Two level systems and ultrastable glasses

Frances Hellman

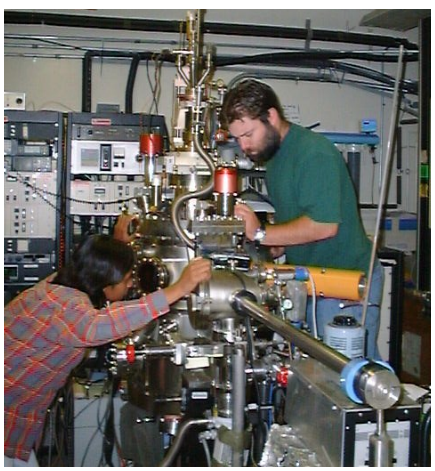
University of California, Berkeley

Keerti Shukla, M. Molina-Ruiz, T. Dauer, D. Queen, B. Zink (Berkeley)

A. Ananyeva, G. Vajente, E. Gustafson (CalTech)

M. Abernathy, T. Metcalf, X. Liu (NRL)

A. Markosyan, R. Bassiri, M. M. Fejer (Stanford)



UHV growth chambers for prototyping materials

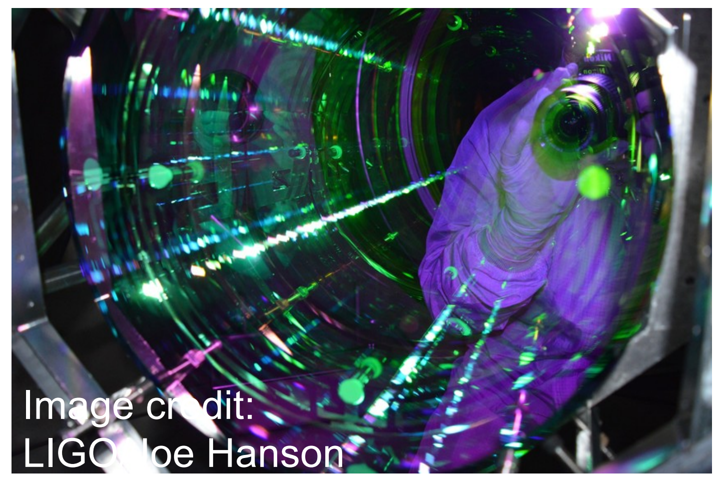


Image credit: LIGO/Joe Hanson

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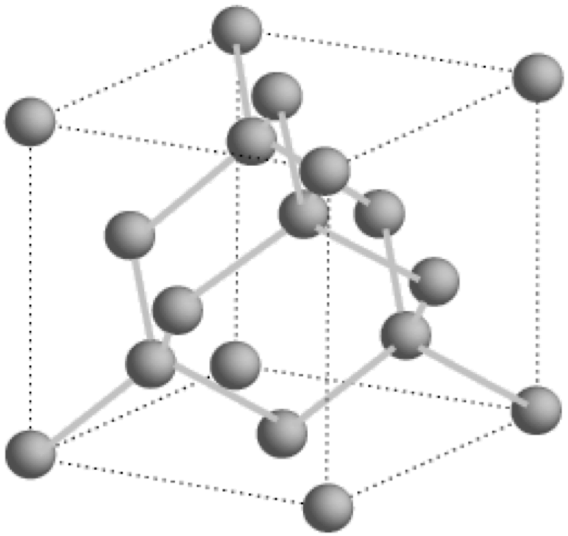
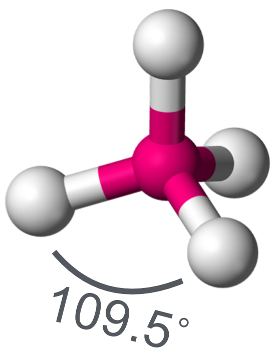
LSC Center for Coatings Research

Current mirror coatings are amorphous
No long range structural order, but have short range order

Traditionally, glasses quenched from liquid
Also can be made by vapor deposition
Structure of Silicon



Xtal Si: diamond structure



Amorphous Si: still has tetrahedral coordination

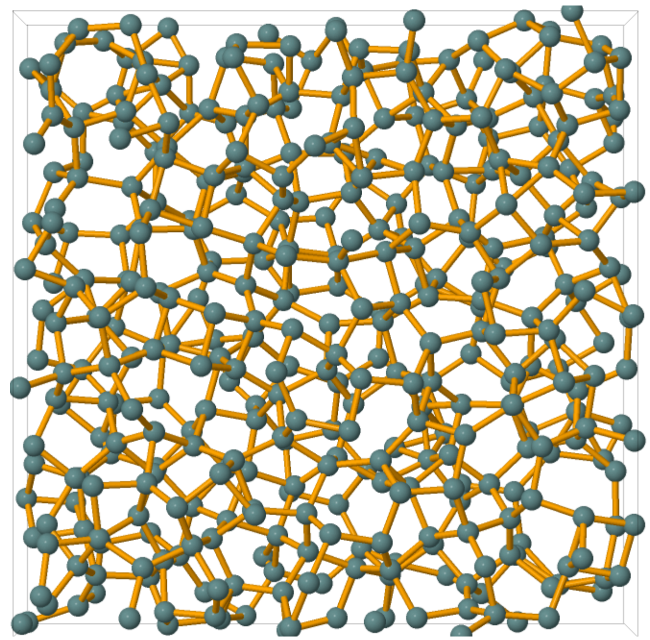
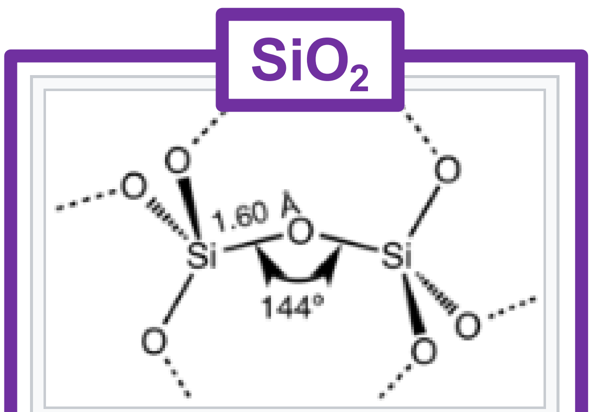


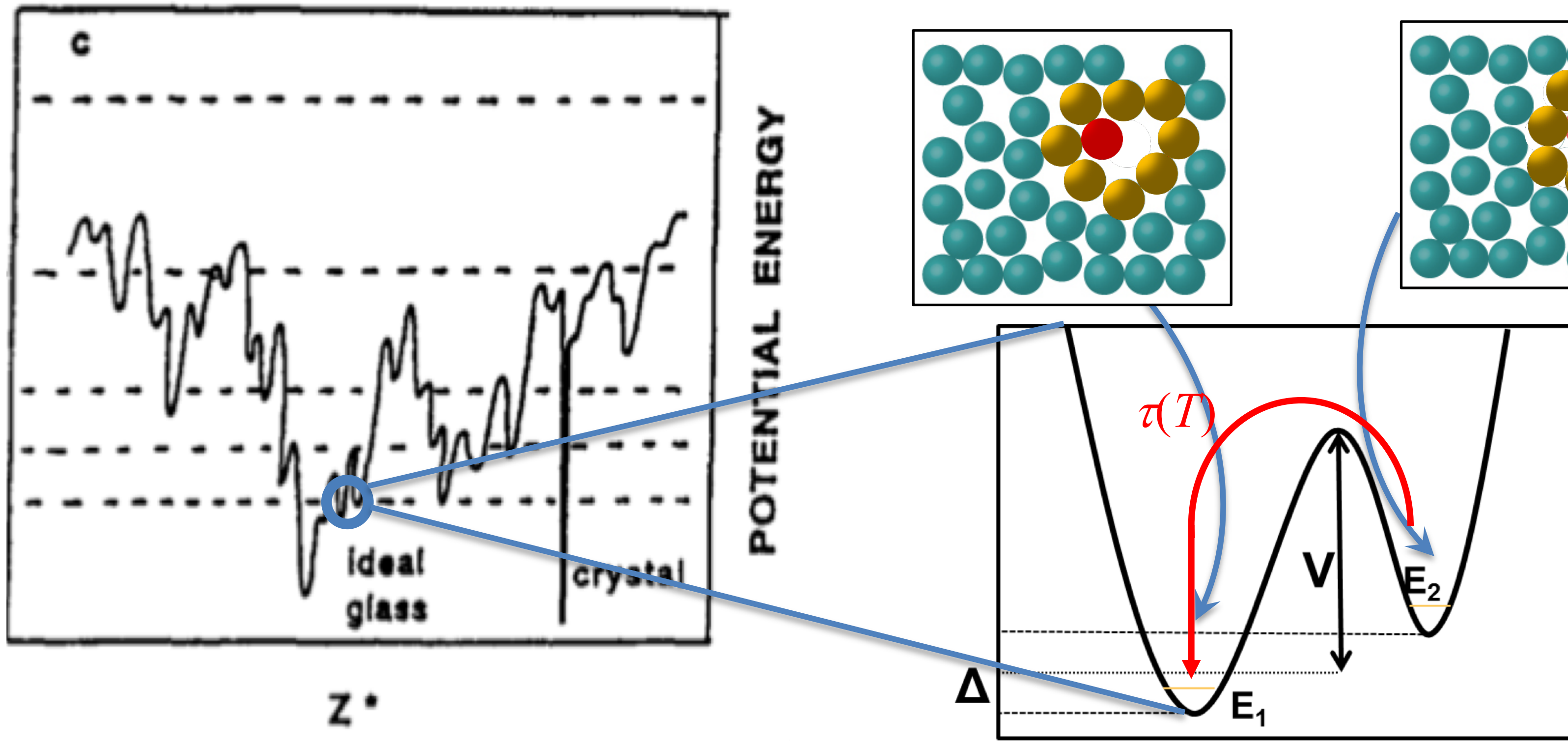
Image credit: Kiran Prasai



O-Si-O bonds are fixed angle but Si-O-Si angle is quite floppy – different energy scales

Energy landscape of configurations: "nearby" minima lead to tunneling *or* thermally-activated motion of groups of atoms

C.A. Angell, Physica D 107, 122 (1997)



Anderson, et al., *Philos. Mag.*, **25** 1 (1972) Phillips, *J. Low. Temp. Phys.*, 7 3-4 (1972)

Two-Level Systems from neighboring energy minima in structural landscape:

- At low T, atomic structure **tunnels** between these ➢ μeV energy splitting $E_{1,2} \pm \Delta$
- At higher T, atomic motion is **thermally activated**, requiring $k_B T$ ~ barrier height V

In both cases, atomic motion leads to dissipation (thermal noise)

For *a single V*, dissipation at frequency ω will have a peak at temperature T

➢ at 1 kHz, 0.5 eV barrier heights has a peak ~ room temperature
50 meV barrier heights has a peak ~ 30K

A *distribution* of μeV tunneling-induced energy splitting leads to T-independent losses

"Universal" mechanical losses at low T (tunneling) Higher T more variable, including peaks (thermally activated)

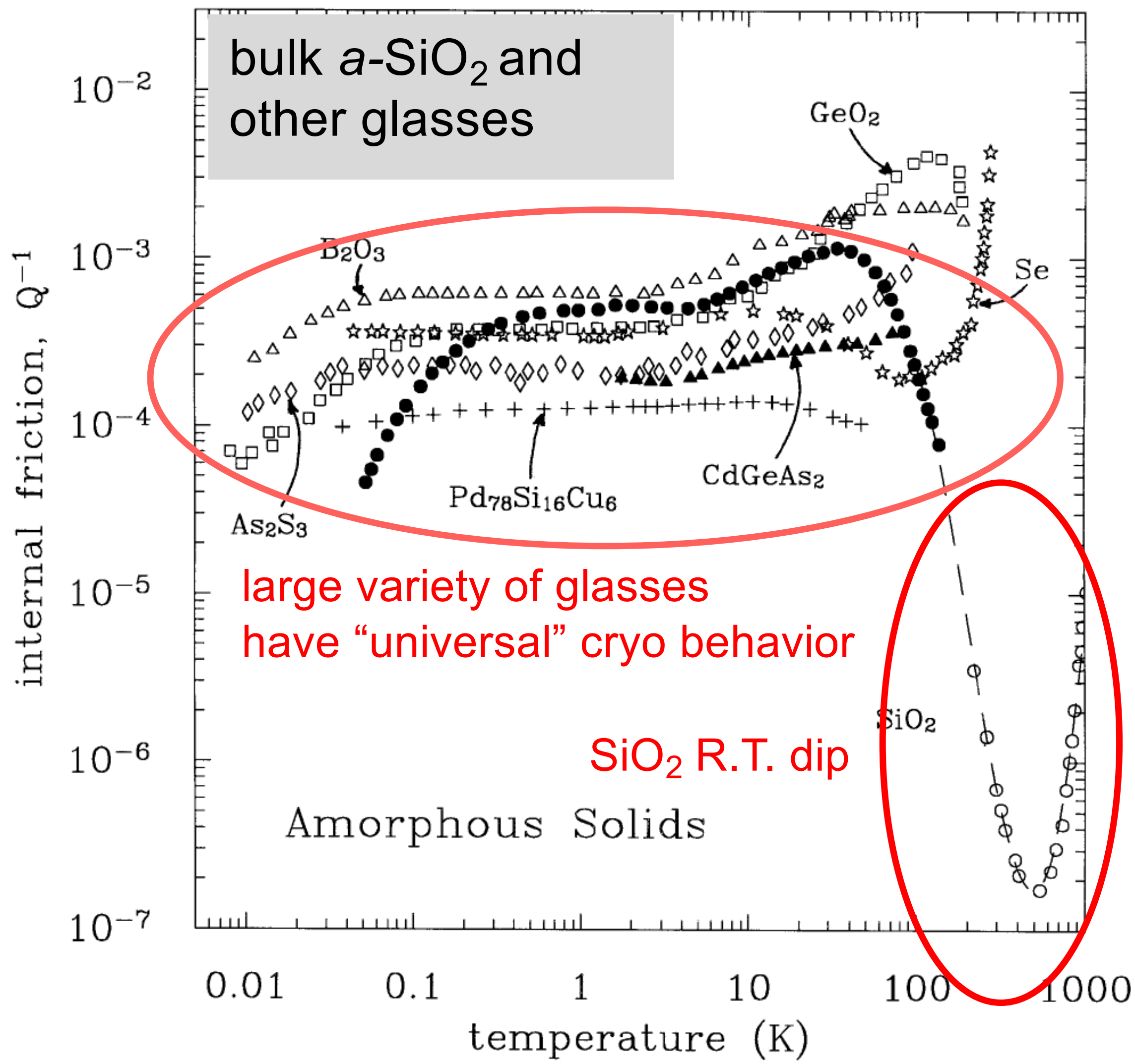
Internal friction $Q^{-1}(T)$ ***low T plateau*** due to *tunneling two level systems* (TLS)-phonon interactions

Q_o^{-1} proportional to $\bar{P}$ (density of TLS) with *poorly understood TLS – phonon coupling parameter* γ

Lower T data (below plateau): TLS model predicts drop off

Higher temp thermally activated regime: a peak implies a single barrier V (or narrow distribution)

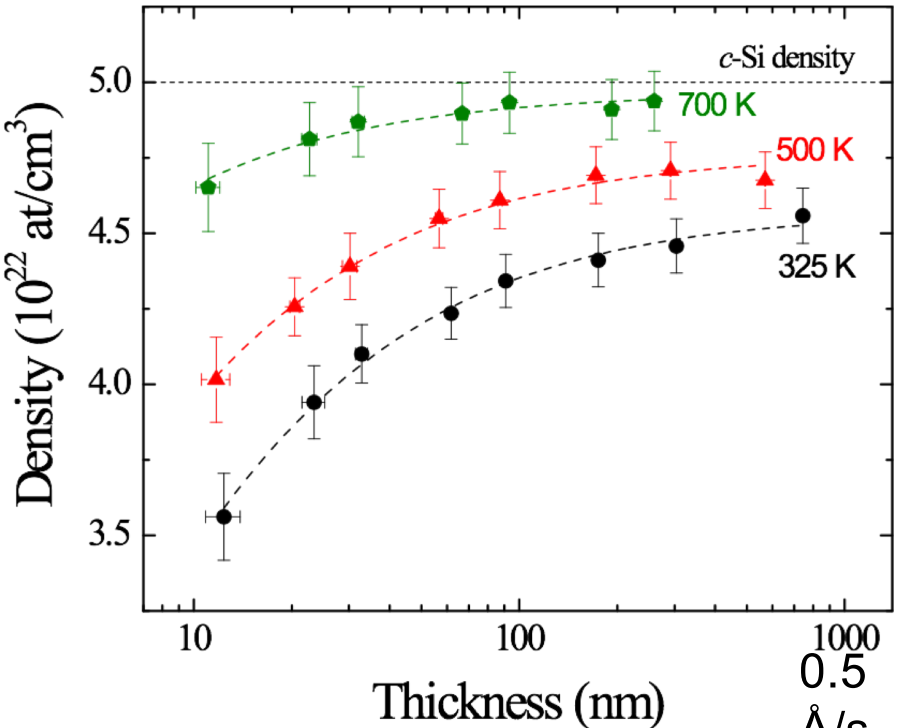
a-SiO_2 dip implies ***a gap*** in the distribution of barriers, followed by α relaxation approaching melting



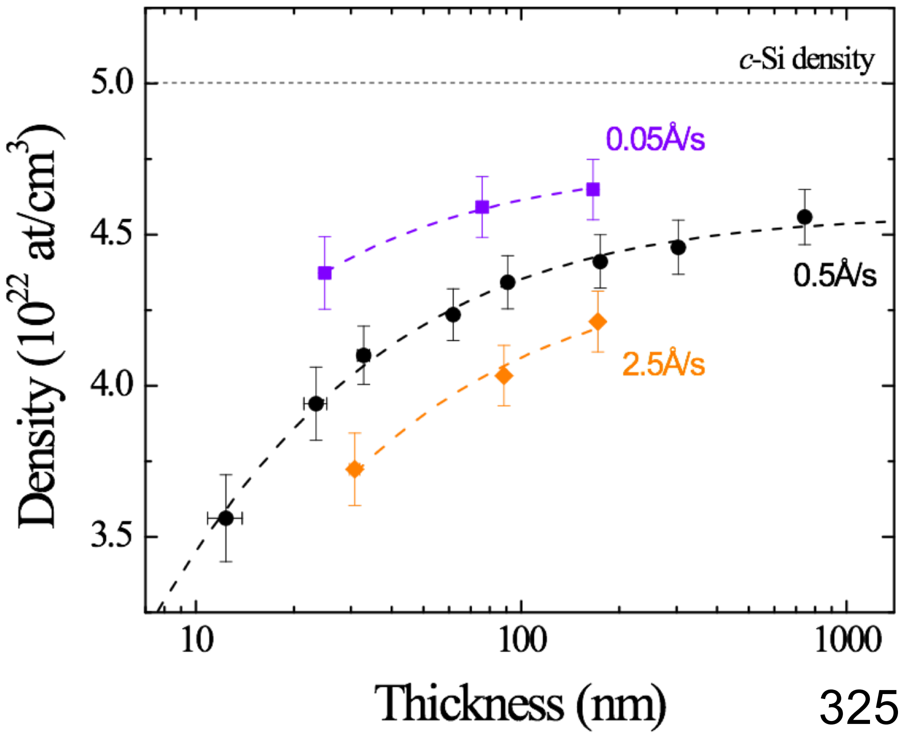
K.A. Topp, *Z. Physik B Condensed Matter* 101 235–45 (1996)

* *Berret & Meissner Z.Phys 1988*

Growth parameters substantially modify amorphous Si film density and some measures of structure



0.5 Å/s

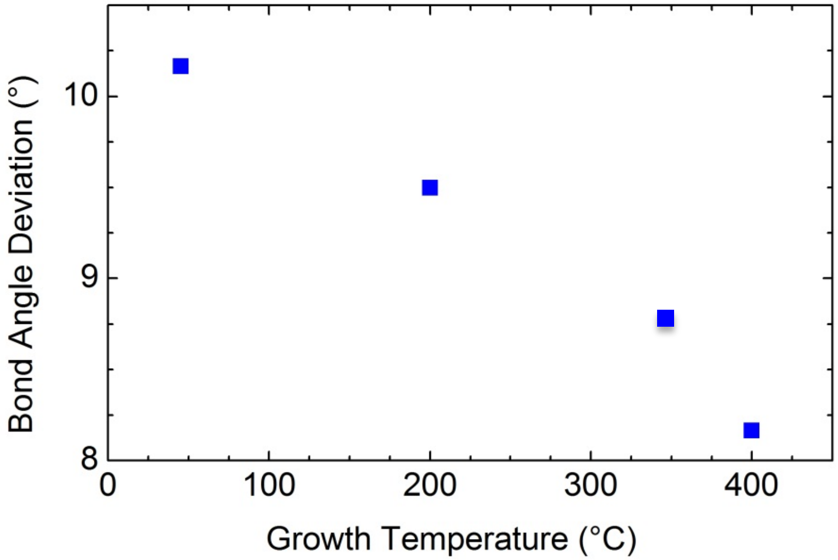


325K

- Thickness, growth temperature T_g, and growth rate affect film density and roughness; room T growth flattest for all thicknesses; higher T_g thin is flat, roughens with thickness (1.5 nm RMS at 300 nm)
- Thinner, low growth T, high growth rate films are less dense
- On what length scale(s) do density changes occur? Little variation in dangling bond density, sound velocity, or macroscale structure, particularly with thickness
- *Variations in bond angle disorder*, *medium range order, nanovoid size and number* (Raman, Fluctuation Electron Microscopy, positron doppler broadening spectroscopy)

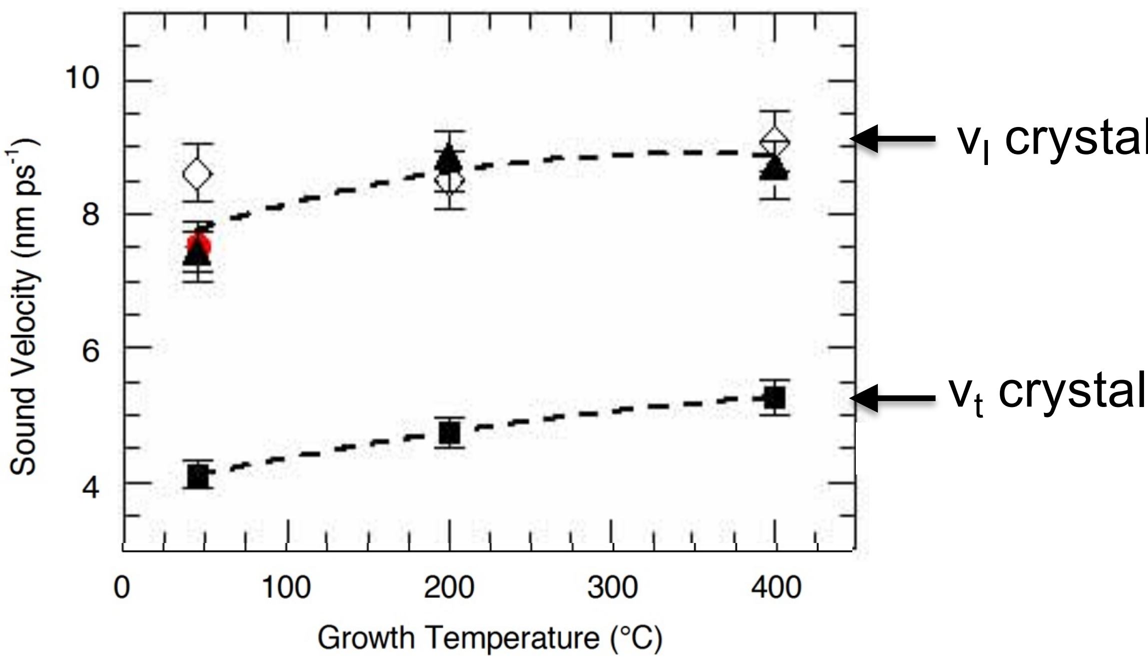
Which of these matter to TLS? ***Appears that nanovoids may be most important***

Amorphous Si: *Disorder decreases with increasing growth T*



Tetrahedral bond angle 109.5° $\pm\ \delta$

Bond angle disorder δ (from Raman scattering width of TO-like peak) decreases with increasing T_s. No dependence on film thickness



Longitudinal and transverse sound velocity v **increases with increasing T_s**

Elastic properties (shear modulus, sound velocity) soften with disorder in amorphous network

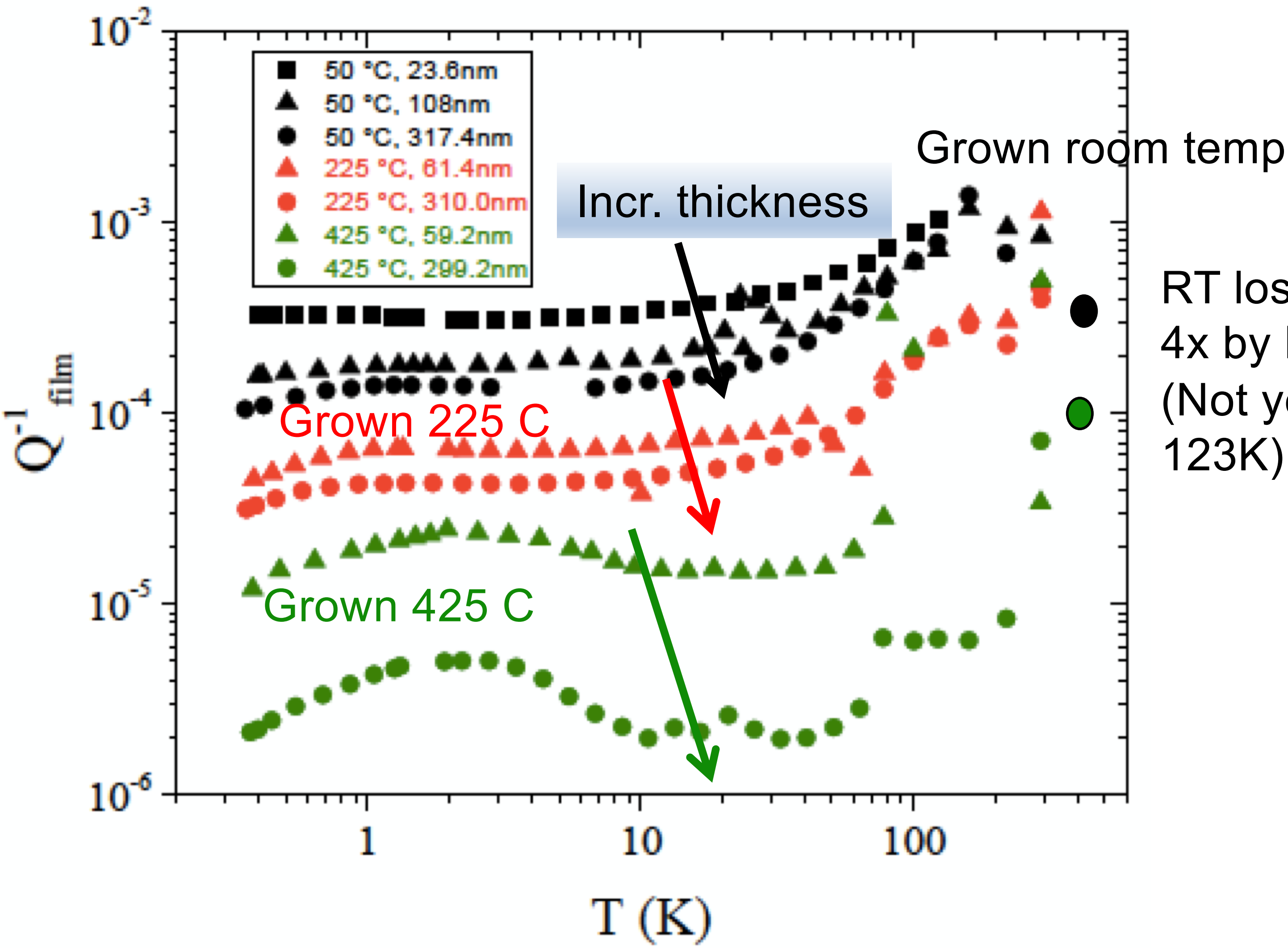
Independent of film thickness

Open symbols: ~100nm films
Closed symbols: ~300nm films

Amorphous Silicon losses: growth T reduces low T losses

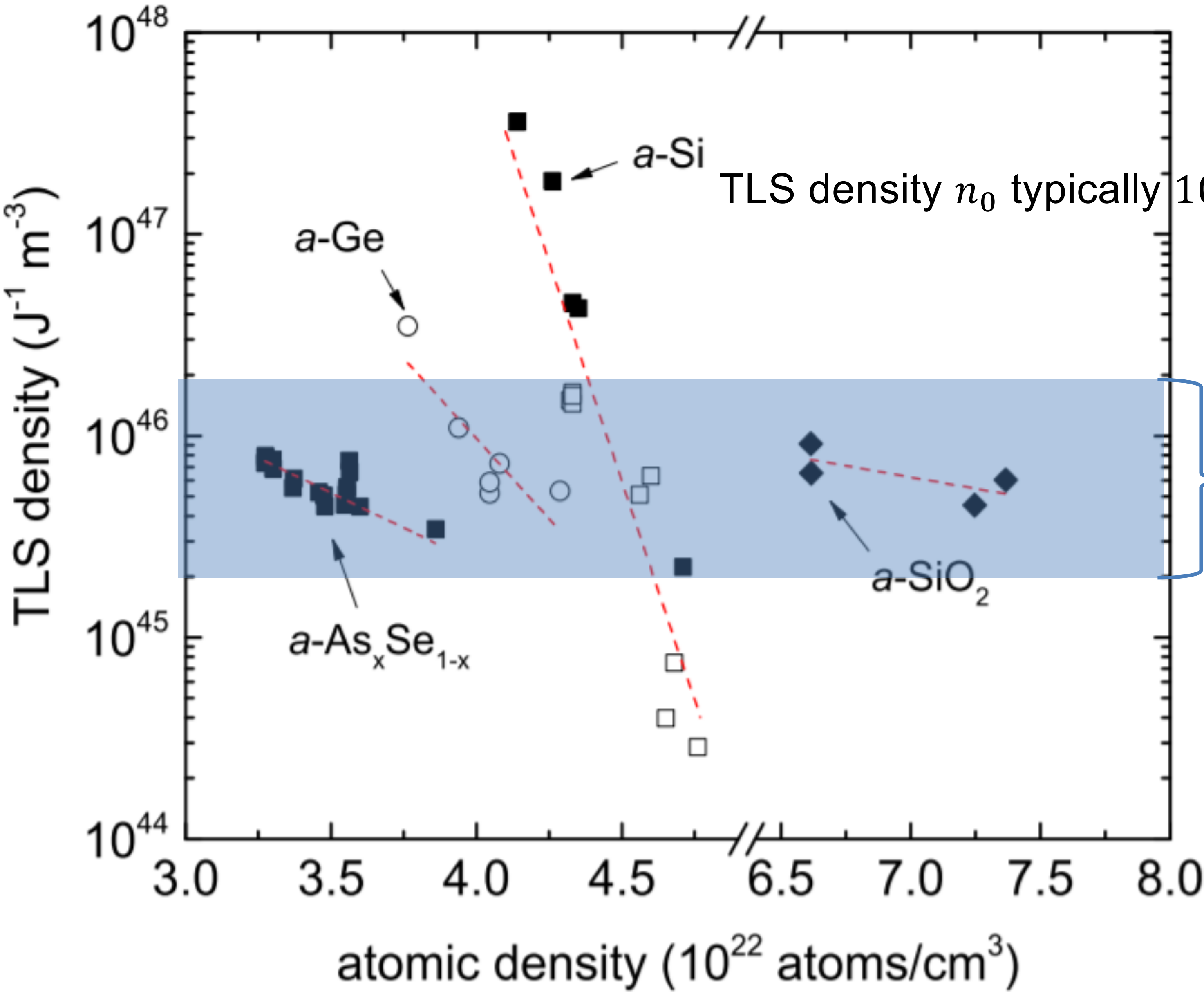
Thin films are more lossy than thick films; correlates with atomic density differences (thick films are denser)

Annealing reduces loss, but not much (at low T) compared to growth T effects



RT losses improved 4x by high T_{growth} (Not yet clear for e.g. 123K)

TLS depends on atomic density in *a*-Si and other amorphous materials

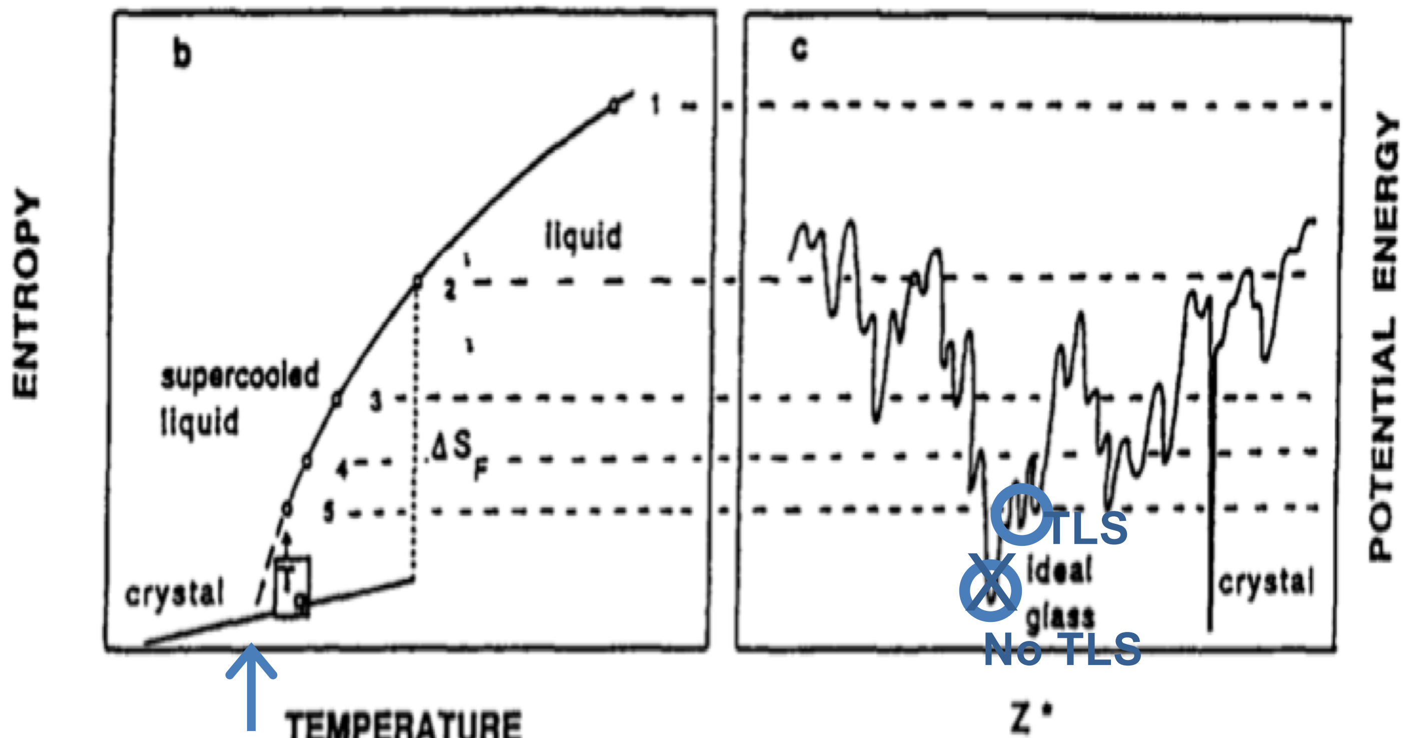


TLS density n_0 typically 10^{45} to 10^{46} J^{-1}m^{-3}

Range of universal glassy behavior

From D.R. Queen et al., JNCS 426 (2015), 19-24

Connection between energy landscape, entropy, and TLS



C.A. Angell, Physica D 107, 122 (1997)

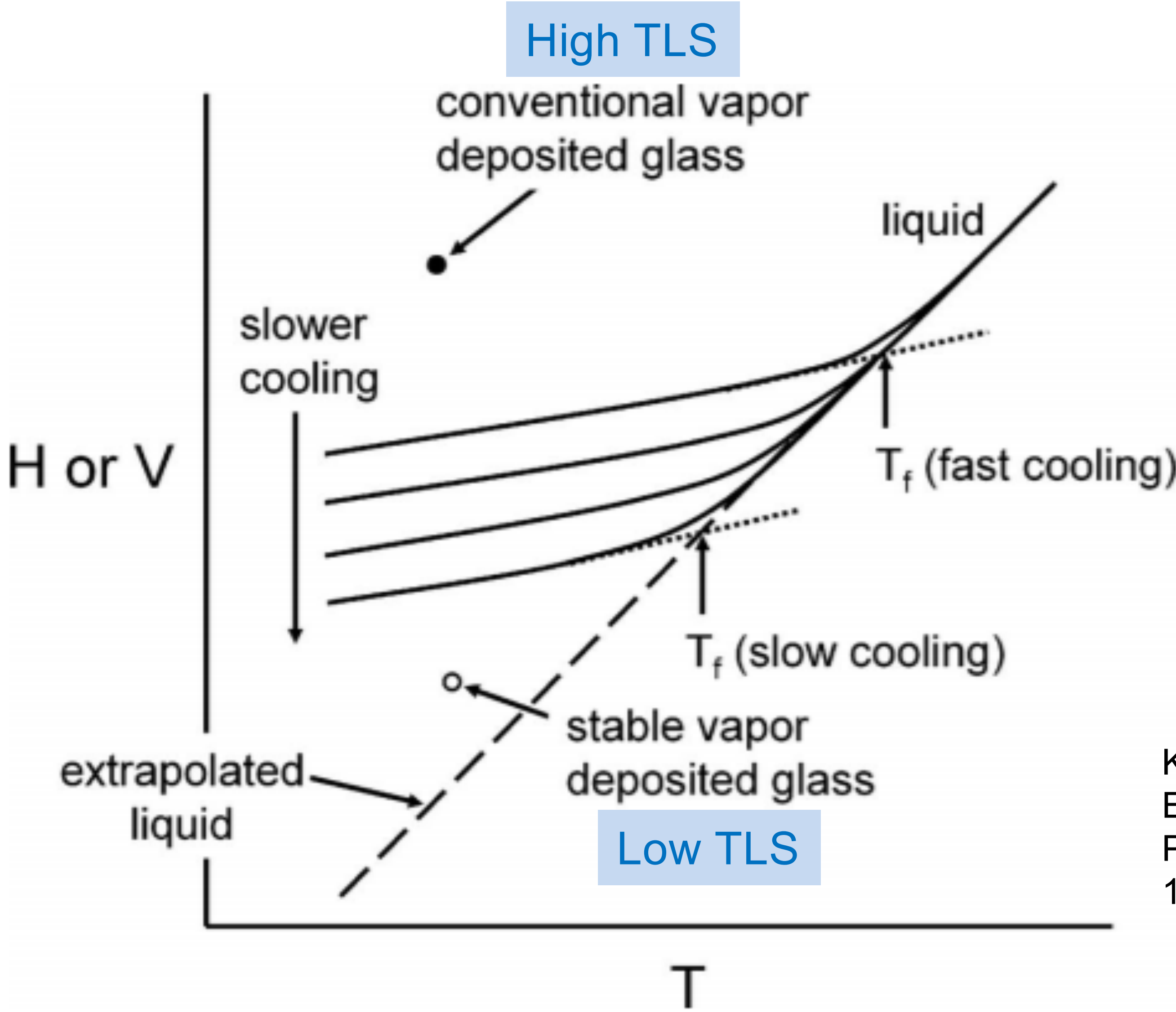
$T_{Kauzmann}$ where (extrapolated) entropy of supercooled liquid crosses crystal!

The energy landscape (right) as related to the glass transition of a liquid (left). Glasses falling out of the equilibrium supercooled liquid at a given dashed line correspond to configurations in the energy landscape.

Hypothesis: vapor deposition offers a way to directly access low lying (ideal) glass state
Due to high atomic mobility at film growth surface despite being at low T.

Hypothesis: Ideal glass has no nearby energy minima, so no TLS, unlike most other states

Enthalpy or Volume (density) as a function of T starting from liquid Vapor deposited compared to liquid quenching of amorphous material



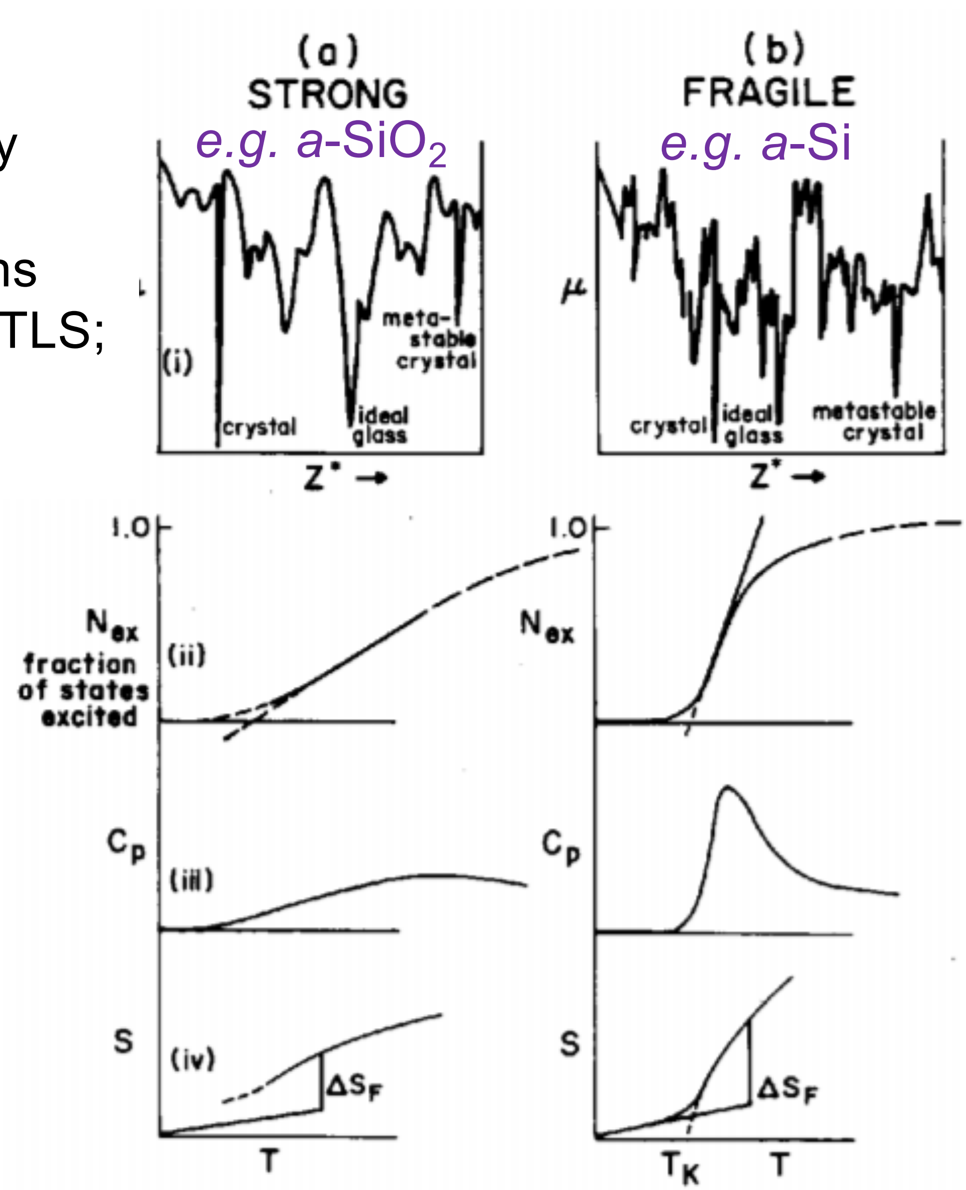
H and V based on simulations of atoms with simple bonds (Lennard-Jones).

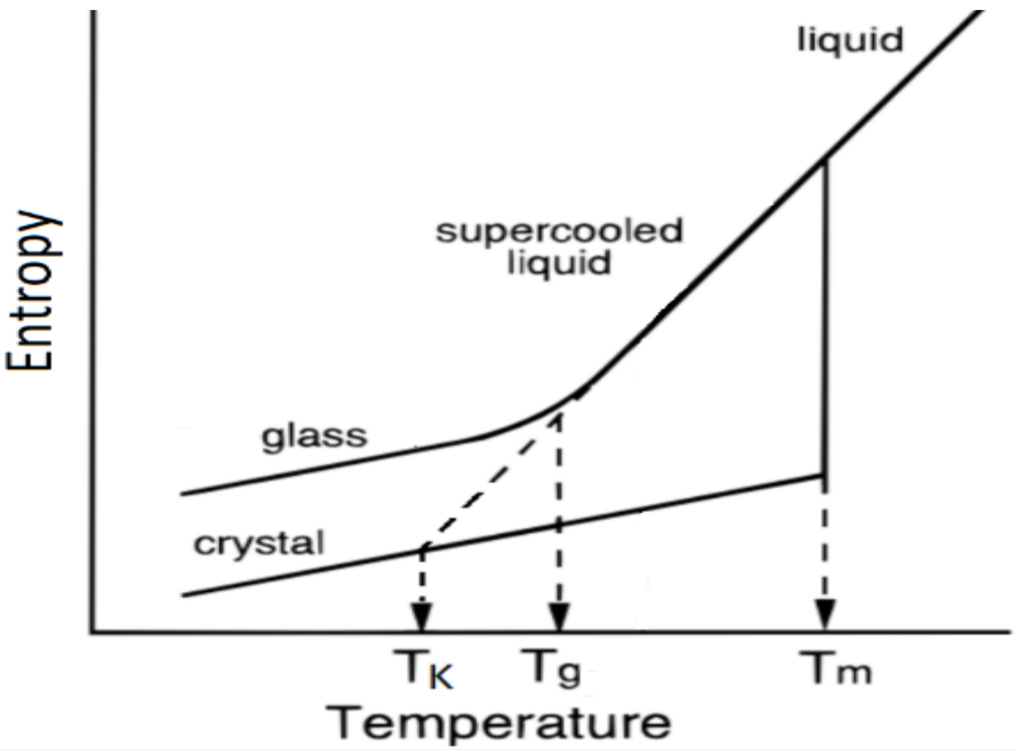
Kearns, Swallow, Ediger, J. Chem. Phys. 127, 154702 (2007)

Could this apply to other materials?
Does this reduce losses at other T?

Kauzmann temperature (and paradox)

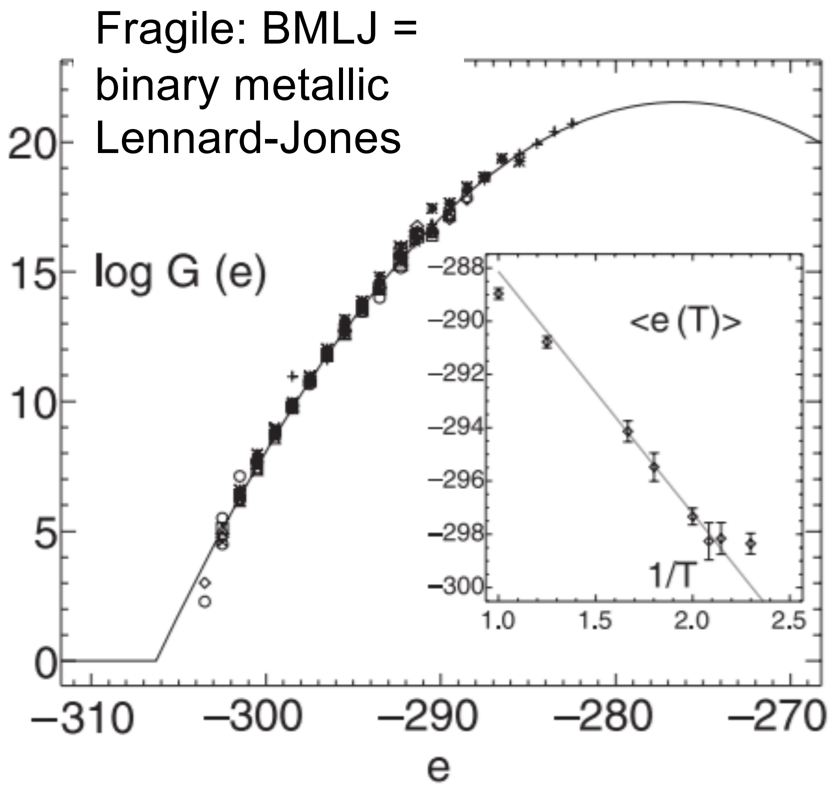
<u>Strong</u>: Liquid develops lots of short range order, so few states left for freezing
<u>Fragile</u>: high density of minima in the energy landscape just above glass transition; large number of locally rearrangable configurations can get frozen in, causing a high density of TLS; vapor dep drops the system lower in this landscape, eliminating TLS

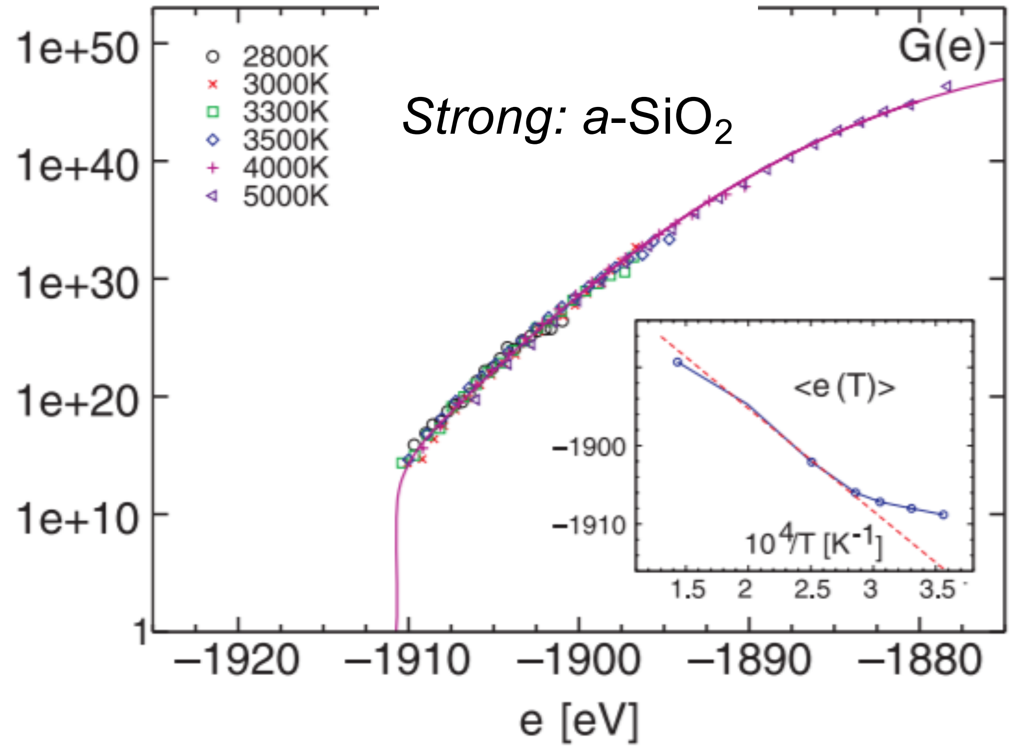




Hypothesis: Ideal glass has no nearby energy minima, so no TLS, unlike most other states
Maybe only accessible for fragile glasses where T_K is at a high temperature

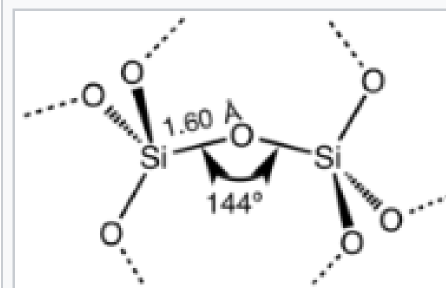
Modes of fragile and strong (a-SiO_2) glasses





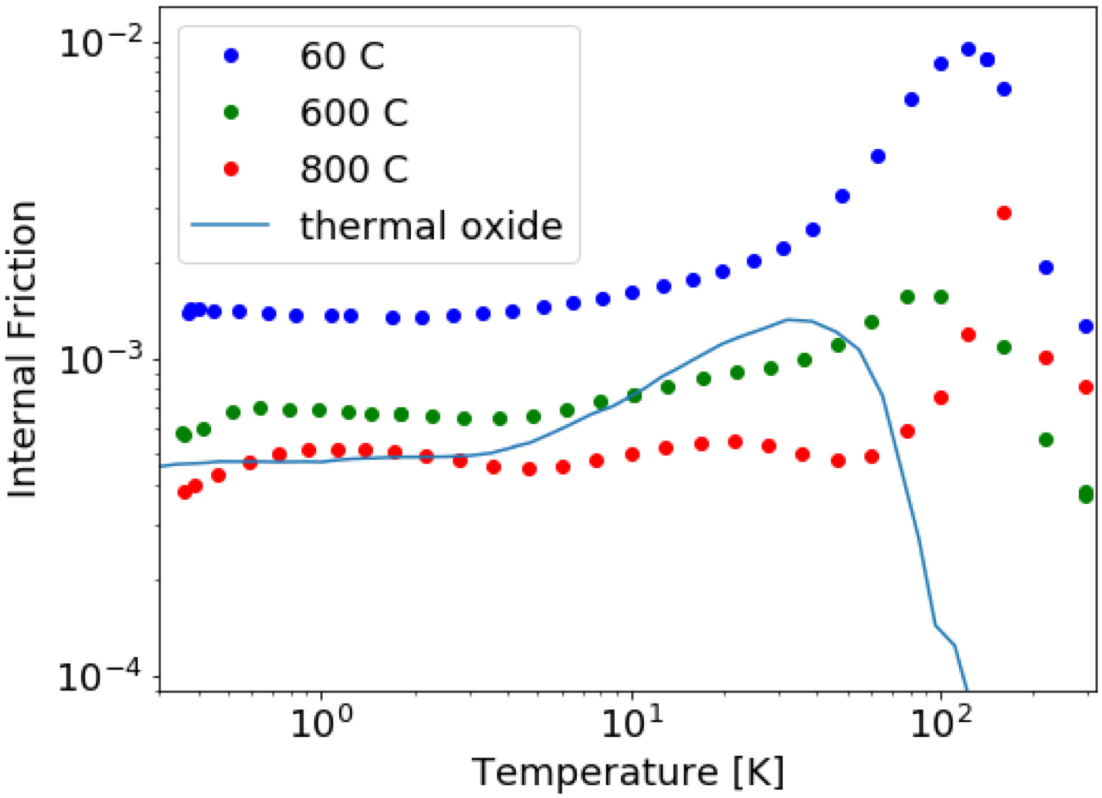
A. Heuer, J. Phys.: Condensed Matter 20, 373101 (2008)

- Low-energy cutoff in $G(E)$ for a-SiO_2 might explain drop in losses at room temperature, yet still allow a highly nearly degenerate ground state where nearly all silicon atoms are fourfold coordinated
- Large degeneracy of such states because Si-O-Si bond angle can vary around $144°$ without much energetic cost ----> many possible disordered networks of similar energy



Structural motif found in α-quartz, but also found in almost all forms of silicon dioxide

DPO Losses in silica ebeam: RT, 600 C , 800 C growth T



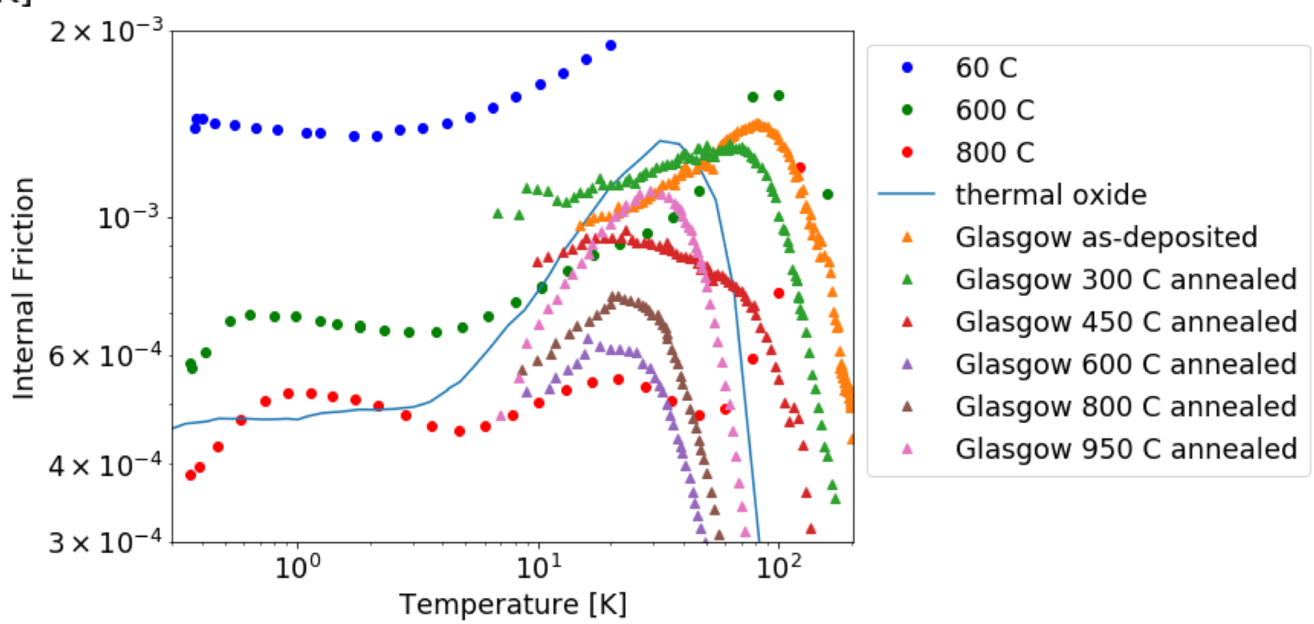
Silica (ebeam) RT deposited
Silica (ebeam) 600 C deposited
Silica (ebeam) 800 C deposited
Thermal oxide (line)

Surface mobility is very low, only a few times higher than bulk mobility, so this violates one premise of ultrastable low TLS glasses (still plan 950C growth)

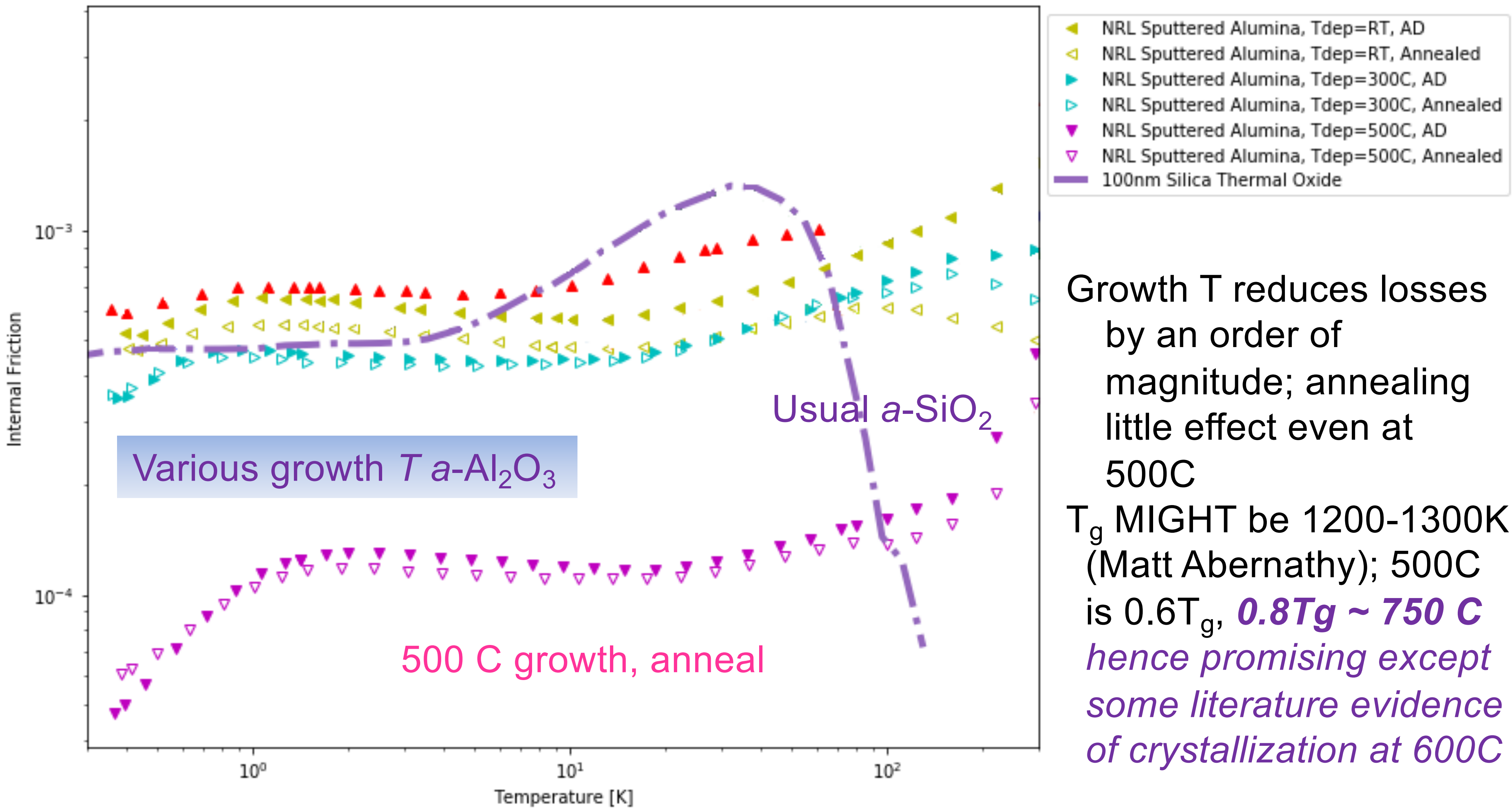
With IBS silica (Glasgow) cantilever data

- As deposited
- 300C anneal
- 450C anneal
- 600C anneal
- 800C anneal
- 950C anneal

Annealing is effective as T_{growth}



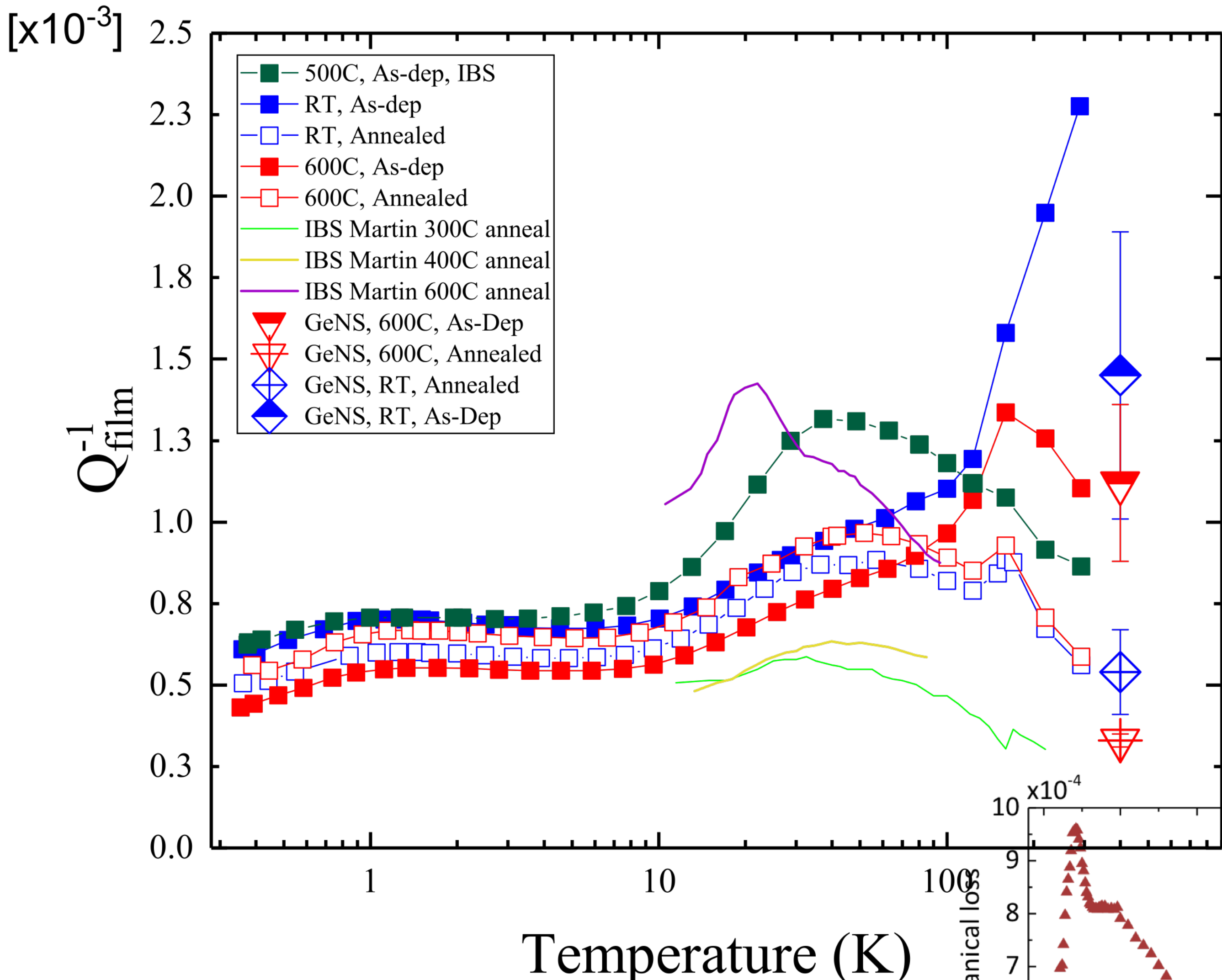
Alumina DPO Measurements: NRL prepared and measured (DPOs)



Growth T reduces losses by an order of magnitude; annealing little effect even at 500C

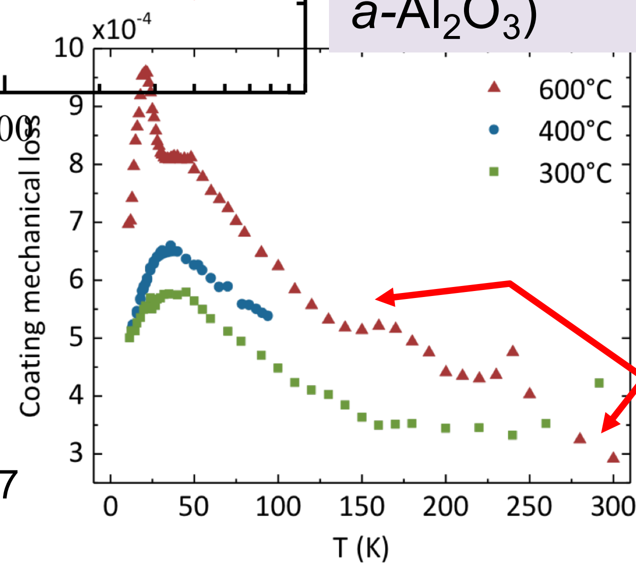
T_g MIGHT be 1200-1300K (Matt Abernathy); 500C is $0.6T_g$, ***0.8Tg ~ 750 C*** *hence promising except some literature evidence of crystallization at 600C*

Losses in *a*-Ta_2O_5: DPOs, cantilevers, and GeNS



Berkeley magn sputt: RT
AD solid; AN 500C open
Berkeley magn sputt: RT
AD solid; AN 500C open
Glasgow IBS 500 C growth
Glasgow IBS 300 C anneal
Glasgow IBS 400 C anneal
Glasgow IBS 600 C anneal

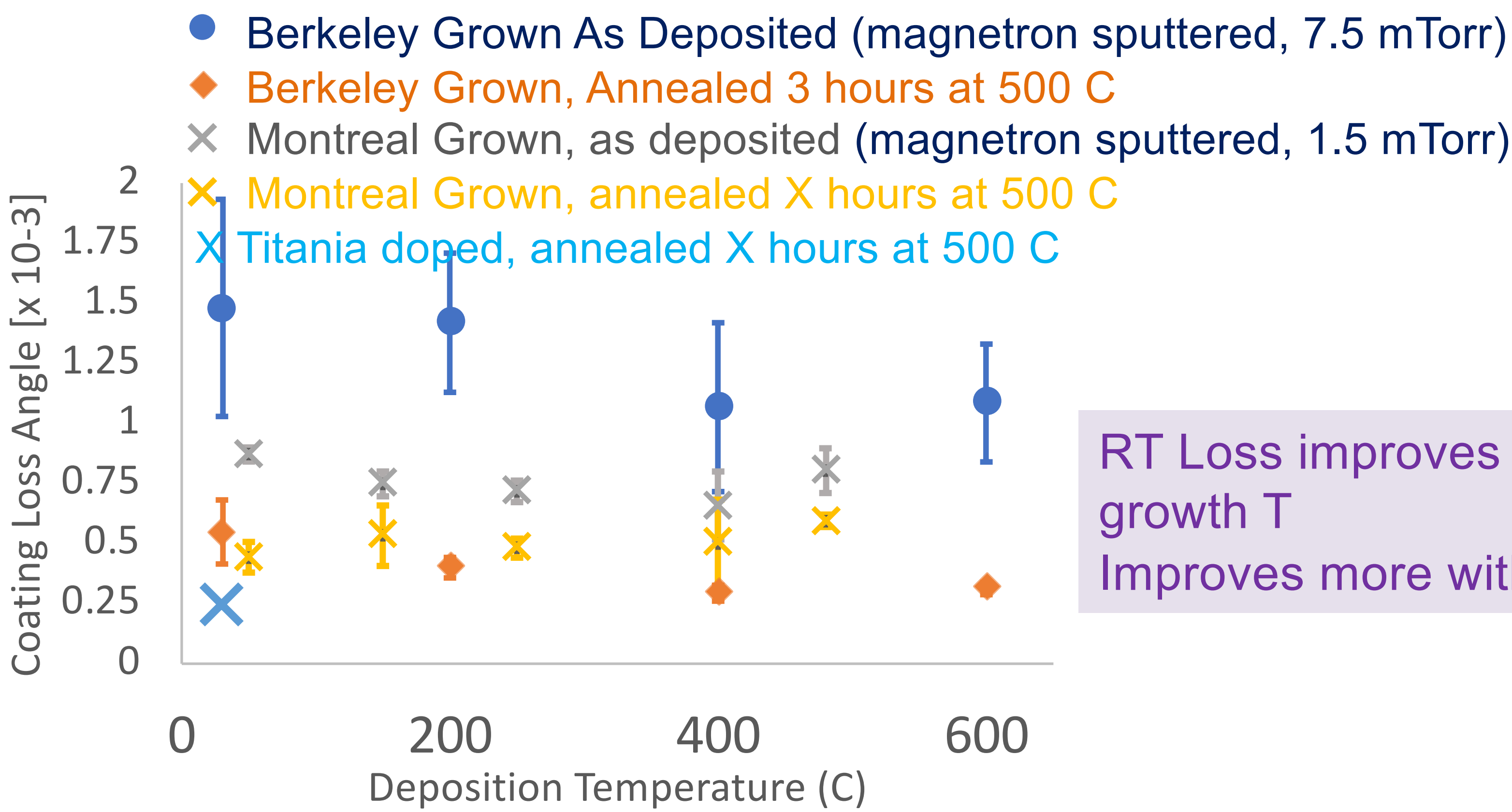
Higher T_{growth} reduces loss all T; annealing decreases loss at 300K, *increases* it at low T (unlike *a*-Si, *a*-SiO_2, *a*-Al_2O_3)



Annealing Decreases loss at 300K, increases it at low T

I W Martin et al, Class. Quant. Grav. 27 225020, 2010; *CQG* **35** 075001

a-Ta_2O_5 Room Temperature GeNS Measurements: Berkeley and Montreal, both magnetron sputtered, various growth temperatures



RT Loss improves a little with growth T
Improves more with annealing

R Flaminio *et al* 2010 *Class. Quantum Grav.* **27** 084030

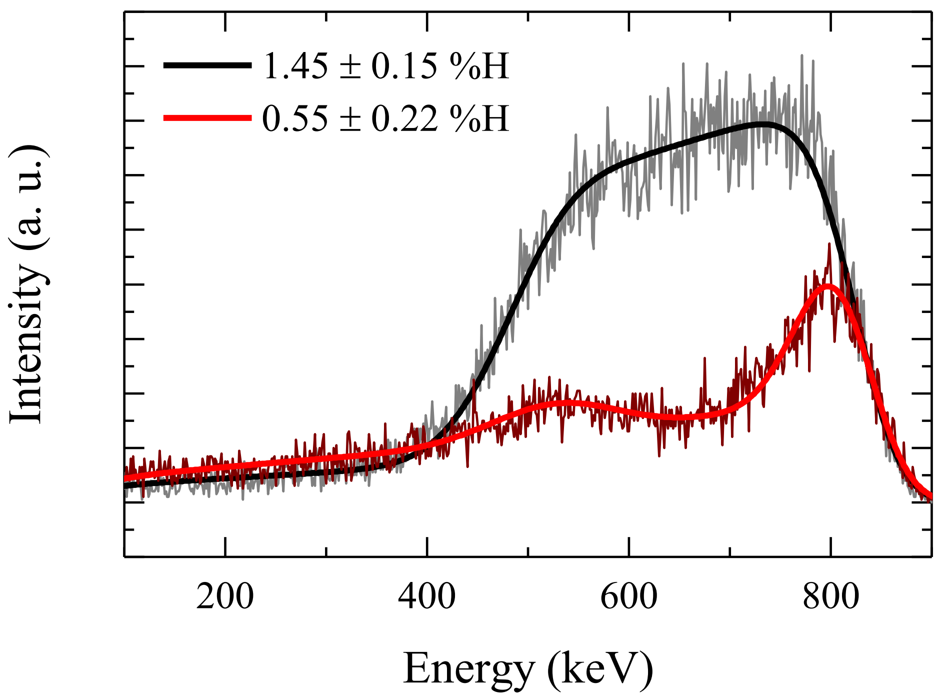
Amorphous Si: Absorption is high, even at 1.5 or 2 μm, due to dangling bonds (~2x10^{18} cm^{-3})

Hydrogenate 500 nm thick *a*-Si, 3-12 hours at 425 ° C in forming gas (5 at.%H) to reduce absorption; measure mechanical losses

Hydrogen Forward Scattering (HFS)

Black 50 ° C: relatively homogeneous 1.45 at.%H

red 425 ° C: inhomogeneous and only 0.55 at.%H

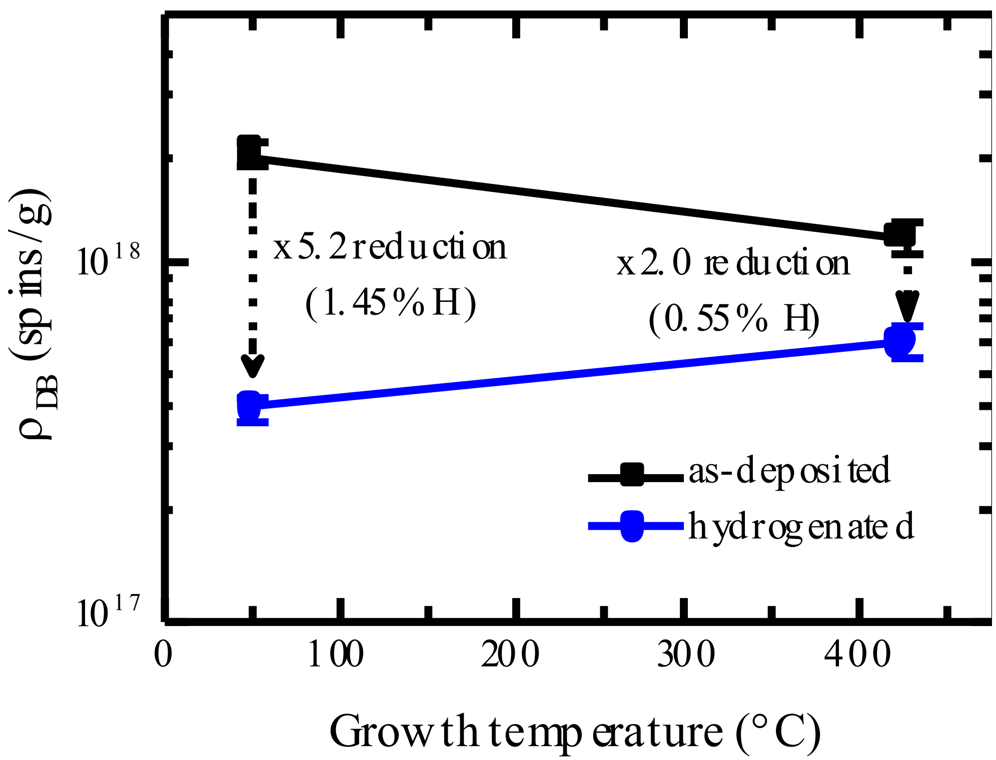


Electron Paramagnetic Resonance – dangling bond density

RT growth: 5x reduction after Hydr.

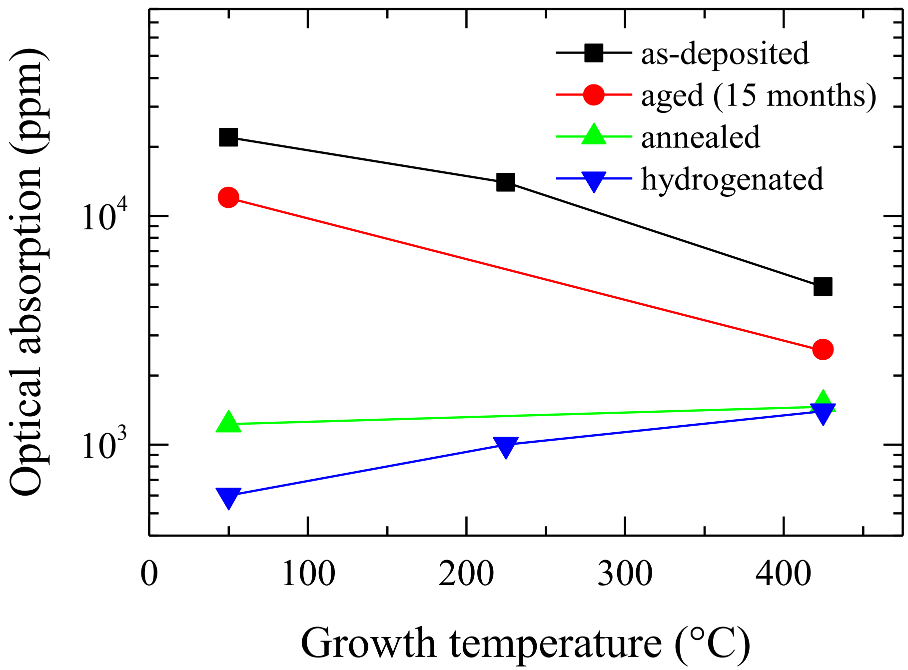
425C growth: 2x reduction after Hydr.

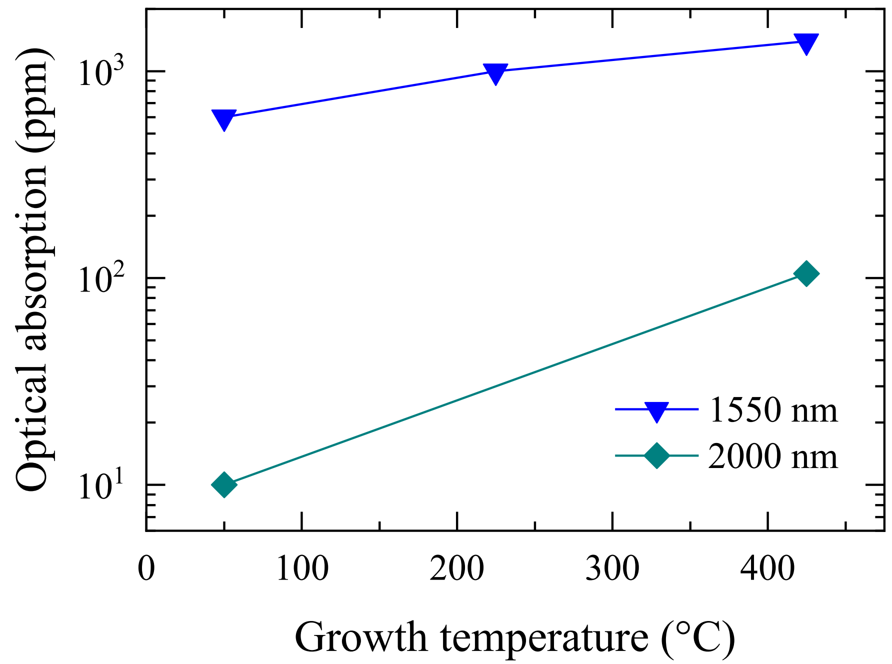
225 C growth pending



Optical absorption

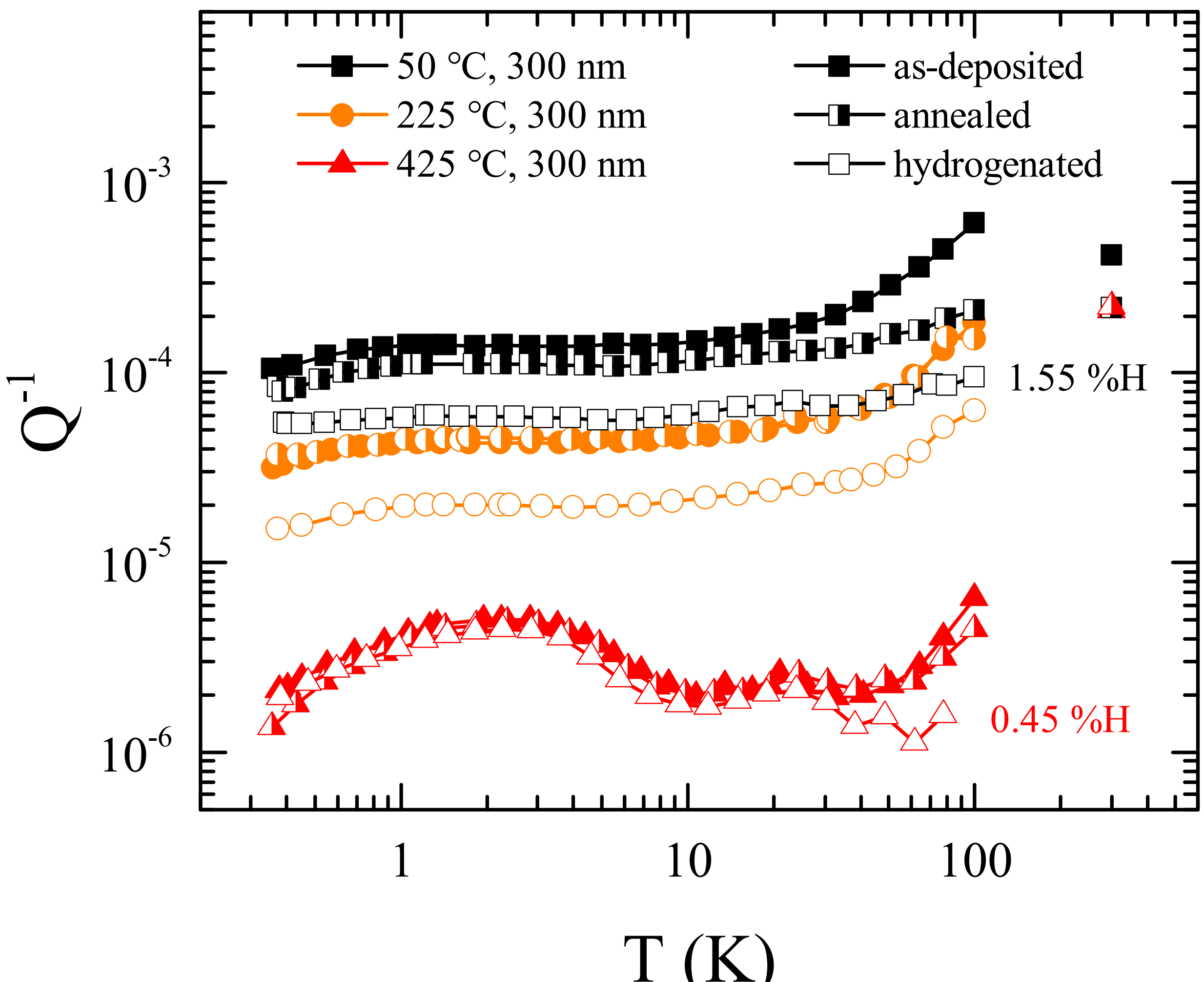
1. as-deposited (500 nm) at 50, 225 and 425 ° C,
2. aged (15 months),
3. annealed (12 hours at 425 ° C) or hydrogenated (12 hours at 425 ° C and 5 at.% H FG).





Optical absorption improves with growth T, and somewhat with annealing, but improves far more with hydrogenation. Best result at 2 mm RT growth, <10 ppm

Mechanical losses in *a*-Si for various growth T, annealing, hydrogenation



As before, low T mechanical losses are improved 100x by increased growth T, improve only slightly on annealing at 425 C, and improve significantly for RT and 225 C growth on hydrogenation. RT losses less affected by any of these.

A trade-off of absorption and losses; likely sweet spot at e.g. 250C growth where H is incorporated, losses 10-5, absorption may be low

Conclusions and Open Questions

- Are low TLS in ultrastable *a*-Si (and IMC) the "exception that proves the rule" of universal low T glass properties? Or, is there a new rule – "universal glass properties" at low T are perhaps due to the universal nature of liquid quenching and domain growth/correlation length growth/boundaries?
- Is low TLS related to growth near T_K? (If (and only if) surface mobility during growth is high). Fragile glasses have T_K near T_g, where mobility is high, so low TLS would be correlated with fragility
- Or is low TLS related to nature of bonding: overconstrained (tetrahedral Si) versus underconstrained e.g. Si-O-Si bonds in *a*-SiO_2 and TLS in *a*-Si due to nanovoids
- Silica, alumina show increased density and reduced loss at low T with increased T_{growth}; not as much as a-Si, but not yet at $T_{growth} = 0.8T_g$.
- Tantala shows reduced losses at low T with increased growth T; not as much as a-Si, and likely at $T_{growth} = 0.8T_g$; annealing big effects, T_{growth} not stabilizing structure.
- Low losses at room temperature in all are not well correlated with low losses at low T
- Route to low room T losses is to find a material like *a*-SiO_2 with strong well formed bonds in liquid state (i.e. strong glass) and moderately high T_g
- Route to low low T losses is fragile glass with moderate T_g and suppress crystallization