Crystallization of Organic Glasses

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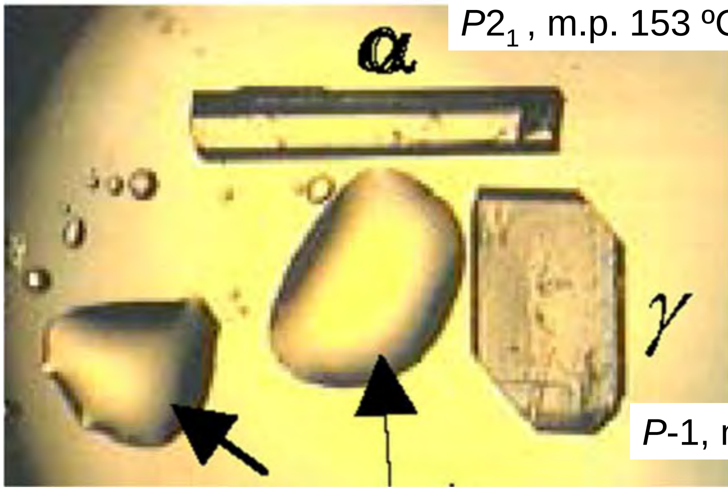
Crystalline and amorphous SiO_2

Crystalline SiO_2 (quartz)
Density 2.65 g/cm^3

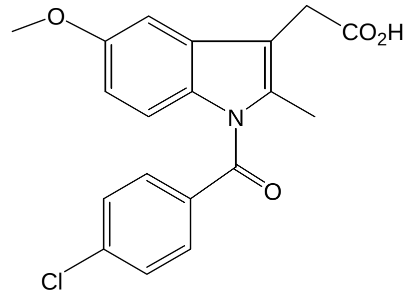
Amorphous SiO_2 (glass)
Density 2.20 g/cm^3

Crystalline and amorphous indomethacin



$P2_1$, m.p. 153 ºC

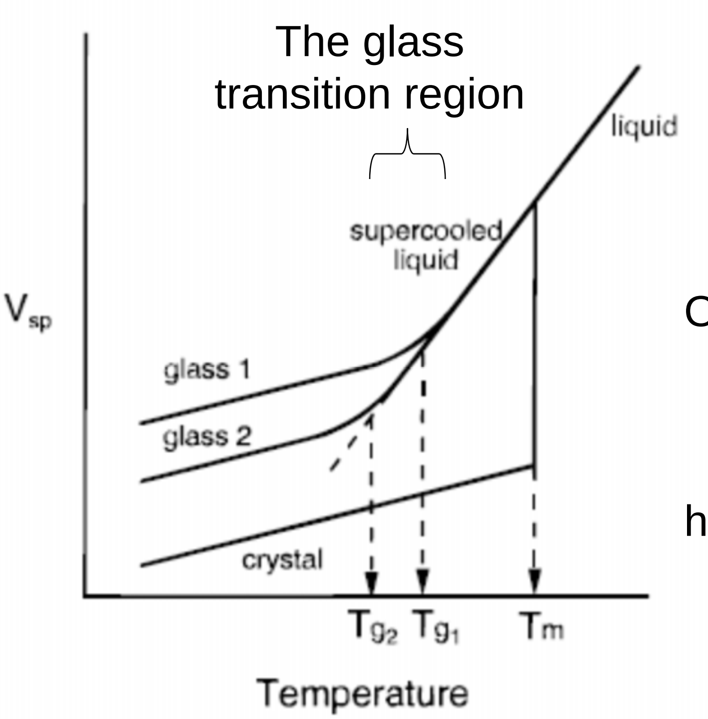
P-1, m.p. 160 ºC



Amorphous solid (glass). T_g = 42 ºC
More soluble than crystals (5 – 17 x)

Figure from Chen, …, Stowell. JACS 2002. Solubilities from Hancock & Parks 2000, Murdande et al.. 2010, Alonzo et al. 2010

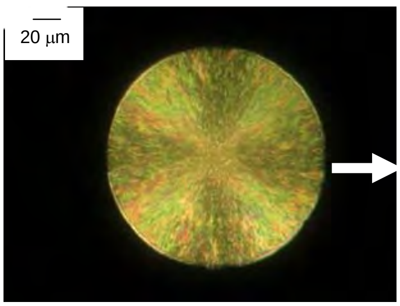
Standard way to make a glass: Cooling a liquid without crystallization



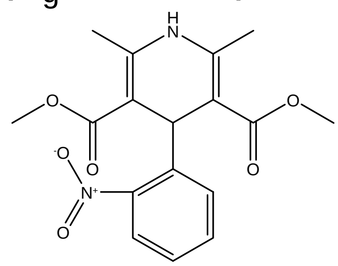
Other ways:
- Grinding
- Freeze or spray drying
- Drying crystalline hydrates
- Vapor deposition

Is there a problem? Can glasses really crystallize?

Obsidian: Natural silicate glass stable for millions of years – but eventually crystallizes



A spherulite growing in amorphous nifedipine at 30 ^{o}C (T_g – 12 ^{o}C)
u = 40 µm/day



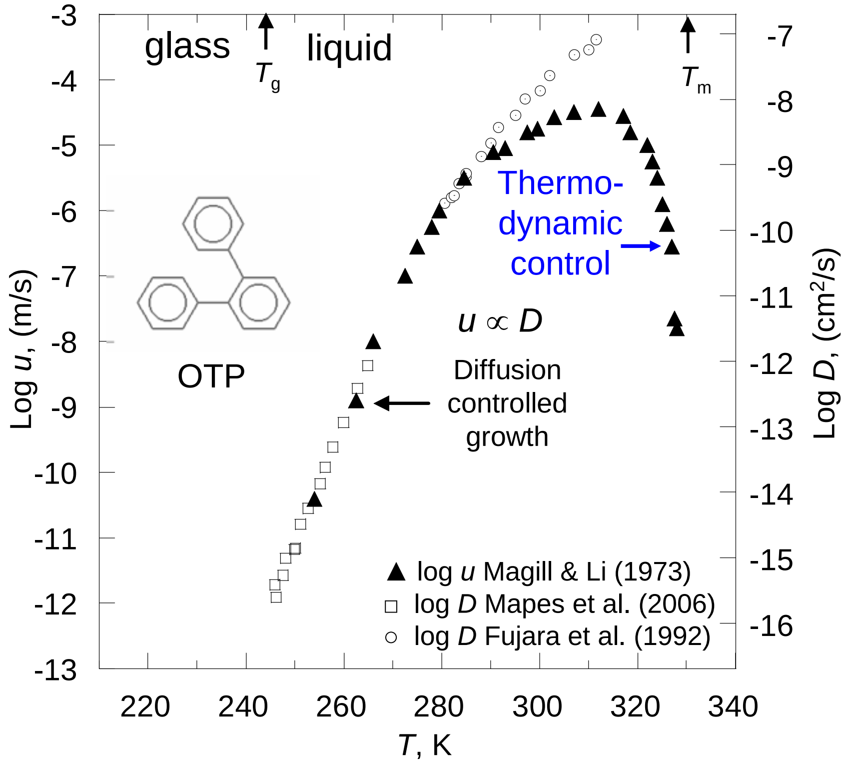
Ishida, Wu, and Yu. *J. Pharm. Sci.* **2007**

This talk
Fast crystal growth in one-component organic glasses

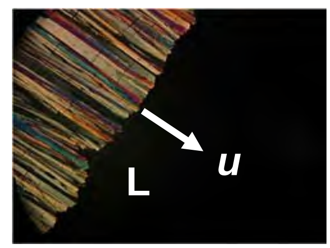
(1) A bulk mode (GC) activated near T_g

(2) A surface mode

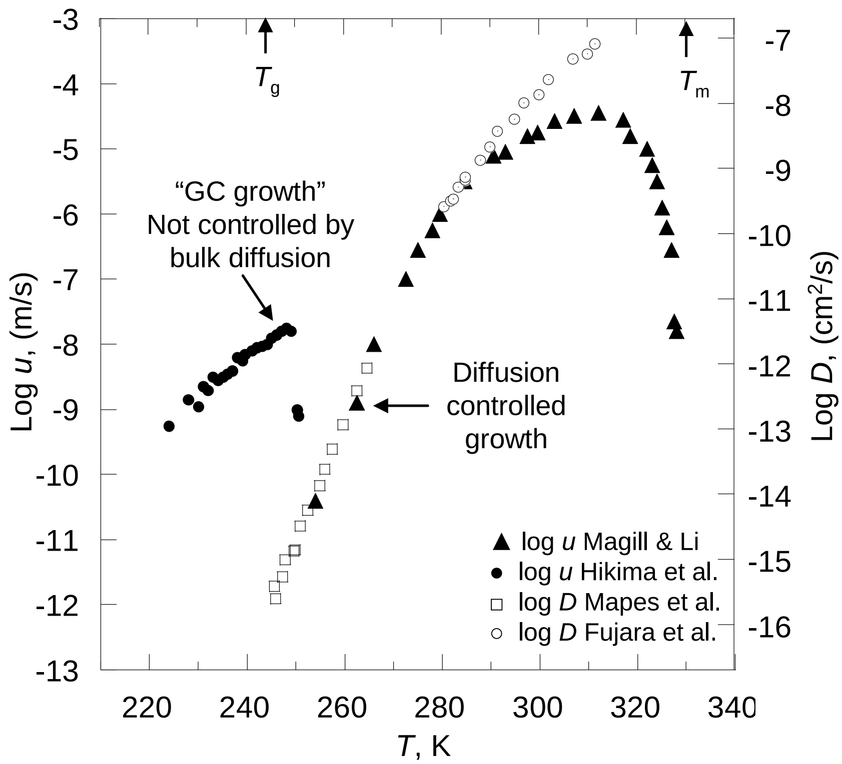
Crystal growth rate in a one-component liquid



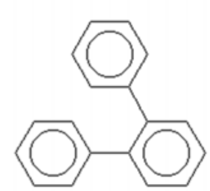
Wilson, Frenkel, Turnbull:
Diffusion defines kinetic barrier of crystal growth



A new, fast growth mode ("GC") is activated near T_g

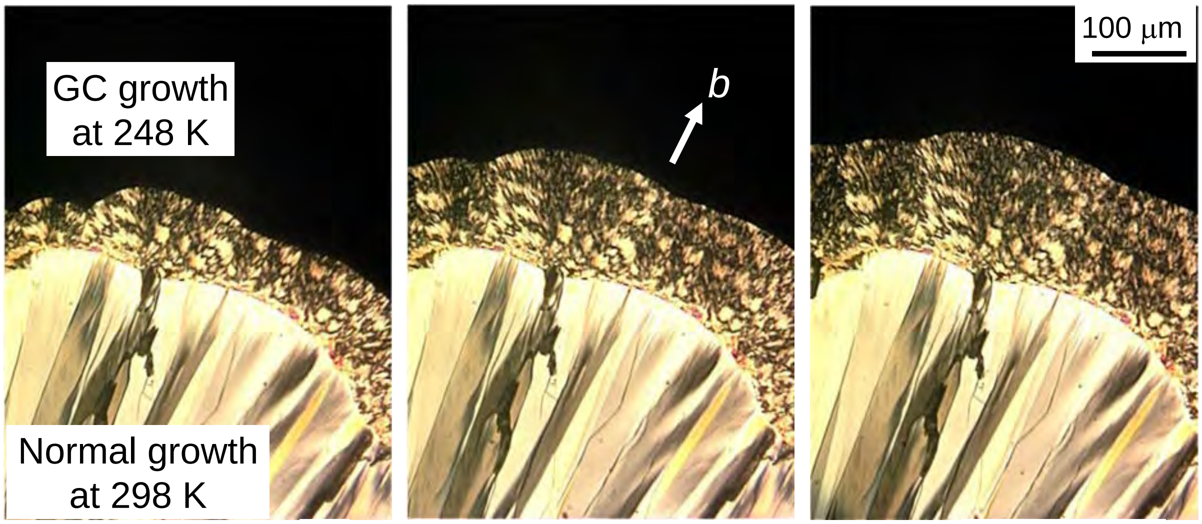


- First observed for OTP by Greet and Turnbull in 1967
- Studied by Oguni and coworkers since 1995
- Unknown for inorganic and polymeric glass formers



OTP

What does GC growth look like?



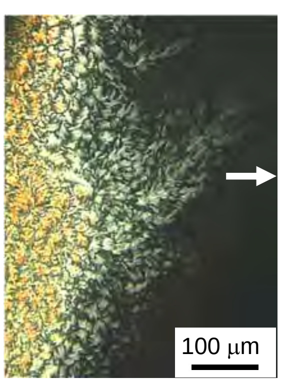
t_0 | t_0 + 40 min | t_0 + 60 min

GC crystals are "real" crystals!

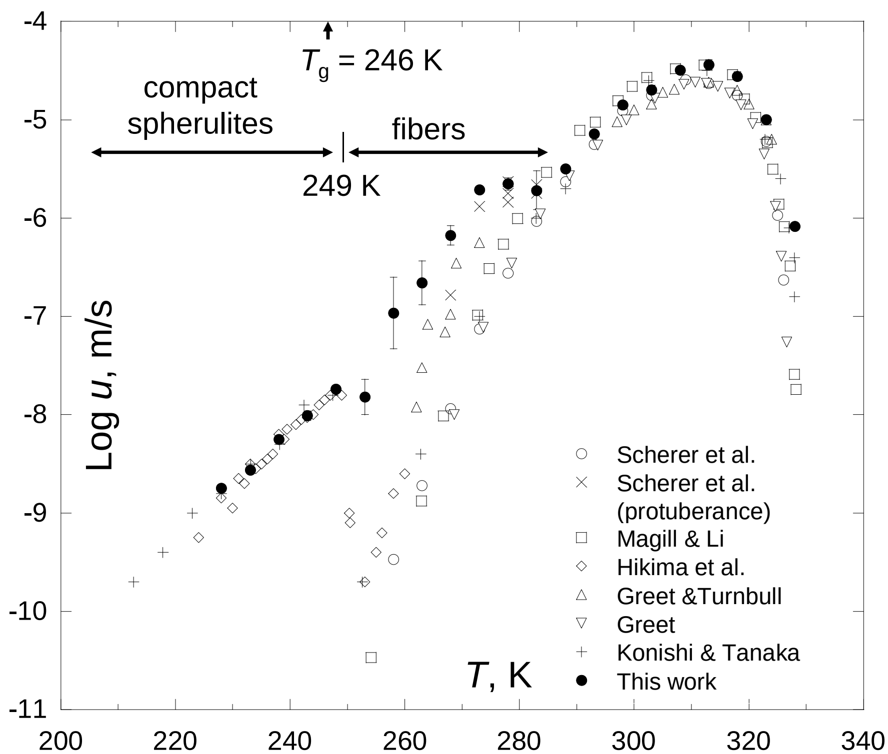
- Same unit cell as normal crystals
- Nearly the same m.p. and ΔH_m
- Growth is also mainly along *b*

GC growth has fast-growing fibers as precursors

Compact growth

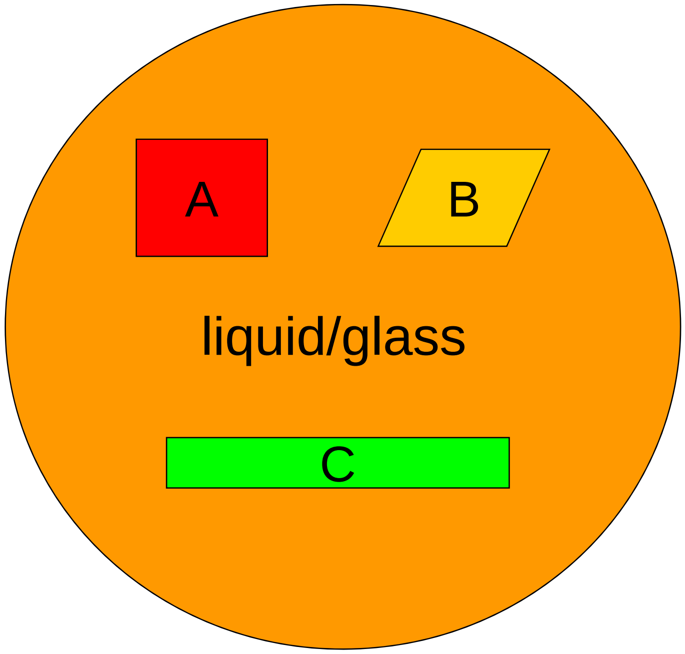


Fiber growth



Sun et al. *J. Phys. Chem. B* **2008**, *112*, 661; Xi et al. *J. Chem. Phys.* **2009**, *130*, 094508

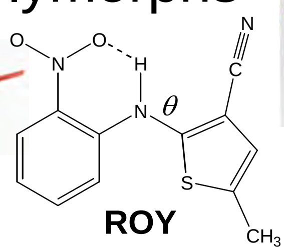
Studying GC growth with polymorphs:
From the same liquid/glass, which polymorph shows GC growth, and which does not?



ROY polymorphs

(1) **R** P-1
mp 106.2 °C
θ = 21.7°

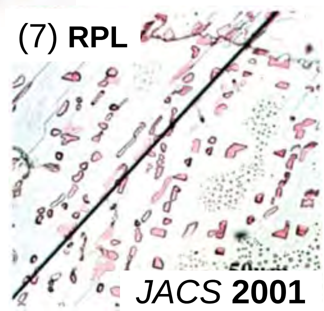
(2) **ON** $P2_1/c$
mp 114.8°C
θ = 52.6°



ROY

(3) **Y** $P2_1/c$
mp 109.8 °C
θ = 104.7°

(7) **RPL**



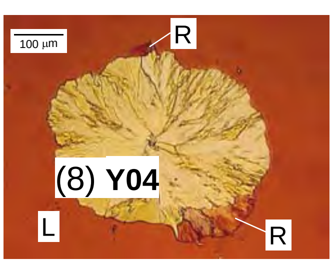
JACS **2001**

(4) **OP** $P2_1/c$
mp 112.7 °C
θ = 46.1°

(5) **YN** P-1,
mp 99 °C
θ = 104.1°

(6) **ORP** Pbca
mp 97 °C
θ = 39.4°

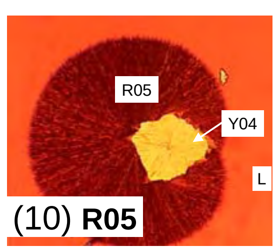
JACS. **2000**



(8) **Y04**

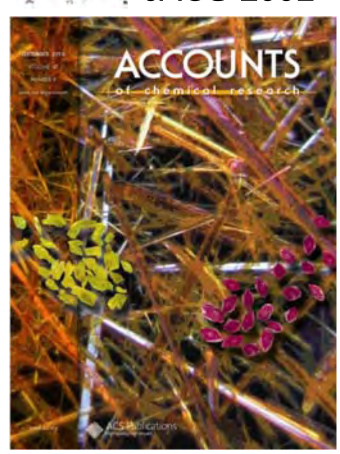
JACS **2005a**

(9) **YT04** $P2_1/c$
mp 106.9°C
θ = 112.8°



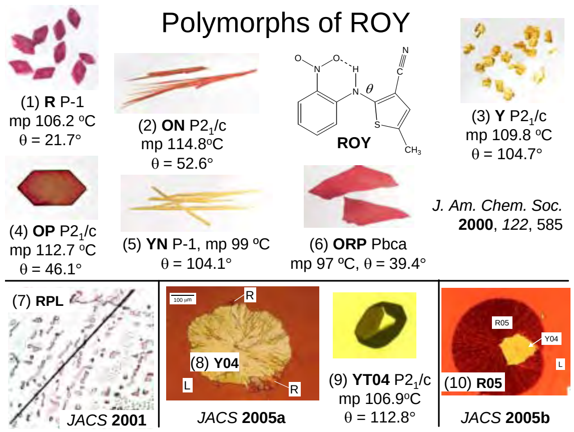
(10) **R05**

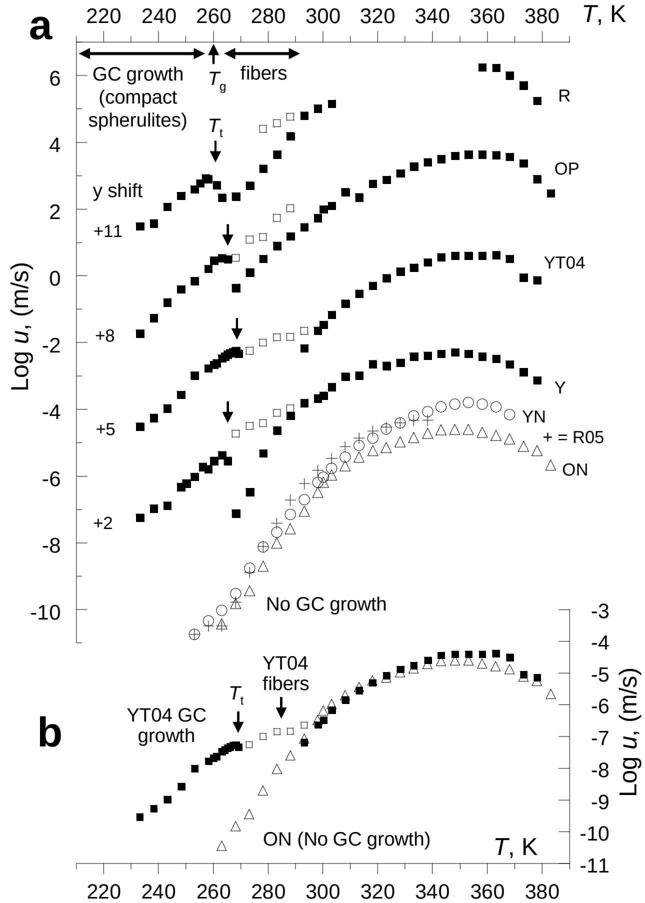
JACS **2005b**



Some ROY polymorphs show GC growth; some do not

Sun, … *J. Phys. Chem. B* **2008**, *112*, 661 and 5594



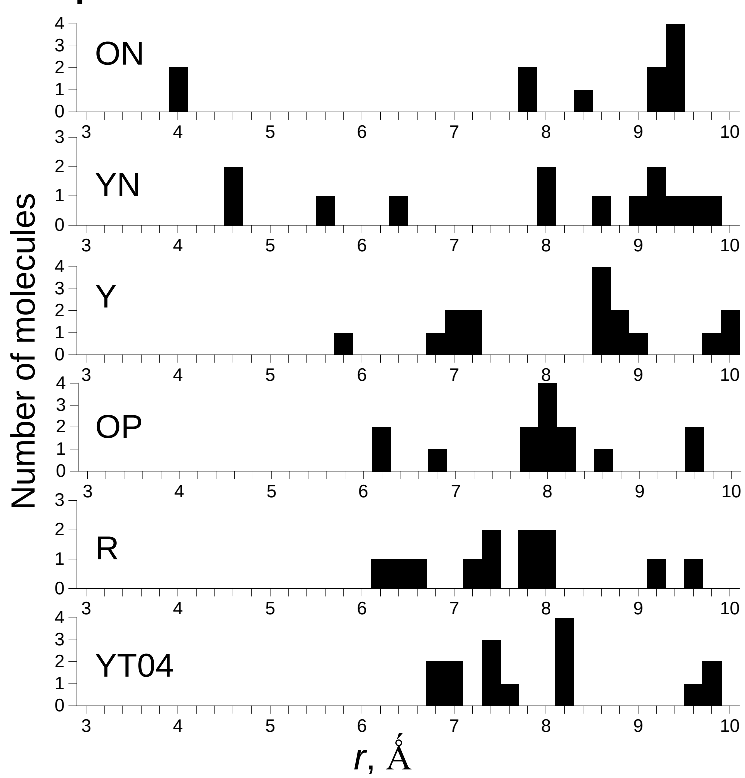


Crystal structures showing GC growth are more "liquid like"

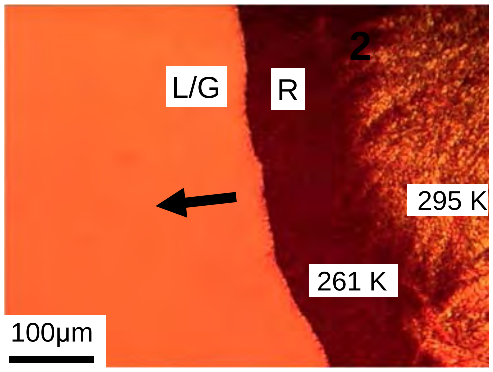
Anisotropic packing: No GC growth

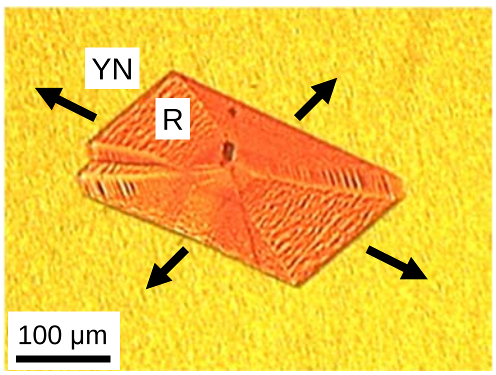
Radial distribution functions

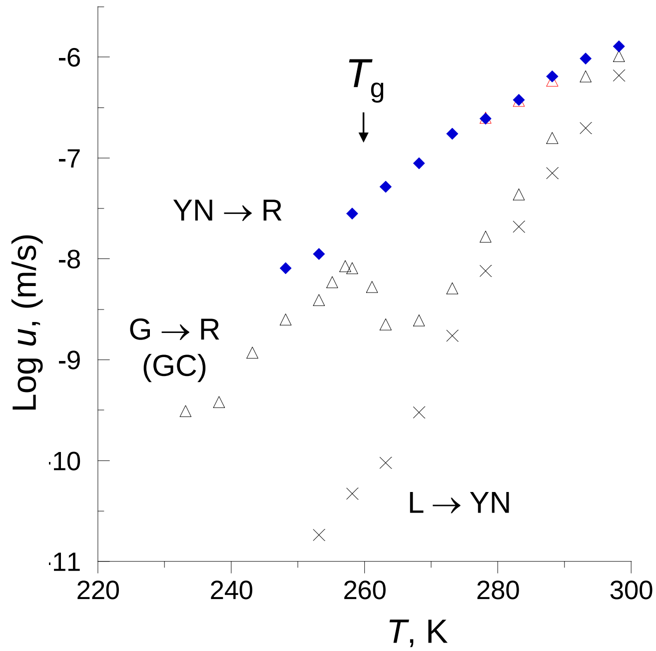
More isotropic packing: GC growth



GC growth is similar kinetically to polymorphic conversion, but “feels” the glass transition







Origin of GC growth: Still an open question

- *Bulk β relaxation*. But the β process is absent in ROY and aged away in OTP
- *Tension at crystal/glass interface*. But fibers grow rapidly above T_g, and no expected “autocatalysis”
- *Solid-state transition similar to polymorphic conversion.* But no predictive power
- *Molecular mobility at grain-boundaries.* But no predictive power
- …

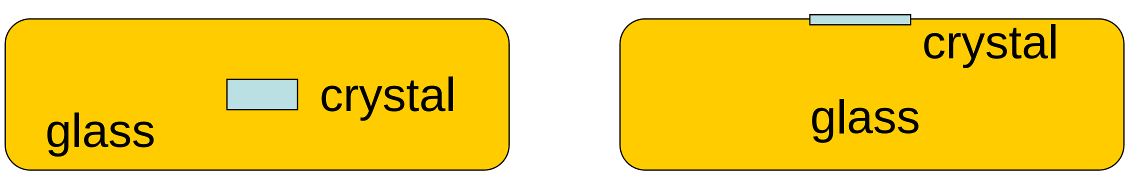
This talk
Fast crystal growth
in one-component organic glasses

(1) A bulk mode (GC) activated near T_g

(2) A surface mode

Crystal growth in the bulk

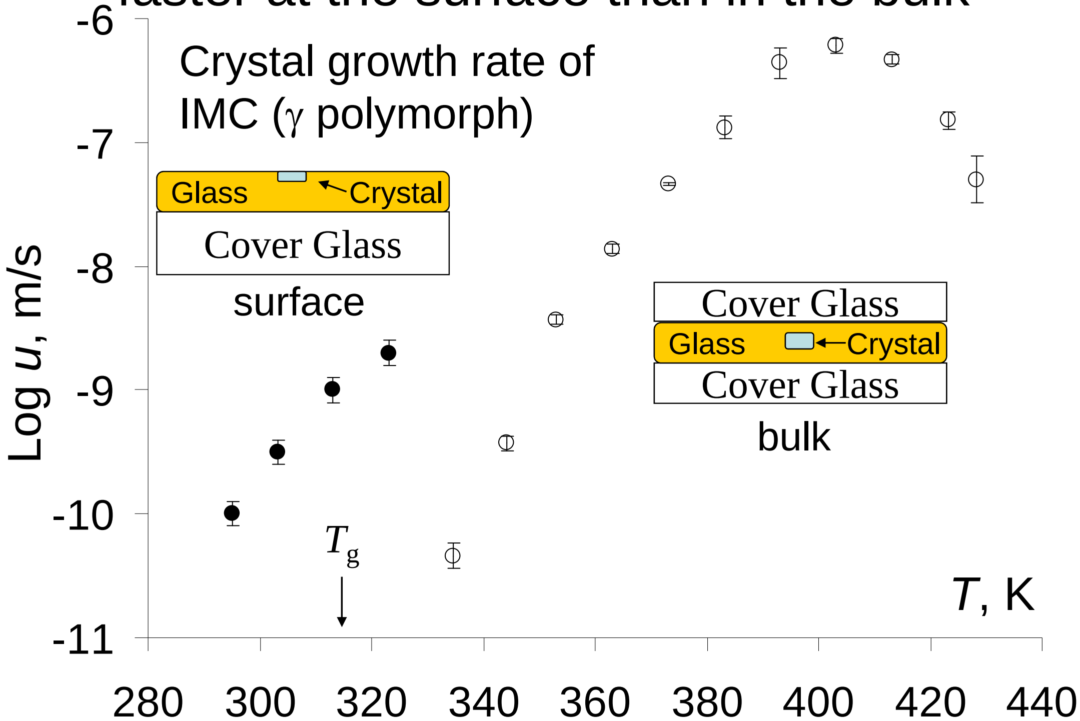
Crystal growth at the free surface



"Whereas in many metallic glasses nucleation has been observed to be enhanced at the surface, growth rates are usually quite comparable with those in the bulk." U. Koster (*Mat. Sci. & Eng.* 1988, *97*, 233)

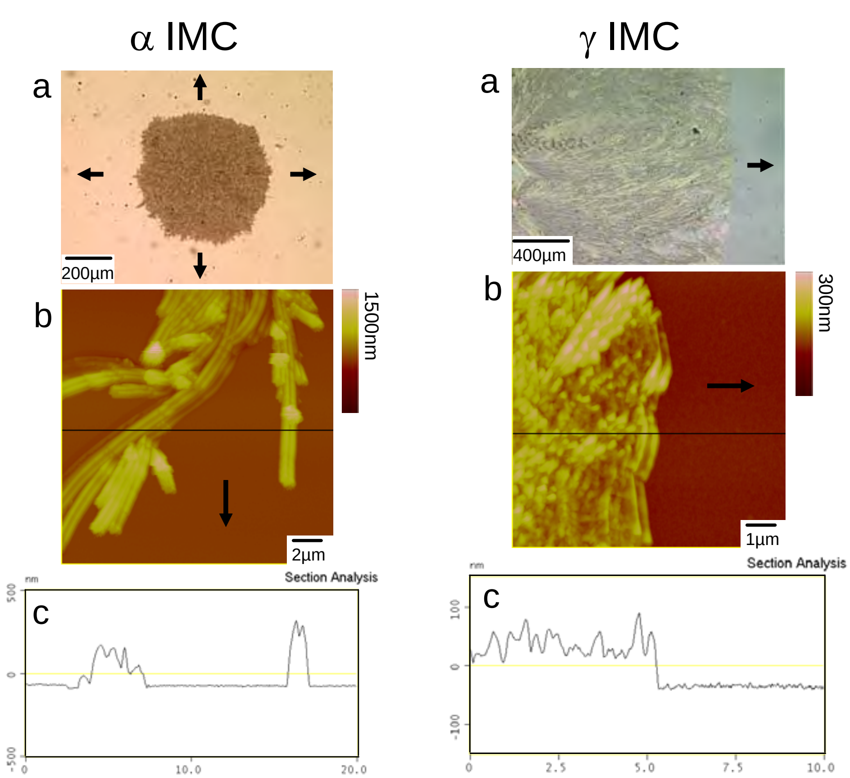
[For silicate glasses,] "The crystal growth velocities of crystals in the volume and of the surface layer in the glass volume, as well as of isolated crystals on the glass surface are equal." Diaz-Mora et al. (*J. Non-Crystalline Solids* 2000, *273*, 81)

For organic glasses, crystal growth can be much faster at the surface than in the bulk



Wu, T.; Yu, L. *J. Phys. Chem. B* **2006,** *100*, 15694**;** *Pharm. Res.* **2006**, *23*, 2350

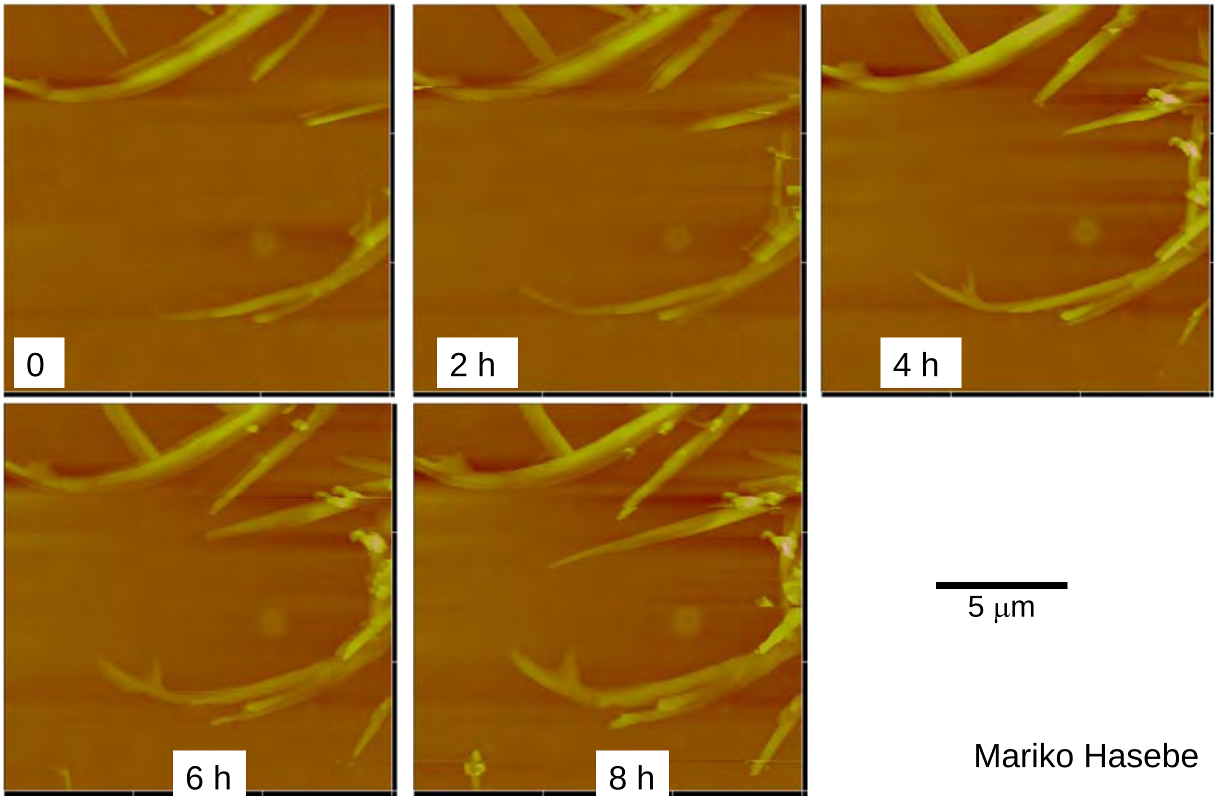
What do surface crystals look like?



Growth front is above glass surface

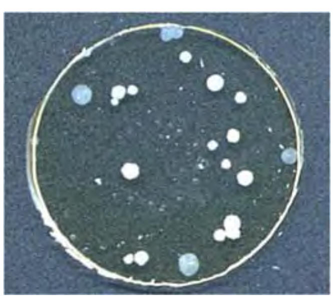
Sun et al. *PNAS*, in press

Growth of α IMC surface crystals at 22 °C



Mariko Hasebe

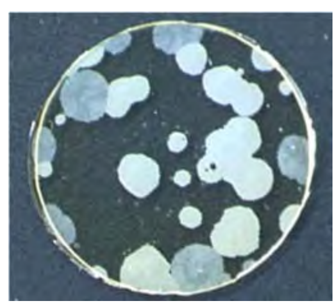
Surface crystallization of amorphous IMC can be inhibited with a nanocoating

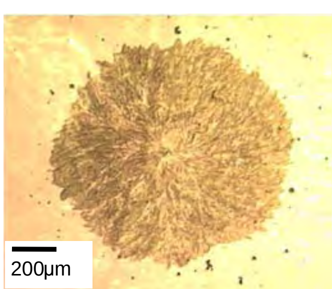


15 mm

Uncoated sample

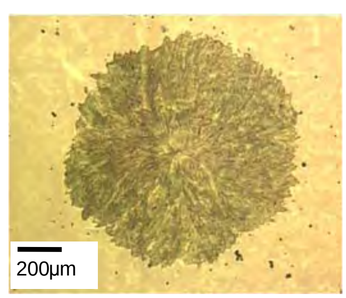
7 days at 40 °C





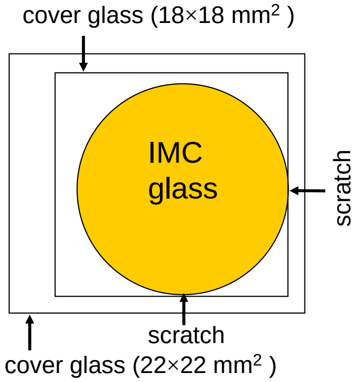
Coated with 10 nm gold or 2 – 30 nm polymer

7 days at 40 °C

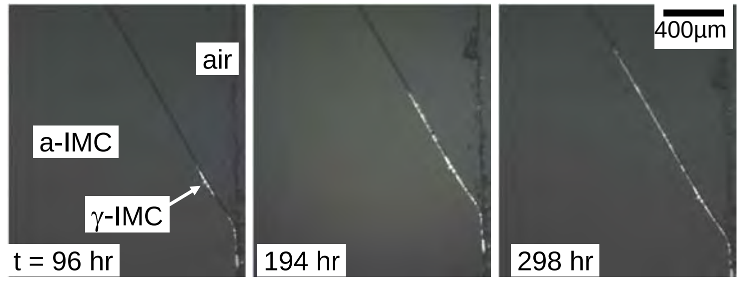


Wu, Sun, Li, de Villiers, and Yu. *Langmuir* **2007**, *23*, 5148

Surface crystal layer can be quite thin

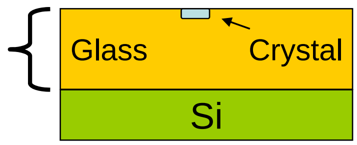


Expt. 1: Direct observation

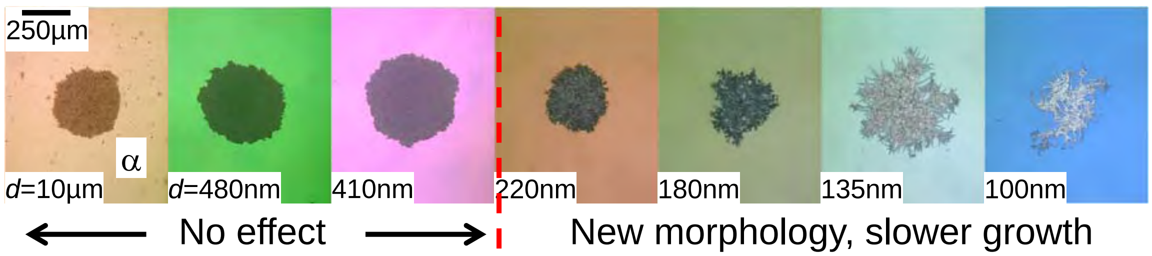


Expt. 2: Vary glass thickness d

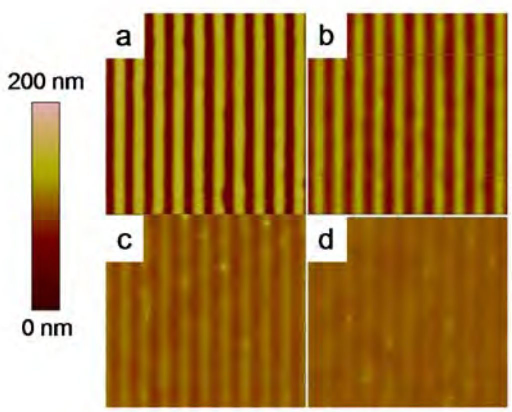
d = 50 nm – 15 µm

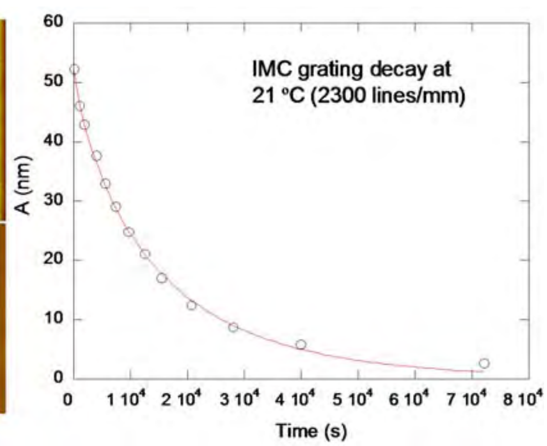


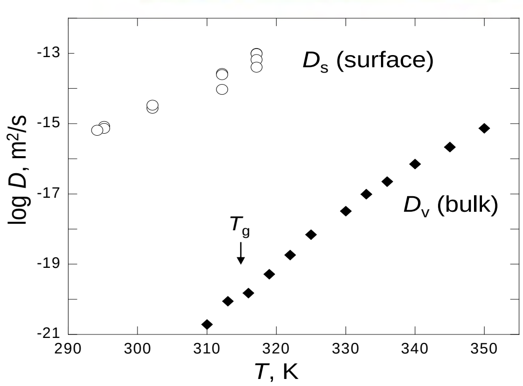
Sun et al. PNAS, in press



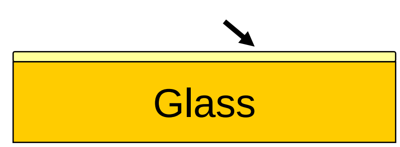
Surface diffusion is fast on amorphous IMC







Mobile surface



Lei Zhu

Origin for surface-enhanced crystal growth: Still an open question

- *Surface mobility*
- *Surface crystals can exploit opportunity to grow upward*
- *Tension from crystal growth is better released at the surface than in the bulk*
- …

All these models imply generality of the phenomenon. But is it?

Summary: Fast crystal growth in organic glasses

GC growth

- A new bulk growth mode is activated near T_g. It is not limited by bulk diffusion
- Favors “liquid-like” structures
- Similar to polymorphic transformation

Surface growth

- Surface enhances growth, not just nucleation
- Inhibited by nano-coating
- Correlates with surface molecular mobility

Both modes are known only or mainly for organic glasses