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

Dieter G. Ast
Cornell University, USA, dga1@cornell.edu

Follow this and additional works at: http://dc.engconfintl.org/ulsic_tft_6
Part of the Engineering Commons

Recommended Citation

This Abstract and Presentation is brought to you for free and open access by the Proceedings at ECI Digital Archives. It has been accepted for inclusion in International Conference on Semiconductor Technology for Ultra-Large Scale Integrated Circuits and Thin Film Transistors VI (ULSIC vs TFT 6) by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
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

Nodes <-> Rigid Nodes <-> Bars under tension

Glass Network

Atoms <-> Bond Bending <-> 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 7ème, 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; ........
Thorpe, Boolchand, Phillips  extension of truss theory to atom
The average of constraints, \( n \), is linked to average valence \( \langle r \rangle \):

\[
\langle r \rangle = \sum_i x_i r_i
\]

\( X_i \) 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 \( \langle r \rangle \) 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 simulations using the pebble game, for a-Si and a-diamond models (from Thorpe, Maxwell solution added)

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

Predicted versus measured Vickers hardness ($H_v$) for $x\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot (89 - x)\text{B}_2\text{O}_3 \cdot \text{1Fe}_2\text{O}_3$ (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.\textsuperscript{28}

From Mauro, calculated with temperature dependent constraint theory
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

$\text{InGaZnO}_4 \quad r = 2.286$

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
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.

Effective Medium Percolation Theory (EMPT) first was used in 1974 to calculate the conductivity of chalcogenide semiconductors as a function of composition.
Resistivity of $\text{As}_x\text{Te}_{1-x}$ as function of composition
The dashed line is the fit with effective medium theory

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

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

_____ solid line : EMPT mixture of Se, + As$_2$Se$_3$ (As < 40%) and As$_2$Se$_3$ + As$_4$Se$_4$ clusters (As > 40%) using $\rho$ of Se, As$_2$Se$_3$, As$_4$Se$_4$

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 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, $\Delta H_{nr}$ 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 $\pm 0.06$. 
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$_x$Ge$_x$Se$_{1-2x}$ glasses

P. Boolchand, M. Micoulaut et al. 2003
Observed reversibility windows from modulated DSC experiments for various glass systems. $\Delta r$ 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 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)

\[ V_{on} = -0.55 \exp \left( -\left( \frac{t}{\tau} \right)^{0.5} \right) - 0.19 \]

\( \tau = 4.8 \) days

D. Lynch - Cornell IGZO Group
How to account for the kinetics?

Network modifiers lower $T_g$

$T_g \quad \text{SiO}_2 \sim 1475 \text{ K}$
$T_g \quad (\text{SiO}_2)_{0.98} \text{Na}_2\text{O}_{0.02} \sim 775 \text{ K}$

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 ($\beta = 3/5$) 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

High power CW laser

Stage Motion

Linear motor

Stage

~1200 µm

~100 µm
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.
Corresponding Photon flux induced transition have previously been seen in \( \text{Ge}_x\text{Se}_{1-x} \) glasses

Raman directly measures network stress !!!

(a) Raman mode frequency variation of corner-sharing (\( n_{CS} \)) tetrahedra in Ge\(_x\)Se\(_{1-x}\) plotted as a function of \( x \).

(b) Non-reversing heat variation, \( \Delta H_{nr}(x) \), in Ge\(_x\)Se\(_{1-x}\) 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 ($\sim 60 \text{ cm}^2/\text{V s}$)
- 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 \( \rightarrow \) narrow process window \( \rightarrow \) avoid excess H too low viscosity too much

- The “molten” state must be “quenched” sufficiently fast freeze in the homogenous structure created by LSA \( \rightarrow \) 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)
Cross-section and plan-view HRTEM images of the highly aligned CAAC IGZO (310 °C/10% O₂) film ((a) and (b)) and the weakly aligned CAAC IGZO (310 °C/100% O₂) film ((c) and (d)) with image FFTs inset.
a) X – sectional HRTEM of highly aligned CAAC IGZO - wavy structure +/- 90° 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
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.

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

Elastic properties:  
- Harder
- Softer

C axis aligned, crystalline + defects, IGZO grows

Zn rich layer crystallizes to (0001) crystalline oxide

IGZO decomposes into ZnO rich phase, and Ga rich phase "dailing up" r to 2.4 in the Ga rich phase

Amorphous IGZO layer r ~ 2.35 strained intermediate phase

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 \( \sim 0.01 \) 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 “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 $300^\circ C$ 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, let's 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 $c \sim (\bar{z} - \bar{z}_f)^\nu$, with the exponent taking the value $1.5 \pm 0.2$.

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 $B_0 = 361$ GPa, which is exactly the computed value for WWW, $\bar{z}_f = 2.25$, and $\nu = 1.6$. (For a measure of the quality of the fit: $R^2 = 0.9907$). If we fix $\nu$ to be 1.5 ($R^2 = 0.9906$), we get 2.33 for $\bar{z}_f$, and if we fix $\bar{z}_f$ to be 2.4 ($R^2 = 0.9904$), we get 1.4 for $\nu$.

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)

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

It accounted for the optical properties and the DOS
But its 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 **


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 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 degrees Celsius below $T_g$ glasses has been since 1873. In a-Si:H hydrogen, the equivalent electronic model is the “defect pool” model.

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