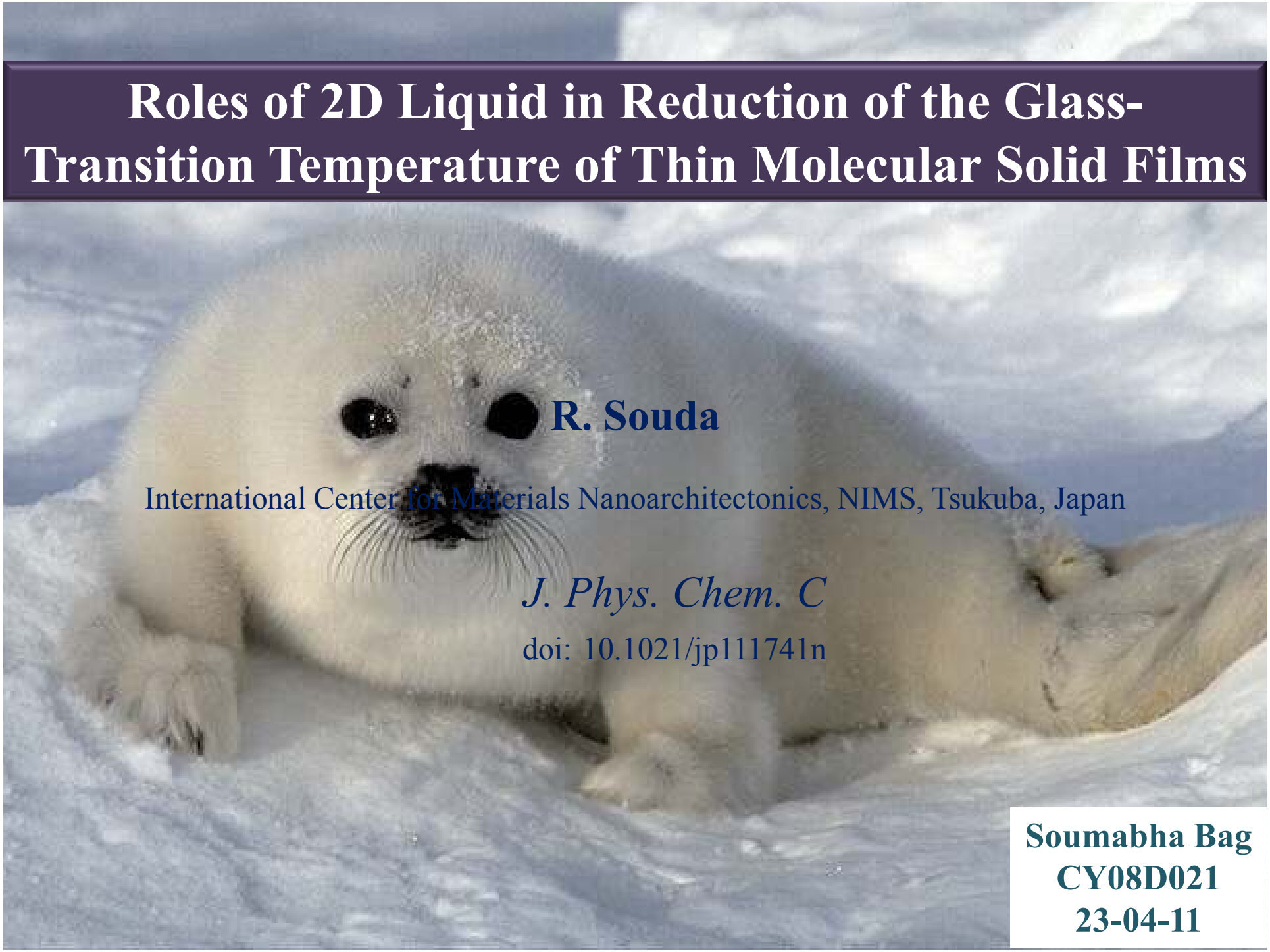
Roles of 2D Liquid in Reduction of the Glass-Transition Temperature of Thin Molecular Solid Films



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Introduction:

❖ Diffusion of particles on the solid surfaces is important in view of catalyst and crystal growth.

❖ Small cluster are more mobile than isolated species as there is less interaction between adsorbate-surface bond. .

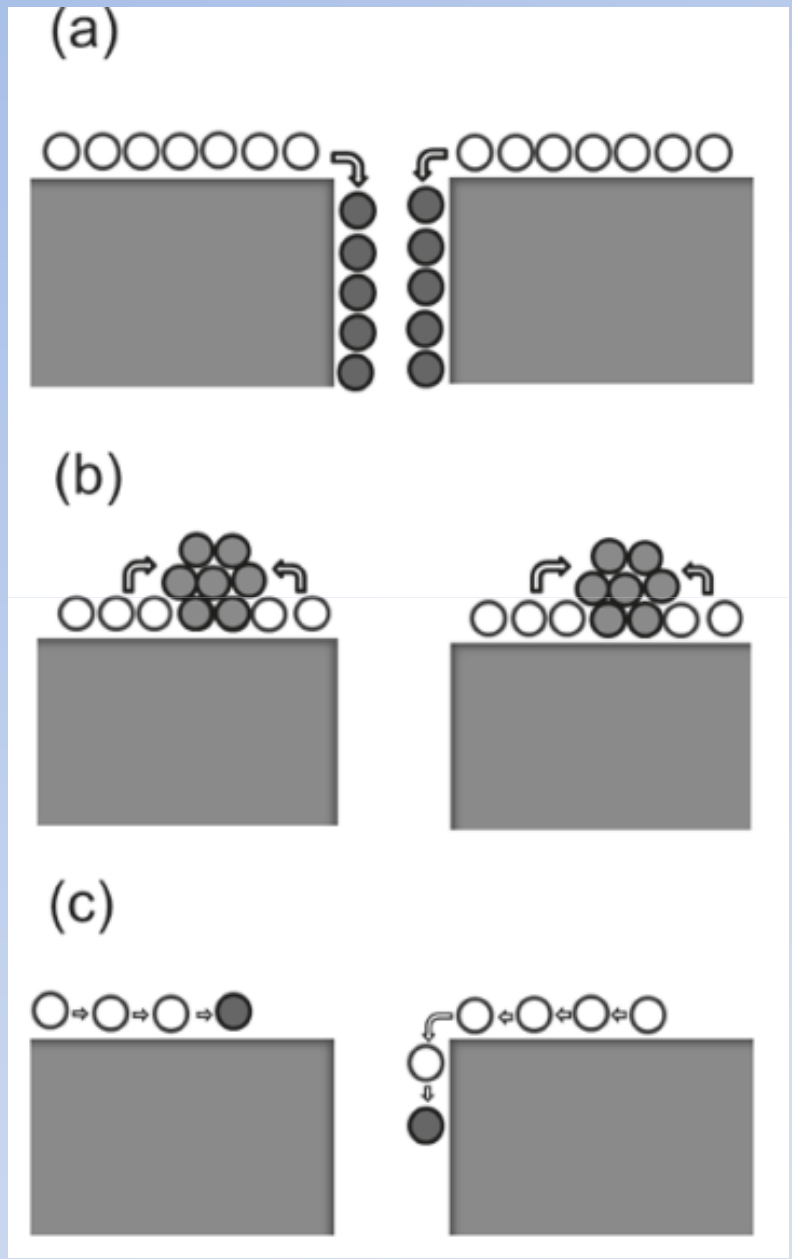
❖ Cooperative diffusion of the cluster is difficult if cluster size increase beyond tetramer.

❖ Computer simulations revealed that stringlike clusters moving cooperatively are formed well above the glass transition; the mean length of the strings increases upon cooling, in accordance with the formation of cooperatively rearranging regions (CRR).

❖ T_g is expected to be modified when sample dimension become ~ 1 nm.

❖ Studies using polystyrene and PMMA revealed some contradiction in understanding in molecular level.

In this paper……

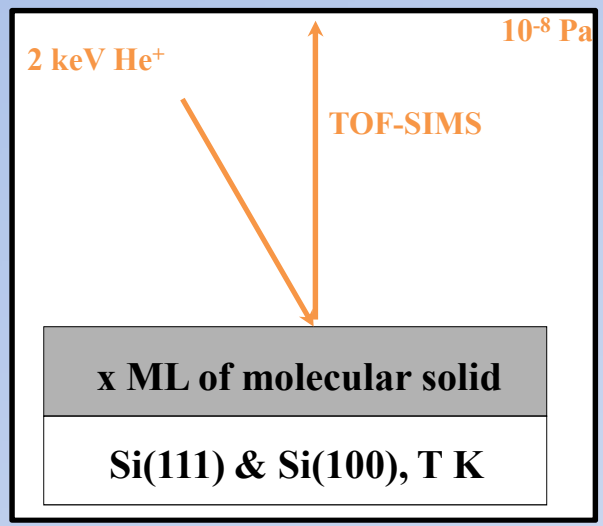


Molecular uptake into pores

Droplet formation

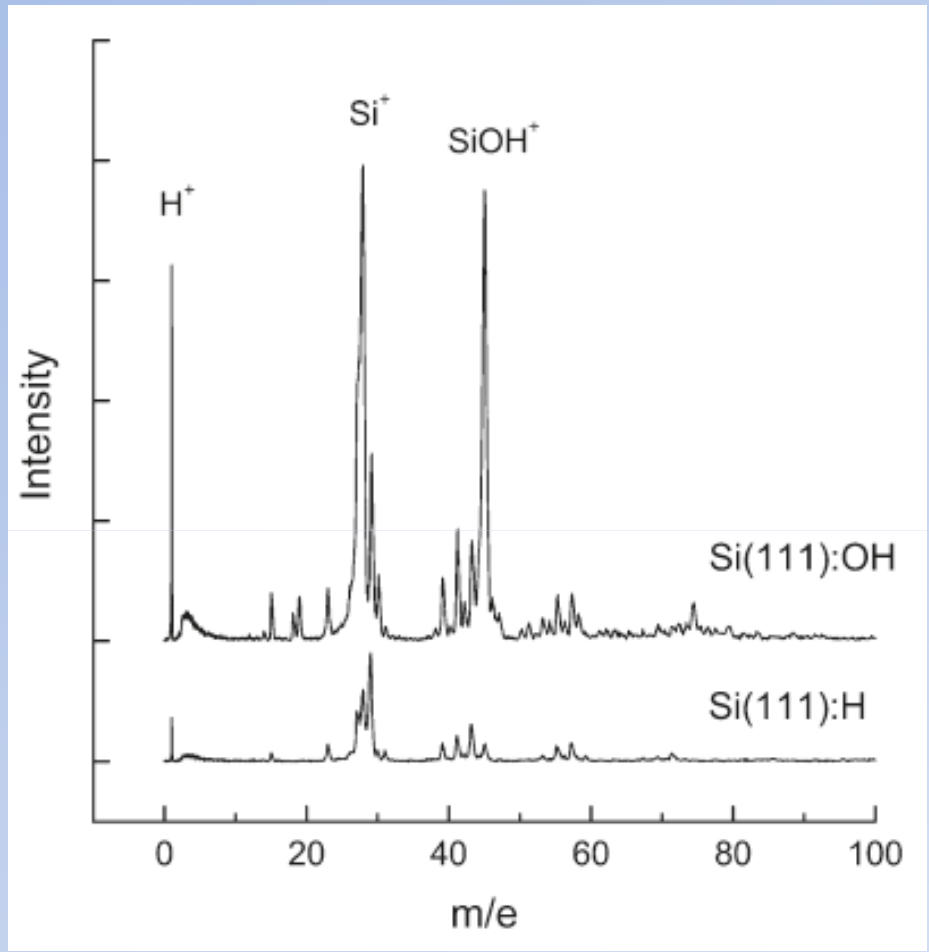
Migration of residues

Experimental section:



Preparation of substrate……

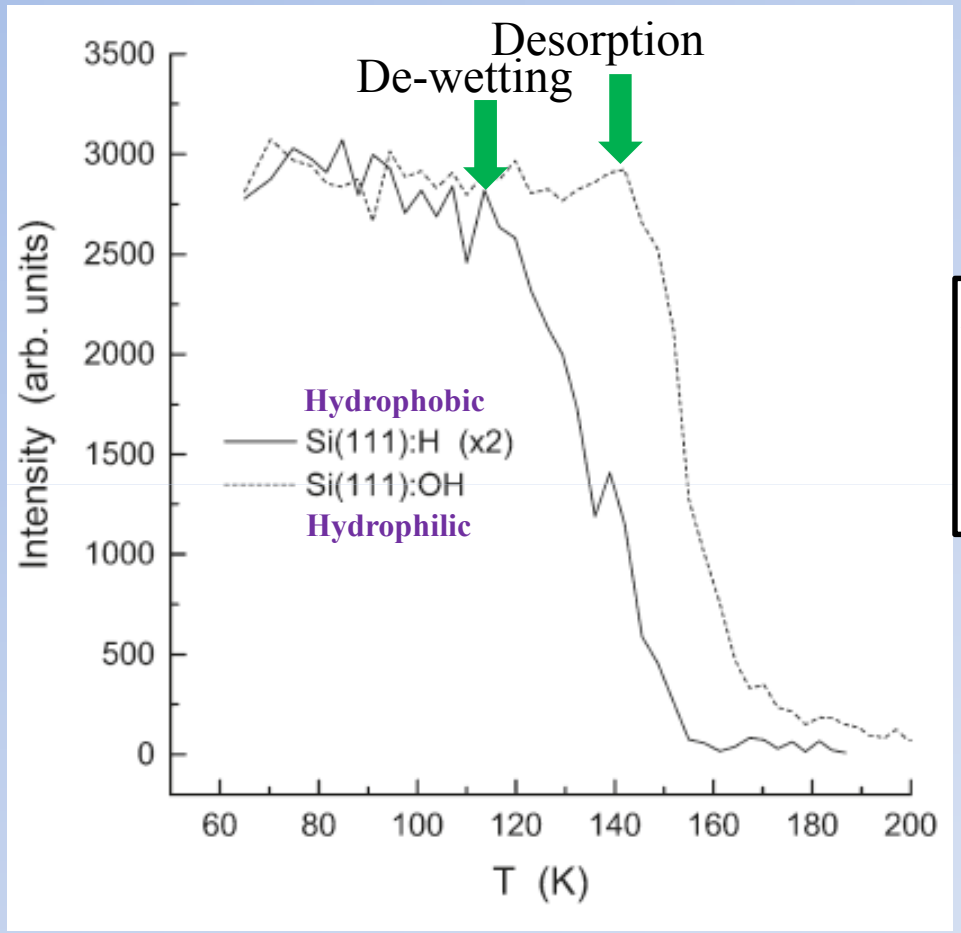
1. Si (111) wafer, p-type → Cleaned ultrasonically in water and ethanol → Etched using 40% NH_4F
2. Kept at N_2 atmos. and H_2-passivated (formation of Si(111):H)
3. Si(111):H irradiated using photon in air to form Si(111):OH
4. p-Si(111) was prepared by electrochemical etching: electrolyte 1:1 (vol.) HF & ethanol, Si(100) anode, current density 100mA/cm^2 for 3 mins. Pore size 10-20 nm diameter. Prepared surfaces are hydrophobic. Hydrophilic surfaces are prepared by irradiating the photon similar way as above.

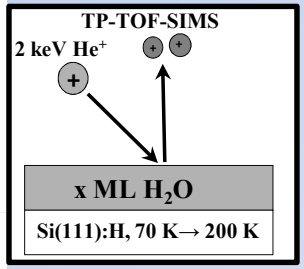


TOF-SIMS from different Si substrate

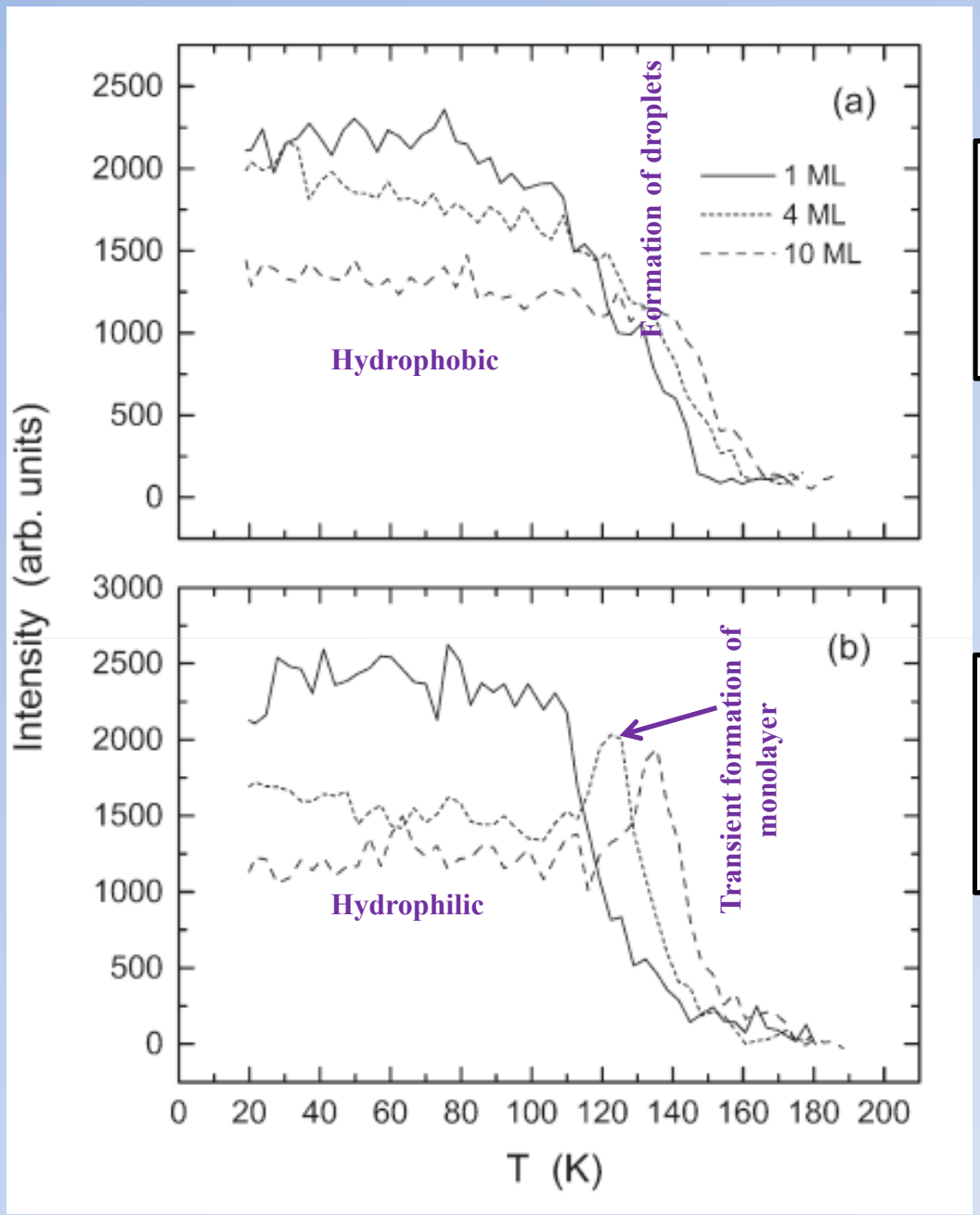
Results:

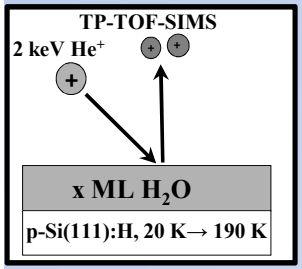
Study using H_2O

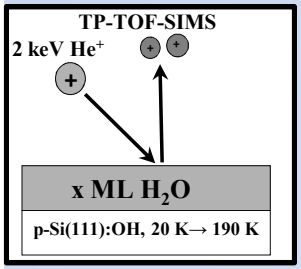


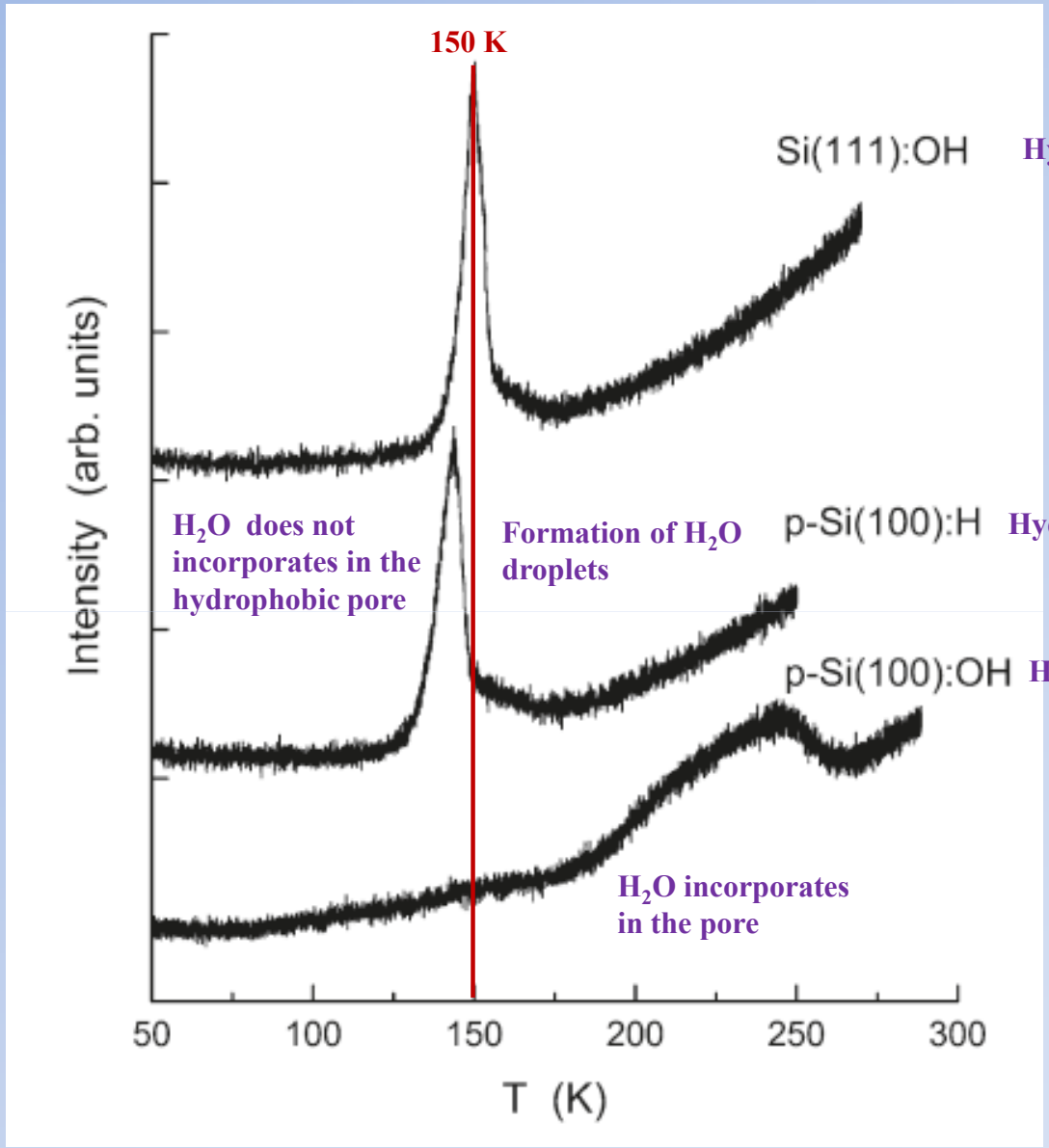


TP-TOF-SIMS intensity of hydronium ion sputtered from water deposited on different Si substrates


(a)
1 ML
4 ML
10 ML
Formation of droplets
Hydrophobic
(b)
Transient formation of monolayer
Hydrophilic
Intensity (arb. units)
T (K)
0
500
1000
1500
2000
2500
3000
0
20
40
60
80
100
120
140
160
180
200

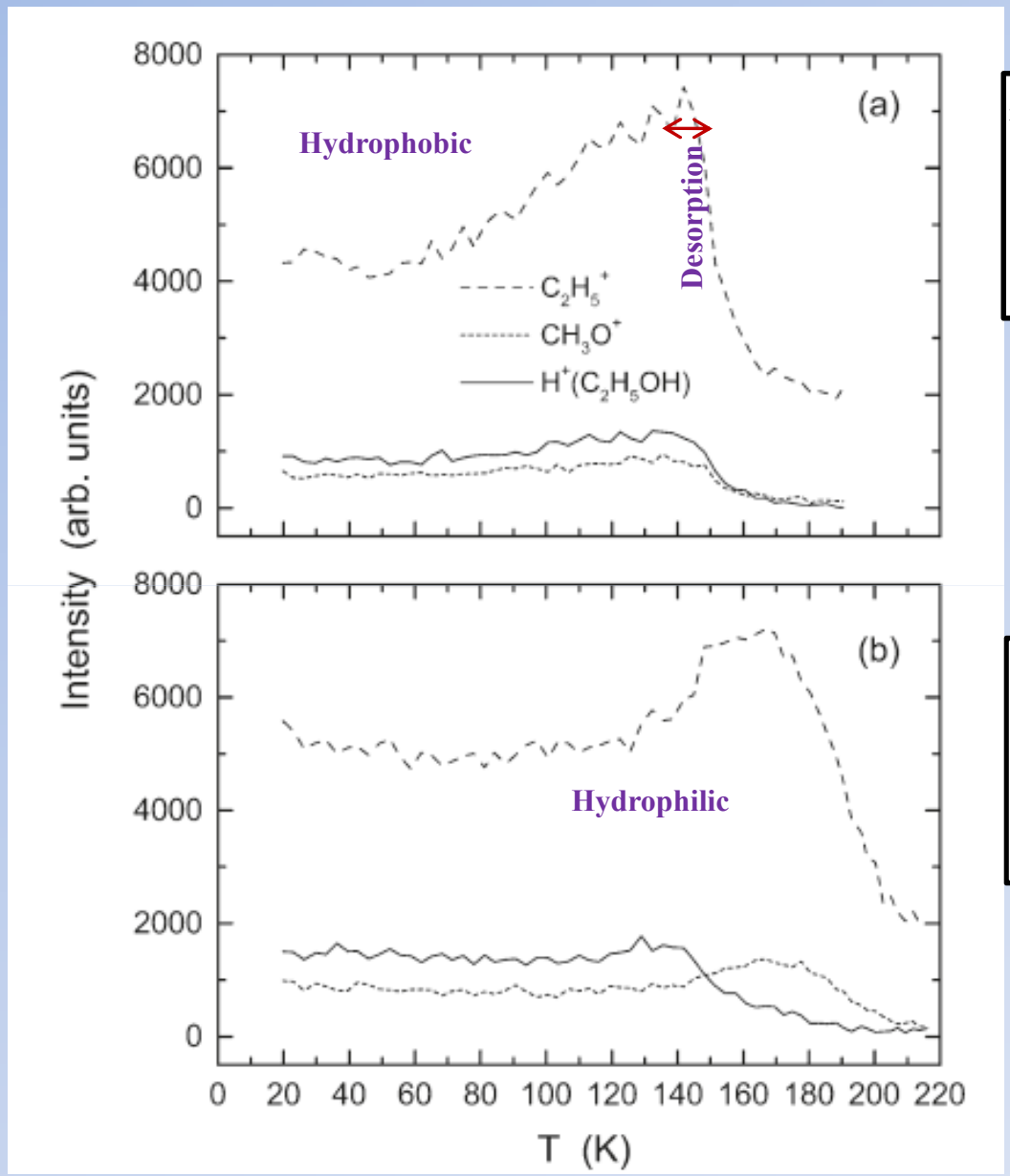

TP-TOF-SIMS
2 keV He+
x ML H2O
p-Si(111):H, 20 K→ 190 K

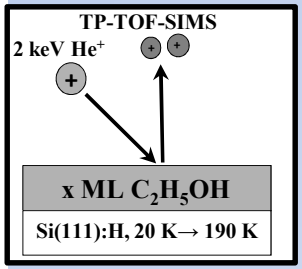

TP-TOF-SIMS
2 keV He+
x ML H2O
p-Si(111):OH, 20 K→ 190 K

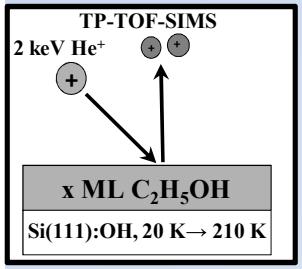


TPD of water deposited on different Si substrates

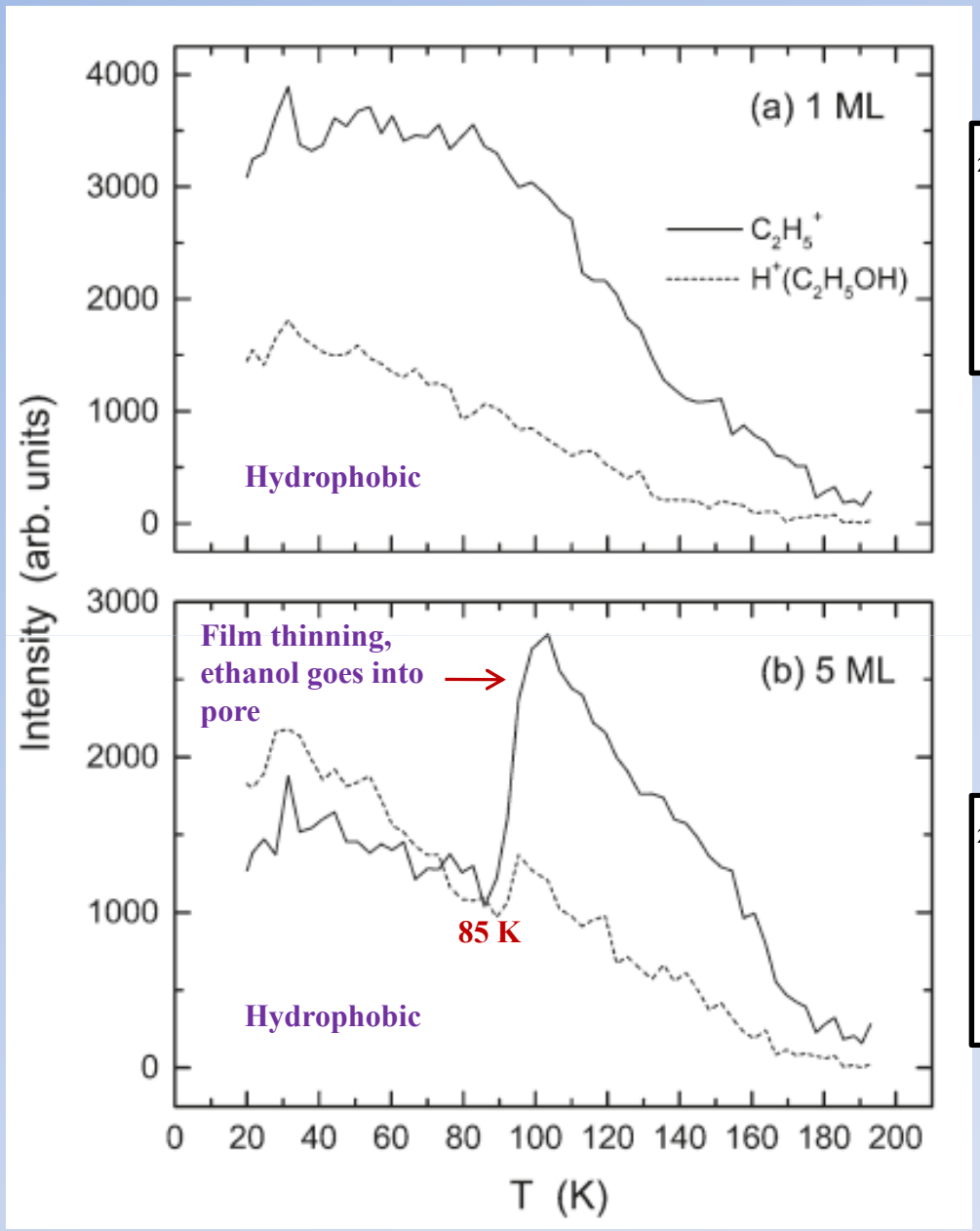
Study using C_2H_5OH

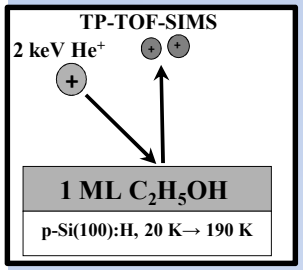


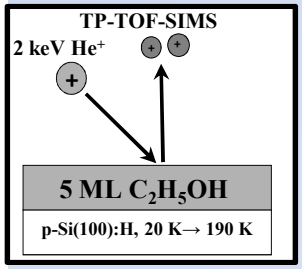




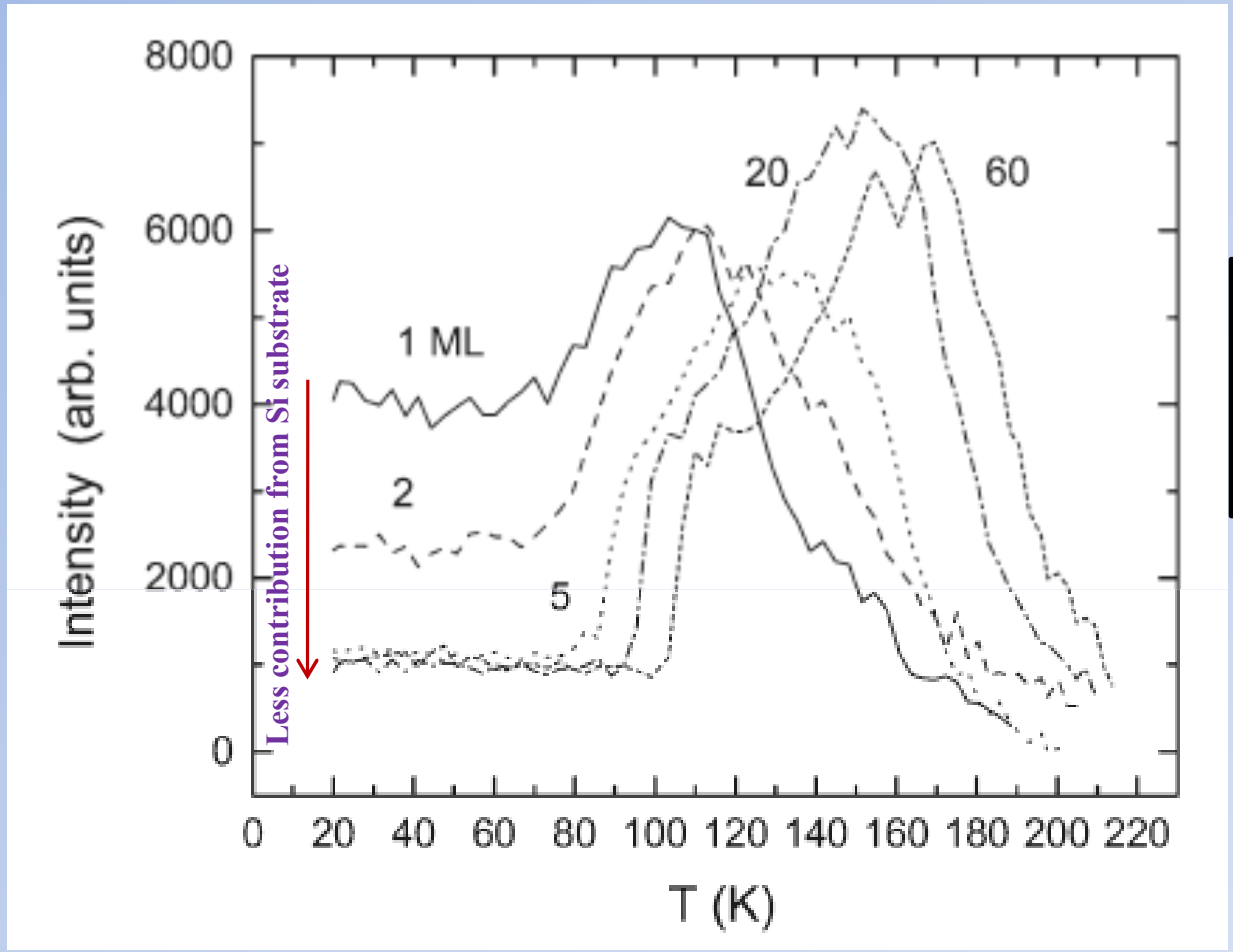
TP-TOF-SIMS of ethanol deposited on different Si substrates

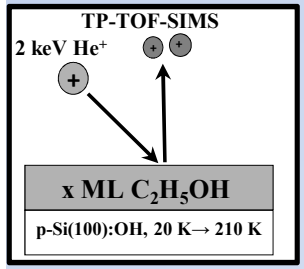




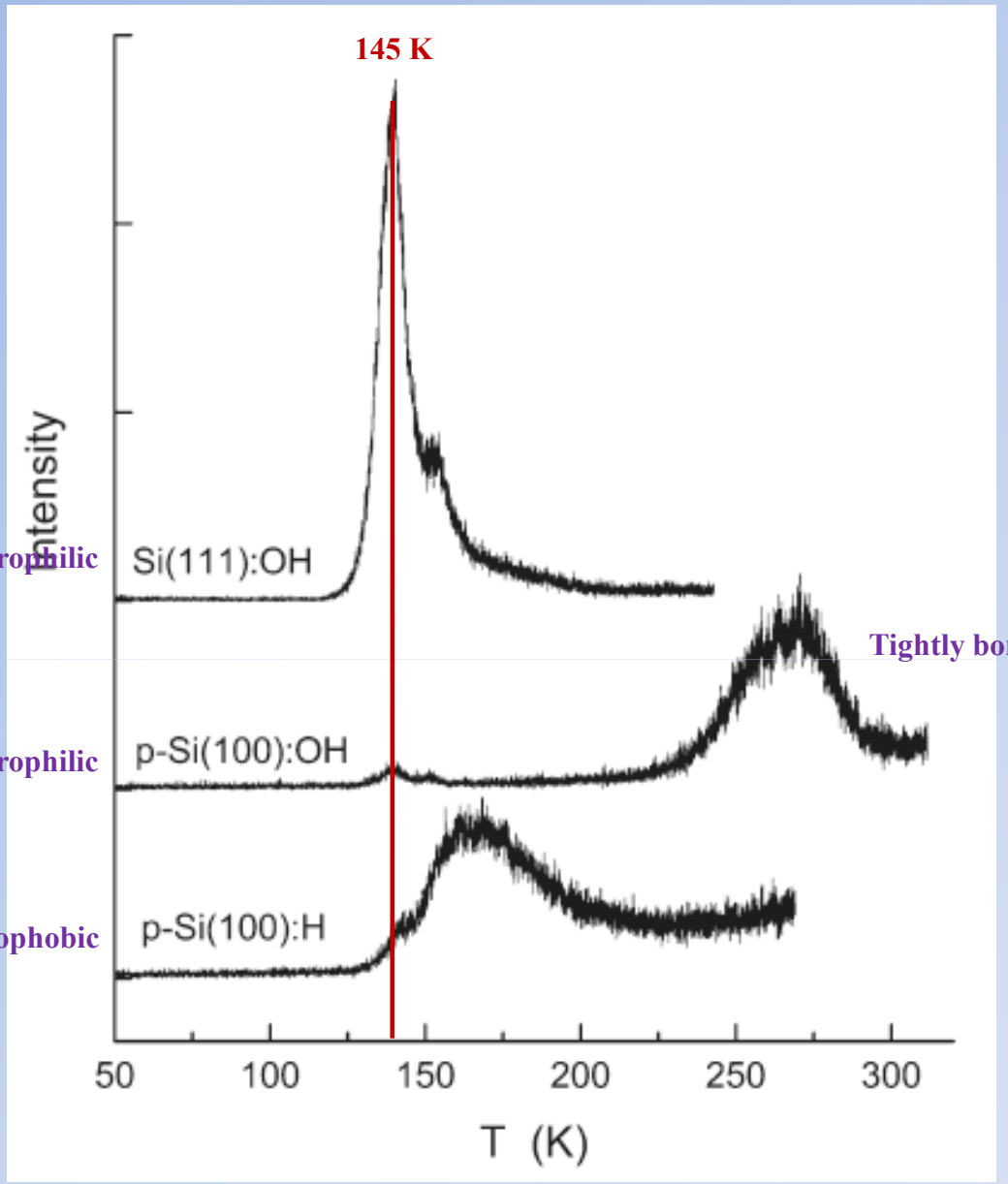


TP-TOF-SIMS of ethanol deposited on p-Si(100):H substrates



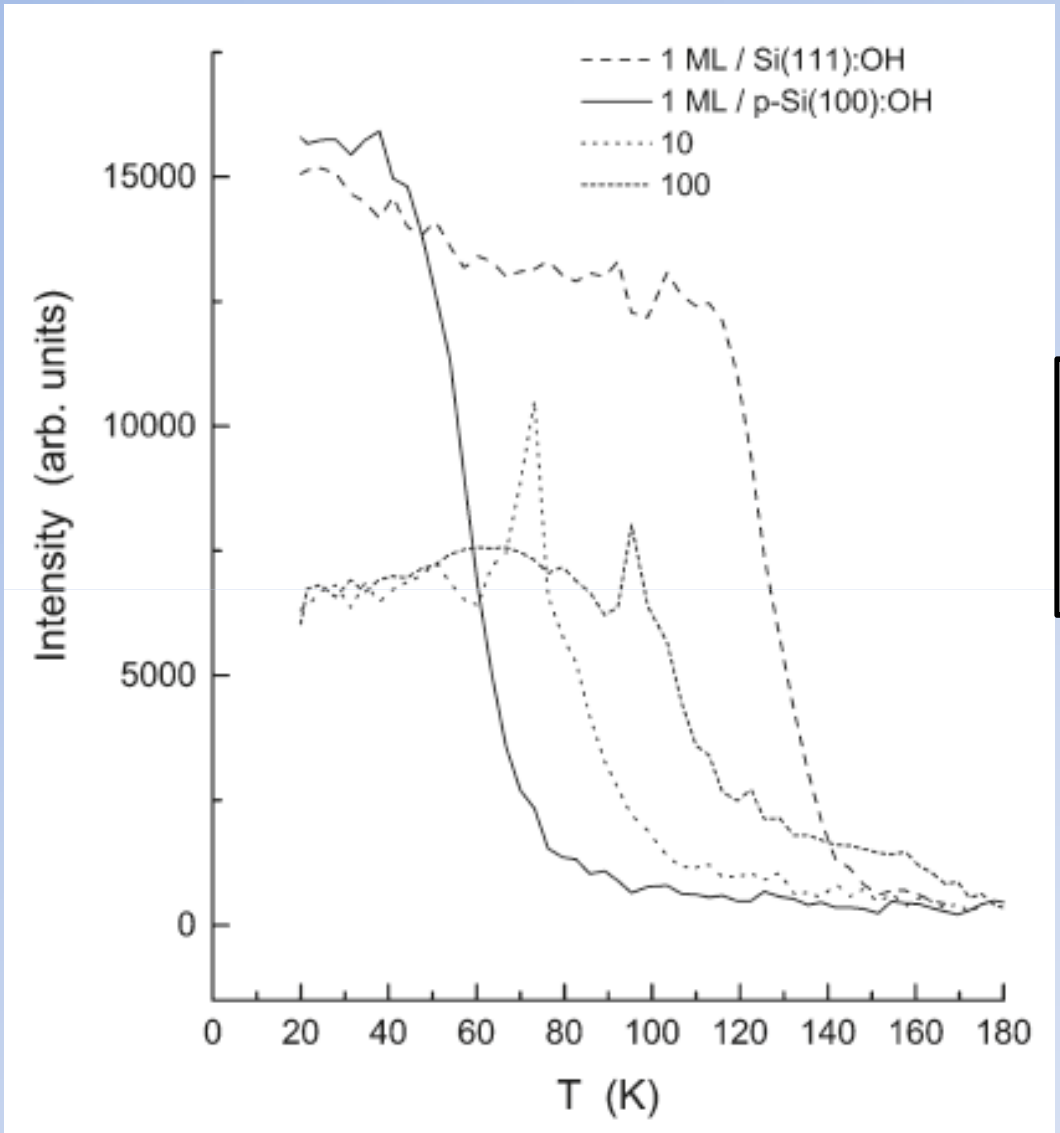


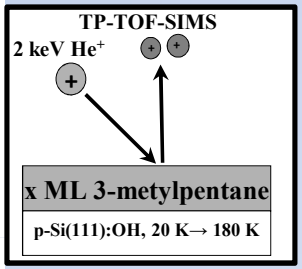
Temperature evolution of ethyl ion from varying layers of ethanol deposited on p-Si(100):OH substrate



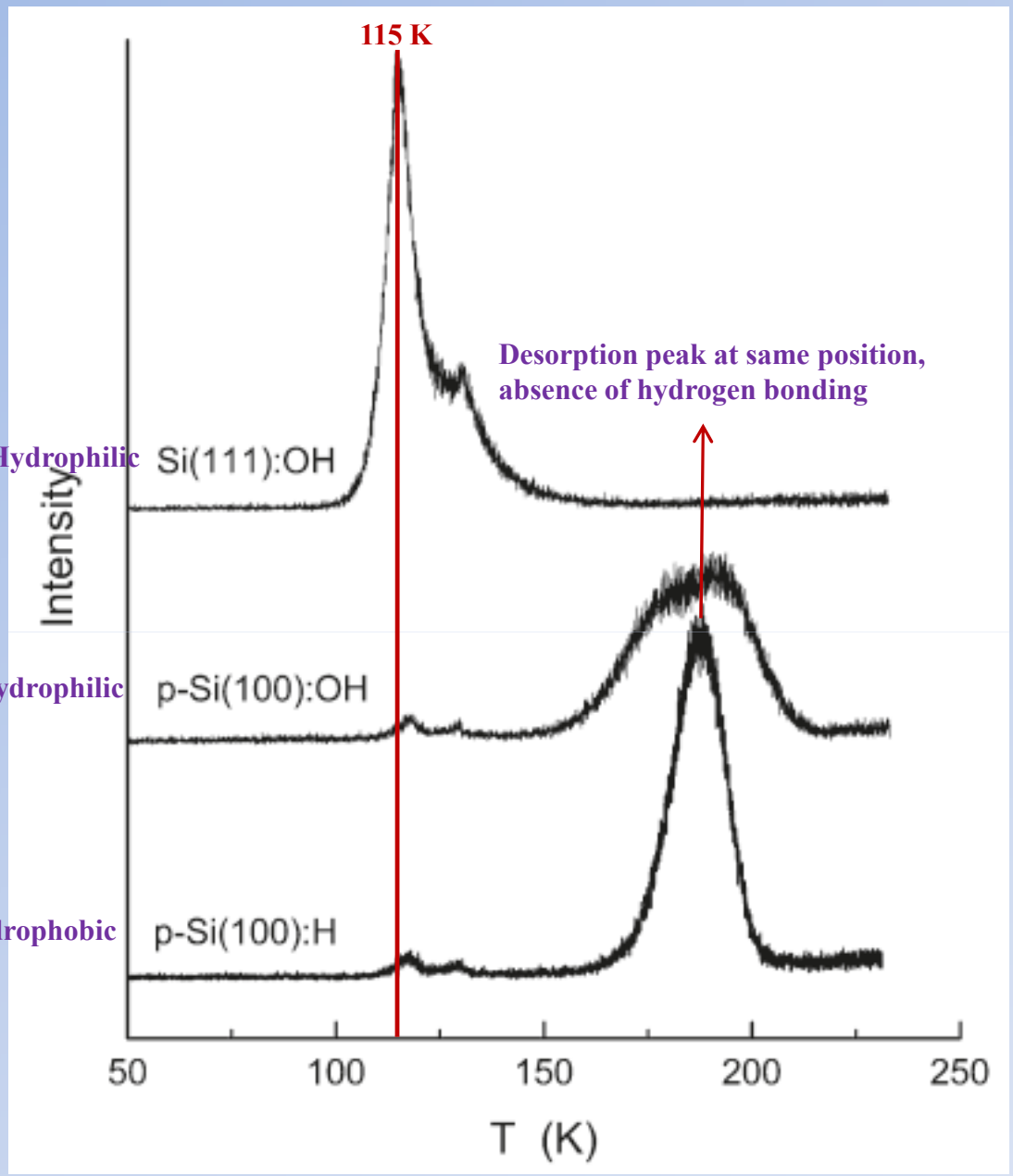
TPD of ethanol (m/e = 31) deposited on different Si substrates

Study using 3-methylpentane

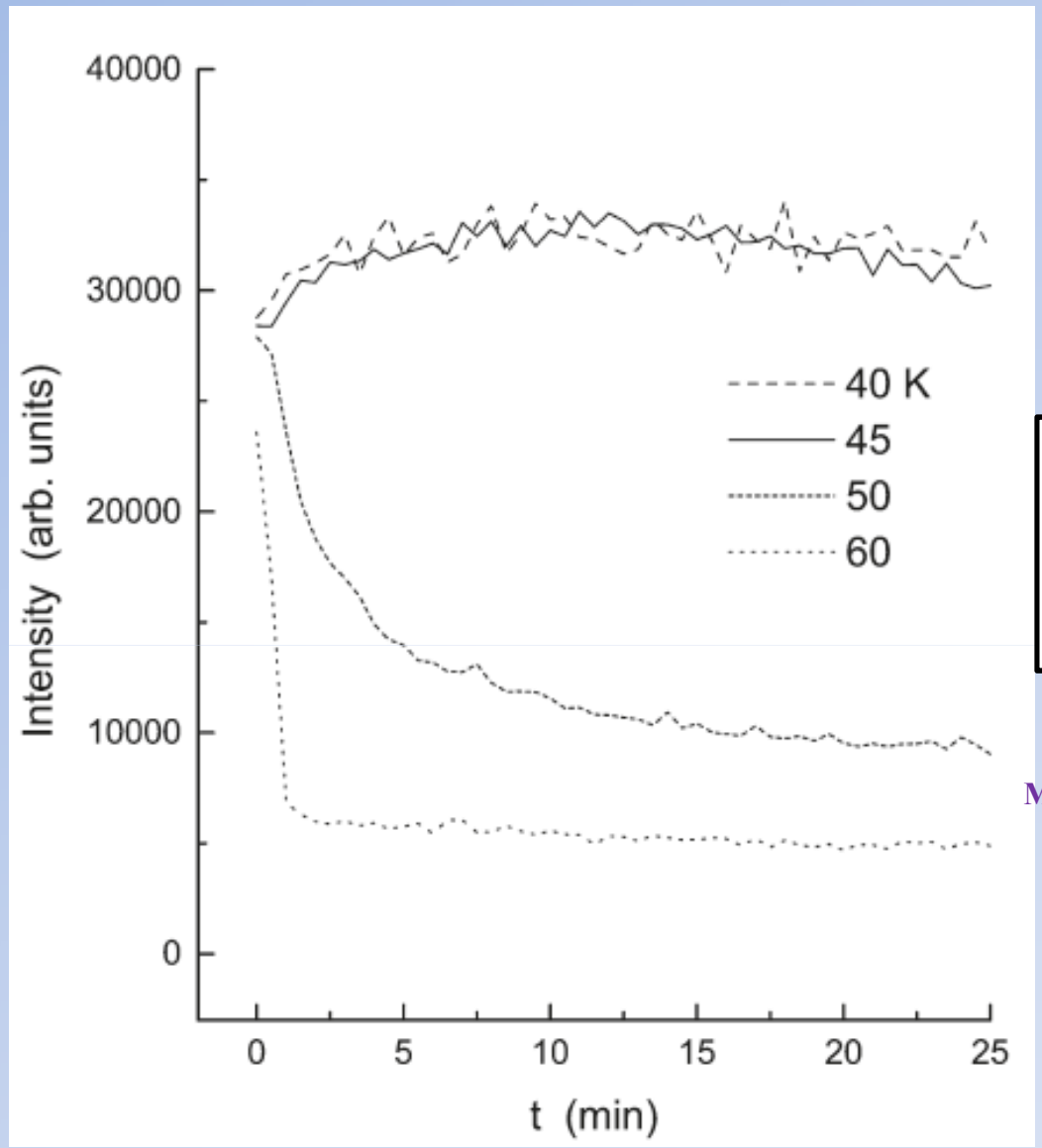


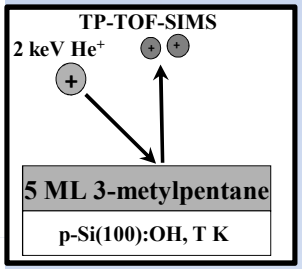


TP-TOF-SIMS of ethyl ion from 3-methylpentane deposited on p-Si(111):OH substrate



TPD of 3-methylpentane (m/e = 56) deposited on different Si substrates





Migration of residues

Isothermal-TOF-SIMS of ethyl ion from 3-methylpentane deposited on p-Si(100):OH substrate

Summary:

- The onset temperatures for monolayers of water, ethanol and 3-methaylpentane to diffuse into pores have been determined as 120, 80 and 50 K respectively.

- The temperatures are lower than corresponding glass transition temperatures (T_g).

- The molecules on the topmost layer are more mobile than bulk thus can be regarded as 2D liquid.

- The onset shift to higher temperature with increasing film thickness is a kinetic effect arising from sequential diffusion of topmost layer molecules.

- The monolayer of water on the –OH terminated Si surface is immobile due to hydrogen bonding.

- On the hydrophobic substrate droplets tend to form because high surface energy of water and instability at the interface.

- The residue of hydrophilic Si substrate yield very little amount of $H^+(C_2H_5OH)$ indicates that the adsorption structures of residues are different from monolayers.

- The residues bind preferentially to the –SiO and –SiOH.

- The onset temp. of surface diffusion is fundamentally lower than T_g because of lack of molecule on the vacuum side.

Thanks!!!!!