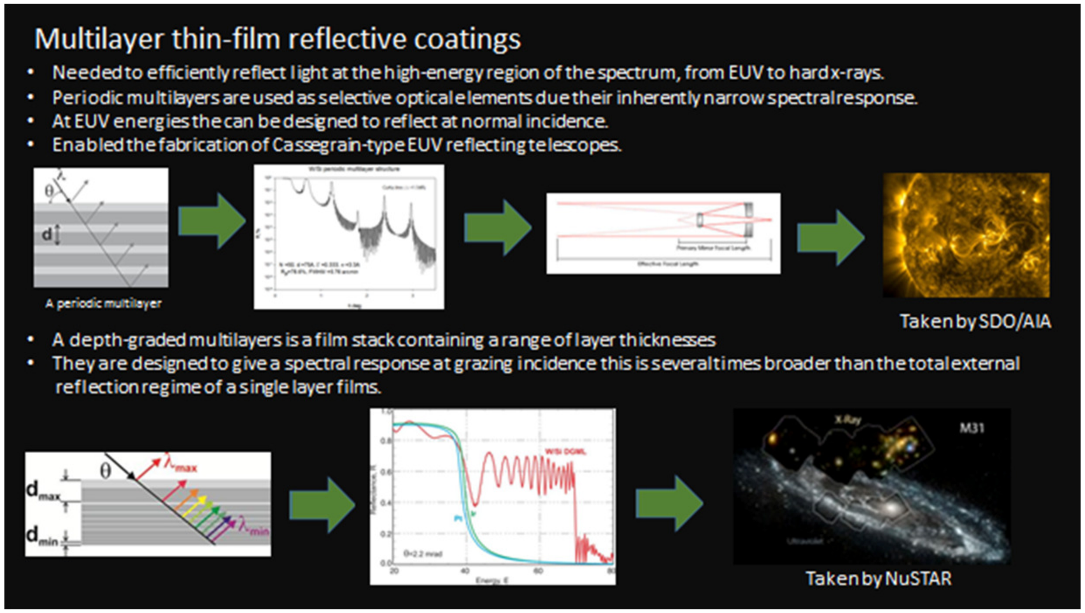
X-ray optical thin film deposition and analysis capability at NASA MSFC

D. Broadway

Talk Outline

- Optical thin film coating capability at MSFC
  - Deposition system
  - X-ray reflectometer (XRR)
  - A method for the deposition of broadband coatings
- Thin film stress measurement:
- Ex-situ example
- In-situ
  - Example: Stress behavior in polycrystalline materials during film growth
  - Current optical methods of in-situ measurement
    - Limitations, sensitivity
  - New method of in-situ stress measurement using fiber optic displacement sensor
    - Two embodiments: circular, cantilever-substrate
    - Sensitivity
    - Repeatability performance
    - Device validation
  - Effect of material interfaces on film stress: Ir/B4C, Ir/Si, Mo/Si, Mo/B4C,…
    - Multilayers to compensate stress in x-ray optical coatings?
      - W/Si example

X-ray optical thin-film coatings



Multilayer thin-film reflective coatings

- Needed to efficiently reflect light at the high-energy region of the spectrum, from EUV to hard x-rays.
- Periodic multilayers are used as selective optical elements due their inherently narrow spectral response.
- At EUV energies the can be designed to reflect at normal incidence.
- Enabled the fabrication of Cassegrain-type EUV reflecting telescopes.

A periodic multilayer

Taken by SDO/AIA

- A depth-graded multilayers is a film stack containing a range of layer thicknesses
- They are designed to give a spectral response at grazing incidence this is several times broader than the total external reflection regime of a single layer films.

Taken by NuSTAR

- Single or multilayers thin-films
- Layer thicknesses

in the range of tens to hundreds of angstroms (Å)

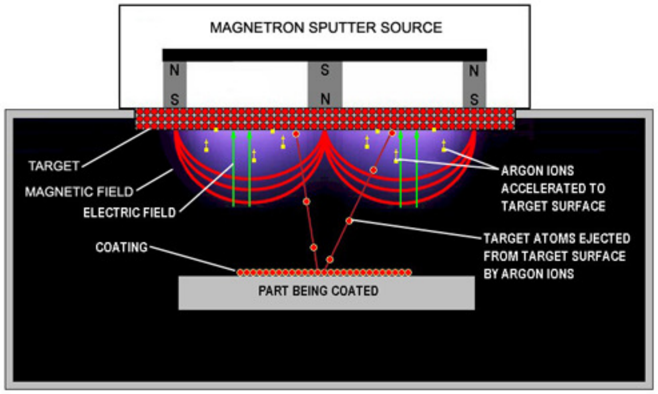
- Multilayers contain hundreds of layer pairs
- Layer thickness can be numerically

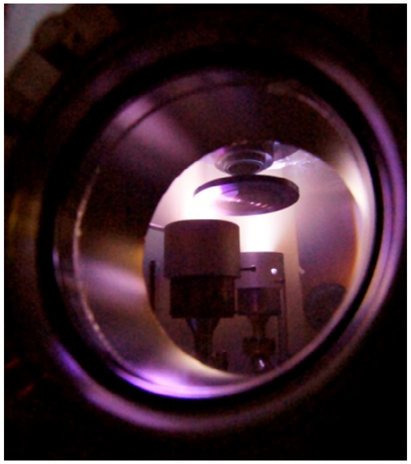
designed to ellicit a specific spectral response

- Optical performance dominated by

interface roughness/diffusion

- Lateral and in-depth thickness gradients enables:
  - ➢ collimating and focusing optics
  - ➢ bandpass filters, notch filters, etc.



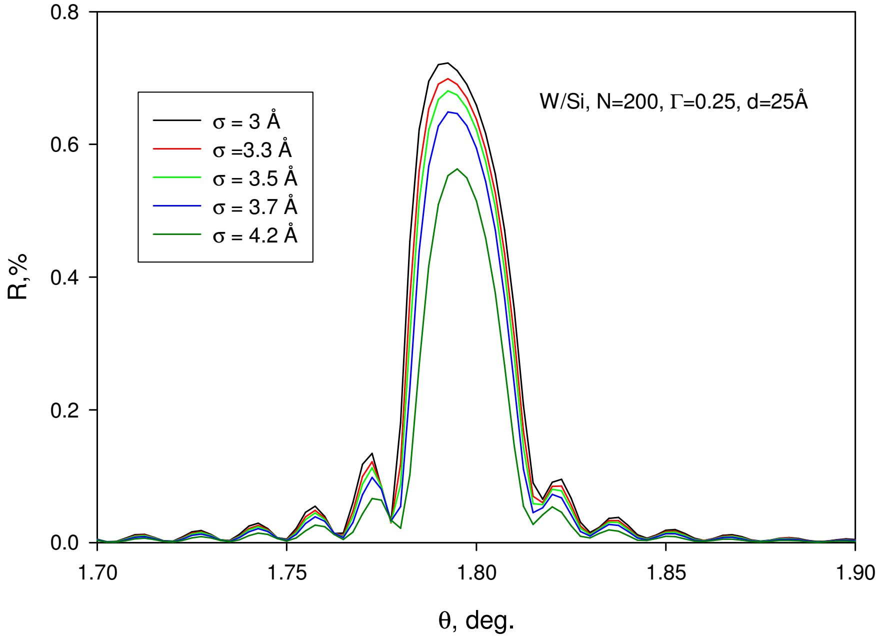


X-ray reflectivity from the multilayer

Modified Fresnel coefficient:

$$r = r_0 e^{\frac{-8\pi^2\sigma^2}{\lambda^2}\sin(\theta_0)^2}$$

Roughness influence on first order reflectivity



$$r^s_{N-j} = \frac{\sqrt{n^2_{N-j}(\lambda) - \cos(\theta_0)^2} - \sqrt{n^2_{N-j+1}(\lambda) - \cos(\theta_0)^2}}{\sqrt{n^2_{N-j}(\lambda) - \cos(\theta_0)^2} + \sqrt{n^2_{N-j+1}(\lambda) - \cos(\theta_0)^2}}$$

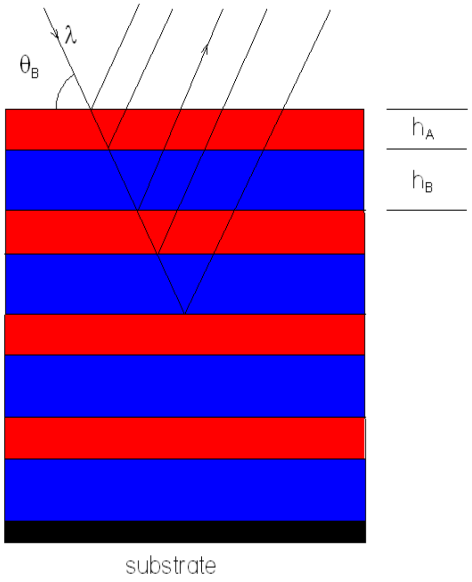
$$r^p_{N-j} = \frac{\left(\frac{n_{N-j}(\lambda)}{n_{N-j+1}(\lambda)}\right)\sqrt{n^2_{N-j+1}(\lambda) - \cos(\theta_0)^2} - \sqrt{n^2_{N-j}(\lambda) - \cos(\theta_0)^2}}{\left(\frac{n_{N-j}(\lambda)}{n_{N-j+1}(\lambda)}\right)\sqrt{n^2_{N-j+1}(\lambda) - \cos(\theta_0)^2} + \sqrt{n^2_{N-j}(\lambda) - \cos(\theta_0)^2}}$$

$$\beta_{N-j} = \frac{2\pi h_{N-j}}{\lambda}\sqrt{1 - \frac{\cos(\theta_0)^2}{n^2_{N-j+1}(\lambda)}}$$

$$S^{\nu}_{j+1} = \frac{r^{\nu}_{N-j} + S^{\nu}_{j} e^{2i\beta_{N-j}}}{1 + r^{\nu}_{N-j} S^{\nu}_{j} e^{2i\beta_{N-j}}}$$

$$R = \frac{1}{2}R^s + \frac{1}{2}R^p$$

$$R^{\nu} = S^{\nu} S^{\nu^*}$$

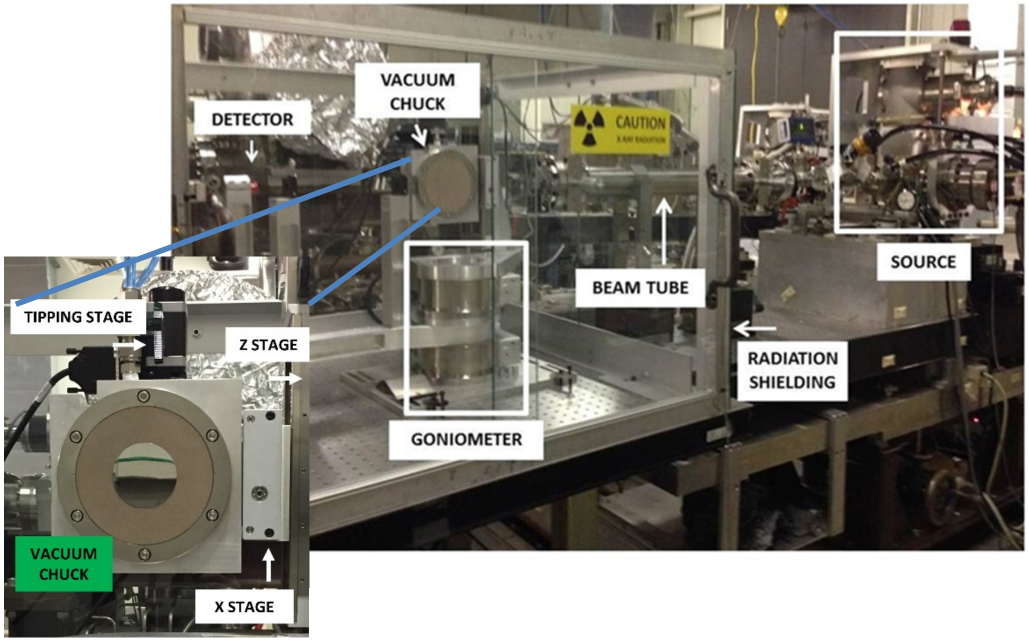


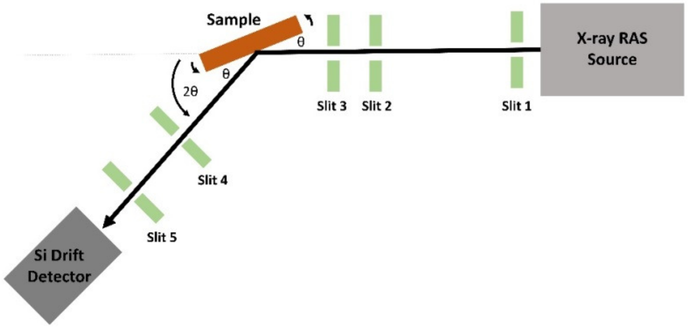
$d \equiv h_A + h_B$

Recently developed XRR system at MSFC

The X-ray Reflectometer System

- High flux rotating anode source
    - Cu target 8 keV X-rays
    - 5-35 kV, 10-150 mA
- Series of Tungsten slits to reduce beam size on sample
- High speed silicon drift detector
    - Amptek
    - (Energy res. of 0.14 keV at 5.9 keV)
- Precision sample alignment and positioning
- Custom control + real-time data collection software (LabVIEW)
- Vacuum chuck sample mount
- No monochromator due high detector resolution
- Interlaboratory study conducted to ensure quality of XRR measurements





Gurgew, Broadway, Gubarev, Ramsey

Thin Film Stress

- The stress can be compressive or tensile.

- Various components of stress:
  - Intrinsic, σ_i, which is related to the film's microstructure.
  - Thermal stress, $\sigma_{\Delta CTE}$,which arises due to the difference in the linear expansion coefficient between the film and substrate and the difference between substrate temperature, T_s, during deposition and subsequent cooling to room temperature: $\boxed{\sigma_{\Delta CTE} = M_f(\alpha_s - \alpha_f)\Delta T}$
  - Extrinsic, σ_{ext}, that results due to external forces applied to the film substrate system such as bending of the substrate to produce a figured optic.

- The film stress can be enormous for some materials (i.e. GPa's)

- The curvature,κ, of the deformed substrate is proportional to the product of film stress and film thickness,σh_f, through a constant that describes the geometric and mechanical properties of the substrate (Stoney's Equation)--namely, the substrate's thickness, h_s, and biaxial modulus, $\frac{E_s}{(1-\vartheta_s)}$:

$$\boxed{\sigma h_f = \frac{E_s h_s^2}{6(1-\vartheta s)}\kappa}$$

N/m

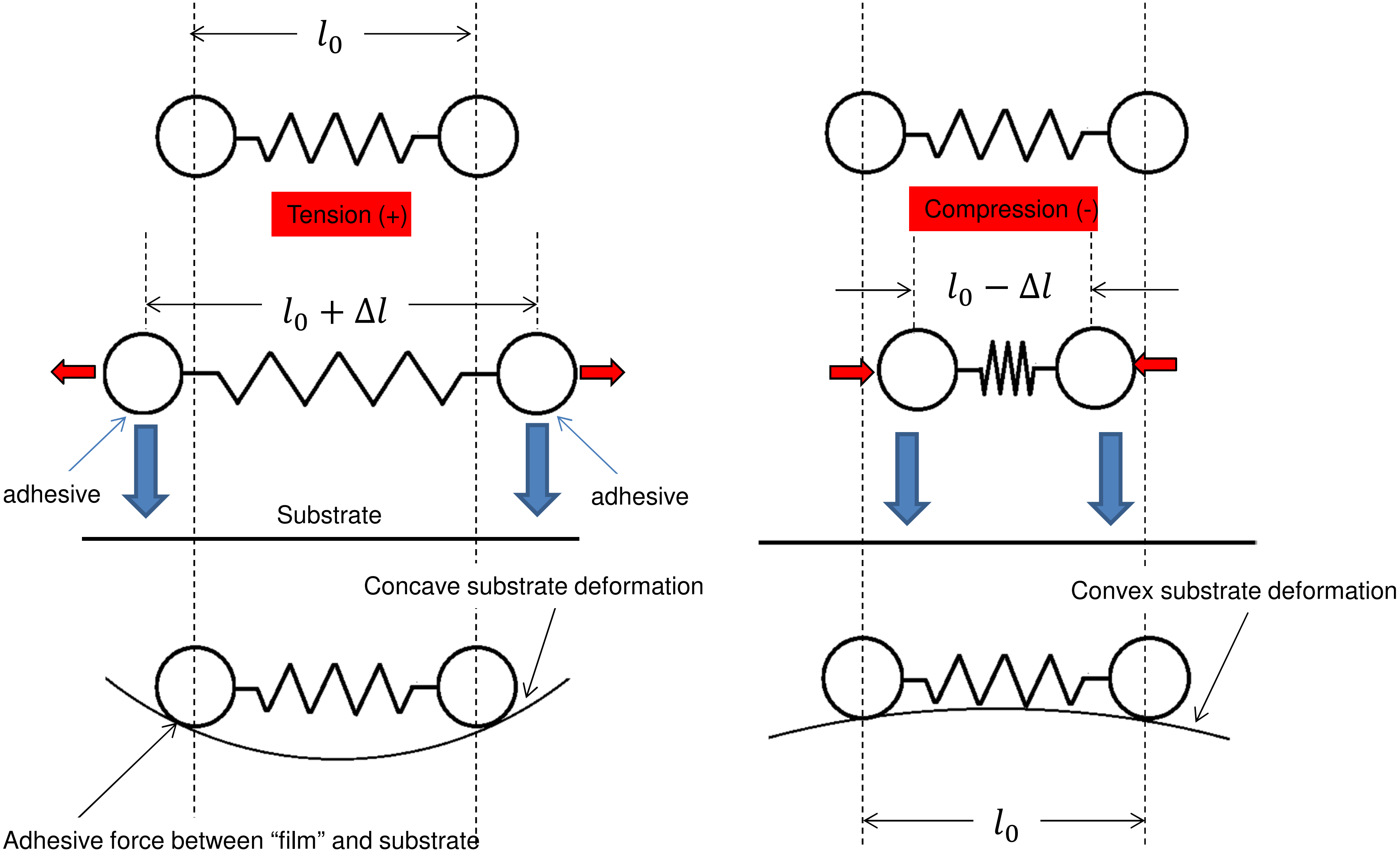
Thin Film Stress (Cont'd))

- In controlling film stress, the aim is to manipulate the energy of the sputtered atoms and influence the adatom mobility at the film surface.

- For a given material, stress is highly process dependent for magnetron sputtering and influenced by deposition conditions:
  - Gas Pressure (stress reversal)
  - Deposition Rate (cathode power)
  - Substrate Temperature
  - Substrate bias

- There is a trade-off between film stress and film quality (i.e. roughness, density).
  - Generally, the deposition conditions needed to achieve good X-ray reflectivity result in high film stress.

Stress/Spring Model



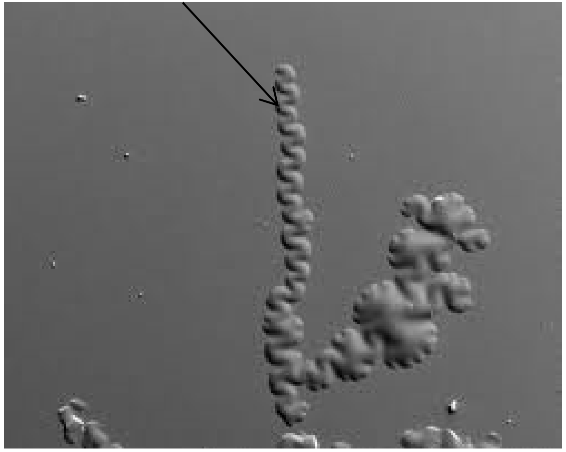
The film will delaminate if the stress is greater than the adhesion between the film as substrate

Detrimental effects of high film stress:

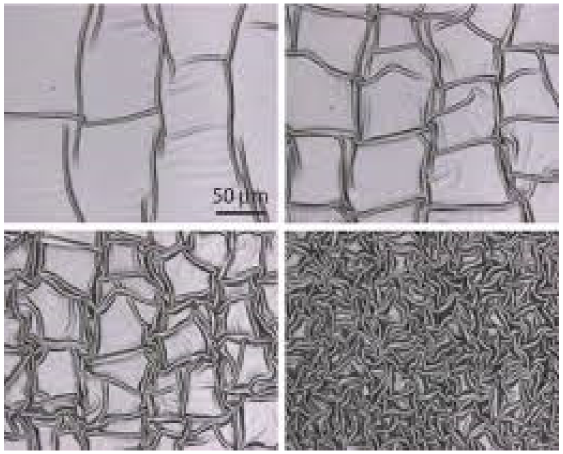
- Cracking, buckling and delamination

  If the force per unit length due to the stress in the film exceeds the adhesive force, delamination of the film will occur.

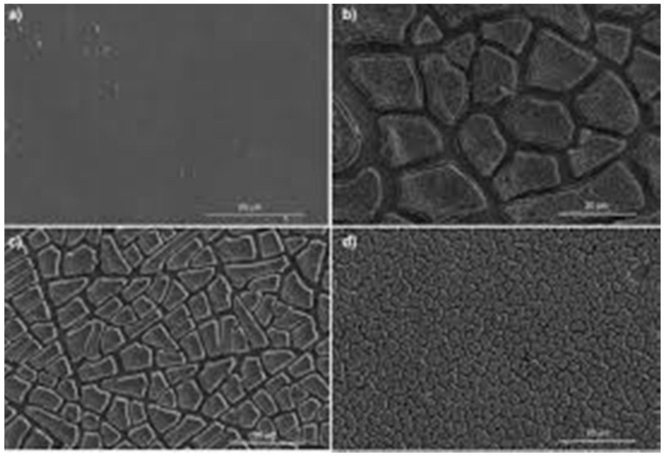
“telephone chord” propagation



High compressive stress (buckling)



High tensile stress (cracking)



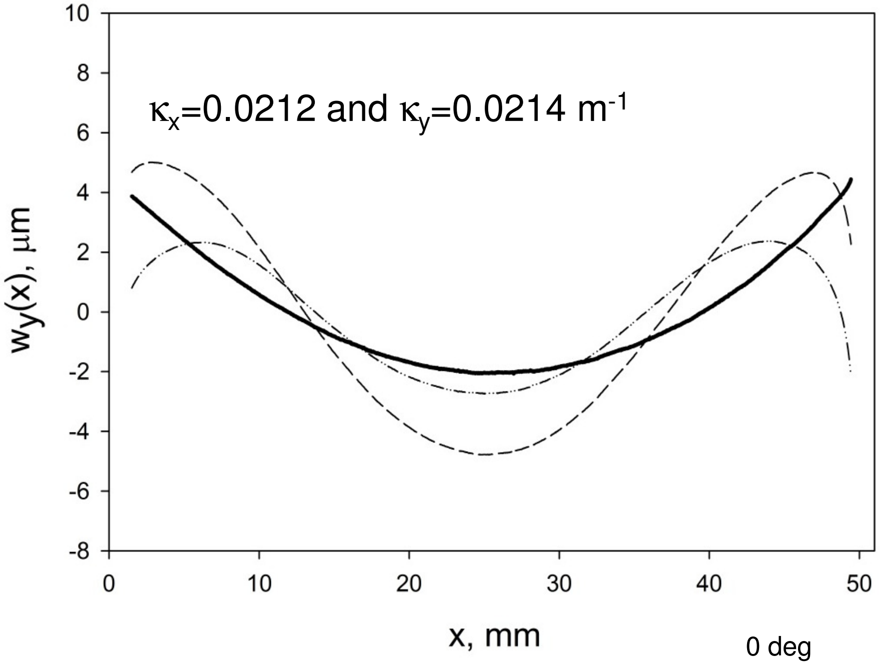
- Substrate deformation
  - Of particular concern for grazing incidence X-ray optics since the stress can alter the precise geometrical figure and degrade its focusing or collimating properties.
    - Significant technological challenge for the next generation of lightweight X-ray space telescopes like Lynx:
    - The desire to achieve sub-second resolution has motivated deposition techniques to correct substrate figure errors which rely on a very low stress film (ie. A few MPa)
    - Substrates are only 10’s of microns thick.
    - The X-ray reflective Ir layer is highly stressed (~4 GPa)

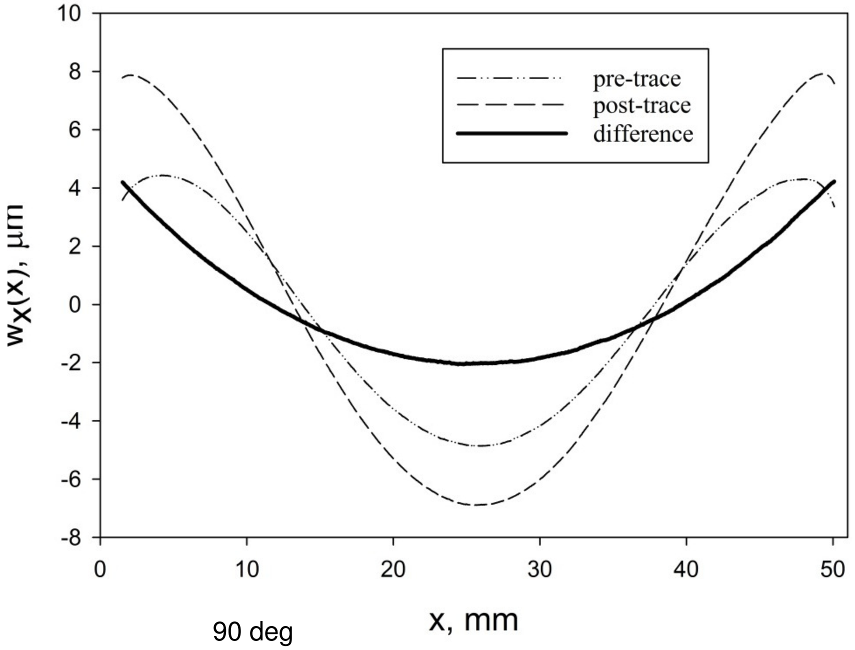
Ex-situ measurement of thin film stress

$$Stoney's\ Eqn{:}\ \sigma h_f = \frac{E_s h_s^2}{6(1-\vartheta s)}\kappa$$

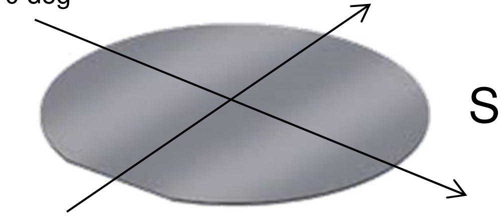
$$Spherical\ Deformation\ Mode{:}$$
$$A = \sigma h_f \frac{D_s^2}{h_s^3}$$

Tallysurf stylus profilometer





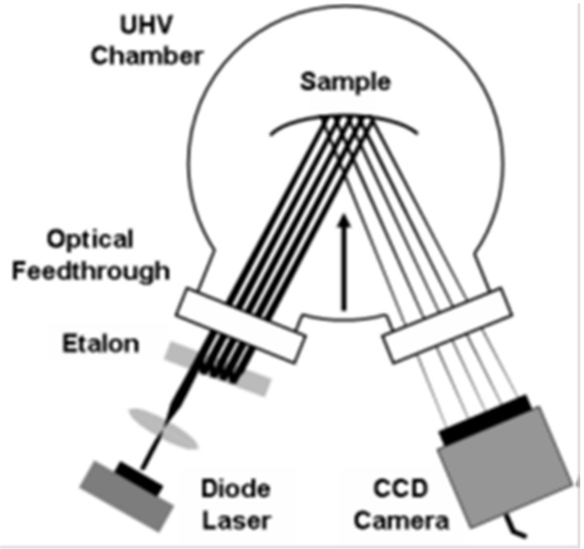
$$\kappa \approx \frac{d^2 w}{d^2 x} = const$$



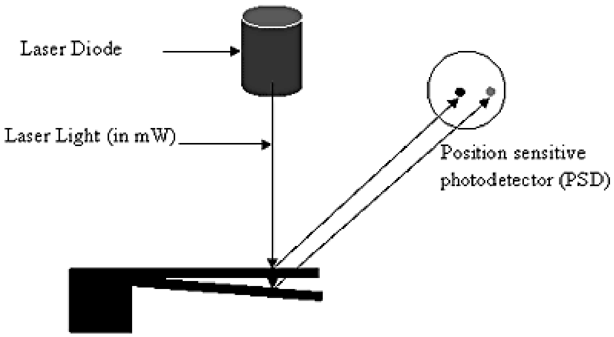
Si <111>

Current methods of optical in-situ thin film stress measurement:

Multi-beam stress sensor (MOSS):



Micro cantilever:



These methods determine the substrate curvature by various optical means from which the integrated stress is calculated from the Stoney Eqn.:

$$\sigma h_f = \frac{E_s h_s^2}{6(1-\nu_s)}\kappa$$

<u>Minimum detectable stress $\Delta\sigma h_f$:</u>

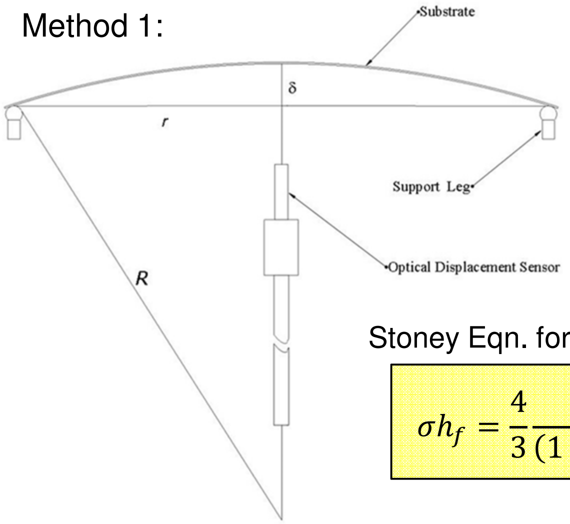
- Ranges from 0.5-50 MPa*nm depending on method and substrate (i.e. geometry and mechanical properties)
- MOSS is 50 MPa*nm for 100 µm thick silicon substrate

<u>Draw backs with current optical methods:</u>

- Requires external optical access to the substrate through angled viewports
- Limited to specific deposition geometries
- Complex
- Requires the use of opaque substrates such as crystalline silicon.
- Film side is measured which can result in destructive interference effects when measuring transparent films.

New approach to in-situ stress measurement

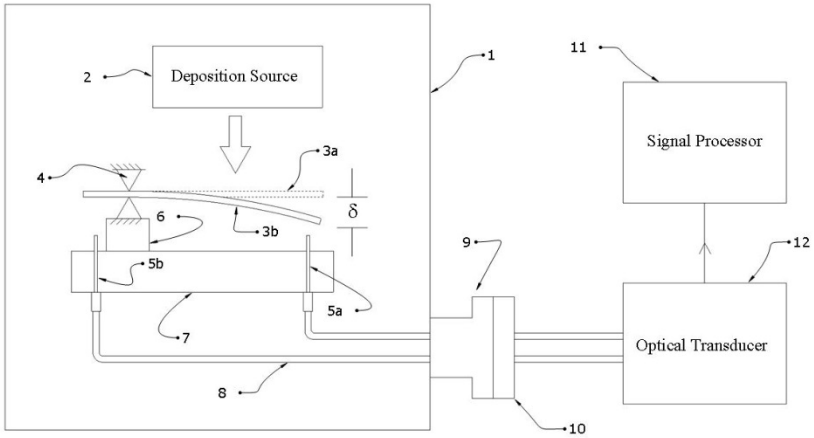
Method 1:



Stoney Eqn. for circular substrate:

$$\sigma h_f = \frac{4}{3}\frac{E_s}{(1-\nu_s)}\left(\frac{h_s}{D_s}\right)^2 \delta$$

Method 2:



Stoney Eqn. for cantilever:

$$\sigma h_f = \frac{E_s h_s^2 \delta}{3(1-\nu_s)L^2}$$

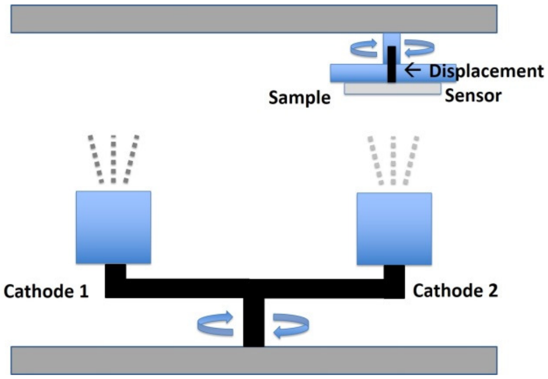
New approach to in-situ stress measurement:

- Utilizes a high resolution (i.e. 5nm) vacuum compatible fiber optic displacement sensor.
- Curvature determined from out-of-plane displacement measurement of the substrate.
- Uses double-side polished substrate.
- Same arrangement can be used for thermal annealing.
- Glass substrates can be utilized.
- Easily implemented into existing deposition systems.
- Very sensitive method.

Ongoing work:

- Adapting to rotating substrates
- Adapting to curved (i.e. segmented) substrates

D.M. Broadway, U.S. Patent 9,601,391 (Granted March 2017).
D.M. Broadway, U.S. Patent Application 15/425,740 (Filed February 2017).
Pending publication in Review of Scientific Instruments



Minimum detectable integrated stress, $\Delta(\sigma h_f)$

- The minimum detectable stress is limited by the combined ambient vibrational background of the substrate and electronic noise of the displacement sensor.
- The sensitivity further depends on the mechanical and geometric properties of the substrate.
- The cantilever approach is more sensitive to a given integrated stress but is also more sensitive to vibrational noise—compensating effect.
- The cantilever approach is advantageous because it is flexible in its orientation and easily adapted to various deposition geometries.

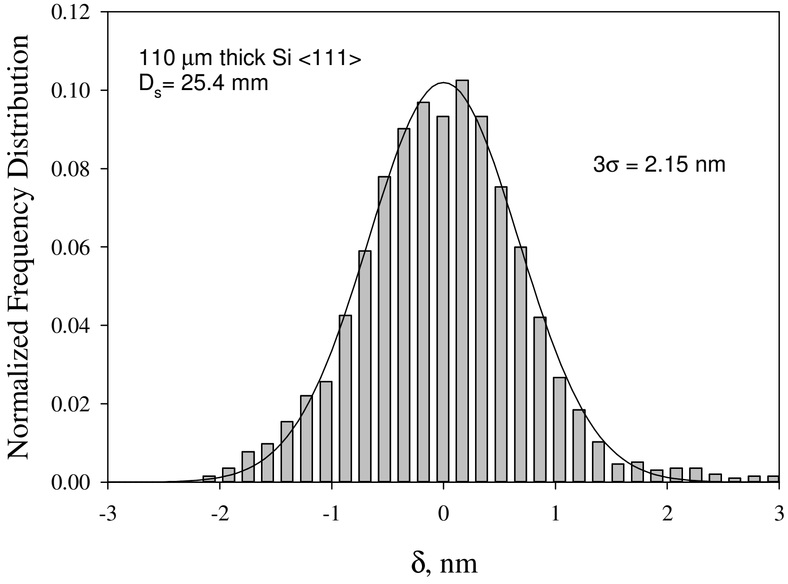
Sensitive enough to measure stress in x-ray multilayers

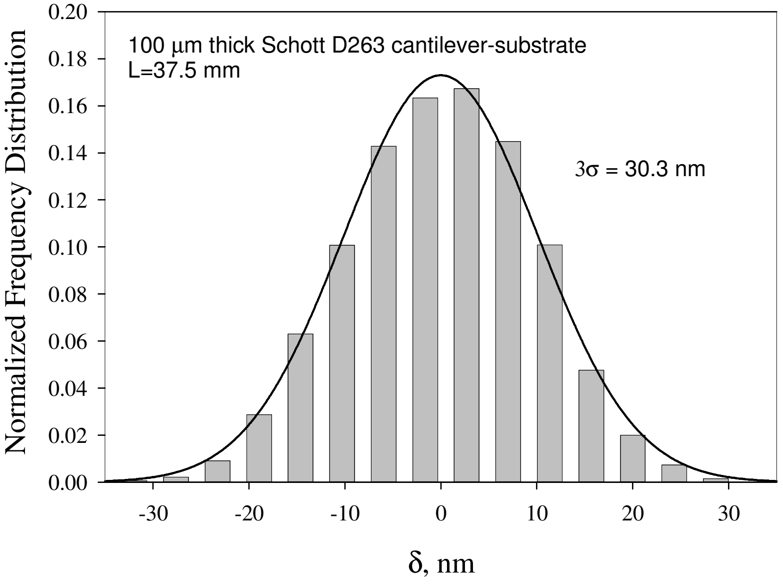
$$\Delta(\sigma h_f) = \frac{4}{3}\frac{E_s}{(1-\nu_s)}\left(\frac{h_s}{D_s}\right)^2 \Delta\delta$$

15 MPa*nm

$$\Delta(\sigma h_f) = \frac{E_s h_s^2 \Delta\delta}{3(1-\nu_s)L^2}$$

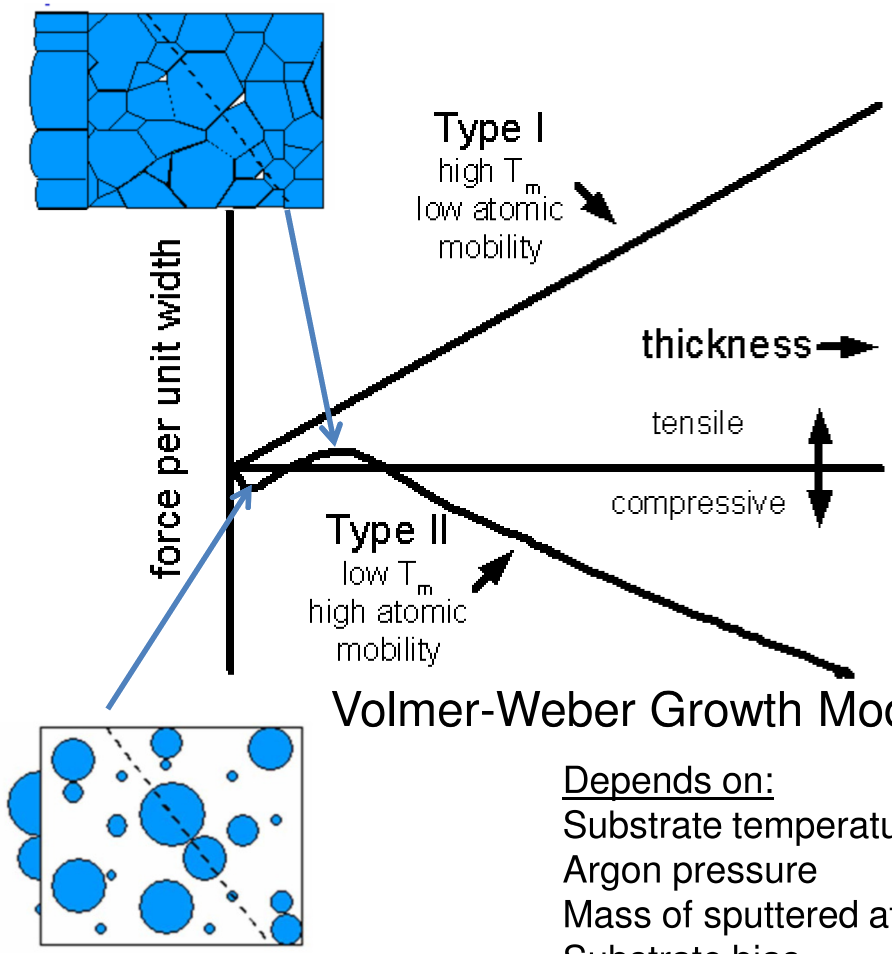
9 MPa*nm





Stress evolution in polycrystalline films

Island coalescence

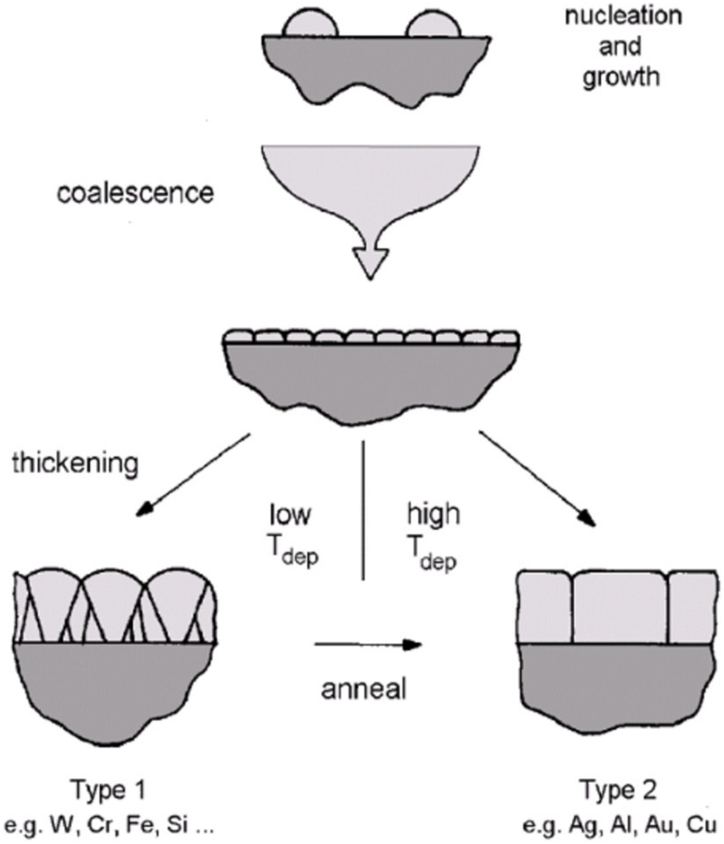


Volmer-Weber Growth Mode

Nucleation & island growth

<u>Depends on:</u>

Substrate temperature
Argon pressure
Mass of sputtered atoms
Substrate bias
Surface energy

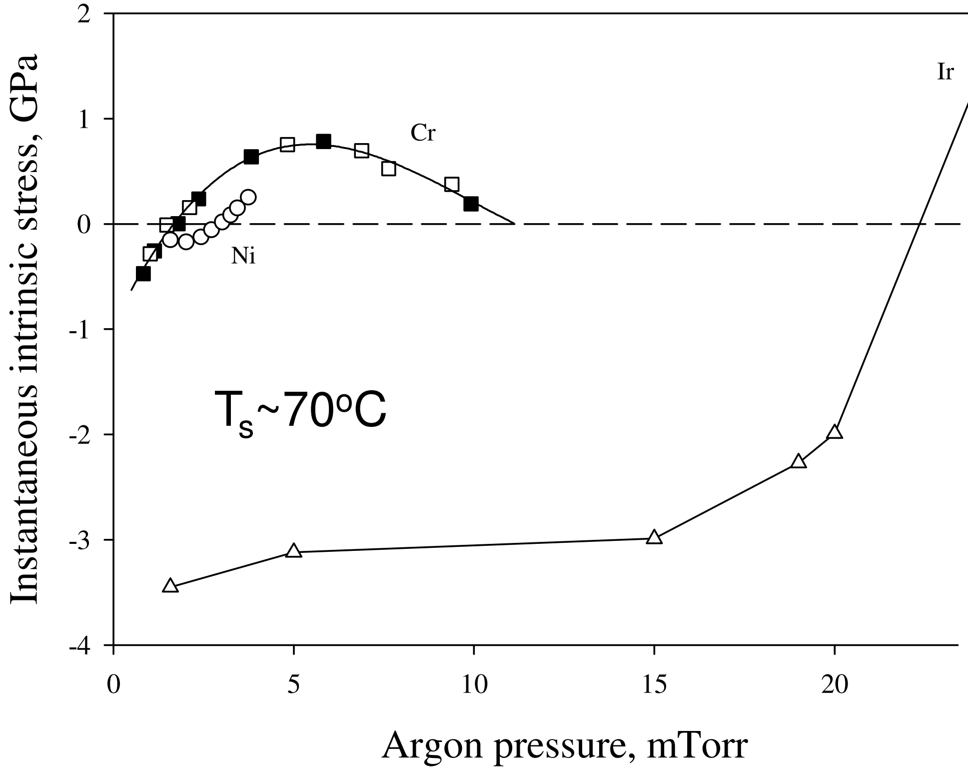


Surface roughness increases with film thickness

Low surface roughness

Stress reversal in polycrystalline films (steady state)

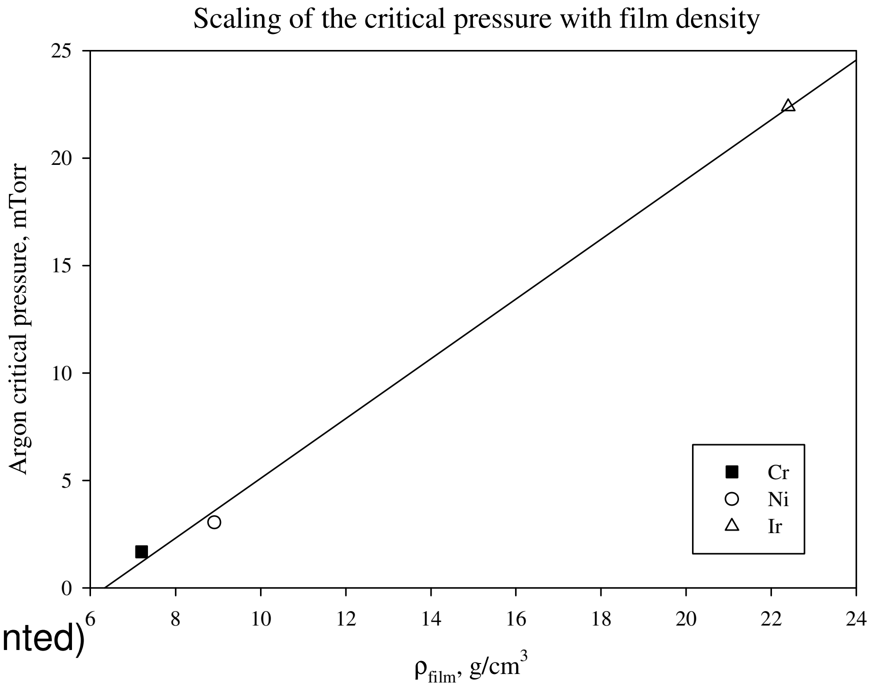
Results are consistent with D.W. Hoffman, Internal stress of sputtered Chromium, Thin Solid Films, 40 (1977) 355-363



Instantaneous stress:

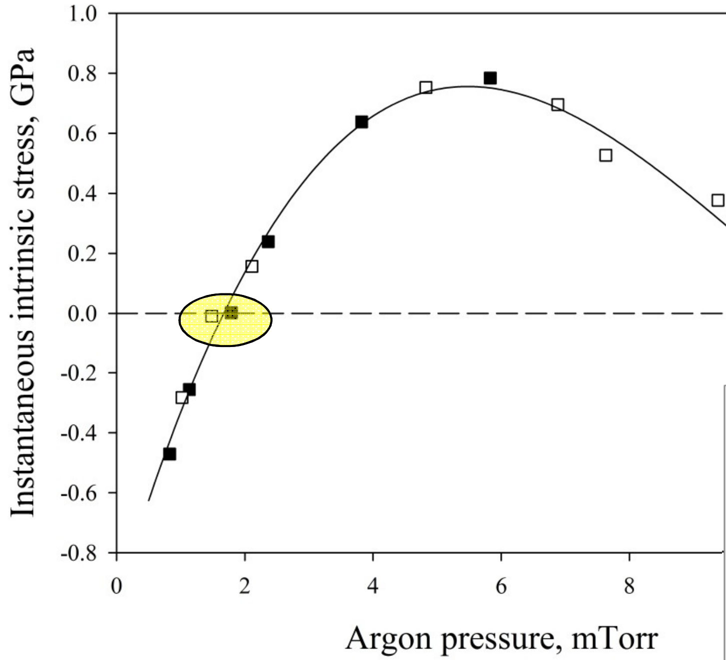
$$\frac{d(\sigma h_f)}{dh_f} = -\frac{E_s}{3\xi(1-\vartheta s)}\left(\frac{h_s}{r}\right)^2 \frac{d\delta}{dt}$$

- Efficient for parametrizing the stress
- Independent of film thickness in the steady-state regime of film growth
- Substrate in thermal equilibrium



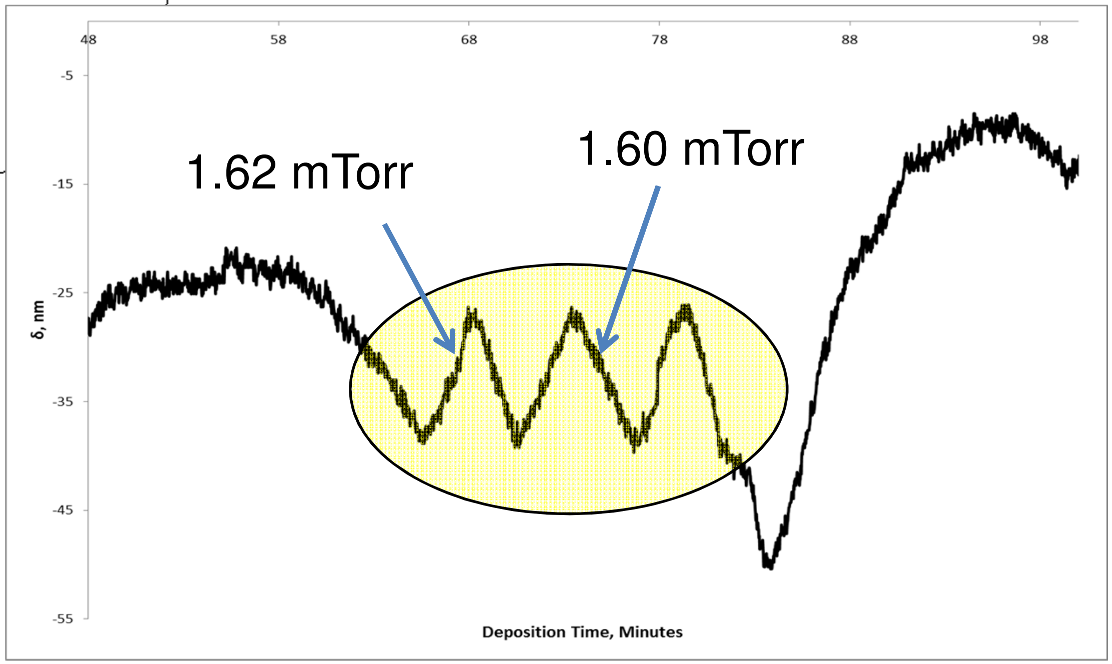
- State of stress (i.e. tensile or compressive) at low pressure is strongly influenced by substrate temperature for low density metals like chromium.
- Therefore, the state of stress will depend on the heat transfer mechanisms of the substrate (i.e. how it is mounted) for a given deposition system.

Sensitivity at the transition pressure (circular substrate)



Stress reversal in Cr with argon pressure has been measured with the instrument. Consistent with the previous work of Hoffman (i.e. stress reversal).

Measurement sensitivity is better than resolution in the control of Argon pressure.

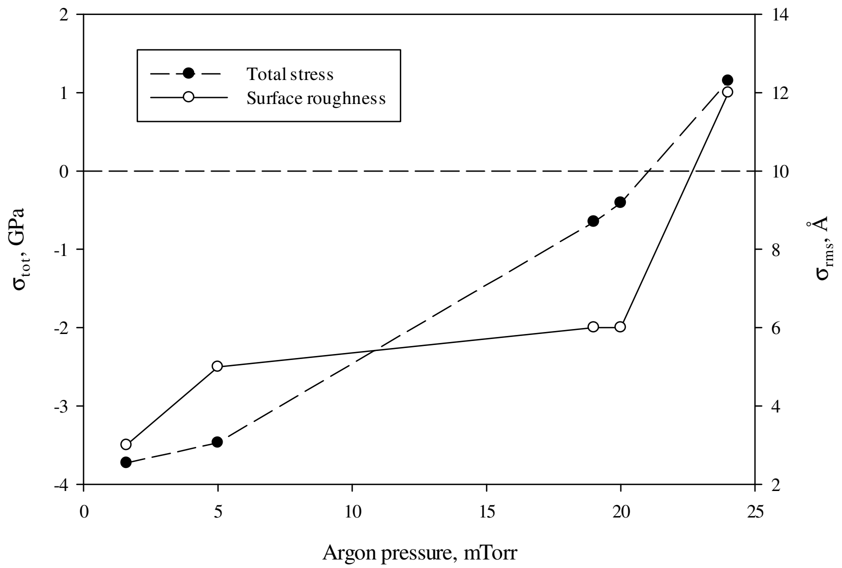


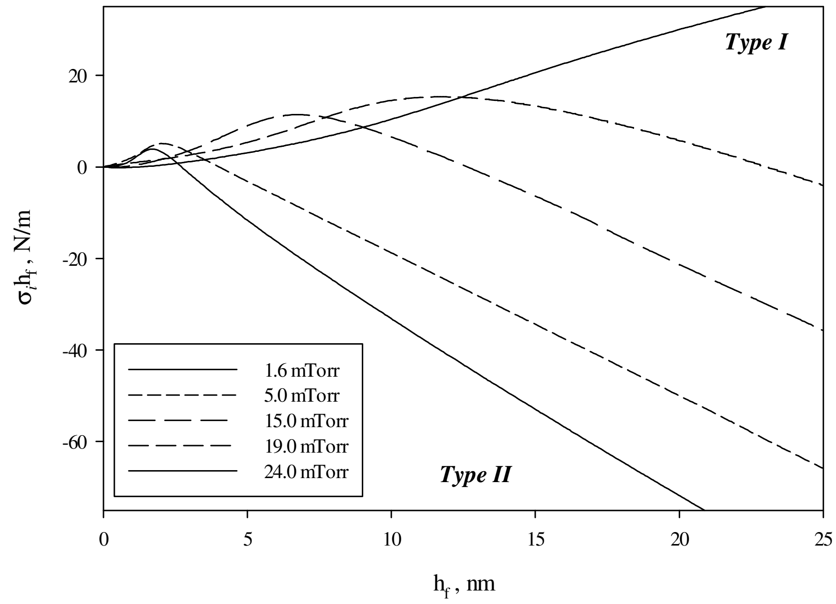
1.62 mTorr

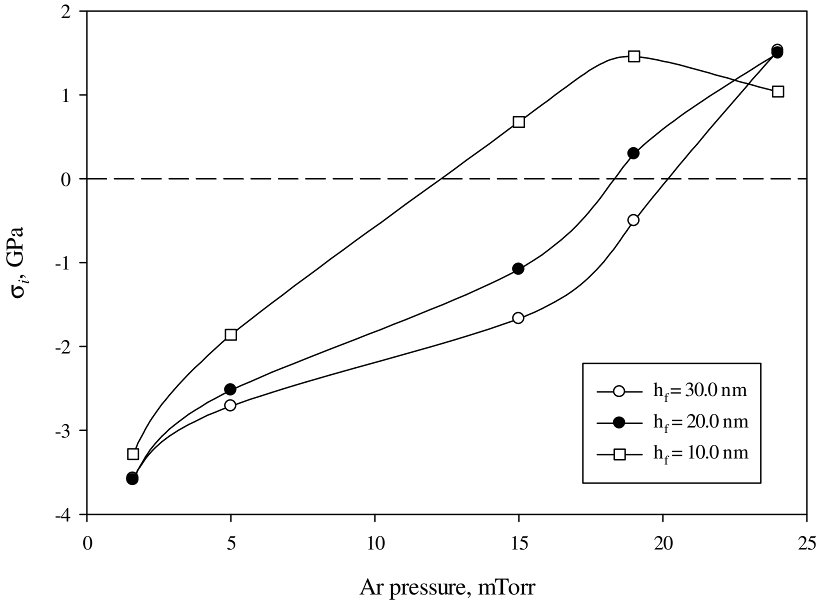
1.60 mTorr

Reduction of Ir film stress with argon pressure optimization

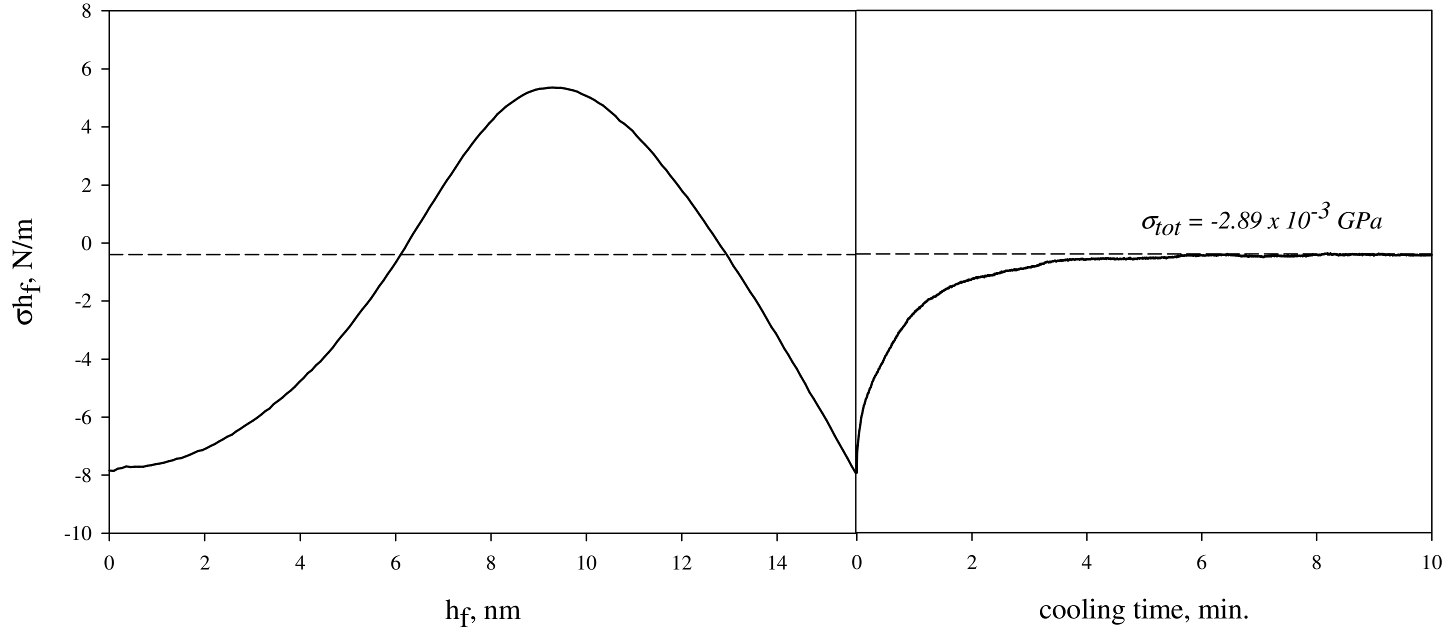
- Surface roughness is to high at the argon critical pressure of ~22 mTorr
- We can achieve low stress and lower argon pressure by exploiting the zero stress that occurs shortly after island coalescence.
- The use of in-situ stress measurement allows use to tune the stress to within a few MPa







Near-zero stress in Iridium (15.0 mTorr)

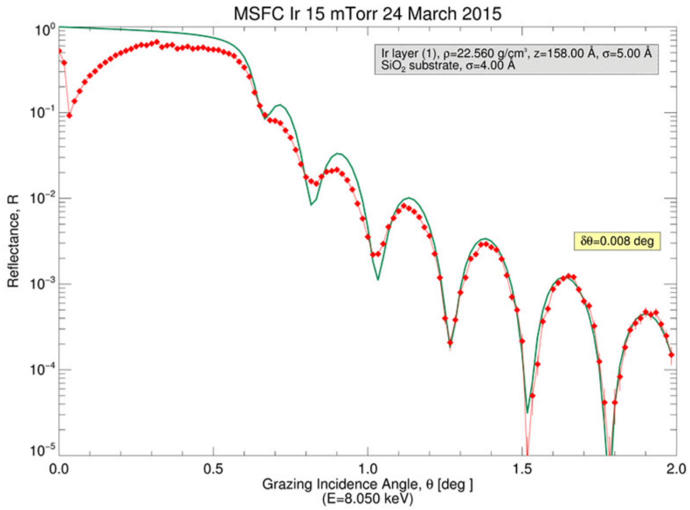


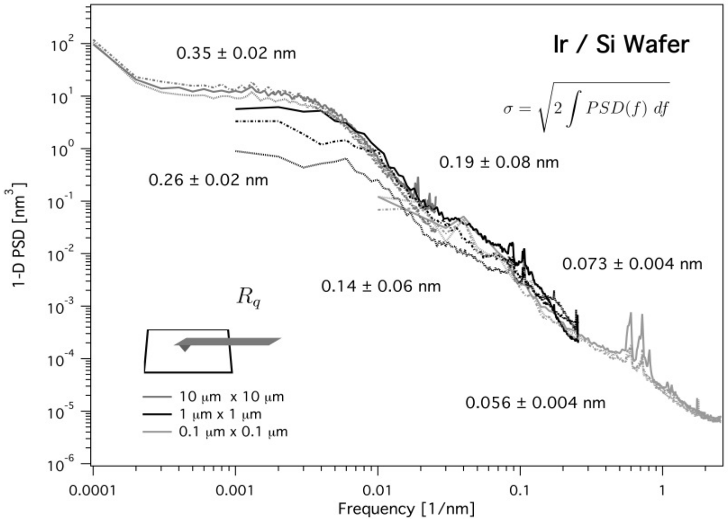
Reduction in the total stress by 3 orders of magnitude (i.e. to -2.89 MPa)

Good adhesion

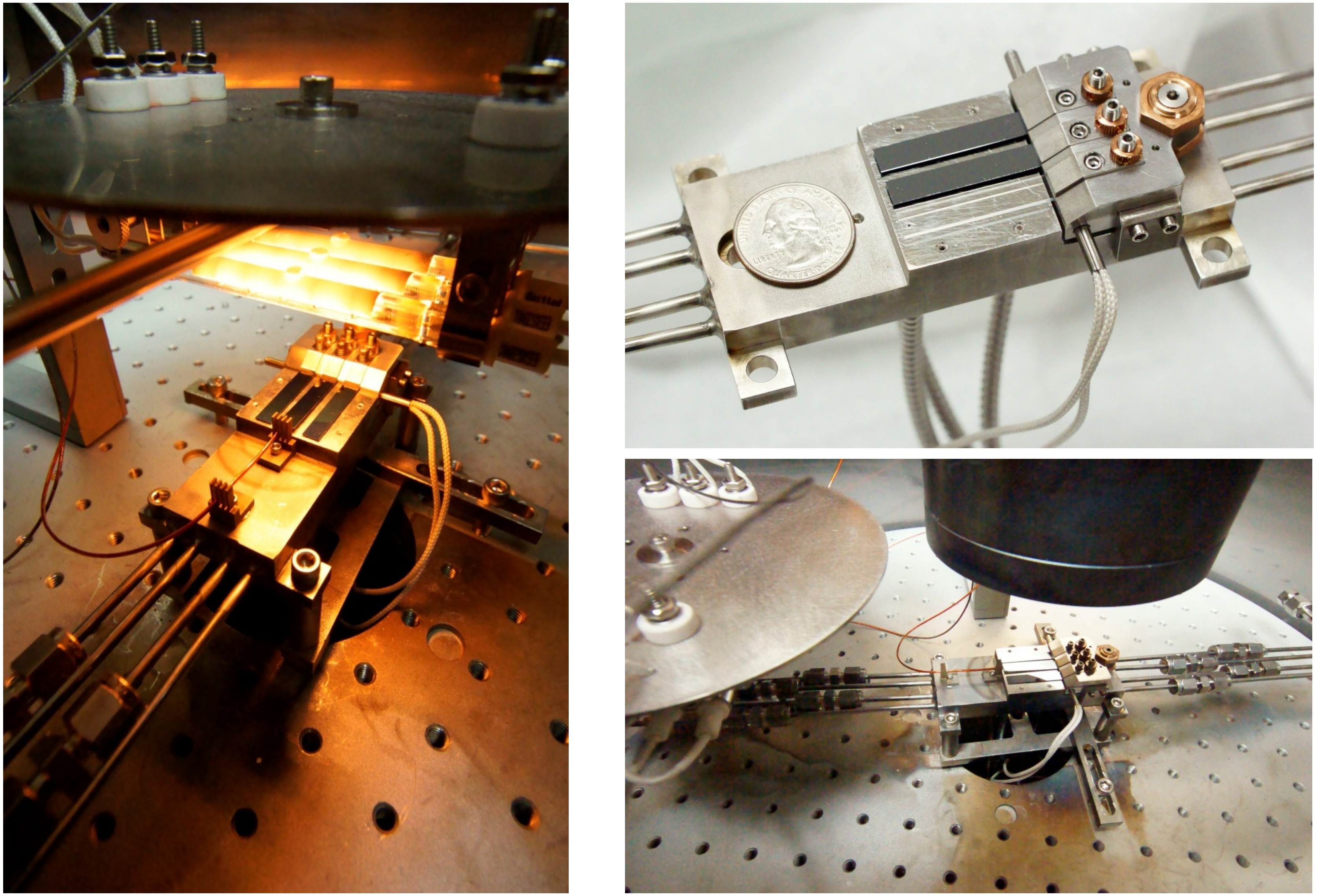
Promising result: 5Å RMS roughness

Further reduction in the roughness is possible through optimization of Ar pressure





Refined in-situ stress sensor

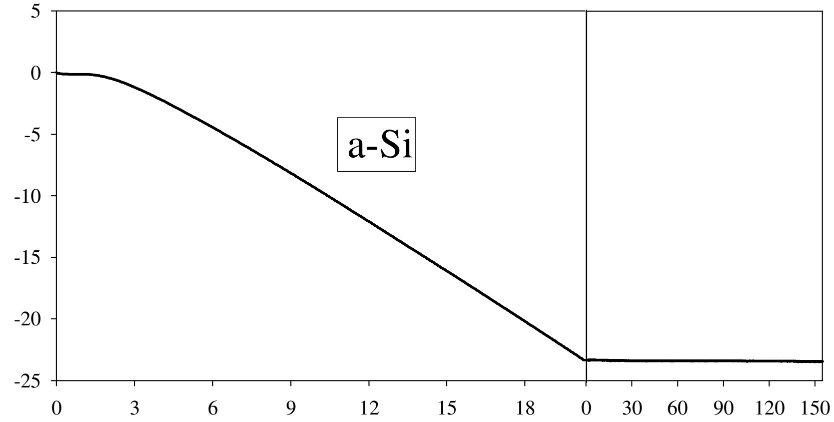


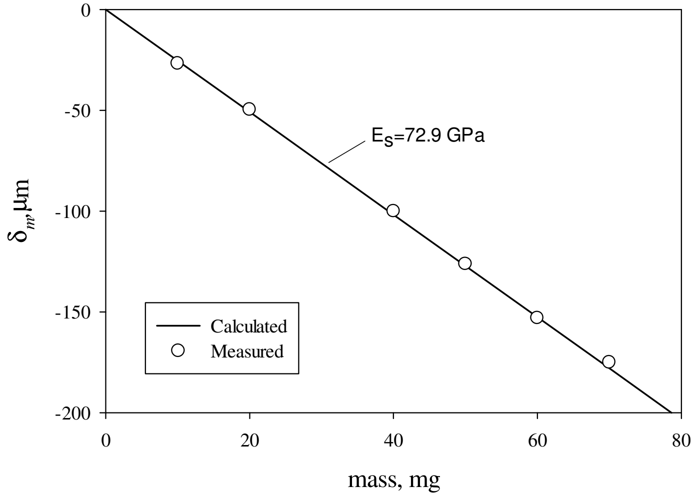
In-situ stress of single layer thin films

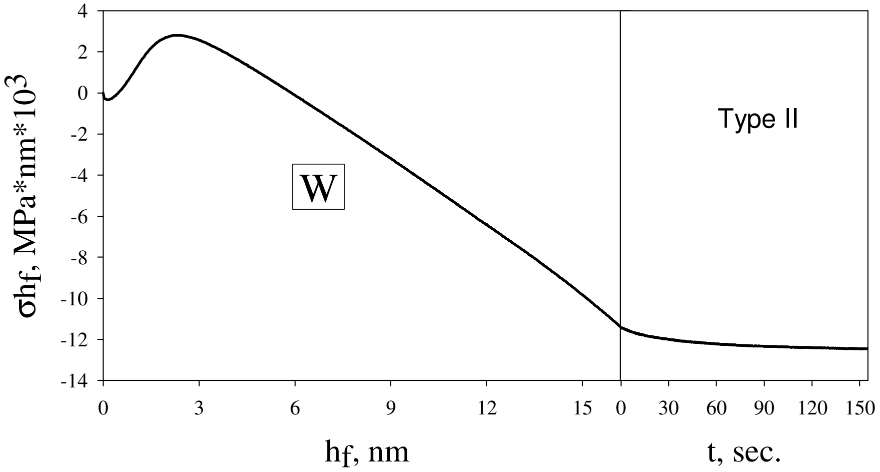
T_s~27-30°C, 2.5 mTorr Ar
100µm thick Schott D263

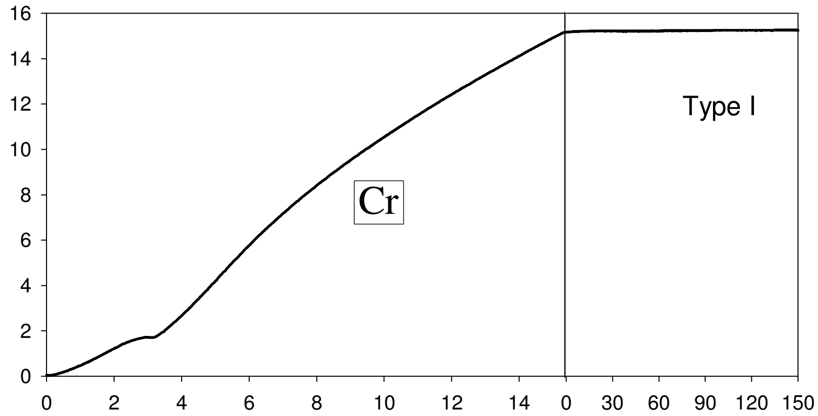
Calibration masses placed on cantilever tip used to validate substrate modulus and linear range of the sensor:

$$\delta_m = \frac{2mgx^2}{E_s b h_s^3}(3L - x)$$

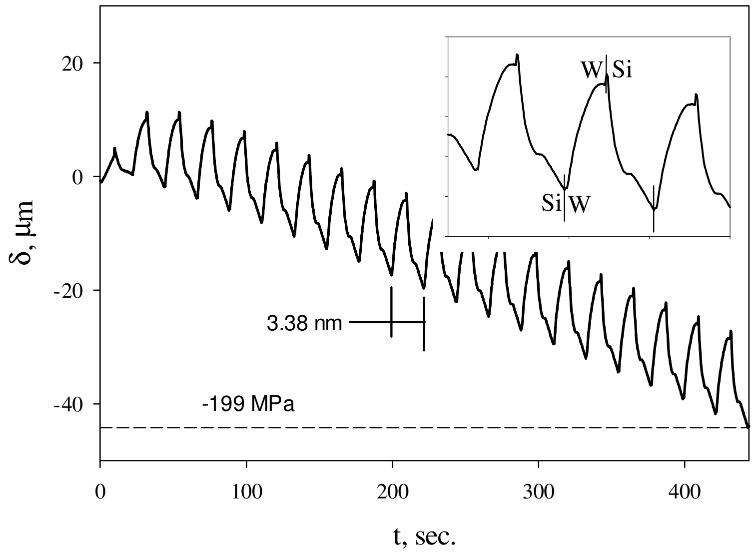


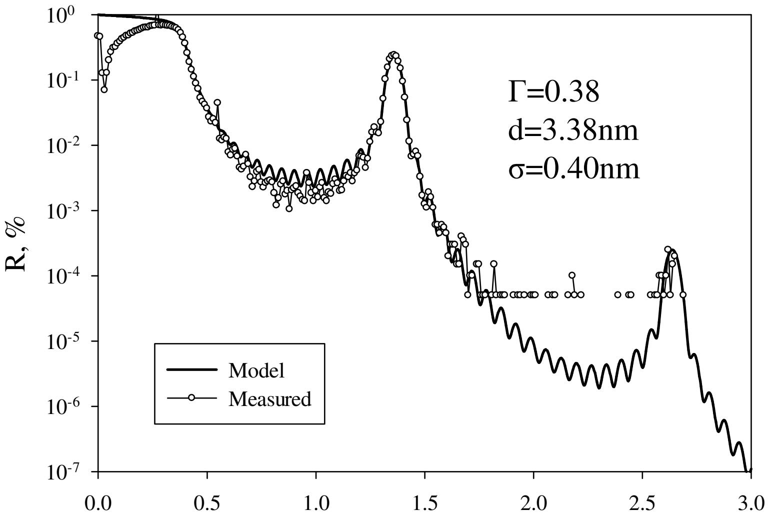






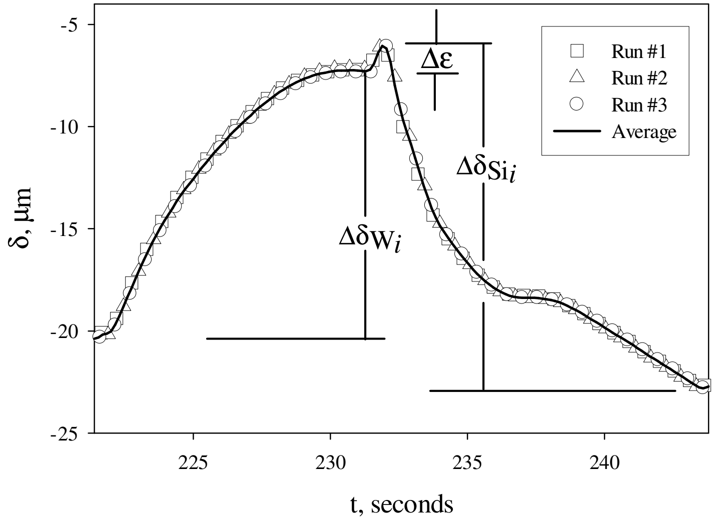
Device performance

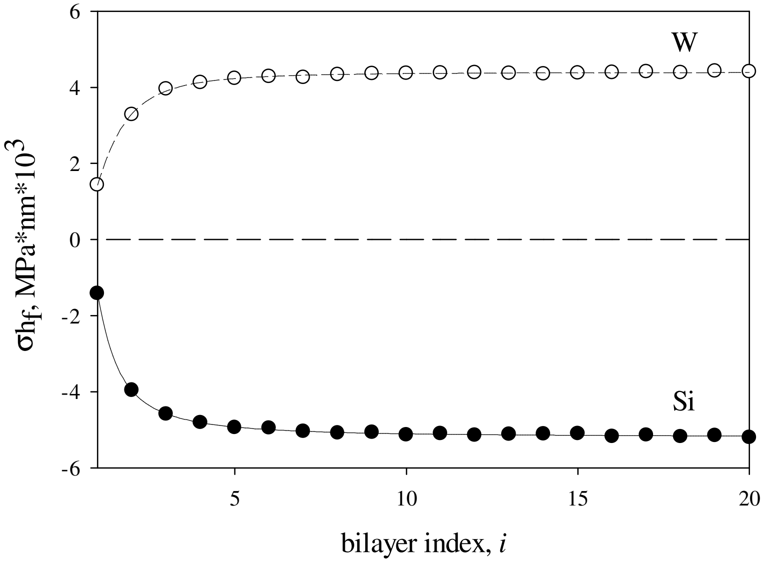




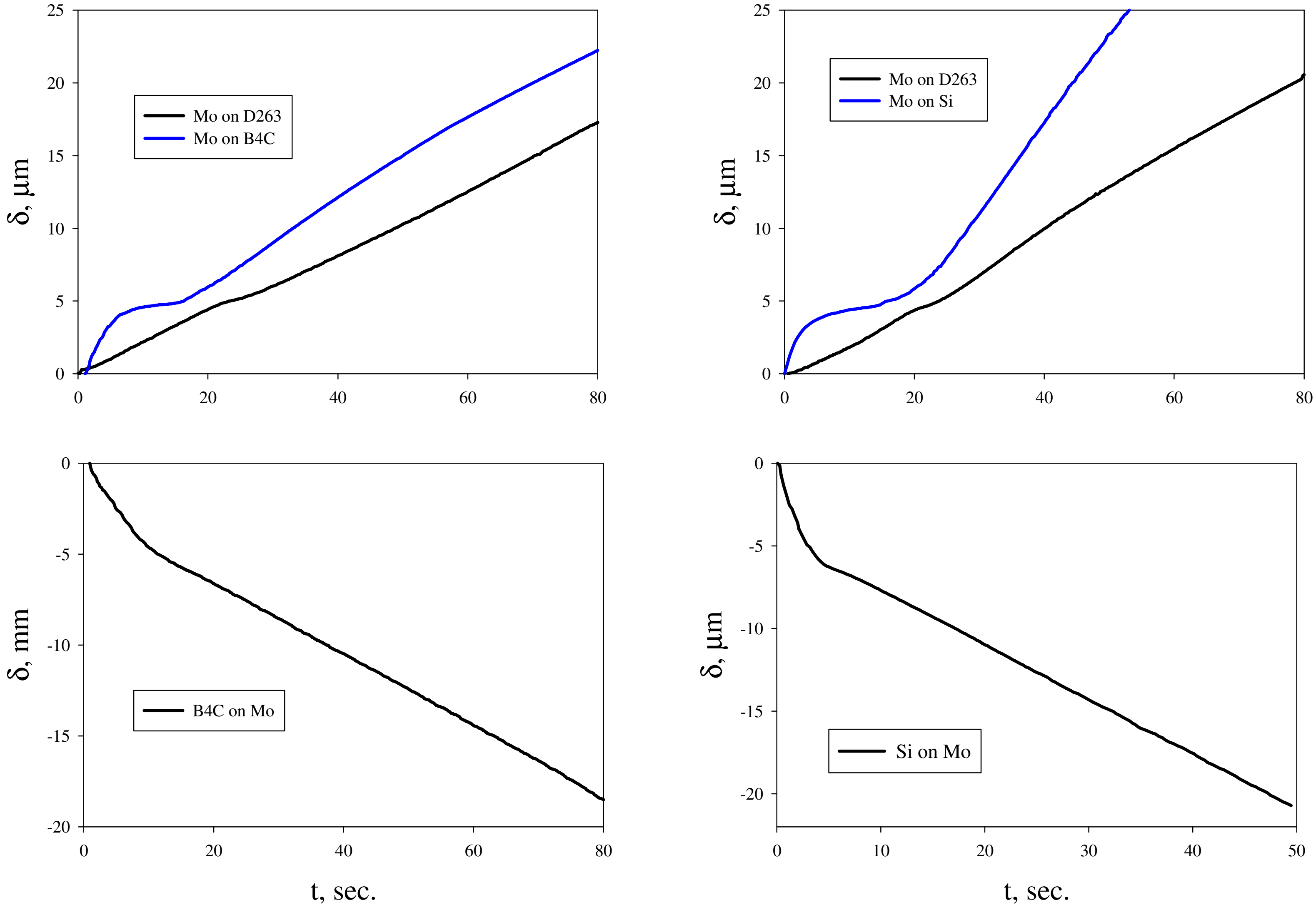
±0.5% within run repeatability

±2.5 % run-to-run repeatability

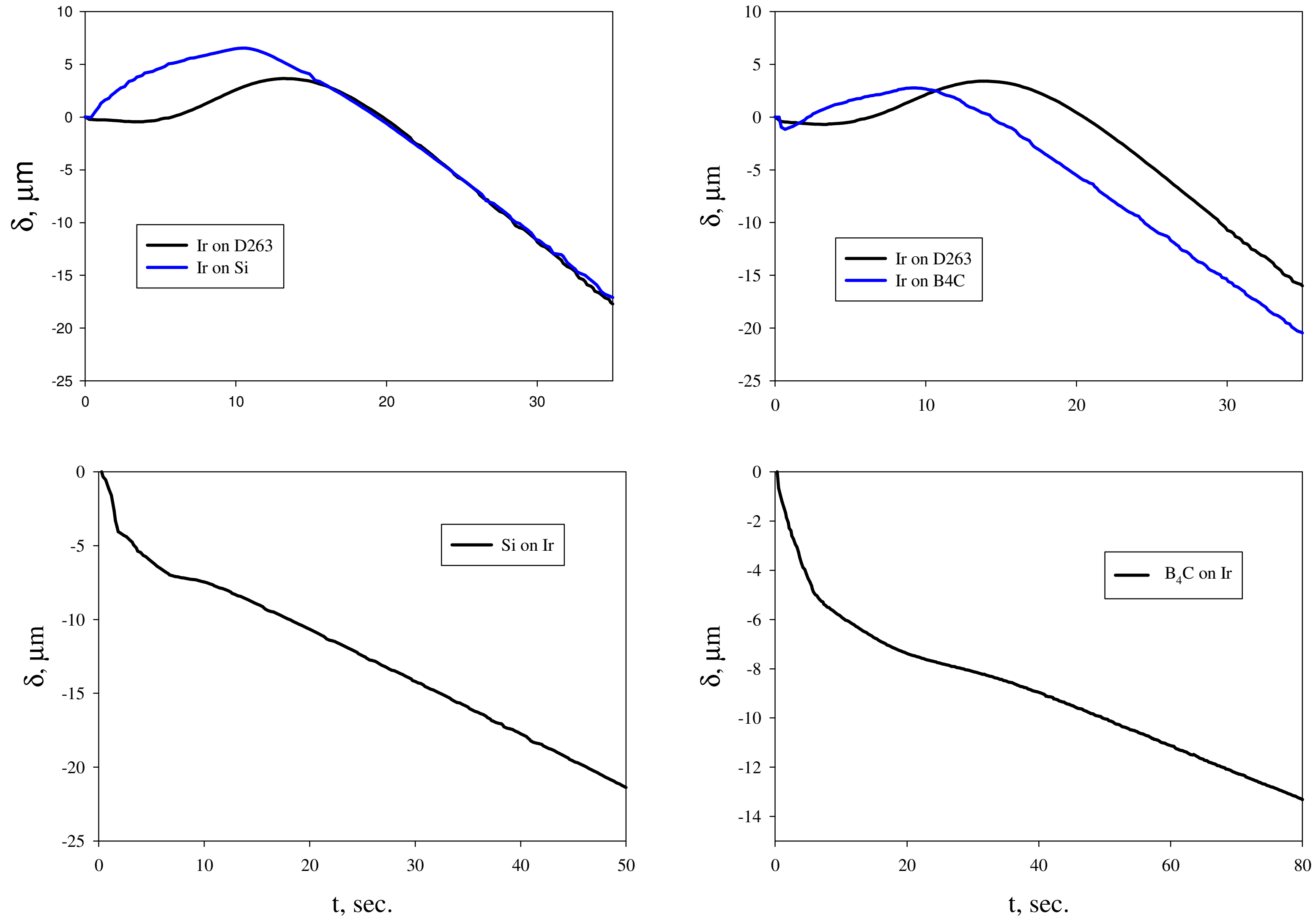




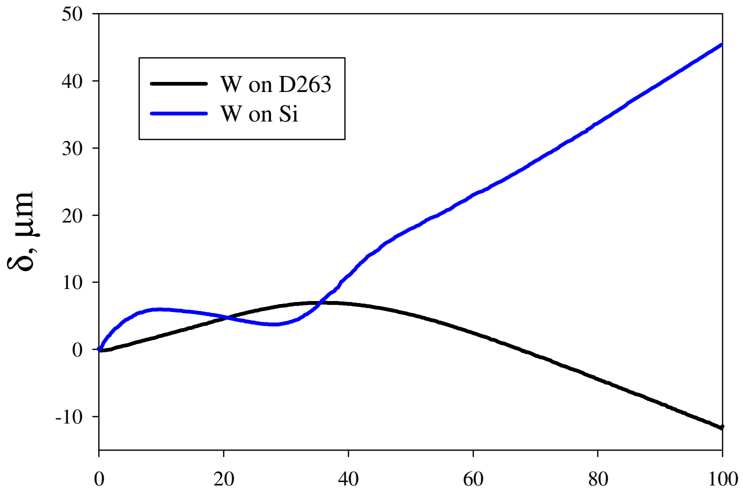
Effect of material interfaces on the film stress (Mo-based)

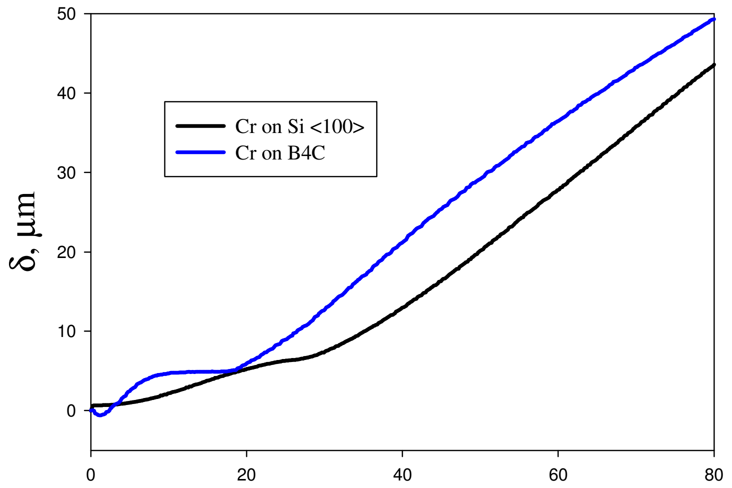


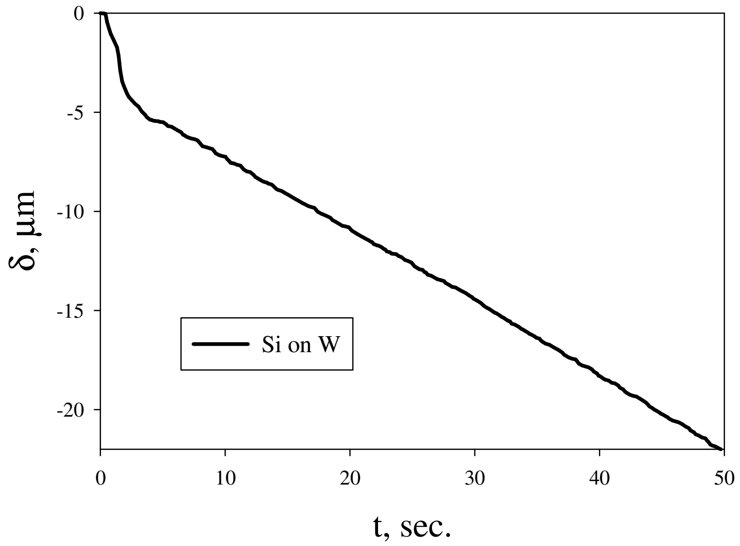
Effect of material interfaces on the film stress (Ir-based)

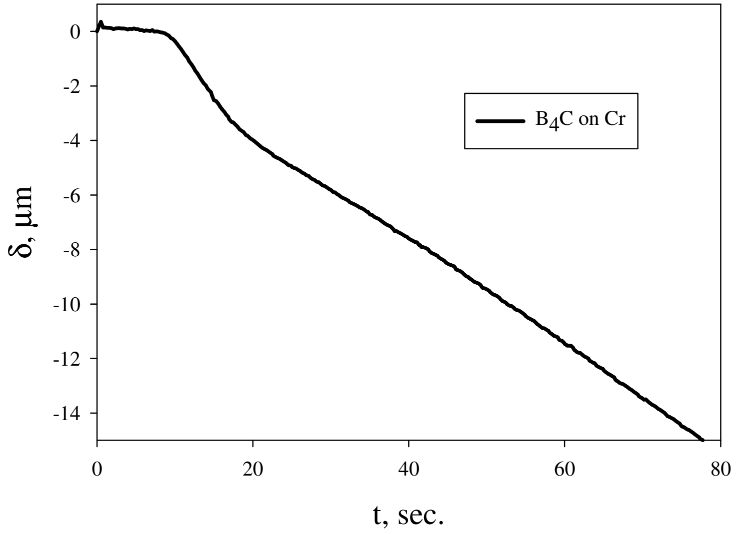


Effect of material interfaces on the film stress (W, Cr-based)









Multilayers to compensate integrated stress

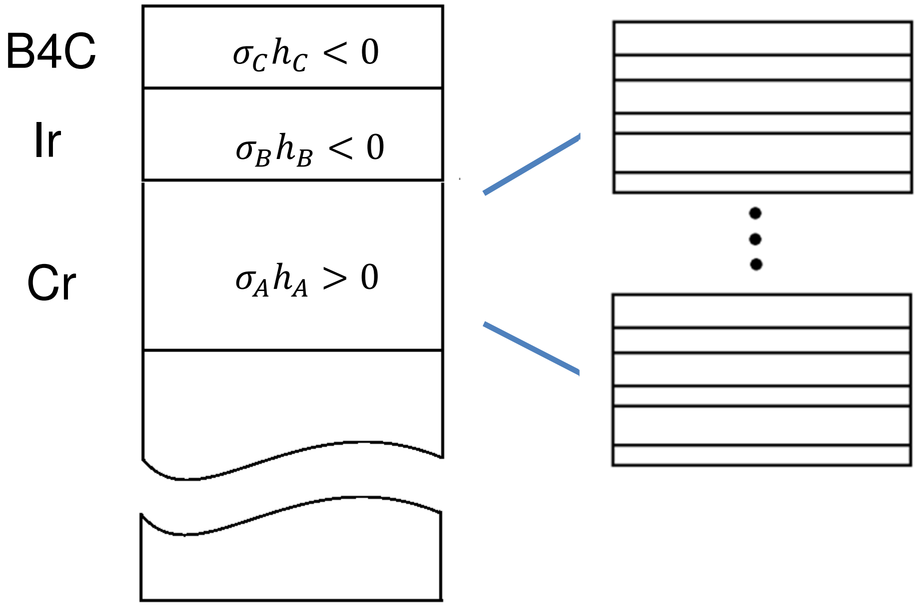
- Currently single layer films (i.e. Cr) with tensile stress are used as one technique to compensate the integrated stress in x-ray optical coatings to near-zero:

$$\left(\sigma h_f\right)_{Net} = \sigma_A h_A + \sigma_B h_B + (\sigma h)_{CTE} \approx 0$$

- The columnar microstructure of metal films in tension results in increasing surface roughness as the film thickness increases—thereby limiting the method’s applicability.
- The increased surface roughness can severely degrade the optical coating’s performance; particularly for high energy broadband multilayers.
- Multilayers interrupt the columnar growth so roughness doesn’t increase with film thickness (for Glass & Si)

Example:

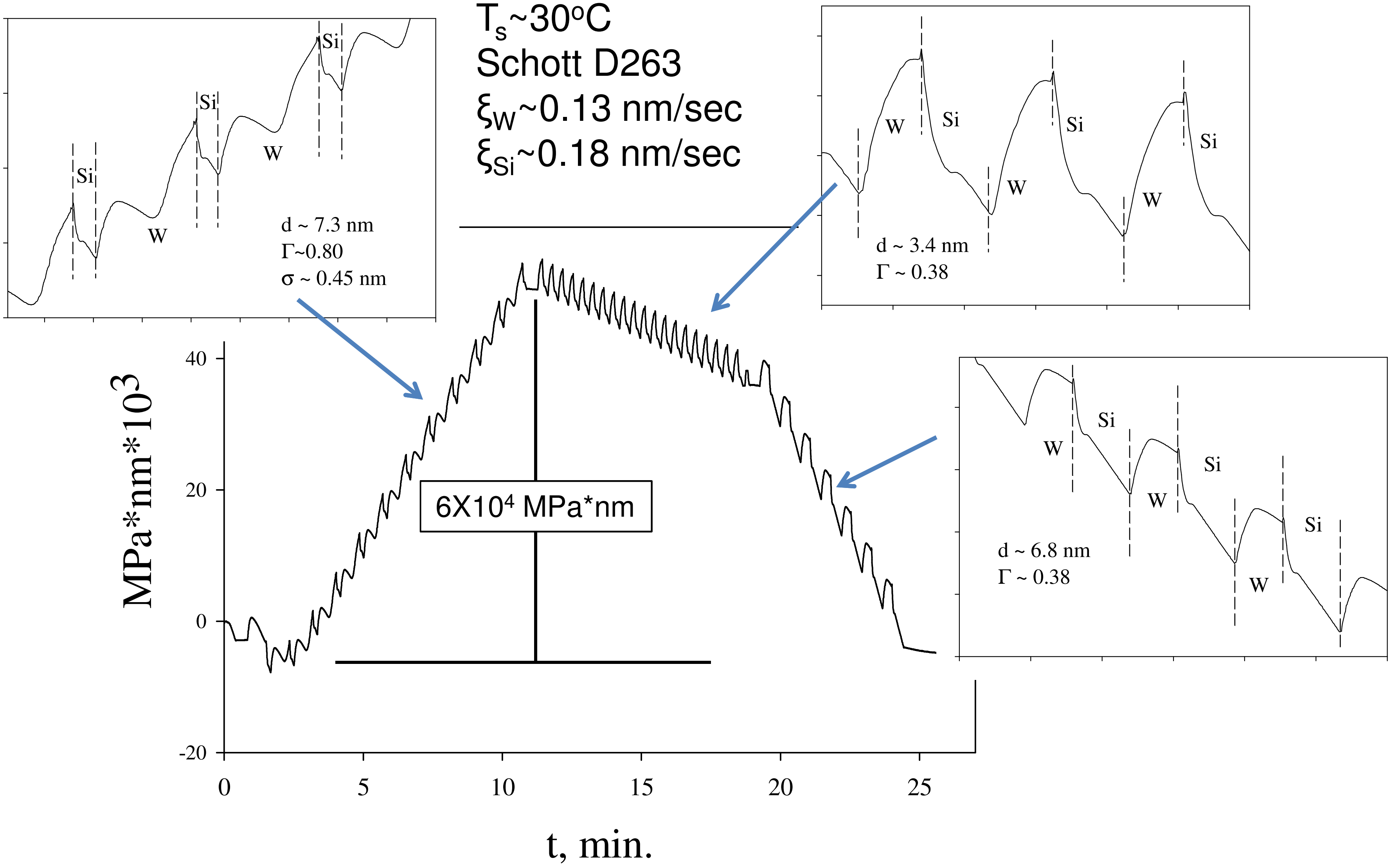
Stress compensating ML: Cr/B4C, Mo/B4C, …



Future work:
- Influence of substrate temperature and deposition rate.
- Impact to total deposition time.
- Optimization of layer thicknesses.
- Surface roughness characterization.
- Addition of N to B4C based ML’s to increase dep. rate and smooth interfaces.

In-situ stress in W/Si multilayers

T_s~30°C
Schott D263
ξ_W~0.13 nm/sec
ξ_{Si}~0.18 nm/sec



Conclusions

- We have introduced a novel method for the in-situ measurement of film stress using a fiber optic displacement sensor.
- The device is less complex than other current optical methods and easily implemented into an existing deposition system.
- The device's sensitivity is 0.009 N/m (9 MPa*nm) for a 100 µm thick glass substrate.
- This sensitivity is capable of detecting changes in stress due to small changes in deposition parameters such as argon process pressure (i.e. ±0.02 mTorr).
- The sensitivity can easily detect changes in the integrated stress in the individual layers of multilayer films of sub-nanometer thickness.
- The in-situ stress measured with the device is in good qualitative agreement with the known behavior of metals films (i.e. stress reversal, Volmer-Weber growth).
- We presented the influence of the material interfaces on the evolution of the film stress for several material pairs including: Mo/Si, Mo/B4C, W/Si, Ir/B4C,…
- We have proposed a new stress compensating method that utilizes multilayers
  - This method might be applicable to balance the stress in broadband multilayer that are more than a micron in total thickness.
  - More investigation is needed to study the impact to the total deposition time through optimization of the layer thicknesses