Controlling smoothness of thin platinum ALD films

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Motivation: X-Ray Diffraction Gratings
- Improvement in grating performance

Making the Pt thinner
- Methods:
  - Deposition
  - Metrology
- Data

Summary
Important questions in cosmology are addressed by analysis of the soft x-ray spectrum:

- Role of Active Galactic Nuclei in galaxy formation
- Characterization of the Warm-Hot Intergalactic Medium and the missing baryon problem

Simulated Spectra of Capella (from IXO studies; assuming ~ 5” PSF)
IXO/CAT: Grating readout spectrum
IXO/XMS Z0: Zeroth order transmitted to microcalorimeter (XMS)
IXO/XMS direct: Not intercepted by gratings

Courtesy of N. Schulz (MIT)
Critical Angle Transmission Gratings

Grating equation:
\[ m \lambda = p (\sin(\theta) + \sin(\beta_m)), \]
\[ m = \text{diffraction order} \]

**Blazing:** \( \beta_m \sim \theta \)

**High reflectivity:**
\( \theta < \theta_c = \text{critical angle of total external reflection} \)

**Strawman:**
- Silicon grating, \( \theta = 1.5^\circ \)
- \( p = 200 \text{ nm} \)
- \( b = 40 \text{ nm} \)
- \( d = 6 \mu\text{m} \)
- Aspect ratio \( d/b = 150 \)

**Total external reflection** \( \theta < \theta_c \)

\( \theta_c \uparrow \implies \theta \uparrow \)
- \( m \uparrow \) (higher order peaks i.e. greater resolving power)
- Higher energy

\( \theta_c \) depends on (material, \( \lambda \))
- \( \theta_c \sim 1.7^\circ \) for (Si,1nm)
- \( \theta_c \sim 2.4^\circ \) for (Pt,1nm)

Case for Pt ALD: increase \( \theta_c \) by conformally coating Si grating with Pt

Heilmann *et al.*, SPIE 9905-65  High Resolution CAT XGS
Manufacturing CAT Grating

Period = 200nm
Opening ~ 130nm
Depth ~ 4micron (open both sides)
Aspect Ratio = 2000/130 ≈ 15:1
Future AR ~ 50

Heilmann et al., SPIE 9905-65  High Resolution CAT XGS
\[ \lambda = 1.0 \text{ nm} \]
\[ \theta = 2.0^\circ \text{ (angle of rotation)} \]

Heilmann et al., SPIE 9905-65 High Resolution CAT XGS

\[ \Theta < \Theta_c(\text{Pt}) : \]
higher order fringes
\[ \approx 2\Theta \]

\[ \Theta > \Theta_c(\text{Si}) : \]
low order fringes

Higher order diffraction peaks => greater resolving power
Access to higher energy (shorter wavelength)
Goal

- Increase efficiency of grating by maximizing open area
  - Thinner film Pt (~ 5nm)
  - High X-Ray reflectivity
    - continuous and smooth
    - high density
    - low impurity
Experimental

- **Deposition:**
  - Savannah 200 (200mm dia reactor)
  - 2” substrates of Si and Si-TOX at reactor center
  - 120sec UV-O3 pre-clean
  - Me$_3$PtCpMe+O2 (270°C), Me3PtCpMe +O3 (150°C)
  - Ozone 120mg/liter

- **Measurement:**
  - Ellipsometry – thickness
  - 4-point probe – resistivity/macroscopic continuity
  - XRR – thickness, density, roughness
  - AFM - roughness
Ellipsometry Validation

- Good quality fit over wide spectral range (1.4-5.9eV)
- Fit parameters tightly bound
- Correlation between optical parameters and thickness is low
- Thickness from ellipsometry is about 4-6 Å more than XRR
Physical considerations

- **Energetics:**
  - Does Pt deposit on previously deposited Pt or on substrate?
  - Does deposited Pt tend to agglomerate into Pt particles vs remain as a film?

- **Kinetics:**
  - What is rate of surface diffusion/agglomeration?
  - How does it compare to rate of deposition?

In-situ TEM at 650°C, 10mbar "air"


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Routes to smoother, thinner films

Low temperature O3
Inhibit surface diffusion

Baseline

Plasma

Higher O2 Dose

Higher deposition rates trump surface diffusion

Buffer Layer:
ZrO2 vs Al2O3
Al2O3 thickness

Lee at al, J Phys. Chem. C, 2014
Mackus et al Chem Mater 2013
Elam et al, ECS Trans 2007
"Standard" (270°C, O₂ process)

Thickness increases linearly with number of cycles
Resistivity increases super-exponentially → percolation?
Percolation

Increasing cycles, increasing thickness

\[ \rho \propto \frac{1}{(t - t_c)^\gamma} \quad t \to t_c, t > t_c \]

\[ \rho = \infty \quad t < t_c \]

“Baseline” process has percolation threshold at \( \sim 50\text{Å} \)
- \( \text{O}_3 \) film is continuous at lower thicknesses
- No sign of percolation threshold
- However, \( \sim 80\text{Å} \) resistivity suggests film quality is poorer
  - X-ray Reflectivity is low
  - Residual carbon?
• Increasing O₃ dose by 4X gives lowest resistivity
• Resistivity improvement is not as much for thicker film
Buffer Layer (Al₂O₃ vs ZrO₂)

- At 80 cycles:
  - Resistivity on ZrO₂ is ~ 35% lower with 10Å thinner film

- At 145 cycles
  - Resistivity is similar for both surfaces

ZrO₂ surface encourages faster nucleation and continuity
Thickness of $\text{Al}_2\text{O}_3$ layer

Pt nucleation enhancement on $\text{Al}_2\text{O}_3$ maintained to 3 cycles of $\text{Al}_2\text{O}_3$

100 cycles Pt
$270^\circ\text{C}, \text{O}_2$
Summary

- Improvement in “device” performance – increase in critical angle for X-Ray CAT grating
- Percolation threshold reduced from ~ 5nm to less than 4nm for ozone process.
  - Film quality improvement required
- Thin (3cycles) Al2O3 is adequate for improved Pt coalasence