6th Annual Tri-Service Workshop on GeSn and SiGeSn
25-26 October 2023, Colorado Springs, CO

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FA9550-15-0001
FA9550-20-F-0005

Characterization of Buffer Layers for Remote Plasma-Enhanced Chemical Vapor Deposition of Germanium-Tin Epitaxial Layers

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Ask me about MS/Ph.D. student positions at NMSU..

New Mexico State University, Las Cruces

Land grant institution, Carnegie R2
Comprehensive: Arts and Sciences, Education, Business, Agriculture
Ph.D. programs in sciences, engineering, agriculture; Ag extension

14,000 students (11,500 UG, 2,500 GR), 1000 faculty

Minority-serving, Hispanic-serving (60% Hispanic/NA, 26% White)
Small-town setting

Military-friendly institution (Army and Air Force ROTC programs)

Community engagement classification
(first-generation students, Pell grant recipients)

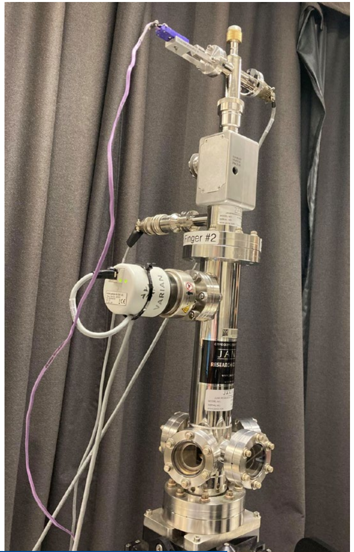
Physics: BS/BA, MS, PhD degrees. 71 UG and 37 GR students.
12 faculty (HE Nuclear and Materials Physics), **1.7 M$ expenditures.**
ABET-accredited BS in Physics and BS in Engineering Physics

Ellipsometry at NMSU

Ellipsometry on anything (inorganic)

- Metals, insulators, semiconductors
- Mid-IR to vacuum UV
- 10 to 800 K

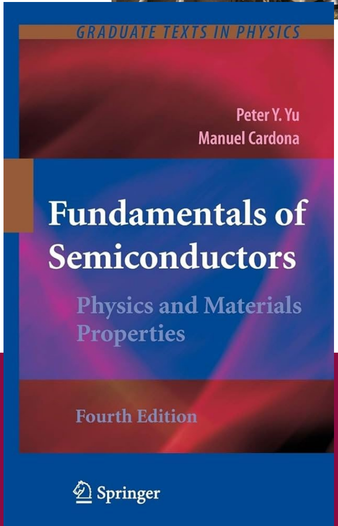
Ellipsometry tells us a lot about materials quality (not necessarily what we want to know).



☐ Optical critical points of thin-film $Ge_{1-y}Sn_y$ alloys: A comparative $Ge_{1-y}Sn_y$ / $Ge_{1-x}Si_x$ study | 429 | 2006
VR D'costa, CS Cook, AG Birdwell, CL Littler, M Canonico, S Zollner, ...
Physical Review B 73 (12), 125207

☐ Growth and strain compensation effects in the ternary $Si_{1-x-y}Ge_xC_y$ alloy system | 404 | 1992
K Eberl, SS Iyer, S Zollner, JC Tsang, FK LeGoues
Applied physics letters 60 (24), 3033-3035

☐ Ge–Sn semiconductors for band-gap and lattice engineering | 322 | 2002
M Bauer, J Taraci, J Tolle, AVG Chizmeshya, S Zollner, DJ Smith, ...
Applied physics letters 81 (16), 2992-2994



GRADUATE TEXTS IN PHYSICS

Peter Y. Yu
Manuel Cardona

Fundamentals of Semiconductors

Physics and Materials Properties

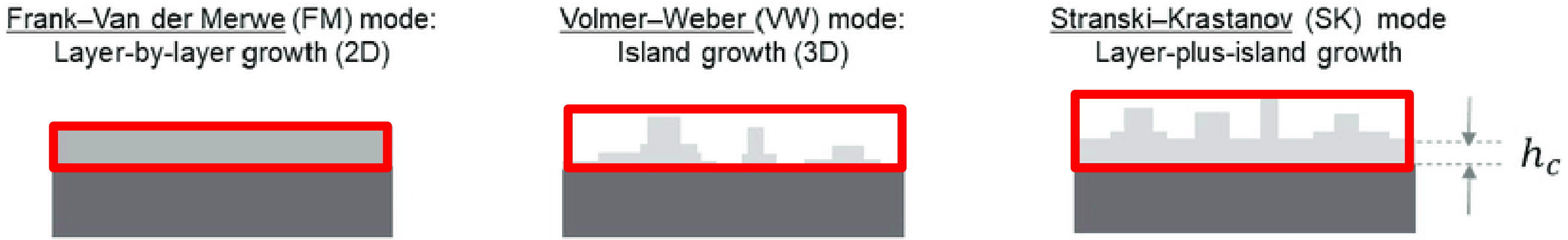
Fourth Edition

Springer

Introduction

- Buffer layers can improve the quality of subsequent growth of epitaxial layers.
- Examples:
  - Buffer grown at different temperature than target layer (encourage 2D layer growth: Ge on Si).
  - Graded buffer layers (ramp up composition).
  - Superlattice buffers (defect and dislocation control).
- Characterization of thin buffer layers (10-20 nm):
  - Spectroscopic ellipsometry (thickness, refractive index, roughness, band gap)
  - X-ray diffraction (crystallinity, lattice constant, composition
  - X-ray photoelectron spectroscopy (composition, thickness)
  - Atomic force microscopy (roughness, morphology)
  - Optical and electron microscopy
- Objective: **Where does the tin go** (substitutional, surfactant, beta-tin, interface, etc)?

Epitaxial growth modes



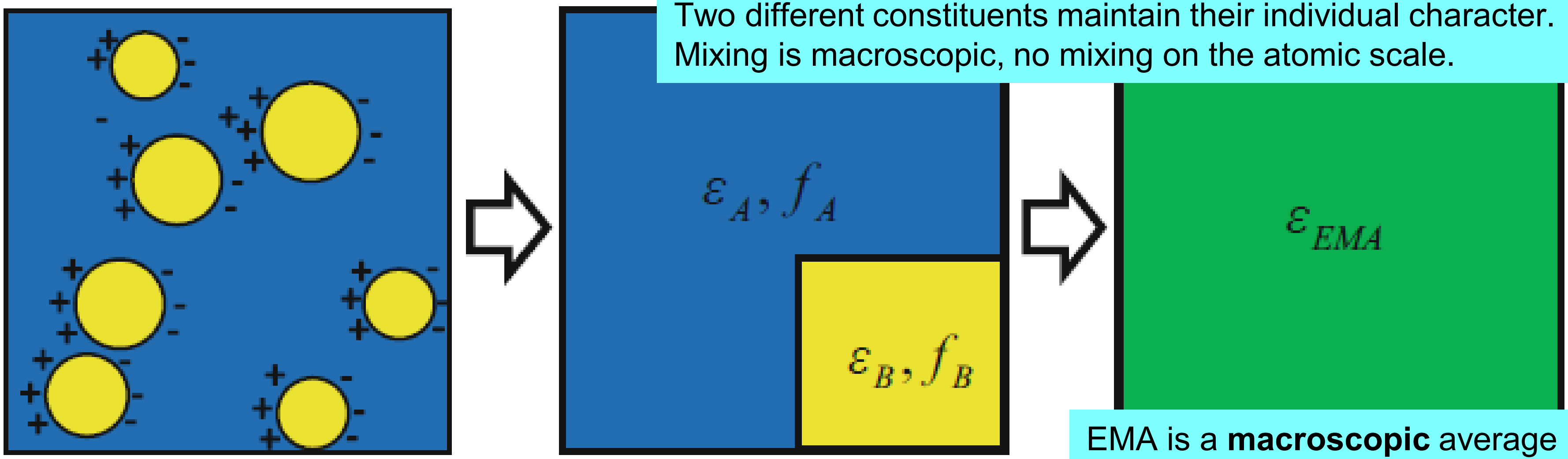
$\langle n \rangle = n_{layer}$

$\langle n \rangle < n_{layer}$

$\langle n \rangle < n_{layer}$

- How does an ellipsometer see such layers?
- Bruggeman Effective Medium Approximation:
  Mixture of Epilayer and Voids: $\langle n_{eff} \rangle < n_{layer}$ for island growth
- Need some idea of thickness
  from growth conditions or XRR, XPS, RBS, etc.

Effective medium approximation (EMA)



Two different constituents maintain their individual character.
Mixing is macroscopic, no mixing on the atomic scale.

EMA is a **macroscopic** average of the two components.

Ignore charge screening: $\varepsilon_{\mathrm{EMA}} = f_A \varepsilon_A + (1 - f_A)\varepsilon_B$

Bruggeman EMA

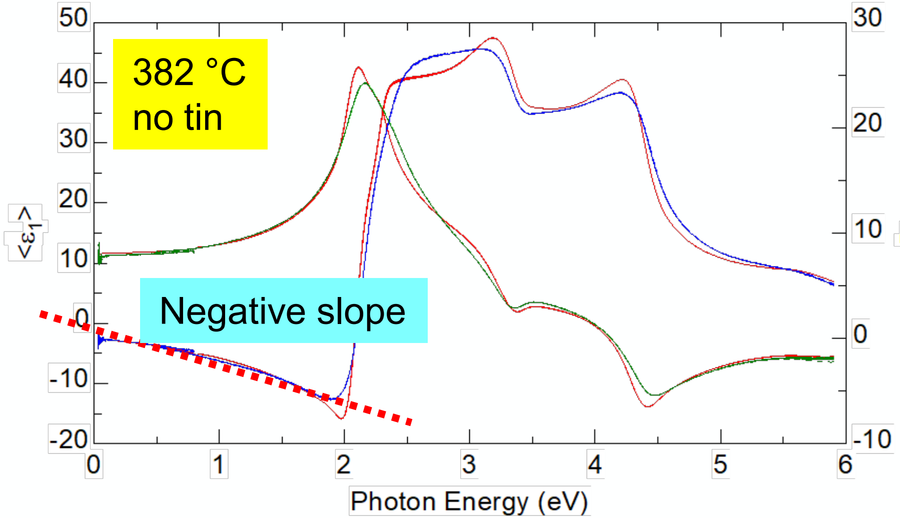
$$f_A \frac{\varepsilon_A - \varepsilon_{\mathrm{EMA}}}{\varepsilon_A + 2\varepsilon_{\mathrm{EMA}}} + (1 - f_A)\frac{\varepsilon_B - \varepsilon_{\mathrm{EMA}}}{\varepsilon_B + 2\varepsilon_{\mathrm{EMA}}} = 0$$

Works well if at least one constituent is amorphous (or air).
Not good for semiconductor alloys.

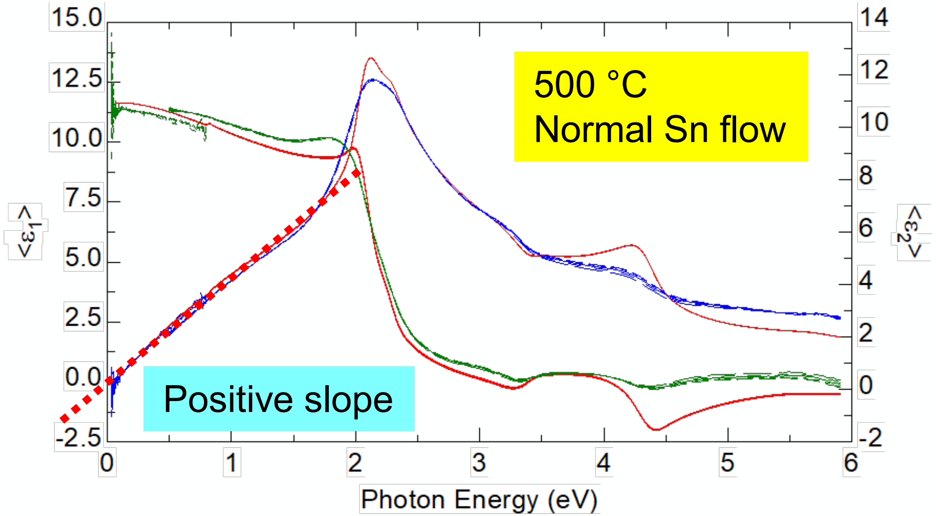
Works well for surface roughness (50/50).

J.N. Hilfiker in *Spectroscopic Ellipsometry for Photovoltaics*, ed. by Fujiwara and Collins (Springer, 2018)

Buffer layers grown at different temperatures


382 °C
no tin

Negative slope

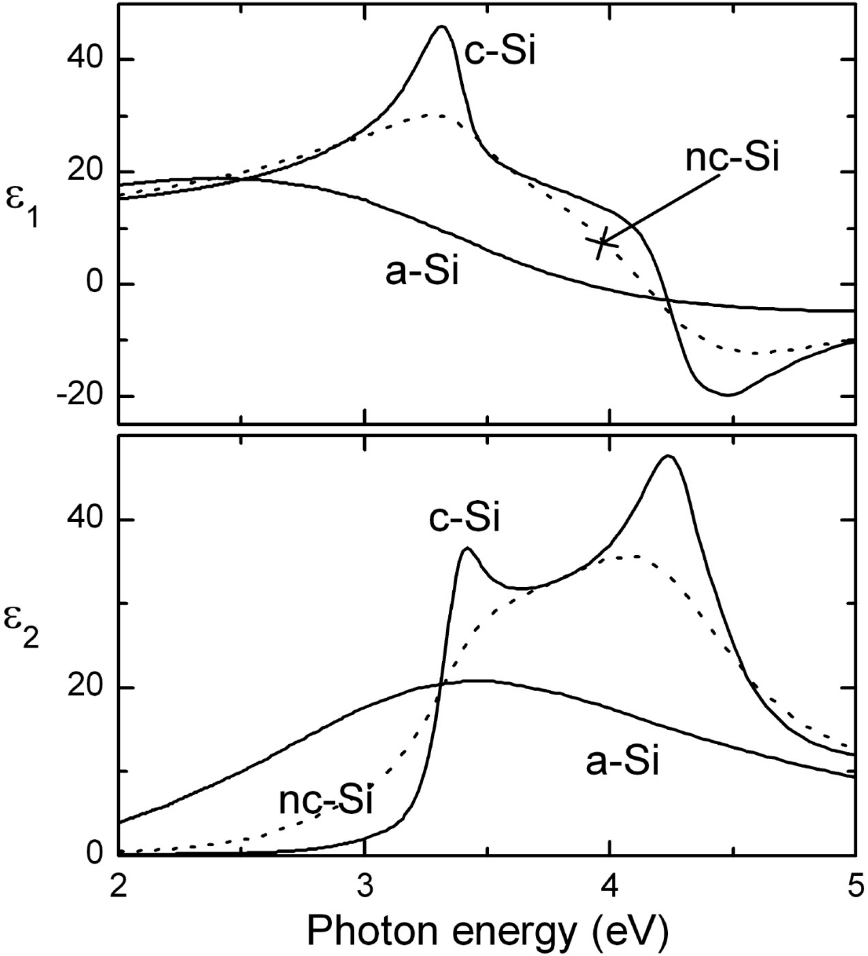

500 °C
Normal Sn flow

Positive slope

$n_{layer} > n_{substrate}$
Layer is similar to bulk Ge.
Probably layer-by-layer growth.

$n_{layer} < n_{substrate}$
Layer is much less dense than Ge, but still crystalline (critical points).
Probably 3D island growth mode.

Crystallinity in ellipsometry spectra

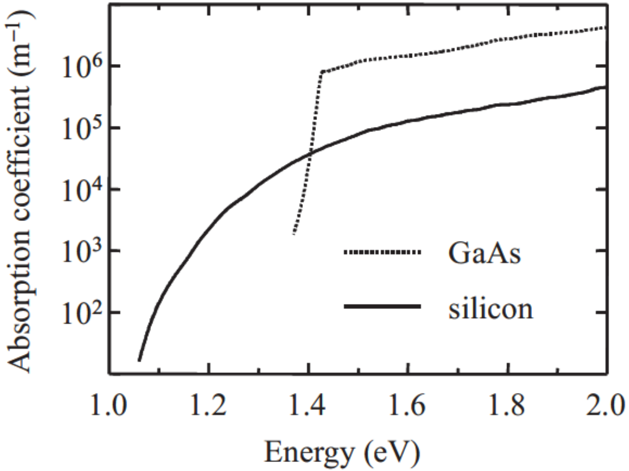


a-Si: Single broad absorption peak

c-Si: Van Hove singularities (critical points) from different directions in the BZ.

nc-Si: Loss of periodicity: (1) critical points are broadened, (2) indirect absorption is stronger.

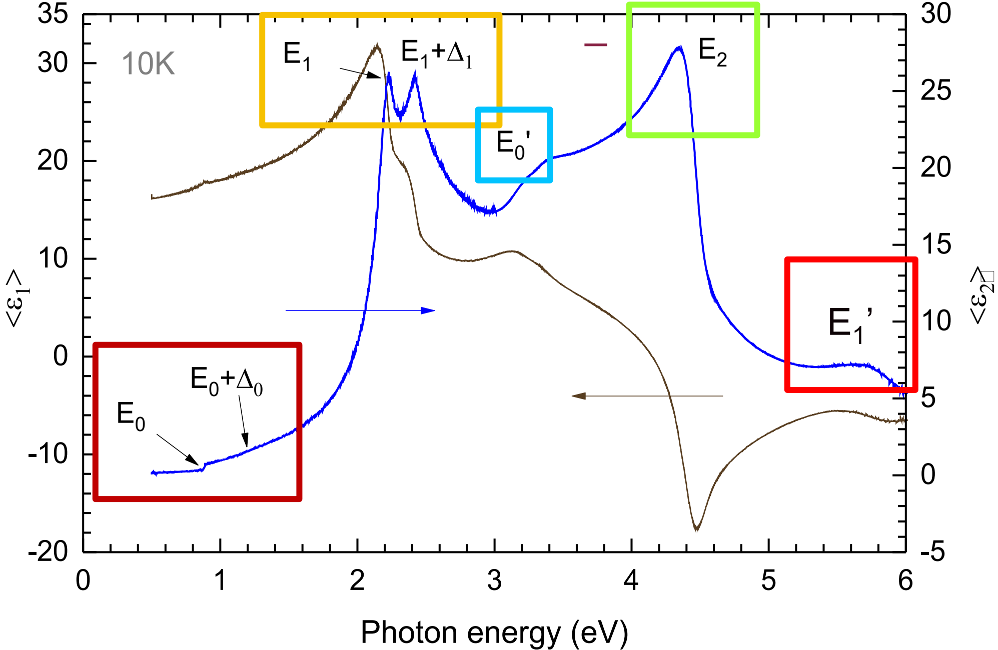
Peter Petrik, 2012

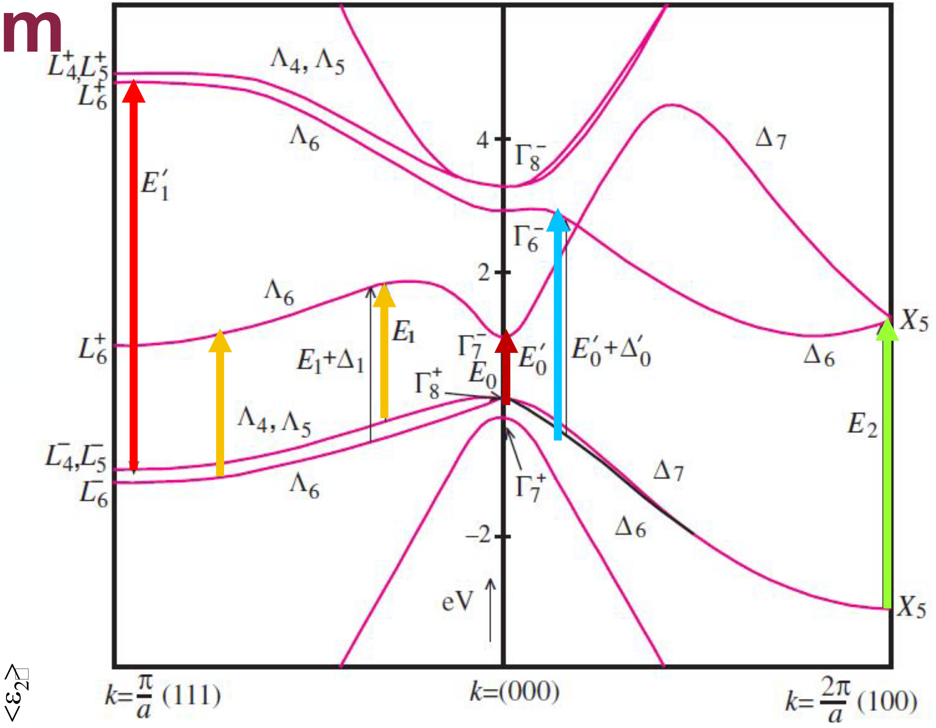


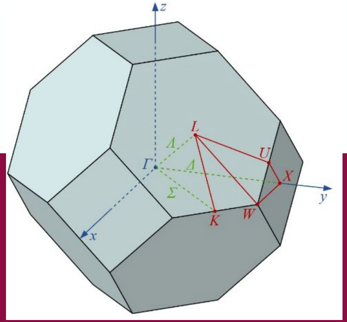
Critical points in germanium

- Structures in ε due to interband transitions
- Joint density of states
- Van Hove singularities

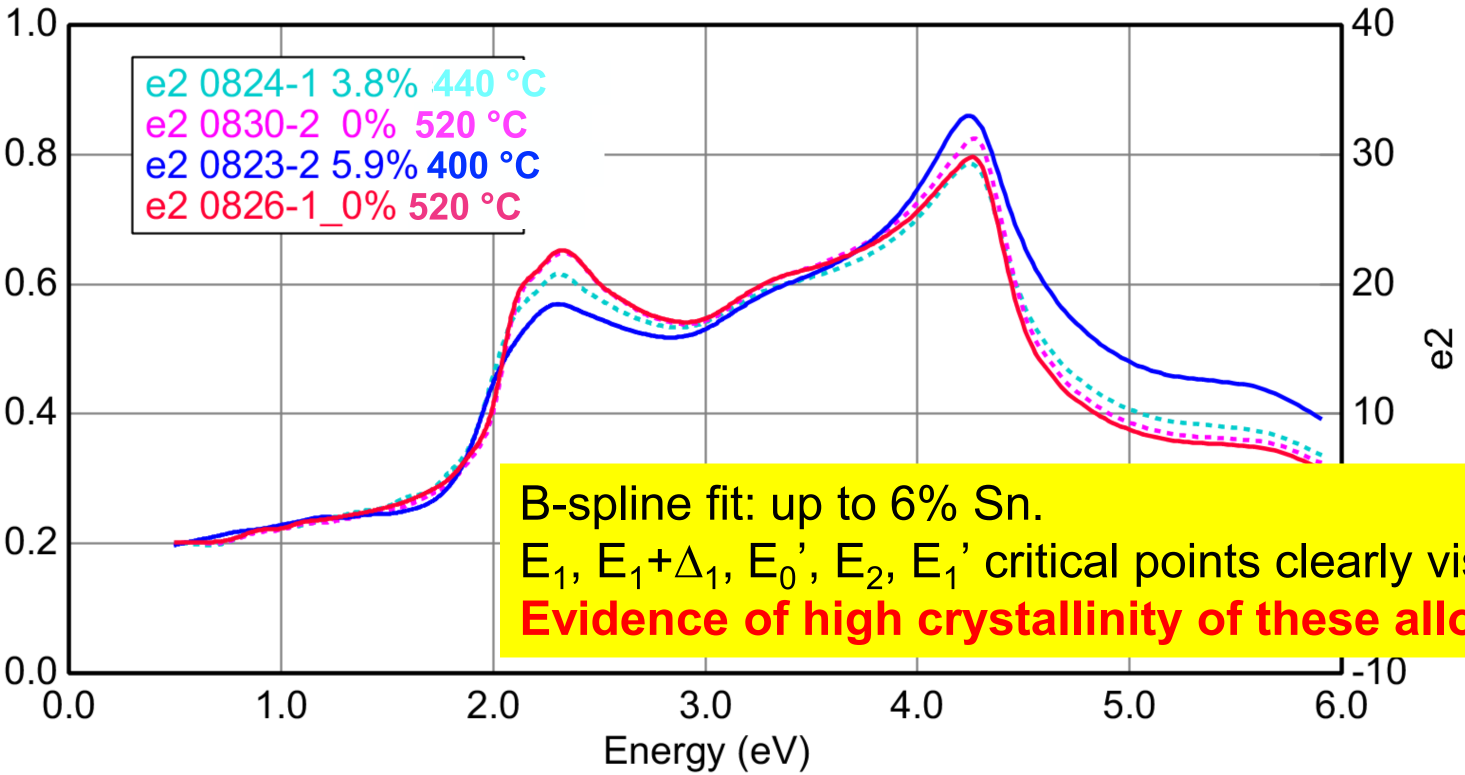
$$D_j(E_{CV}) = \frac{1}{4\pi^3}\int \frac{dS_k}{|\nabla_k(E_{CV})|}$$







Thick crystalline Ge-Sn alloys grown by RPECVD

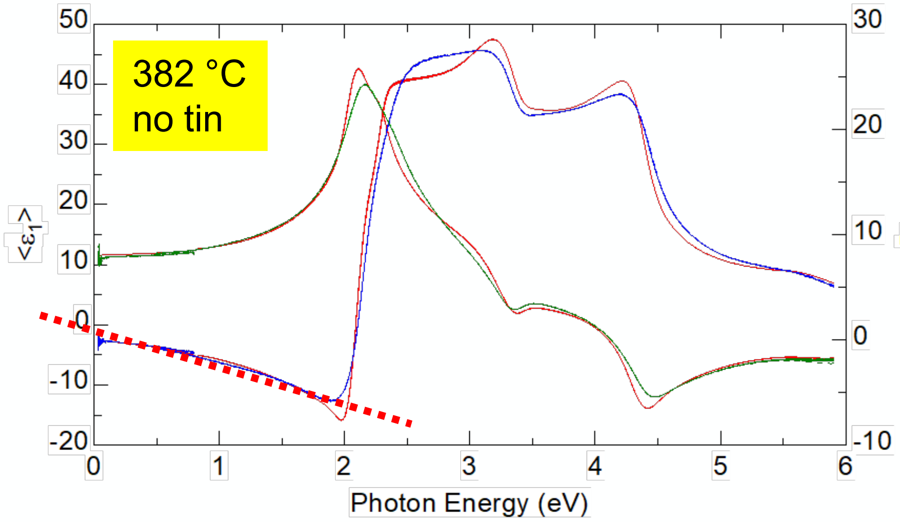


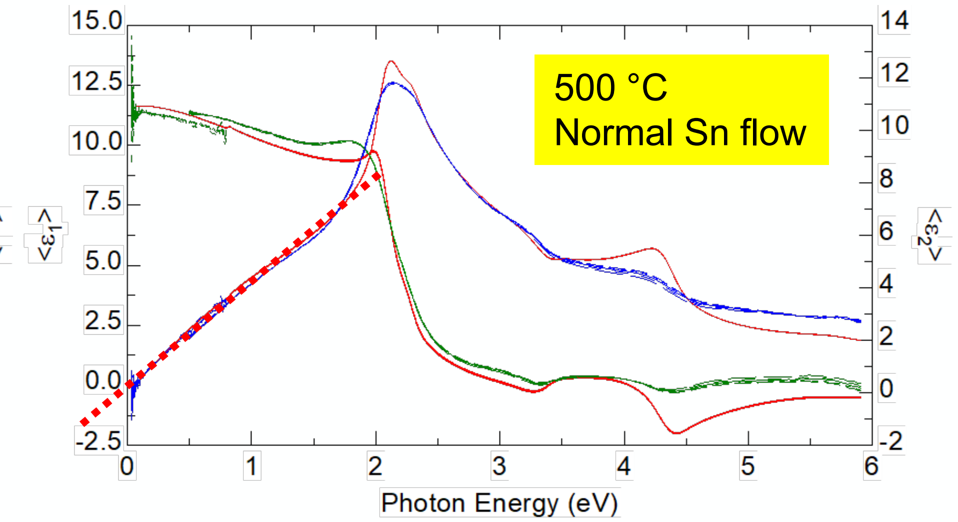
B-spline fit: up to 6% Sn.

E_1, $E_1+\Delta_1$, E_0', E_2, E_1' critical points clearly visible.

Evidence of high crystallinity of these alloys.

Buffer layers grown at different temperatures

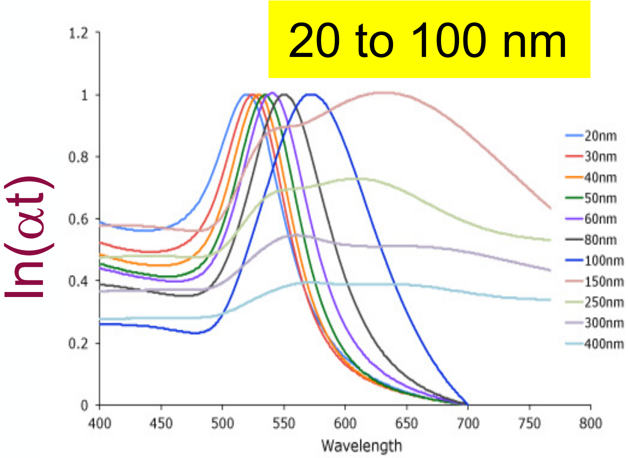


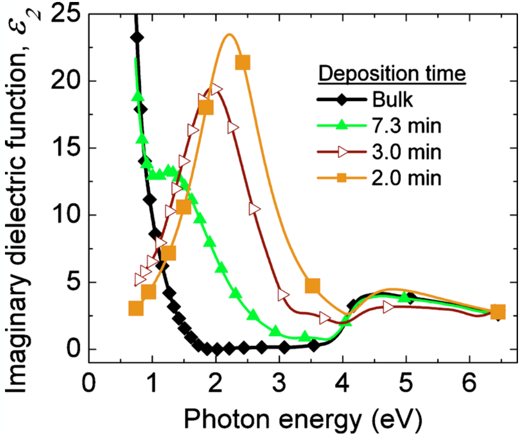


$n_{layer}>n_{substrate}$
Critical points similar to Ge.

$n_{layer}<n_{substrate}$
Low density, large roughness,
but critical points similar to Ge:
Buffer layer is crystalline, Ge-like.

Plasmon Resonance in Gold Nanoparticles


20 to 100 nm



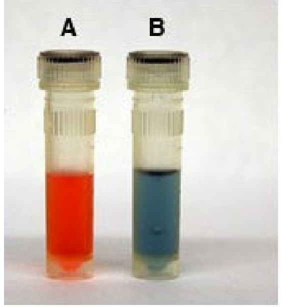
Gold is not always yellow.

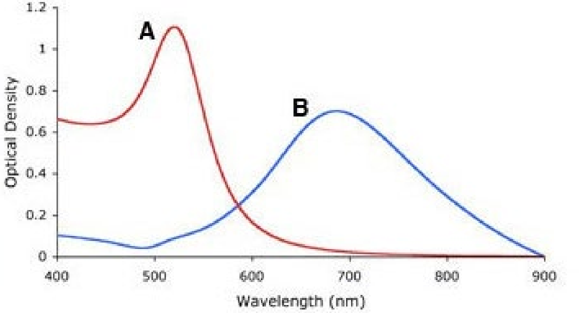
Nanoparticle radius a<λ

$$\alpha = 4\pi a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\epsilon_d}$$

m: metal, d: dielectric

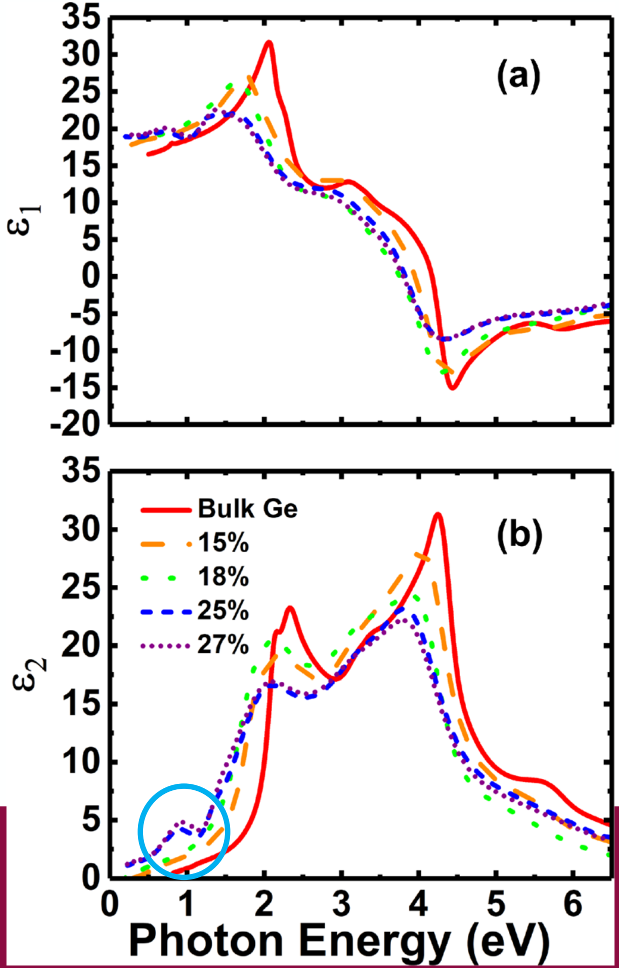
Enhance molecular absorption.





Fox, *Optical Properties of Solids*
Little, *APL* **98**, 101910 (2011)

Plasmon Resonance in β-Tin Nanoparticles



Ge-Sn alloys with high tin content grown by MBE
“have a broadened peak in ε_2, near 0.9 eV.”

“possibly caused by an intrinsic feature such as from the **band structure**, an extrinsic one such as from a **defect**, or an **interference fringe** from the substrate”.

Answer:
None of the above.
This peak is likely a **plasmon resonance**
of metallic β-Sn precipitates.

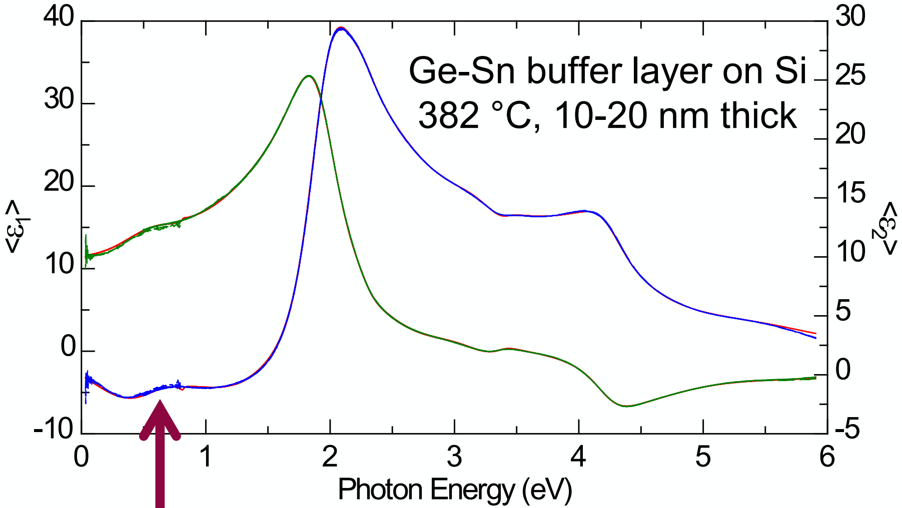
Ellipsometry cannot determine if the beta-tin particles are on the surface, embedded in the layer, or at the substrate/epilayer interface.

Future.

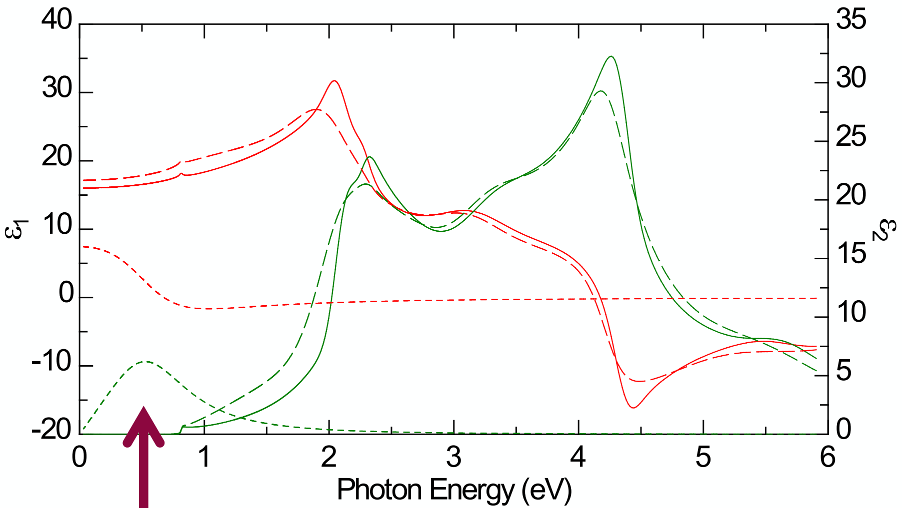
D. Imbrenda, APL **113**, 122104 (2018)

Plasmon Resonance in β-Tin Nanoparticles

Pseudodielectric function



Dielectric function



Not an interference fringe.

This Lorentzian peak (0.6 to 0.7 eV) is likely a **plasmon resonance** of metallic β-Sn precipitates.

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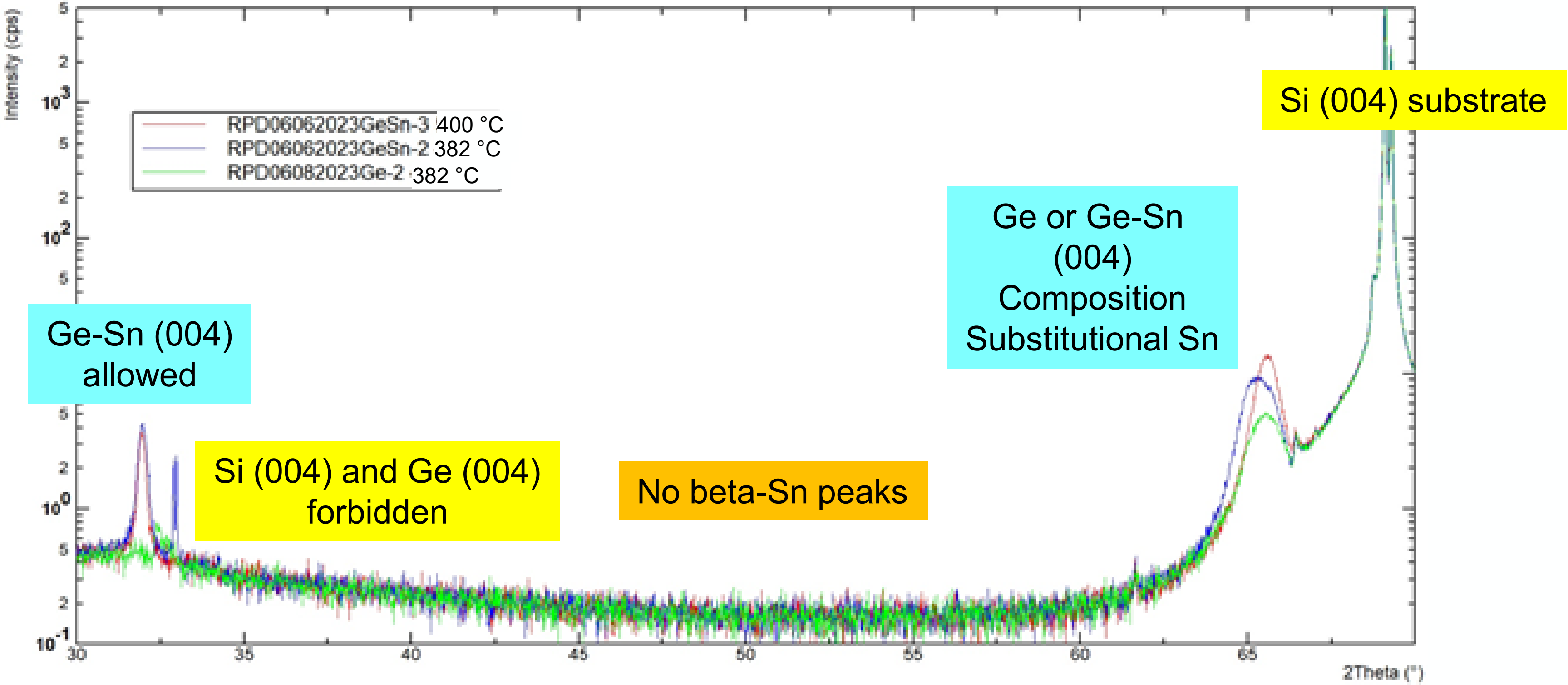
Low-resolution (powder) x-ray diffraction



Si (004) substrate

Ge or Ge-Sn (004)
Composition
Substitutional Sn

Ge-Sn (004) allowed

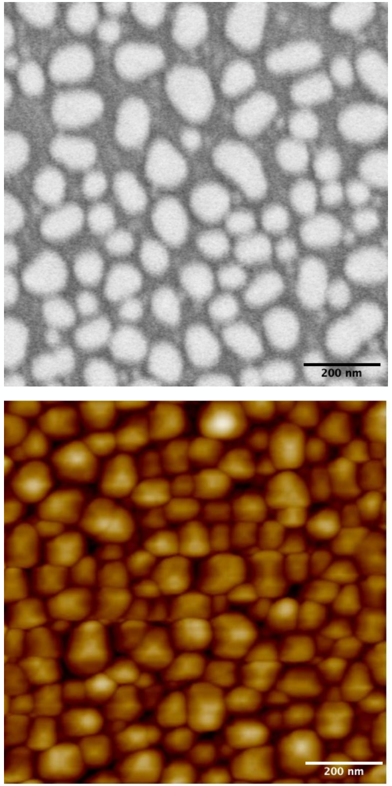
Si (004) and Ge (004) forbidden

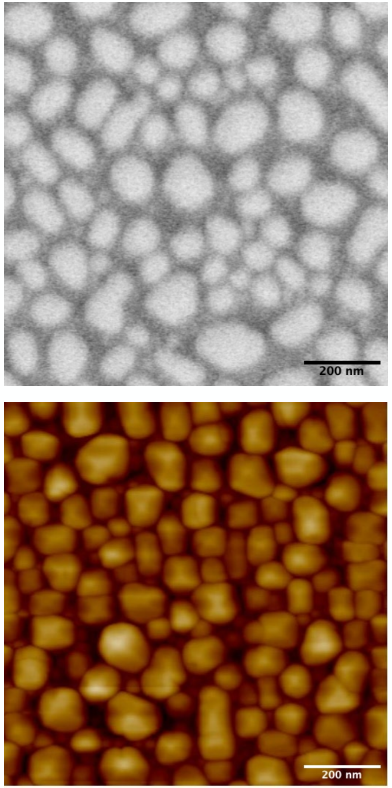
No beta-Sn peaks

SEM and AFM micrographs

RPD03032023GeSn-2

500°C substrate
30 sccm He flow through
$SnCl_4$ bubbler
RMS roughness≈9.3 nm



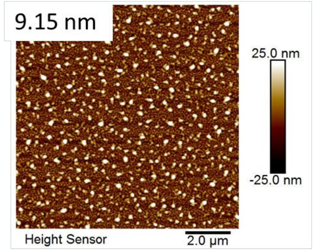


RPD02282023GeSn-4

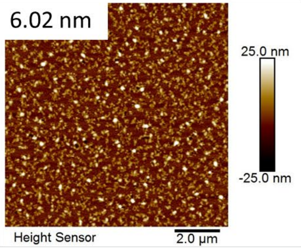
489°C substrate
30 sccm He flow through
$SnCl_4$ bubbler
RMS roughness≈11 nm

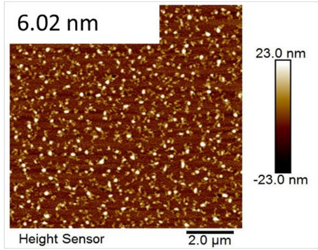
Atomic force microscopy

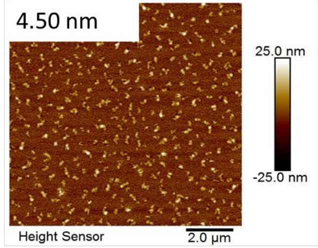
RMS roughness

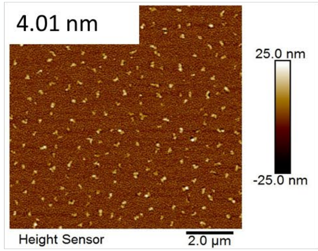


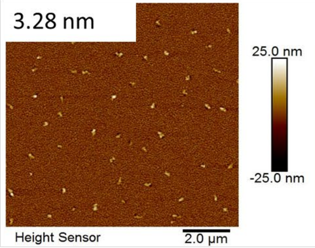
520 °C Lower Sn Flow

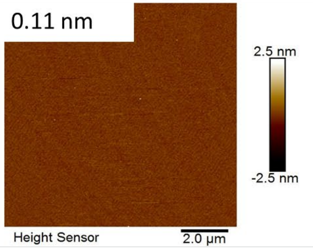


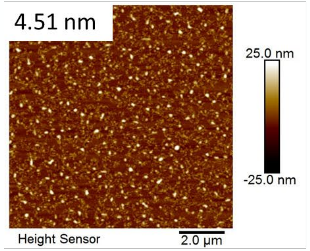












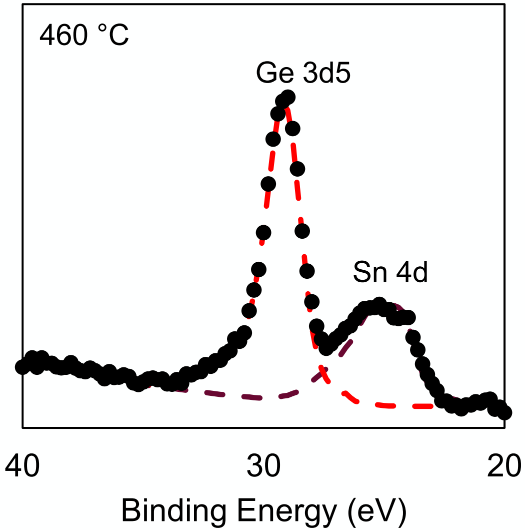
Higher Temp

X-ray photoelectron spectroscopy

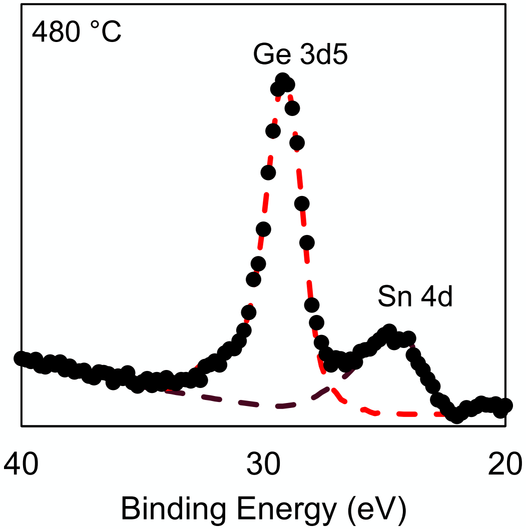
- Analysis Conditions
  - Phi 5500 XPS instrument
  - Non-monochromatic Mg $K\alpha$ x-rays (350 W, 25 kV)
  - 93.9 eV pass energy for high resolution spectra
  - As received and sputter cleaned surfaces analyzed
    - 5 keV Ar^+ ions
    - Rastered over 4 mm x 4 mm area
    - Sputtered until oxygen peak minimized (≈ 120 seconds)
- Quantitation
  - Empirical sensitivity factors
  - Determined from pure element samples
  - Ge 3d5 and Sn 4d transitions used (similar analysis depth for these transitions)
  - Line shapes acquired from standards used for Ge 3d and Sn 4d curve fitting.

X-ray photoelectron spectroscopy

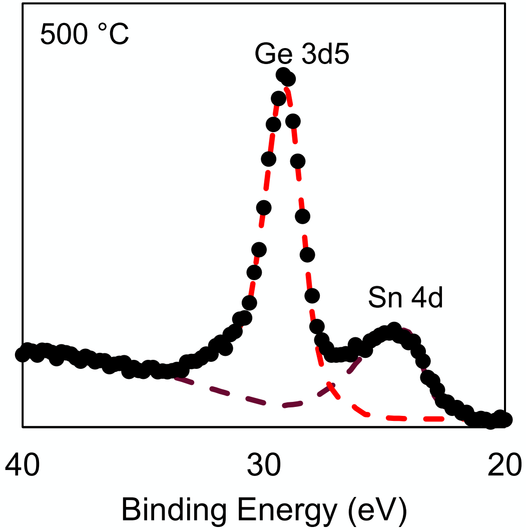
As Received: ≈ 49% Sn
Sputtered: ≈ 22% Sn



As Received: ≈ 40% Sn
Sputtered: ≈ 15 % Sn

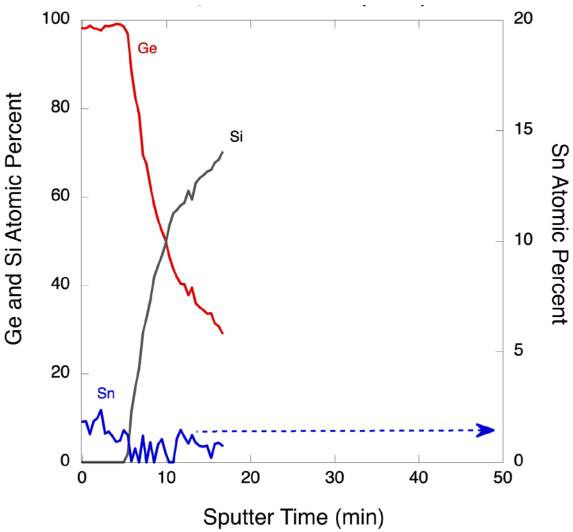


As Received: ≈ 40% Sn
Sputtered: ≈ 17 % Sn



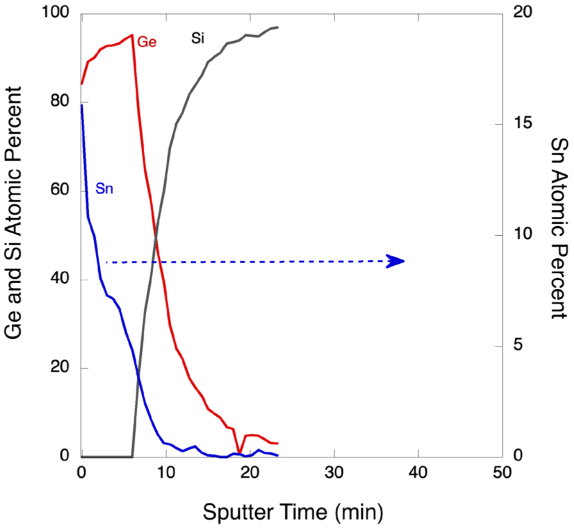
XPS Depth Profiles (acquired in 2022)

1 minute deposition
≈345°C substrate
Low He through bubbler



Interface: 9.8 minutes

1 minute deposition
≈345°C substrate
High He through bubbler



Interface: 9.1 minutes

- Films about same thickness
- ↑ He through bubbler ↑ Sn content in film
- Sn gradient through thickness
- Sn-enriched surface

Interface defined at point where Ge signal drops to one–half its maximum value.

Conclusion

- Multiple characterization tools are available for thin buffer layers.
- Spectroscopic ellipsometry:
  - Density, void fraction, crystallinity, thickness (with limits)
- Powder x-ray diffraction:
  - Substitutional alpha-Sn
  - Large beta-Sn clusters
- Atomic force microscopy
  - Morphology and surface roughness
- X-ray photoelectron spectroscopy
  - Total tin content, depth profile

Thank you!