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 $\sim 1$ 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% NH₄F
2. Kept at N₂ atmos. and H₂-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/cm² 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 H₂O**

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

Formation of droplets

TP-TOF-SIMS
2 keV He⁺

x ML H₂O

p-Si(111):OH, 20 K → 190 K

Hydrophilic

Transient formation of monolayer

TP-TOF-SIMS
2 keV He⁺

x ML H₂O

p-Si(111):H, 20 K → 190 K
Hydrophilic $\text{H}_2\text{O}$ incorporates in the pore

Hydrophobic $\text{H}_2\text{O}$ does not incorporate in the hydrophobic pore

Formation of $\text{H}_2\text{O}$ droplets

TPD of water deposited on different Si substrates
Study using $\text{C}_2\text{H}_5\text{OH}$

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.
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-methyloctane 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 $\text{H}^+(\text{C}_2\text{H}_5\text{OH})$ 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!!!!!