Next Generation Chalcogenide Glass for Active and Passive Applications

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Industry Day and Exhibition
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Outline

• Chalcogenide Glass - Introduction
• Glass Manufacture – Improving Foundations
• Improving Materials – Building for the Future
• Device Challenges – Current and Planned
Chalcogenide Glass Manufacture

- First Produced in 1950’s
- Sealed Ampoule Techniques
- Driven by Defence Applications

Commercially Established

SCHOTT

glass made of ideas

Amorphous Materials Inc.

umicore
Why are they Interesting?

- Glass is semiconducting, conducts electricity
- Easily switched between amorphous & crystalline state
- Transparent in the infrared, to beyond 15 microns
- Photosensitive (in 44 ways!)
- Highly non-linear, low two photon absorption at telecoms wavelengths
- Easily doped with rare earth elements, transition metals
- Easily cut, polished, extruded, drawn into fibre, formed as thin films
- Commercially importance proven: memory and defence
- Bright Future: 2D materials, beyond CMOS electronics
Initially – An IR Optical Material

Oxide Glass Transmission

Atmospheric Transmission Windows

Imaging

Sensing

Defence
Why more Materials Research?
Glass Quality Far from Ideal

ORC Silica Fibre Fabrication
Typical Loss: < 0.2 dB/km

ORC Non-Silica Fibre Fabrication
Typical Loss: < 2 dB/m

Ten Thousand Times Higher Loss

A radical change in glass preparation is needed!
Ga:La:S Melt Quenching

- Raw Materials batched in nitrogen purged glove box
- Sulphides melted in vitreous carbon crucibles
- Typically 24 hours at 1150°C in flowing argon
- Quenched to below glass transition temperature
- Annealed at 500°C, depending on ingot size
Focus on Glass Melt Facility

Gas Inlet

Gas Purification

System Capability:

• Designed completely in-house for flexibility
• Instrumented to guarantee consistency
• National Instrument and Labview code, provide recipes and automation.
• MFC flow controls
• Online dew point measurement
• State of the art purifiers include 3nm particulate filters and up to 100 ppt removal in certain gases.
• Gas detection and automated shutoff
• UPS power backup for 8 hours

Daily Monitoring of Gas Purity

- Argon line – Conversion Rig
- H₂S line
- Nitrogen Purge
Current Glass Purity

Glass Purification Progress

2011 - As melted Glass
Loss Minimum 31.6 dB/m
approx 100 fold reduction in transmission loss

2014 - Improved Purification
Loss Minimum 0.3 dB/m

Absorption (cm⁻¹)
Wavelength (microns)
GLS Infrared Transmitting Glass

A radically new chalcogenide glass and long-awaited alternative to toxic arsenic-based

- Optical transparency from the visible to infrared wavelengths and thermal stability up to 550°C
- Safer and more economical production; can be melted in a large-scale without the need for sealed ampoule processing
- Over 200 times greater performance and overall transparency in the 3-5 micron band as compared to early glasses of the same family; this is a result of substantially reduced impurity levels, in particular OH and SH absorption bands at around 3 and 4 microns
- A wide range of applications, e.g. IR and non-linear optics, high efficiency thin-film solar cells, high-capacity batteries and sensors with potential as the choice semiconductor for developing beyond CMOS electronics and all optical processing technologies

Physical data and characteristics

<table>
<thead>
<tr>
<th>Physical Data and Characteristics</th>
<th>2.403</th>
<th>1 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index @ 0.589 μm</td>
<td>75</td>
<td>μm</td>
</tr>
<tr>
<td>Zero material dispersion</td>
<td>6.53 - 10.5</td>
<td>μm</td>
</tr>
<tr>
<td>Temperature dependence dN/dT</td>
<td>&lt;0.001 cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>Bulk transmission at 50% (1 mm thickness)</td>
<td>&gt;35</td>
<td>MW/cm²</td>
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<tr>
<td>Bulk absorption @ 4.8 μm</td>
<td>&gt;250</td>
<td>kW/cm²</td>
</tr>
<tr>
<td>Damage threshold @ 1064 nm (coated)</td>
<td>380</td>
<td>°C</td>
</tr>
<tr>
<td>Damage threshold @ 1.54 μm (uncoated)</td>
<td>400</td>
<td>°C</td>
</tr>
<tr>
<td>THERMAL</td>
<td>550</td>
<td>°C</td>
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<tr>
<td>Glass transition</td>
<td>830</td>
<td>°C</td>
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<tr>
<td>Softening point</td>
<td>16</td>
<td>°C</td>
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<tr>
<td>Maximum use temperature</td>
<td>6.54</td>
<td>1/g K</td>
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<tr>
<td>Melting temperature</td>
<td>9.43</td>
<td>W/m K</td>
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<tr>
<td>Thermal expansion</td>
<td>4.04</td>
<td>g/cm³</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>4.5</td>
<td></td>
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</tbody>
</table>

Standard formats

Available as bulk glass or polished optical components, thin and thick films and emerging as an optical fibre; dimensions for discs, rods, windows, prisms on request. Raw glass ingots (up to 500 grams) can be supplied for your own in-house glass processing.

Bespoke specifications

Specifications beyond the typical formats outlined here may be available, including:

- Raw glass ingots cut and polished to your specification
- Other glass compositions, which we can provide under standard material transfer agreement for rapid evaluation by industry and academia

Please contact us to discuss your specific requirements.

Contact us

Professor Dan Hewak
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Corrosion resistance

Chemical vulnerability weakness for previous chalcogenides

IG4 (Ge:As:Se) 4 day 23% mass loss in ethylenediamine (EDA)

- GLS surface after 1 month exposure to
  - Cleaning Agents
  - Amine Solvents

Significantly improved chemical resistance
Many Properties  
= Many Applications

Markets
- Chemical Sensing
- Defence & Security
- Consumer Electronics
- Aerospace

Applications
- Bulk IR optics - imaging / sensing
- Active elements - remote sensing / imaging
- Laser / light delivery
- Laser / Light generation
- Memory and Transistors

Physical properties
- Infrared transmit
- Multi-state
- Stable to 600°C
- Multi-format - film, fibre, bulk
- Semiconducting / metallic
- Photosensitive
- Actively Doped

Chalcogenide content of systems will increase

slide courtesy of John Lincoln
Emerging Devices

Demonstrated and Challenges:
Glass Optimization (The Hard Way!)

Paul Bastock, Chris Craig

10:90 50:50 90:10

Glass Optimization (The Efficient Way!)

High Throughput Material Discovery

Brian Hayden
Jaffar Saleh Subaie
Phase Change Memory
High Throughput Screening Chip

90% of Compositional Space

625 unique devices

Optimum Composition GLS Switch

![Graph showing reset currents vs. cell area]

- **GLS Reset Currents**
- **GST Reset Currents**
Modifying chalcogenides through non-equilibrium doping via ion implantation

(collaboration with Richard Curry, University of Surrey)
Thermoelectric Devices

Waste Heat → Electrical Power

Figure of merit ($ZT$) depends on Seebeck coefficient $S$, thermal conductivity $\lambda$, and electrical resistivity $\rho$.

$$ZT = \frac{S^2 T}{\rho \lambda}$$

Research directions:
- Thin film TE
- Nanostructuring
- Novel design of TE
Thermoelectric Device Fabrication

(p & n) pairs

Metal pads

Load

Hot side

Schematic and real device image of TFTE on PI substrate

(collaboration with Harish Baskharim, University of Oxford)
3D Photonic Bandgap Structures

Backfill with Ge-Sb-S by CVD

(a) woodpile structure template before backfill process;
(b) SEM image fabricated by FIB showing the quality of in-filling

Collaboration with John Rarity, University of Bristol)
There remain hundreds of layered materials that could still yield monolayers.
Summary

• Chalcogenide glass clearly has broad reaching potential

• With long term funding radical changes in their processing and applications were enabled

• The fascinating application space ensures the future of these materials.

• If you’d like some glass or thin films, please ask!

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EP/G060363/1  ChAMP – Chalcogenide Advanced Manufacturing Partnership

More details at  http://chalcogenides.net