Engineering Novel Infrared Glass Ceramics for Advanced Optical Solutions

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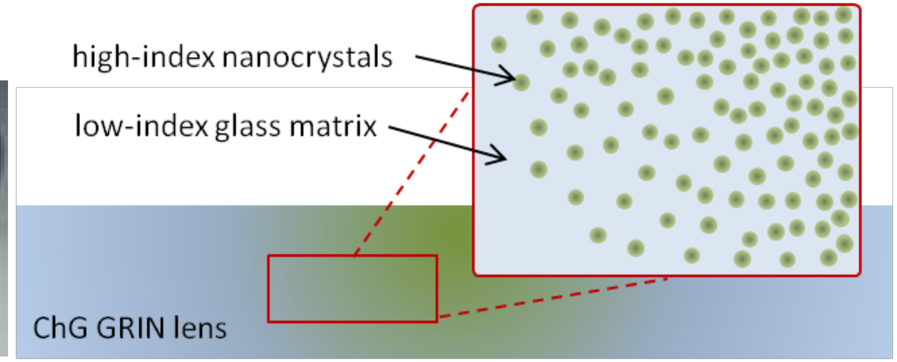
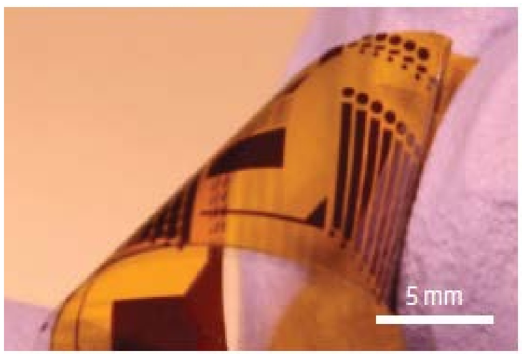
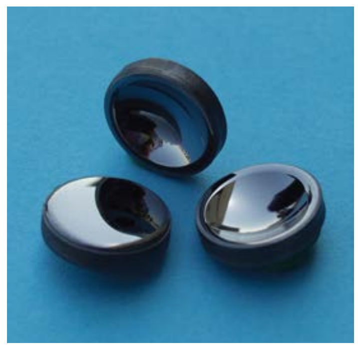
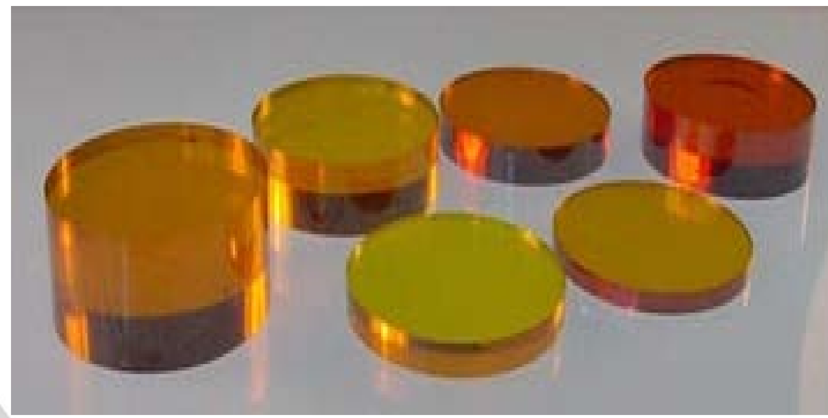
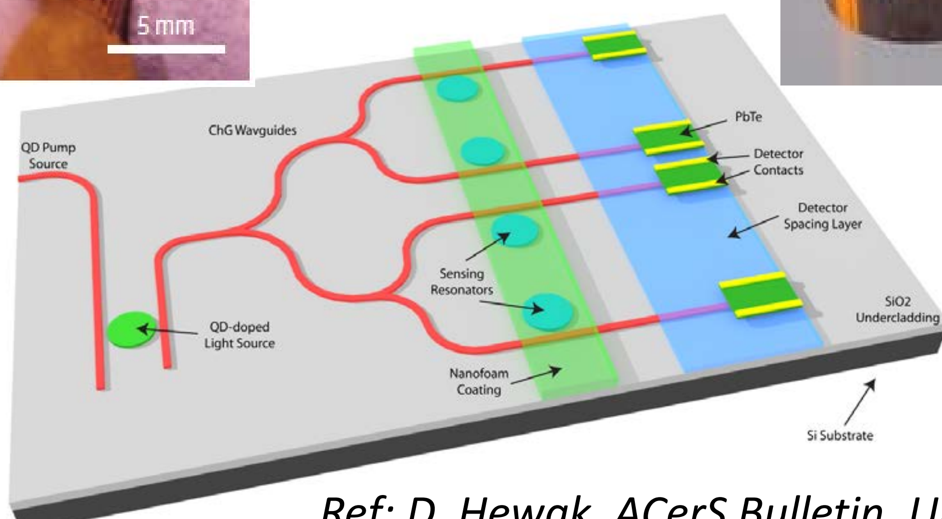
When we think of *infrared* glass....





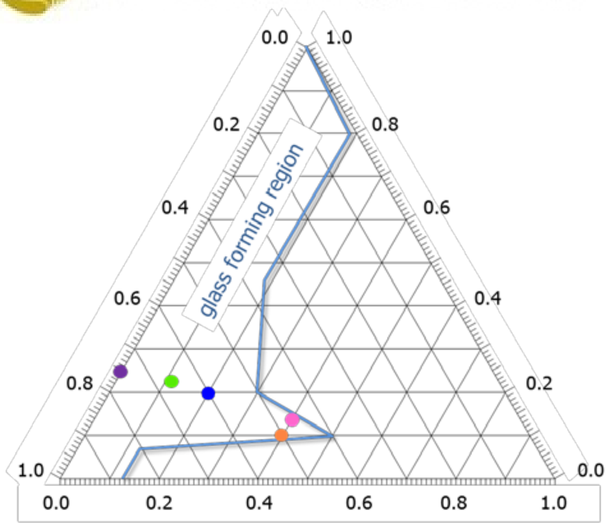


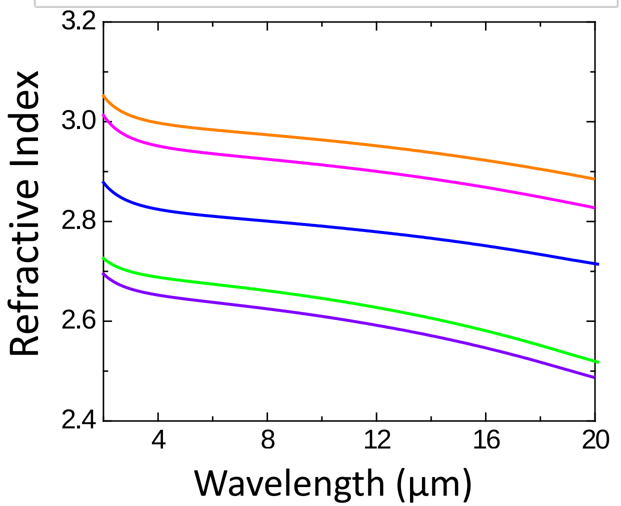


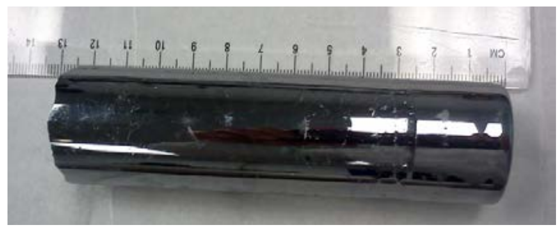


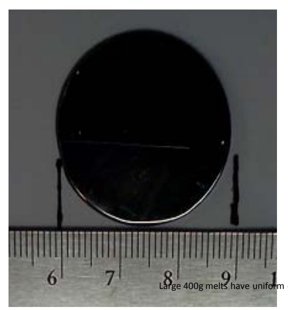
Ref: D. Hewak, ACerS Bulletin, Umicore Corp., and IRradiance Glass

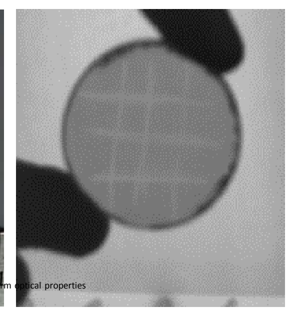
Compositionally tunable optical nanocomposites: MWIR/LWIR glass and glass ceramic

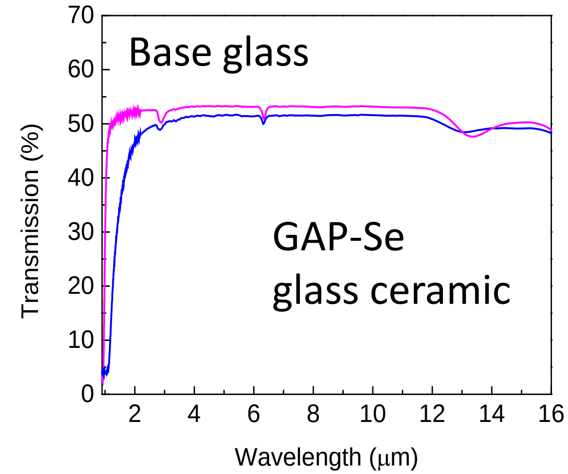


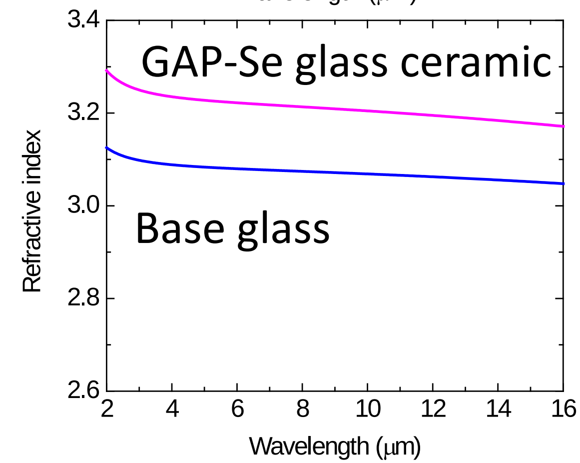












Compositional tuning of multicomponent chalcogenides increases the number of glasses available for optical designers

M-GRIN: Innovative Design and Manufacturing of Gradient-Index-Based Transformation Optics Components
T. Mayer, D. Werner, C. Rivero-Baleine, K. Richardson, Research grant # 4970-UCF-AFRL-7225

ChG GRIN Physical Properties: GAP-Se

Property	As_2Se_3*	GRIN	GRIN + thermal
Transmission Window (µm)	1.0-12	1.1-16	2.0-16
Refractive Index (at 4 µm)	2.7946	2.9565	3.2968
dn/dT (x 10^{-6} °C^{-1}) (at λ, µm)	36.1-32.7	47 (3.39)	--
Glass transition temperature, Tg (°C)	185	189	189
Softening point, (°C)	--	213	--
Crystallization Temp, T_x, (°C)	--	250	250
Upper Use temperature (°C)	--	162	163
Dispersion value (3-5 µm)		69	41
Thermal expansion (ppm/°C)	20.8	18.82	19.31
Density (g/cm^3)	4.63	5.5677	5.5394
Micro-hardness (GPa)	1.04	1.657	1.785

**from: SCHOTT IR Materials data sheets – IRG 26 (May 2013)*

Engineered *chemistry and morphology* enables novel optical materials with manufacturability comparable to existing deployed materials

ChG-GRIN: Motivation

- Need for new materials to support advances in SWIR/MWIR/LWIR optical system applications
  - ✓ *Crystalline materials available (Si and Ge); chalcogenide glasses – ChG and heavy metal oxides (HMOs)*
  - ✓ *Well–characterized chemistry/structure/property know-how needed*

    - input for optical designers (absorption, refractive index, dispersion, thermo-optic properties, nonlinear optical behavior)
  - ✓ *Component/device manufacturing compatibility or flexibility*

    - bulk, thin film and fiber-based materials

    - focus on SWaP: size, weight and power
  - ✓ ***MGRIN -** Low loss, manufacturable mid-infrared glass and glass ceramic materials with tailored and graded refractive indices*

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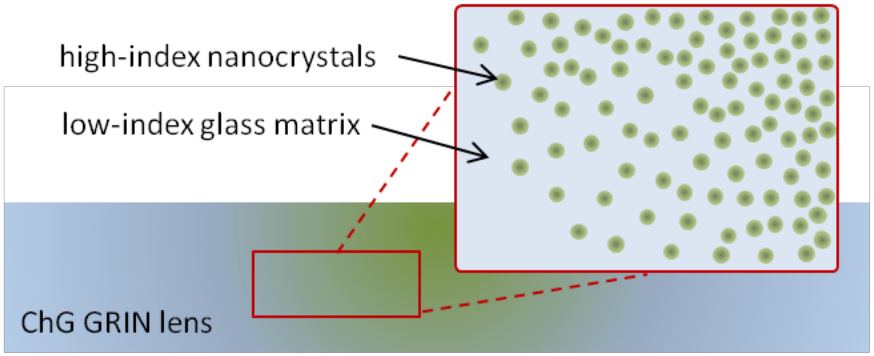
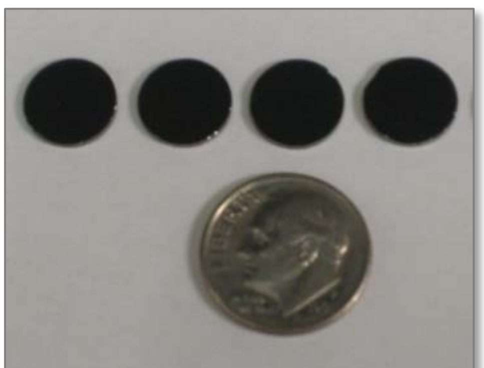
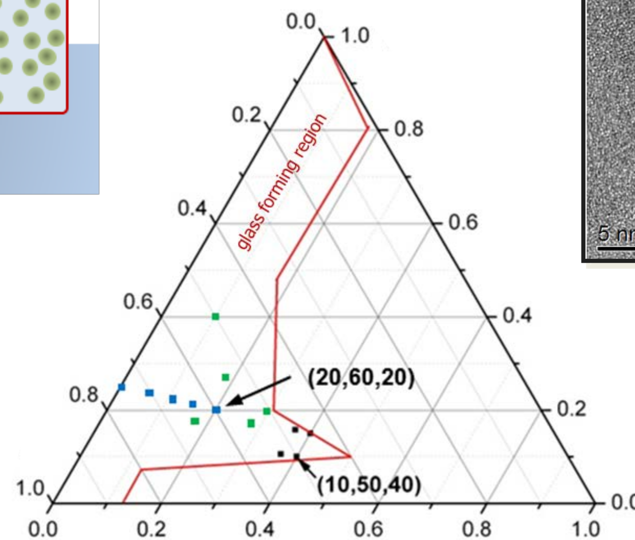
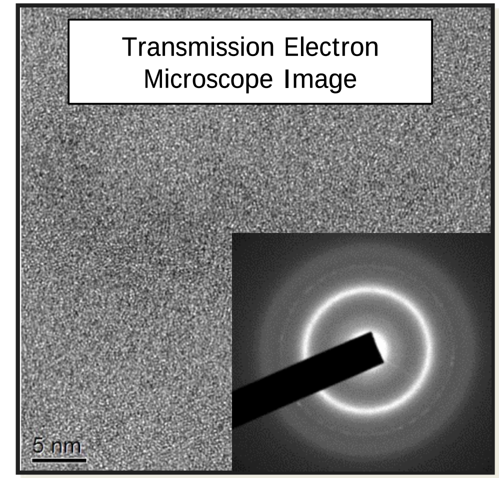
Our M-GRIN solution uses a multicomponent chalcogenide nanocrystal composite material









- Develop compositionally agile, highly transmissive ChG-based material system with extraordinary $\Delta n \geq 0.25$ throughout the infrared spectral range.
- Controlled nucleation and growth of monosized nanocrystals within a ChG glass matrix to form tailorable GRIN profiles in both the radial and axial directions.

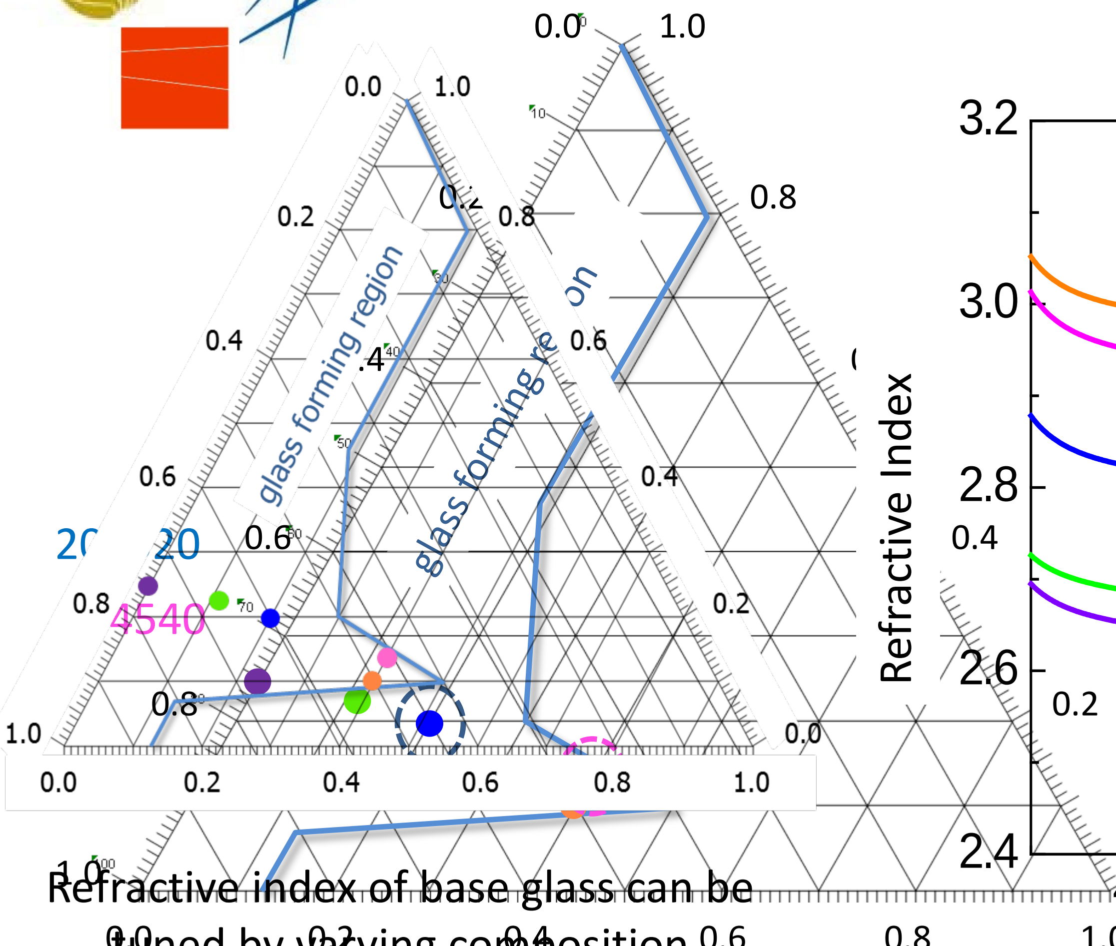
Multicomponent ChG Nanocomposite GRIN System

Key attributes for MWIR glass ceramic (GC) nanocomposite GRIN elements:

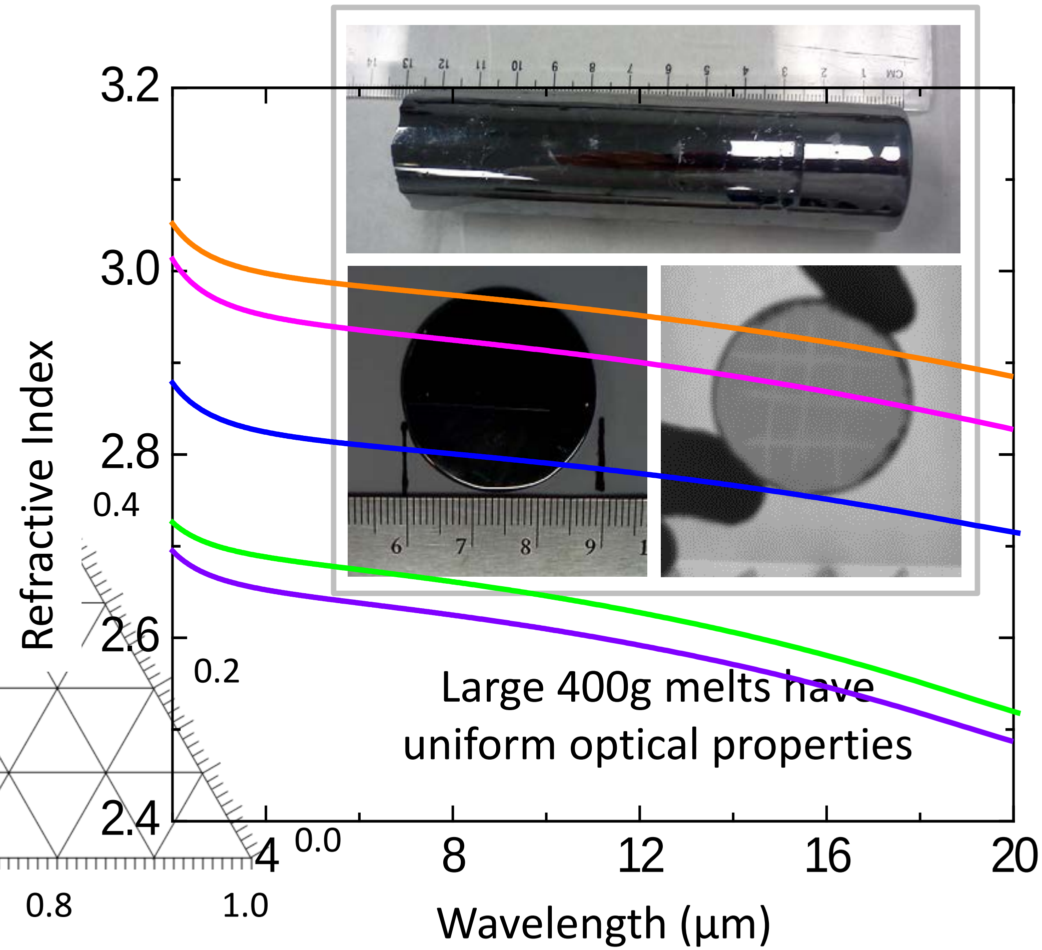
- ✓ All phases (glass and crystal) have low MWIR *absorption* loss
- ✓ Nanocrystals ($n_{crystal}$) have high refractive index relative to base glass (n_{glass})
- ✓ Low *scatter* loss with sub-100 nm diameter crystals
- ✓ Nanocrystal-to-glass filling fraction ($V_{crystal}$:V_{glass}) is tailorable knowing nucleation (I) and growth (U) rates of desired crystal phase(s)

TARGET: $(n_{eff:GC}) - (n_{glass}) = \Delta n_{max} > 0.1$

Chalcogenide Glass GRIN System



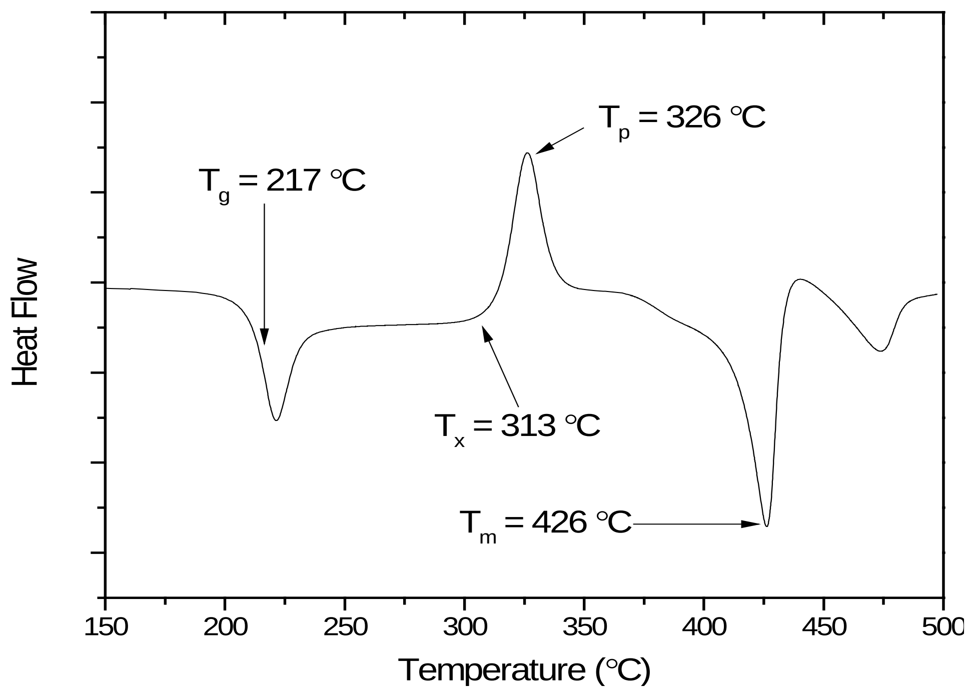
Refractive index of base glass can be tuned by varying composition

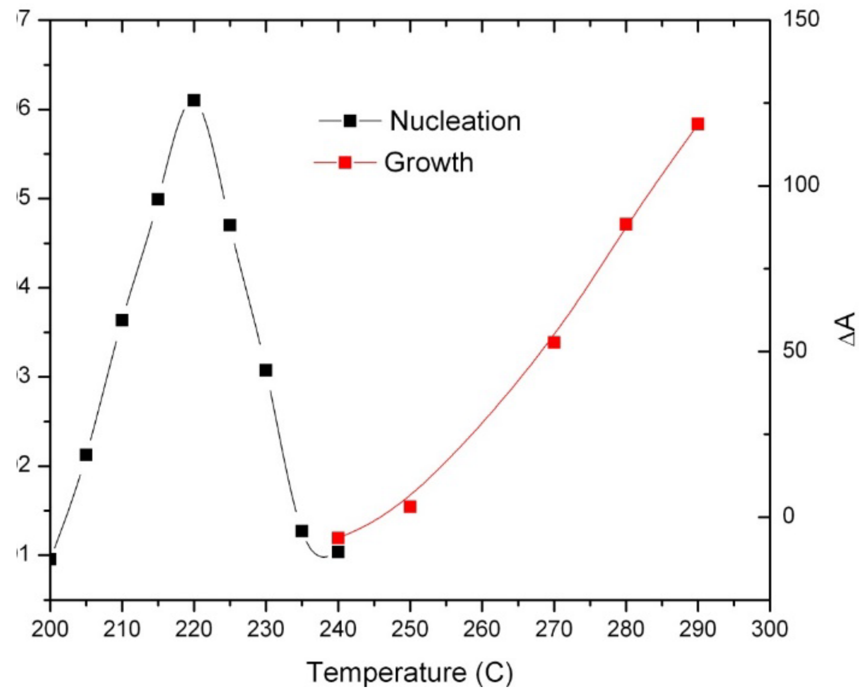


MWIR transparent glass with tailorable refractive index

Process to Create Spatially-Controlled GRIN Profile

Controlled crystallization (nucleation and growth) is required to precipitate high index crystal phase with mono-size distribution within a low index glass matrix





Glass' unique thermal analysis signature yields distinct, *composition-specific* nucleation (I) and growth (U) rate curves

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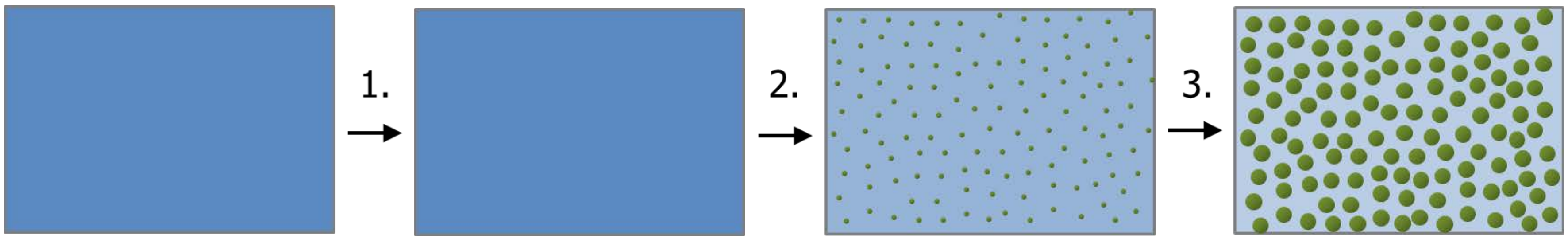
Thermally Driven High-Index Nanocrystal Formation

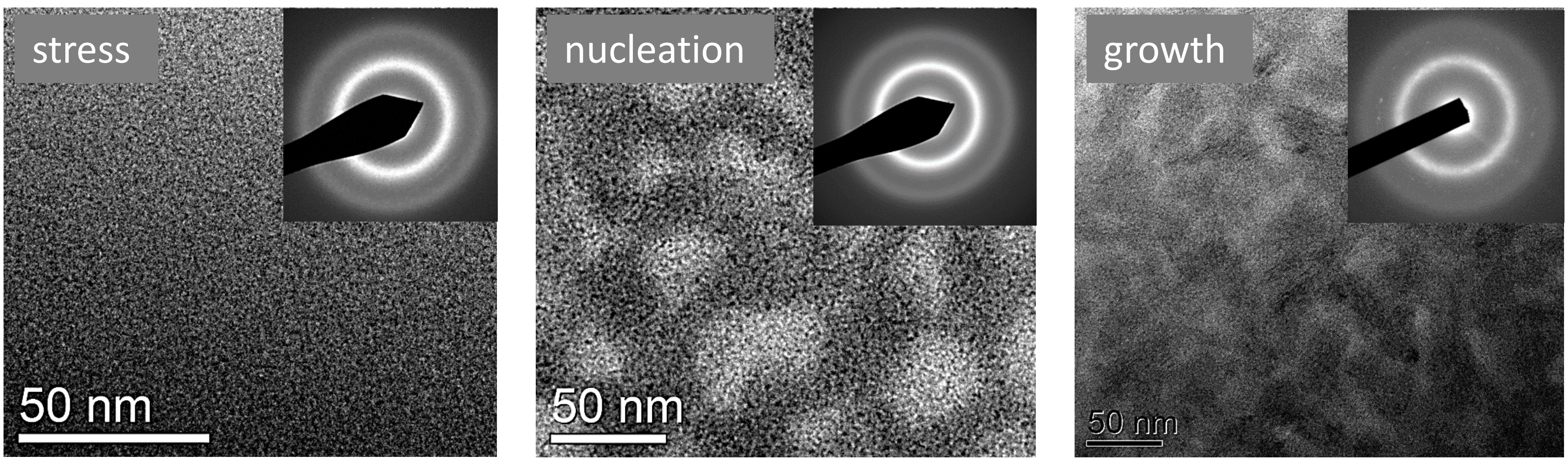
Melt: GAP-Se base ChG glass

Anneal: stress relieved

Nucleation: phase separation→ *number density of crystals defined*

Growth: nanocrystals formed→ *volume fraction defined*





Thermal processing results in controlled phase separation and growth of high-index nanocrystals within multicomponent ChG glass

Using I-U curve for *thermal* GRIN

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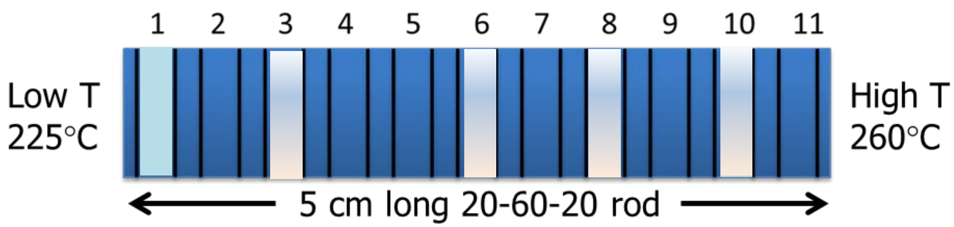
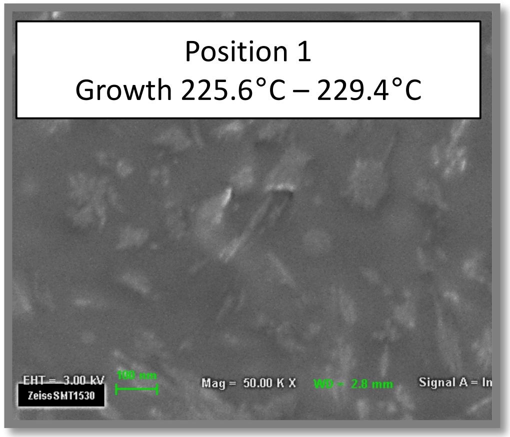
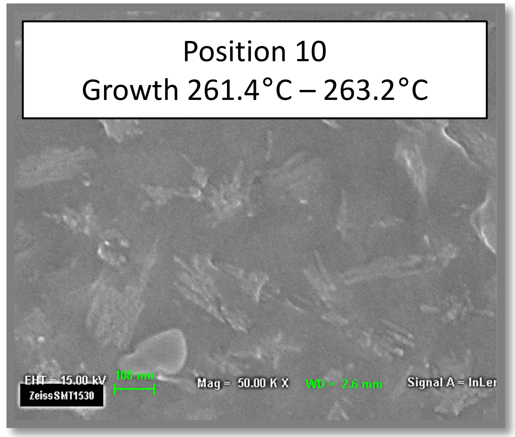


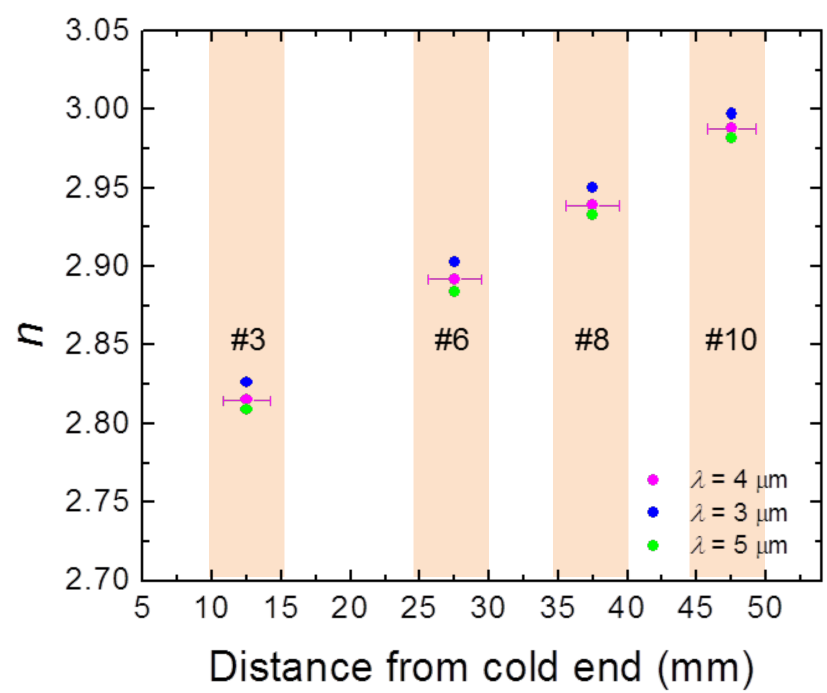
1D Thermal-Thermal Gradient

A 5-cm long GAP-Se rod was thermally treated (nucleated) and then placed in a gradient furnace with a linear (growth) temperature profile that varied from 225°C to 260°C (n_{glass} =2.7946 @ 4µm)





Sample	λ = 3 µm	λ = 4 µm	λ = 5 µm	Abbe number
2-3	2.83	2.81	2.81	103.7
2-6	2.90	2.89	2.88	99.8
2-8	2.95	2.94	2.93	115.6
2-10	2.99	2.98	2.98	129.4

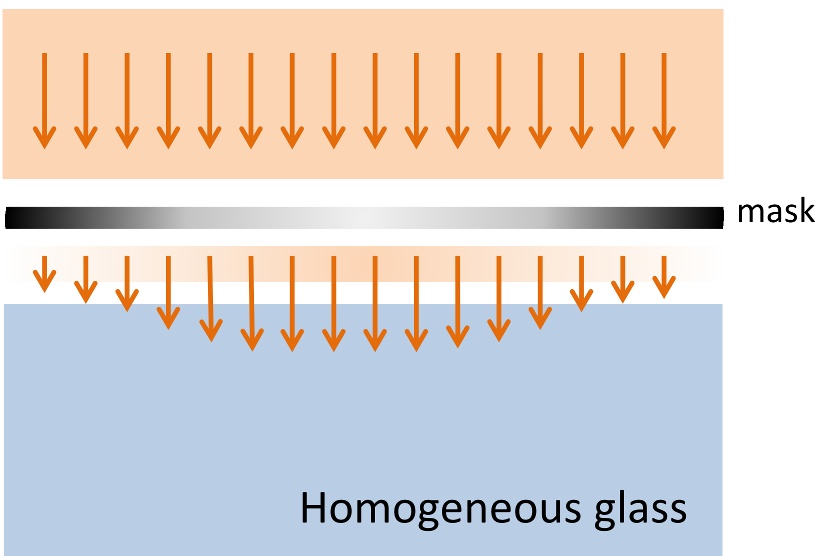


1D GRIN profile with Δn ~ 0.17 introduced by enforcing a 1D thermal gradient across a 5 cm long GAP-Se rod; infrared index and dispersion quantified with morphology

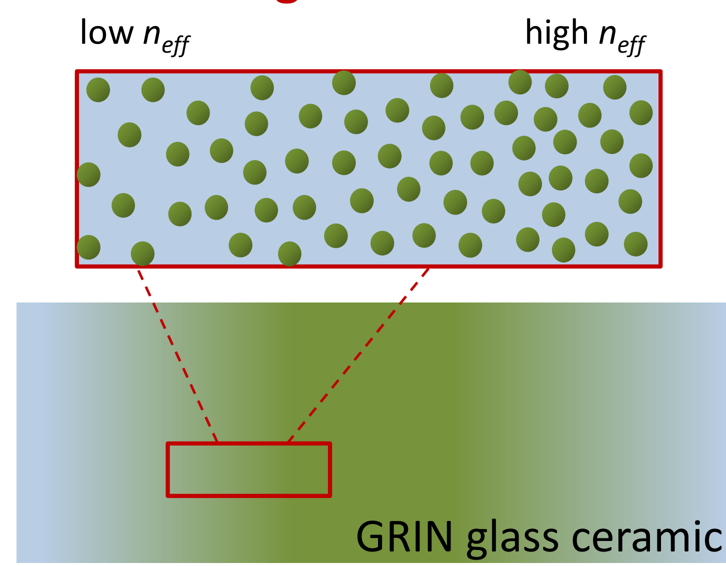
Process to Create Spatially-Controlled GRIN Profile

Controlled crystallization (nucleation and growth) is required to precipitate high index crystal phase with mono-size distribution within a low index glass matrix

1. Spatially varying laser exposure - **nucleation**



2. Thermal treatment – **growth**



$$n_{eff} \sim (n_{glass} \times V_{glass}) + (n_{crystal} \times V_{crystal})$$

Laser exposure is used to locally engineer n_{eff} by controlling the spatially defined concentration of nuclei and high-index nanocrystals

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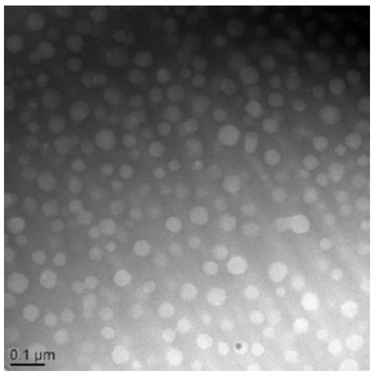
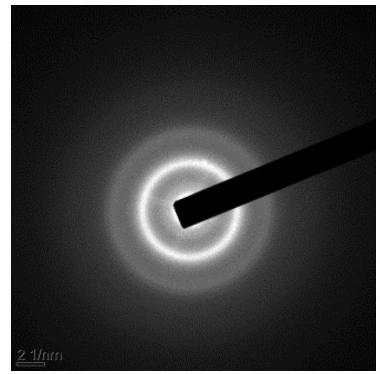
TEM on base glass and *laser irradiated* bulk samples - bright field microscopy

- Initial base glass has nanoscale phase separation → low stability phase
- 1064 nm laser exposure on bulk glass imparts optical absorption, leading to laser-thermal crystal nucleation; post processed with furnace growth

Control



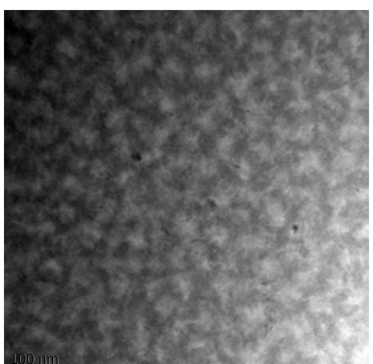
BASE GLASS
Phase separation represented by dark (Pb-rich) matrix and bright (Pb-deficient) droplet regions (100 nm)



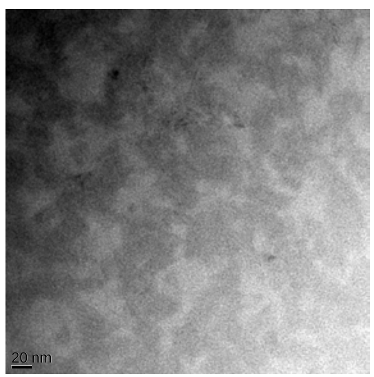
Diffuse ring: amorphous

Laser Exposed

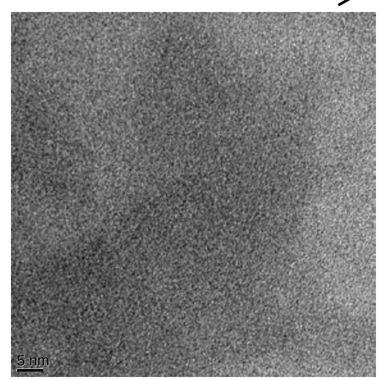
Higher magnification →



Phase Separation represented by dark and bright regions (100 nm)



Size of each phase-separated region ~ 50 nm (20 nm)

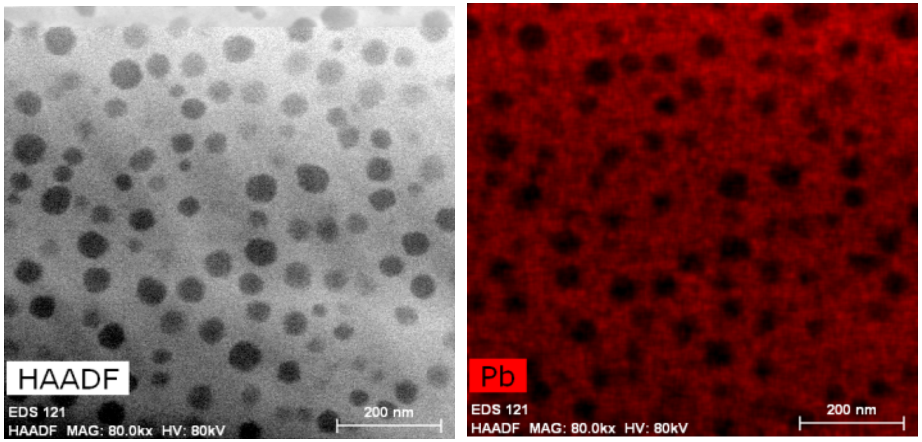


The fringed dark Pb-rich crystalline phase; Bright region: Pb-deficient glass matrix (5 nm)

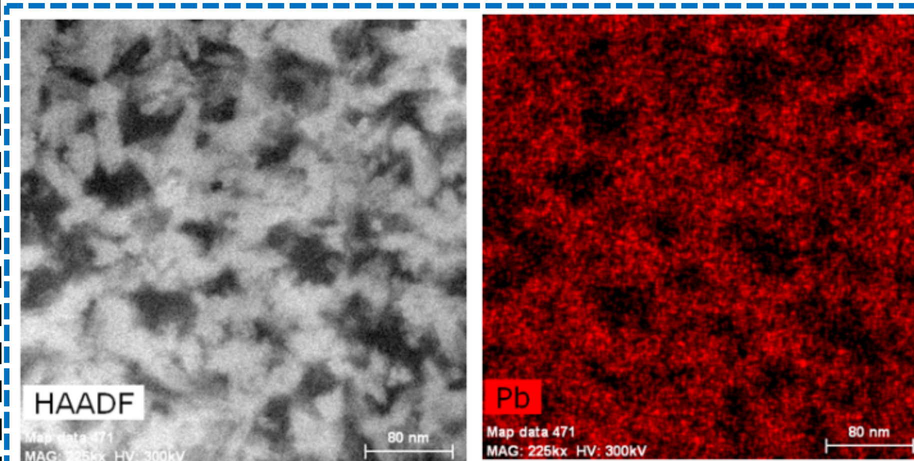
Spotty patterns (crystalline) + a diffuse ring (amorphous)

XEDS can chemically assess phase separation and species segregation- dark field

As-quenched BASE GLASS control sample



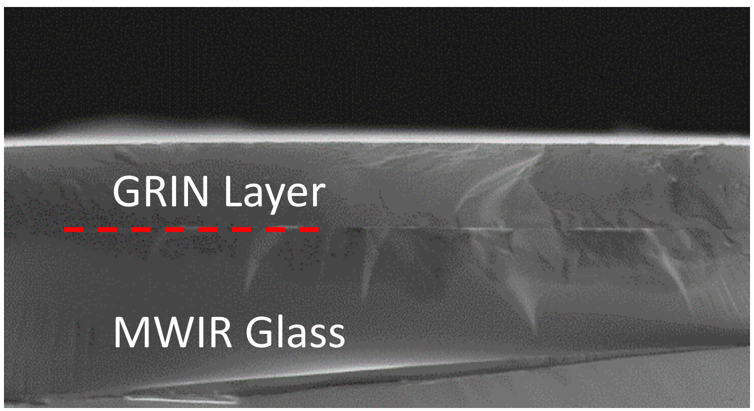
Laser-irradiated BASE GLASS sample

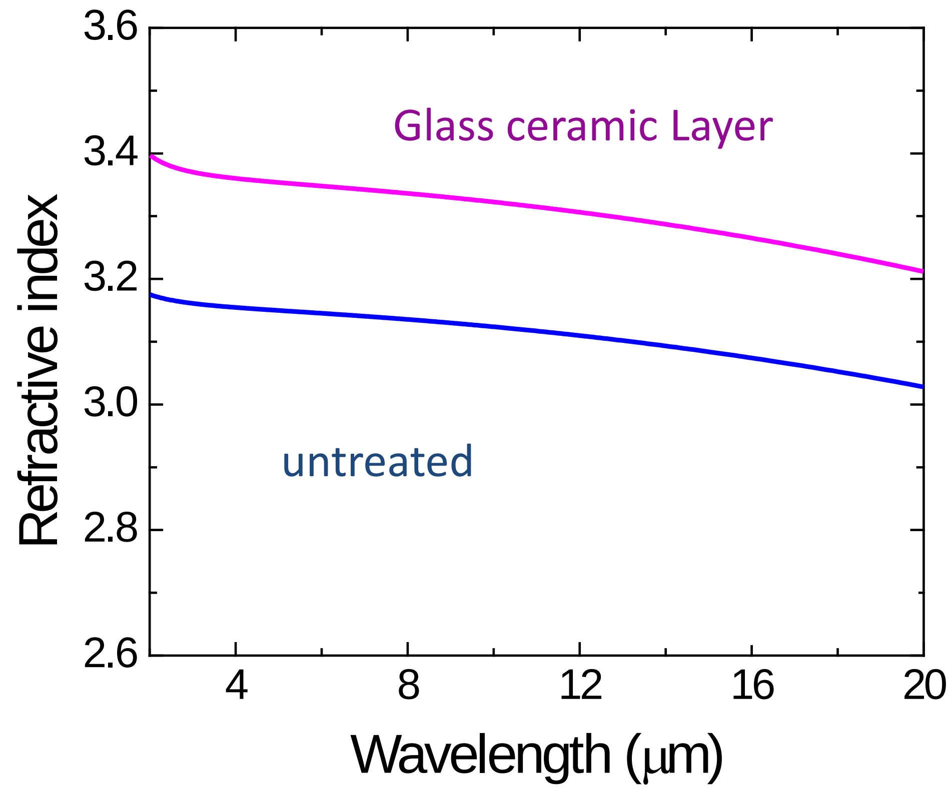


- Pb atoms are segregated by melt/quench protocol into Pb-deficient droplets.
- Pb distribution matches well with the dark region in the BASE TEM image.
- Laser-induced Pb segregation is maintained during laser irradiation.
- Pb-rich matrix regions subsequently (preferentially) crystallize with further thermal treatment

Layered GRIN films on homogeneous bulk MWIR Glass

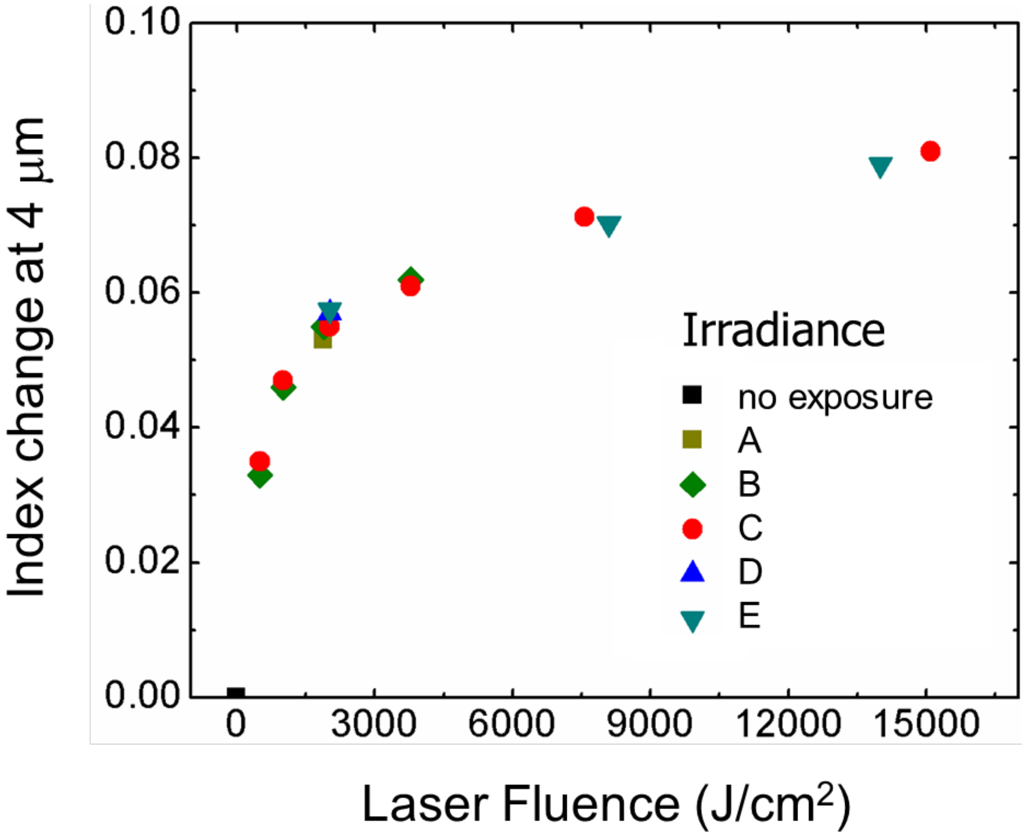
Cross-section of GRIN layer on CTE-matched MWIR glass component (*Class 4 – IRG*)





Homogeneous post-deposition thermal processing introduces uniform distribution of high-index nanocrystals giving a maximum index change of Δn_{eff} ~ 0.2

Index Change versus laser irradiance and fluence

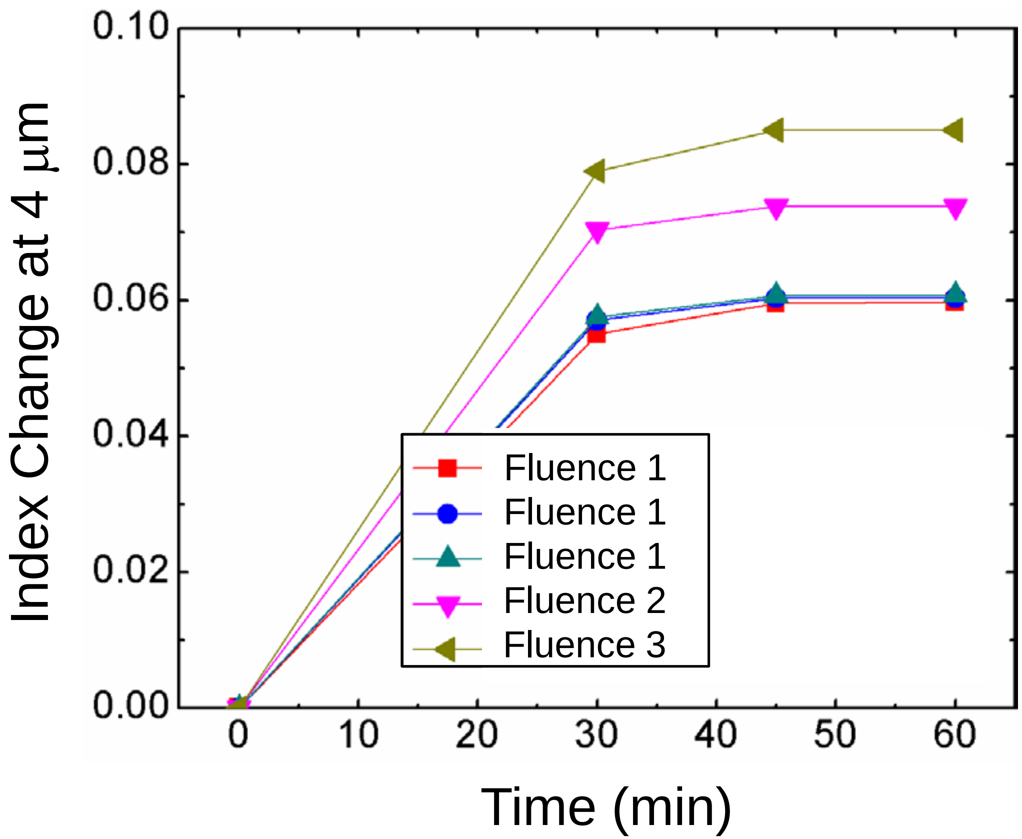


Treatment Details:

- 1.4 μm GAP-Se films with SiO_x AR layer on fused silica substrate
- Constant 190°C for 30 min thermal treatment
- Higher index changes are expected with higher fluence exposures

Identified laser exposure and thermal treatment conditions that give controlled and reproducible index change

Index change versus thermal treatment time



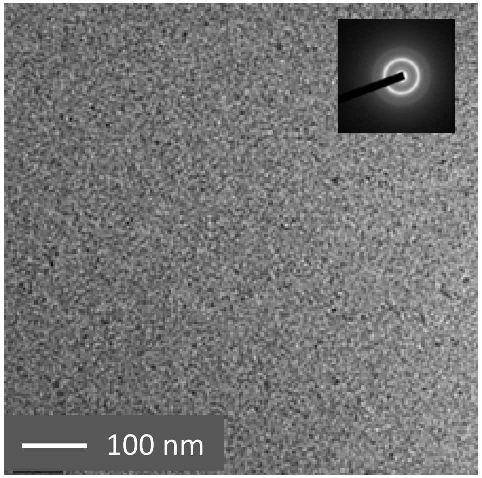
Treatment Details:

- 1.4 µm GAP-Se films with SiO_x AR layer on fused silica substrate
- Sequential thermal treatment at constant 190°C for 30 min

Index change increases with thermal treatment time below 45 mins, and then saturates → **defines process window**

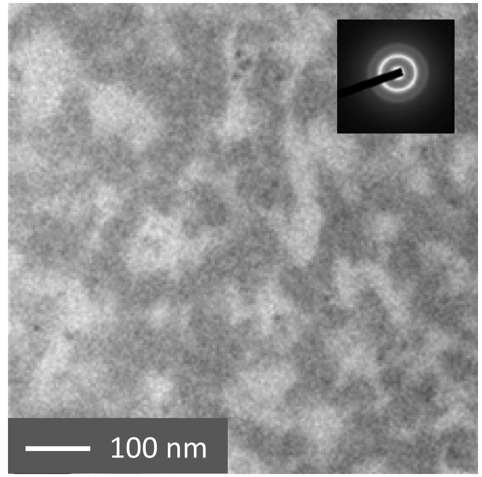
Layered GRIN films on homogeneous bulk MWIR Glass

As-deposited



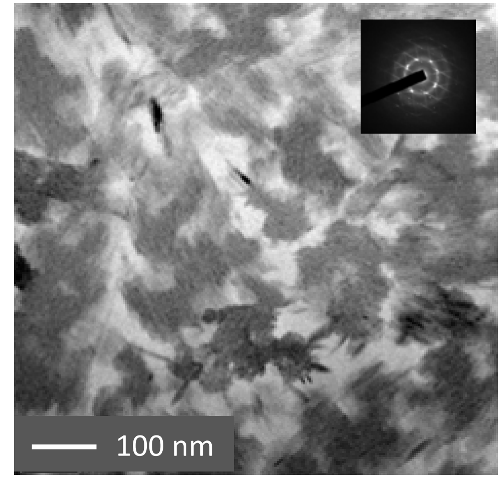
Homogeneous
Amorphous

Laser Exposed



Phase Separation
Amorphous

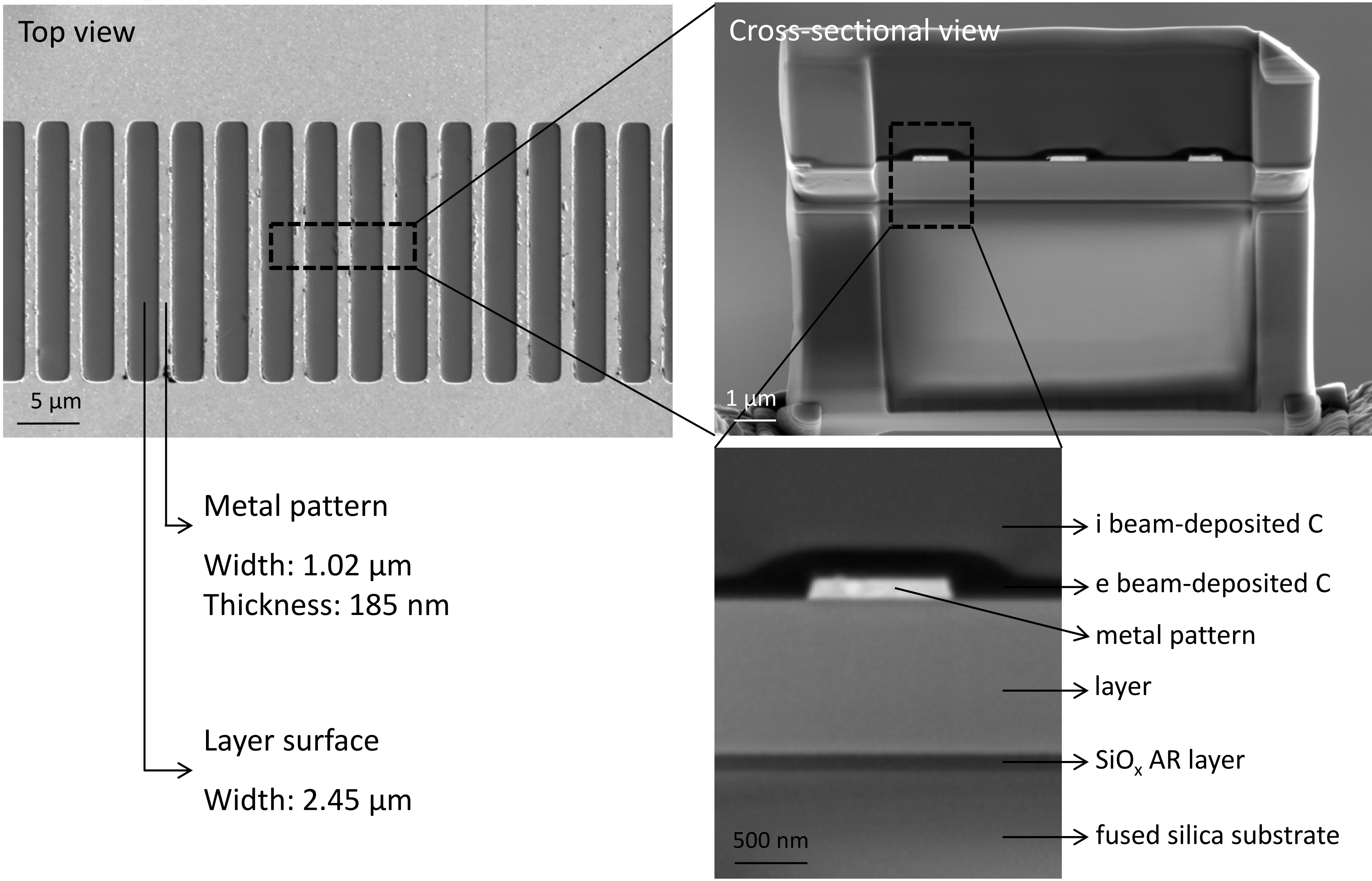
Thermal Treatment



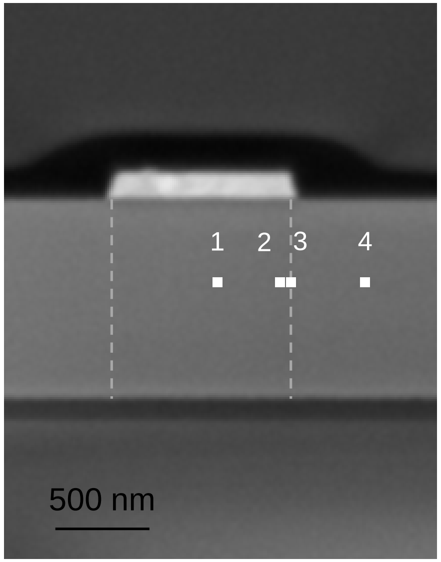
Nanocrystal Growth

- Laser exposure induces controlled phase separation in amorphous film
- Thermal treatment creates sub-60 nm high-index nanocrystals
- Nanocrystal concentration varies with laser exposure and post- exposure thermal treatment conditions → spatial control of dose yields spatial GRIN
- Knowing laser + HT process window, *what is the spatial resolution of the GRIN?*

Laser Exposure through Grating Mask

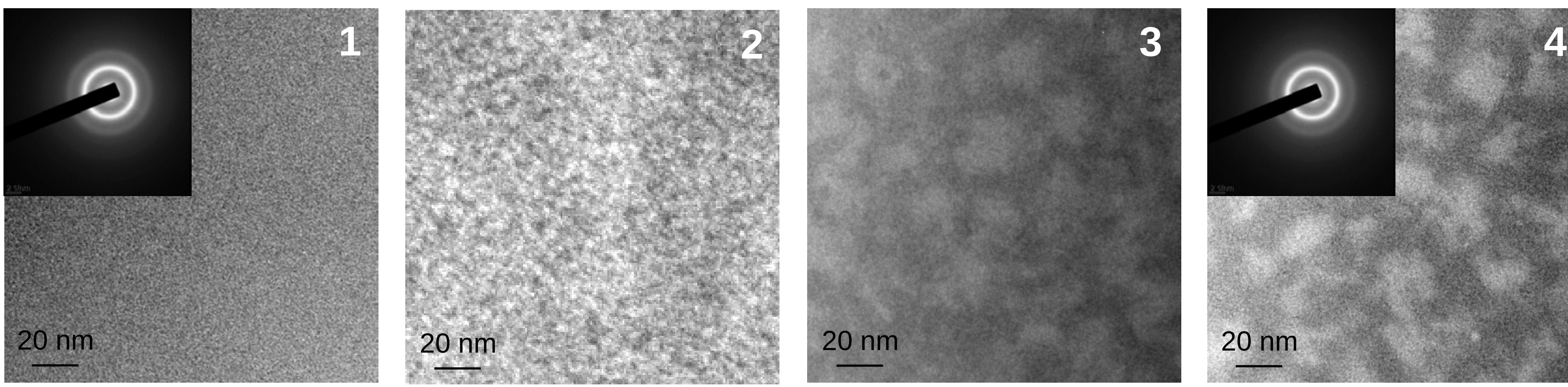


Laser Exposure through Grating Mask



Following *laser exposure only*:

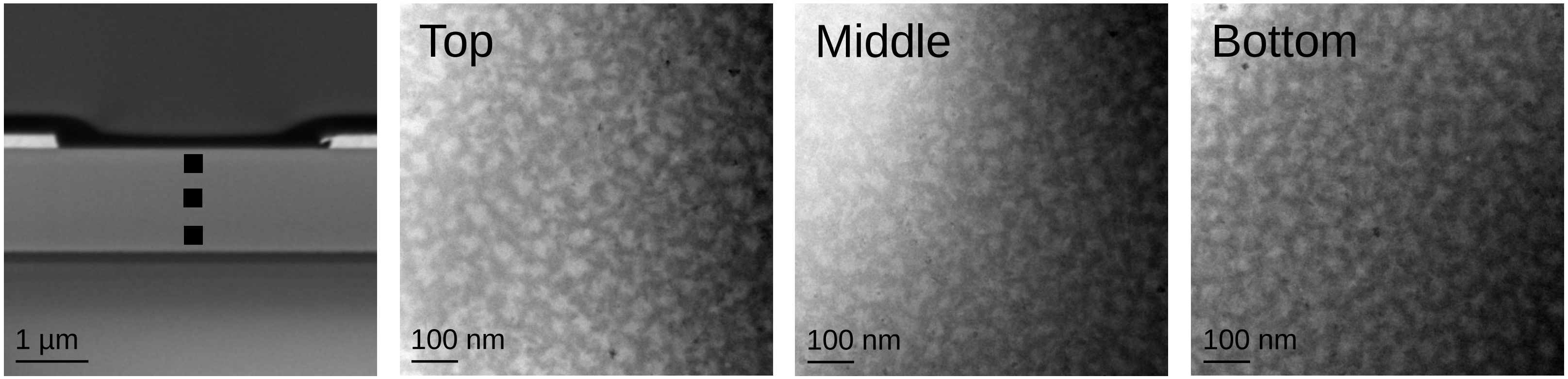
- 1.4 µm layers with SiO_x AR layer on fused silica substrate
- Benchmark fluence prior to thermal treatment
- Microstructure in exposed areas are consistent with broad area experiments, while unexposed areas remain unchanged
- High spatial resolution of < 100 nm



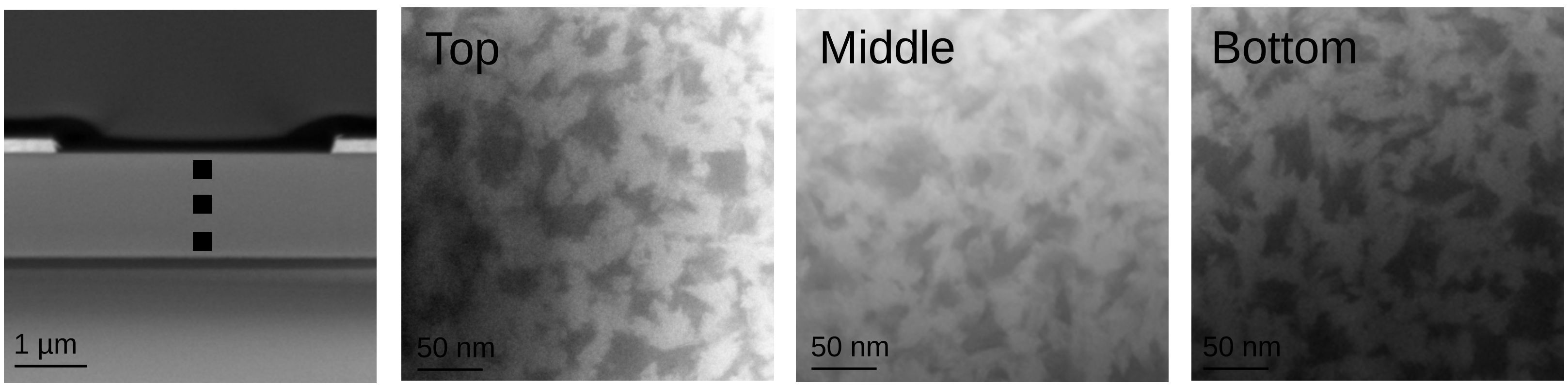
High spatial resolution indicates a photonic driven laser-induced phase separation process with superb spatial control of nucleated microstructure

Laser Exposure + thermal treatment

Following laser exposure – in non-masked region (100 nm scale bar)



Following laser exposure and thermal treatment (50 nm scale bar)



Heat treatment yields uniform nanocrystal formation throughout the *thickness* of the deposited layer – fill fraction variation yields Δn_z in glass below transparent regions of the mask

Conclusions

- Current and next-generation infrared optical systems require **robust materials** based with tunable and/or tailorable optical and physical properties that extend component functionality
- Chalcogenide-based glass ceramic materials have been developed with ***tunable optical properties that can be optimized for desired refractive index and GRIN applications*** to support novel optical system designs
- Physical properties required for optical design optimization have been quantified to enable **optical design and system optimization using graded index optical components**
- Spatially varying (tunable) index profiles (2D or 3D) based on **optical design requirements exceeding Δn of 0.25** have been realized in multi-component ChG glass ceramics which possess low infrared loss enhanced thermal-mechanical robustness;
- **Material scale-up** is ongoing