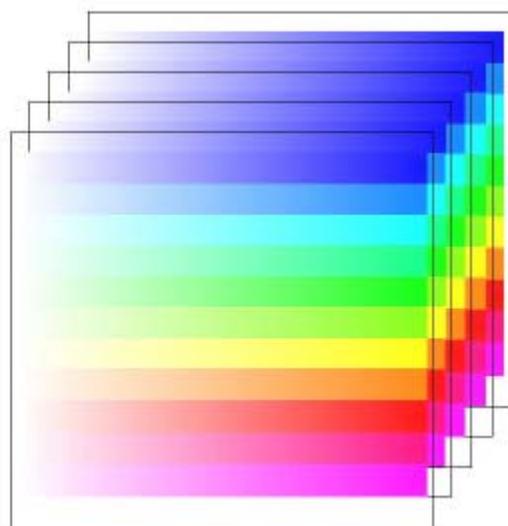


Combinatorial Tools for Inorganic Thin Films

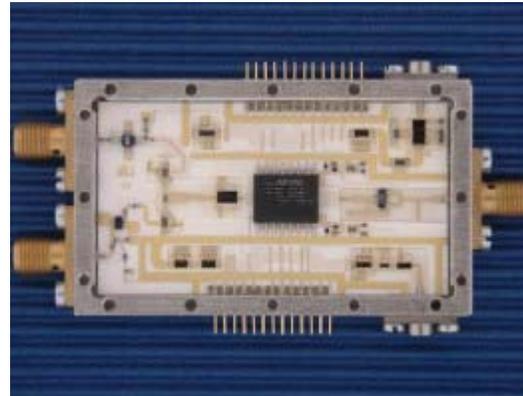


Introduction

Applications of Inorganic Thin Films



optoelectronics



electronics



magnetics

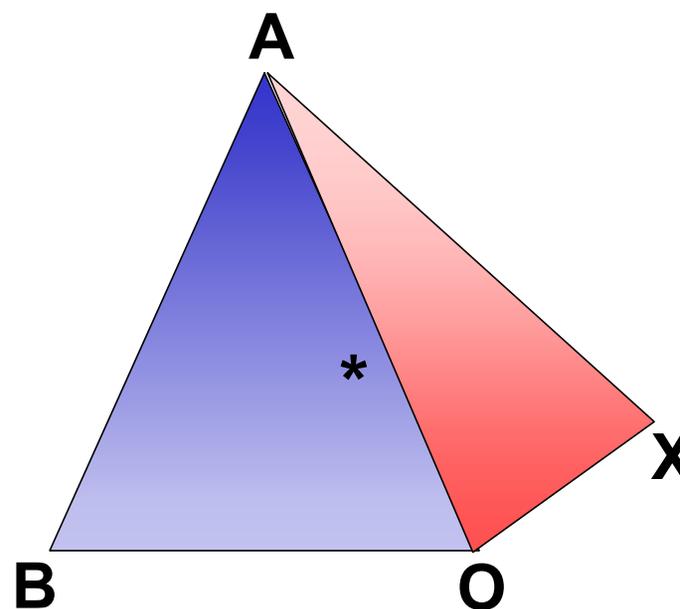


photonics

Introduction

Multicomponent Inorganic Systems

- **Composed of 3 or more elements**
- **Properties depend on composition and structure**
- **Search composition space to:**
 - **optimize specific property**
 - **discover new materials**
- **Explore multiparameter processing space to:**
 - **optimize structure**
 - **optimize specific property**



Quaternary composition space A- B-O-X

Introduction

Combinatorial Studies of Inorganic Films

Material class

Superconductors

Magnetoresistors

Phosphors

Dielectric oxides

Ferroelectric superlattices

Semiconductors

Optical phase change

Investigators

Hanak (1970); Xiang (1995)

Briceno (1995)

Sun (1997); Danielson (1997)

Chang (1998), van Dover (1998)

Koinuma (1999)

Matsumoto (1999)

Cremer (2001)

Introduction

Objective of our Work

Develop combinatorial tools that are applicable to a broad range of inorganic materials:

- ***Library fabrication***

Pulsed laser deposition: dual-beam, dual-target

- ***Property assays***

Thickness & refractive index mapping by spatially-resolved spectroscopic reflectometry

- ***Structural evaluation (preliminary)***

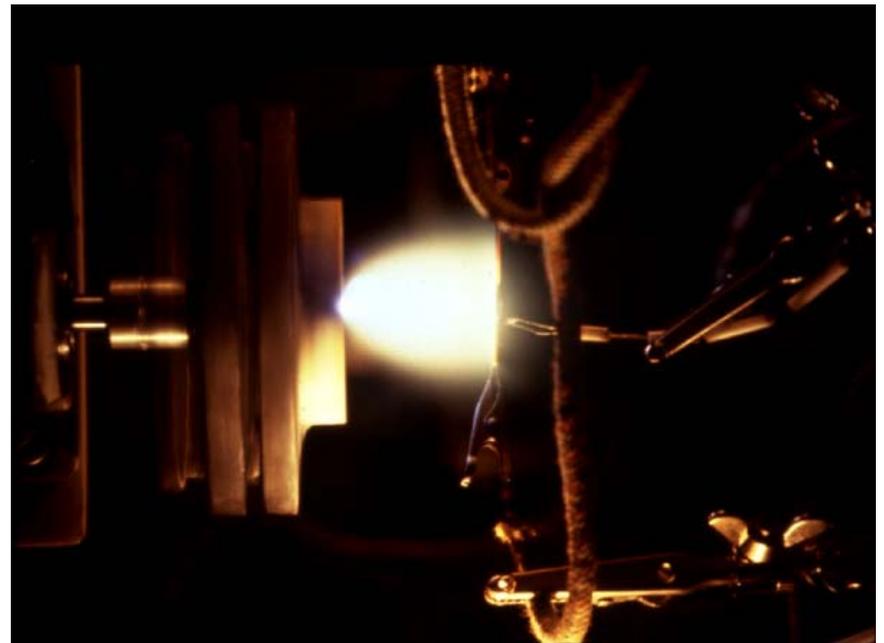
Phase evolution measurements by x-ray diffraction and spectroscopic reflectometry

Library Fabrication

PLD as a Rapid Prototyping Tool

Advantages:

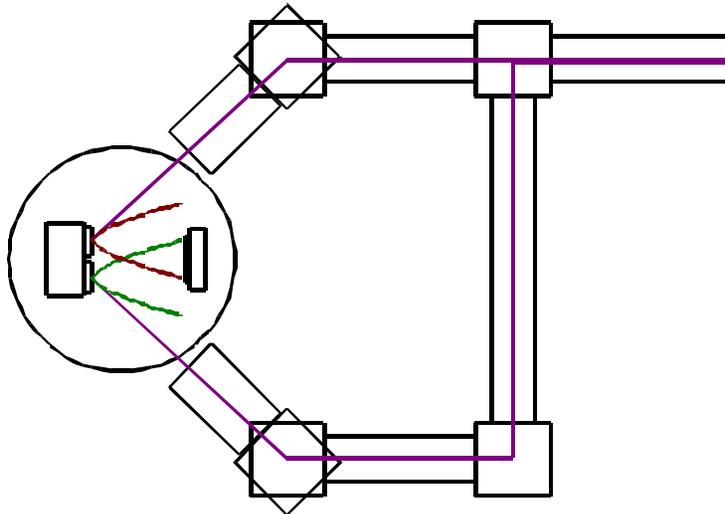
- **Complex target compositions are possible**
- **Congruent vaporization leads to stoichiometric material transfer**
- **High energy process**
- **Higher deposition rates**
- **Lower substrate temperatures**



Laser plume from a single target

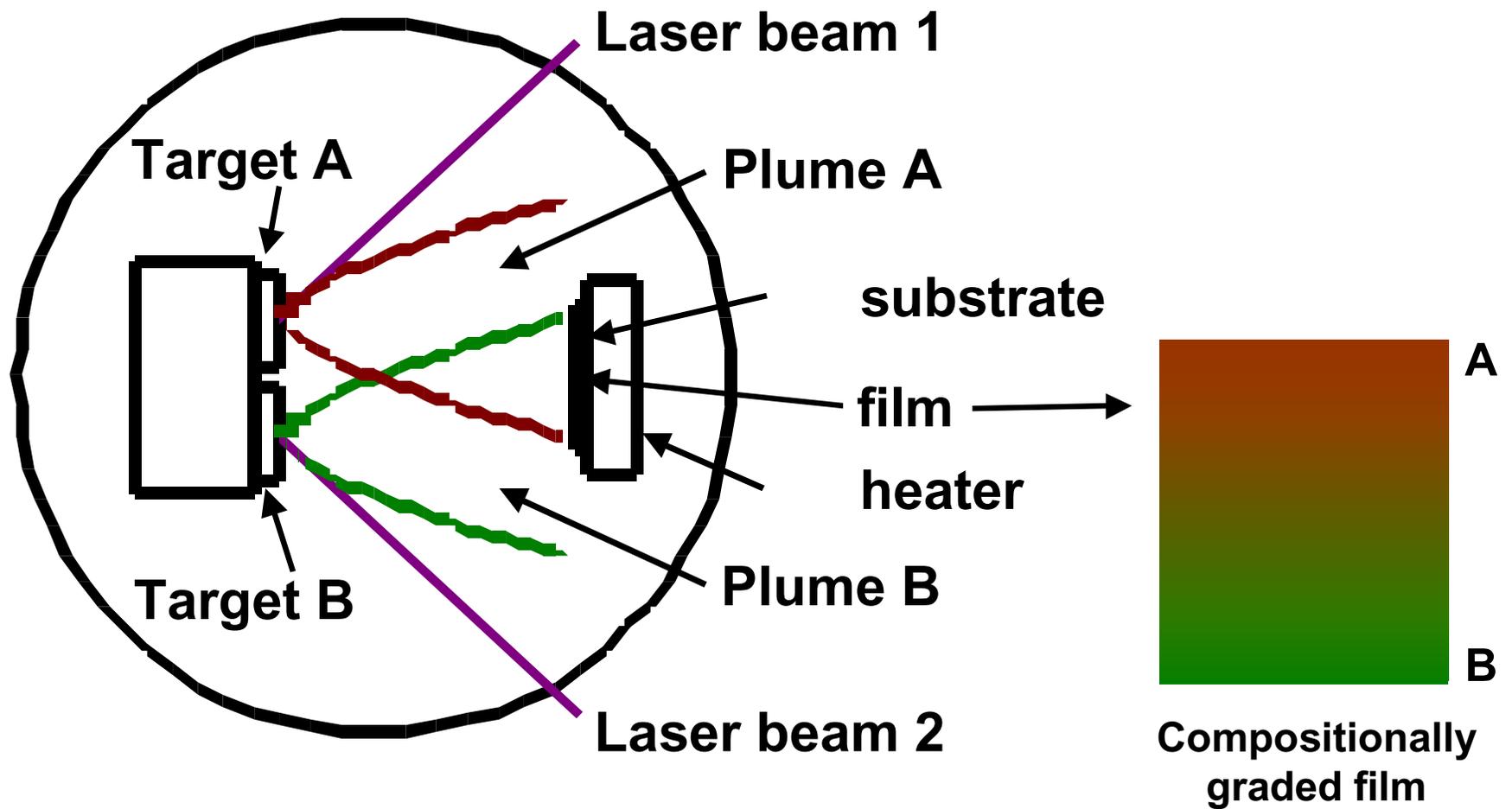
Pulsed Laser Deposition

Dual Beam Design



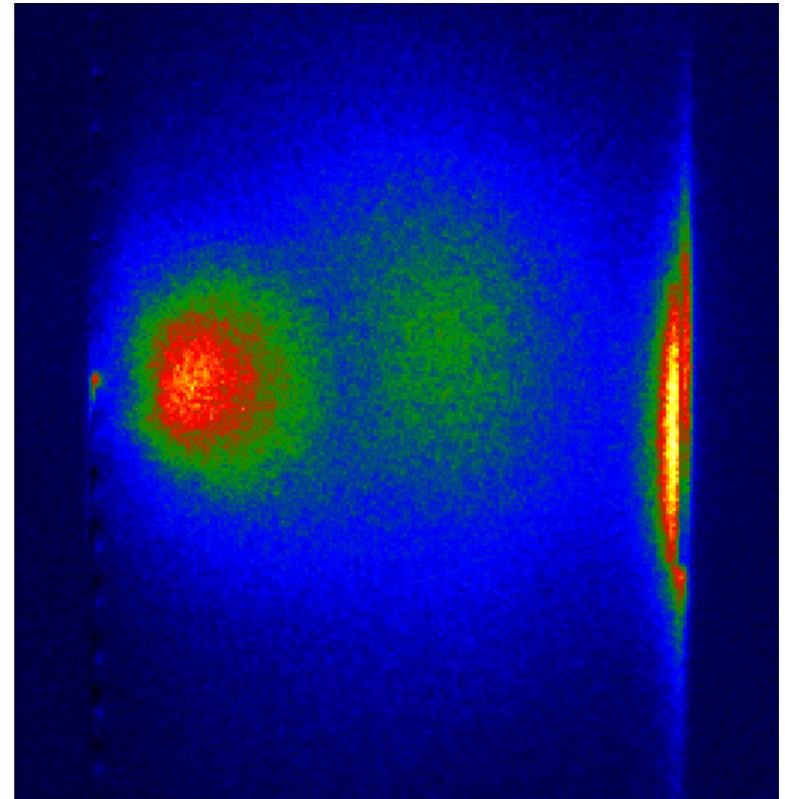
- *Dual Beam Delivery System*
 - Adjustable beam dividing mirror apportions the laser energy to the two targets.
 - Independent adjustment of focus to control spot size on targets.
- *Deposition Chamber*
 - Oil-less pumping and controllable buffer gas pressure.
 - Computer controlled heater.
- *Dual Target System*
 - Targets rotate and raster in two dimensions relative to laser impact points.
 - Utilizes whole target and reduces particulates.

Pulsed Laser Deposition Co-deposition from Two Targets



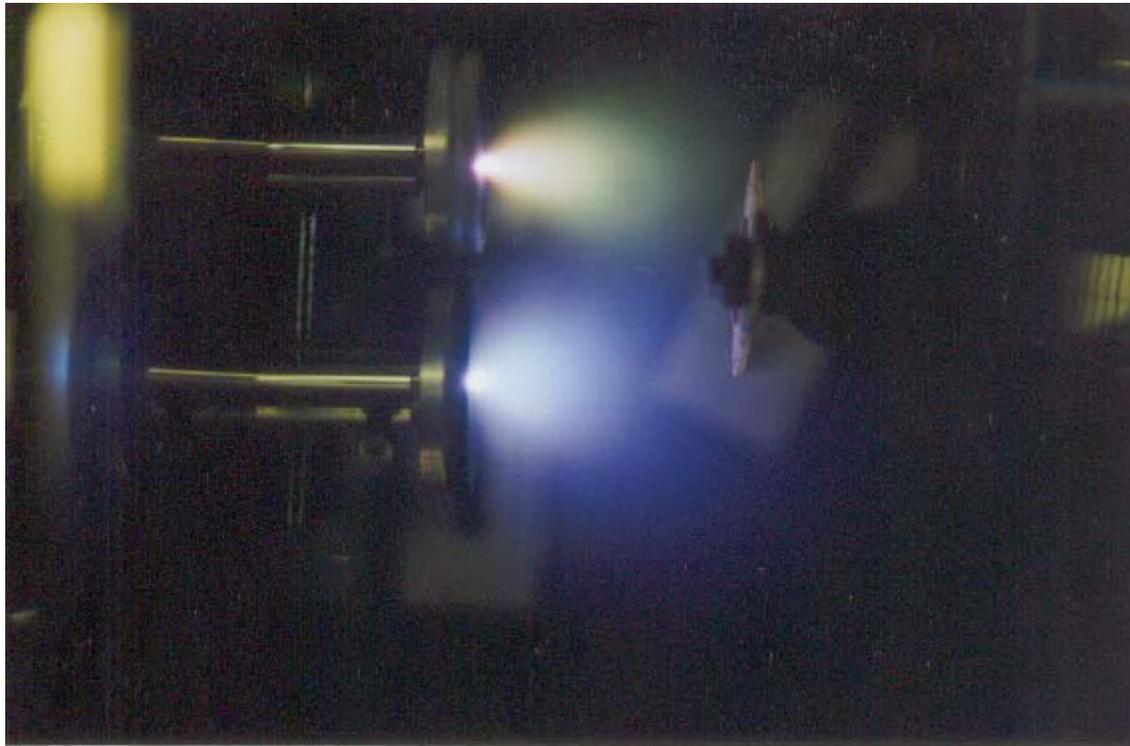
Pulsed Laser Deposition **In-Situ Process Monitoring**

- High speed ICCD camera for imaging laser generated plumes:
 - 5 ns resolution
 - 1 cm field of view
 - 200-900 nm coverage
- Dual crystal deposition rate monitor
- Adjustable parameters: *laser spot size, energy, target spacing*
- Fine-tune parameters to get films of a particular composition spread or thickness distribution



False color ICCD UV image of BT plume at $\sim 1 \mu\text{s}$ after laser pulse (20 ns exp., 3 cm target to substrate)

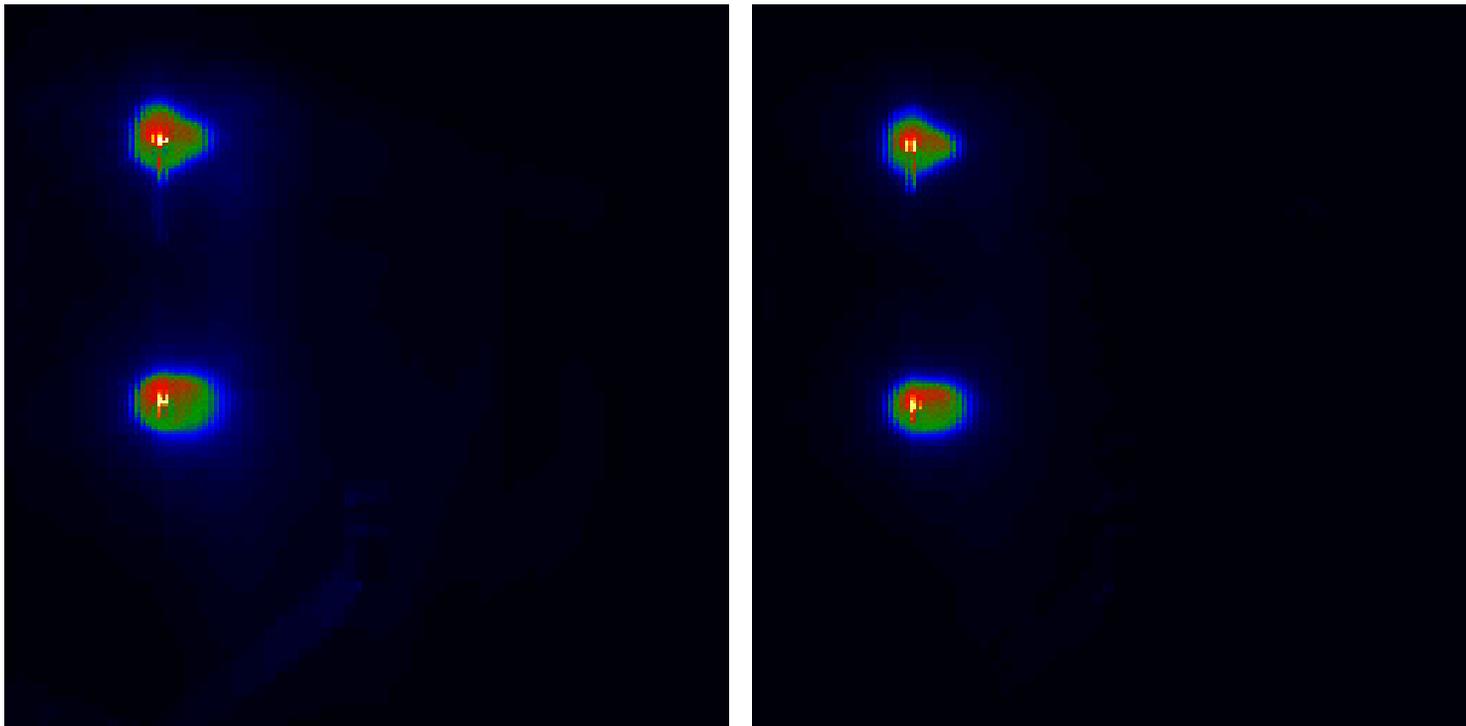
Pulsed Laser Deposition **Plume Imaging**



Target - heater distance 3 cm
BaTiO₃ - yellow SrTiO₃ - blue

Pulsed Laser Deposition Plume Evolution

ICCD Images of Dual PLD Plume Evolution



Visible Light

UV Light

0.5 μs exposure, 15 μs total time

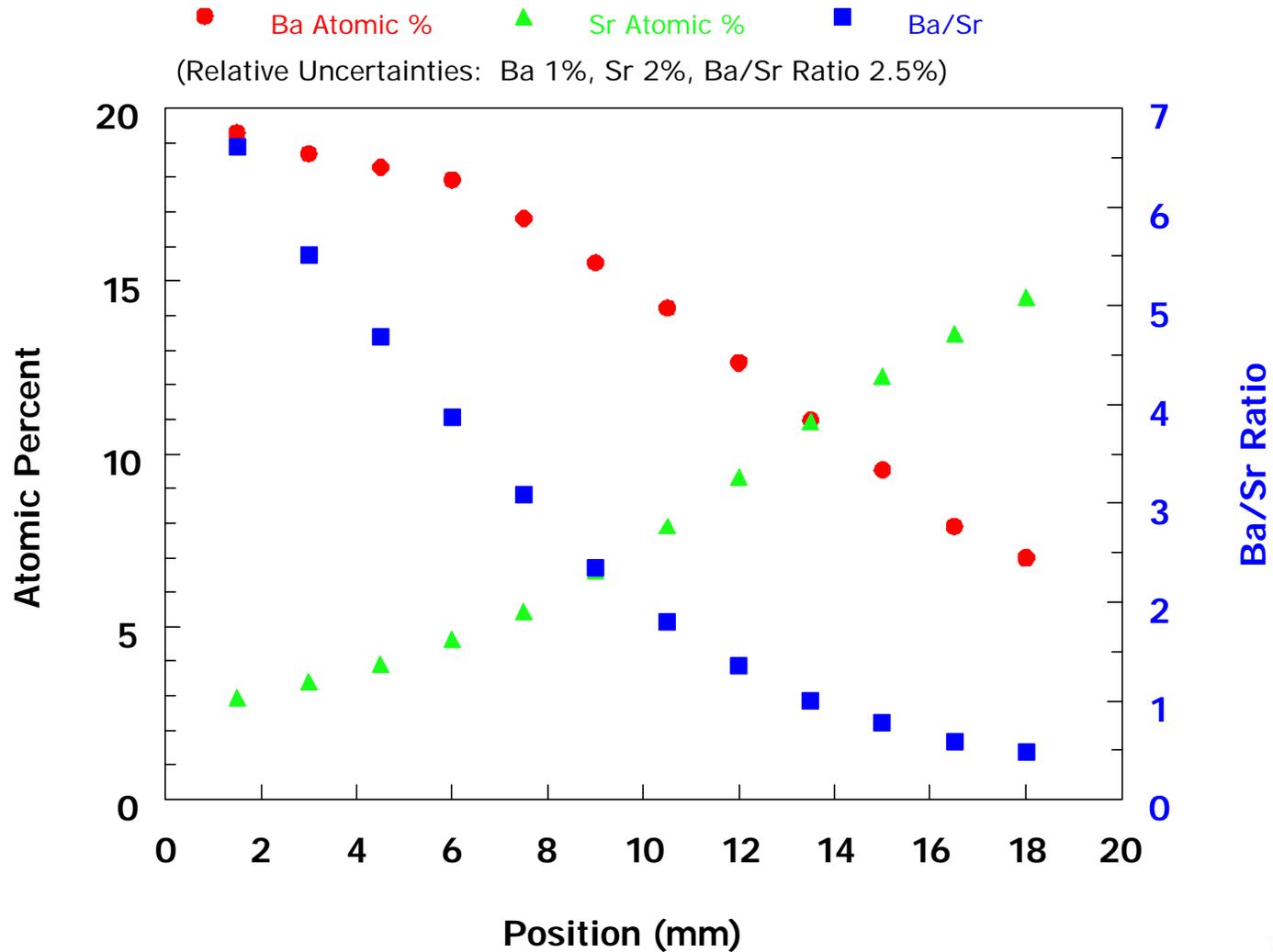
Pulsed Laser Deposition

Library Deposition Conditions

| | <u>Experiment</u> | <u>Range</u> |
|--|--|---|
| Laser Fluence (excimer @ 248 KrF) | ~5 J/cm² | threshold to >100 J/cm² |
| Buffer Gas | 2.5 Pa O₂ | 10⁻⁶ to 40 Pa O₂ |
| Substrate Temperature | 600°C | RT to 800 °C |
| Material System | BaTiO₃ - SrTiO₃ | infinite |
| Targets | pure BT, ST ~ 26 mm centers | |
| Time | 60 minutes / 10 Hz | |
| Deposition rate | 300 to 500 nm/h | |

Composition Assay: BT-ST library

EMPA / WDS measurements



High Throughput Assays

Thickness and Refractive Index

- **Film thickness**

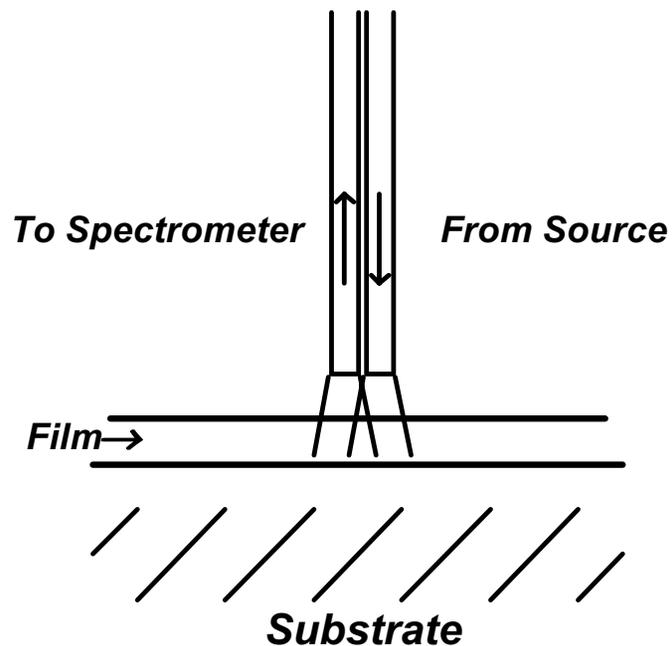
- Key parameter in property measurements
- Thickness may not be uniform in a library film – mapping is needed

- **Refractive index, n**

- Measure of light propagation in a material
- Speed of light in vacuum/speed of light in material
- Critical property for optical and transparent conducting materials

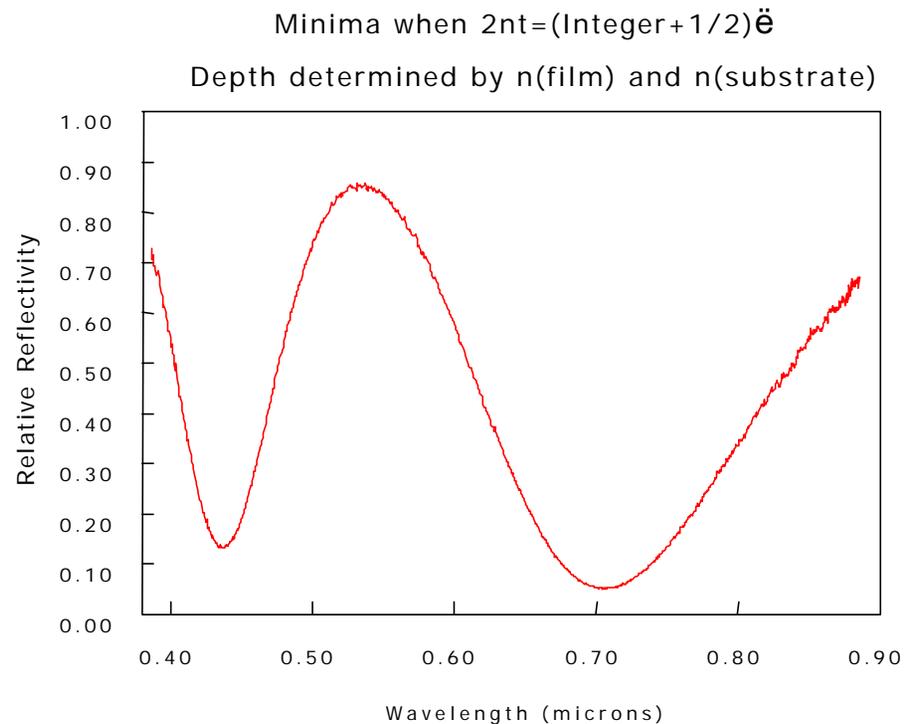
Thickness Mapping Spectroscopic Reflectometry

Bifurcated Fiber Optic Probe



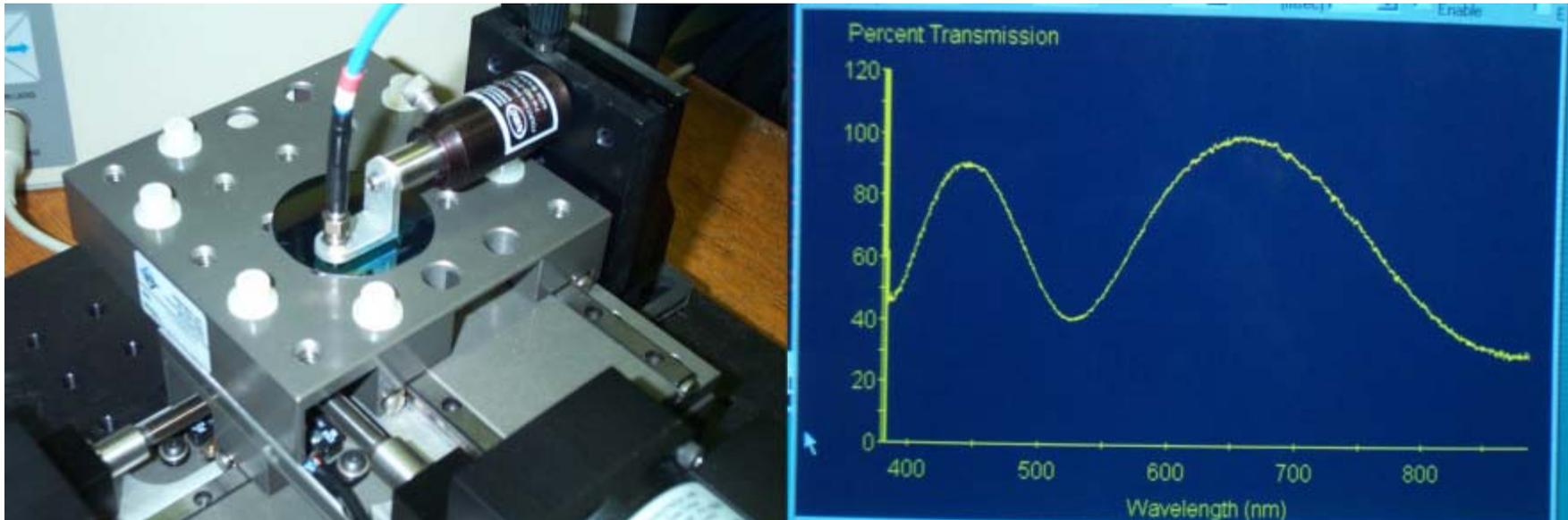
Spatial resolution: 0.5 mm

Film Thickness (t) and Index (n)



Spectrum from 317 nm BST film on a silicon substrate

Thickness Mapping **Spatially-resolved Spectroscopic Reflectometry**

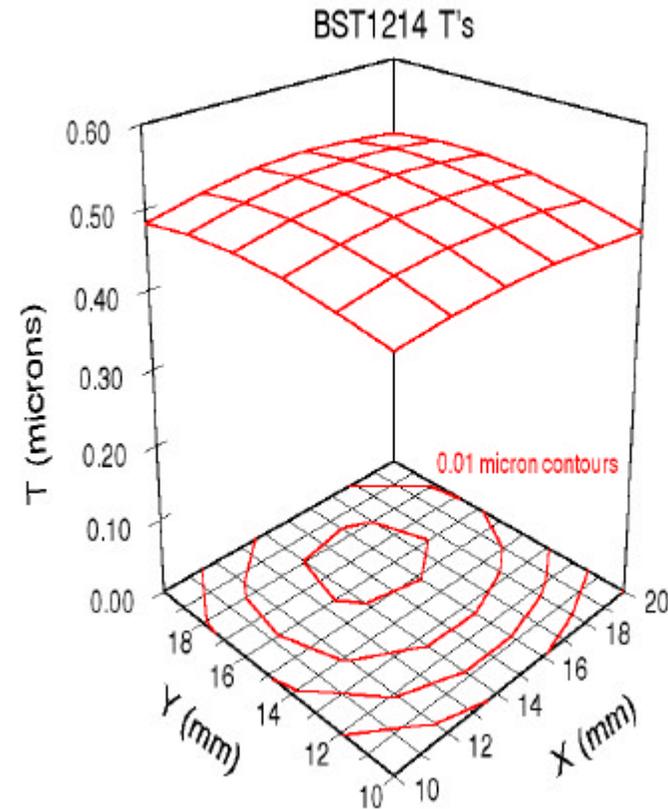


**Fully automated mapping of thickness: ~5 s/point
(1-2 s spectrum, 3-4 s for fit)**

Thickness Mapping

Uniform thickness films

- Uniform thickness films can simplify analysis of property measurements
- Laser plumes were fine-tuned using the *in situ* diagnostics
- Thickness uniformity of ~3% over a 1 cm x 1 cm area was achieved



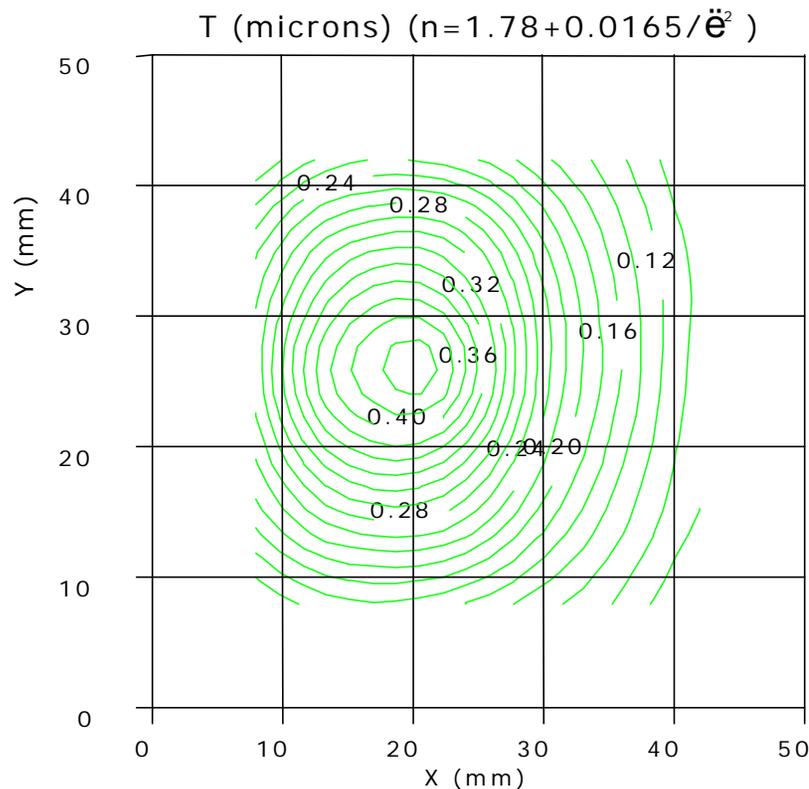
Thickness map of a BT-ST library film

Predicting Composition Maps

Measuring the Deposition Pattern

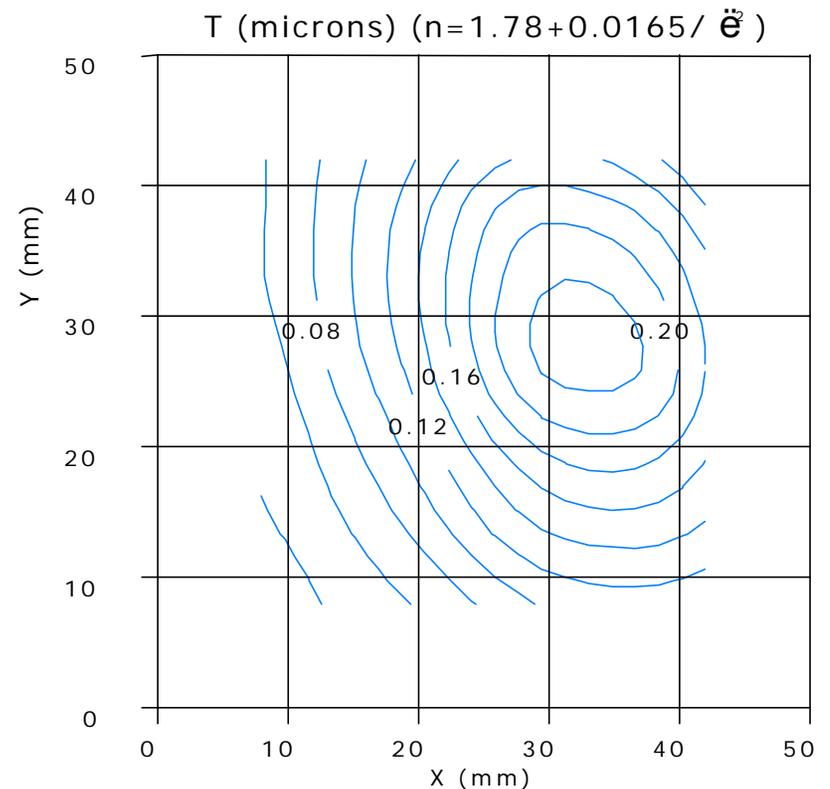
Deposition Patterns from Individual Targets

BST0403 BT only



**Thickness contours from
BT target only**

BST0404 ST only



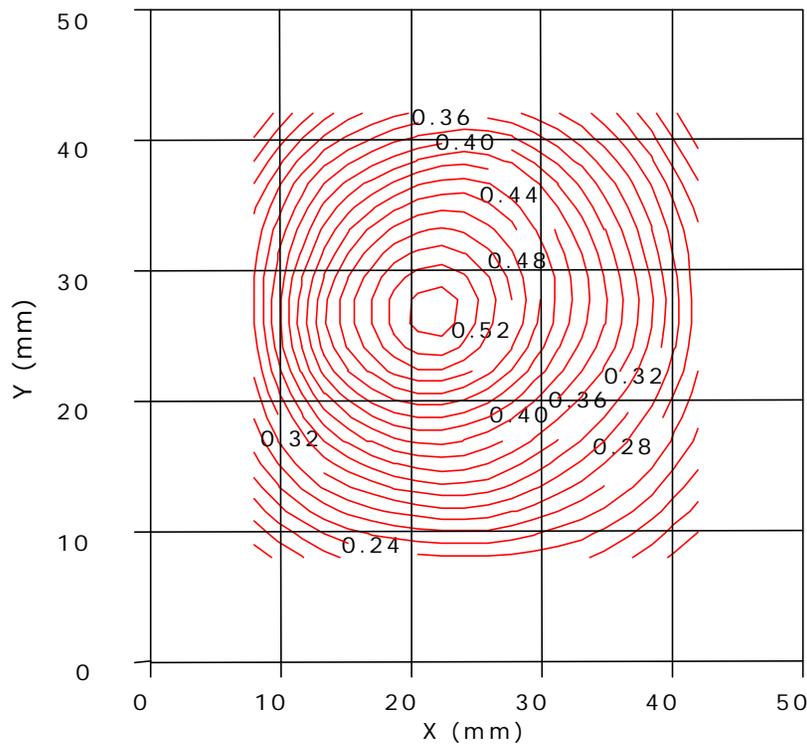
**Thickness contours from ST
target only**

Predicting Composition Maps

Comparing Deposition Patterns

BST0403+0404 BT + ST

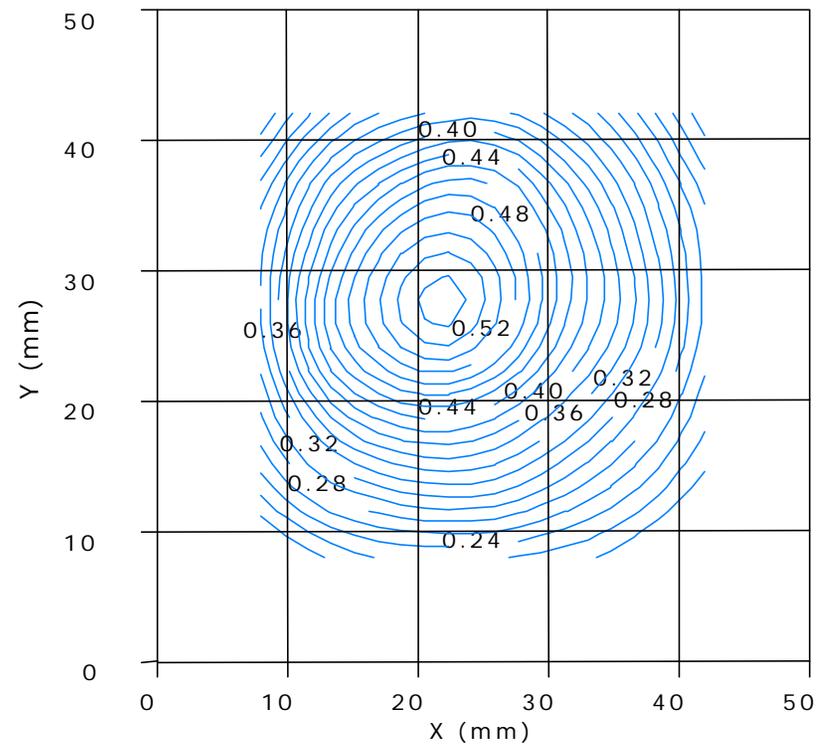
T (microns) ($n=1.78+0.165/\bar{\epsilon}^2$)



Thickness contours obtained by summing contours for films deposited from individual targets

BST0402 BT&ST

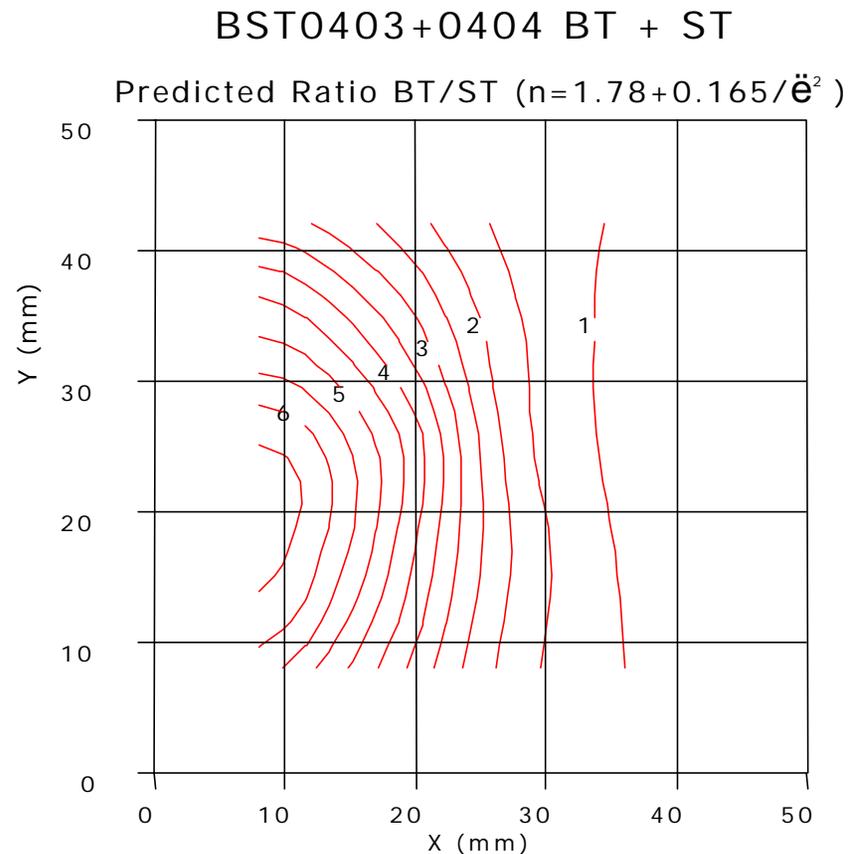
T (microns) ($n=1.78+0.0165/\bar{\epsilon}^2$)



Thickness contours for a film deposited from both targets

Predicting Composition Maps From Thickness Maps

- **Excellent correlation of deposition pattern from both targets with pattern obtained by summing individual target patterns**
- **Assume negligible diffusion**
- **Predict composition map from individual target patterns**



**Predicted composition ratio
Ba/Sr contours**

Phase Evolution Measurements

Tools Under Development

Objective:

Develop high throughput methodologies to measure phase evolution in thin films as a function of temperature, atmosphere & time

Approach:

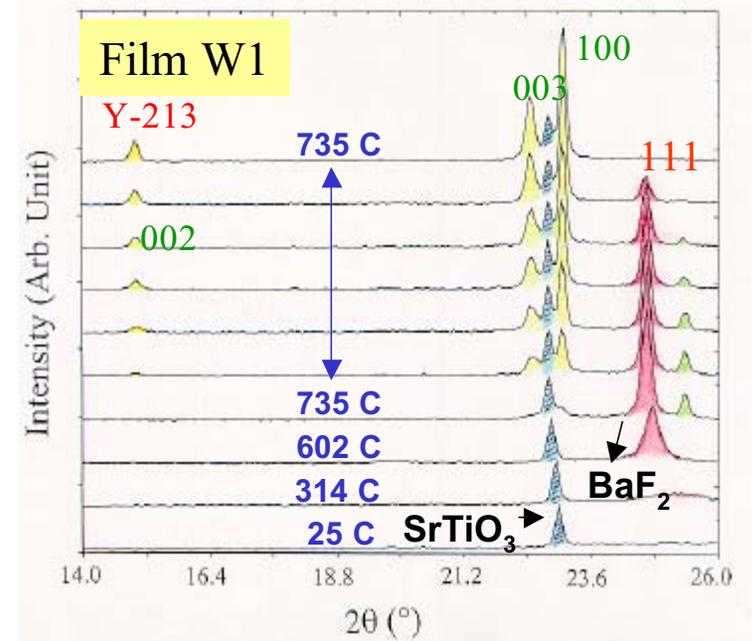
- High temperature XRD: *modify existing system to increase measurement rate*
- Spectroscopic reflectometry: *detect phase changes via changes in refractive index*

Status:

- Demonstrated feasibility of using HTXRD to monitor phase changes in films
- Preliminary results on crystallization of ZrO_2 films by XRD and optical methods

Future work:

- Establish high throughput measurement protocol for films

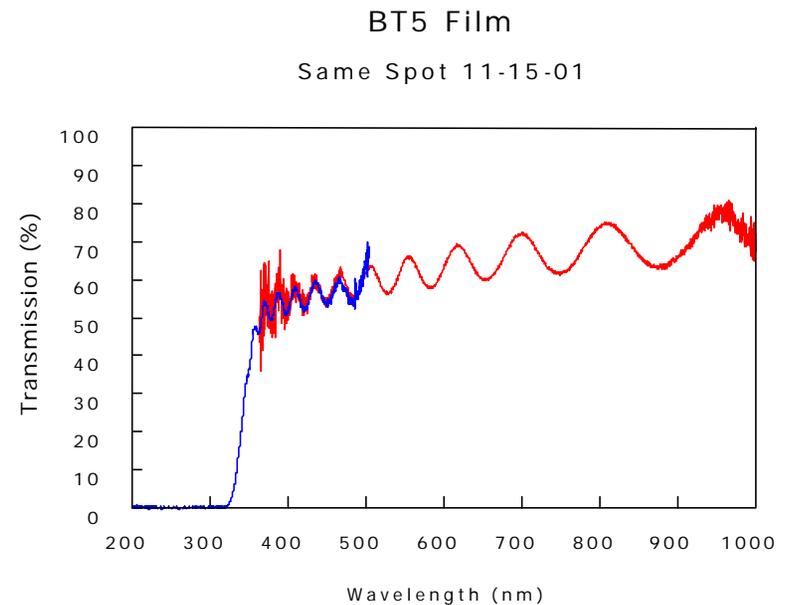


HTXRD results on a 1 μm Y-Ba-Cu-O-F film on a SrTiO₃ substrate

Future Direction

Spectroscopic Reflectometry

- **Expand measurements into the near UV to 200nm**
 - **New UV source, spectrometer, fiber optic probe**
 - **More complex data analysis, models for n and k**
- **Include transmission measurement capability**



Future Direction

Gold-Nickel Oxide Library Films

- **Au-NiO films: transparent electrodes for III-nitride devices**
- **Informal project with GE's CRD Lab**
- **Two approaches, both dual target:**
 - **Au and NiO deposited on heated substrate with O₂**
 - **Au and Ni deposited, then annealed in air**
- **Measure optical transmission and electrical conductivity**

Summary

Combinatorial tools broadly applicable to inorganic films:

- ***Dual-beam, dual target pulsed laser deposition system for library fabrication***
- ***Spatially-resolved spectroscopic reflectometry technique for high throughput thickness and refractive index mapping***

NIST Collaborators

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Materials Science and Engineering Laboratory

Library fabrication, high-throughput thickness assays

John T. Armstrong, Ryna B. Marinenko

Chemical Science and Technology Laboratory

Composition measurements

Mark D. Vaudin, Igor Levin, Peter K. Schenck

Materials Science and Engineering Laboratory

Phase evolution measurements

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NIST