Measurement of stress evolution in thin films using real-time \textit{in situ} wafer curvature (k-Space MOS)

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- Intro to k-Space MOS (multi-beam optical sensor)
  - theory
  - capabilities
  - analysis
- Examples
  - polycrystalline films
    - steady-state stress
      - Scaling with D/RL
    - stress vs thickness
  - sputtering
  - tin whisker formation
  - battery materials
Stress in thin films is a generic problem
Leads to decreased performance, deformation, failure

Cracks in Sn-Li electrodes
Chao and Guduru, MRS, 2012

Deformation in Ni MEMS devices

Stress voiding/electromigration

Sn Whiskers
NASA website: http://nepp.nasa.gov/whisker

Stress in electroplated NiW
Mizushima et al., Electrochimica Acta. 2006

Diamond on Si delamination
diamond.kist.re.kr/DLC/mwmoon/gallery.htm

Want to:
understand stress,
control stress,
predict stress

First need to measure it

Thin Solid Films review, 2012
Measure thin film stress via wafer curvature

Stressed film bends the substrate
Stoney’s equation

MOSS (multi-bean optical sensor)
Curved surface deflects array of parallel beams

\[ K = \frac{1}{R} = \frac{6 \overline{\sigma} h_f}{M_s h_s^2} \]

For multiple layers:

\[ \frac{1}{R} = \frac{6}{M_s h_s^2} \sum_i \bar{\sigma}_i h_i \]

Curvature measures product of average stress x thickness

\[ \overline{\sigma} h_f = \frac{\delta d}{d} \frac{M_s h_s^2}{12L} \cos \alpha \]
Multibeam approach (MOSS): easy to implement/robust

- Simple, stable optics (aligned outside processing chamber)
- in situ, real-time, high sensitivity
- $R > 20 \text{kM}$, $\sigma h_f < 1 \text{ GPa-Å}$
- Can see 0.1 ML Ge on Si(001)

- System requirements:
  - Ports to measure specular reflection
  - Reflective surface (backside ok)
- Measurement technique
  - Etalon produces array of parallel beams
  - CCD measures change in beam spacing ($\delta d/d$)

$$\Rightarrow \frac{1}{R} = \frac{\delta d \cos \alpha}{d} \frac{1}{2L}$$

Multi-beam technique reduces sensitivity to vibration

Measure difference between beams not absolute position
Interpreting curvature measurements: How does curvature relate to evolving stress distribution?

**Average stress:**

\[ \bar{\sigma} = \frac{1}{h_f} \int_0^{h_f} \sigma(z) \, dz \]

Film with non-uniform stress distribution

- Thickness changes with time (deposition)
- Curvature changes as film grows over time
- Shows stress is not uniform throughout film

Curvature vs. time

**Ag on SiO₂, 23°C**
**Stress distribution:**
Study change of curvature with time

\[
\frac{d\kappa}{dt} \propto \sigma(h_f, t) \frac{\partial h}{\partial t} + \int_0^{h_f} \frac{\partial \sigma(z, t)}{\partial t} dz
\]

(1) Stress in new layers at the surface, \(\sigma(h_f, t)\)

Incremental stress proportional to slope of \(\kappa\) vs \(h\)

- But only if stress not changing in rest of film

*Ag on SiO\(_2\)*

\(23^\circ C\)
**Stress distribution:**
Study change of curvature with time

\[
\frac{dK}{dt} \propto \sigma(h_f, t) \frac{\partial h}{\partial t} + \int_0^{h_f} \frac{\partial \sigma(z, t)}{\partial t} \, dz
\]

(2) Change in stress of existing layers

*Ag on SiO₂ 23°C*

Stress changes when growth stopped
Layer thickness doesn’t change

Measure film stress under different conditions to understand mechanisms controlling it
MOS can be implemented on many platforms

**Deposition techniques**
- CVD
- sputtering
- PVD
- MBE
- PLD
- electrodeposition

**Materials systems**
- heteroepitaxy  
  \((\text{SiGe/Si, InGaAs/GaAs})\)
- optoelectronics  
  \((\text{GaN, AlGaN, GaSb})\)
- hard coatings  
  \((\text{DLC, a-C})\)
- oxides \((\text{TiO}_2, \text{CeO}_2)\)
- polycrystalline metals

MOS on GaN rotating disk CVD reactor  
( Hearne et al)
Examples from stress evolution studies

1. Residual stress in polycrystalline films
   - Electrodeposition/evaporation
   - Dependence on growth conditions, material
   - Evolution with film thickness

2. Sputter deposition
   - Effect of processing parameters
     (surface roughness)

3. Mechanical properties of Sn films
   - stress leads to whiskers
   - enhance stress relaxation

4. Strain in battery materials
   - large volume changes
   - associated with phase changes
Features of stress evolution in polycrystalline films

**Stress changes with microstructure**

*Ag on SiO₂, 23°C (Floro et al, 2001)*

Stages of film/stress evolution:
- Nucleation
- Coalescence
- Tensile rise
- Continuous film

Steady-state compressive (for high atomic mobility)

**Stress depends on kinetics (temperature, material, deposition rate)**

*Ag on SiO₂ (Chason, Hearne, JAP 2013)*

*Fe on MgF₂ (Thurner and Abermann, TSF, 1990)*

- Lower T, same growth rate:
  → more tensile
- At 30 °C:
  Fe: tensile, Ag: compressive
Simple model for stress evolution in polycrystalline films

Consider stress as balance between different generation/relaxation mechanisms occurring at triple junction (top of grain boundary)

- Tensile $\rightarrow$ grain boundary formation
  \[ \sigma_T \propto \left( \frac{\gamma E}{L} \right)^{1/2} \]

- Compressive
  $\rightarrow$ insert atoms into grain boundary (driven by surface supersaturation)
  \[ \sigma_C = \frac{\delta \mu_s}{\Omega} \]

- Mediated by kinetic processes on surface:
  - Growth rate $R$, diffusivity $D$, grain size $L$
Write equations for evolution of stress

\( \Delta \mu \) drives atoms into or out of gb

1) \( \Delta \mu = \delta \mu_S + \sigma_{ij} \Omega \)

2) \( \frac{\partial N_{ij}}{\partial t} \approx 4C_s \frac{D}{a^2} \frac{\Delta \mu}{kT} \)

Master equation for stress evolution at triple junction:

\[
\sigma_{ij} = \sigma_C + (\sigma_T - \sigma_C) \cdot e^{-\Delta t_{ij}/\tau}
\]

where \( \Delta t_{ij} = a / \dot{h}_{gb} \)

Combine stress as grain boundary forms (tensile) with stress as atoms are inserted into it (compressive)

3) Induced stress: \( \sigma_{ij} = \sigma_T - M_f \frac{N_{ij} \cdot a}{L} \)

Rate of growth of grain boundary
Steady state stress: dependence on growth rate

Electrodeposited Ni on Au, Hearne et al, JAP 97 (2005)

Stress reaches steady-state (constant slope)
- Different $\sigma_{SS}$ for each growth rate

Model prediction:
$$\sigma_{SS} = \sigma_C + (\sigma_T - \sigma_C) \cdot e^{-\alpha D/RL}$$

Key parameter:
$$\frac{D}{RL}$$

- $\frac{D}{RL} << 1$  
  Low D, high R  
  $\rightarrow$ tensile

- $\frac{D}{RL} >> 1$  
  High D, low R  
  $\rightarrow$ compressive

→ Determines growth rate for stress-free films

Grain size remains $\sim 1 \mu m$
Stress vs thickness: effect of coalescence of islands

Data: Stress changes with thickness
Depends on temperature

PVD Ag on SiO$_2$, (Hearne)

Model:

\[
\sigma_i = \sigma_C + (\sigma_T - \sigma_C) \cdot \exp\left(-\frac{\alpha D}{L \frac{\partial h_{gb}}{\partial t}}\right)
\]

- \(\partial h_{gb}/\partial t\) changes during coalescence

- Model islands as cylindrical caps to calculate grain boundary velocity

Grain boundary growth rate changes as film grows
Stress changes with grain boundary velocity
Consider process of coalescence

- Calculate how $\partial h_{gb}/\partial t$ changes during coalescence
- Model islands as cylindrical caps
- Initial spacing is L

**Grain boundary velocity changes as islands grow**

Before coalescence, $\partial h_{gb}/\partial t = 0$

(no grain boundary)
Consider process of coalescence

- Calculate how $\partial h_{gb}/\partial t$ changes during coalescence
- Model islands as cylindrical caps
Consider process of coalescence

- Calculate how $\partial h_{gb}/\partial t$ changes during coalescence
- Model islands as cylindrical caps
Consider process of coalescence

- Calculate how $\partial h_{gb}/\partial t$ changes during coalescence
- Model islands as cylindrical caps

Slows down as film gets thicker
Consider process of coalescence

- Calculate how $\partial h_{gb}/\partial t$ changes during coalescence
- Model islands as cylindrical caps

$\dot{h}_{gb}$ approaches average growth rate ($R$) as film gets thicker (steady-state)
Model fits Ag on SiO$_2$ data
Change atomic mobility ($D$) at constant $R$, $L$

**PVD Ag on SiO$_2$, (Hearne)**

**Model:**

$$\sigma_i = \sigma_C + (\sigma_T - \sigma_C) \cdot \exp\left(-\frac{\alpha D}{L h_{gb}}\right)$$

- Islands are cylindrical caps, contact angle $\sim$68 deg,
- Fitting parameters: $\sigma_c$, $\sigma_T$, $\tau$
  Use same $\sigma_T$ (442 MPa) and $\sigma_C$ (-359 MPa) for all temperatures
- $\tau$ different for each $T$ (proportional to $1/D$)

→ Grain boundary model captures change with thickness, temperature
Monitor stress during electrochemical deposition

1) Evaporate seed layer of Sn (1 µm)
2) Electrodeposit Sn film at constant voltage

Look at effect of growth interrupts
Stress behavior during interrupt & regrowth

\[
\sigma_{ss} = \frac{\sigma_T + (\alpha D / RL) \sigma_C}{1 + (\alpha D / RL)}
\]

Shin and Chason, PRL 2009
Interpretation of stress behavior at interrupt & regrowth

Decay rate depends on layer thickness

$$\delta \mu_S = 0 \quad R = 0$$

$$\sigma = \sigma_f + (\sigma_i - \sigma_f) e^{-t/\tau_{relax}}$$
Interpretation of stress behavior at interrupt & regrowth

\[ \sigma_{SS} = \frac{\sigma_T + (\alpha D / RL) \sigma_C}{1 + (\alpha D / RL)} \]
Stress is independent of layer thickness:

- confirms role of grain boundary in stress evolution

Stress during etching:

- negative chemical potential on surface induces tensile stress in film
- confirms role of surface chemical potential in stress evolution

Equivalence between growth and etching:
Stress evolution during sputter deposition

Additional parameters: ion energy, gas pressure

MOSS with magnetron sputtering sources (Mo films, Fillon, Abadias, et al. TSF 2010)

Lower pressure $\rightarrow$ more energetic particles
Stress becomes more compressive

Dependence on growth rate different than evaporation
Don’t know grain size or grain evolution
Stress evolution during sputter deposition (LLNL)
Be targets for NIF: need films with low stress (thick > 100 µm)

*Higher growth rate (power) → more tensile*
*Higher T → more compressive*

![Graph showing stress evolution during sputter deposition with different conditions and their corresponding stress values.](image)
Be sputtering results (LLNL): effect of pressure
Lower pressure → more compressive initially

Why? Lower pressure means less scattering, more energetic incident particles: implant into surface, produce higher density.
Be sputtering results
Lower pressure $\rightarrow$ more compressive initially

BUT: Incremental stress changes from compressive to tensile as layer gets thicker $\rightarrow$ kept same temperature, growth rate
**Reason:** Stress change correlated with rougher surface morphology

Film structure: roughening instability
(Zepeda-Ruiz, APL 2010)

Greater roughness $\rightarrow$ Turns off compressive stress generation
Film becomes tensile
Sn whisker growth: driven by stress from IMC (intermetallic) formation

Whiskers form in Pb-free Sn coatings on Cu – cause systems failure (satellites, pacemakers)

Measure stress evolution with MOSS
Water curvature measures total force exerted by film.

1. Remove Sn

2. IMC forms at Cu-Sn interface

Correlate IMC/stress/whiskering (Chason & Jadhav, APL 2009)

Remove Sn layer – change in curvature gives stress in Sn
Reduce whiskering by enhancing stress relaxation

- Measure mechanical properties of layers: Sn and Sn alloys
- Find coatings that have low stress even after IMC grows

Use thermal expansion mismatch to create strain

- These results agree with conclusions from whisker studies
- More relaxation with larger grain size - thickness - horizontal grain boundaries
Stress evolution during charging/discharging of batteries
(lithiation of Sn anode)

Put MOSS on electrochemical cell

Simultaneously measure C-V and stress-thickness

Measure stress associated with phase changes
Need to know layer thicknesses to interpret MOSS data

(Chen, Guduru 2013)
Summary

- Multi-beam wafer curvature (MOS) enables stress evolution to be monitored in real-time
  - useable on wide variety of platforms
  - sensitive, robust, easy to interpret

- Stress dynamics provide more information than single stress measurement
  - Key for
    - modeling
    - understanding sources of stress
    - controlling stress (optimizing processing conditions)

- Frontiers
  - Understanding multi-component materials
  - Energetic particle effects

**Take home point:**
In situ monitoring useful for understanding stress evolution
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