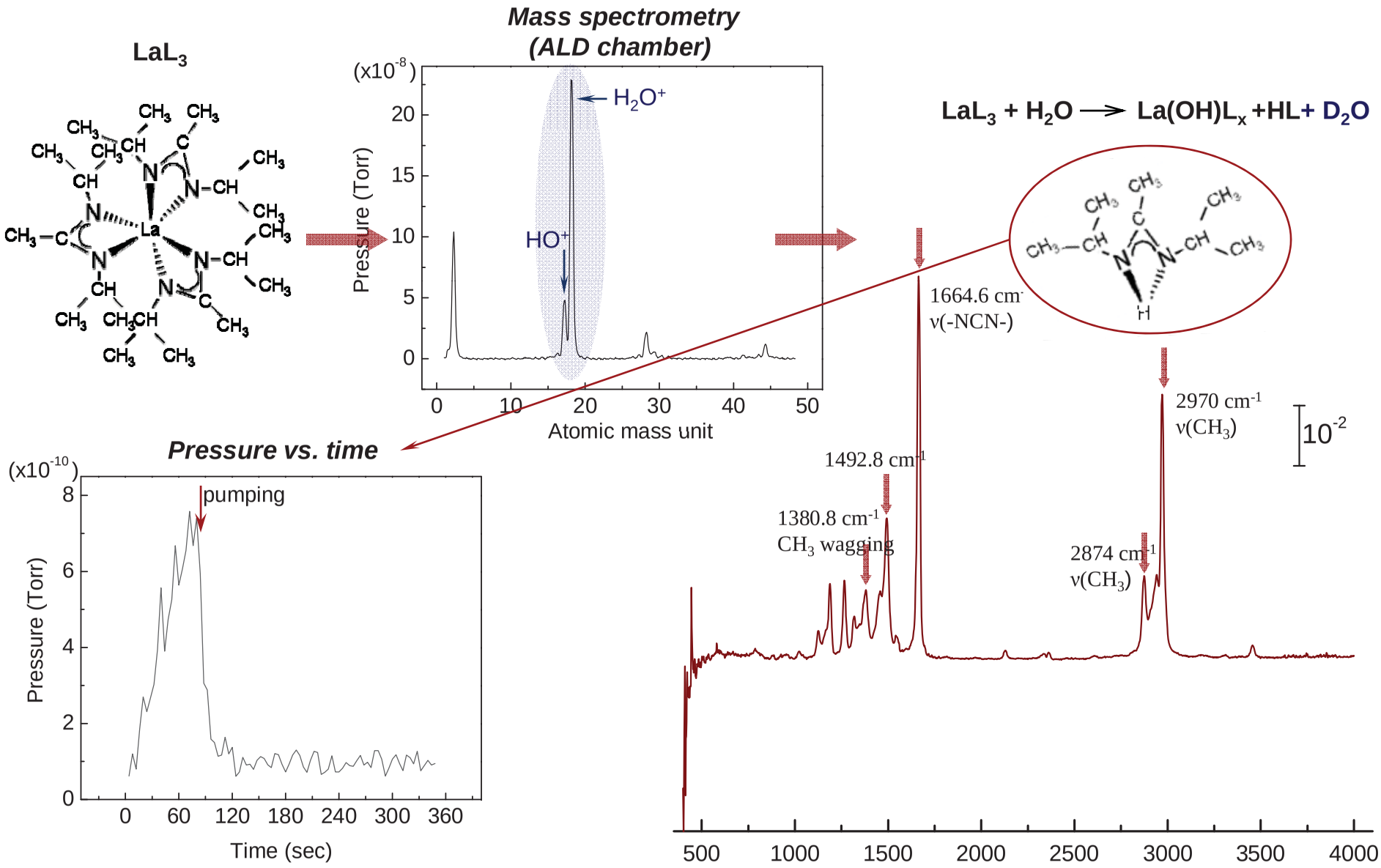
D_2O

Single beam



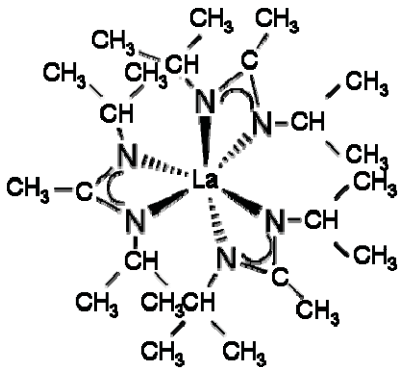


FTIR of gas phase La(^{i}Pr$_2$amd)$_3$

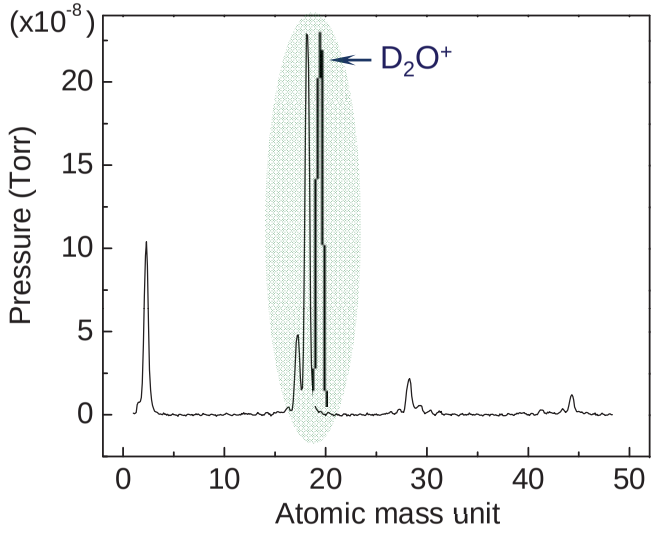


FTIR of gas phase La(^{i}Pr$_2$amd)$_3$

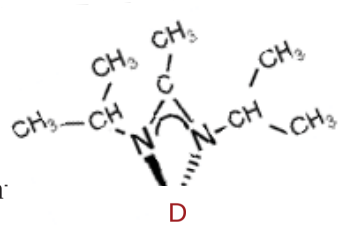
LaL_3

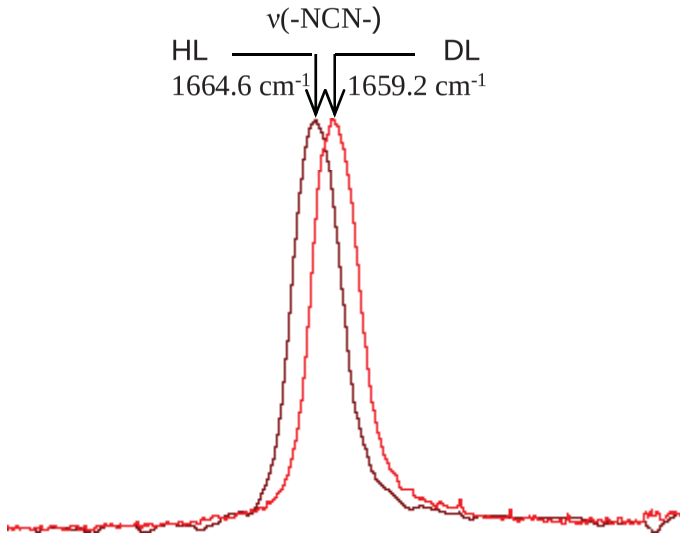


Mass spectrometry

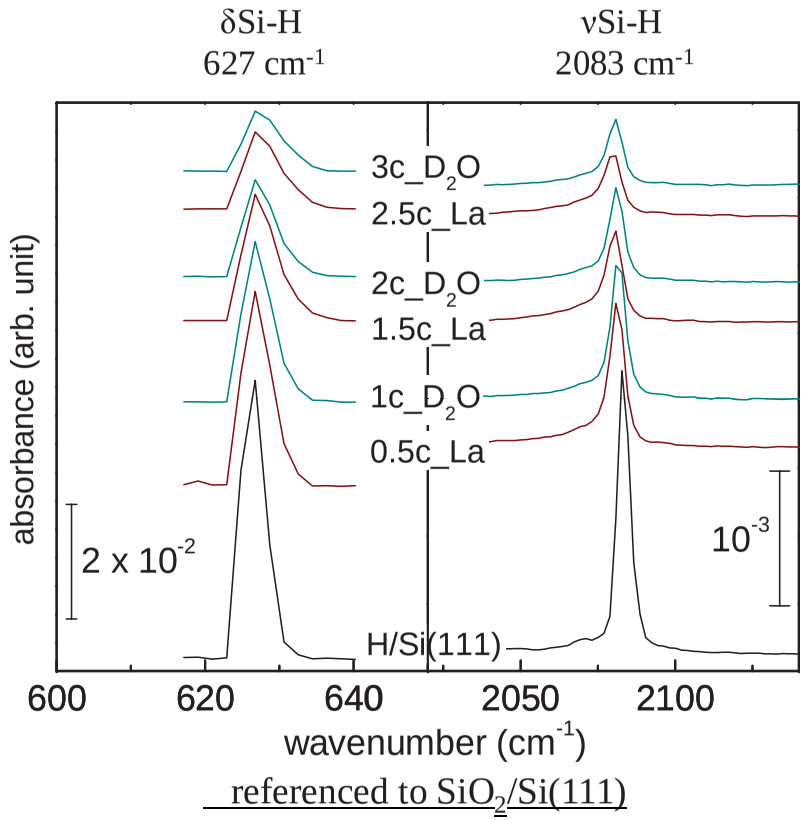


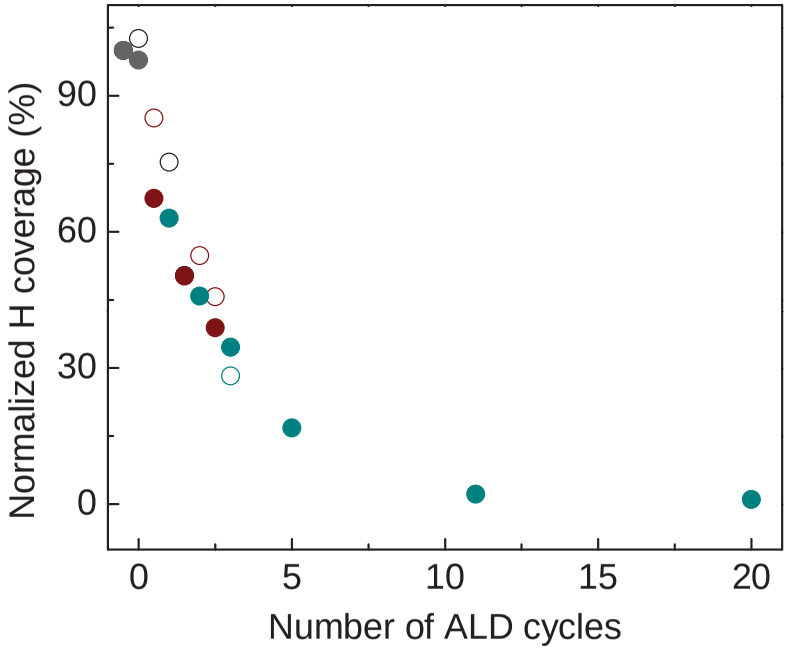
$LaL_3 + D_2O \longrightarrow La(OD)L_x + DL$





ALD of La_2O_3 on H/Si(111) at T_s = 200°C



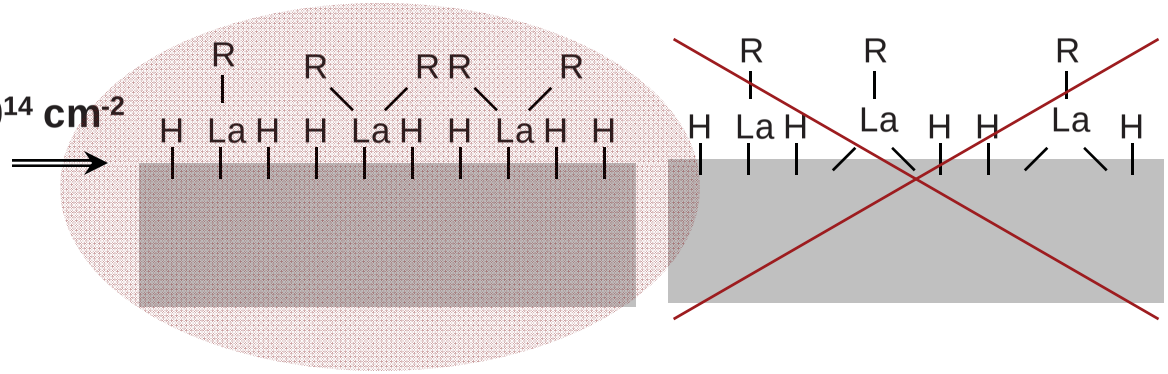


- **40 % (70 %) H loss after 1 (3) cycle**
- **Density of Si-H on Si(111) = 7.8 x 10^{14} cm^{-2}**

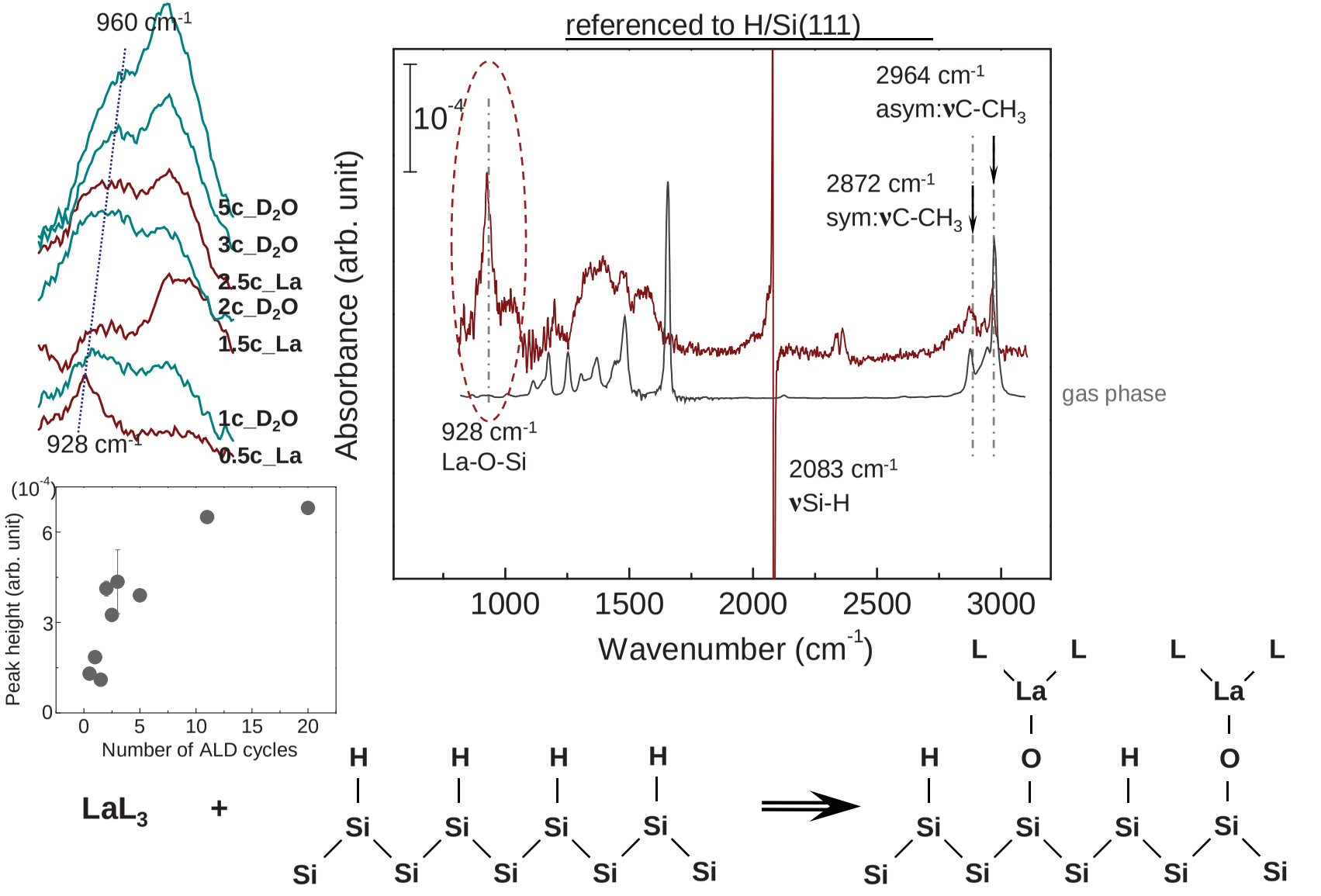
  40 % H loss = 3.1 x 10^{14} cm^{-2}

  La atoms/cm^2 (RBS) after 1 cycle

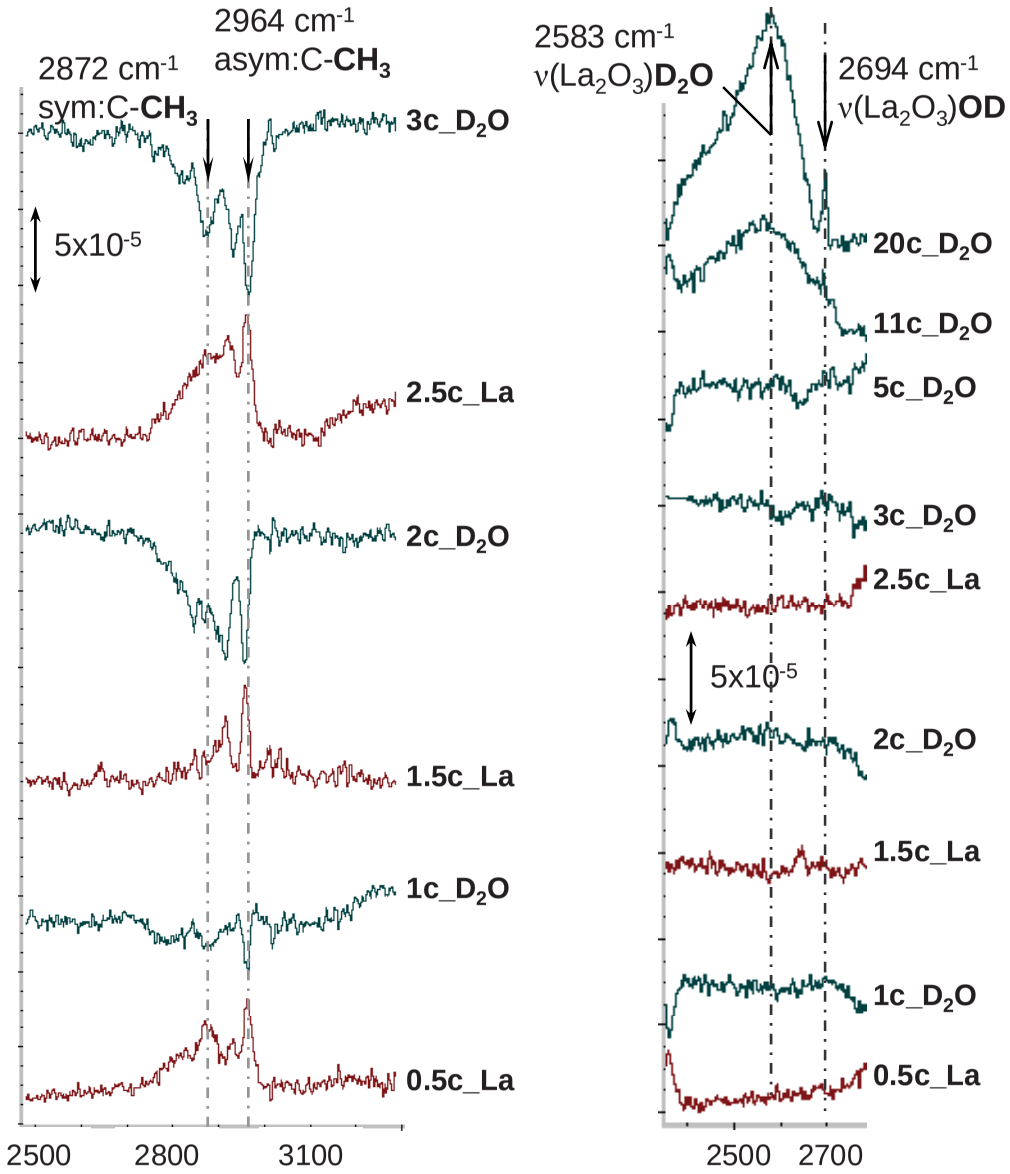
  = ~3 x 10^{14} cm^{-2} (± 7%)



Reaction between 1st La(iPr2amd)3 and H/Si(111) at Ts = 200oC

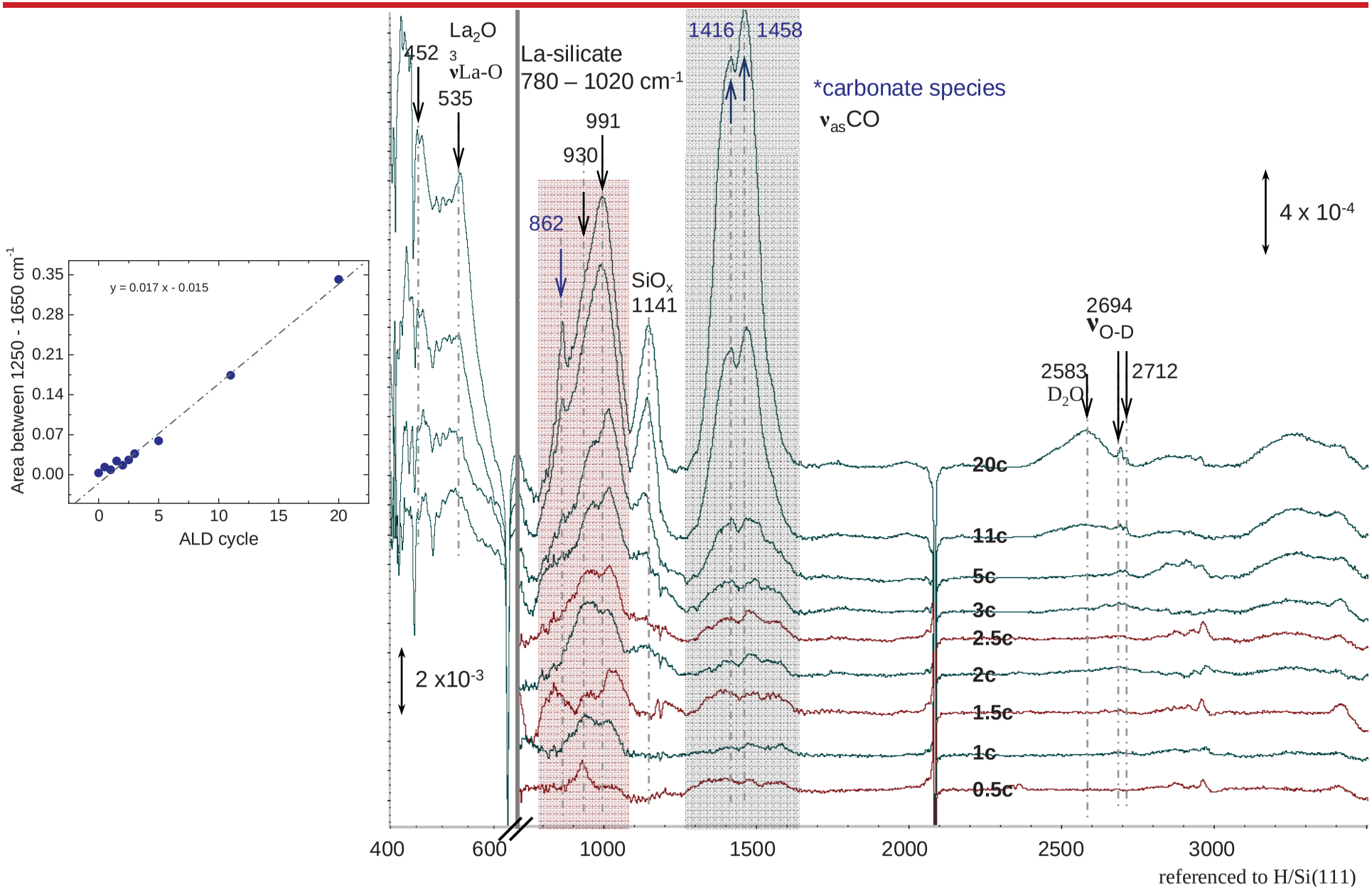


ALD of La_2O_3 on H/Si(111) at T_s = 200°C

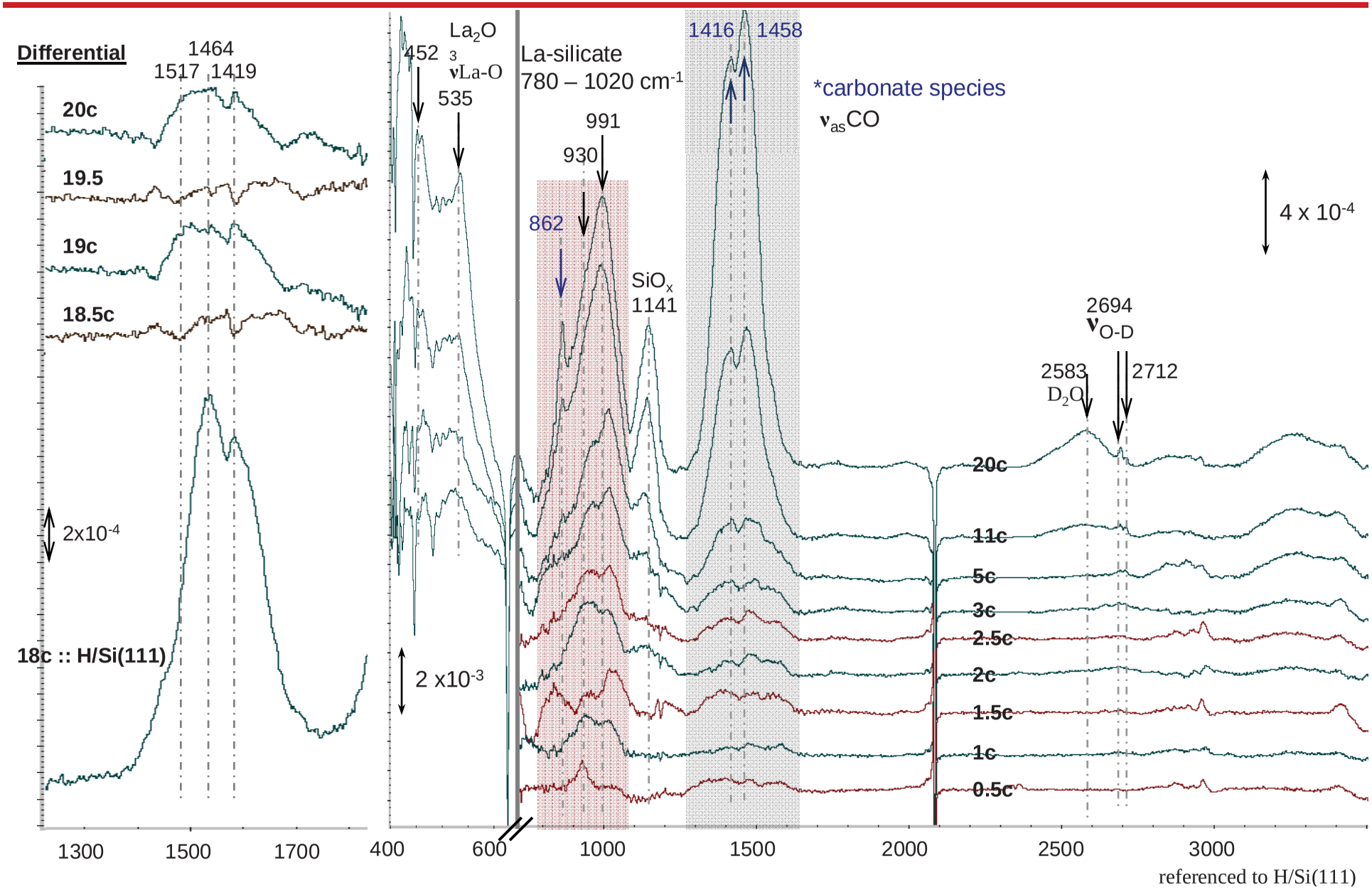


Differential

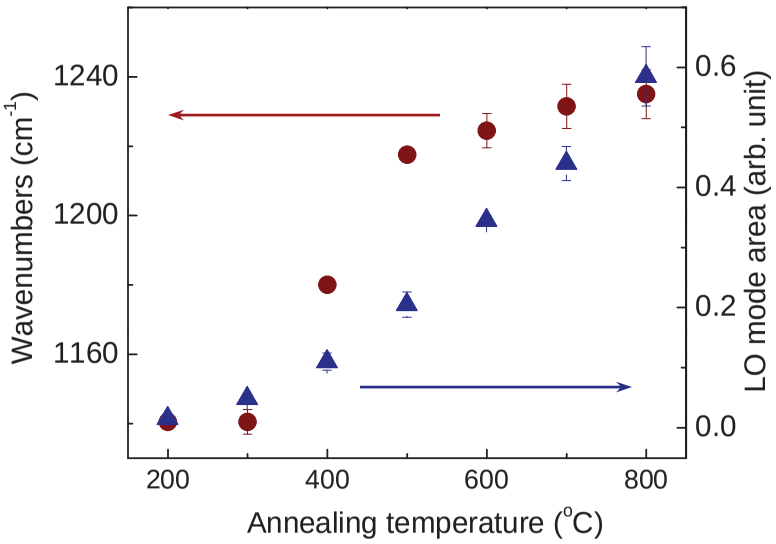
ALD of La_2O_3 on H/Si(111) at T_s = 200°C

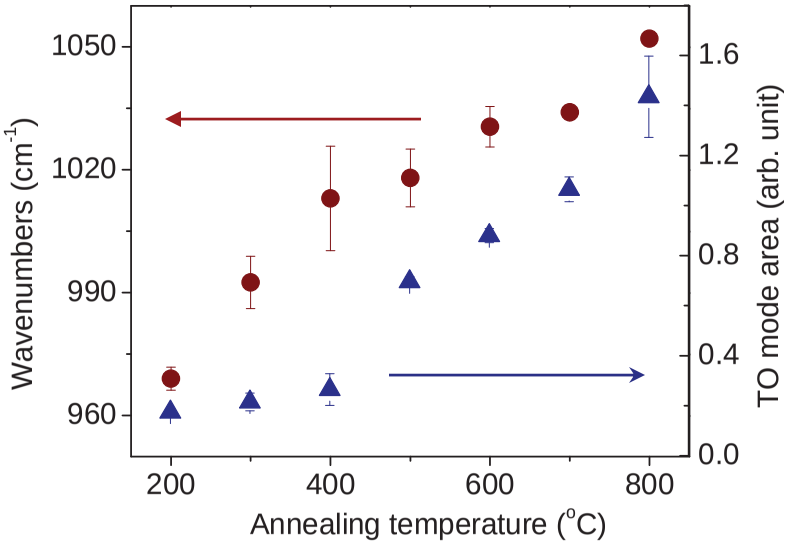


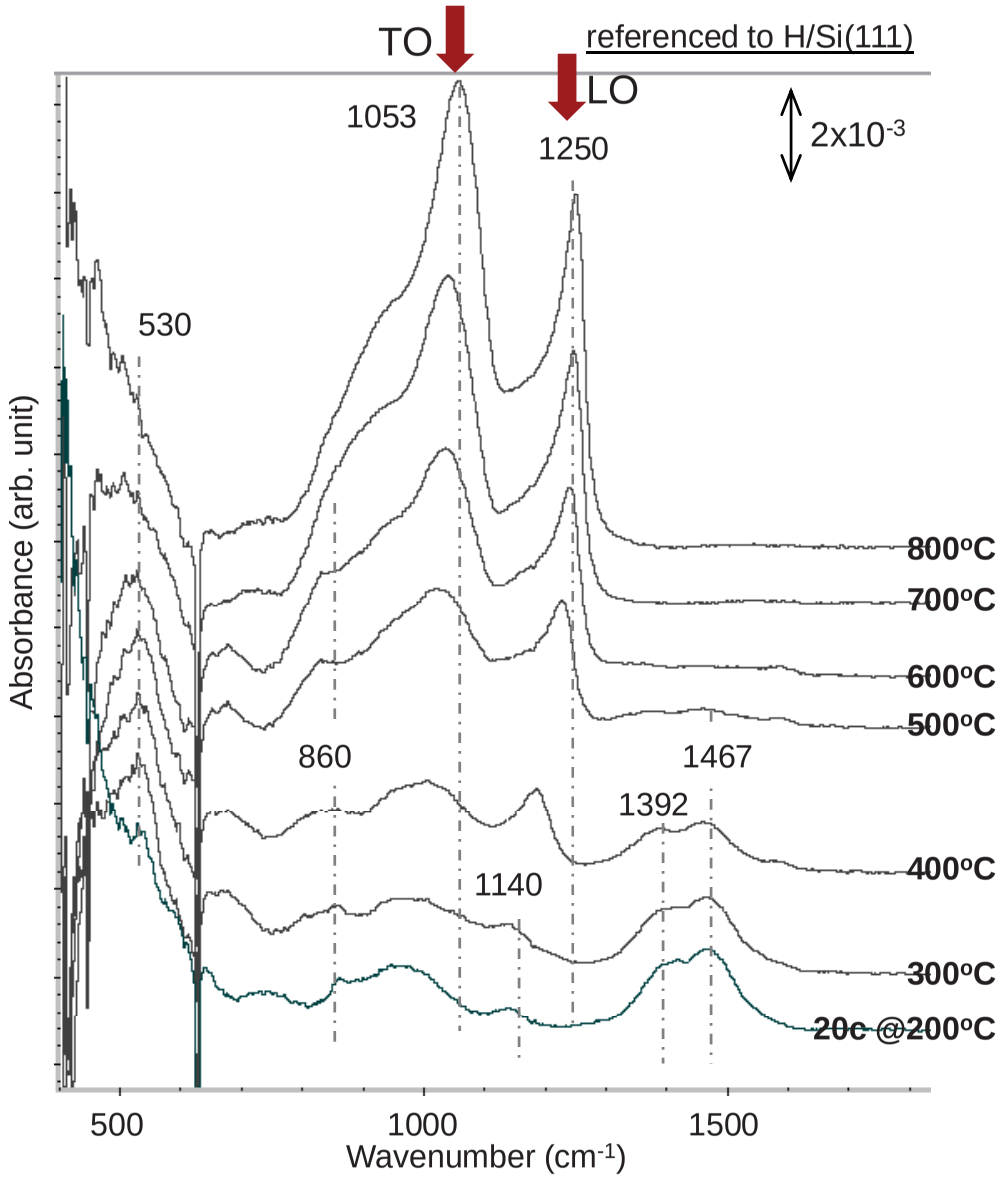
ALD of La_2O_3 on H/Si(111) at T_s = 200°C



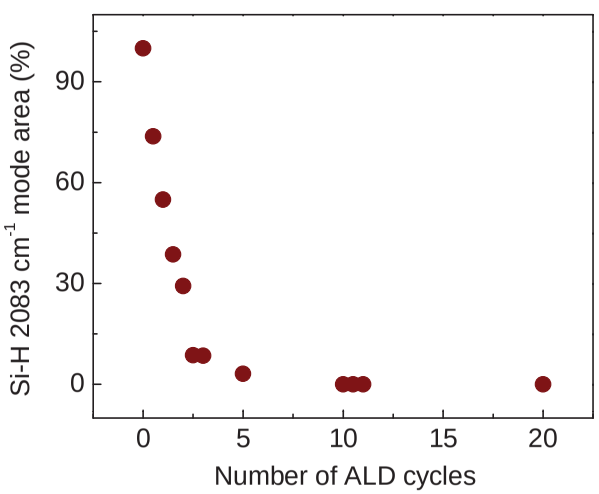
Post deposition annealing



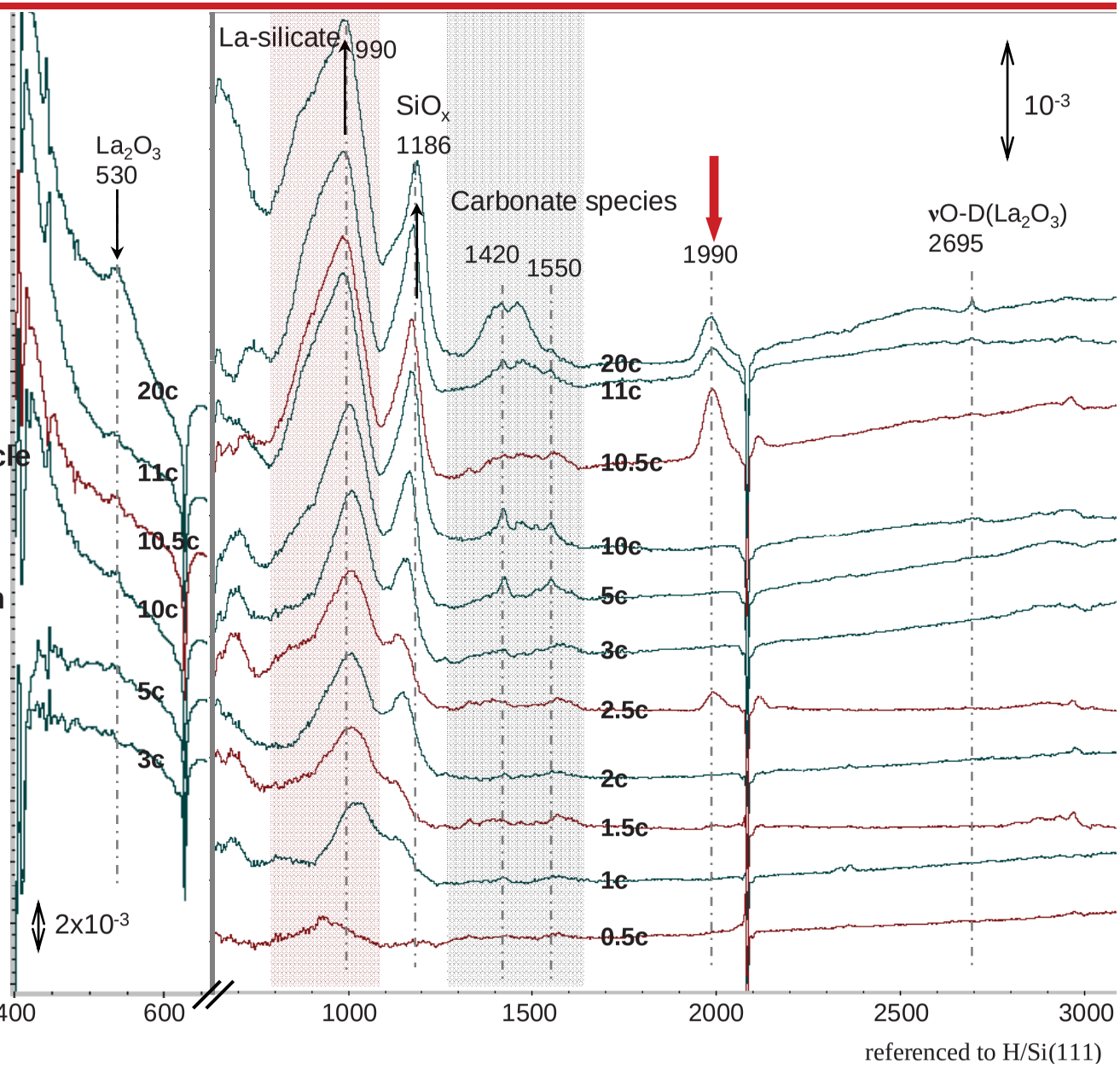




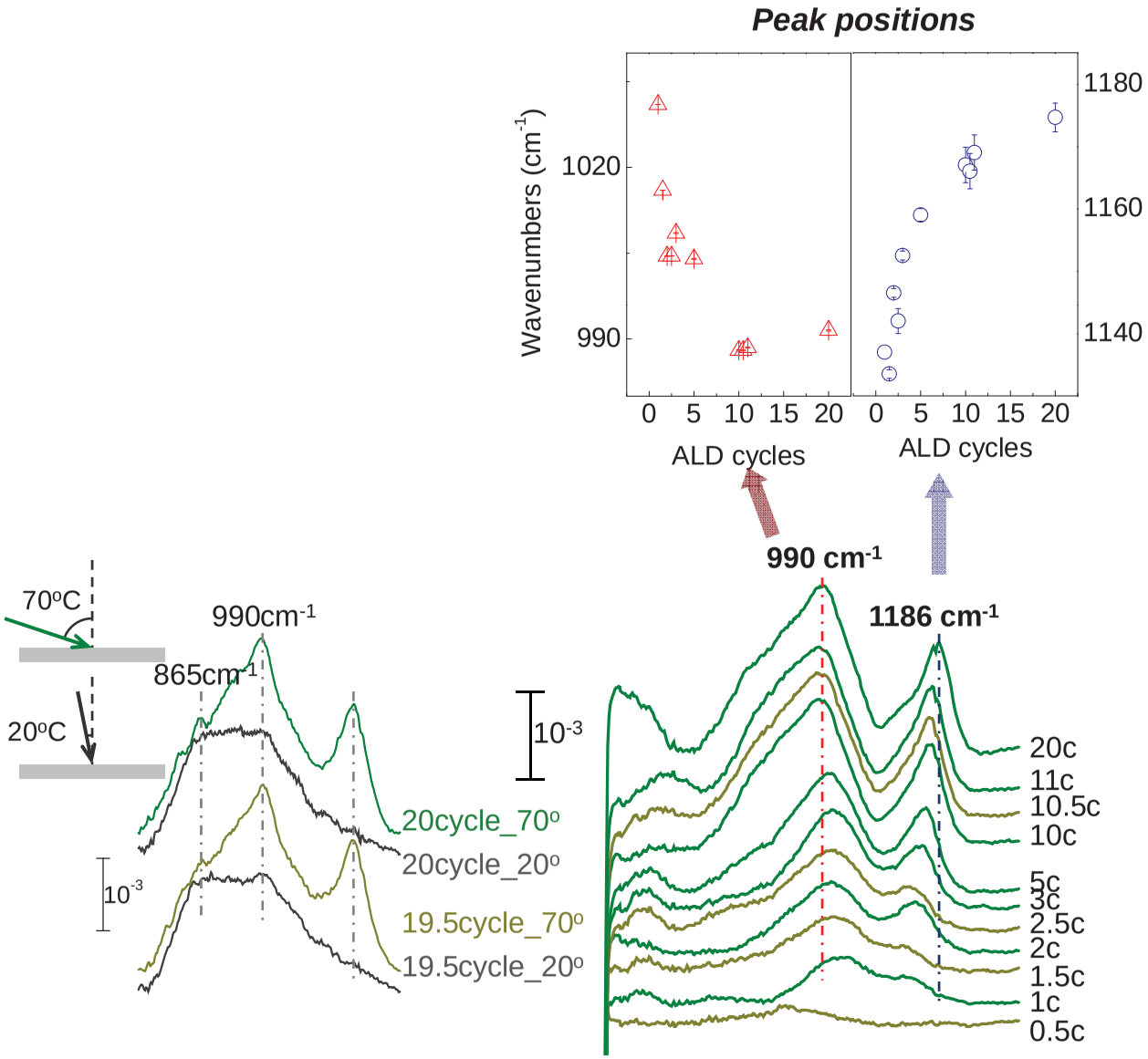
ALD of La_2O_3 on H/Si(111) at T_s = 300°C



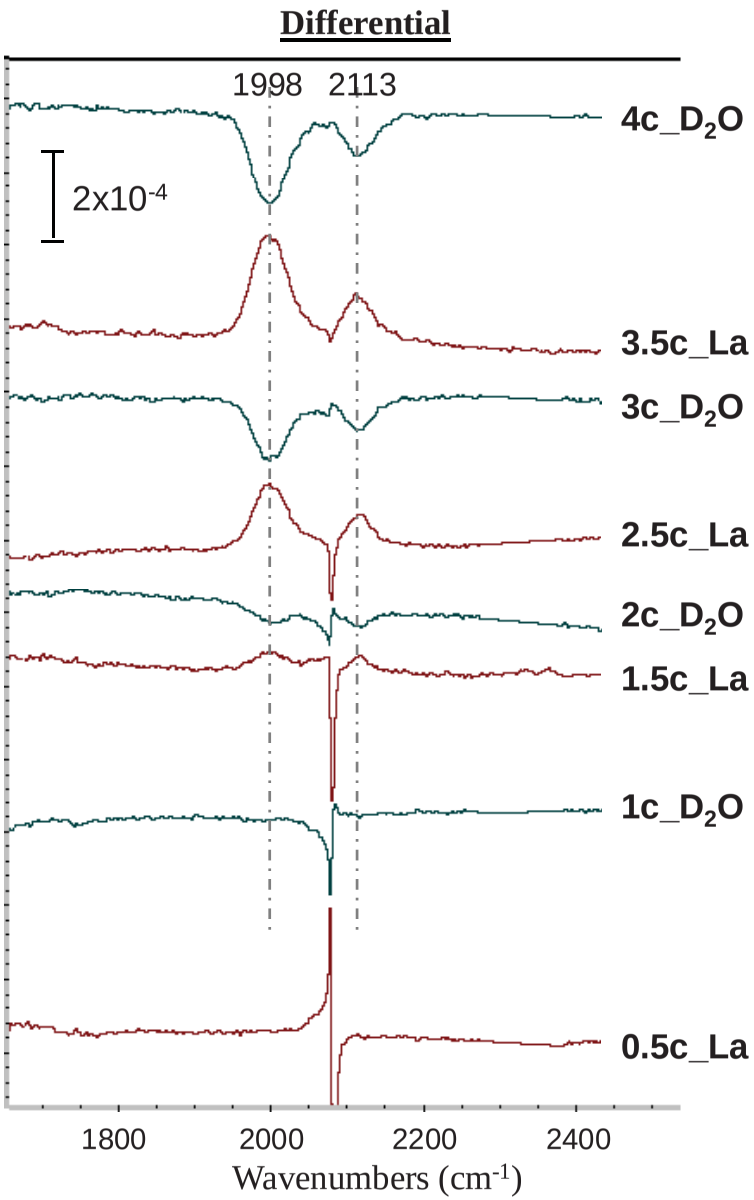
- **~100% H loss by the end of 5th cycle**
- **La_2O_3 LO mode at 530 cm^{-1}**
- **Less carbonate species in the film (1400 – 1600 cm^{-1})**
- **Interfacial SiO_x formation (1100 – 1200 cm^{-1})**
- **La-silicate formation (800 – 1100 cm^{-1})**
- **1990 – 2100 cm^{-1} modes**



ALD of La_2O_3 on H/Si(111) at T_s = 300°C

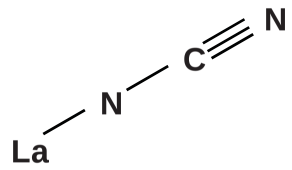


ALD of La_2O_3 on H/Si(111) at T_s = 300°C



Decomposition of La-precursor

→ cyanamide $[N\text{-}C{\equiv}N]^{2-}$ (or carbodiimide $[N{=}C{=}N]^{2-}$)



$\nu_{as}(CN_2)$
1900 ~ 2120 cm^{-1}

Verbindung	ν_s/cm^{-1}	ν_{as}/cm^{-1}	δ/cm^{-1}
Li_2CN_2	1275	2152	575/**653**
Na_2CN_2	*1242*	*2008*	*662/672*
K_2CN_2	*1225*	*1945*	*670*
Rb_2CN_2	*1214/**1227***	*1936*	*665*
Cs_2CN_2	*?*	*1921*	*653*
$MgCN_2$	*1301*	*2114*	*681*
$CaCN_2$	*1271*	*2033*	*670*
α-$SrCN_2$	*1251*	***1989**/2023*	***663**/677*
β-$SrCN_2$	*??*	*1986*	*665/677*
$EuCN_2$	*1244*	***1969**/2087*	***655**/666*
$BaCN_2$	*1238*	*1947*	***662**/673*
$Si(CN_2)_2$	*?*	*2174*	*?*
$Si_2(CN_2)N_2$	*?*	*2170*	*?*
$CuCN_2$	1212	2025	561/596/**665**/686
Ag_2CN_2	*1191*	*1980*	*633*
$ZnCN_2$	*1293*	*2048*	***677**/694*
$CdCN_2$	1264	*2071/**2113***	***655**/668*
Hg_2CN_2	*1270/1320*	*2075*	*647*
$HgCN_2$(I)	*1214*	***1942**/2036*	*653/**666***
$HgCN_2$(I)	*1219*	*1948/2031*	*616*
$HgCN_2$(II)	*1219*	*1949/2097*	*616*

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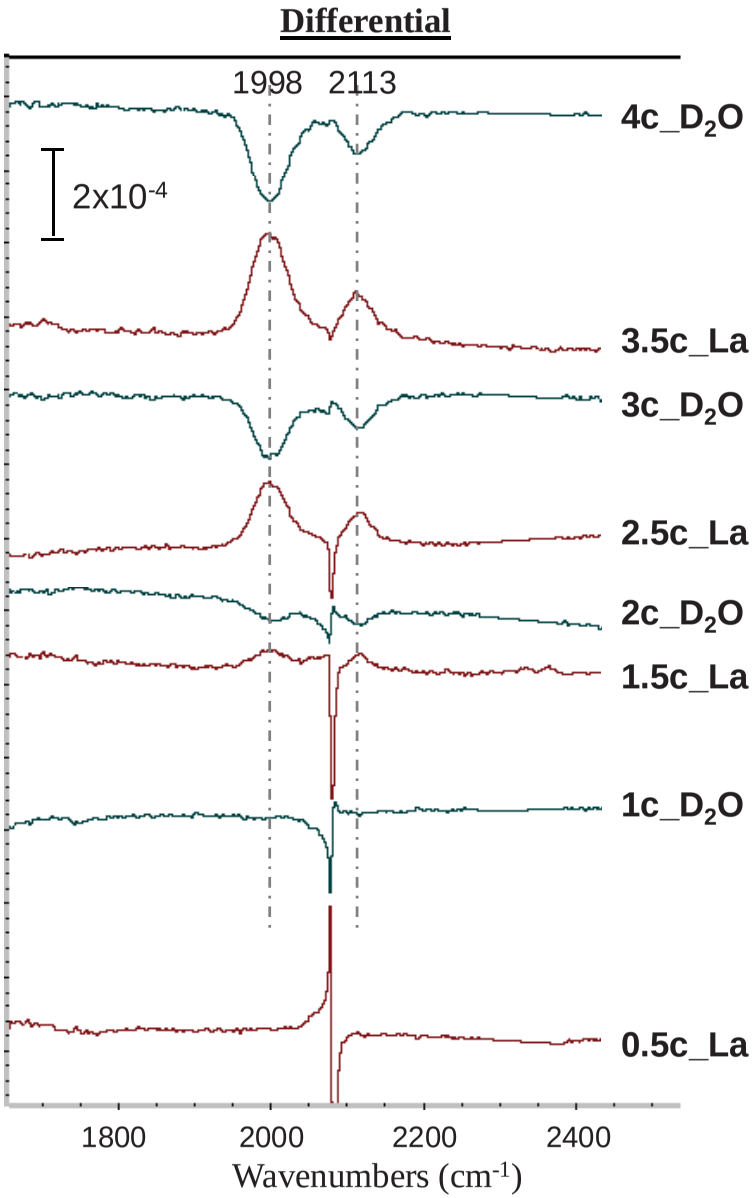
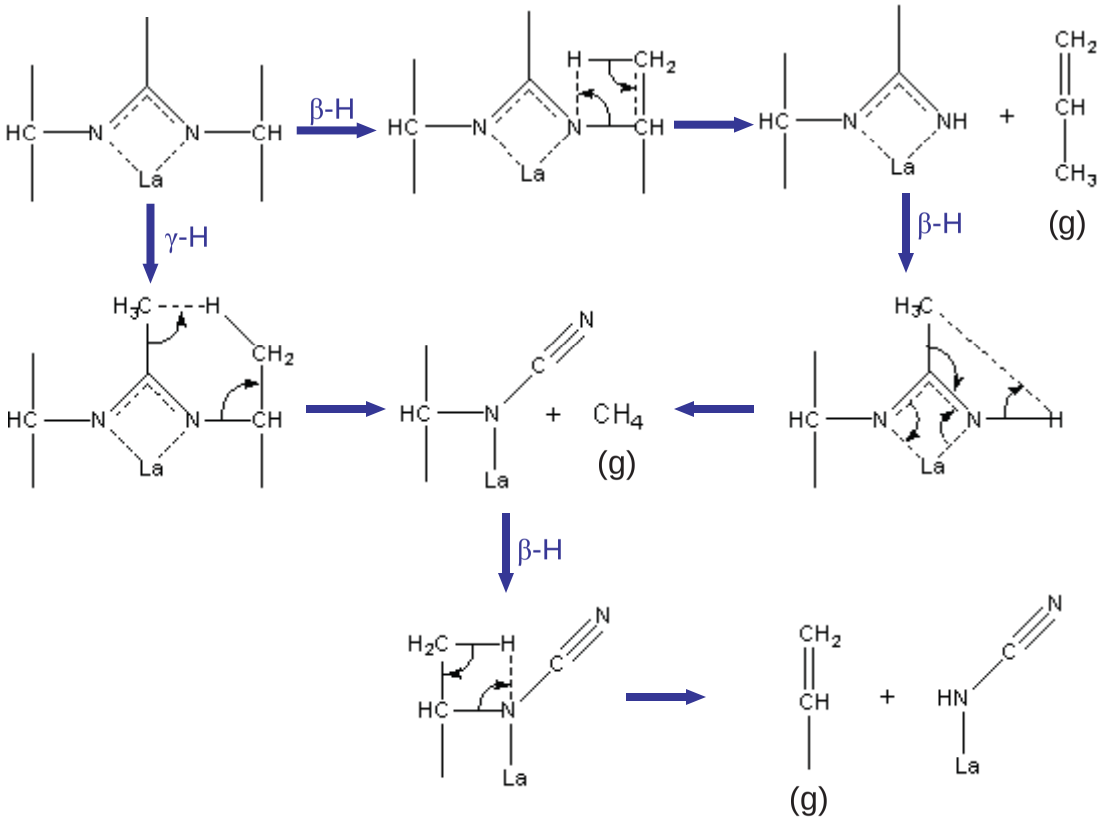
ALD of La_2O_3 on H/Si(111) at T_s = 300°C





Summary

- $La(^{i}Pr_2amd)_3$ is hydrolyzed by residual water in the ALD chamber
- Complete H loss by the end of 5^{th} cycle ($T_s = 300^{o}C$)
- La-silicate and SiO_2 formation along with La_2O_3
- Carbonate impurities in the films $\longrightarrow$ removed by annealing at $500^{o}C$
- $La(^{i}Pr_2amd)_3$ decomposed to cyanamide at $T_s = 300^{o}C$