Effect of Glass Formation-Thin Films

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Glass – ancient transmission medium

Photo courtesy of the Optoelectronics Research Centre (ORC) at the University of Southampton, UK

…..beauty can have function too!

Its not just what its made of…

...its the secret of the manufacturing technology that makes the final part unique and functional ....

Photos courtesy of National Geographic (left) and the Optoelectronics Research Centre (ORC) at the University of Southampton, UK (below)
Processing history dictates properties

Formation-induced attributes dictate the form, performance and lifetime on a resulting glass part. Here, residual stress frozen into a Prince Rupert’s drop during its formation (which appears as birefringence under crossed polarizers) ultimately limits the drop’s mechanical stability and life.

Photos courtesy of National Geographic
Outline

- Formation of glassy films – the basics
  - Vapor deposition
    - CVD
    - PLD
  - Thermal Evaporation
  - RF Sputtering
  - Others: e⁻ beam deposition, ion beam assist, sol gel

- Amorphous versus non-crystalline films
- Effect of processing parameters
- Defects and damage
- Characterization tools
- Bulk/film variations
Volume versus Temperature Plot

Graph showing the transition of materials from crystal to glass to liquid to gas as a function of temperature and time. The graph includes markers for $T_g$, $T_f$, and $T_b$. The time scales are marked as $10^3$ sec, $10^{12}$ sec, and $10^{10}$ yrs.
Viscosity Temperature curve

Difference in cooling rates --> stress
outside (compression), inside (tension)
Schematic Sketches of the Atomic Arrangements in Solids

(a) CRYSTAL  (b) GLASS
Schematic of the Radial Distribution Functions
Difference in cooling rates leads to
- stress, anisotropy ($\Delta n$, $\Delta \rho$, $\Delta T_g$, $\Delta$bonding),
- relaxation rates
Bulk optical glass manufacturing process

- Batching
- Melting
- Refining
- Stirring
- Forming
- Annealing
- Relaxation to equilibrium

Thin film glass manufacturing process

- Target processing
- Deposition (means of energy deposition influences residual “stored energy”)
- Annealing
- Relaxation to equilibrium
Type of deposition influences structure

- Heating rate analogy
- Higher energy process creates glass structure “further” from equilibrium
- Glass film structure is “further” from that of parent bulk glass
- Stability of film structure over time influenced by distance from equilibrium
Deposition rate \sim \text{condensation rate}

\textit{Film final volume}

\textit{equilibrium solid}

\textit{Vapor phase}

\textit{Final film volume dictates film properties and stability}
Films – key issues

- Maintaining compositional similarity
  - Bulk-film properties vary when thermal history varies
  - Compositional variation (from the vapor or plasma phase)
    - Vapor phase > variation than plasma
    - Preferential target removal
      - variation in vapor pressures
    - Preferential film condensation
      - Molecular units present in vapor or plasma may be “fragments of structural units” OR “clusters of structural units”
- Structural variation
  - Results from composition and condensation rate differences
Film Deposition Techniques

Thermal Evaporation

- Substrate (Glass/Si)
- Molybdenum Boat
- Bulk Glass Target
- Target heaters

Pulsed Laser Deposition

- Laser beam
- Port with quartz window
- Heatable sample stage
- Substrate
- Laser plume
- Vacuum chamber
- Rotating target
Targets for deposition

- Bulk glass can be utilized as starting “parent” glass

**Melting**
- $t=30$ min

**Crush to form pieces of target glass**

**Quenching**

**Annealing**

- Polished bulk piece of glass
Film Deposition Techniques - Targets

- **Single component targets**
  - Good chance at maintaining stoichiometry
  - Deposition environment (Ar, O$_2$, air) influences

- **Bi-component targets**
  - Some variation may result due to variation in constituent properties (Tm, vapor pressure, etc)
  - Stablity versus crystallization depends on similarity

- **Multi-component targets**
  - Selectivity of deposition rate can result in non-uniform film
  - Preferential deposition rates can lead to graded properties
    - Near-substrate properties $\neq$ top of film properties $\neq$ bulk glass properties
  - Target fabrication technique is crucial
    - Uniformity in target composition yields higher probability of uniform film $\rightarrow$ structure and properties
Target fabrication

- Multi-component glass: oxide/oxy-sulfide

Target fabrication

- Melting
  - GeO$_2$ – Na$_2$B$_4$O$_7$
  - GeO$_2$ – Sb$_2$O$_3$
  - GeO$_2$ – NaPO$_3$
  - GeO$_2$ – B$_2$O$_3$
  - $t=30$ min

- Sulfination
  - H$_2$S Flow
    - 50°C below the Tg

- Quenching

- Annealing

- Pulverize to form a powder

- Press to form pellet target
Sulfination process (crystalline GeO$_2$)

$\text{SULFINATION OF CRYSTALLINE GeO}_2$

- $\text{GeS}_2$

- Confirmation of substitution of oxygen by sulfur

Raman spectrum $\lambda_{\text{exc}} = 632 \text{ nm}$

* Raman spectrum $\lambda_{\text{exc}} = 632 \text{ nm}$
Confirmation of mixed oxysulfide

![Diagram showing reaction of GeO$_2$ with H$_2$S forming GeO$_{1.6}$S$_{0.4}$]

- **IR Spectra**

  - **IR Forbidden mode of [GeS$_4$]**
  - Asymmetrical stretch Ge – S – Ge in [GeS$_4$]
  - Asymmetric stretching S$_3$Ge – GeS$_3$

**IR absorption peaks for GeO$_{1.6}$S$_{0.4}$** $\Rightarrow$ Presence of Ge – S vibrations
Compositional tailoring of target

X-ray pattern of sulfinated GeO$_2$ powder

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sulfur percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO$_2$</td>
<td>0</td>
</tr>
<tr>
<td>GeO$<em>{1.42}$S$</em>{0.58}$</td>
<td>29</td>
</tr>
<tr>
<td>GeOS</td>
<td>50</td>
</tr>
<tr>
<td>GeO$<em>{0.42}$S$</em>{1.58}$</td>
<td>79</td>
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<tr>
<td>GeS$_2$</td>
<td>100</td>
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</table>
Physical Vapor Deposition (aka RF sputtering)

- Argon pressure of $10^{-2}$ mbar
- Power applied of 15 mW

Homogeneous thin films obtained

High deposition speeds can be attained

Deposition speed of the material is correlated to O/S ratio of the target

No apparent selectivity of constituents in film

Film thickness can be controlled
Oxide and oxy-sulfide films: morphology

SEM image of GeO$_2$ thin film

SEM image of GeO$_{1.42}S_{0.58}$ thin film
Auger data: compositional variation

Auger spectroscopy measurements

- Films deposited on Al foil

Homogeneity from the surface to the depth of the films
Enhancement of optical and physical properties example: oxysulfide thin films

Blue-shift with decreasing sulfur content (UV and multiphonon); increased \( T_g \), thermal stability and mechanical integrity of resulting film material

Absorption spectra

```
α (cm⁻¹)
```

```
GeS₂
GeO₀.₄²S₁.₅₈
GeOS
GeO₁.₄²S₀.₅₈
GeO₂
```

```
300 400 500 600 700 800
0
2500
5000
7500
10000
12500
15000
17500
```

Micro-Raman spectroscopy: structural origin of changes

Vibration of tetrahedral unit peak shifts with sulfide to oxide ratio

Other applications driving film processing technology: Portable Energy Sources are Critical Technologies
Anode and Cathode Combinations Determine the Energy Density

Li-ion Batteries

$C_6$ is a common anode material for Li-ion batteries.

The maximum capacity of graphite ($LiC_6$): 372 mAh/g
1339 C/g

Good cycle-life

But, low capacity for new portable devices

Li$_x$C$_6$  Li$^+$ conducting electrolyte  Li$_{1-x}$CoO$_2$
Anode:  Li$_x$C$_6$  $\rightarrow$  xLi$^+$ + xe$^-$ + C$_6$
Cathode:  Li$_{1-x}$CoO$_2$ + xLi$^+$ + xe$^-$  $\rightarrow$  LiCoO$_2$
Polymer Li\textsuperscript{+}- ion Conducting Electrolytes

- Li ion conducting polymer electrolytes
  - advantages
    - Polypropylene oxide + LiClO\textsubscript{4} (Salt + polymer electrolyte)
    - High Li\textsuperscript{+} ion conductivity
    - Excellent thin film properties
    - Enable multitude of “form factors” for use
  - disadvantages
    - Chemically unstable
    - Degrades with time
    - Soft
    - Cannot be used high energy anodes such as Li
Lithium Dendrite Formation in Li ion Batteries with polymer electrolyte membranes

Non-epitaxial deposition of lithium after each cycle leads to the growth of uneven “fingers” or dendrites

Internal connection results which short circuits the battery

Li\(^+\) - ion Conducting Glasses (FIC) as Alternative Electrolytes

**Advantages**

- Inorganic chemistry can be more chemically stable
  - No reaction with high activity anodes
- Stronger bonding (ionic) gives higher mechanical strength
  - No Li penetration from dendrites
- Chemically bonded anion (Si-O\(^-\), Ge-S\(^-\)) is immobile
  - Unit transference number for Li\(^+\)
  - Higher Li\(^+\) ion conductivity
- Smaller temperature dependence of the conductivity
  - Polymers are used above Tg in liquid state
  - Glasses are used below Tg in solid state
Li$^+$- ion Conducting Glasses as Alternative Electrolytes

- **Disadvantages**
  - Solid structure does not accommodate volume changes
  - Anode and cathode shrink and swell during discharge
  - Anode and cathode swell and shrink during recharge cycle
  - Volume changes promote debonding between electrode and electrolyte
  - Debonding creates open circuit and reduces battery performance
Thio-Oxynitride FIC Thin Films

- Combine electrochemically durable inorganic electrolyte with flexible and volume accommodating polymer electrolyte
  - Thin strong Li\(^+\) ion conducting film will block dendrite growth
  - Polymer electrolyte will allow required volume changes in the battery
- Oxide chemistry to enable atmospheric stability for ease of handling
- Sulfide chemistry to enable fast Li\(^+\) ion conduction and transport across thin film electrolyte
- Nitride chemistry to enable electrochemical stability in contact with metallic Lithium
Thio-Oxynitride FIC Thin Films

Solution
- Back Lithium metal anode with copper current collector on back side
- Coat Lithium metal anode with inorganic glass FIC electrolyte on front side
- Sandwich the two layers together to create new stable anode
- Copper protects backside and collects electrons
- Inorganic glass protects front side – carries Li\(^+\) ions to polymer electrolyte
- Strippable polymer film is removed when battery is manufactured

Thin glass film
- Limits dendrites, hard inorganic glass
- Protects polymer electrolyte from reactive Lithium
Thio-Oxynitride FIC Thin Films

- Problems with existing glasses
  - Glass compositions that are stable in contact with metallic Li are not conductive enough to Li$^+$ ions
    - Oxide Glasses
    - Li$_2$O + P$_2$O$_5$
  - Glasses that have high enough Li$^+$ ion conductivities are not stable enough in contact with Li
    - Chalcogenide Glasses
    - Li$_2$S + GeS$_2$

- Solutions
  - Can oxy-sulfide mixtures be both conductive enough and stable enough?
Bates at Oak Ridge also found that nitrogen added to oxide glasses makes them stable in contact with Li

- Li$_3$PO$_4$ + N (RF reactive sputtering) produces Li$_{3.3}$PO$_{3.9}$N$_{0.17}$
- Good stability with Li
- But poor conductivity $10^{-6}$ (Ωcm)$^{-1}$ at RT

Sulfides can be sputtered in Ar and have excellent conductivities, but poor stabilities

Will Thio-Oxynitride thin films combine properties of all three components?
Thio-Oxynitride RF sputtered thin films

- Objectives of the ISU project
  - Build RF magnetron reactive materials sputtering system capable of sputtering chalcogenide targets
  - Test with Li$_3$PO$_4$ in Ar and N
    - Characterize Li$_3$PO$_4$ and LiPON
  - Sputter Chalcogenide Targets, Li$_4$GeS$_4$
    - Sputter in Ar and N
    - Oxygen as a ubiquitous contaminate used to advantage
    - Characterize structure, properties, conductivities
    - Improved atmospheric stability?
    - Improved stability with Li metal?
    - Improved conductivity?
Thionitride Thin Films – ISU effort

- 2004-2005
- Construction of RF magnetron sputtering system
  - Attached to a N₂ filled glove box
  - Tested and debugged sputtering system, glove box, and vacuum system
- Purchased commercial Li₃PO₄ target
  - Sputtered Li₃PO₄ target in Ar – No N incorporation
  - Sputtered Li₃PO₄ target in N₂ – N incorporation
    - ~ the same amount of N reported in literature
    - ~ the same atomic ratios of Li, P, and O
  - Achieved ~ 1μm/hr deposition rate
  - Controllable sputtering gases, power, time, and pressure
  - Connected to glove box so targets and deposited films can be handled without contamination
Reactive Materials RF Sputtering System

Load lock chamber
Sputtering Head
Sputtering anti-chamber
Sputtering Chamber
Glove box
x load lock arm
y load lock arm
Li$_4$GeS$_4$ plasma in N$_2$ at ~ 20 mTorr
Li$_4$GeS$_4$ Target Preparation

- Commercial source for Li$_2$S – Lorad, Alfa, Cerac
- Ge + 2S $\rightarrow$ GeS$_2$ – Sealed SiO$_2$ tube, 800 °C for 8 hours with rotation @ 5-8 rpm
- 2Li$_2$S + GeS$_2$ $\rightarrow$ Li$_4$GeS$_4$, 900°C for 2 hours
  - Vitreous carbon crucibles
  - Slowing cooling to ensure crystallization of the melt
  - Milling of the powder to ~ 5-25 microns
- Dry pressing to a 1/8” x 2” pellet
- Sintering 700, 720, 740, 800 °C, 2 – 6 hours
Sample preparation facilities at ISU
Li$_4$GeS$_4$ Target Characterization - XRD
Li$_4$GeS$_4$ Target Characterization

- Effects of Sintering Time and Temperatures
  - Green bulk density 1.91 g/ml
  - Theoretical density 2.25 g/ml

<table>
<thead>
<tr>
<th>Time</th>
<th>Temp (C)</th>
<th>Apparent Density (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 hrs</td>
<td>730</td>
<td>2.052</td>
</tr>
<tr>
<td></td>
<td>740</td>
<td>2.173</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2.203</td>
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<tr>
<td>4 hrs</td>
<td>740</td>
<td>2.147</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2.399</td>
</tr>
</tbody>
</table>
Sputtering of Li$_4$GeS$_4$ thin films

- Raman Spectra
- Li$_4$GeS$_4$ shows sharp lines from GeS$_4^{4-}$ tetrahedra
- Sputtered films in N$_2$ and Ar are very similar
- Shows evidence of bridging sulfur units
- Under modified with Li
- GeS$_2$ is more easily sputtered than Li$_2$S
Film Deposition Techniques

Thermal Evaporation

Deposition parameters:
112 Evap-Sputter Station (PVD Systems Inc)
Thermostat stage held to 25 °C
Base pressure: $2.0 \times 10^{-7}$ Torr
Deposition rate: $\sim 2$ nm/s

Pulsed Laser Deposition

Laser parameters:
Mode-locked Nd:YVO₄ laser
Frequency tripled – 355 nm
Repetition rate: 28 MHz
Pulse width: 12 ps
Peak intensity: $\sim 10^{10}$ W/cm²

Deposition parameters:
Target-Substrate distance: 160 mm
Base pressure: $5.0 \times 10^{-7}$ Torr
Ablated using 2.5 cm spiral pattern
Characterization tools - films

- Composition and thickness – **SEM w/EDS**
- Refractive Index, thickness and extinction coefficient - **Ellipsometry**
- Refractive Index change ($\Delta n$) -
  - Stress birefringence measurements (magnitude and sign of stress)
  - Induced refractive index change
- Thermal properties ($\mu$TMA, thermal conductivity) - **Micro-thermal analysis**
- Bonding and local structure/structural changes - **Micro-Raman and Waveguide Raman Spectroscopy (WRS)**
- Composition/stoichiometry, thickness, density - **Rutherford Backscattering Spectroscopy (RBS)**
Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>Target</th>
<th>Thickness</th>
<th>% Ge</th>
<th>% Sb</th>
<th>% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>Ge$<em>{0.23}$Sb$</em>{0.07}$S$_{0.70}$</td>
<td>1400 nm</td>
<td>23</td>
<td>11</td>
<td>66</td>
</tr>
<tr>
<td>PLD</td>
<td>Ge$<em>{0.23}$Sb$</em>{0.07}$S$_{0.70}$</td>
<td>1000 nm</td>
<td>23</td>
<td>7</td>
<td>70</td>
</tr>
</tbody>
</table>

- PLD film appears to have a composition closer to that of the bulk target
- Difference is close to limit of error for the measurement (2 at.%)
- Both films appear to have homogenous structure through the thickness
Helpful relationships

1. \[ c = \frac{c_0}{n} \] where:
   - \( c_0 \) = speed of light in vacuum
   - \( n \) = refractive index of medium
   - \( c \) = speed of light in medium of refractive index \( n \)

2. Heavier atoms (higher Z) with more polarizable electrons can be influenced (rearranged by an E-field); these materials have a higher \( n \) [i.e. S, Se have \( n > 2 \); Si, Ge have \( n \) between 3 and 4]

3. Index tends to track with density \( \rho \) ----> \( n \)

Fresnel single surface reflection, \( r \)

\[ r = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \]
index measurement: Swanepoel Method

The transmission of a substrate material alone is given by the well-known formula

\[ T_s = \frac{(1 - R)^2}{1 - R^2} \]

with \( R = \left[(s - 1)/(s + 1)\right]^2 \)

Where \( s \) is the refractive index of the substrate. For a thin film deposited on a substrate, interference fringes occur for:

\[ 2nd = m\lambda \]

In the transparent region of the spectrum, Swanepoel showed that the envelope function of the maxima is the same as the substrate and the minima are given by:

\[ T_m = \frac{4n^2s}{n^4 + n^2(s^2 + 1) + s^2} \]

Thus, we can solve for \( n \) by:

\[ n = \left[M + \left(M^2 - s^2\right)^{1/2}\right]^{1/2} \]

with \( M = \frac{2s}{T_m} - \frac{s^2 + 1}{2} \)

Transmission spectrum fitting procedure (Swanepoel)

\[ T_s \]
\[ T_M \]
\[ T_m \]

\[ s = \frac{1}{T_s} + \left( \frac{1}{T_s^2} + 1 \right)^{\frac{1}{2}} \]

\[ N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 - 1}{2} \]

\[ n = \left[ N + \left( N^2 - s^2 \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} \]

\[ T_i = 2 \frac{T_M T_m}{T_M + T_m} \]

\[ F = 2 \frac{8n^2s}{T_i} \]

\[ x = \frac{F - \left[ F^2 + \left( n^2 - 1 \right)^3 \left( n^2 - s^4 \right) \right]^{\frac{1}{2}}}{\left( n^2 - 1 \right)^3 \left( n - s^2 \right)} \]

\[ \alpha = \frac{-\ln(x)}{d} \]
Refractive Index/Band Gap estimation from transmission spectra

Transmission spectra of the films

Refractive index estimation

Absorption band gap estimation

• Index of the films similar within error

• Absorption band gap of TE film is red-shifted compared to PLD film.

• Not possible to compare bulk values by this technique.
Refractive index from Spectroscopic Ellipsometry

Refractive index dispersion

Optical model includes:
Simultaneous fitting at two angles (55° & 75°)
Cauchy dispersion relation
Surface roughness layer (2-5 nm)

Correction for non-idealities:
Multiple internal reflections
Thickness non-uniformity (approx. 5%)
Spectral bandwidth (20 nm)

Ellipsometry can confirm estimation of index from transmission spectra
Ellipsometry to measure physical properties


Figure 2.2 The absorption coefficient of Si measured at several different temperatures using spectroscopic polarization modulation ellipsometry. (After Reference 21.)
\[ \Delta \phi = \frac{2 \Delta (OPD)}{\lambda} \]

The factor of 2 is needed because the light travels through the sample twice.

\[ \Delta (OPD) = n_{\text{irradiated}} d_{\text{irradiated}} - n_{\text{film}} d_{\text{film}} \]

From prior measurements, we know:

- \( n_{\text{film}} \) - Transmission Spectrum
- \( d_{\text{film}} \) - Surface Profile with Zygo
- \( d_{\text{irradiated}} \) - Photoexpansion from Zygo

Thus, we can find \( n_{\text{irradiated}} \) and the induced \( \Delta n \).
The $\Delta n$ value relates to the measured phase shift $\Delta \phi$ by:

$$\frac{\Delta \phi}{2\pi} = \frac{2d}{\lambda} \Delta n$$

$\Delta n = 0.044$

**photo-darkening:** increase of absorption and index upon exposure
Δn measurement: Interferometric method

- 3D optical profilometer
- 0.1 nm height resolution, independent of surface texture,
- Submicron X-Y features resolution
- Profile areas up to 100 x 100 mm
Spatial surface characterization
Thermal properties from micro-thermal analysis

Sample Thermogram of PLD film

Probe penetration temperature is higher for films than for the bulk glass
μ-thermal analysis

- AFM tip
  - Surface topography
  - nm resolution

- Thermal tip
  - Local thermal analysis (transitions)
  - Thermal conductivity
  - Local thermal expansion
  - Maps of thermally-active defects
Thermal analysis of film

- AFM probe for topographic characterization
- Thermal probe for thermal characterization – requires reference
- Heating rates: 10°C/sec (versus 10°C/min)
- Film thickness and Substrate dependent (heat flow)
Laser written structures in As$_2$S$_3$ films

Surface profile (Zygo white light interferometer microscope)
(a) of a relief grating (10$^6$ pulses)
(b) of a phase grating (10$^6$ pulses)
(c) of a Y-coupler

Typical width $\sim$10 $\mu$m (FWHM)
► localized photo-expansion

Micro-thermal analysis: characterization of laser-written structures

- As$_2$S$_3$ aged film; written with high intensity
- AFM analysis showed minimal surface relief
- µTA analysis shows an increase in thermal conductivity in same regions as the increase in refractive index
- fs-modification to local bonding arrangement leads to small variation in local thermal signal
- measurements being repeated on fresh films, freshly written structures.
Characterization of the glass structure of the film

- Raman spectroscopy
- Excitation source
- 180° geometry

Diagram:

-Incoming light
-\( \lambda = 752 \text{ nm} \)
-Beam splitter
-Polarized backscattered light
-To spectrometer / camera

XYZ stage

Sample
Raman Spectroscopy: fs-written bulk glass

Depletion of 345 cm\(^{-1}\) As-S bonds

Creation of 236 cm\(^{-1}\) As-As bonds

Waveguide Raman spectroscopy

WRS parameters:
- \( \lambda_{pump} = 840 \text{ nm} \)
- Power < 25 mW

- Ideally, As-S vibrations only (bulk); broad band centered at 345 cm\(^{-1}\): vibrations in (As-S\(_{3/2}\) pyramidal sites
- Bulk and fiber: Small concentration of As-As (236 cm\(^{-1}\)) and S-S (494 cm\(^{-1}\)) bonds
- Waveguide (film) shows As\(_4\)S\(_4\) molecular units and As-As, S-S bonds; no crystallinity
Bulk versus film: micro- vs WG Raman

Effective coupling into the waveguide is required to get film-specific structural information.

**Figure 23.8:** Waveguide Raman spectra of single layer, As$_2$S$_3$ channel structure. Panels (a) to (d) show a sequence traversing along the lateral direction (L to R) on the endface of the waveguide traversing from channel to channel. Excitation wavelength is 840 nm.

**Figure 23.9:** Structural features in film and bulk As$_2$S$_3$ Raman spectra as compared with high-purity crystal (from [66]). (Crystalline specimen courtesy of Prof. M. Frumar, University of Pardubice, Czech Republic.)

Rutherford Backscattering Spectroscopy

The basis of RBS lies in the energy profile of ions that are backscattered from a sample. When a monoenergetic beam of ions is incident on a sample, a small fraction of the ions backscatter, and emerge from the sample at a reduced energy. The energy loss of the ions is due to interaction as they traverse in and out of the target material, and to the transfer of momentum that occurs during a single binary elastic collision (SBEC) with a target atom (Fig 2). By energy analyzing these rebounding ions at a given angle, a spectrum of events occurring throughout the volume of the sample is obtained. Application of conservation laws of energy and momentum translates this spectrum into sample composition as a function of depth.
RBS: principles

By application of classical mechanics to surface collisions, the relationship of the mass $M$ of the target atom, to the known mass $m$ of the ion is defined by

$$\frac{M}{m} = \frac{1 + E_f / E_i - 2 \cos \theta \sqrt{E_f / E_i}}{1 - E_f / E_i}$$

Energies $E_i$ and $E_f$ denote the energy of the ion just prior and immediately after the collision, while $\theta (\theta = 2\pi - \phi_1 + \phi_2)$ is the angle from the incoming beam to the detector. The equation can be rearranged, giving $E_f / E_i$ as a function of the mass of the target atom.

$$\frac{E_f}{E_i} = \left( \frac{\cos \theta \pm \sqrt{(M / m)^2 - \sin^2 \theta}}{1 + M / m} \right)^2 = K$$

The ratio between $E_f$ and $E_i$ is defined as the kinematic factor, $K$. The kinematic factor is only a function of the scattering angle and the ratio of the target mass to the ion mass.
Principles, continued: how do we get compositional information

The stopping cross-section $\varepsilon$ is fundamental to establish the change in energy, where $N$ represents the atomic density of the target sample, $x$ is the depth of the scattering event, and $E_1$ is the energy detected.

$$\Delta E = KE_0 - E_1 = [\varepsilon]N_x$$

The derivation of these equations from the classical mechanical theory gives an accurate estimation of the stoichiometry and density measurements proposed throughout this project. A more detailed analysis regarding the RBS theory is given in

RBS experimental conditions

The experiment employed a **1.7 MeV Tandetron Rutherford Backscattering System** which features a tandem accelerator. A helium ion beam was used to probe the sample. In a tandem accelerator, the source, which emits negative ions, is at ground potential. The negative ions are injected toward the positively charged terminal of the accelerator. He\(^+\) ions are first generated from a duoplasmatron source. Extracted into a lithium charge exchange canal, a small fraction of the ions gain two electrons becoming He\(^-\). In the accelerator, the charge state of the ion is once again changed. Passing through a \(\text{N}_2\) stripper gas cell, most of the ions are converted to He\(^{+2}\) resulting in repulsion from the positive terminal towards ground potential. The charge multiplication of the system, in transforming the He\(^-\) to the He\(^{+2}\) ions, allows for ion energies in excess of 5MeV. The probe ion beam had a diameter of 1mm. Beam current at the target ranged from 18 to 20 nA, for each experiment. The sample was mounted with multiple axis goniometer control in a chamber evacuated to 7 x 10\(^{-7}\) Torr. The backscattered ions were detected using surface barrier detectors at near-normal (165°) and grazing incidence (100°), optimizing the mass and depth resolution, respectively. Pulses from the detector were formed and amplified by a pre-amp and amplifier and then subsequently distinguished by the multichannel analyzer.

For additional info, see

- A. B. Wittkower and H. D. Betz, At. Data, 5, 133 (1973) and
**RBS-example**

1000 Å Ni film on Si

*(Top) incidence of MeV $^4$He ions on film*

-Nearly all of the $^4$He beam penetrates microns into the target before it is stopped

-Particles scattered from the front surface of the Ni have an energy given by the kinematic equation

\[ E_1 = E_0 K, \]

where the kinematic factor $K$ for $^4$He back-scattered at the incidence angle of 170° is 0.76 and 0.57 for Si

-As particles traverse the solid, they lose energy at a rate (64eV/Å) ~ the Ni density (8.9 g/cm³)

$H$ is proportional to relative compositional fraction Energy of peak is related to stopping energy and thickness

*(bottom) reaction product Ni$_2$Si*

$\Delta E_{Ni}$ has spread slightly owing to the presence of Si atoms contributing to the energy loss The Si signal exhibits a step ~ Si in Ni$_2$Si

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*Figure 3.10 Schematic backscattering spectra for MeV $^4$He ions incident on 1000 Å Ni film on Si (top) and after reaction to form Ni$_2$Si (bottom). Depth scales are indicated below the energy axes.*

*from Fundamentals of Surface and Thin Film Analysis, L. Feldman and J. Mayer, North Holland (1986)*
Composition ratios from peak heights

- Ratio of heights $H_{\text{Ni}}/H_{\text{Si}}$ of Ni to Si in the silicide layer gives the composition of the layer, by

\[ \frac{N_{\text{Ni}}}{N_{\text{Si}}} \approx \frac{H_{\text{Ni}}}{H_{\text{Si}}} \cdot \frac{\sigma_{\text{Si}}}{\sigma_{\text{Ni}}} = \frac{H_{\text{Ni}}}{H_{\text{Si}}} \cdot \left( \frac{Z_{\text{Si}}}{Z_{\text{Ni}}} \right)^2, \]  

where we have ignored the difference in stopping cross sections along the outward path for particles scattered from Ni and Si atoms. The yield from the Ni or Si in the silicide is given closely by the product of signal height and energy with $\Delta E$. Therefore a better approximation to the concentration ratio of two elements A and B uniformly distributed within a film is

\[ \frac{N_A}{N_B} = \frac{H_A \Delta E_A \sigma_B}{H_B \Delta E_B \sigma_A}. \]  

In this case of Ni$_2$Si the difference between application of Eqs. (3.26) and (3.27) corresponds to a 5% difference in the determination of the stoichiometry of the silicide.
RBS is considered a non-destructive profiling tool. High-energy He$^{+2}$ ions probe the structure interacting primarily with the electron shells of atoms within the target. Most probe ions penetrate deep below the region of interest losing energy to electrons by inelastic collisions with little or no damage to the lattice, except for those very rare ions that are backscattered through large angles. Almost all damage occurs near the end of range of the probing ions; approximately 17.3 $\mu$m into the silicon substrate in the case of 4 MeV He ions.

Site repetition analysis (below) confirms the continued integrity of the film subsequent to analysis at 4 MeV. Here, multiple measurements were made at the same site under identical probe conditions. Spectra reveal no displacement of constituent atoms within the sample following repeated analysis. Radiation damage, although assumed nonexistent, would not be observable in the spectra.

![Site Continuity on annealed Single Layer Sample](http://www.TRIM.org)
The common plateau width defined by the trailing edge of each species indicates their mutual existence in the compound layer. **Grazing angle spectra (bottom) confirms the elemental designation of the leading edges.** No variation in the density-thickness product is evident between the nonannealed and annealed samples. Density ($\rho$), was calculated based on a 1.66 $\mu$m layer thickness, $t$, determined using a Scanning Electron Microscope (SEM), where

$$\rho_{\text{RBS}}t_{\text{RBS}} = \rho_{\text{REAL}}t_{\text{SEM}}$$

The stoichiometry of the films was determined by taking the ratio of the parametric equation that defines the areal thickness, $A$, for each element (A & B), where the ratio $m/n$, represents the relevant abundance of element A and B (i.e. stoichiometry), given by:

$$\frac{m}{n} = \frac{A_A \sigma_B (E_o)}{A_B \sigma_A (E_o)}$$
Results:

A measured As to S ratio, prescribing a 1.5 molar percent, was used to produce the bulk glass [As$_{0.4}$S$_{0.6}$]. RBS analysis of annealed and nonannealed films (below) are comparatively sulfur-deficient with respect to the original parent glass composition (often seen in thermal deposition). In addition, the RBS spectra show a slight density variation between the annealed and nonannealed structures; however, the discrepancy results within the deviation error presented by RBS analysis.

<table>
<thead>
<tr>
<th></th>
<th>Nonannealed</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry</td>
<td>As$<em>{0.416}$S$</em>{0.584}$</td>
<td>As$<em>{0.403}$S$</em>{0.597}$</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>1.66</td>
<td>1.66</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.93±10%</td>
<td>2.91±10%</td>
</tr>
<tr>
<td>% Uncertainty</td>
<td>0.65-1.12</td>
<td>0.68-1.11</td>
</tr>
</tbody>
</table>

Although variations in stoichiometry are within the experimental uncertainty, it may also be associated with a reconfiguration of the molecular structure of the film during annealing. As$_4$S$_4$ molecular clusters form during the thermal deposition of the films. These As$_4$S$_4$ sub-molecular features, represented by the sharp peaks in the Raman spectra, undergo reconfiguration with annealing and time. The near infrared Raman spectra show that the annealed and photoinduced waveguide have less As$_4$S$_4$ molecular clusters than the as-deposited structure. These results imply that the variations observed in the Raman data are due only to a rearrangement of the molecular species in the glass matrix, which might induce modifications in the thickness (density) of the film, however it does not appear to affect the final stoichiometry of the film structure.

Structural changes in glassy films

- With composition
- With deposition condition
  - Target configuration, properties
  - Film deposition/formation rate
- With film age
  - Relaxation behavior
  - Stability of properties for device applications
- With external modification
  - Ion implantation (chemical changes)
  - Thermal history (cycling)
  - With induced optical modification
    - Photo-induced structural response
    - Need to know “before and after structure”
    - Assessment of bonding mechanism changes