Ideality and Tunneling Level Systems (TLS) in Amorphous (*a*)-Si, *a*-Si:H, and *a*-Ta_2O_5 Films

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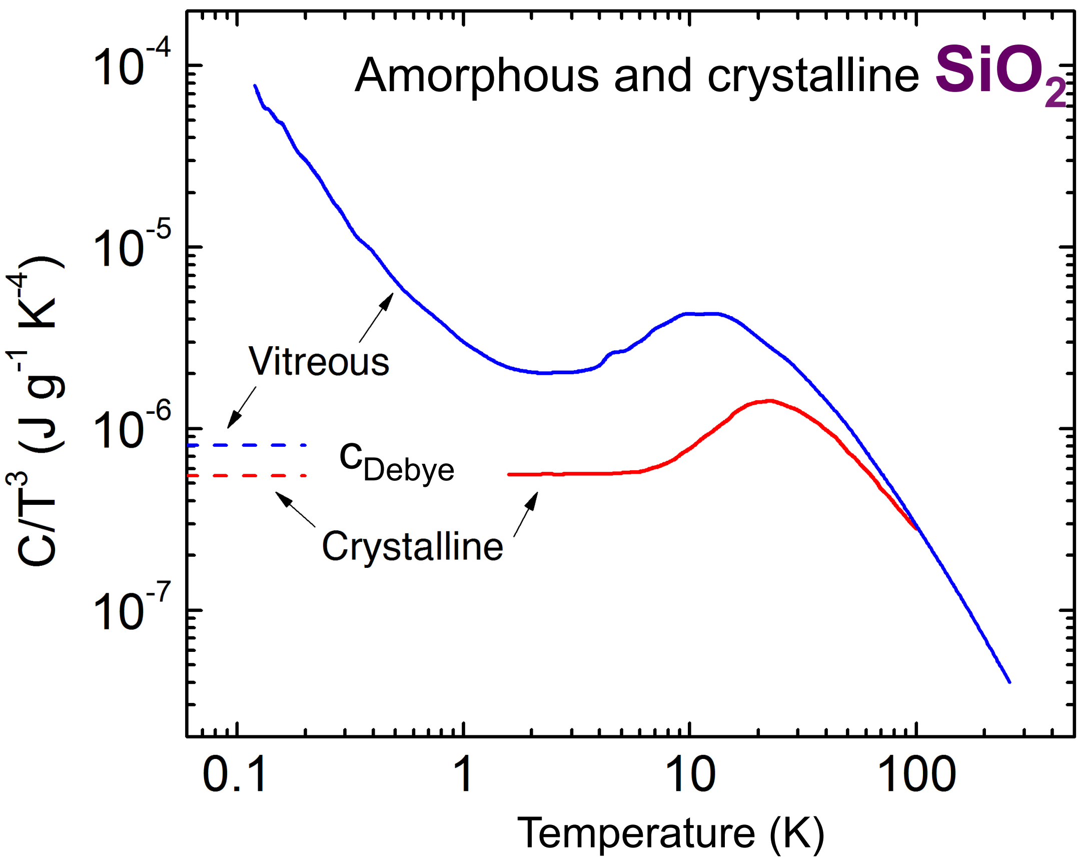
Thermodynamics of amorphous materials: Low T (<10K) specific heat – excess, non-T^3 specific heat



R. C. Zeller and R.O. Pohl, Phys. Rev. B 4, 2029 (1971).

In amorphous (glassy) materials,

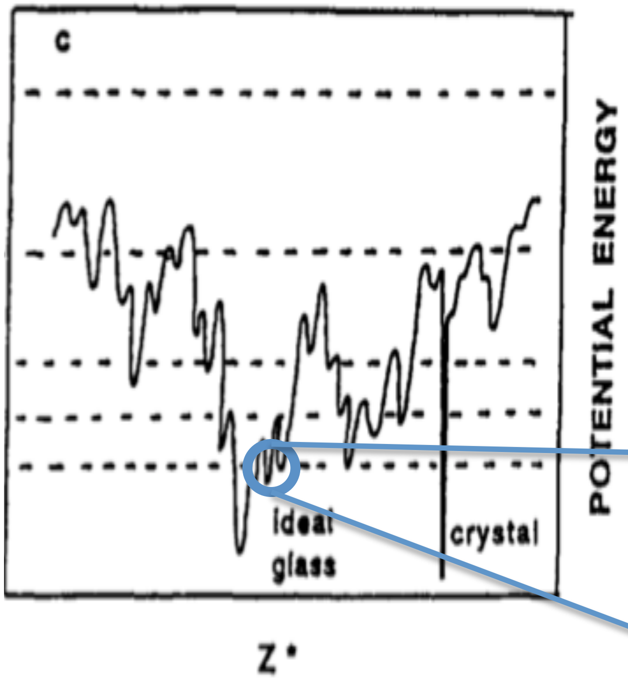
$C(T) = c_1T + c_3T^3$ below 10K

Linear term unexpected in an insulator

$c_3 > c_{Debye}$

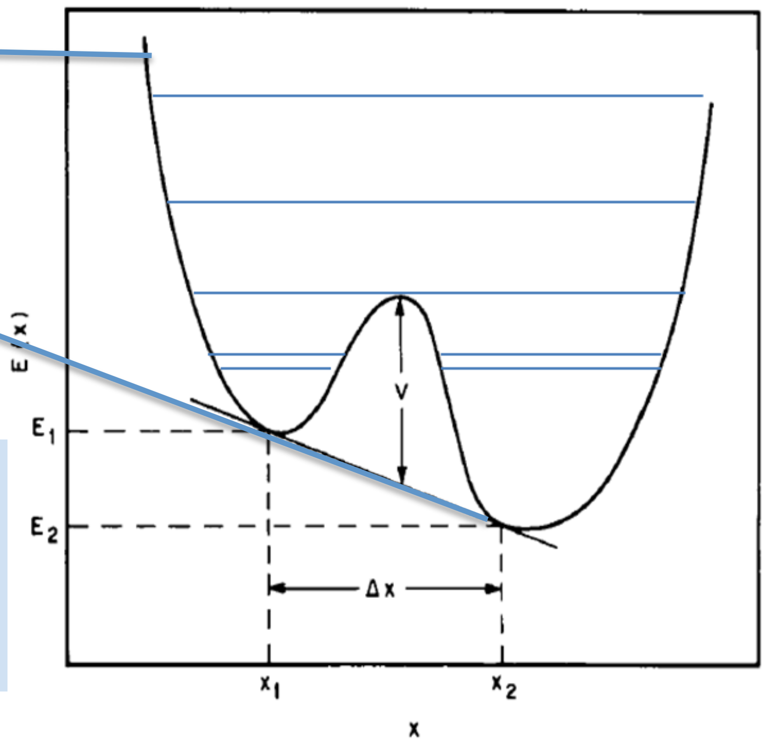
And, c_{Debye} (amorphous) often > c_{Debye} (crystalline)

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)

Two-Level Systems (TLS) from neighboring energy minima in structural landscape; atomic structure tunnels between these at low T. Splitting is μeV



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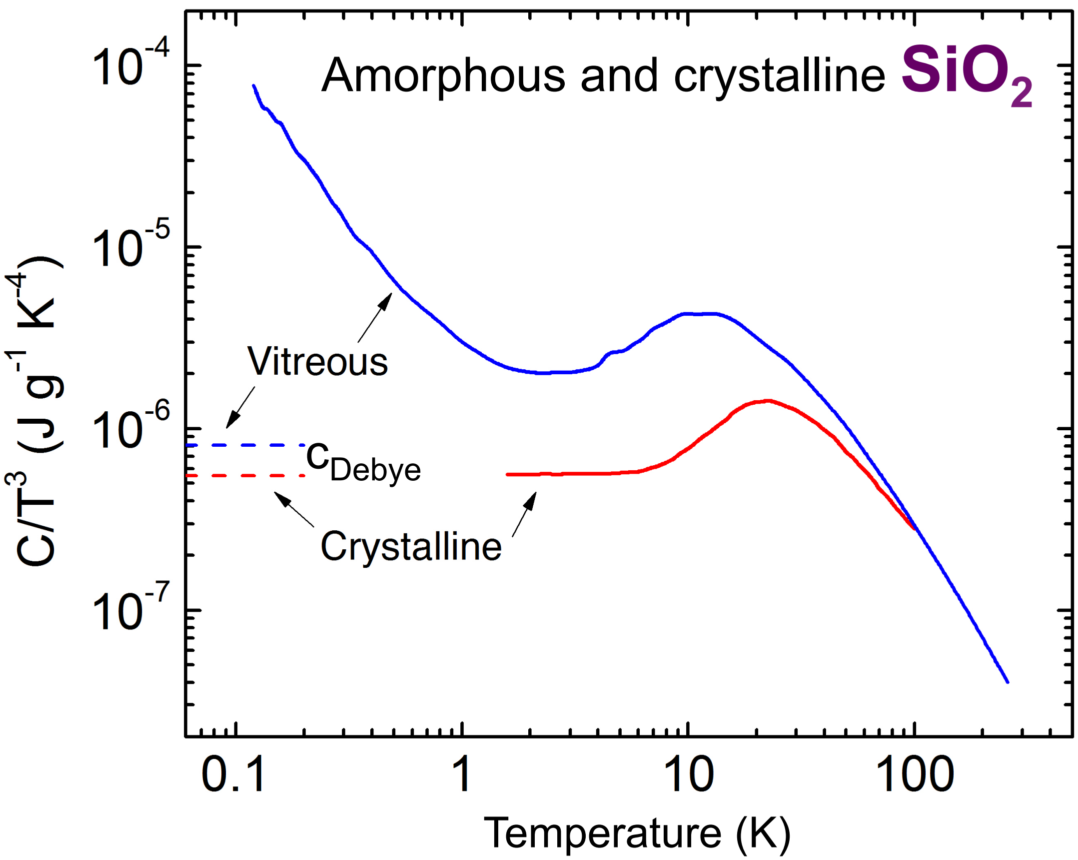


R. C. Zeller and R.O. Pohl, Phys. Rev. B 4, 2029 (1971).

Tunneling/two level systems (TLS)

$C = c_1 T + c_3 T^3$ below 10K

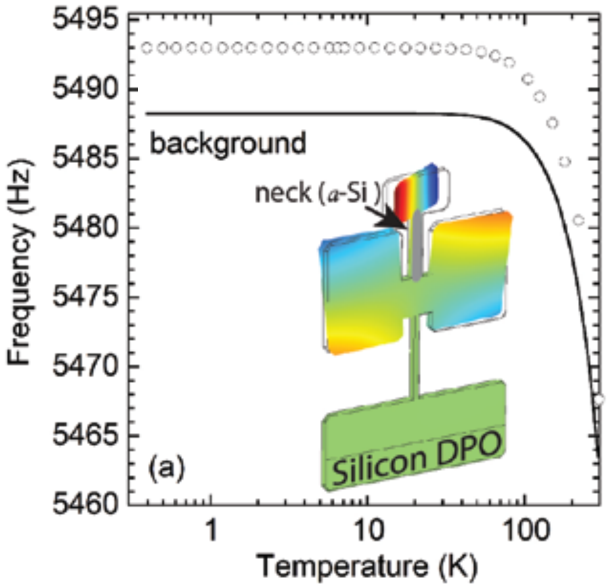
$c_1 = \frac{\pi^2}{6} k_B^2 n_0$ TLS n_o (no electron *C*)

$c_{ex} = c_3 - c_{Debye}$

***n_0* = density of TLS is "universal" (within factor of ~10) in amorphous systems independent of preparation or material type**

Origin of c_{ex} not clear and not part of TLS model. Often c_{Debye} not known/measured (!)

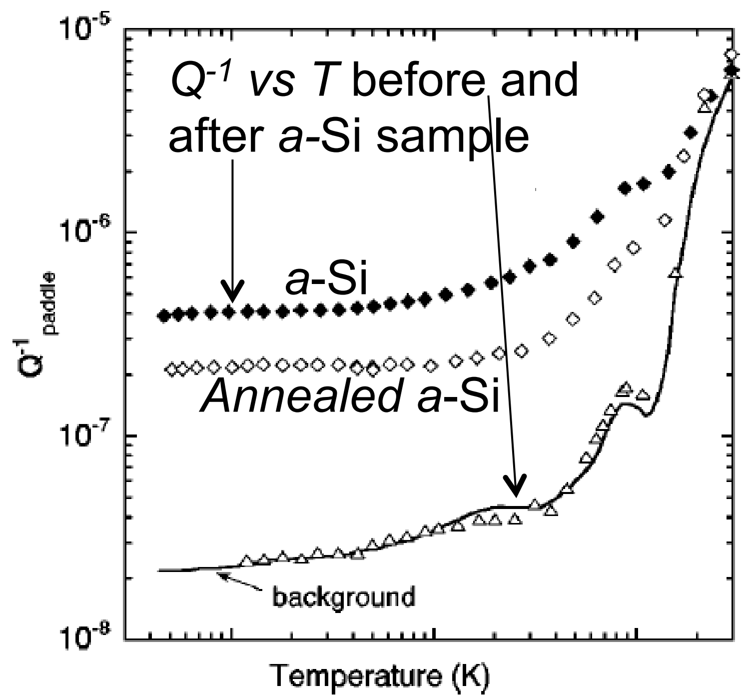
Other "Universal" low T properties of glasses (also TLS): Internal friction (can be measured on thin films)



Measure resonant frequency and internal friction (damping) Q^{-1} of a double paddle oscillator (DPO) as a function of T before and after depositing a film

Change in frequency gives shear modulus and transverse sound velocity

X. Liu and R.O. Pohl, Phys. Rev. B **58**, 9067 (1998)



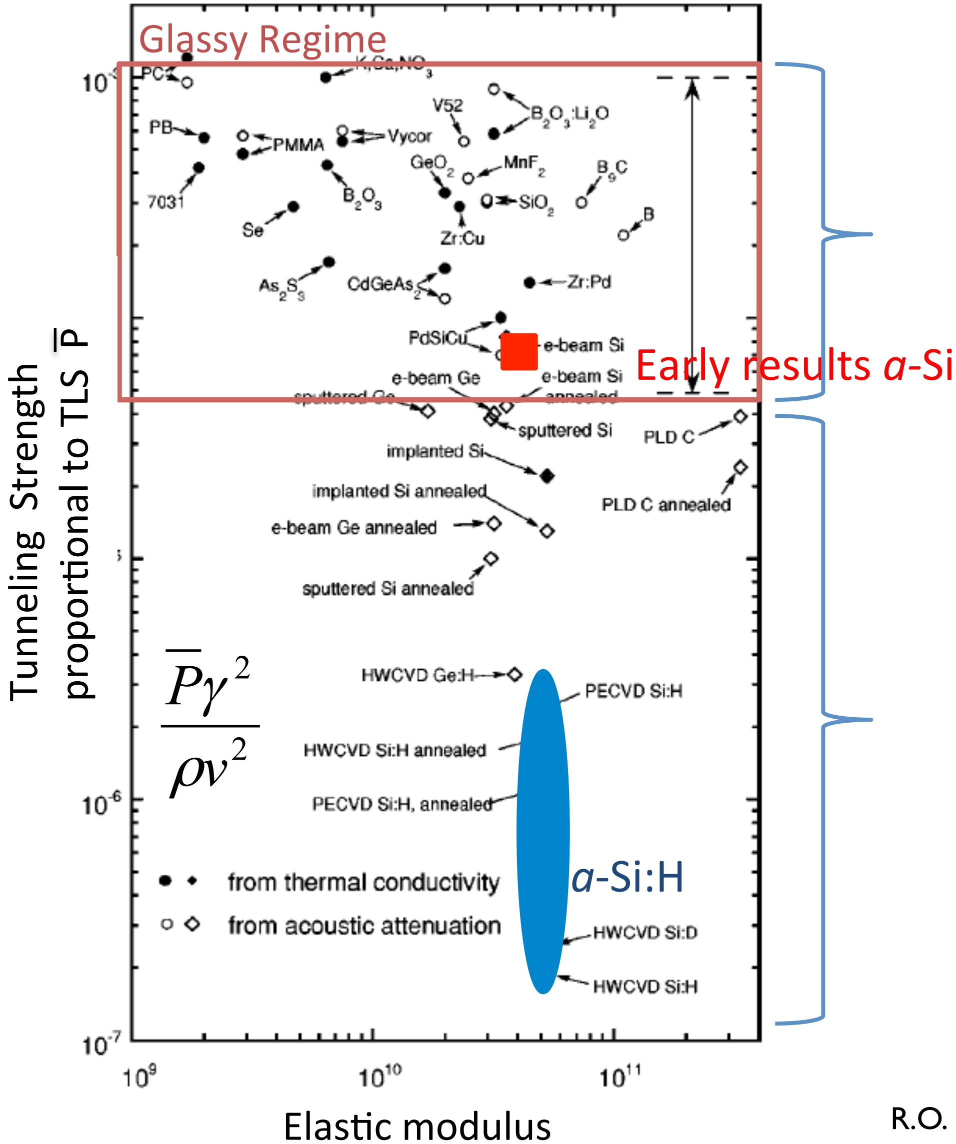
Internal friction $Q^{-1}(T)$ has a low T plateau due to TLS

- TLS damp acoustic waves
- Low T plateau Q_o^{-1} is due to TLS-phonon interaction
- Q_o^{-1} proportional to $\bar{P}$ (density of TLS) with a poorly known coupling parameter γ

  $Q_0^{-1} = \pi\bar{P}\gamma^2/2\varrho v^2$

  γ is TLS-phonon coupling parameter, ρ is density, and v is the sound velocity

"Universal" low T thermodynamic properties of glasses: Internal friction Q_0^{-1} proportional to TLS; thermal conductivity plateau; dielectric losses



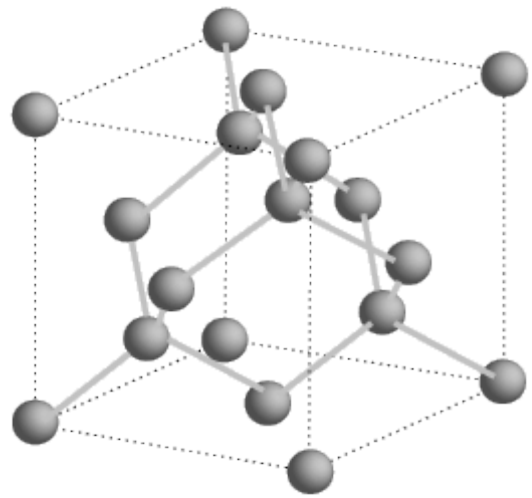
Universal glassy behavior
i.e. *a*-SiO_2, PMMA, etc
High density of TLS

Materials with TLS in range considered "outside" of glassy regime are all covalently bonded Si, Ge related, particularly *a*-Si:H (low dangling bond density and low TLS)

R.O. Pohl, X. Liu, and E. Thompson, Rev. Mod. Phys. **74**, 991 (2002).

Structure of Glassy/Amorphous Si?

Xtal Si: diamond structure



Si: Tetrahedrally-bonded (both xtal and “glass” = amorphous)
“overconstrained” - predicted to not have TLS (Phillips)

Amorphous state: cannot be quenched from liquid (high density, not tetrahedrally bonded), BUT is easily made by vapor deposition techniques, hence only available in thin film form

μg quantities too small for traditional heat capacity measurements

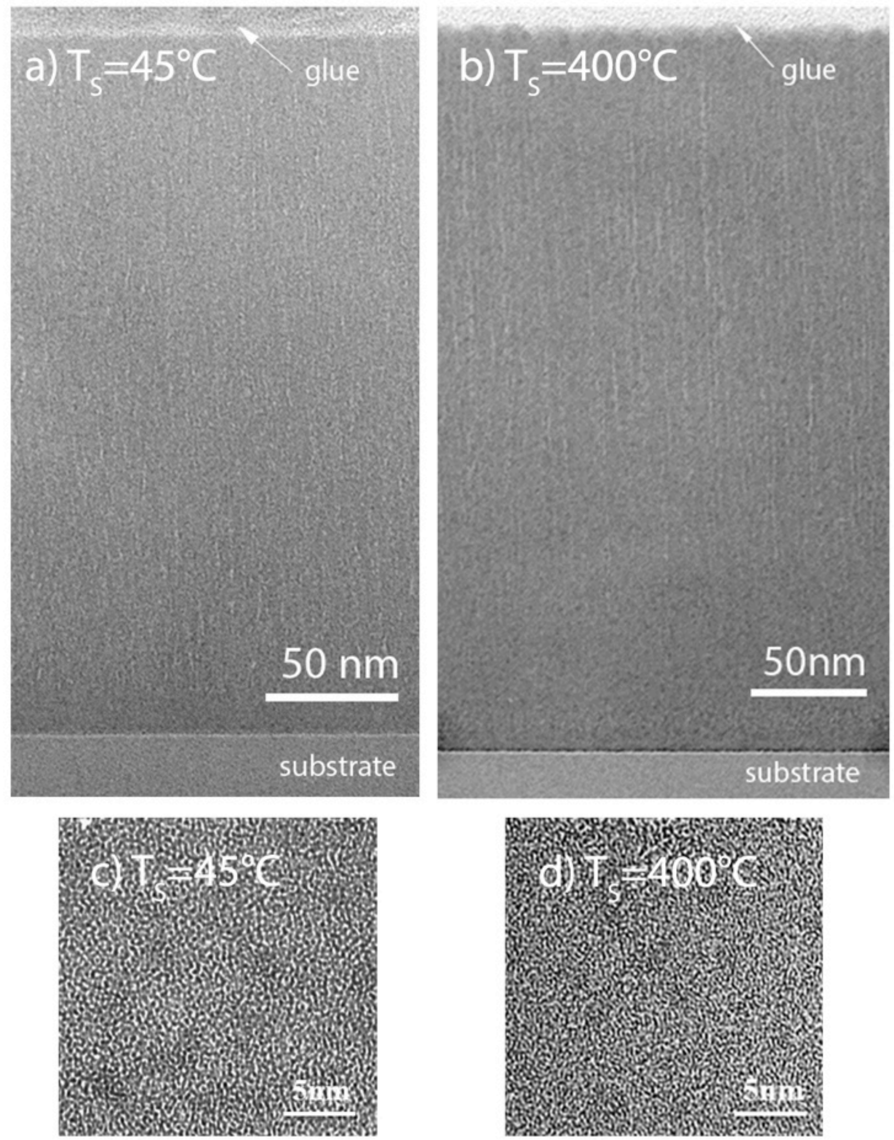
Amorphous Si: preparation and characterization

e-beam evaporation

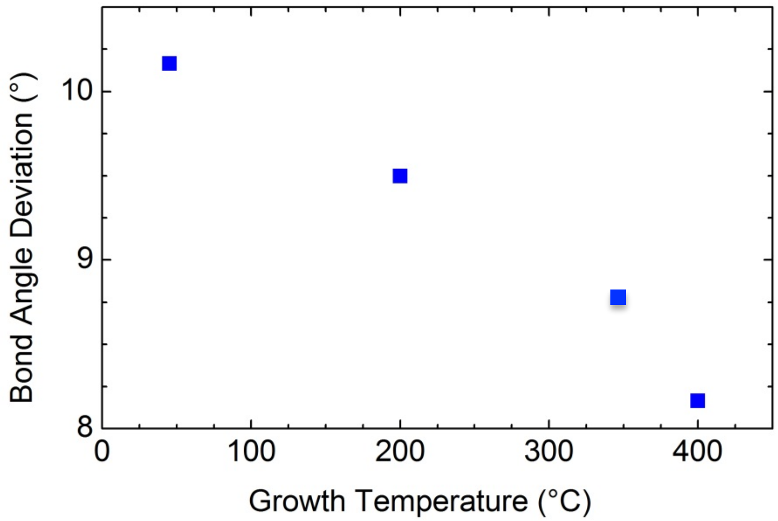
- P_{base}= 10^{-9} Torr
- T_s = 45°C -425°C
- Growth rate 0.005 − 0.25nm/s
- Thickness t from 10-400 nm
- Roughness varies with T_s and t
- n_{DB} ~ 10^{19} cm^{-3} (dangling bonds)
- ρ = 2.02 – 2.2 g/cm^3 (xtal: 2.33)

Characterization

- RBS (Rutherford back-scattering)
- AFM (atomic force microscopy)
- XRD (x-ray diffraction)
- Raman Scattering (bond angles)
- Sound velocity (transverse and longitudinal); shear modulus
- HR-TEM (high resolution transmission electron microscopy), also low resolution
- Fluctuation electron microscopy to get medium range order
- Dangling bond density (ESR)

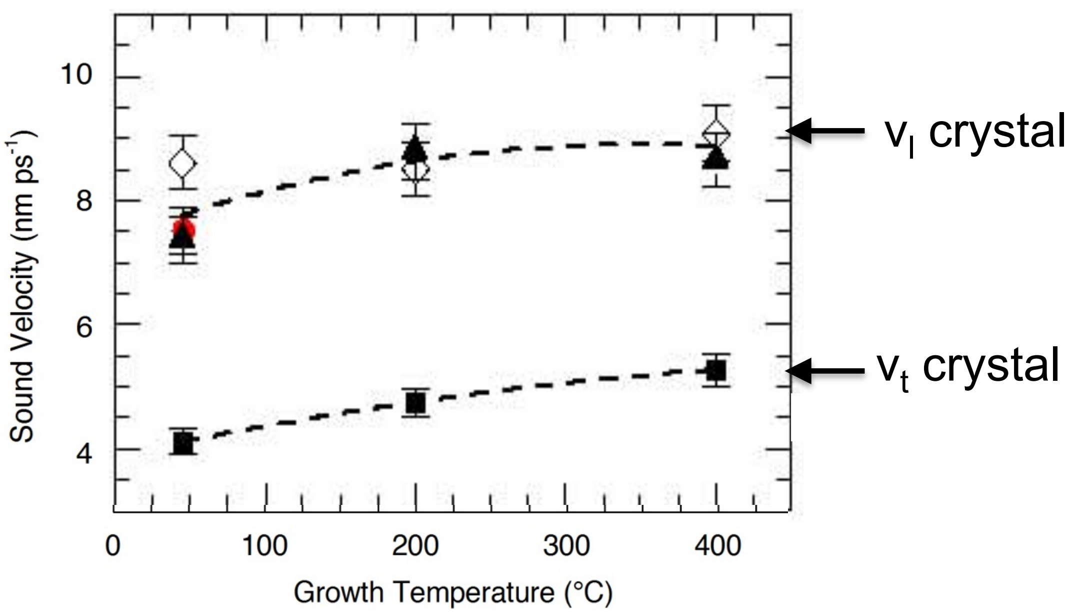


Amorphous Si: *Disorder decreases with increasing growth T*



Tetrahedral bond angle 109° ± δ

Bond angle disorder δ (from Raman scattering width of TO-like peak) decreases with increasing T_s



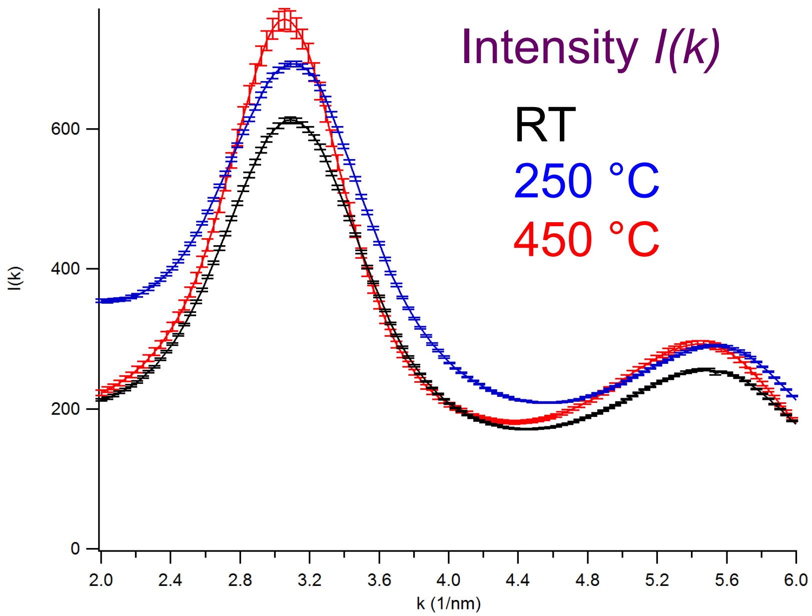
Longitudinal and transverse sound velocity v **increases with increasing T_s**

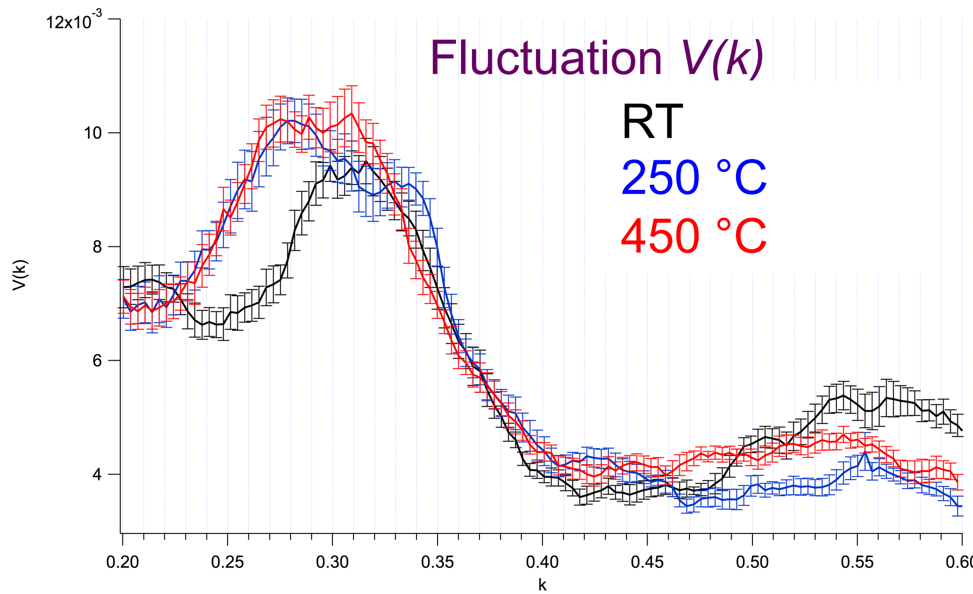
Elastic properties (shear modulus, sound velocity) soften with disorder in amorphous network

Independent of film thickness

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

Electron microscopy: intensity *I(k)* independent of growth T; fluctuation *V(k)* shows *shifts in medium range order*





25 nm films; grown at RT, 250 and 450 °C

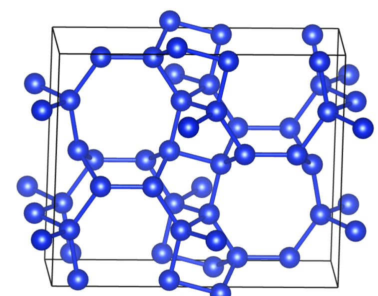
Room temp growth: like other a-Si: peaks in *V(k)* near the peaks in *I(k)*

250 and 450 °C growth: *I(k)* unchanged (short range order) and clearly amorphous

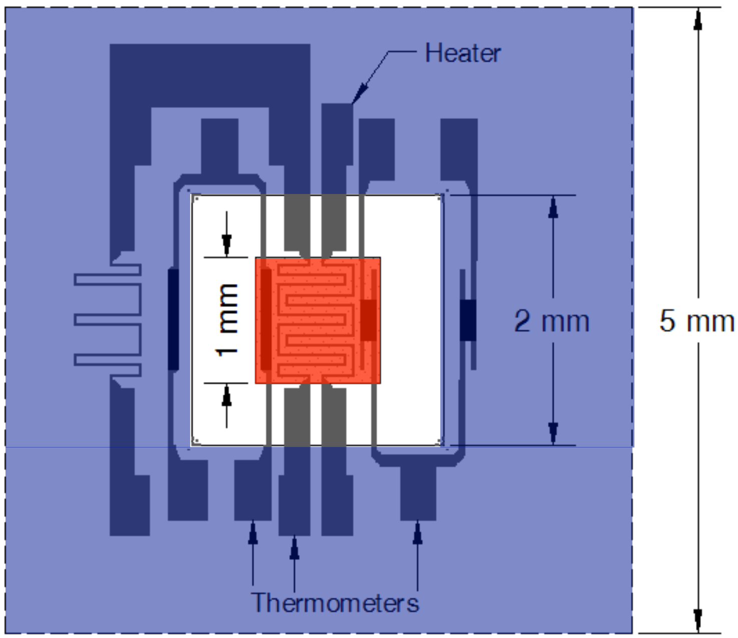
New peak in *V(k)* at lower *k*, which means larger *d = 1/k*

Suggestive *perhaps* of 8 member rings – interpretation unclear

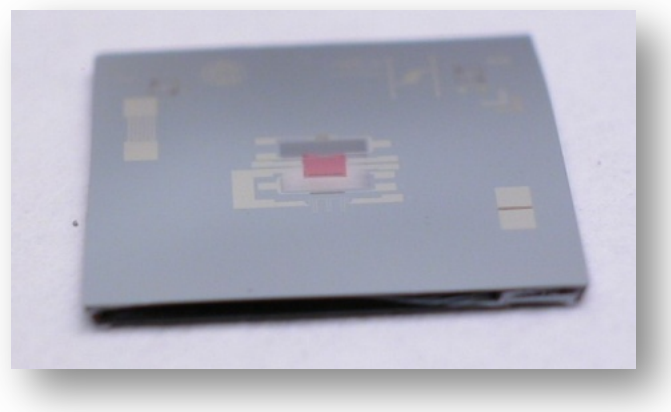
(like in high pressure crystalline Si_{24})



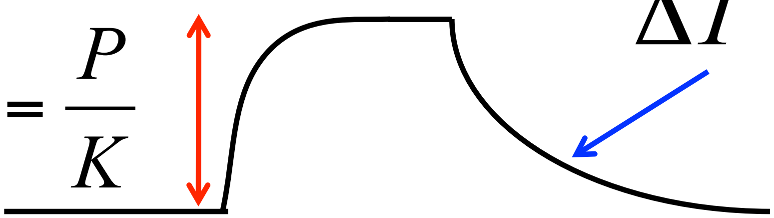
Heat Capacity Measurement: nanocalorimetry



- 50 nm thick *a*-SiN membrane
- Addenda: 2×10^{-10} J/K at 2K
- Temperature: 2 - 300K
- Magnetic Fields: 0-8T
- C_p - Small ΔT Technique
- In-situ rapid (pulse) annealing



$$\Delta T = \frac{P}{K}$$

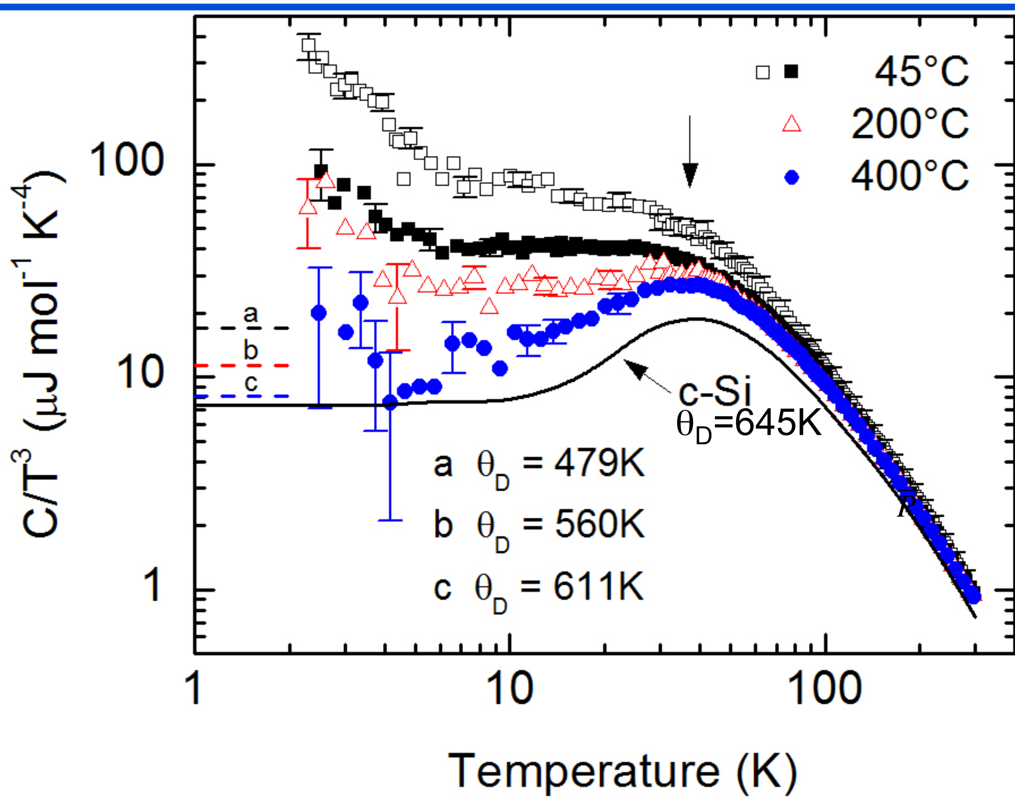


$$\Delta T \sim e^{-t/\tau}$$

$$\tau = C_P / K$$

D.R. Queen and F. Hellman, Rev. Sci. Instrum. **80**, 063901 (2009)

Variable TLS in e-beam *a*-Si: specific heat



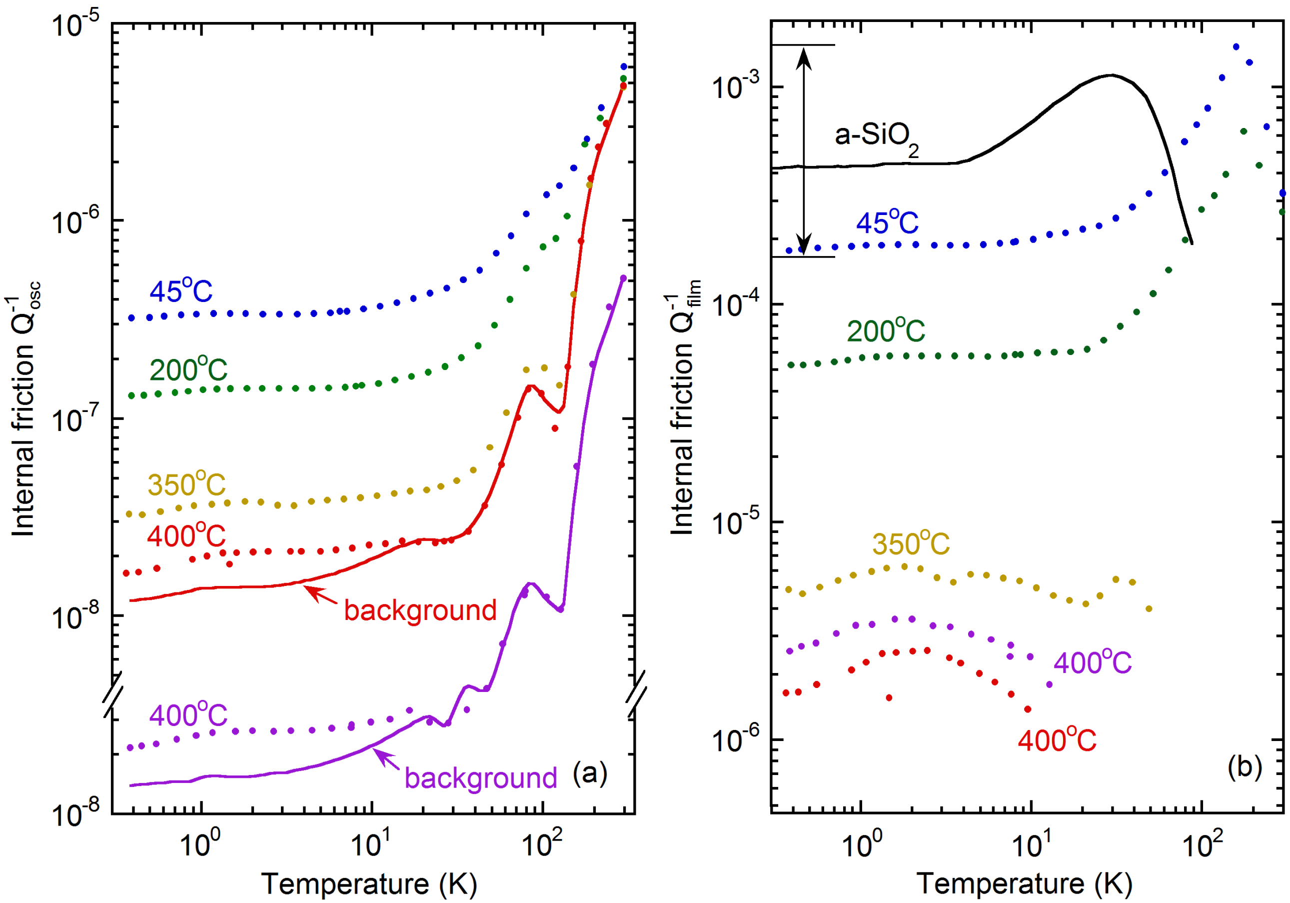
Linear term in C: $c_1 \sim n_0$
Excess T^3 term (c_{ex})

Films grown at 400°C have *C(T)* only a little above *c*-Si; small n_0 and small c_{ex} (Also, thermal conductivity shows no plateau)

Films grown at lower T_s have excess Q^{-1} and *C(T)* above Debye value (from transverse and longitudinal sound velocity measurements)

Fit low T *C(T)* to $c_1T + C_3T^3$; both n_0 and c_{ex} depend on T_s ***but also on film thickness (unlike sound velocity)***

Variable TLS in e-beam *a*-Si: internal friction



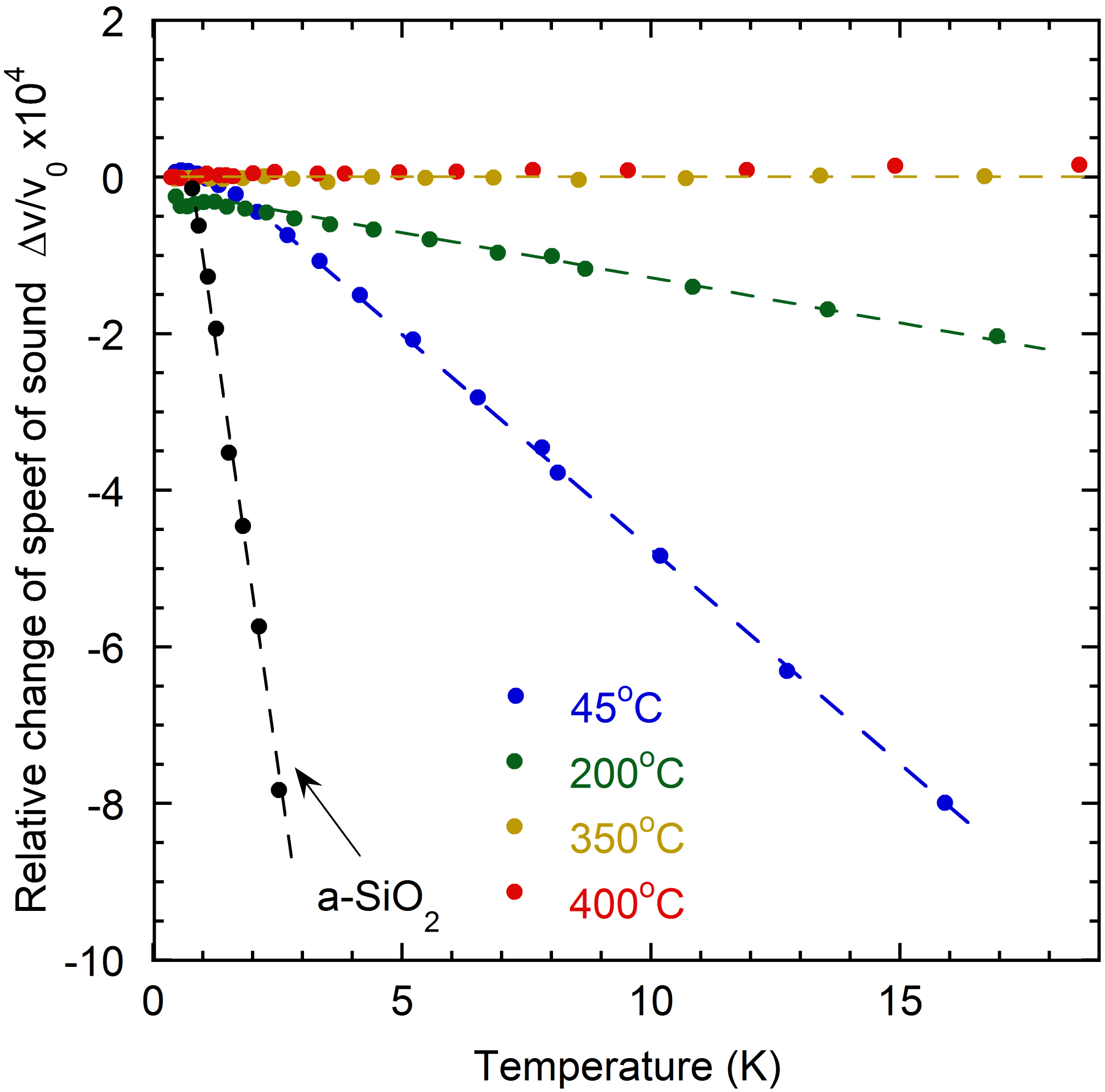
Internal Friction:
$Q_0^{-1} \sim \overline{P}\gamma^2$
γ is TLS-phonon coupling parameter

Films grown at 400°C have *very low* Q^{-1} *hence low* $\overline{P}$

Films grown at lower T_s have larger Q^{-1} *and higher* $\overline{P}$

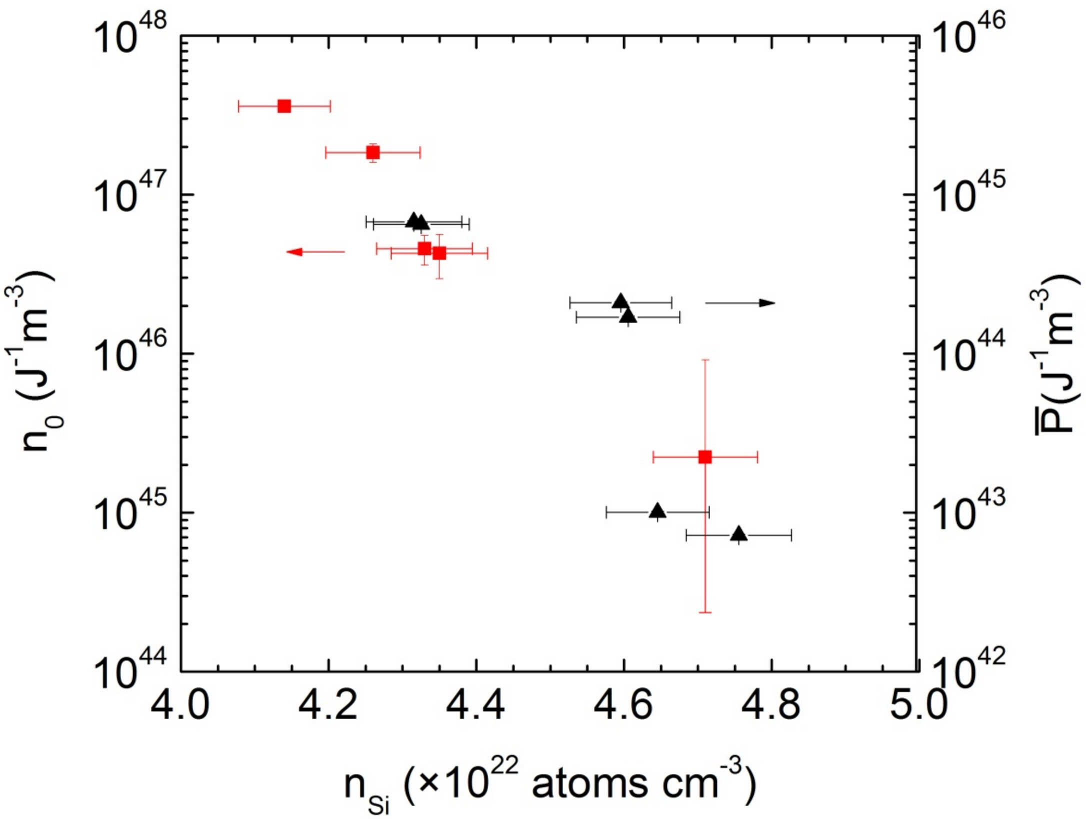
Like *C(T)*, Q^{-1} depends **on** $\boldsymbol{T_s}$

Temperature dependence of sound velocity (due to thermal activation of TLS) in e-beam a-Si



Δv/v is due to thermally activated relaxation of TLS dominating the quantum tunneling rate; low *Δv/v* for higher T_s consistent with low TLS density for higher T_s

TLS density from specific heat and internal friction are proportional to each other, *and depend on film density*

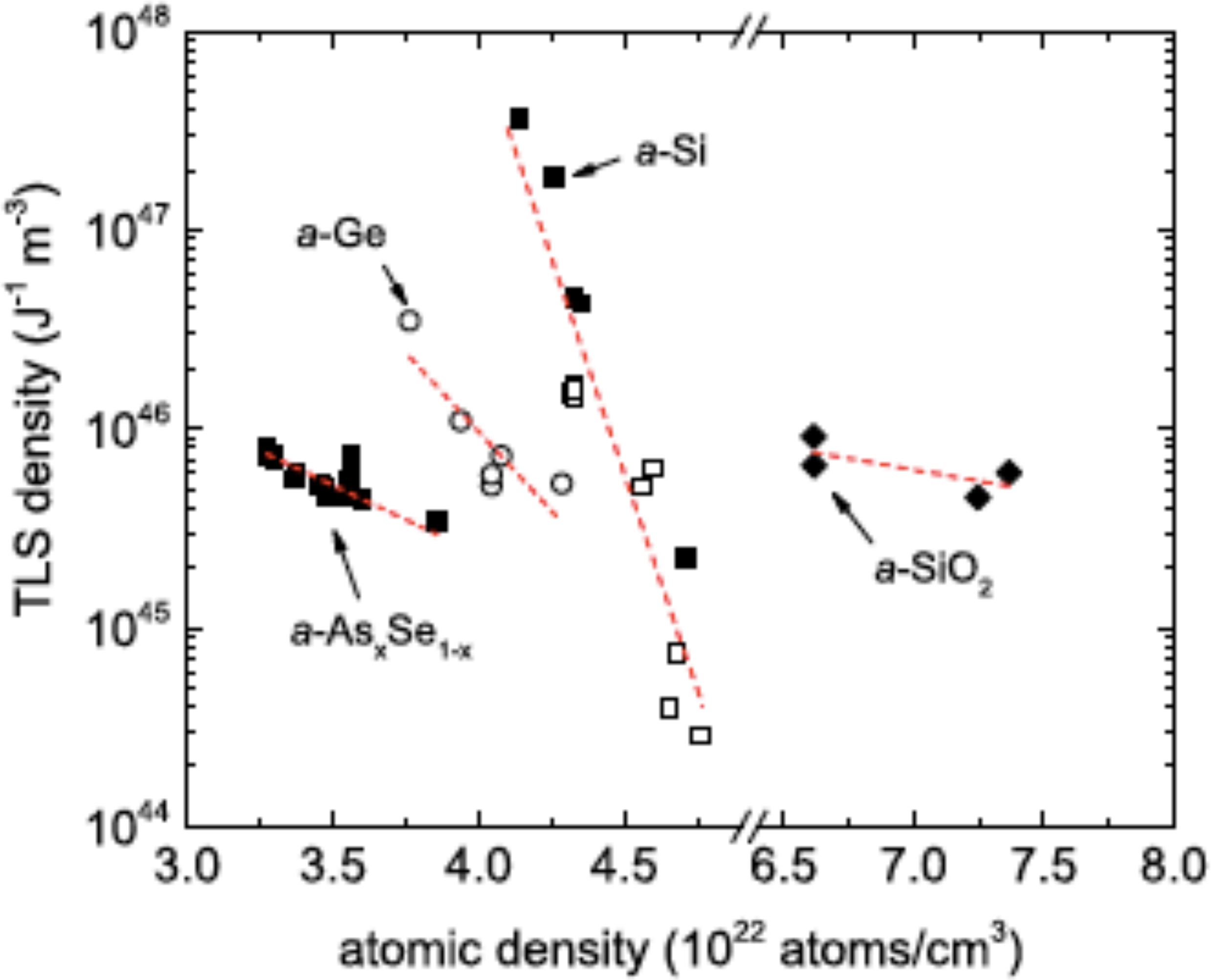


$$C = c_1 T + c_3 T^3$$
$$c_1 = \frac{\pi^2}{6} k_B^2 n_0$$
$$c_{ex} = c_3 - c_{Debye}$$
$$n_0 \propto \overline{P} \ln(4t/\tau_{min})$$

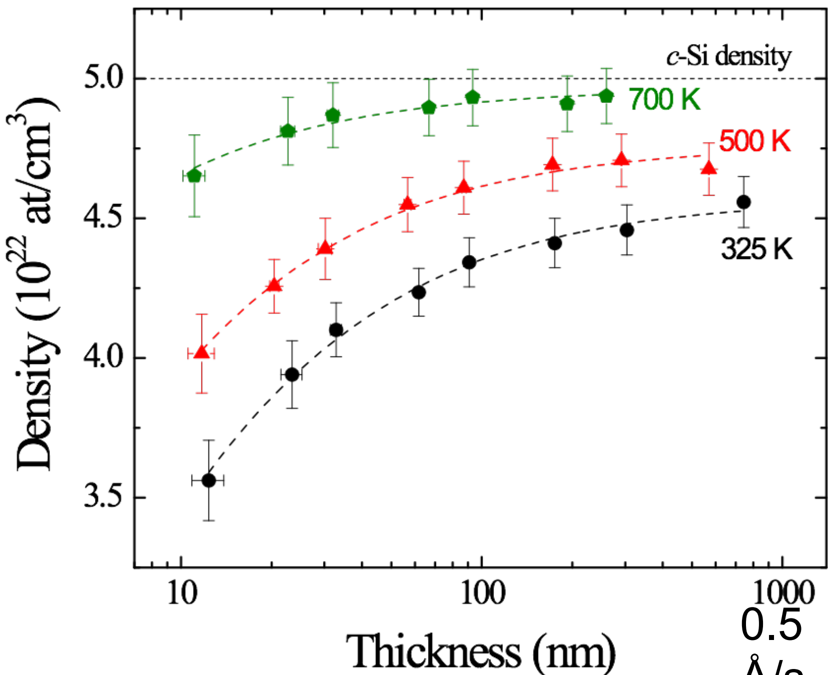
Crystalline Silicon:
$n_{Si}=5\times10^{22}$ cm^{-3}

- *n_o and $\overline{P}$ vanish as $n_{Si} \rightarrow n_{crystalline\ Si}$*
- $n_0/\overline{P}$ ~ 8 – similar to other glasses. n_o and $\overline{P}$ proportional in usual TLS model
  τ is time scale of C ~ 1 msec; τ_{min} is TLS minimum relaxation time ~10^{-9}sec
- TLS vanish with increasing n_{Si} – associated with low density regions/nanovoids??
- Correlation is over nearly 3 decades

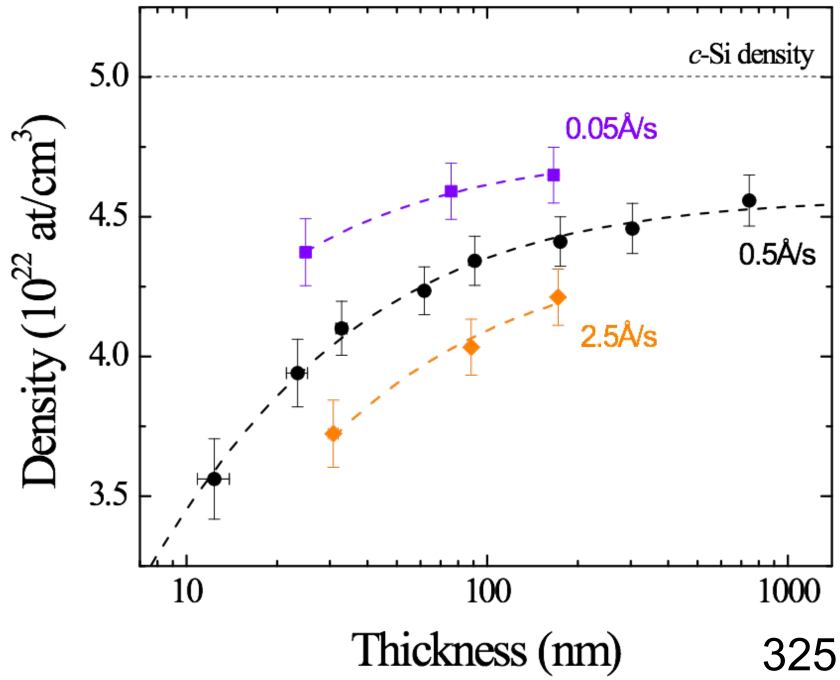
TLS (either n_o or $\bar{P}$) dependence on density seen in a range of amorphous materials



Growth parameters substantially modify film density and some measures of structure



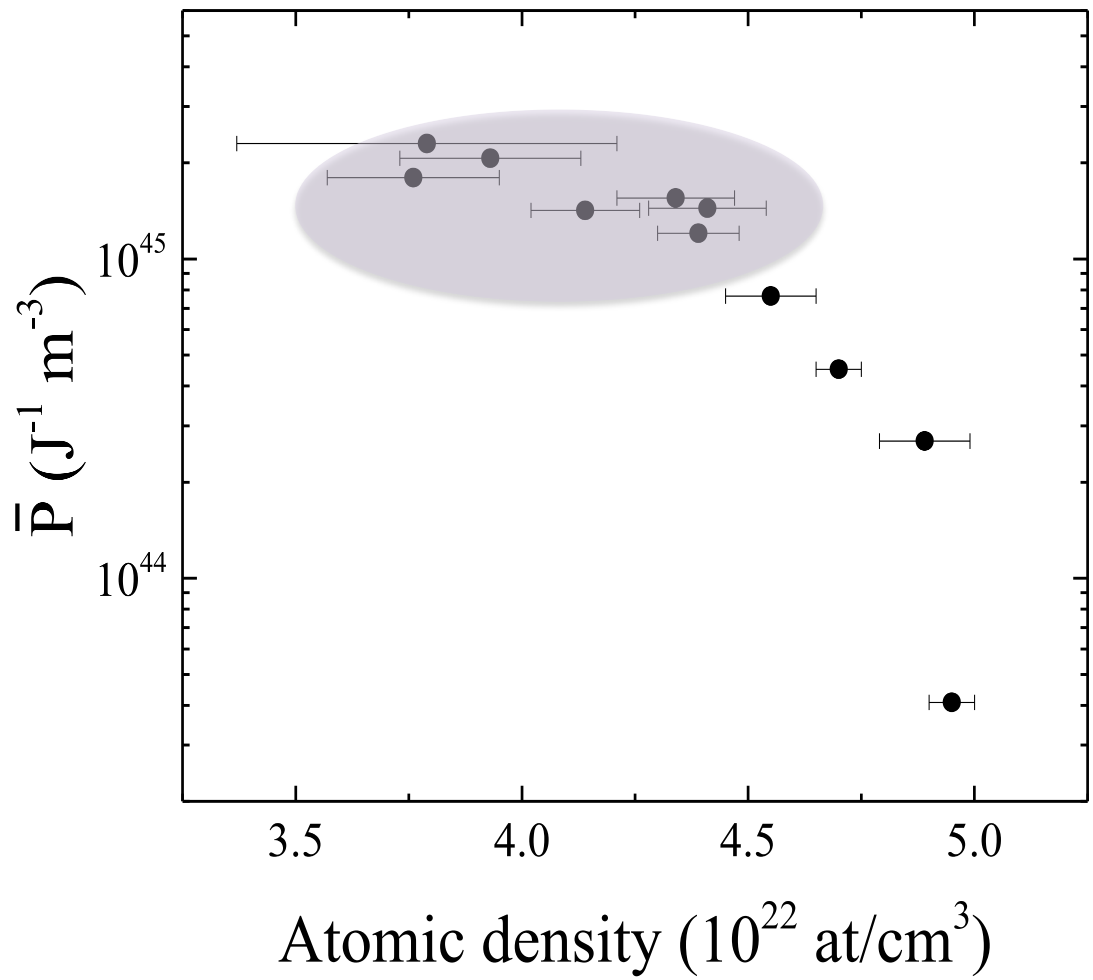
0.5 Å/s



325K

- Thickness, growth temperature, and growth rate affect film density and roughness; room T growth flattest for all thicknesses; higher T 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 or macroscale structure
- *Variations in bond angle disorder*, *medium range order, nanovoid size and number* (Raman, Fluctuation Electron Microscopy, positron doppler broadening spectroscopy)

More recent data on internal friction (IF) derived TLS density (specific heat still in progress)



Low density plateau shows that IF-derived TLS do not continue to increase with lower density samples

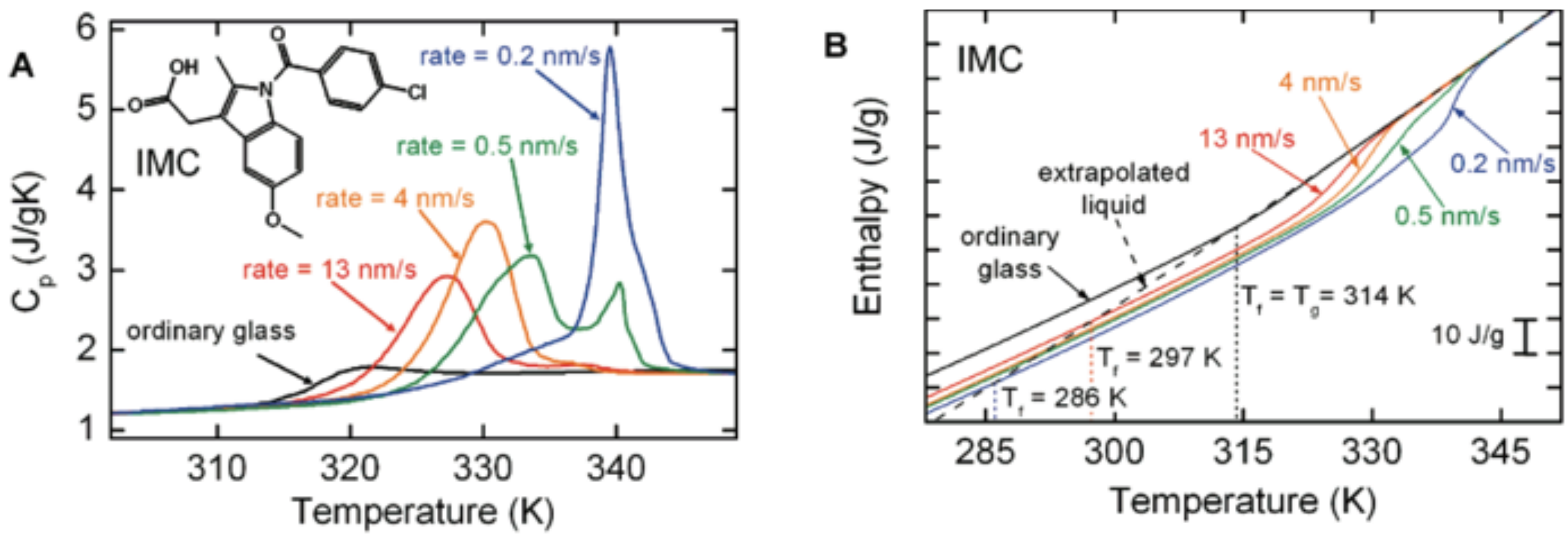
Two possible conclusions:

a) Larger nanovoids in the lower density (thinner, faster growth rate, lower growth temperature) do not create more TLS (then specific heat n_0 would also plateau)

b) TLS decouple from phonons in lower density films (then specific heat n_0 would continue to increase)

What does any of this have to do with ideality?

Vapor deposited films of indomethacin (IMC); ultrastable glasses



Heat capacities and enthalpies for vapor deposited glasses of indomethacin (IMC) with decreasing deposition rates; grown at "magic" $T_s \sim 0.8\ T_g$. As rates are lowered, T_f decreases, as does enthalpy, indicating a more stable glass.

These films also have low TLS!!

T. Perez-Castaneda, C. Rodriguez-Tinoco, J. Rodriguez-Viejo, M.A. Ramos, "Suppression of tunneling two-level systems in ultrastable glasses of indomethacin," PNAS 111(31), 11275 (2014)

M.D. Ediger, "Vapor-deposited glasses provide clearer view of two-level systems," PNAS 111(31), 11232 (2014).

Hypotheses re vapor deposited *a*-Si

Vapor deposited films of covalent materials such as *a*-Si or *a*-SiO_x have to date not been probed for ideality/ultrastability

The glass transition of a-Si has never been measured (because it can't be quenched) but theory suggests 850K (C.R. Miranda and A. Antonelli, J. Chem Phys 120, 11672 (2004).

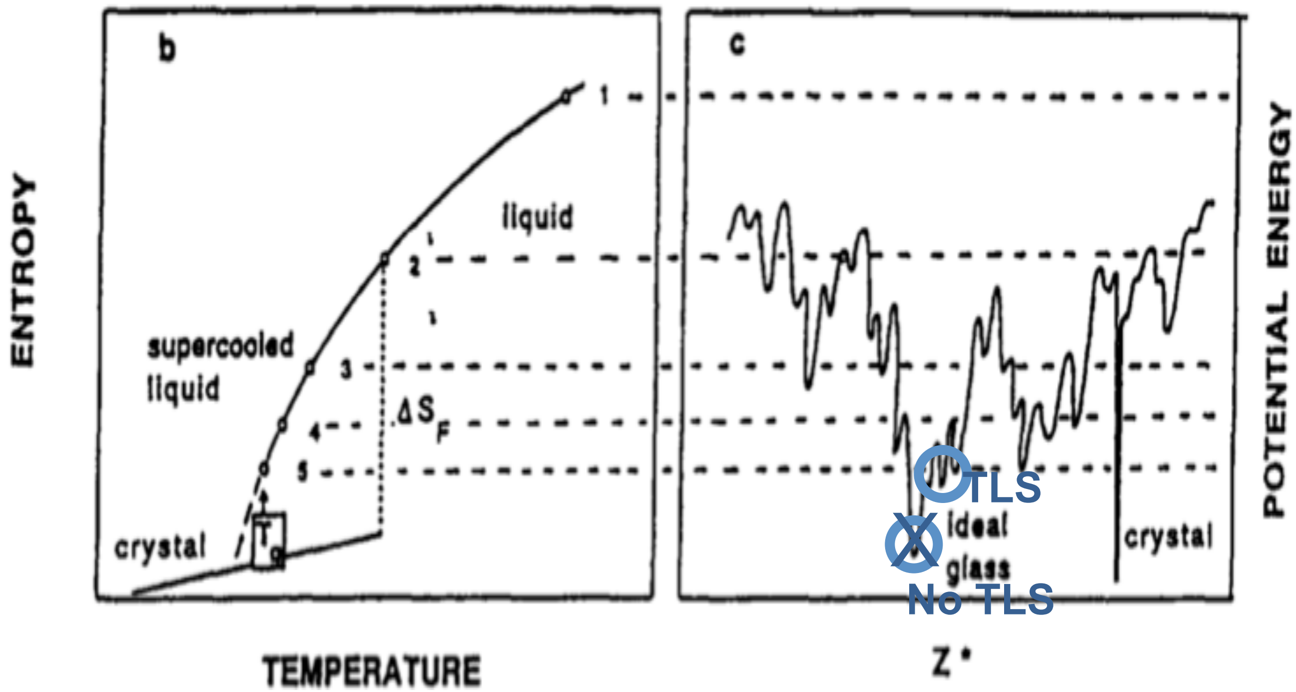
Our growth T to get low TLS is 673K ~ 0.8 T_g!! (similar to IMC work)

We have also seen effects of deposition rate and thickness on density, similar to IMC work; TLS measurements in progress on these other films

Hypothesize that ideal glasses are grown under these conditions and have high density/low defects = low TLS

Important role of Kauzmann temperature *T_K* , *connection to fragile/ strong glass character*

Energy landscape ideas for vapor deposition growth of amorphous materials



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

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.

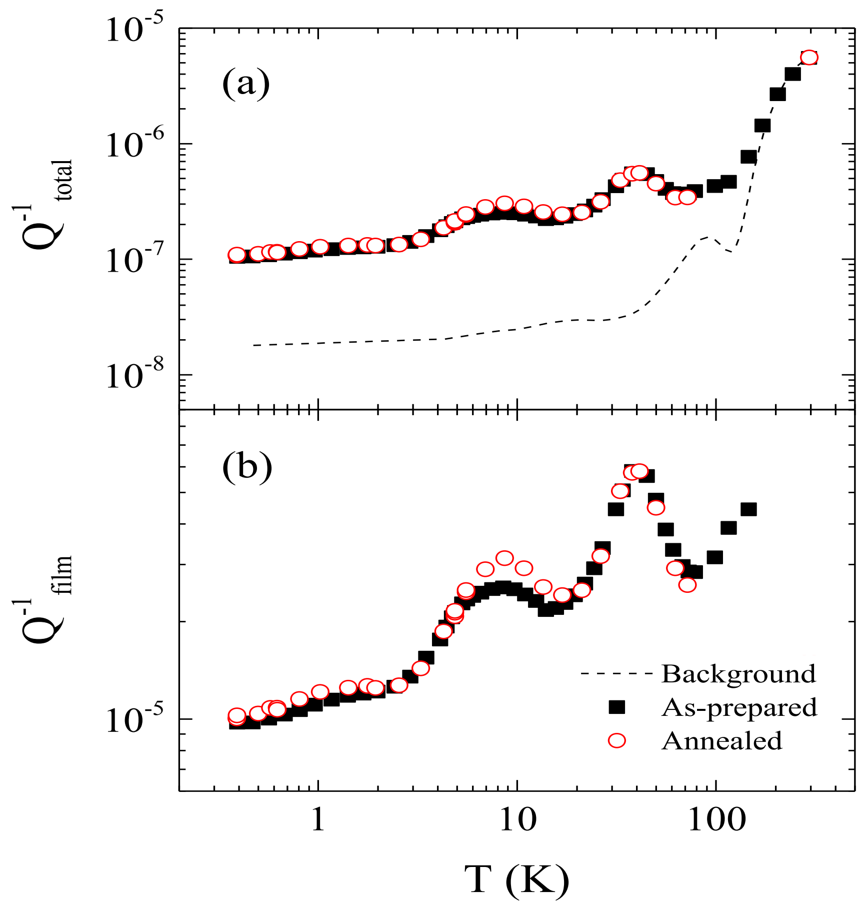
Hypothesis: vapor deposition offers a way to directly access low lying (ideal) glass state
Due to high atomic mobility at film growth surface despite being at low T.

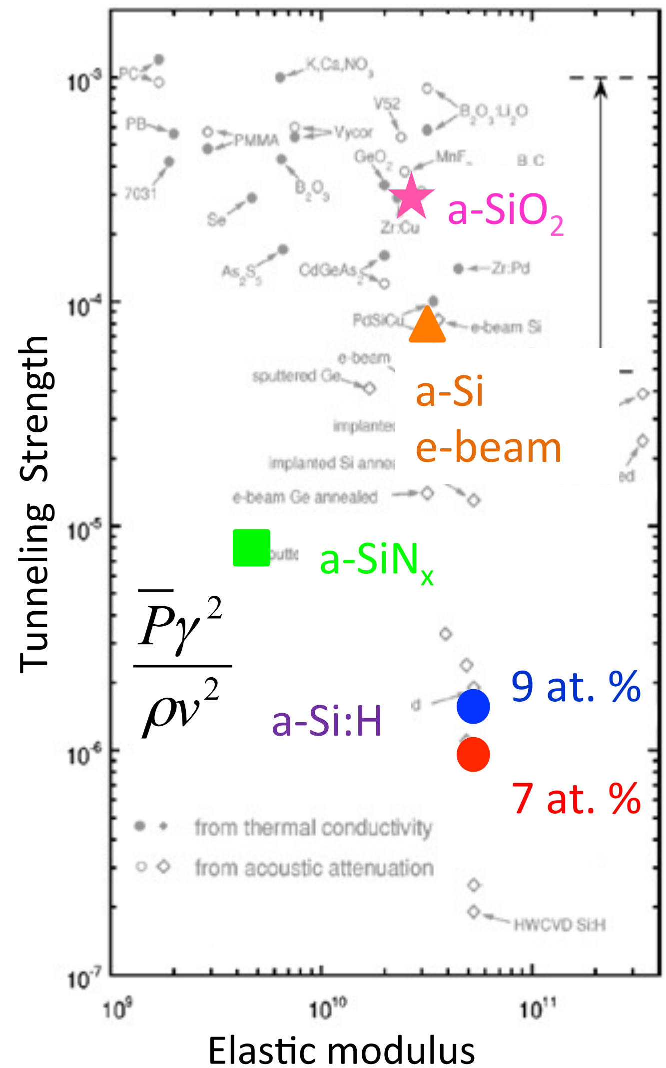
Hypothesis: Ideal glass has no nearby energy minima, so no TLS, unlike most other states

More comments on vapor deposition

- *NOT vapor quenching, contrary to common terminology*
- *Atoms land and have high mobility until buried*
- *Allows equilibration at some relatively low T (compared to T_g)*
- *Annealing further relaxes this structure but is ineffective compared to growth temperature – "best" amorphous films are grown at the highest possible temperature that doesn't permit crystallization*
- *Inherently anisotropic (in-plane vs out of plane); annealing eliminates this anisotropy*
- *Growing at elevated temperature stabilizes the structure against annealing-induced relaxation at that temperature, e.g. 200°C growth is very different than growth at 30°C followed by annealing at 200°C*

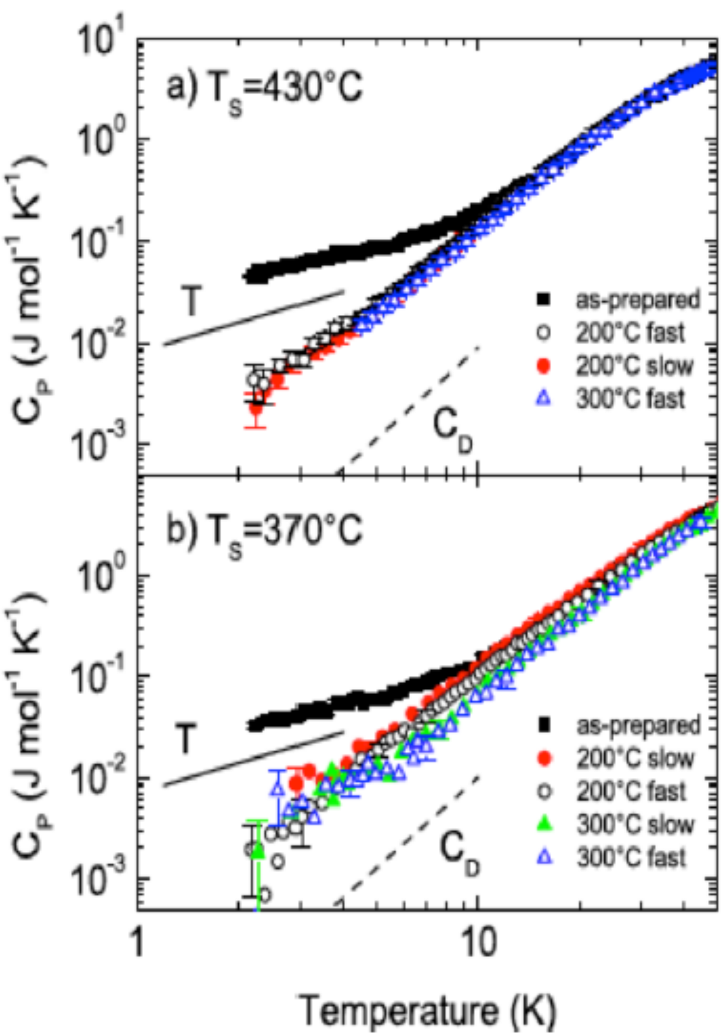
Amorphous Si:H (hot wire CVD – "device quality" – low dangling bond density ~10^{16} cm^{-3}) Internal friction measurements: low TLS

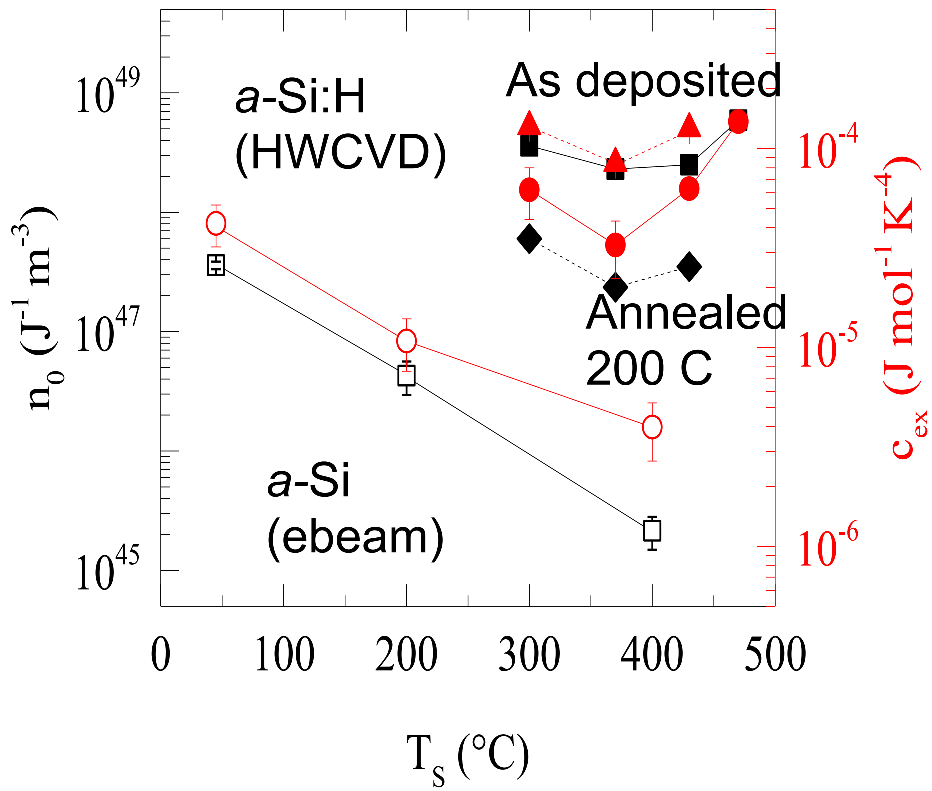




R.O. Pohl, *et. al.,* Rev. Mod. Phys. **74**, 991 (2002).
X. Liu Mater. Res. Soc. Symp. Proc. **989**, A22, (2007).

Amorphous Si:H (hot wire CVD – "device quality" – low dangling bond density ~10^{16} cm^{-3} Heat capacity high TLS

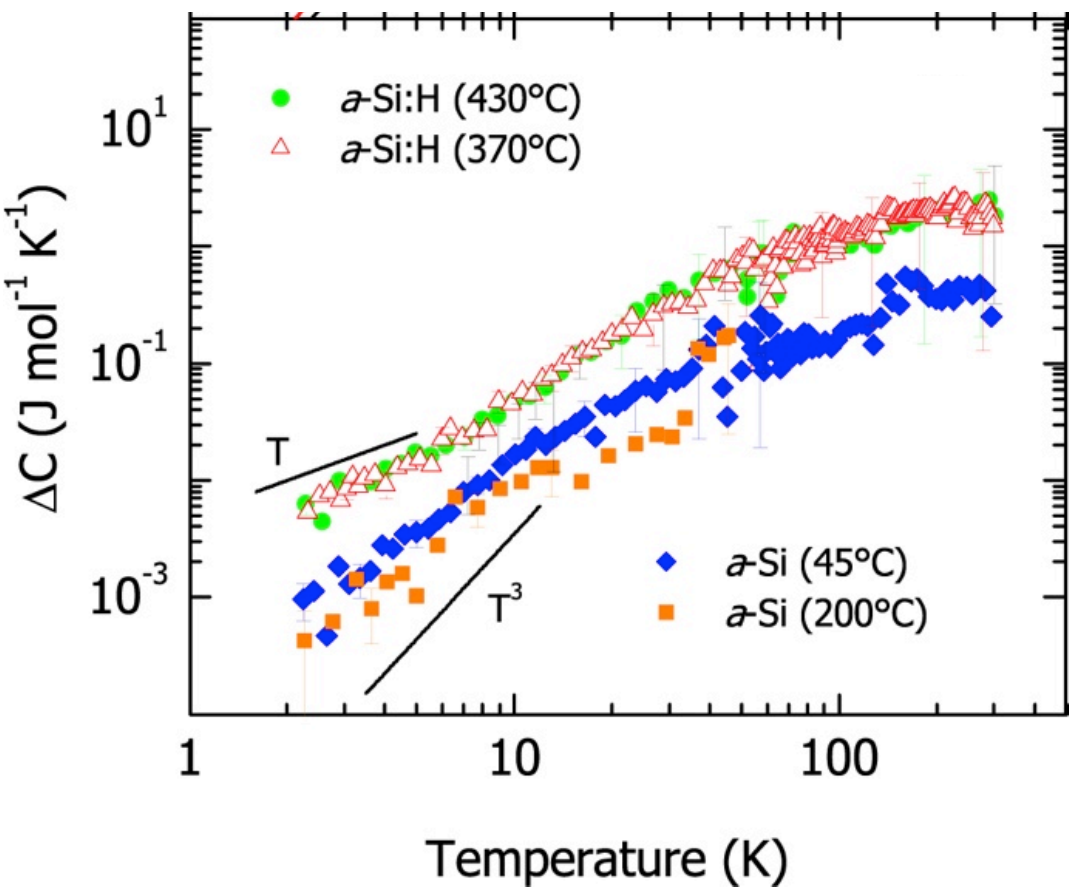




TLS due to H but not proportional to at.%H

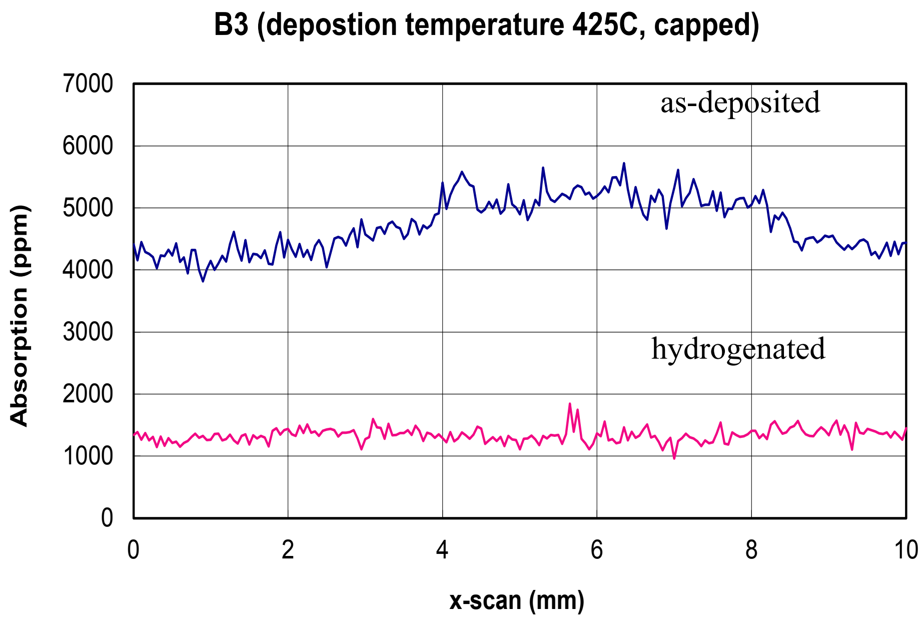
Low TLS as measured by IF, but very high TLS as measured by heat capacity – decoupling of TLS from acoustic waves (γ)

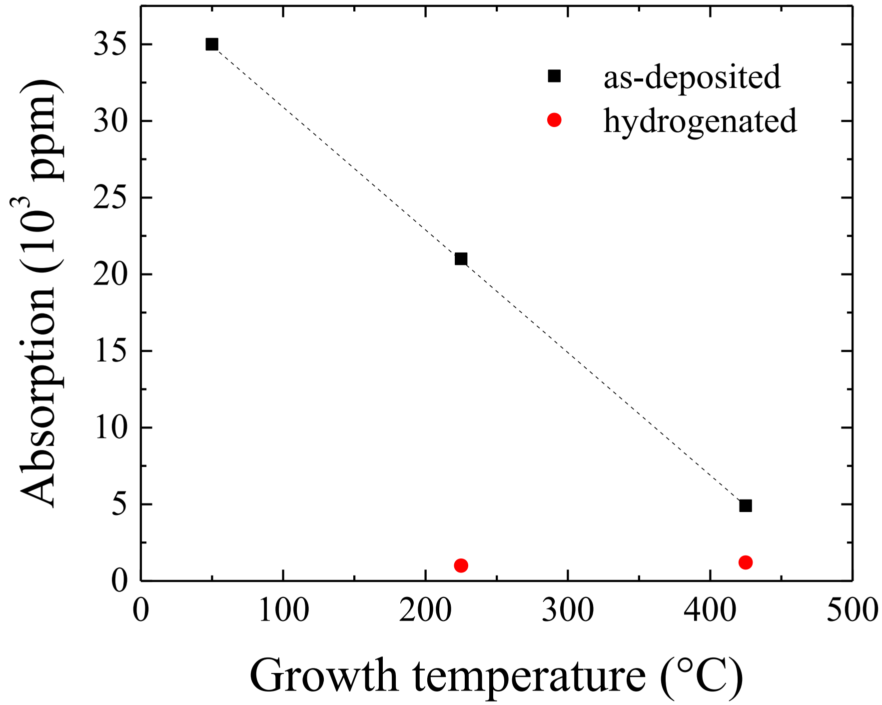
Reversible change in specific heat *C(T)* with light soaking, low T (150C) annealing – both *a*-Si and *a*-Si:H



- Effect larger in a-Si:H, but similar in a-Si
- Changes in n_o and c_{ex}, also $\overline{P}$, ***but direct proportionality is gone – change in γ ??***
- Associated with structural rearrangements, facilitated by H, but H not required
- NOT directly connected with dangling bonds, even though dangling bonds matter

Absorption measurements on *a*-Si

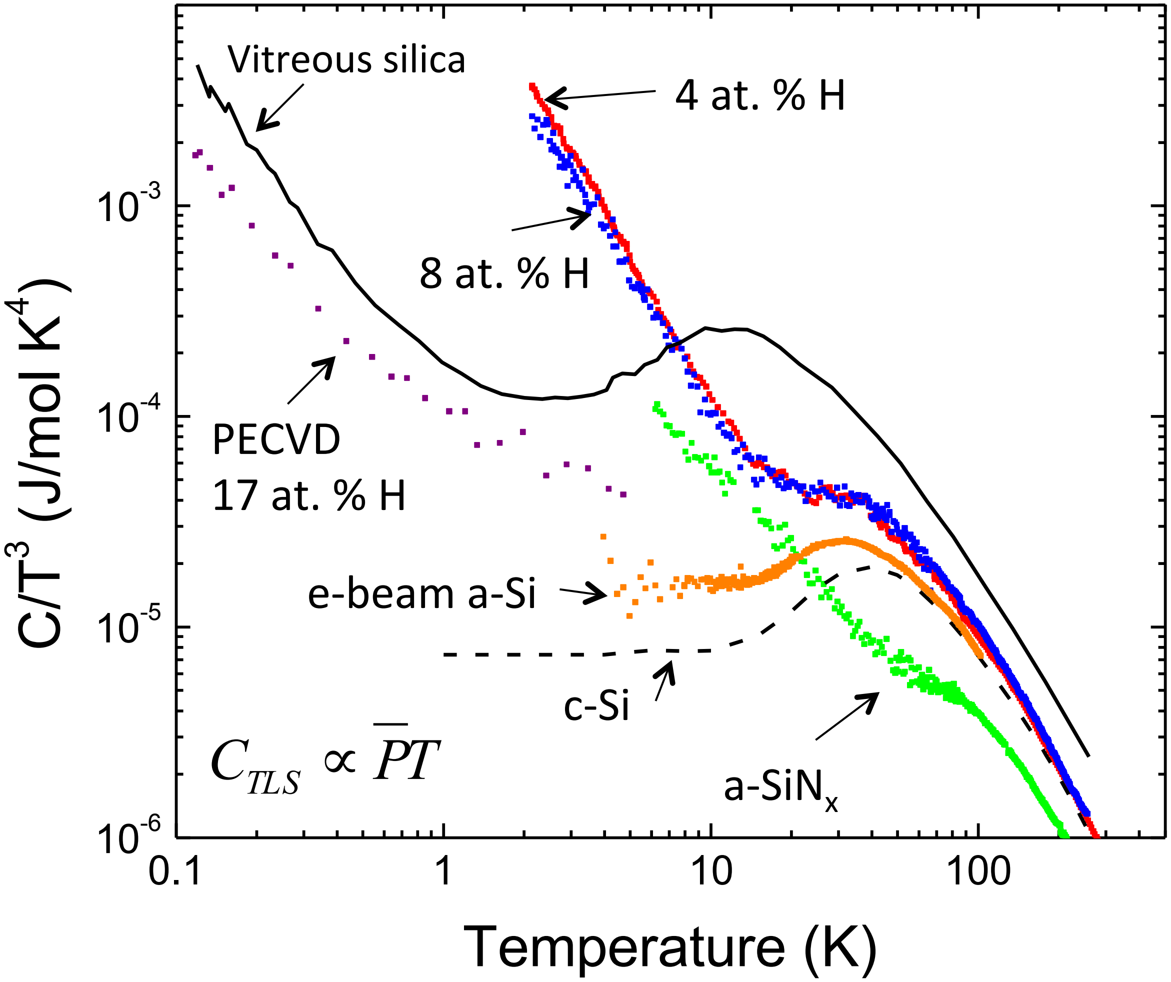


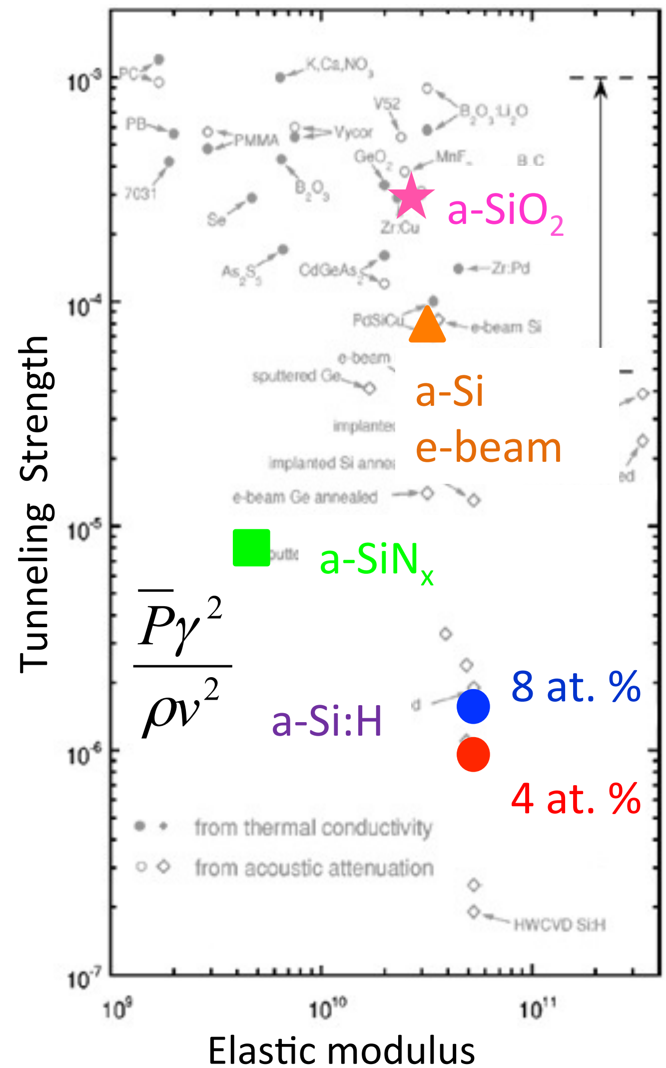


0.5 A/s, 500 nm + 20 nm capping (a-Al_2O_3)

Note: adding H to reduce absorption may CREATE TLS, even if Internal Friction does not see this

a-SiN_x by LPVCD: low TLS by IF, high by heat capacity; maybe influenced by H content (1-2 at.%)





a. D.R. Queen and F. Hellman, Rev. Sci. Instrum **80**, 063901 (2009).
b. B.L. Zink, R. Pietri, and F. Hellman, Phys. Rev. Lett. **96**, 055902 (2006).
c. R.C. Zeller and R.O. Pohl, Phys. Rev. B **4**, 2029 (1971).
d. Graebner *et al.,* Phys. Rev. B **29**, 3744 (1984).

R.O. Pohl, *et. al.,* Rev. Mod. Phys. **74**, 991 (2002).
X. Liu Mater. Res. Soc. Symp. Proc. **989**, A22, (2007).

a- Ta_2O_5 - techniques to reduce TLS: Growth T, Annealing, Dopants (Ti ,Zr)

Ti and Zr different valences than Ta. Why does this not disorder the amorphous structure, leading to increased TLS.

Possible explanations:

a) Their "incorrect" valences/different bonding enhance mobility by creating vacancies. Both surface and bulk.

b) Mixture of TiO2 and Ta2O5, with O connecting the structures. Effectively, Ti and Zr reduce the coordination number of the oxide units, and thereby increase the fragility hence increase TK hence makes growth a more effective tool

c) Only the phonon-coupling gamma has changed; the TLS themselves have not changed. They are measuring TLS by IF like measurements. (I plan to show the a-Si:H data as an example tomorrow of this effect).

a-Ta_2O_5 Hellman lab possible goals:

- Use growth T (up to 600 C) to produce lower Ts films
- Oxide films could be grown by three different techniques :
  - (1) direct e-beam evaporation of the oxide, with concurrent use of an *in situ* oxygen plasma source as needed.
  - (2) RF magnetron sputtering of the oxide
  - (3) DC reactive magnetron sputtering of Zr metal in an Ar/O2 plasma. Ti or Zr easily introduced
- Perhaps more work with Ti or Zr, to try to understand why these work
- Perhaps then look for other dopants?
- Perhaps multilayer coatings? Nanometer-scale thickness wherein the material susceptible to crystallization (typically the high-index material) is sandwiched between layers of a material with a high crystallization temperature (typically fused silica, the low-index material).

References:

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