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Equilibrium mobility in IGZO TFT: Existence of the intermediate boolchand phase?

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IGZO and a-Si:H: A topological constraint theory view

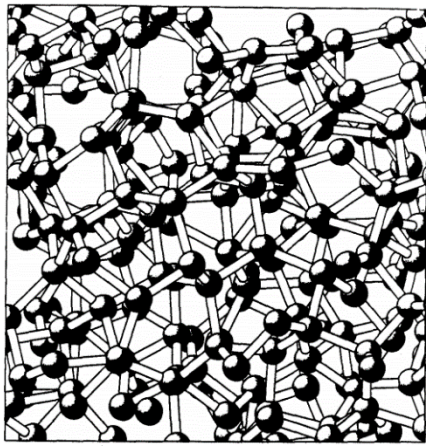
D.G.Ast

Cornell U

IGZO is an oxide glass that is replacing a-S-:H in TFTs

Modern glass theory analyses glass network as truss network

It all goes back to the Eifel Tower and Maxwell…



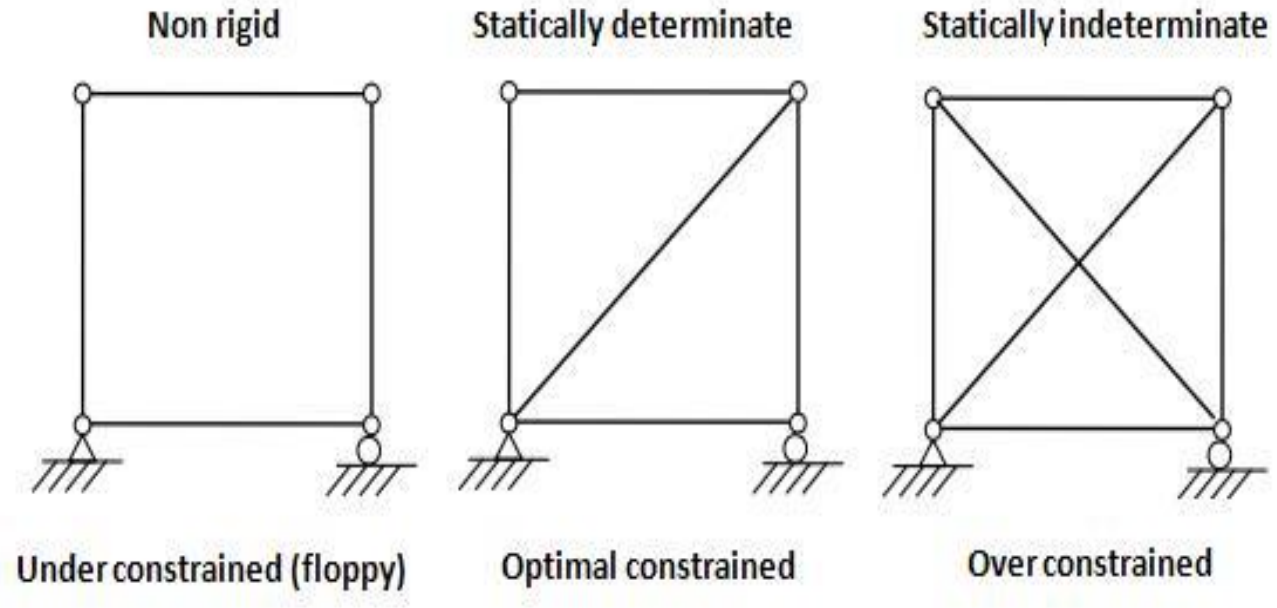
Truss Network

Glass Network

Nodes	<->	Atoms
Rigid Nodes	<->	Bond Bending
Bars under tension	<->	Bond stretching

After matthieu.micoulaut@upmc.fr

Coordination and rigidity



Glass forming is maximized when the system is optimally constraint.

Such networks are also termed to be isostatic

The first statistical analysis of truss networks
was carried out by J. Clerk Maxwell 151 years ago

From the publication in Phil Mag

L. *On the Calculation of the Equilibrium and Stiffness of Frames.* *By* J. Clerk Maxwell, *F.R.S., Professor of Natural Philosophy in King's College, London**.

THE theory of the equilibrium and deflections of frameworks subjected to the action of forces is sometimes considered as more complicated than it really is, especially in cases in which the framework is not simply stiff, but is strengthened (or weakened as it may be) by additional connecting pieces.

I have therefore stated a general method of solving all such questions in the least complicated manner. The method is derived from the principle of Conservation of Energy, and is referred to in Lamé's *Leçons sur l'Elasticité*, Leçon 7me, as Clapeyron's Theorem; but I have not yet seen any detailed application of it.

If such questions were attempted, especially in cases of three dimensions, by the regular method of equations of forces, every point would have three equations to determine its equilibrium, so as to give $3s$ equations between e unknown quantities, if s be the number of points and e the number of connexions. There are, however, six equations of equilibrium of the system which must be fulfilled necessarily by the forces, on account of the equality of action and reaction in each piece. Hence if

$$e = 3s - 6,$$

the effect of any external force will be definite in producing tensions or pressures in the different pieces; but if $e > 3s - 6$, these forces will be indeterminate. This indeterminateness is got rid of by the introduction of a system of e equations of elasticity connecting the force in each piece with the change in its length. In order, however, to know the changes of length, we require to assume $3s$ displacements of the s points; .....

On the calculation of the equilibrium and stiffness of frames
J. Clerk Maxwell FSR
Phil Mag 27, 1864

Thorpe, Boolchand, Phillips extension of truss theory to atom

The average of constraints , n , is linked to average valence <r > :

$$\langle r \rangle = \sum_i x_i r_i$$

X_i is the atomic fractions, and r_i the valences

$$n = \frac{\langle r \rangle}{2} + (2\langle r \rangle - 3)$$

In a 3 D network , n= 3 , and solving for <r > yields

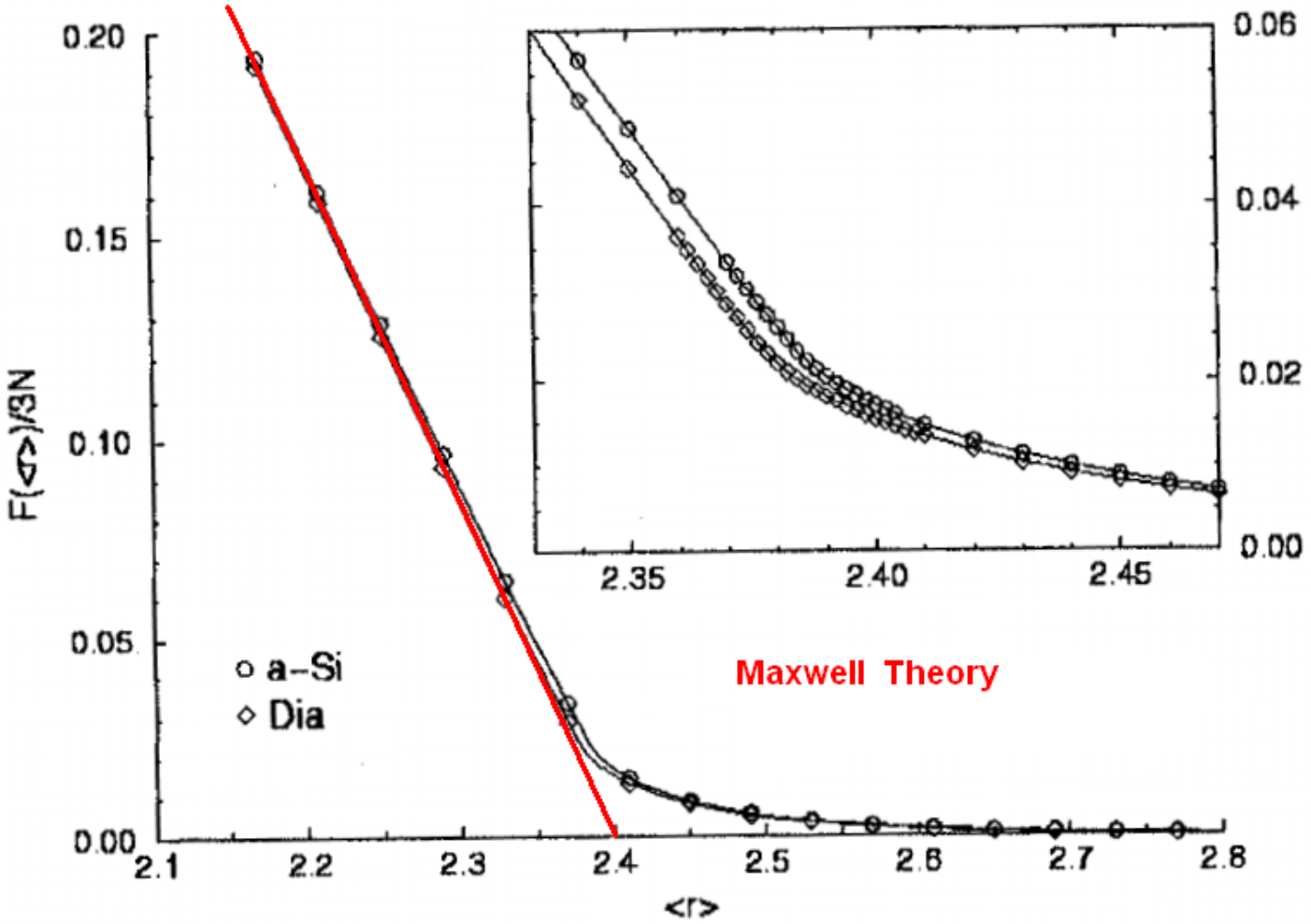
$$\frac{\langle r \rangle}{2} + (2\langle r \rangle - 3) = 3$$

$$\langle r \rangle = 2.4$$

Summary

When beams are replaced with bonds and nodes with atoms, analysis shows that in three dimensions networks are optimally constrained at the average atomic coordination of r=2.4 , a value first derived by Phillips in 1979

Numerical calculation using percolation theory to locate the floppy to rigid transition back up the topologically derived value

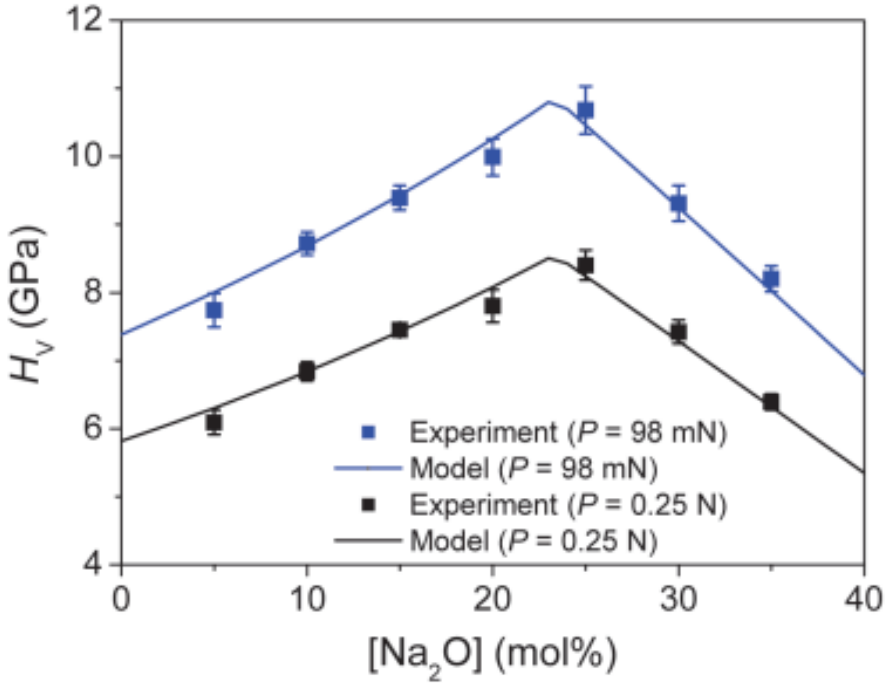


Fraction of floppy modes as function of <r> . Red line : Maxwell Theory, black lines numerical simulation s using the pebble game, for a-Si and a-diamond models (from Thorpe, Maxwell solution added)

Generic Rigidity Percolation: The pebble game D.J. Jacobs, M.F. Thorpe PRL **75**,22, 4541 (1995)

Topological Constraint Theory quantitatively calculates glass properties as function of composition that agree with experiment.

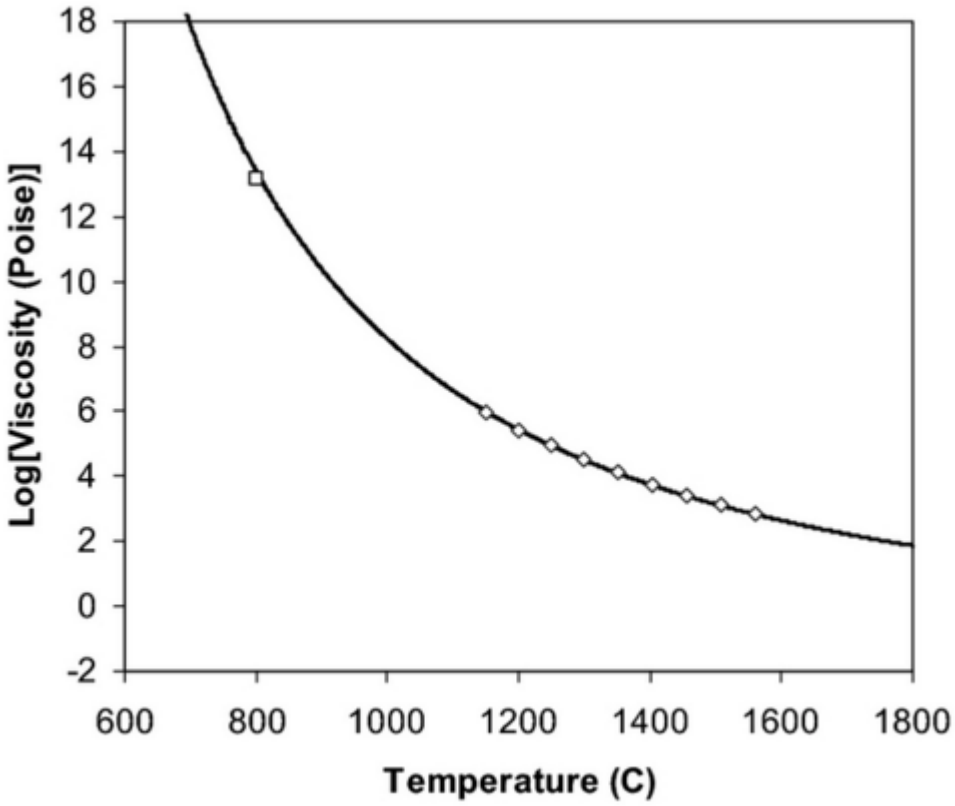
Hardness



Predicted versus measured Vickers hardness (H_V) for $xNa_2O{\cdot}10CaO{\cdot}(89 - x)B_2O_3{\cdot}1Fe_2O_3$ (mole percent) glasses at loads (P) of 98 millinewtons and 0.25 newtons, solid lines represent model predictions using temperature-dependent constraint theory. Reproduced from Smedskjaer et al.[28]

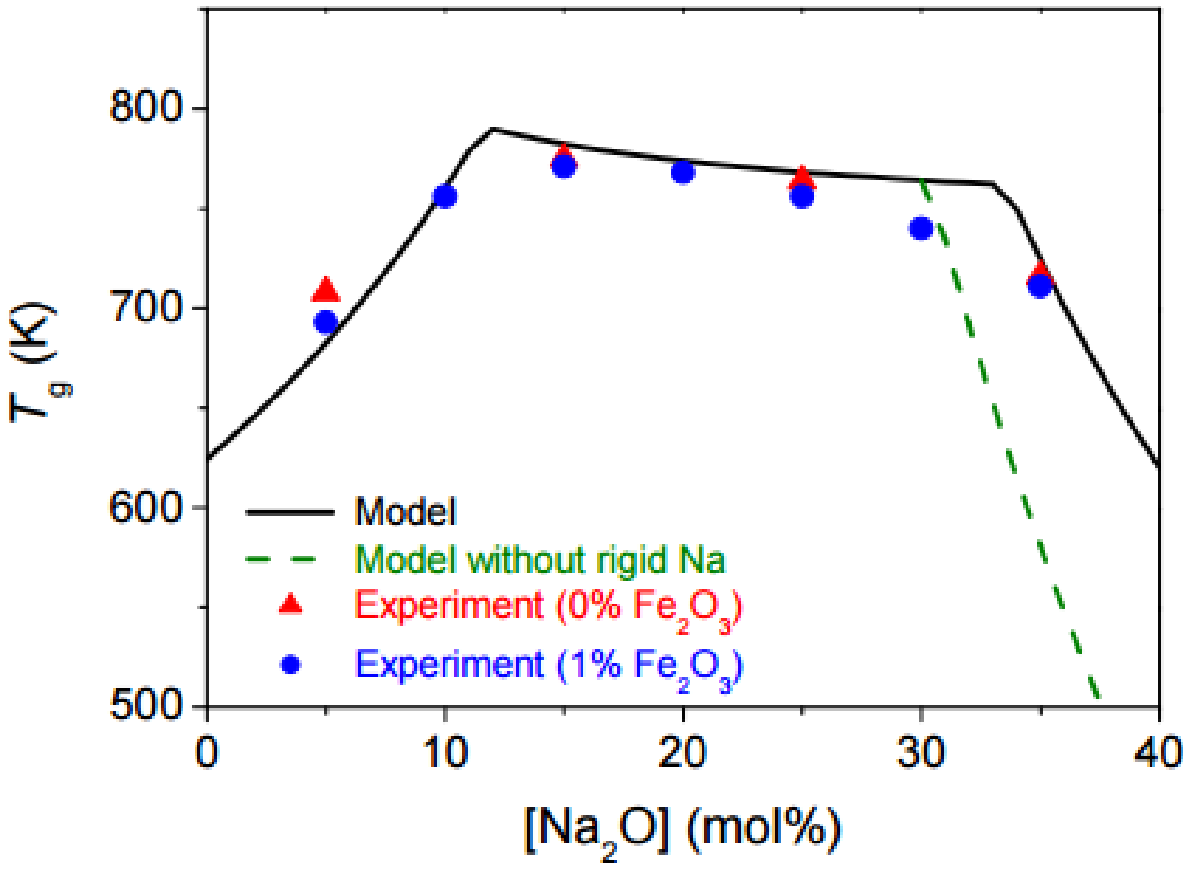
From Mauro, calculated with temperature dependent constraint theory

Viscosity



Example of predicted viscosity versus temperature curve for an alkaline earth aluminosilicate composition. The prediction was made with the glass composition as the only input to the model.

Mauro et al., Applied Glass Science , 6 December 2012



Experimental and calculated glass transition temperature in Calcium Borate Glass

IGZO SEEN AS AN OXIDE GLASS

$InGaZnO_4$ $r = 2.286$

But film composition from such a target are invariably short of Zn. Our measured compositions of films corresponds to

$r \approx 2.30$

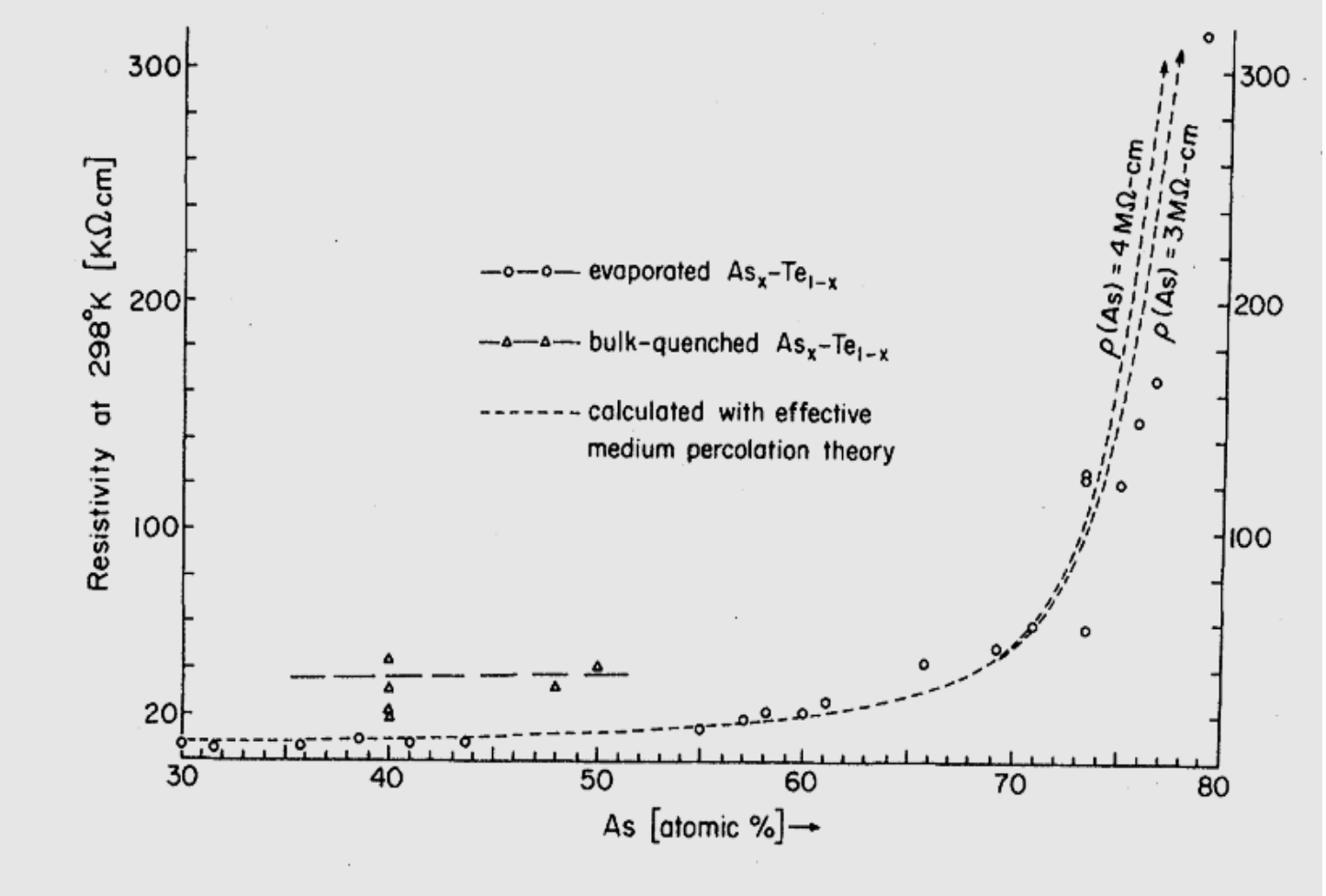
Once can speculate that Zn sticking coefficient is function of <r> with Zn less firmly bonded in the floppy regime, “dialing up” the composition towards the isostatic value of 2.4

Electrical conduction in non-oxide glass

"Rigidity percolation is similar conceptually to the more familiar connectivity percolation except that instead of demanding a connected pathway across the sample, the more stringent condition that the connected pathway is also rigid is required"

Thorpe MF, Stinchcombe RB. 2014 Two exactly soluble models of rigidity percolation. Phil. Trans. R. Soc. A 372: 20120038.

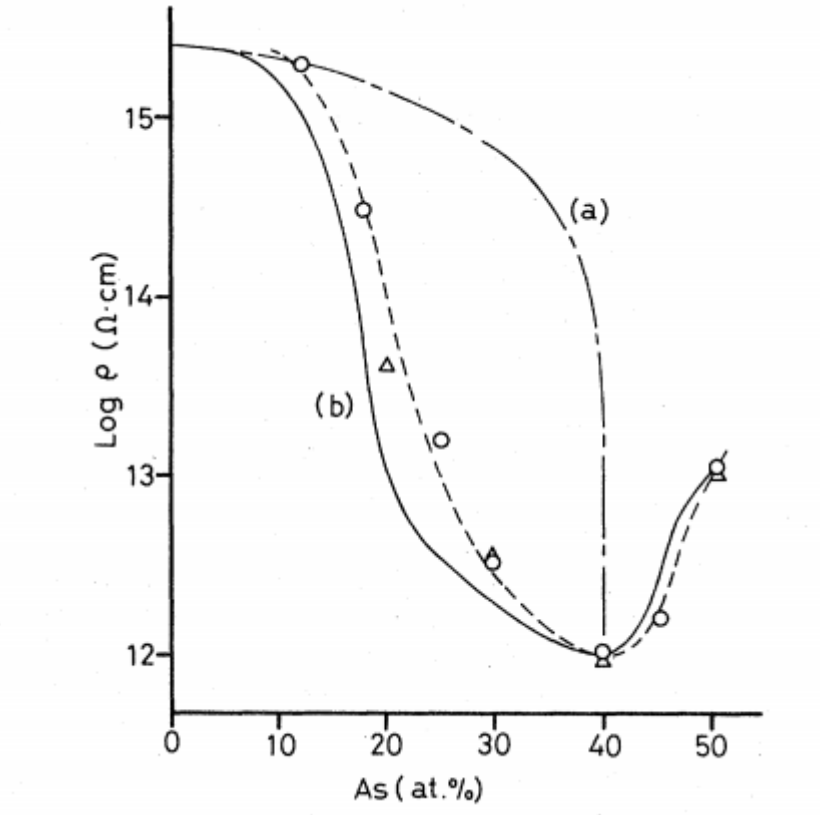
Effective Medium Percolation Theory (EMPT) first was used in 1974 to calculate the conductivity of chalcogenide semiconductors as a function of composition



Resistivity of As_x-Te_{1-x} as function of composition
The dashed line is the fit with effective medium theory

Ast Phys. Rev. Lett. 1974

Extension to As-Se glasses



Variation of the room-temperature resistivity in the As-Se system

-------- dashed line : Random mixture EMPT

_____ solid line : EMPT mixture of Se, + As_2Se_3 (As < 40%) and As_2Se_3 + As_4Se4 clusters (As > 40%) using ρ of Se, As_2Se_3, As_4Se4

Shimakawa and Shoji Nitta Phys. Rev. B 1978

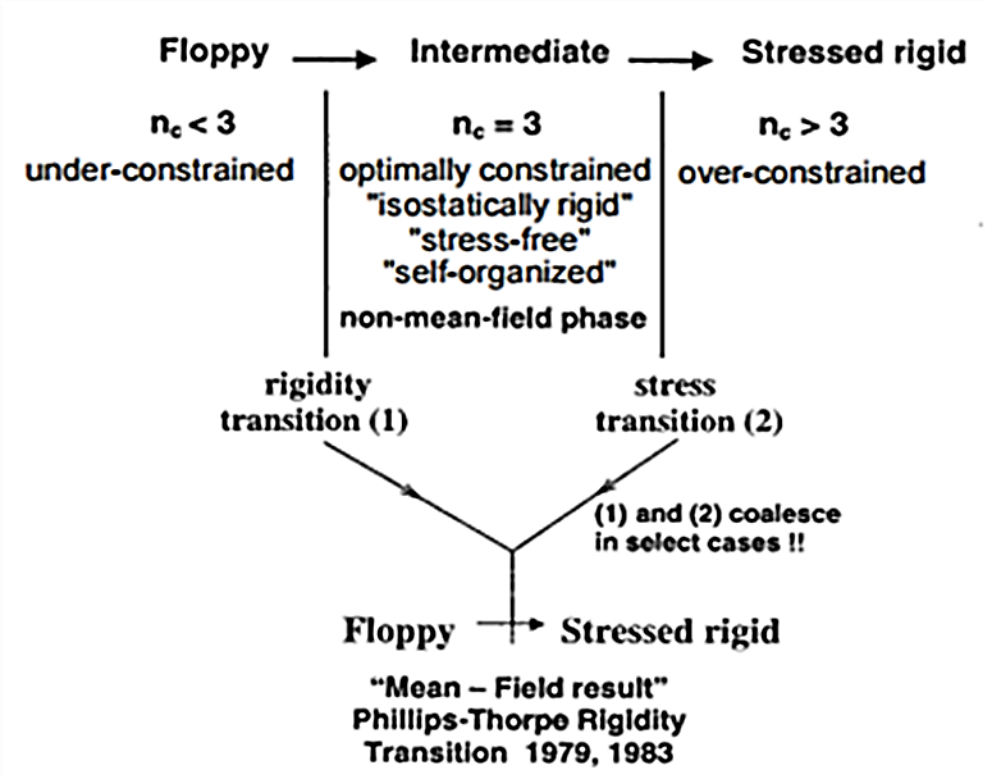
Historically, the EMPT cluster models to fit the electrical properties of chalcogenide glasses preceded the network models but the two fields never linked up

From the semiconductor point of view what matters is

- Network Stress (stressed bonds <-> traps)
- Network stability (stable electronic properties)

To consider above , we need to move to the intermediate phase concept introduced by Boolchand

The intermediate phase

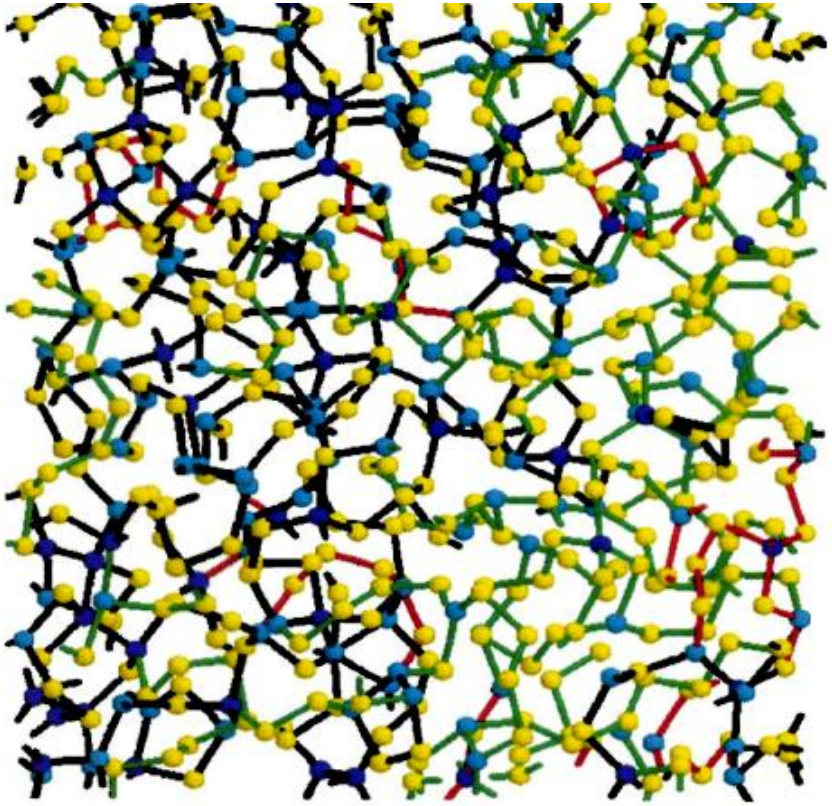


The ideal network ($r = 2.4$, $n_c = 3$) has an existence range

Deviations from the ideal network are accommodated by "defects"

Useful to think of intermediate phase as being "phase separated"

"Covalent glass near the phase transition at a mean coordination r= 2.4
green bonds are hinges, the red bonds isostatic and the black bonds hyperstatic"

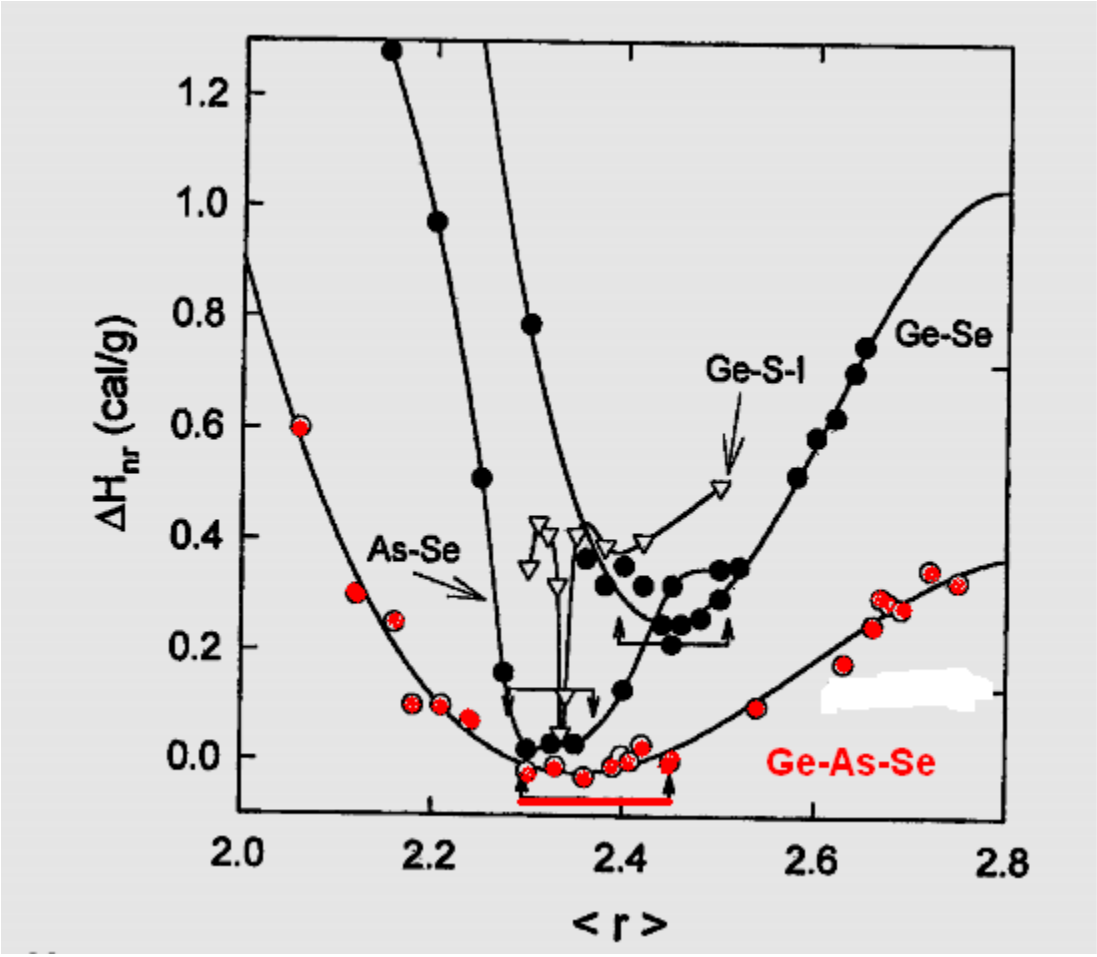


The blue, green and red clusters => can *conceptually* be seen as an incipient phase separation on the intermediate Length Scale of glass

Green: floppy Red: Stress free Black : Over constrained

From Networks, Flexibility and Mobility by Thorpe

The intermediate phase was discovered by Boolchand using MDSC



Non-reversing heat, ΔH_{nr} as a function of mean coordination number <r> for four different glass systems. (After Boolchand)

The intermediate phase is centered at 2.36 and with a range of~ +/- 0.06

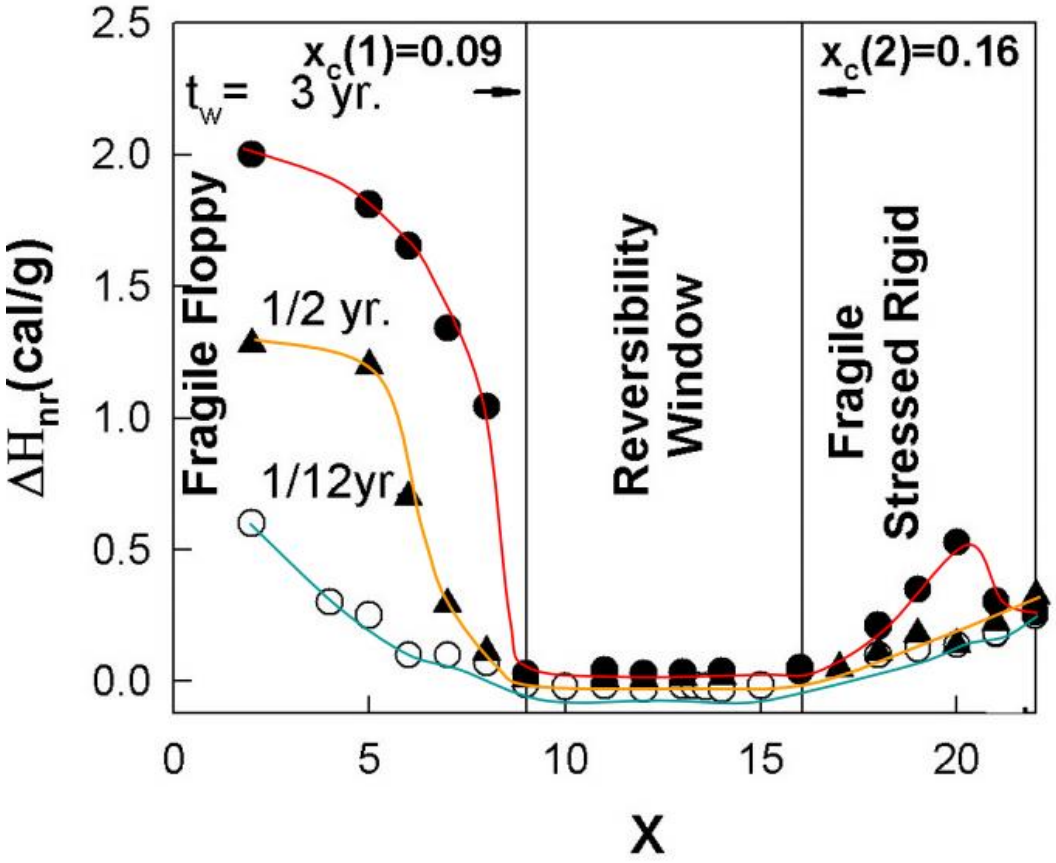
The intermediate phase is *a meta-stable* phase.

Although not crystal , the network is in its lowest energy state.

The lowest energy state *is stress free* – isostatic.

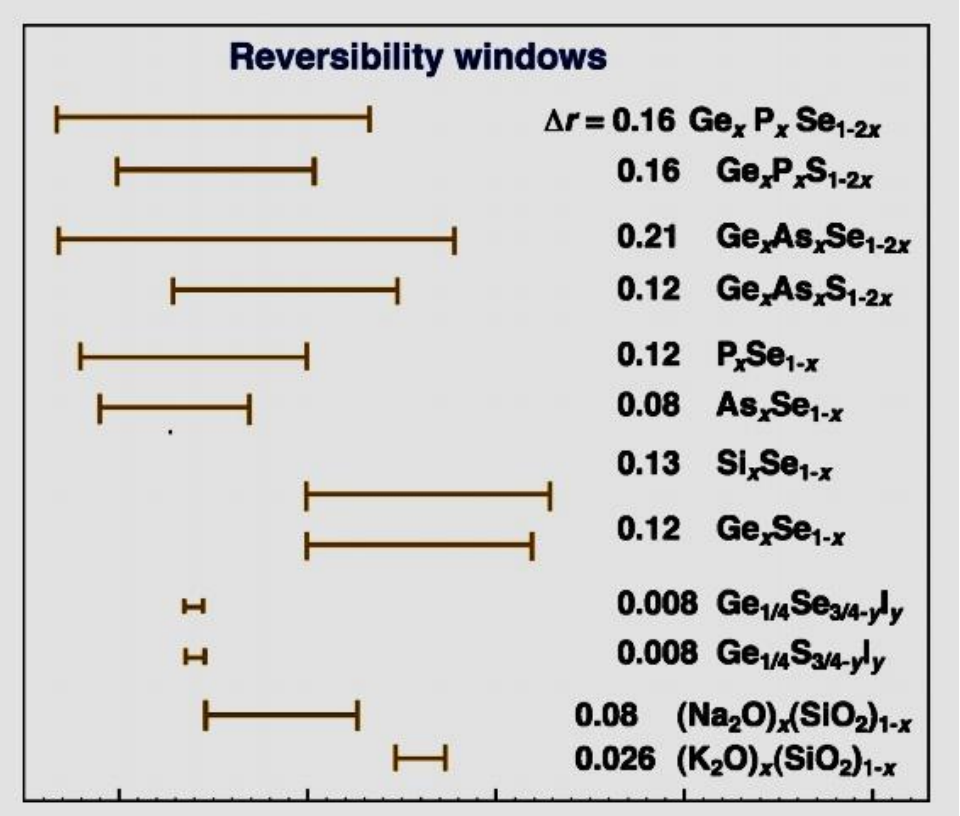
A glass with a composition in the center of the metastable phase $r \approx 2.4$ will return the metastable phase when disturbed by external forces such as for example applied electric fields

Long term stability in amorphous semiconductors
requires to operate in the intermediate phase



Temporal Stability of Elastic Phases in $As_xGe_xSe_{1-2x}$ glasses

P.Boolchand, M.Micoulaut et al 2003



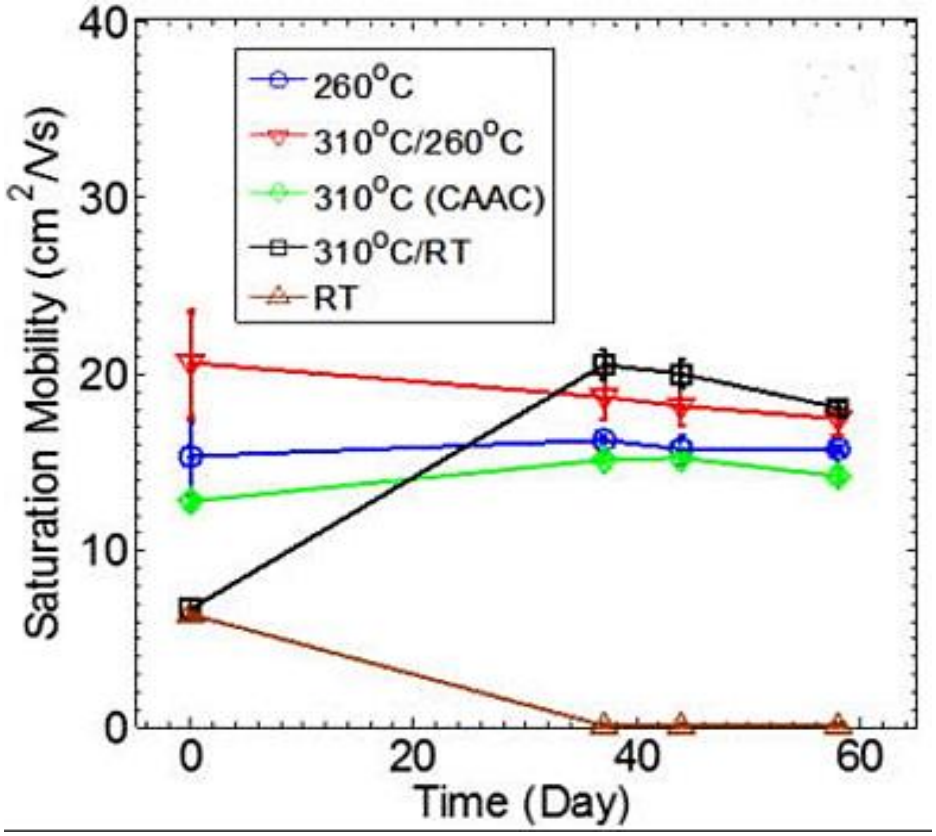
Observed reversibility windows from modulated DSC experiments for various glass systems. Δr is deviation from the average coordinate number.

The existence range of IGZO is unknown

If as in the two oxide glasses, it might be of order 0.05

Lessons for IGZO

- Long term stability requires to use compositions in the reversibility window (rough guess $r \approx 2.35 \pm 0.06$)
- MDSC of IGZO would yield quantitative information on the width of the reversibility window.
- Indirect evidence for IGZO being in equilibrium phase is furnished by reversible electronic properties that are stable in time

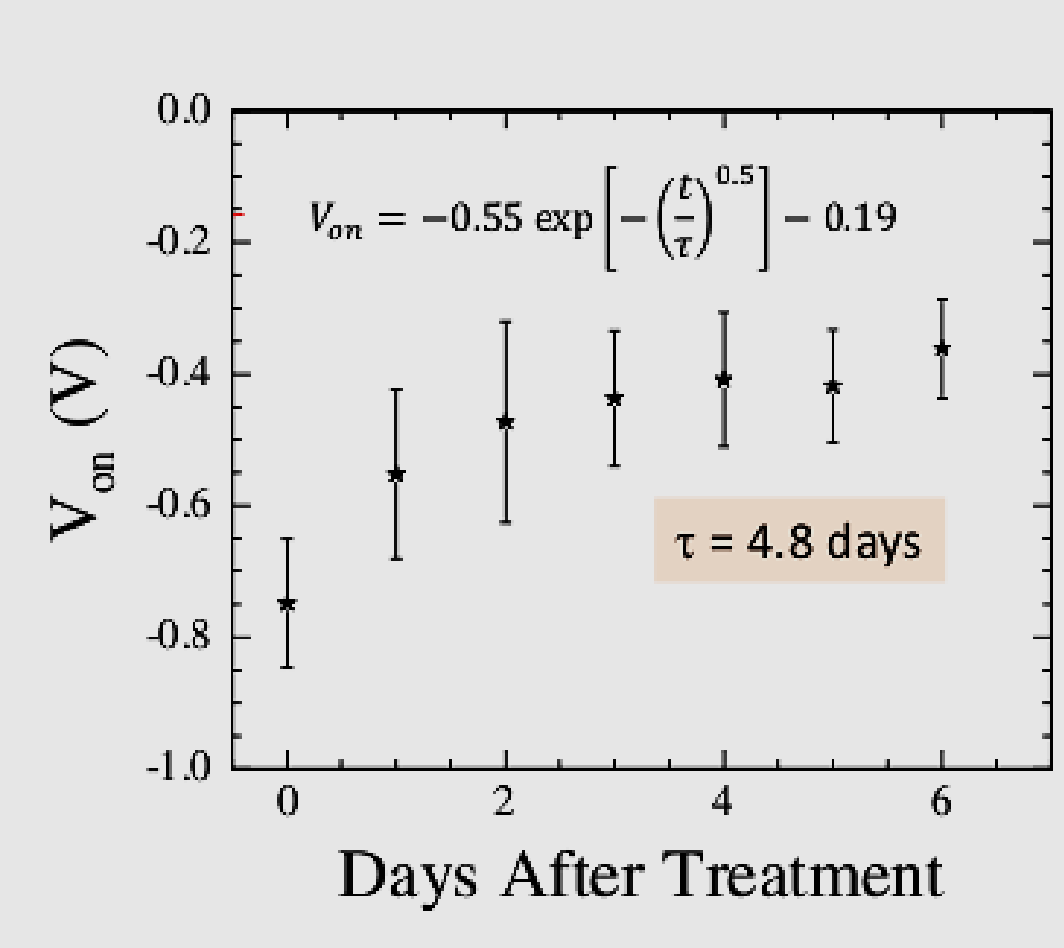


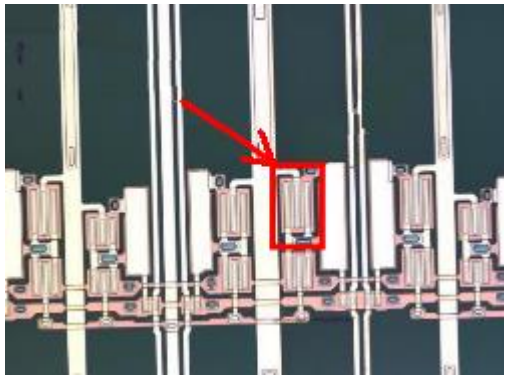
Time scale: Days

Time dependence of saturation mobility of variously prepared IGZO transistors

The brown data are from a RT deposited sample where $r \approx 2.26$

Threshold recovery of commercial display transistors in a TV display after photoresist treatment (15 devices)





D. Lynch - Cornell IGZO Group

How to account for the kinetics ?

Network modifiers lower T_g

Tg SiO_2 ~ 1475 K

Tg $(SiO_2)_{0.98} Na_2O_{.02}$ ~ 775 K

Glass view : Alkali lower T_g

Atomistic view : Na takes out highly strained bridging oxygen bonds,

Extension to IGZO : H will act as a "super alkali" lowering the local T_g

Kinetics of return to equilibrium mobility in IGZO transistors is compatible with the diffusion of hydrogen

SUMMARY OF EXPERIMENTAL OBSERVATIONS

- The electronic properties of well prepared IGZO return, after being stressed, to their equilibrium value

- The kinetics is compatible with the diffusion of hydrogen and the stretch exponent is compatible with diffusion (ß = 3/5) within the accuracy of the experimental data

- The temperature dependence of the recovery is compatible with the diffusion of hydrogen

Implications for IGZO :

Device quality IGZO needs to be in the Boolchand intermediate phase.

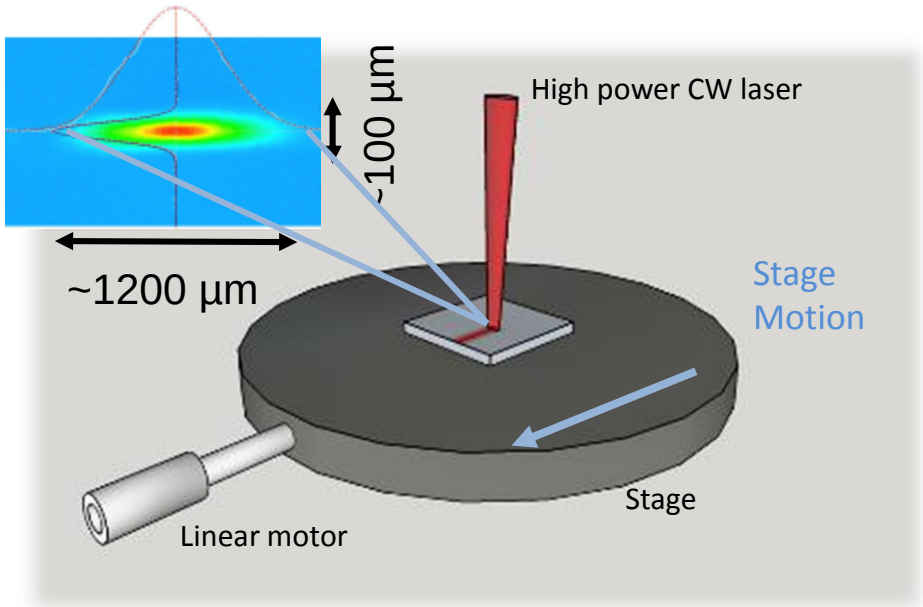
Thus prepared, devices will exhibit equilibrium electronic properties

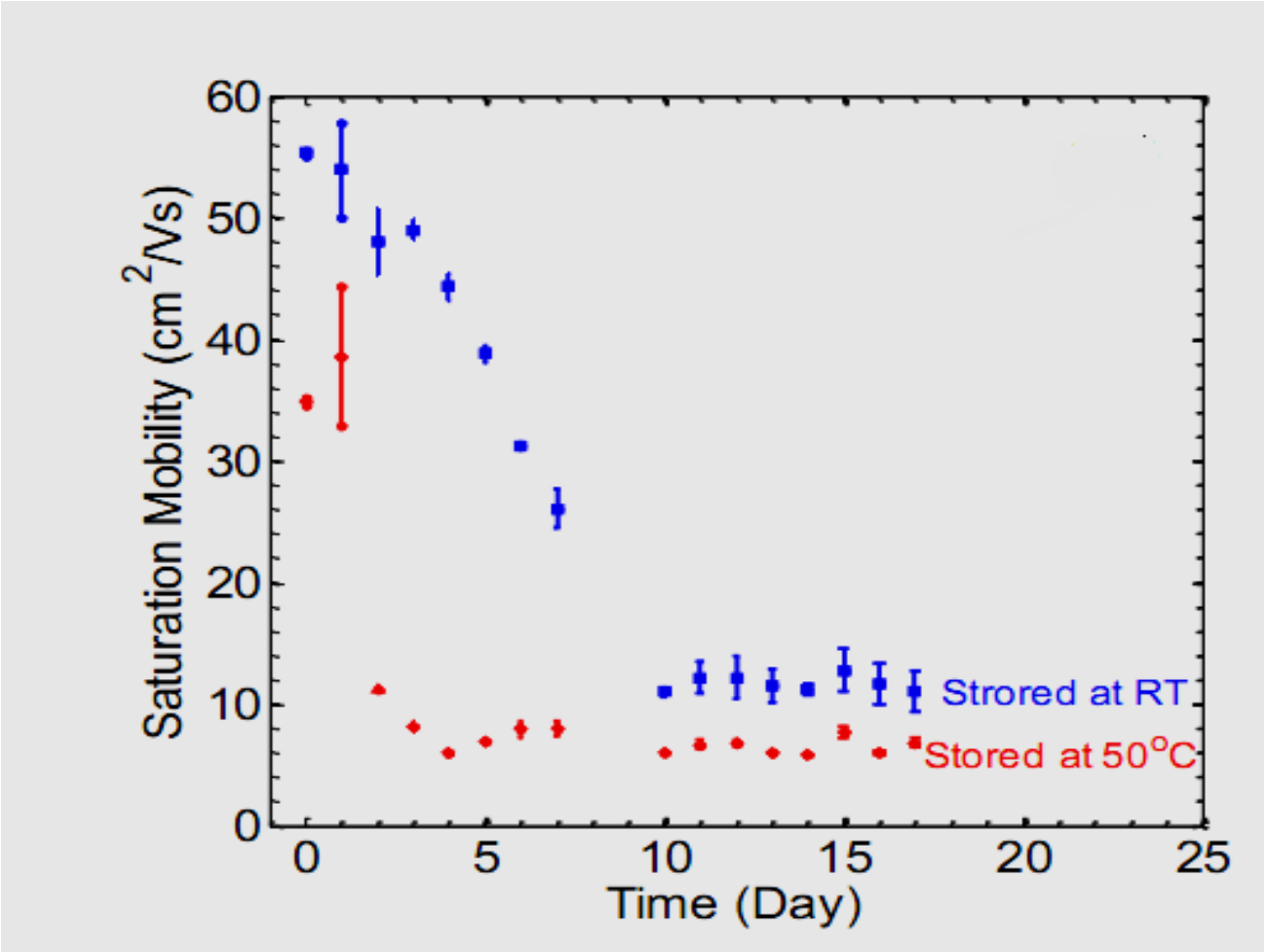
Hydrogen enables the network to return to equilibrium on a time scale of days

Control of hydrogen :

H is required to allow the network to relax below T_g but excess H will decrease network stability by "dialing down" r and move the network to the floppy regime

Laser spike annealing (LSA) of IGZO



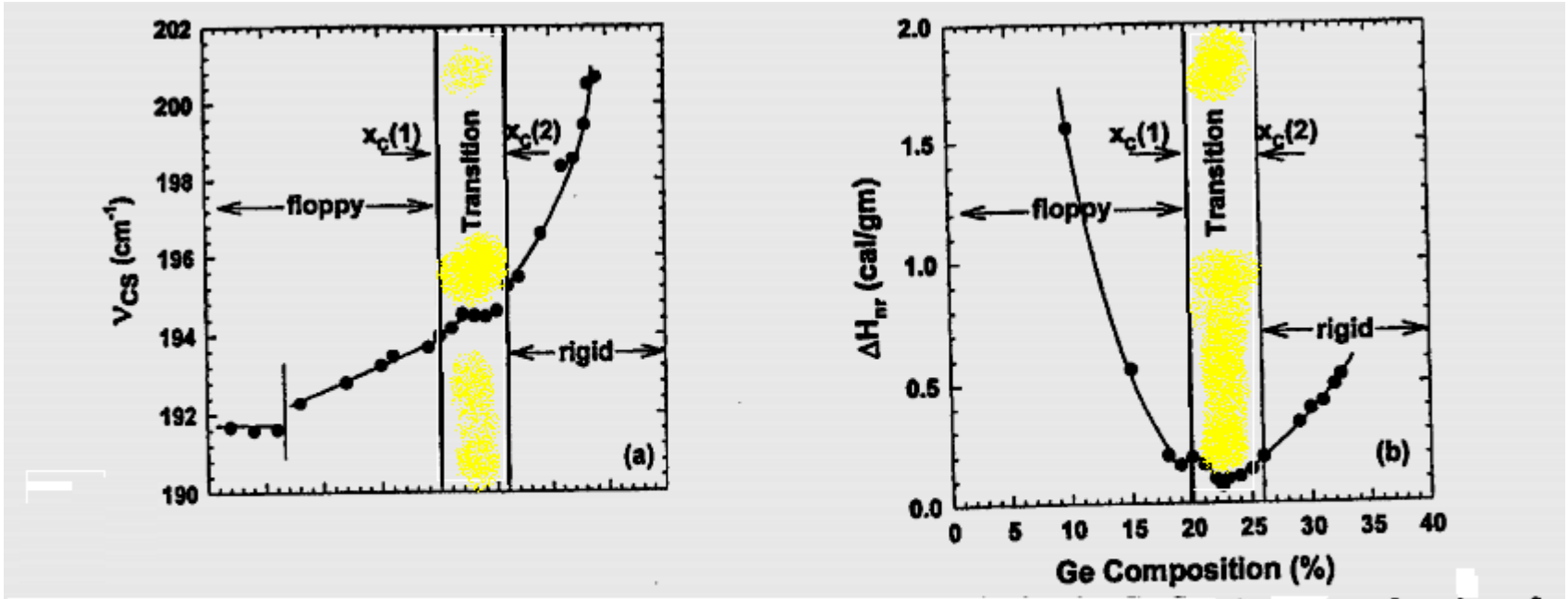


LSA introduces a temporary increase in the mobility close to the intrinsic band mobility of oxide semiconductors that returns to the equilibrium value on a time scale of days *with a kinetic compatible with H diffusion*

Cornell IGZO group

Corresponding Photon flux induced transition have previously been seen in Ge_xSe_{1-x} glasses

Raman directly measures network stress !!!

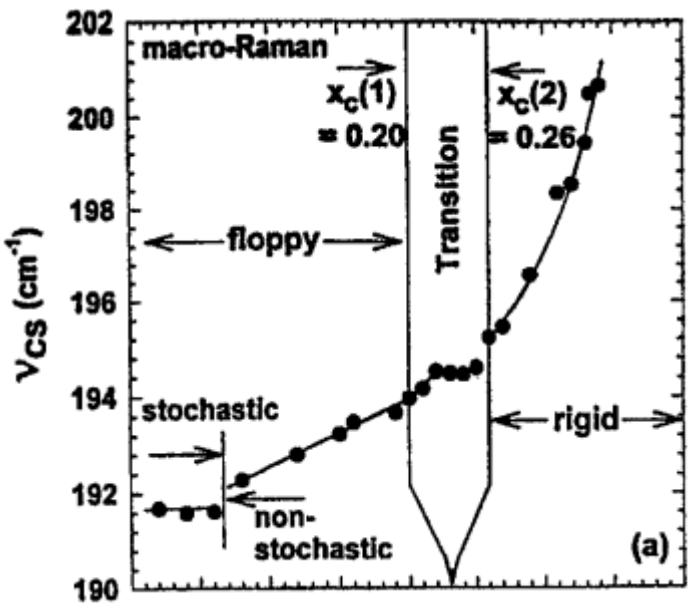


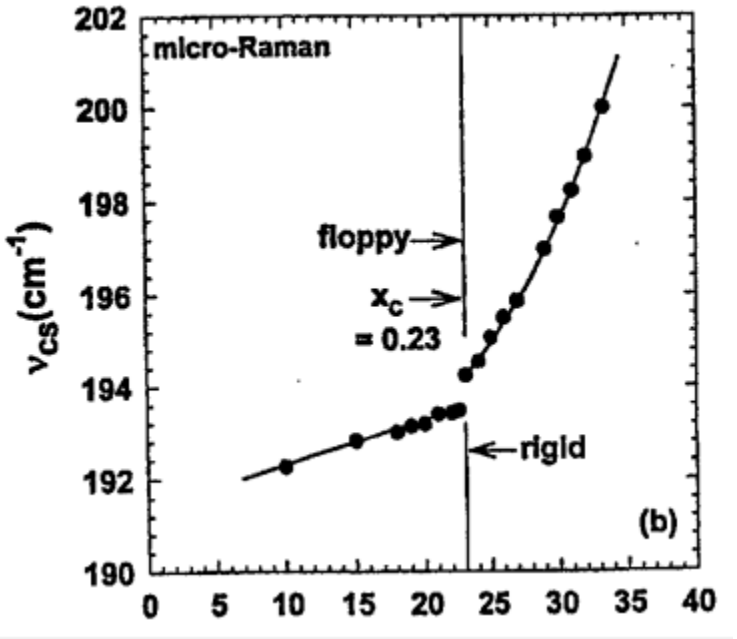
(a) Raman mode frequency variation of corner-sharing (n_{CS}) tetrahedra in Ge_xSe_{1-x} plotted as a function of x
(b) Non-reversing heat variation, $DH_{nr}(x)$, in Ge_xSe_{1-x} glasses.

Network stress is lowest and constant in the intermediate phase

P. Boolchand, D. G. Georgiev, B. Goodman 2001

Effect of increasing photon flux density by 10^4



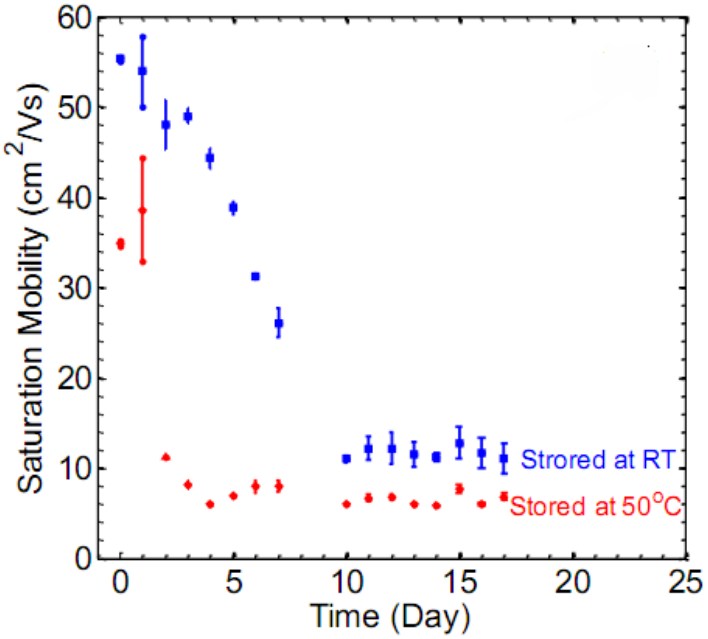


(a) Macro Raman
Photon Flux Density 1 (normalized)

(b) Micro Raman
Photon Flux Density 10 000

"Photo- Melting" collapses the intermediate phase

LSA of IGZO as explained by topological glass theory



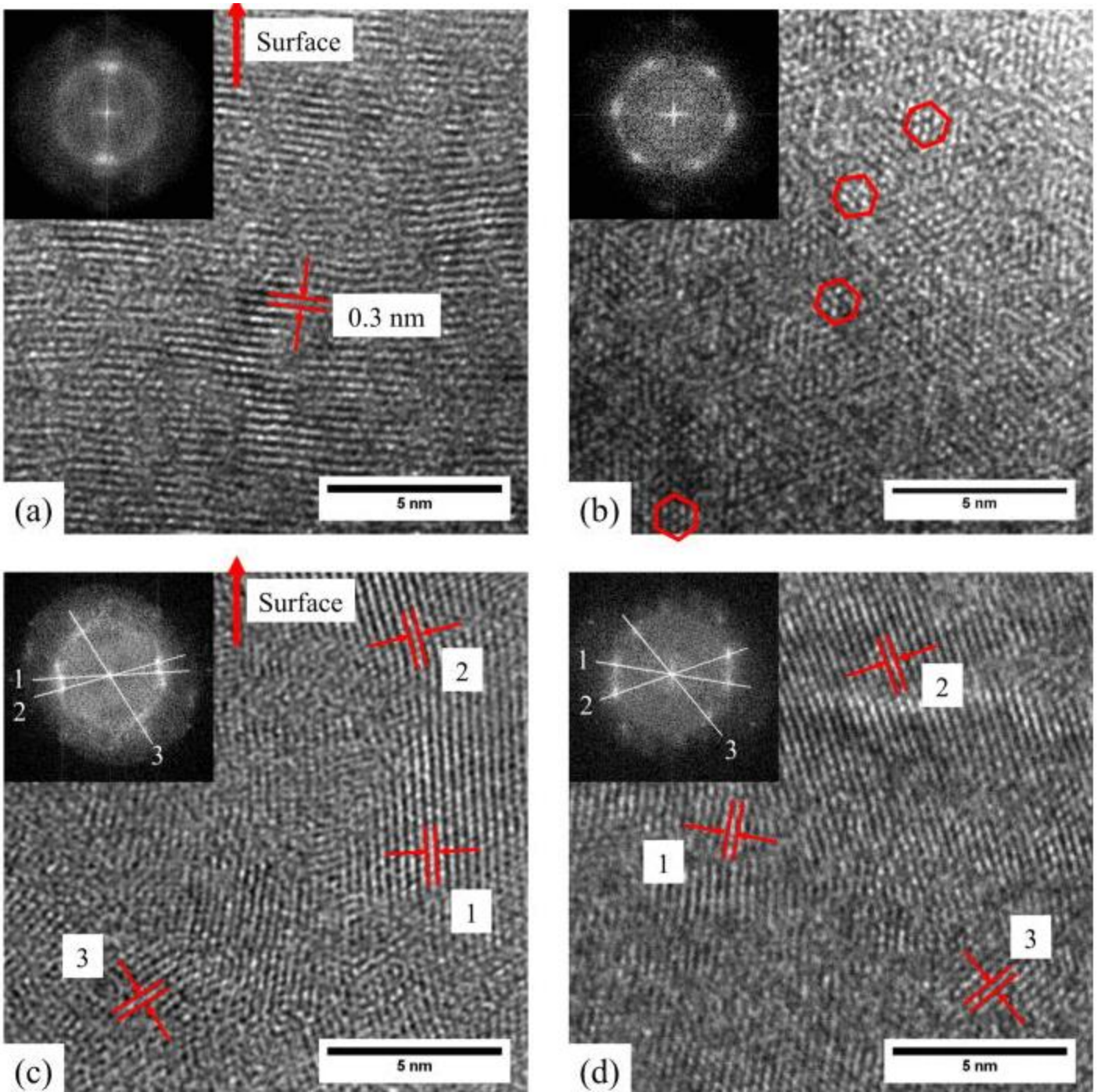
- Intermediate phase collapses into a narrow compositional range, becoming spatially homogenous on the intermediate length scale of glasses.
- The E_c conduction band energy landscape becomes flat and the activation barrier to carrier transport disappears. *
- Electron mobility increases to the intrinsic limit for oxide semiconductors (~ 60 $cm^2/V\ s$)
- In time, the system “de-mixes” the intermediate phase occupies a range of local arrangements , and electron mobility returns to its “equilibrium ” value of the roughened energy landscape of the intermediate phase

- The energy landscape roughness model was first introduced by Fritzsche in 1983

Process window per topological constraint theory

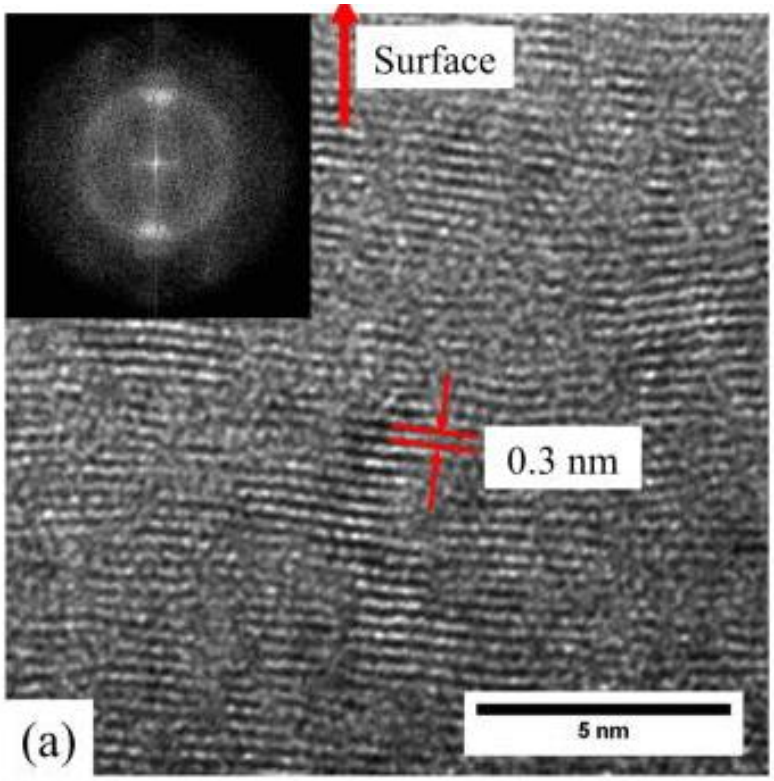
- LSA needs to “melt” the intermediate phase without crystallizing the material <-> narrow process window <-> avoid excess H too lower viscosity too much
- The “molten” state must be “quenched” sufficiently fast freeze in the homogenous structure created by LSA <-> narrow process window.
- The two conditions above, plus having the correct r to collapse to a singularity set a very tight process window
- The experimental observation are in agreement with above.

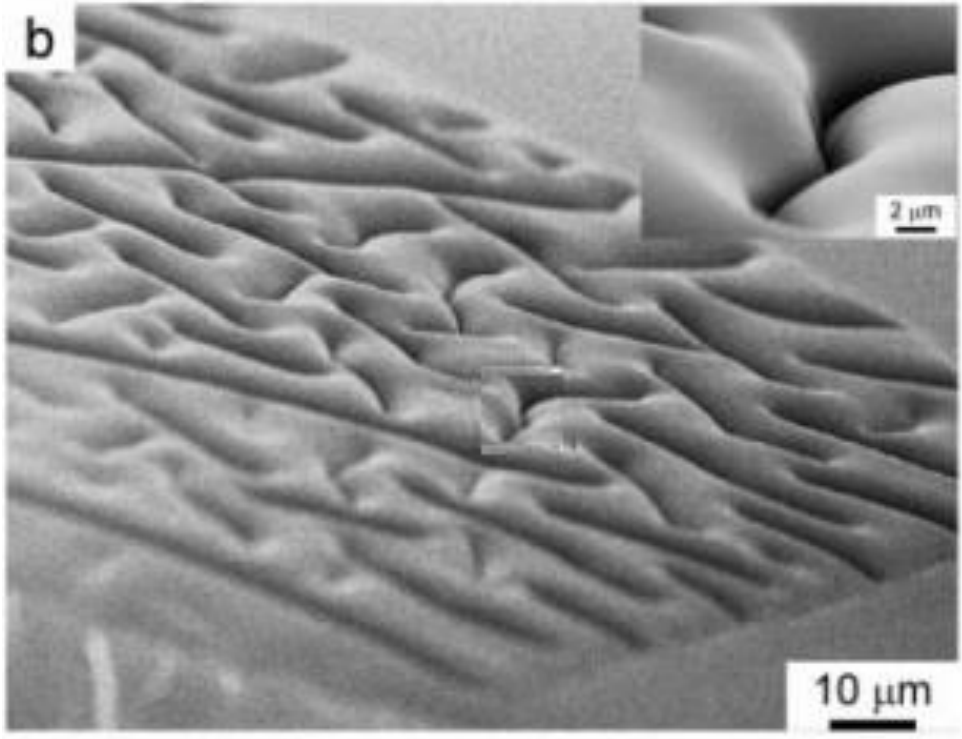
C-Axis aligned crystalline IGZO (CAAC)



CAAC IGZO

Cross-section and plan-view HRTEM images of the highly aligned CAAC IGZO (310 °C/10% O_2) film ((a) and (b)) and the weakly aligned CAAC IGZO (310 °C/100% O_2) film ((c) and (d)) with image FFTs inset.





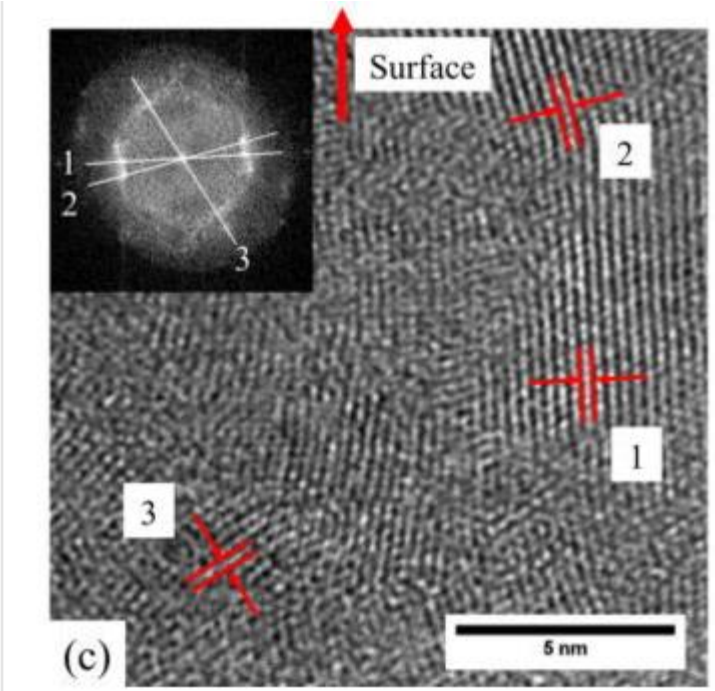
a) X – sectional HRTEM of highly aligned CAAC IGZO - wavy structure +/- 9^0 parallel to substrate

b) buckling pattern formed on a PDMS film comprised of a stiffer top layer and more pliant bulk . Stress generated by solvation (after Chan and Crosby , Soft Matter)

c) The "wavy" geometry suggest stress relief by "wrinkling" during nucleation

IGZO D.Lynch et al 308 • SID 2015 DIGEST **Polymer :**Chan and . Crosby . (Communication) *Soft Matter*, 2006**, 2**, 324-328

Weakly aligned CAAC

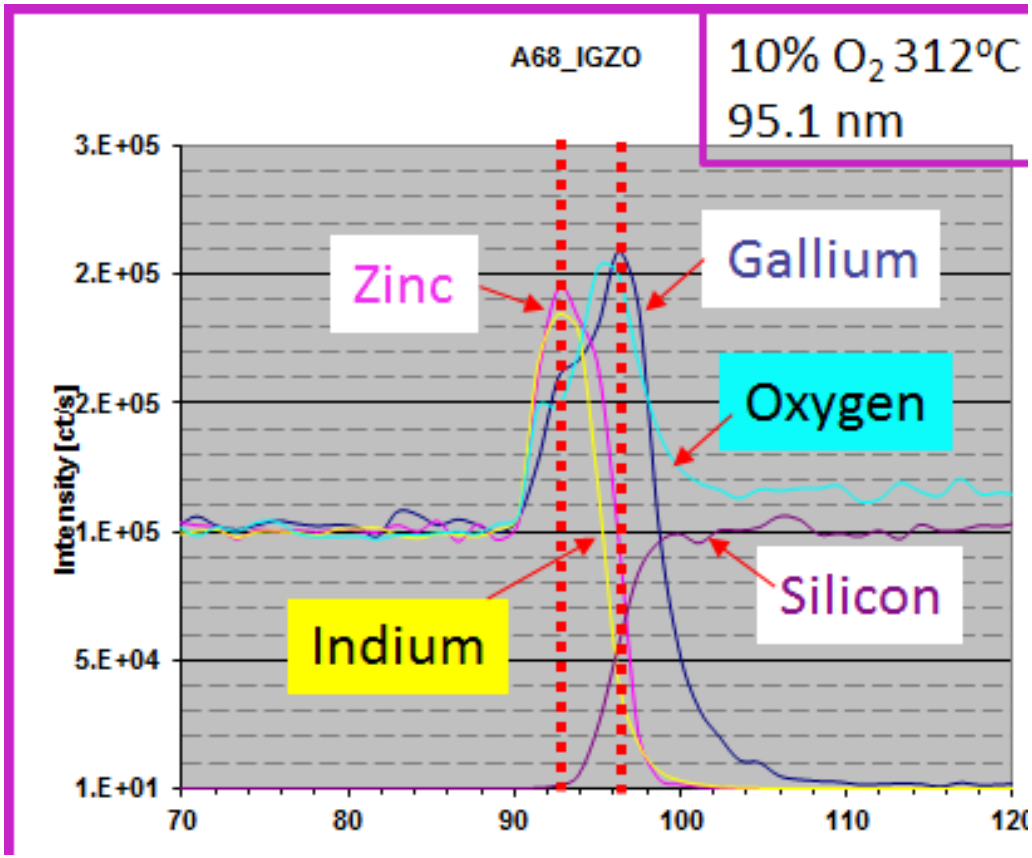


X-Sectional view of a weakly aligned CAAC film highlighting the increasingly random orientation of the grains. The numbered FFT diffractogram spots correspond to planes labeled within the images.

D.Lynch et al J. Appl. Phys. **119**, 145304 (2016); 10.1063/1.4945580

CAAC nucleation proceeds via a 3 to 5 nm thick amorphous layer that subsequently transforms into wavy CAAC

SIMS of “optimal" CAAC IGZO film (10% O2, ~310C - same as in APL letter)



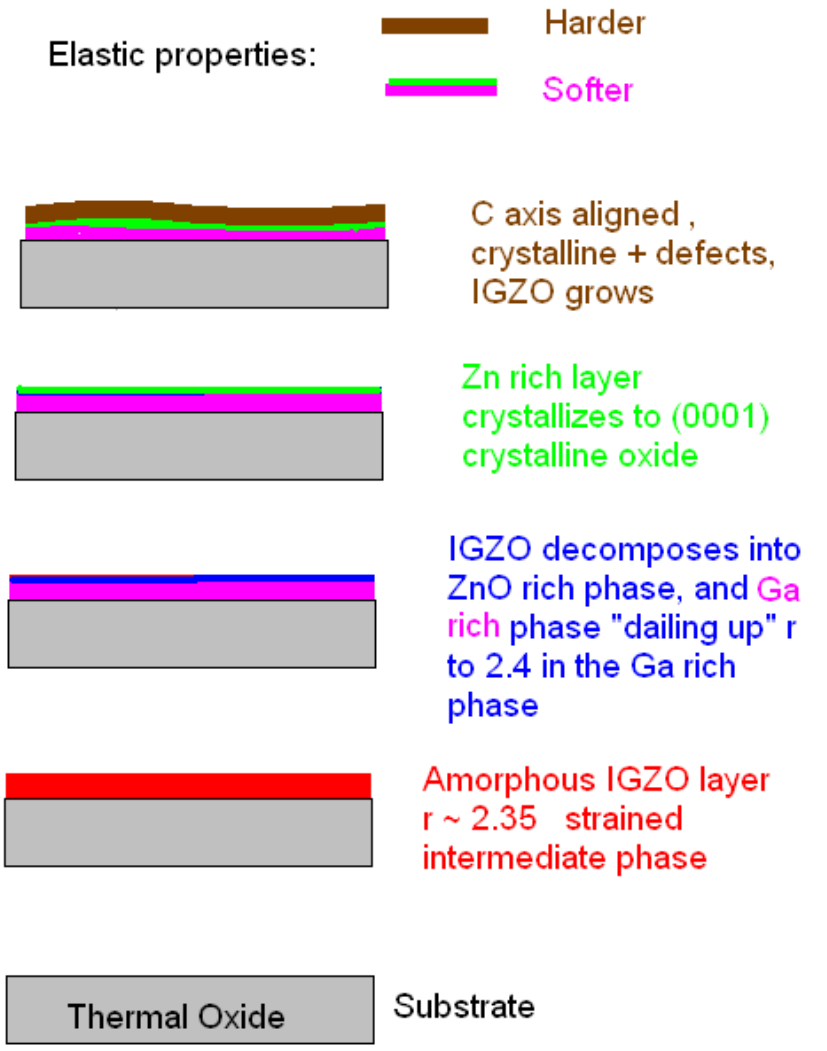
A Ga rich layer is inserted between the CAAC and the thermally oxidized Si substrate.

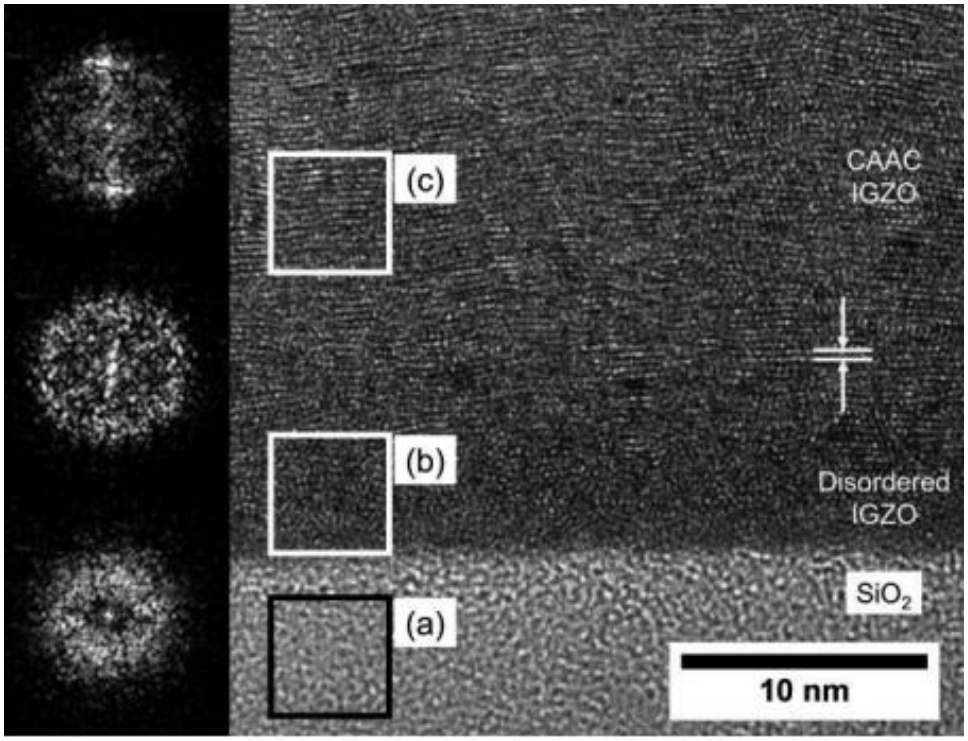
The "bumps" in the In/Ga/Zn/O signals are due to matrix effects from the local electronic structure changing during SIMS sputtering - but all four bumps should occur at the same point. They do not.

Corning Inc . SIMS group

Stress relief by "wrinkling"

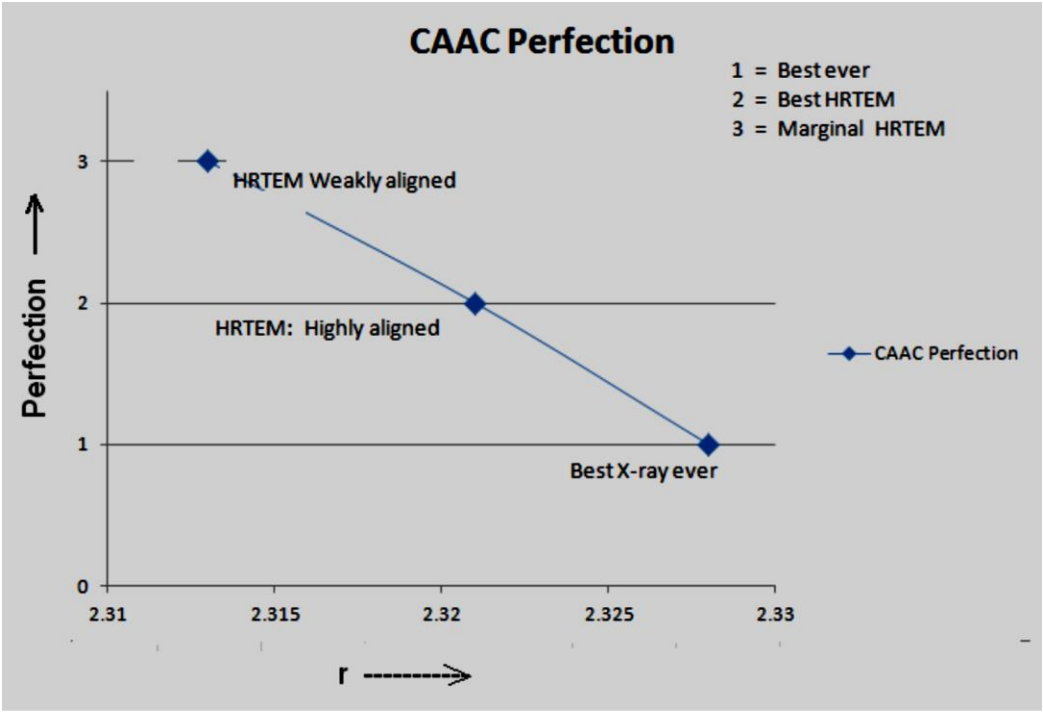
Nucleation of CAAC as explained by topological constraint theory





Cross-section HRTEM of highly aligned CAAC

D. M. Lynch, Bin Zhu, B.D.A. Levin et al
SID 2015 DIGEST • 309



Classification of CAAC by X ray and HRTEM and corresponding r value

Best X ray CAAC ever of Cornell IGZO group r= 2.328
Best highly aligned CAAC (by HRTEM previous slide) r =2.321
Weakly aligned CAAC (HRTEM previous slide) r =2.313

The classification corresponds to steps in r of ~ 0.01
but more work will be required to put this result on a firm footing

Topological Constraint Theory View of Optimal CAAC Formation Conditions:

- Select a film (not necessarily target !) composition that moves IGZO to the into the "edge" of intermediate phase range
- Control hydrogen - it changes T_g (classical glass view), dials down r (topological constraint theory view), eliminates bridging oxygen bond (atomic view)
- Operate under conditions that favour heteroepitaxial growth of subsequent CAAC on the (0001) ZnO template "floating" on the "phase separating "amorphous IGZO

Substrate :

We use high T thermal oxide on Si as substrate. Inserting a Si wafer into a sputter system, heating it to 300^{o}C prior to deposition will result in the formation of a low quality porous oxide that will interact with the deposition in irreproducible ways.

(Kawata et al 2016-SID Symposium Digest of Technical Papers)

Summary

To achieve optimal IGZO based devices
select conditions that deposit IGZO
in the Boolchand intermediate phase .

In the Boolchand intermediate phase, electrical properties will recover after electrical, photon, and chemical stress

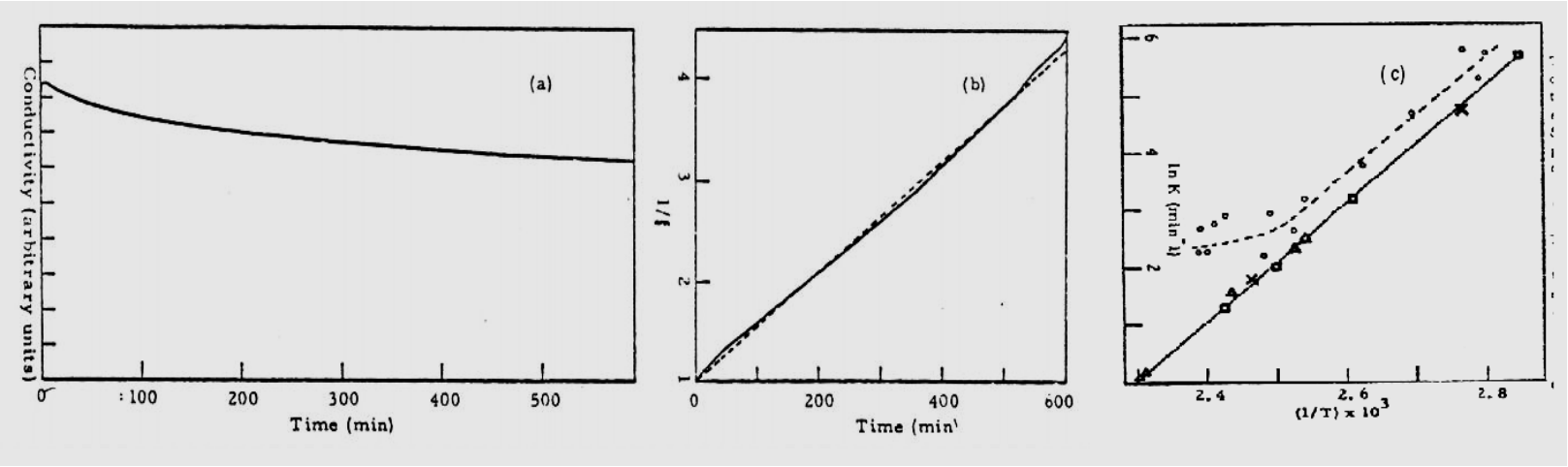
In processing IGZO into the Boolchand phase, the two agents most likely to shift r out of the optimal phase range are Zn and H

Amorphous Si:H

Internal stress is not easily measured, and often ignored in semiconductor physics.

J.C. Phillips

Reversible thermally induced transitions in Amorphous Si:H



a) Isothermal decay of quenched-in excess conductivity
b) Test for second order kinetics. The dashed line is a least square fit
c) Temperature dependence of the second rate order constant of various device structures, dashed intrinsic a-Si:H , solid P-doped a-Si:H

Reversible electronic properties as f(cooling rate)

Brodsky and Ast, 1979

Network view of the defect pool model

- a-Si:H is a hybrid glass, in an intermediate phase
- The presence of H “dials down” r and moves the network to a more stress free state
- Microscopically, the network consists of 5,6, and 7 membered rings
- If sufficiently decoupled by H to be treated as rings MO theory tells us a rough energy landscape (Even rings having higher HOMO LUMO splits)
- See as such the network is “phase separated” on the intermediate length scale of glass - leading support to the quantum well model of Brodsky

Before the audience concludes that I am too far out, lets have a look at a-Carbon

Structure, stability, and stress properties of amorphous and nanostructured carbon films
M.G. Fyta , C. Mathioudakis, G. Kopidakis , and P.C. Kelires

Abstract

"Structural and mechanical properties of amorphous and nanocomposite carbon are investigated using tight-binding molecular dynamics and Monte Carlo simulations. In the case of amorphous carbon, we show that the variation of sp3 fraction as a function of density is linear over the whole range of possible densities, and that the bulk moduli follow closely the power-law variation suggested by Thorpe."

http://arxiv.org/abs/cond-mat/0605381v1

Network view

Thorpe and collaborators suggested that the elastic moduli of bond-depleted crystalline diamond lattices and of bond-depleted "amorphous diamond" networks (WWW model) follow a power-law behavior c ∼ (¯z−z¯f) ν , with the exponent taking the value 1.5 ± 0.2.

TBMD simulations and the EDTB model

The computed data can be fitted to the power-law relation

$$B_{eq} = B_0 \left(\frac{\bar{z} - \bar{z}_f}{\bar{z}_0 - \bar{z}_f} \right)^{\nu},$$

Letting all fitting parameters in Eq. (2) free, we obtain B0 = 361 GPa, which is exactly the computed value for WWW, ¯zf = 2.25, and ν = 1.6. (For a measure of the quality of the fit: R2 = 0.9907). If we fix ν to be 1.5 (R2 = 0.9906), we get 2.33 for ¯zf , and if we fix ¯zf to be 2.4 (R2 = 0.9904), we get 1.4 for ν.

We thus conclude that the variation confirms the constraint-counting theory of Phillips and Thorpe

a-Si:H

Its electronic properties have been most difficult to calculated from first principles and still have difficulties to match glow discharge deposited a-Si:H

An early attempt to explain its bandgap was the QW model of Brodsky (IBM)

* First-principles study of hydrogenated amorphous silicon K. Jarolimek, R. A. de Groot, G. A. de Wijs, and M. Zeman Phys. Rev. B **79**, 155206 ,20 April ** A first principles analysis of the effect of hydrogen concentration in hydrogenated amorphous silicon on the formation of strained Si-Si bonds and the optical and mobility gaps Merid Legesse, Michael Nolan, and Giorgos Fagas Citation: Journal of Applied Physics 115, 203711 (2014

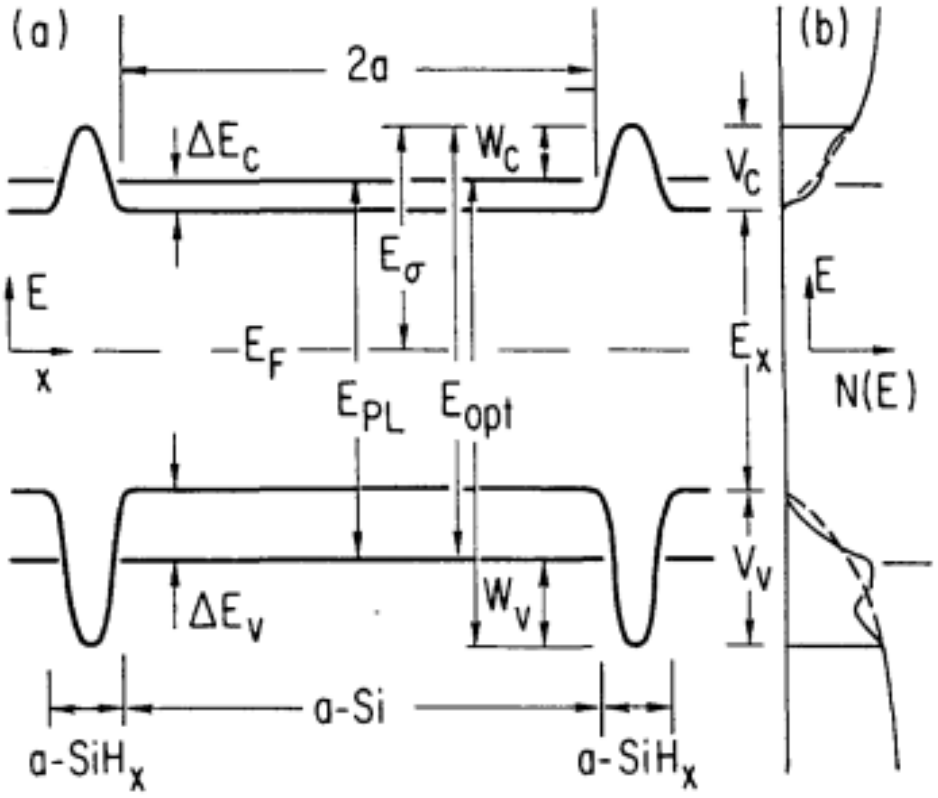


Figure 2. a) Real space band structure of an a-SiH_x-bounded region in pure a-Si. b) Schematic density of states N(E) vs energy E averaged over many regions.

a) Real space band structure of an a-SiH-bounded region in pure a-Si.
b) Schematic density ofstates N(E) vs energy E averaged over many regions.

M.H. Brodsky SolidState Communications, QUANTUM WELL MODEL OF HYDROGENATED AMORPHOUS SILICONVol.36, pp.55—59.

Structurally, the 1980 Q.W. Model of a-Si:H was an early attempt to use network theory to account for the optical properties of a-Si:H. It postulated QW of spatial extend of ~ 4 Å

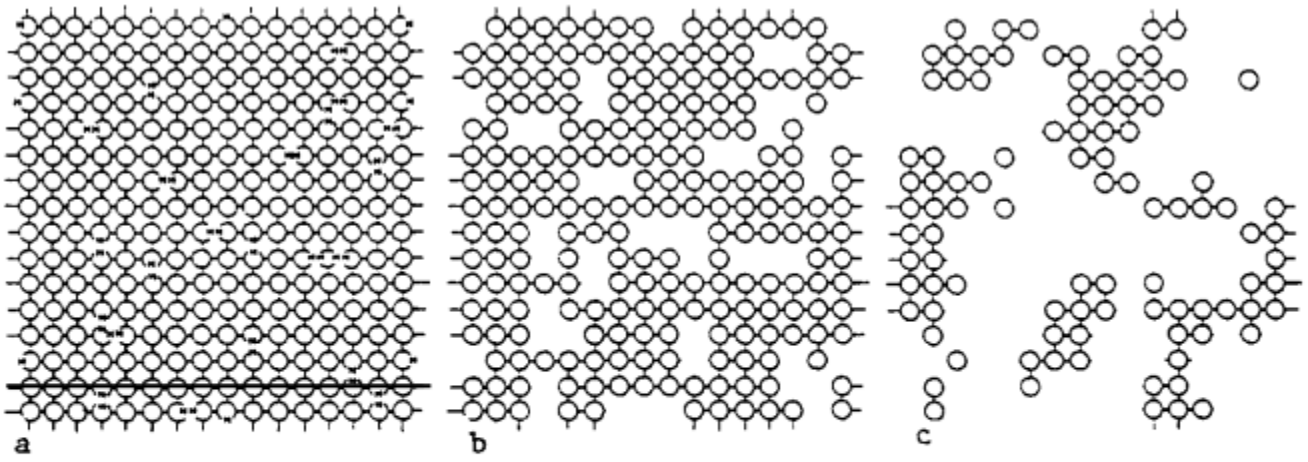


Figure 1. a) 2-D square lattice of Si atoms with two H atoms at each broken bond. b) Those Si atoms with only Si nearest neighbors. c) Those Si atoms without any nearest neighbor H atoms or any nearest neighbor Si atoms attach to H atoms. This figure is based on a similar one for correlated sites of H_2O molecules in Ref.3.

It accounted for the optical properties and the DOS
But it's structural underpinning remained mysterious

Modern network view would see a-Si:H as a Hydride Glass

Given enough H, the network might be sufficiently decoupled such that 5, 6, and 7 membered rings become legitimate building block.

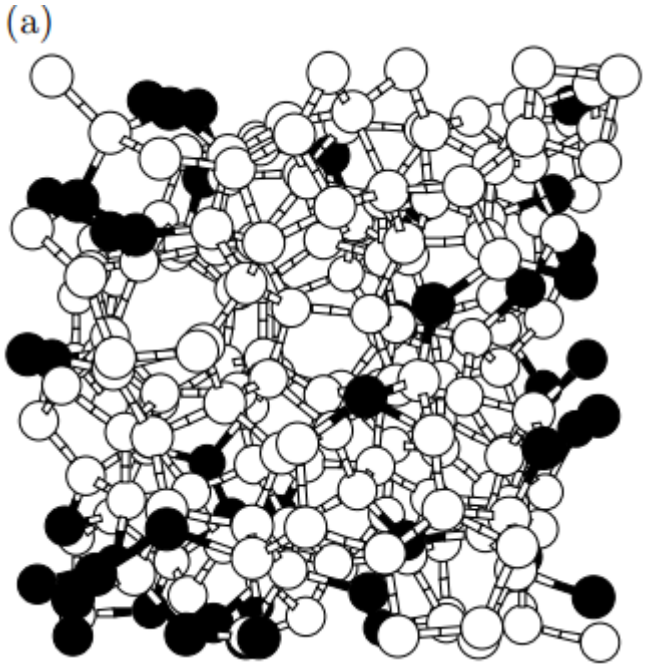
If so, quantum confinement will increase the bandgap, with a rough energy landscape (even numbered rings having higher Homo-Lumo gaps than odd ones)

If so, the material would be inhomogeneous on the length scale of the diameter of rings , 4.4 Å

How much H would be required? Using a Pareto guess that 20% of rings account for 80% of stress, back-of-the-envelope calculations are leading to reasonable number, but clearly more work is required to put this most speculative model onto a firmer footing.

Ab initio calculations of the bandgap of a-Si:H renders a value 0.92eV *

To analyze a-Si:H by network theory requires to identify the (most) relevant structural units, units that result from the introduction of H that breaks up the continuous network. a-C models are a start



Cluster formation in a-C network with a density of 2.99 gcm−3 and 79% sp3 Open atoms sp3 , dark atoms sp2 **

* First-principles study of hydrogenated amorphous silicon K. Jarolimek, R. A. de Groot, G. A. de Wijs, and M. ZemanPhys. Rev. B **79**

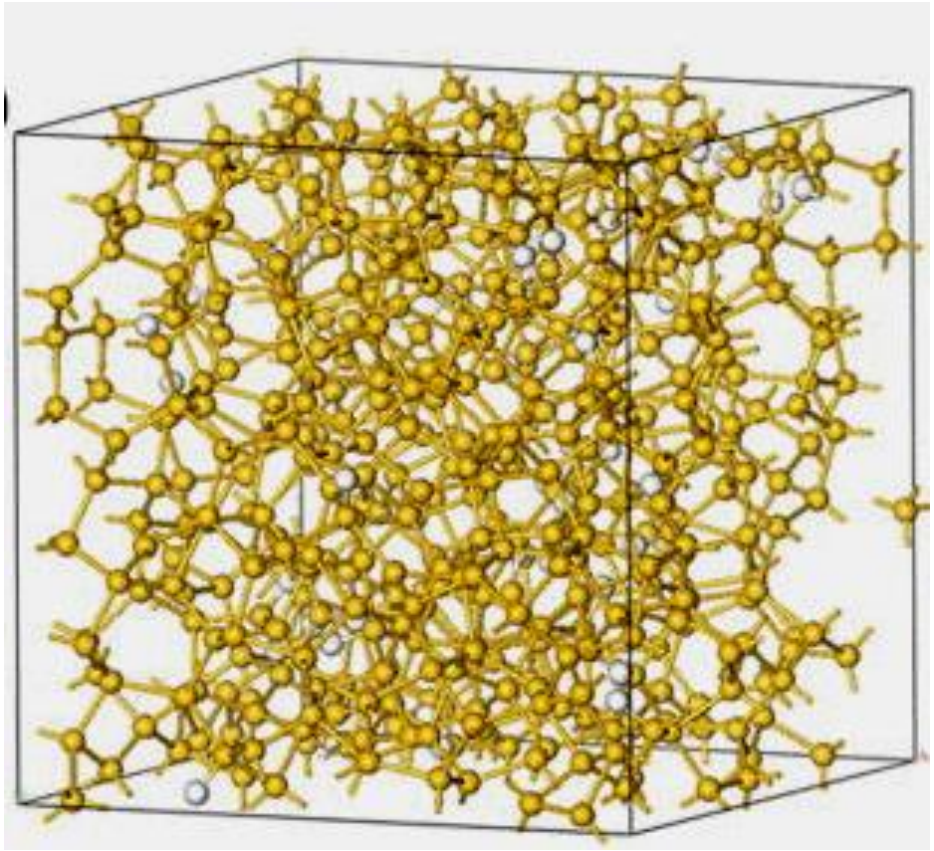
** Structure, stability, and stress properties of amorphous and nanostructured carbon films M.G. Fyta , C. Mathioudakis, G. Kopidakis , and P.C. Kelires Thin Solid Films, 482, 56 (2005)

To my coworkers at Cornell

Chen Yang Chung (now at Intel)
David Lynn (soon at Intel)
Michael Thompson (now Assoc. Dean of Undergraduate Education)
Bin Zhu (now at Corning Inc)

J.C. Phillips for most valuable encouragement and comments

Financial support by Corning Inc



A 512 atom model of a-Si:H constructed with Tersoff potentials

MD + DFT

A first principles analysis of the effect of hydrogen concentration in hydrogenated amorphous silicon on the formation of strained Si-Si bonds and the optical and mobility gaps Merid Legesse, Michael Nolan, and Giorgos Fagas Citation: Journal of Applied Physics 115, 203711 (2014

Historical Note

It has long been known that the presence of alkali in oxide glasses enables stress relaxation at room temperature

“Thermometer Effect”

Structural “relaxation” in alkali containing oxide glasses hundreds of degree Celsius below T_g glasses has been since 1873.
In a-Si:H hydrogen , the equivalent electronic model is the “defect pool” model.

A. Thermometer aus Thüringer Glas.

SiO_2	Na_2O	K_2O	CaO	Al_2O_3
68,30	12,08	8,27	10,41	1,28

Angefertigt: 5. Juni 1878.

Datum der Beobachtung	Ice point / Eispunkt: Before boiling (vor d. Kochen)	Ice point / Eispunkt: After boiling (nach d.)	Depression	Erhöhung des Alters nach Anfertigung
23. Oktober 1878	+0,497°	+0,095°	0,402°	$4^1/_2$ Monate
17. Mai 1879	0,507	0,064	0,443	7 „
27. Januar 1881.	0,65	0,20	0,45	20 „
22. Juli 1881	0,60	0,27	0,33	6 „
22. Mai 1882	0,66	—	—	— „
7. Juni 1883.	0,65	—	—	— „
31. Oktober 1883	0,68	0,20	0,48	27 „

Elimination of Alkali greatly reduced the effect, but thermometers still need to be recalibrated

2009

NIST Special Publication 1088

Maintenance, Validation, and Recalibration of Liquid-in-Glass Thermometers

C. D. Cross
W. W. Miller
D. C. Ripple
G. F. Strouse

http://ws680.nist.gov/publication/get_pdf.cfm?pub_id=900914