Ideality and Tunneling Level Systems (TLS) in Amorphous Silicon Films

Frances Hellman
University of California, Berkeley

UCSD and UCB; *now U. Denver, *now Northrup Grumman

X. Liu, M. Abernathy, and T.H. Metcalf, Naval Research Laboratory

R.S. Crandall, E. Iwaniczko and Q. Wang, National Renewable Energy Laboratory

D.G. Cahill, D.Y. Li, UIUC

P. Voyles, U. Wisconsin

Marc Weber, Washington State U.

Junqiao Wu, UCB

M. Fejer, R. Bassiri, K. Prasai (Stanford, LIGO)

G. Valiente (Caltech, LIGO)
Thermodynamics of amorphous materials: Low T (<10K) specific heat – excess, non-$T^3$ specific heat

In amorphous (glassy) materials,

\[ C(T) = c_1 T + c_3 T^3 \]

below 10K

Linear term unexpected in an insulator

\[ c_3 > c_{\text{Debye}} \]

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

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

Two-Level Systems from neighboring energy minima in structural landscape:
- At low T, atomic structure tunnels between these $\gg \mu$eV energy splitting $E_{1,2} \pm \Delta$
- At higher T, atomic motion is thermally activated, requiring $k_B T \sim$ barrier height $V$

C.A. Angell, Physica D 107, 122 (1997)
Thermodynamics of amorphous materials:
Low T (<10K) specific heat – excess, non-$T^3$ specific heat

Temperature (K)

Amorphous and crystalline SiO$_2$

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 $n_0$ (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)

- 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 understood TLS – phonon coupling parameter $\gamma$, also the deformation potential
  - $Q_0^{-1} = \pi P \gamma^2 / 2 \rho v^2$
  - $\rho$ density, $v$ sound velocity

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

At room T, another technique (GeNS) used

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

---

bulk $a$-SiO$_2$ and other glasses

[Graph showing a variety of glasses with similar cryo behavior]

SiO$_2$ R.T. dip

“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. $\alpha$-SiO$_2$, PMMA, etc

High density of TLS

Early results $\alpha$-Si

Materials with TLS in range considered “outside” of glassy regime are all covalently bonded Si, Ge related, particularly $\alpha$-Si:H (low dangling bond density and low TLS) – is that the important variable?

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
- $P_{\text{base}} = 10^{-9}$ Torr
- $T_S = 45^\circ$ C - 400$^\circ$ C
- Growth rate $0.005 - 0.25$ nm/s
- Thickness from 10-400 nm
- $n_{\text{DB}} \sim 10^{19}$ cm$^{-3}$ (dangling bonds)
- $\rho = 2.02 - 2.2$ 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: $109.5^\circ \pm \delta$
- Bond angle disorder $\delta$ (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
Heat Capacity Measurement: nanocalorimetry

- 50 nm thick $\alpha$-SiN membrane
- Addenda: $2 \times 10^{-10}$ J/K at 2K
- Temperature: 2 - 300K
- Magnetic Fields: 0-8T
- $C_p$ - Small $\Delta T$ Technique
- In-situ rapid (pulse) annealing

\[ \Delta T = \frac{P}{K} \]

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

\[ \tau = \frac{C_p}{K} \]

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 $c_1 T + c_3 T^3$; both $n_0$ and $c_{ex}$ depend on $T_s$ but also on film thickness (unlike sound velocity)
Thin film amorphous Silicon: internal friction $Q^{-1}$ (and excess heat capacity) is strongly reduced (decades) by increased growth $T_s$

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

Crystalline Silicon:
\[ n_{\text{Si}} = 5 \times 10^{22} \text{ cm}^{-3} \]

- \( n_0 \) and \( \bar{P} \) vanish as \( n_{\text{Si}} \rightarrow n_{\text{crystalline Si}} \)
- \( n_0/\bar{P} \sim 100 \) – somewhat larger than expected 15 in usual TLS model with \( \tau \) the time scale of \( C \sim 1 \text{ msec} \), \( \tau_{\text{min}} \) the TLS minimum relaxation time \( \sim 10^{-9} \text{ sec} \)
- TLS vanish with increasing \( n_{\text{Si}} \) – associated with low density regions/nanovoids??
- Correlation is over 2+ decades
Excess specific heat $c_{ex}$ and $n_o$ also correlate over nearly 3 decades.

- Correlation between $n_0$ and $c_{ex}$ over nearly 3 decades – not independent phenomena
- TLS models do not discuss an excess $T^3$ term
- Model of glasses at low $T$ should include both terms
- Have also looked at a-Si:H. Large, correlated $n_0$ and $c_{ex}$ seen there, BUT not with $P$, which is low – perhaps due to low $\gamma$??

$\text{Crystalline Silicon: } n_{Si} = 5 \times 10^{22} \text{ cm}^{-3}$

$n_0$ and $c_{ex}$ vanish as $n_{Si} \rightarrow n_{cr}$

$n_0$ and $c_{ex}$ have same dependence on $n_{Si}$!
TLS (either $n_o$ or $\bar{P}$) dependence on density seen in a range of amorphous materials.
Temperature dependence of sound velocity (due to thermal activation of TLS) in e-beam a-Si

Δν/ν is due to thermally activated relaxation of TLS dominating the quantum tunneling rate; low Δν/ν for higher Ts consistent with low TLS density for higher Ts.
Comparison of sound velocity decrease with internal friction losses in relaxation regime

Line is $\beta = 0.5*Q_0^{-1}$ (in units of K$^{-1}$)

For $\alpha$-Si, $\beta \sim 0.5*Q_0^{-1}$ (in units of K$^{-1}$) over two decades
Growth parameters substantially modify film density

- Thickness, growth temperature, and growth rate affect film density
- 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, short range order or macroscale structure; some variation in bond angle disorder. Likely associated with medium range order and/or nanovoids
- Nanovoids seen in positron doppler broadening spectroscopy, not in HRTEM
Amorphous Silicon losses: thickness also matters

Thin films are more lossy than thick films (not per volume, absolute)
Correlates with atomic density differences (thick films are denser)
Annealing reduces loss, but not much (at low T) compared to growth T effects
Recent data on internal friction (IF) derived TLS density

Recent data on internal friction (IF) derived TLS density

Low density plateau suggests 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 heat capacity would continue to increase)
Recent data on internal friction (IF) derived TLS density: some specific heat (rest still in progress)

Low density plateau in $P$ 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) – one data point supports this low $\gamma$ idea
Amorphous Si:H (hot wire CVD – “device quality” – low dangling bond density $\sim 10^{16}$ cm$^{-3}$

$C_p$ Schottky anomaly in as-deposited, gone on annealing at 200C (H mobility)

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

Low TLS as measured by IF including $dv/dT$, and unchanged on annealing, but very high TLS as measured by heat capacity; no/P $\sim 10^4$, completely outside TLS models suggests TLS decoupling from acoustic waves ($\gamma$)
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!!


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.
Energy landscape ideas for vapor deposition growth of amorphous materials

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

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


Does this lower losses at all T, for all materials?
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.
Strong-fragile glass classification: strongly affects $T_K$


Fragile glass-formers have a high density of minima in the energy landscape just above the glass transition, hence a large number of locally rearrangable configurations would get frozen in, causing a high density of TLS.
Random first order transition (RFOT) theory predicts divergence of correlation length $\xi$ of supercooled liquid as $T \rightarrow T_K$

Also predicts TLS density $\sim \xi^{-3}$, supporting the hypothesis that TLS density if highly suppressed for deposition $T$ near $T_K$

But, surface diffusion needs to be fast near $T_K$, argues $T_K$ needs to be $\sim T_g$, which means fragile glasses like $a$-Si and indomethacin, and not $a$-SiO$_2$ which has a high density of low energy floppy modes and a low $T_K$

Recent work on $a$-SiO$_2$ (silica) and $a$-Ta$_2$O$_5$ (tantala) show increasing atomic density with increasing growth temperature (similar to $a$-Si); TLS measured by internal friction is reduced significantly by increasing growth $T$, also in $a$-Al$_2$O$_3$ (alumina; Matt Abernathy NRL) but not the 2+ orders of magnitude of $a$-Si. BUT, have not yet grown at 0.85 $T_g$ ($T_g$ high)
Comments 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 – the “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. Se) and Si-O-Si bonds in SiO$_2$

• Test with amorphous SiO$_2$ and particularly Se$_x$Ge$_{1-x}$ alloys!!

• Can this be connected to jamming theory? Test with *overdense* glasses, which should be higher in the energy landscape with higher TLS.

• What is $c_{ex}$ and how is it connected to TLS?

• How does $\gamma$ as deformation potential (which varies from TLS site to site) compare/translate to $\gamma$ as TLS-phonon coupling parameter, particularly when TLS are small compared to phonon wavelength
Conclusions

• Tunneling/two level states (TLS) are found only in lower density a-Si
  – Linear and excess T^3 term in C(T), low T plateau (P) in internal friction Q^-1
  – Over 2 decades of variation in each correlate with atomic density n_{Si}
  – Independent of the elastic properties of the material
  – Lower density films associated with nanovoids, measured by positron DBS
  – POSSIBLE decoupling of acoustic waves from TLS at low density; need C_p(T)

• Excess T^3 term increases with increasing TLS (n_0 and P)
  – Correlation of n_0 and c_{ex} need to be included in TLS models

• Growth temperature dependence argues for connection to ideal glass
  – T_s ~ 0.8 T_g; high stability of material against annealing-induced relaxation
  – Measurements of excess entropy, enthalpy needed

• Need to look at other vapor deposited materials, including a-SiO_2 and Ge-Se