Deposition and Characterisation of Chalcogenide Materials with the J/Lab FEL

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Overview

- PLD of ZnSe thin films.
- NIR absorption of Ga:La:S glasses.
Pulsed Laser Deposition of Zinc Chalcogenide Optical Thin Films using JL-FEL.

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Jefferson National Laboratories
Aim

- Deposition of epitaxial thin films.
- Low optical loss.
- Room temperature IR Laser.
- High refractive index for waveguiding.
Materials

- ZnS and ZnSe host materials.
- Low Phonon energy.
- Cr$^{2+}$ dopant shown to lase at 2.35µm.
- Sapphire and SrF$_2$ substrate layers.
- Close lattice match with substrate.
- Good thermal conductivity.
- Refractive Indices allow waveguiding.
Why PLD?

- Retains target stoichiometry.
- High plume energy means lower substrate temperatures required.
- High deposition rate, easily adjustable using pulse rate.
- Deposition controlled by laser - no shutters needed to stop film growth.
<table>
<thead>
<tr>
<th><strong>KrF Excimer</strong></th>
<th><strong>Free Electron Laser</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>• $\lambda = 248\text{nm}.$</td>
<td>• $\lambda = 1050\text{nm}$, frequency doubled to 525nm.</td>
</tr>
<tr>
<td>• 1-50 Hz.</td>
<td>• 18 MHz.</td>
</tr>
<tr>
<td>• Pulse Energy = 0.4J.</td>
<td>• $\mu$-pulse energy $\sim 0.25\mu\text{J}$</td>
</tr>
<tr>
<td>• Average power $\sim 4\text{W}$</td>
<td>• Laser power 5-10W (green)</td>
</tr>
<tr>
<td>• 40 ns pulses.</td>
<td>• 0.5 -1.7 ps pulses.</td>
</tr>
</tbody>
</table>
Why go to J-Labs?

- The ps/ns particulate debate.
- High average powers available.
- Excellent beam quality.
FEL Experimental Parameters

- $\lambda = 525\text{nm}$
- 50% doubling efficiency.
- Frequency = 18MHz
- Incident Power = 4.3W

Cubic ZnSe [1]

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorption depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>619.9</td>
<td>1.233</td>
</tr>
<tr>
<td>500.0</td>
<td>0.796</td>
</tr>
<tr>
<td>459.2</td>
<td>0.228</td>
</tr>
</tbody>
</table>

Vacuum Chamber

Typical pressure reached = \(1 \times 10^{-6}\) Torr.
Target to substrate distance = 55mm.

- Compressed Air
- Cooling Gas
- Heater & Thermocouple
- Electrical Connections
- Rotating ZnSe Target
- Target Motor
- Electrical Connections

- Vacuum Pump Pipe
  Diameter = 100mm

- Removable Substrate
  Holder Assembly

- \(\text{N}_2\) Venting Gas
- Silica Laser
  Entry Window
Vacuum chamber under test
Optical Beam Path

Focal lens scanning motor.

Moving platform which scans laser point across target.

Vacuum chamber.

Focal length of final Silica lens = 49cm

LBO doubler crystal.
Laser Focus Alignment

- Initial Deposition on large area glass substrates.
- Check parallel alignment of target and substrate mount.
- Focus laser onto target surface.
- Ensure laser does not scan over target edges - film contamination from target holder.
- Positioning of central deposition area (‘bull’s eye’) over substrate centre.
- Check PLA occurring, not thermal evaporation.
Alignment Deposition Fringes
Ablation Target Patterns

Right: KrF ZnSe target, showing typical ablation pattern.

Left: FEL ZnSe target.

Thermal Evaporation groove - rough surface.

Typical Ablation pattern - smooth glassy surface.
Glass Substrate, Post Deposition
Hiccups from a rushed transatlantic flight!

- Susceptibility of substrate heater element to failure.
- Lack of time to degas replacement heater (with brazed element).
- Running at 525nm, not 263nm - comparison films deposited using KrF laser (247nm).
- Need to recaesiate FEL during the experiment.
But, even so…4 Interesting Films

1. Substrate temperature 518°C.
   Deposition over 1 minute. Thickness = 240 nm.

2. Substrate temperature 395°C.
   Deposition over 1 minute. Thickness = 248 nm.
   Heater broke.

3. Substrate temperature 503°C.
   Deposition over 1 minute. Thickness = 334 nm.

4. Substrate temperature 565°C.
   Deposition over 1 minute. Thickness = 213 nm.
   Brazed heater degassing - probable contamination.
Deposited ZnSe Film

Film #1 - fringes visible

Aluminium Substrate mount shield with visible fringes
XRD Analysis of FEL Films

Film 1 - Substrate Temperature 518°C

Counts (a.u.)

2 theta (degree)

FWHM = 0.3518°

Peak at 44.6°
XRD Analysis of FEL Films

Film 4 - Substrate Temperature 565°C

Counts (a.u.)

Polycrystallinity and film defects - possibly caused by contamination

Peak at 44.58°

FWHM = 0.3425°
XRD Analysis of KrF Films

Cr:ZnSe film - Substrate Temperature 550ºC

Peak at 43.62º

FWHM = 0.0708º
XRD Analysis of KrF Films

ZnSe film - Substrate Temperature 575°C

Peak at 43.7°

FWHM = 0.2218°
UV/visible Spectroscopy Analysis

Comparison of Film 3 with ZnSe optical window

Transmission edge intercept at 440nm for film. 450nm for ZnSe.
### FEL and KrF film Comparison

<table>
<thead>
<tr>
<th>Film Type</th>
<th>Temperature (°C)</th>
<th>XRD Peak</th>
<th>FWHM</th>
<th>Transmission Edge (nm)</th>
<th>Thickness (nm)</th>
<th>Deposition Rate (nm/s/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEL #1</td>
<td>518</td>
<td>44.6°</td>
<td>0.352°</td>
<td>449</td>
<td>0.240</td>
<td>0.80</td>
</tr>
<tr>
<td>FEL #2</td>
<td>395</td>
<td>44.56°</td>
<td>~2°</td>
<td>445</td>
<td>0.243</td>
<td>0.39</td>
</tr>
<tr>
<td>FEL #3</td>
<td>503</td>
<td>~44.8°</td>
<td>~2°</td>
<td>451</td>
<td>0.334</td>
<td>1.12</td>
</tr>
<tr>
<td>FEL #4</td>
<td>565</td>
<td>44.58°</td>
<td>0.343°</td>
<td>446</td>
<td>0.213</td>
<td>0.71</td>
</tr>
<tr>
<td>KrF</td>
<td>574</td>
<td>43.7°</td>
<td>0.222°</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>KrF</td>
<td>550</td>
<td>~43.6°</td>
<td>~3°</td>
<td>458</td>
<td>0.9242</td>
<td>0.13</td>
</tr>
<tr>
<td>KrF</td>
<td>499</td>
<td>–</td>
<td>–</td>
<td>459</td>
<td>1.1681</td>
<td>0.16</td>
</tr>
<tr>
<td>KrF</td>
<td>402</td>
<td>–</td>
<td>–</td>
<td>460</td>
<td>1.3564</td>
<td>0.19</td>
</tr>
</tbody>
</table>

- Deposition rate for FEL greater by a factor of 5, compared to KrF.
- XRD peak for SrF$_2$ substrate close to ZnSe peak (SrF$_2$ = 41.96°).
Conclusions

- Too few results to reach any definite conclusions.
- The ps/ns debate remains to be resolved.
- Preliminary results indicative of epitaxial films.
- UV/visible spectroscopy look good but there are some questions.
- Plenty of scope for more collaboration and return visits to J-Labs.
Calorimetric Measurements of Near-IR Optical Absorption of Ga:La:S Glasses using JL-FEL.

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Jefferson National Laboratories
Outline

- Ga:La:S glass technology.
- Achievements and current efforts.
- Ga:La:S transparency limit.
- Laser calorimetry.
- Results, conclusions & further work.
Why not silica glass?

**Advantages**
- Stability & Inertness.
- Low attenuation.
- CDV fabrication.
- EDFA devices.
- Mature Technology.

**Limitations**
- Opaque above 2μm.
- Limited rare earth solubility.
- High Phonon Energy.
- Small nonlinearity.
Fibre Amplifiers for Optical Telecoms

- Traditional
- Zero OH

Wavelength [nm]
- 1100 - 1350
- 1400 - 1700

Attenuation [dB/km]
- 0 - 1

EDFA

- 1310 nm band
- S-band
- C-band
- L-band

50 THz

Pr, Nd, Tm-Ho, Er (C-ZBLAN), Tm-Tb
Ga:La:S glasses for photonic applications

- Visible to Mid-Infrared Transmission.
- High Rare Earth solubility.
- Low Phonon Energy.
- High Nonlinearity.
- Fiberisable.
- Good durability.
- Non toxic.
- Highly photorefractive.
# Ga:La:S vs. Silica Glass

<table>
<thead>
<tr>
<th>Property</th>
<th>Ga:La:S</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency window (μm)</td>
<td>0.55 - 5</td>
<td>0.16 - 2</td>
</tr>
<tr>
<td>Refractive Index n (@1.5 μm)</td>
<td>2.4</td>
<td>1.44</td>
</tr>
<tr>
<td>Nonlinear Refractive index n₂ (10⁻¹⁹ m²/W)</td>
<td>20</td>
<td>0.25</td>
</tr>
<tr>
<td>dn/dT (10⁻⁵ K)</td>
<td>10</td>
<td>1.2</td>
</tr>
<tr>
<td>Phonon Energy (cm⁻¹)</td>
<td>425</td>
<td>1150</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (10⁻⁶ K)</td>
<td>10.6</td>
<td>0.55</td>
</tr>
<tr>
<td>Glass Transition Temperature (°C)</td>
<td>560</td>
<td>1175</td>
</tr>
<tr>
<td>Melting Temperature (°C)</td>
<td>840</td>
<td>&gt;2200</td>
</tr>
<tr>
<td>Specific Heat (J/kg/K)</td>
<td>540</td>
<td>880</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m/K)</td>
<td>0.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Low Phonon Glass Host

Fluoride/Oxide Glass

\( \text{P} \text{r}^{3+} \)

1.3 \( \mu \text{m} \) Emission

Non-radiative Decay

Pump power

High Phonon Energy

Sulphide/Chalcogenide Glass

\( \text{P} \text{r}^{3+} \)

1.3 \( \mu \text{m} \) Emission

3.4 \( \mu \text{m} \) Emission

4.7 \( \mu \text{m} \) Emission

Pump power

Low Phonon Energy
Ga:La:S Fabrication Technology

- Raw material Synthesis/Purification.
- Glass melting.
- Polishing of Rods and Disks.
- Preform manufacture by Extrusion or by the Rod-in-Tube method.
- Etching.
- Fibre drawing.
- Characterisation.
Ga:La:S Fabrication Technology

Rods, Canes and Fibers

Multimode Fiber  Holey Fiber  Planar Waveguide

Single-mode Fiber
Ga:La:S-based glasses for photonic applications: state of the art

- **Ga:La:S glass** (fibre amplifiers & lasers)
  - 65Ga₂S₃:30La₂S₃:5La₂O₃ “low oxide” composition.
  - Low phonon energy host for active rare earths (Pr, Dy, Er, Tm, ...).
  - Glass stability upon reheating (devitrification) is an issue.
  - Single mode fibre achieved, although only in short lengths and poor quality.

- **Ga:La:S:O glass** (nonlinear devices, microstructured fibers)
  - 78Ga₂S₃:22La₂O₃ “oxysulphide” composition.
  - Better thermal stability makes fibre drawing easier.
  - Lower QEs of rare earth ions, but nonlinearity as high as in Ga:La:S.
  - Multimode fibers pulled in hundred meter lengths. Holey fibre demonstrated.
Current Limitation: High Loss

Sources of Optical Loss
- Impurities (Fe$^{3+}$, ...).
- Scattering (Crystals, ...).
- Core/clad interface defects.
- Weak Tail.

Target for a Practical Device:
1 dB/m Single Mode Fibre
(≈2μm core diameter)
WAT in Chalcogenide Glasses

- Typical of covalent Chalcogenide Glasses (As$_2$S$_3$, GeS$_2$, ...).
- Limits intrinsically the NIR glass transparency to $\approx$1 dB/m.
- Caused by additional electron. states in the bandgap.
  (Defects, Disorder)
Key issues:

- **Is there a Weak Tail in Ga:La:S?**
- **What is the Transparency Limit of Ga:La:S?**
- **Is it feasible to fabricate optical devices based on this glass system?**
Measurement of Low Levels of Attenuation in High Index Media.

- Assuming $n = 2.4$ & $\beta = 1\text{dB/m}$ (no scattering considered).

\[ \alpha \approx 2\sigma + \beta L \approx 0.2\% \]

\[ R \approx 28.9\% \]

\[ T \approx 70.9\% \]

\[ L \approx 1\text{cm} \]
Why is conventional “transmission” measurement hard?

- High refractive index causes a big Fresnel Loss (*two orders higher* than Bulk Absorption).
- Inhomogeneity in thick samples.
- Interference effects in thin samples.
- Beam defocussing and steering in UV/VIS and FTIR spectrometers.
- Cannot distinguish scattering from absorption.
Laser Calorimetry

- Direct Measurement of the Bulk Absorption.
- High sensitivity.
- Independent on Scattering.
- Can discriminate bulk from surface absorption.

**Which source?**

\[ AI_0 = C_p \frac{d}{dt}(\Delta T) \]
Why using the FEL at Jefferson Labs?

- Tuning Range.
- High average Power.
- Ability to change the peak power while maintaining constant the average power.
- Beam Quality.
Setup: Calorimeter

- Vacuum Chamber.
- Additional Ext. Shielding.
- Sample Mount.
- Signal Feedthrough.
- Vacuum connections.
- Silica WF ‘Front’ Window.
- CaF$_2$ Brewster ‘Back’ Window.
- Gas Inlet for Thermal Re-Equilibration.
Setup: Sample Mount & RTDs

**Sample Mount**
- Low Thermal Leakage.
- Steady, Low Thermal Capacity.
- Conduction sample-sensors.

**Sensors & Wiring**
- Pt film RTDs (8).
- Th. conductive vacuum epoxy.
- Cu wiring (0.07mm), PTFE coated.

**Temperature monitoring**
- Four Wire Method.
- Control of Thermal emfs.
- Keithley 2000, PC-interfaced
Setup: Optical Path

- Beam Dump
- Sample
- Higher order Harmonics Filter (Si Brewster’s window)
- Chamber Temperature RTD monitor
- CaF$_2$ Brewster’s back window
- Optical Power Meter
- To Keithley 2000
Pulsed method:

\[ \Delta T(t) = \alpha \frac{Q}{m c_p} (e^{-t/\lambda} - e^{-t/\tau}) \]

- \( \alpha \): absorbance 
  \( (\alpha \approx \beta L + 2\sigma) \).
- \( Q \): \( P_0 \Delta t_{\text{pulse}} \).
- \( m c_p \): total heat capacity 
  \( (\text{sample} + \text{holder}) \).
- \( \lambda \): rise time const.
- \( \tau \): decay time const.
Nonlinear and wavelength effect

Experimental Data

Transmitted Laser Power (W) vs. Time (s)

Temperature Increase $\Delta T$ (ºC) vs. Time (s)

- 1.9±0.2 kJ @ 1.55$\mu$m 37MHz
- 2.0±0.3 kJ @1.55$\mu$m 74MHz
- 1.9±0.3 kJ @1.7$\mu$m 37MHz

Fit Curves:
- 1st Heating
- 2nd Heating
- 3rd Heating

Laser Power

- Experimental Data
- Fit Curve 1st Heating
- Fit Curve 2nd Heating
- Fit Curve 3rd Heating
Absorption vs. Pulse Rep. Rate

- Fixed wavelength: $\lambda = 1.55\mu m$
- $\beta(I) = \beta_0 + \beta_1 I$
- No evidence of nonlinear absorption
Absorption vs. Sample Thickness

Temperature Increase $\Delta T$ (°C)

Time (s)

Absorbance

Thickness $L$ (cm)

$T$ (ºC)

$Q = 1$KJ

$\lambda = 1.55 \mu m$

$\Delta t_{\text{pulse}} = 150s$

$L = 2.0mm$

$L = 3.2mm$

$L = 8.5mm$

$\alpha \approx \beta L + 2\sigma$

<table>
<thead>
<tr>
<th>Glass Composition</th>
<th>$\beta$ (10^{-2} cm^{-1})</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga:La:S</td>
<td>1.2 ± 0.1</td>
<td>≈ 0</td>
</tr>
<tr>
<td>Ga:La:S:O</td>
<td>2.1 ± 0.2</td>
<td>≈ 0</td>
</tr>
</tbody>
</table>
Results

• Calorimetric Measurements of Optical Absorption of two sets of samples (Ga:La:S and Ga:La:S:O compositions) have been performed at 1.55 μm and 1.7 μm wavelengths.

• The Bulk Absorption is in the region of 10^{-2} cm^{-1} and is the principal mechanism of optical loss at both the wavelengths. No evidence of surface absorption results from our measurements.

• No evidence of nonlinear absorption was found.

• Our measurements also allow to establish a lower limit to the damage threshold in Ga:La:S glasses, that is 14 W Average CW Power with 0.2 KW/cm^2 Power Density (>6 MW/cm^2 Peak).
Conclusions and further work

- The value of absorption is higher than expected, but still compatible with the fabrication of short in-fibre and planar waveguide devices.
- Additional Measurements at different wavelengths are required to assess if the absorption is due to impurities or to a Weak Tail.
- Characterisation of nonlinear properties vs. the wavelength by the z-scan technique.
- Many other interesting glass systems yet to be investigated....
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