Stress in thin films

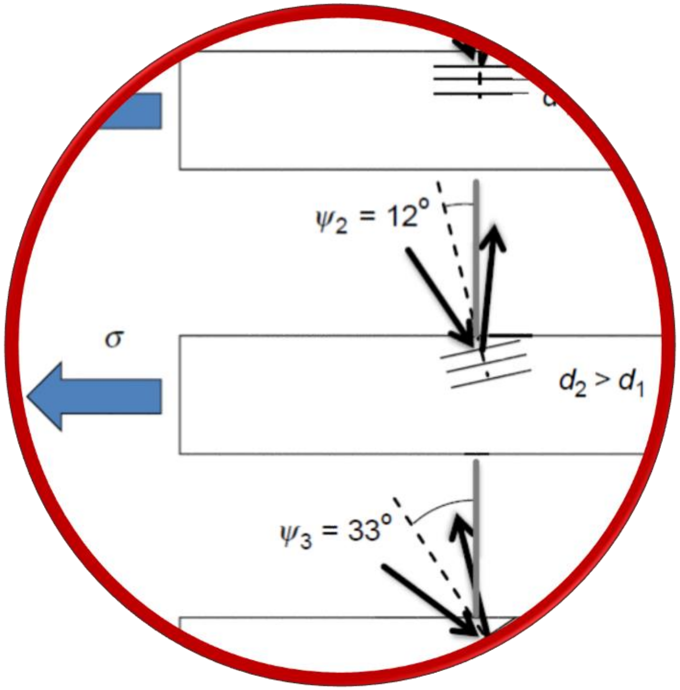

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Table of contents II

Importance of stresses

Strain energy release drives
- interfacial cracks and film fracture
- morphology evolution during film growth
- all type of microstructure changes

Strain engineering of physical properties

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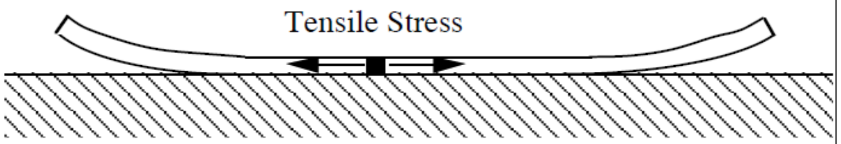
Importance of stresses

Thin Film Debonding

Thin Film Peeling

* Caused by Tensile Stresses

* Interfacial Strength is Important

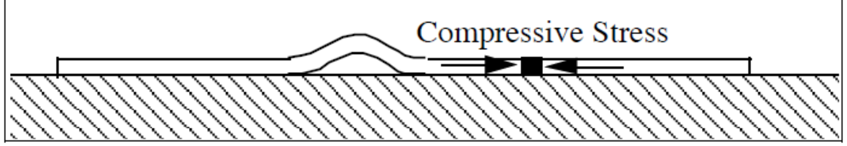


(for some geometries the curvatures also indicate tensile stress gradients in the film)

Thin Film Buckling

* Caused by Compressive Stresses

* Interfacial Strength is Important



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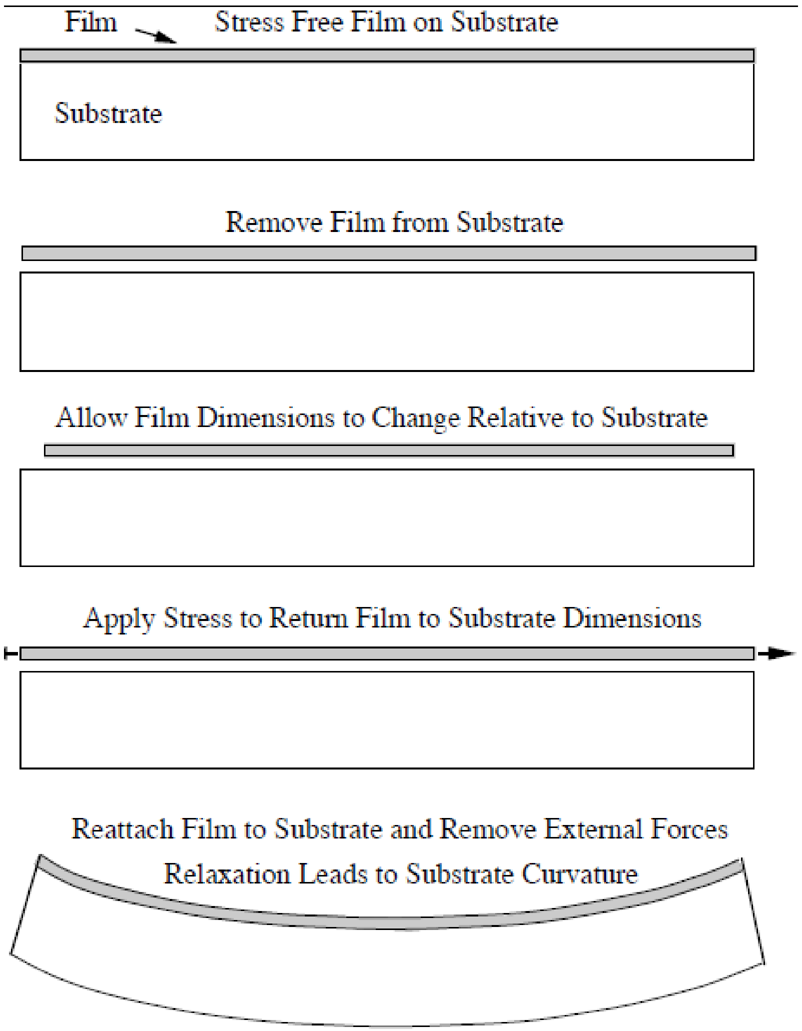
Substrate curvature



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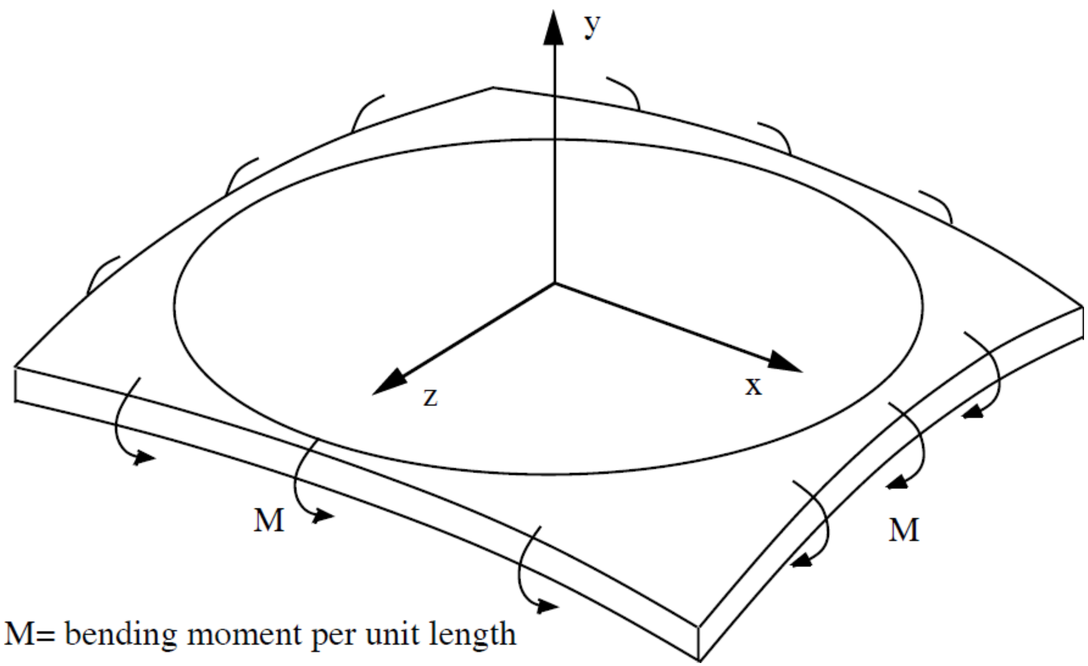
Bending of a plate (without film)

M = moment per unit length applied along edges of plate.

Biaxial Bending of a Thin Plate



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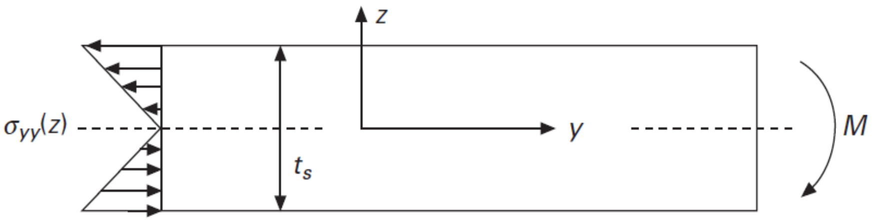
Bending of a plate (without film)

We now develop a relationship **between the curvature** and involved **strains**.

the stresses vary linearly through the thickness of the plate, such that the in-plane stresses are expressed as $\sigma_{xx} = \sigma_{yy} = c_1 z$, and where c_1 is a constant determined by the bending moment (per unit length along the edge)

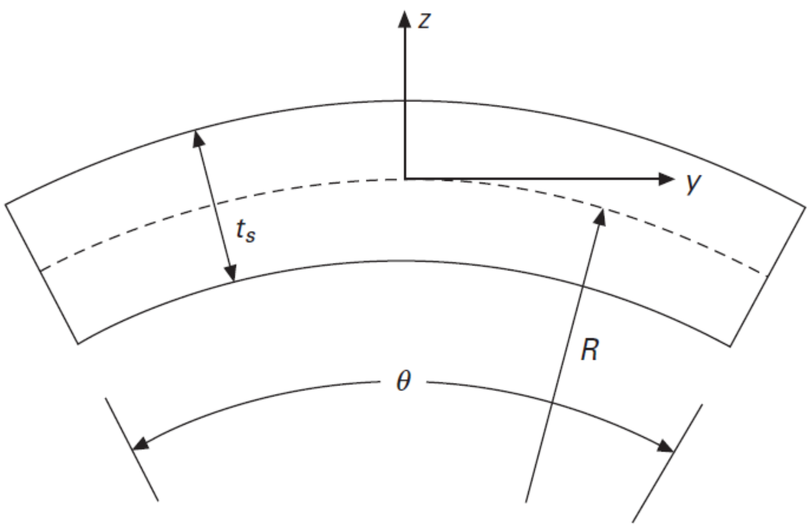


$$M = \int_{-t_s/2}^{t_s/2} \sigma_{yy} z dz = \int_{-t_s/2}^{t_s/2} c_1 z^2 dz = \frac{c_1 t_s^3}{12}$$

Solving for c_1

$$\sigma_{xx} = \sigma_{yy} = \frac{12M}{t_s^3} z,$$

The biaxial bending stress in the substrate. The bending causes the substrate to curve and from geometry



$$\varepsilon_{yy}(z) = \frac{(R+z)\,\theta - R\theta}{R\theta} = \frac{z}{R} = -\kappa z$$

where κ is the resulting curvature of the substrate. We note that the negative curvature shown in the figure results from the positive bending strain for z > 0.

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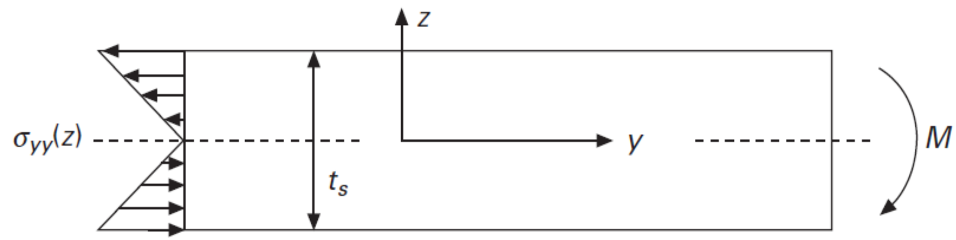
Bending of a plate (without film)

We now develop a relationship between the **curvature** and the imposed **bending moment**.



We have seen that the inplane, biaxial elastic strains in the plate can be used to find the curvature:

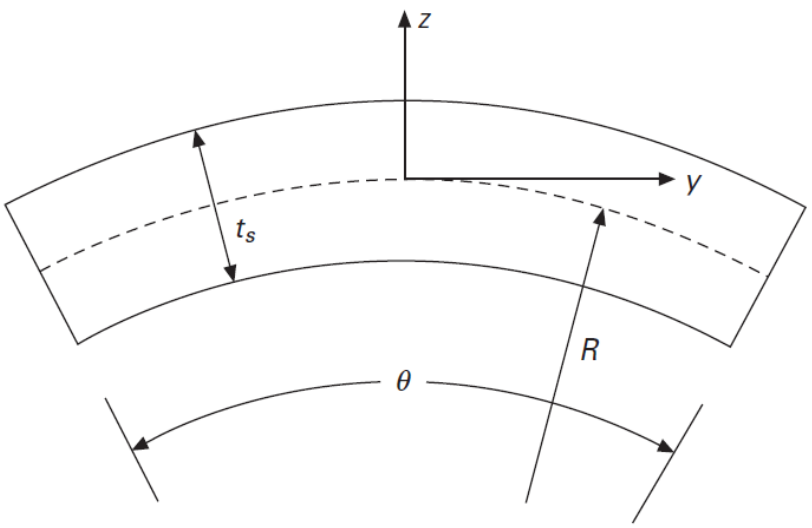
$\kappa = -\varepsilon_{yy}(z)/z = -\varepsilon_{xx}(z)/z.$

Using Hooke's law for an elastically isotropic solid we can express the strain as

$$\varepsilon_{yy} = \frac{1}{E_s}\left(\sigma_{yy} - \nu_s\left(\sigma_{xx} + \sigma_{zz}\right)\right)$$

where E_s is Young's modulus, ν_s is Poisson's ratio, both of the plate (or substrate), $\sigma_{yy} = \sigma_{xx}$, are the in-plane biaxial stresses in the plate and $\sigma_{zz} = 0$. Using this

$$\kappa = -\frac{(1-\nu_s)}{E_s}\sigma_{yy}/z \qquad \text{or} \qquad \kappa = -\frac{(1-\nu_s)}{E_s}\frac{12M}{t_s^3}$$



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Stoney equation

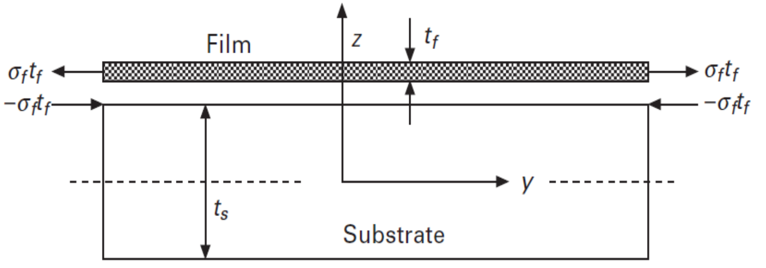
We consider now a **thin film** on a **much thicker substrate** initially in a stress free state.

The forces exerted onto the substrate by the film cause it to bend.

If the biaxial stress in the film is σ_f,

then an edge force (per unit length), $\sigma_f\ t_f$,
where t_f is the thickness of the film,
must be exerted onto the film, as shown on the right.

That edge force, in turn, exerts an equal and opposite edge force (per unit length) on the substrate at the top corner of the substrate.



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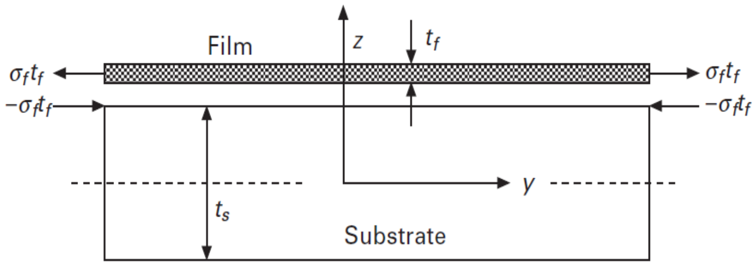
Stoney equation

The result is that a bending moment,

$M = -\sigma_f\, t_f\, (t_s/2)$,

is imposed onto the substrate by the film and that causes the substrate to bend.



We neglect the film thickness and calculate the plate curvature

$$\kappa = -\frac{(1-\nu_s)}{E_s}\frac{12M}{t_s^3} \quad \text{or} \quad \kappa = \left(\frac{1-\nu_s}{E_s}\right)\frac{6\sigma_f t_f}{t_s^2}$$

With this relation we see that the **biaxial stress in the film** can be found by **measuring the curvature**. To be more precise we take into account the curvature the substrate might had before film deposition:

$$\sigma_f = \left(\frac{E_s}{1-\nu_s}\right)\frac{t_s^2}{6t_f}(\kappa - \kappa_o) = \left(\frac{E}{1-\nu}\right)_s \frac{t_s^2}{6t_f}\Delta\kappa$$

The famous **Stoney equation**. The term $E_s/(1 - \nu_s)$ is called the biaxial elastic modulus of the substrate. We see that the stress in the film can be determined from the substrate curvature.

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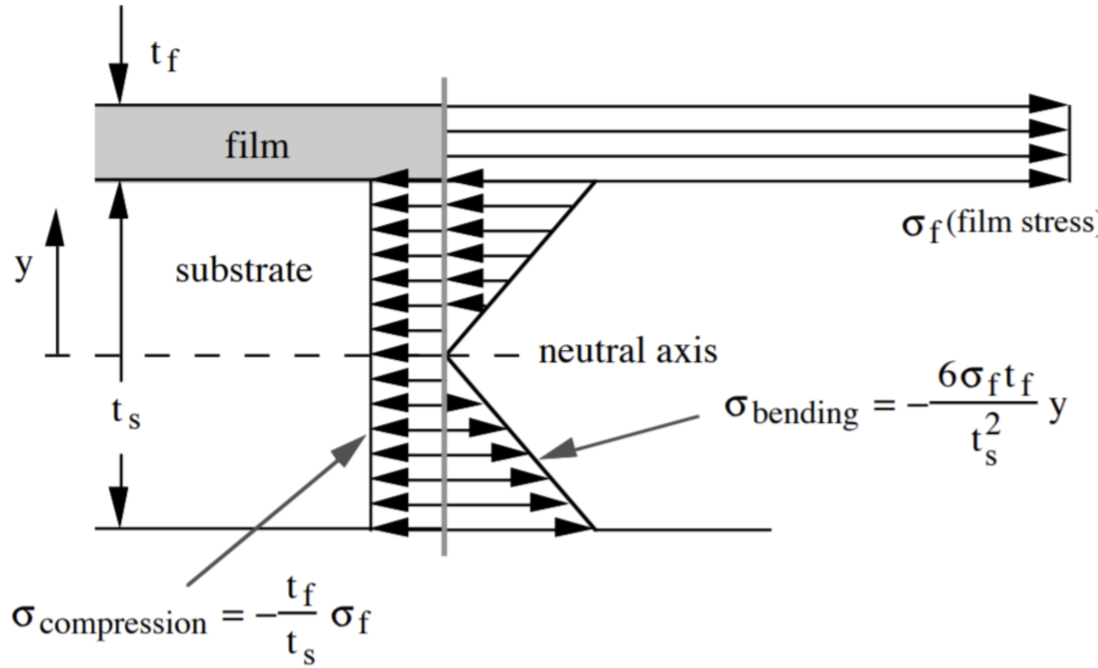
The result is independent of the film properties

Stresses in multilayer film and substrate

The substrate stresses are about **100 times smaller than the film stresses** for typical ratios of film/substrate thickness

For **multiple thin films** that are all very thin compared to the substrate, the biaxial stress in each film causes the substrate to curve according to the Stoney equation, as if the other films were not present.

Under these conditions one might determine **the stresses in all of the films** by starting with the measured curvature of the **bare substrate** and then determining the curvature **after each of the films is deposited**.



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Young's Modulus

If you try to measure the Young's moduls of a thin film one has to take into account grain size, porosity, anisotropy, creep, anelasticity, measurement uncertainties and load case to understand the results.

grain size

Consider a material consisting of continuum cubic grains with side d having boundaries of width δ.
The ratio of grain boundary to grain interior volume is

$3\delta/d$.

If the grain interiors have modulus E_{grain}, and the boundaries have a modulus of zero (an extreme change in bonding), then using an isostrain model (i.e., the same strain in grains and boundaries), the composite modulus of the material is:

$$E = (1-3\delta/d)E_{grain}.$$

For δ=0.2 nm (big!), we would need a grain size of d 6 nm (small!) to achieve a modulus reduction of only 10%.

grain size

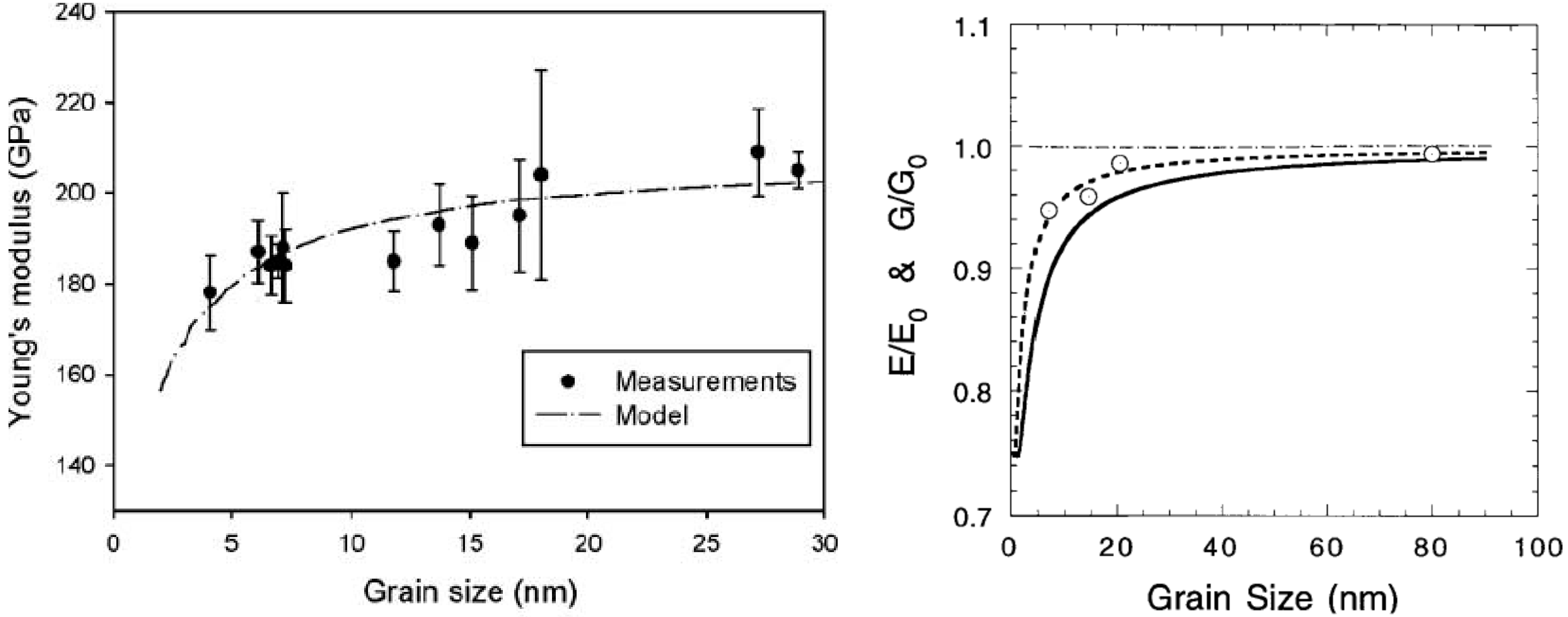


Figure 1-4 (a) Young's Modulus of electrodeposited nanocrystalline Ni and NiP alloys as a function of grain size [79]; (b) Young's and shear moduli of nanocrystalline Fe produced by mechanical attrition expressed as ratios of the conventionally accepted, coarse-grained bulk values. The dashed and solid curves correspond to a grain boundary thickness of 0.5 and 1nm, respectively. The open circles show the E/Eo values of nanocrystalline Fe versus grain size [76].

[76] T.D. Shen, C.C. Koch, T.Y. Tsui, G.M. Pharr, J. Mater. Res., 10 (1995) 2892.
[79] Y. Zhou, U. Erb, K.T. Aust, G. Palumbo, Z. Metallkd., 94, 10 (2003) 1.

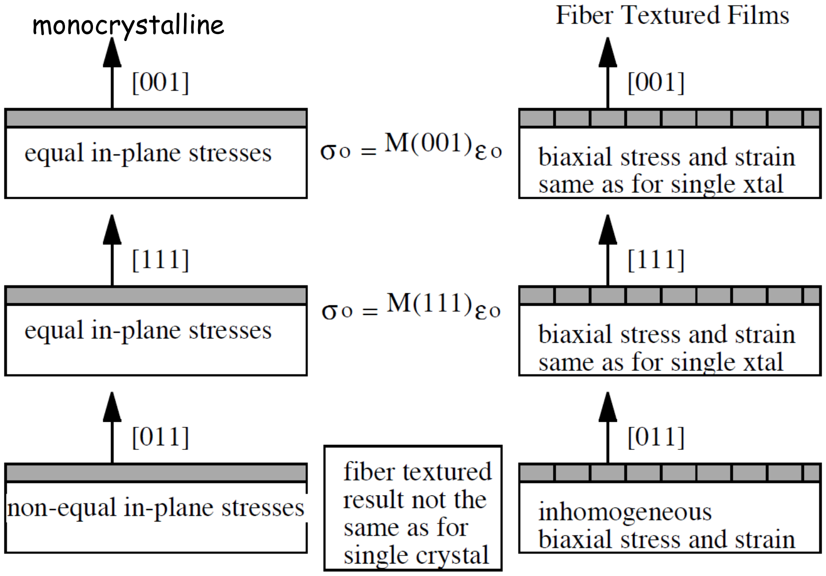
Textured films

The isotropic elastic expressions are **valid** for many thin film/substrate systems, even though the materials involved are **elastically anisotropic**.

The reason is that only the **biaxial elastic moduli enter these relations** and these key elastic properties are isotropic for many epitaxial or strongly textured films.

The elastic properties of cubic metal crystals are expressed in terms of the stiffnesses, (c11, c12, c44) (or compliances (s11, s12, s44)) which describe the elastic properties in the crystal coordinate system.

For the common **<001> and <111> cubic textures we can use a modified biaxial modulus**:



$$B_{\{111\}} = \frac{6c_{44}(c_{11} + 2c_{12})}{c_{11} + 2c_{12} + 4c_{44}} \qquad B_{\{001\}} = c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}$$

The {011} plane for cubic solids is not elastically isotropic and the inplane stresses are different in different directions, which makes the analysis more complicated.

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Textured films

	c_{11} (GPa)	c_{12} (GPa)	c_{44} (GPa)	a_o (nm)	α $10^{-6}K^{-1}$	$B_{\{001\}}$ (GPa)	$B_{\{111\}}$ (GPa)
Ag	120	91	46	0.4090	18	73	172
Al	113	67	28	0.4050	23	101	116
Au	186	157	42	0.4078	14	78	189
Cu	168	121	75	0.3620	16.5	115	260
Ni	246	147	124	0.3520	13.4	217	388
Pd	227	176	72	0.3890	11.8	130	288
Pt	347	251	77	0.3924	9	235	339
Cr	352	73	101	0.2885	6	395	335
Fe	237	141	116	0.2870	11	210	367
Mo	460	179	109	0.3147	4.8	500	427
Nb	246	134	29	0.3330	7.3	234	142
Ta	265	159	83	0.3303	6.3	233	317
V	228	119	43	0.3028	8.4	223	188
W	500	198	151	0.3160	4.5	541	541
GaAs	118	53	59	0.5653	5.4	123	172
Ge	129	48	67	0.5640	5.6	141	183
Si	166	64	80	0.5431	2.6	181	230
MgO	296	95	154	0.4212	8	330	407

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porosity

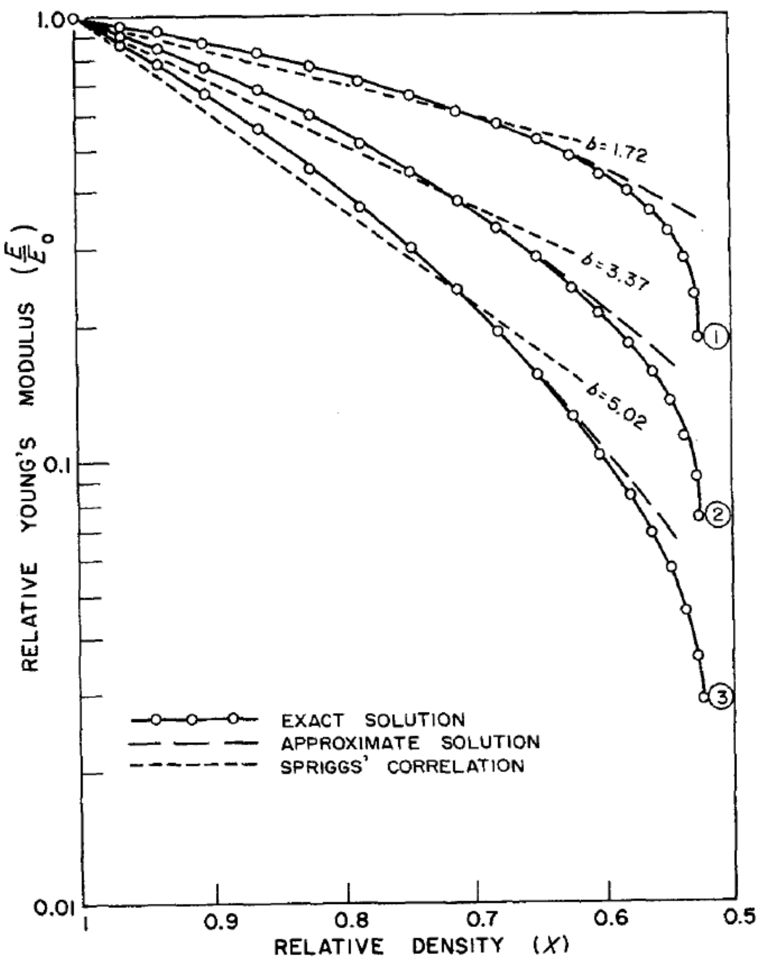


Figure 3 Young's modulus of porous materials. Solid curves are the theoretical curves, broken curves are the approximate solutions and the dotted lines are the Spriggs' correlation lines.

Three various porosity ranges can be usually identified, e.g., Danninger *et al*. [8] observed for sintered iron the following porosity ranges:

1. porosity·3%: fully isolated pores of nearly spherical or elliptical shape
2. porosity ¸20%: fully interconnected pores of complex shape
3. porosity between 3% and 20%: both isolated and interconnected pores are present in various amounts.

H. DANNINGER, G. JANGG, B. WEISS and R. STICKLER, *pmi* **25** (1993) 170 and 219.

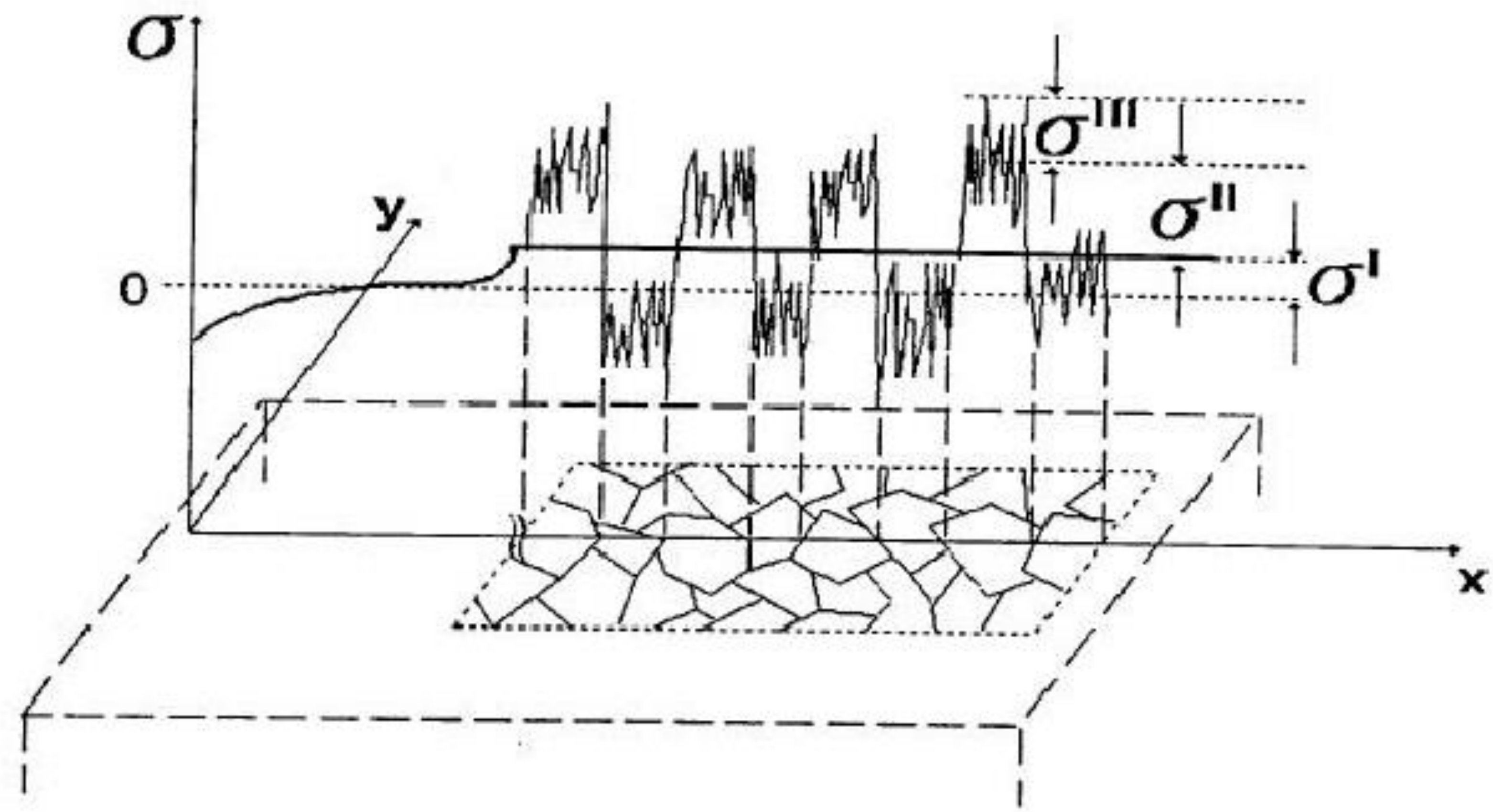
JOURNAL OF MATERIALS SCIENCE 19 (1984) 801–808

Young's modulus of porous materials

Part 1 *Theoretical derivation of modulus–porosity correlation*

JAMES C. WANG*
State University of New York, Stony Brook, New York 11794, USA

residual stress



substrate curvature methods

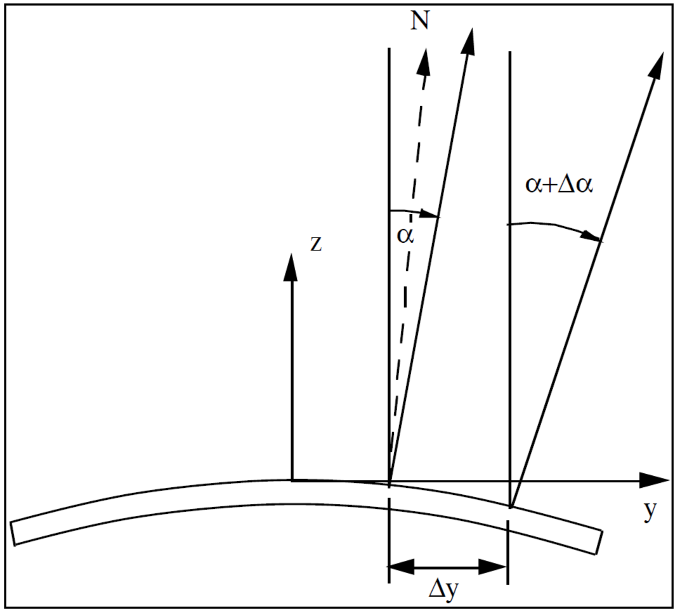
The **most popular technique** for measuring thin film stress is based on **measurements of the curvature** of the substrate on which the film is deposited.

As shown earlier the stress in the film is given by

$$\sigma_f = \left(\frac{E_s}{1-\nu_s}\right)\frac{t_s^2}{6t_f}(\kappa - \kappa_o) = \left(\frac{E}{1-\nu}\right)_s \frac{t_s^2}{6t_f}\Delta\kappa$$

where $\Delta\kappa$ is the curvature change induced by the stress in the film (**Stoney equation**)

In most systems, the curvature (or radius of curvature) is measured by **scanning a laser beam across the wafer (or substrate) and deflecting the position of the reflected beam.**



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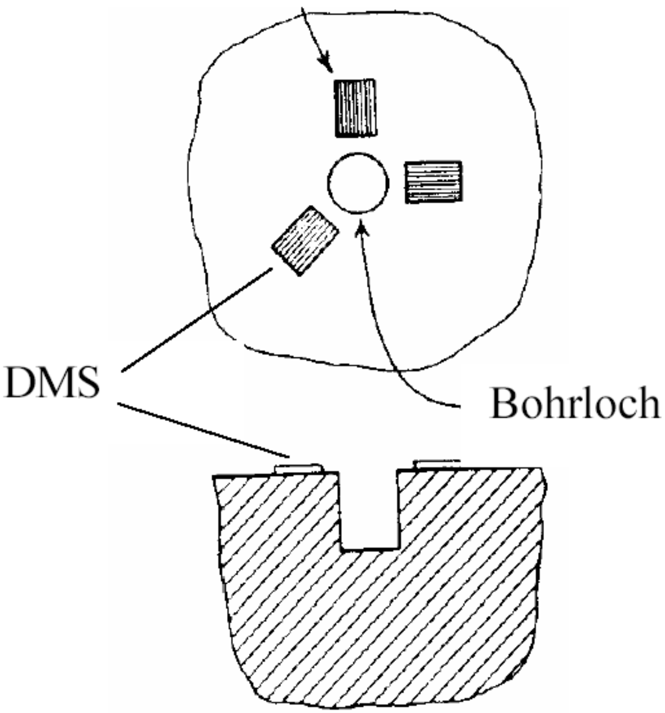
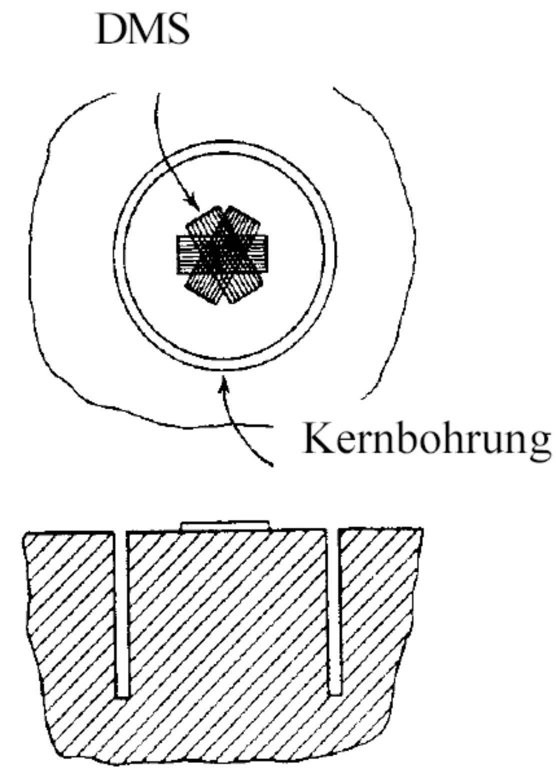
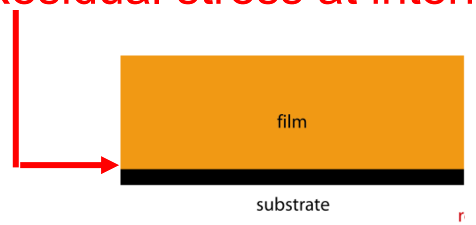
hole drilling method

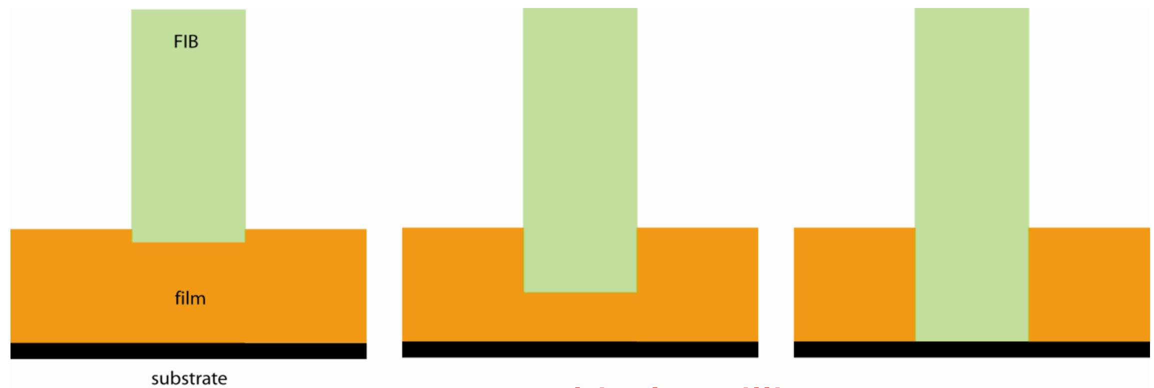




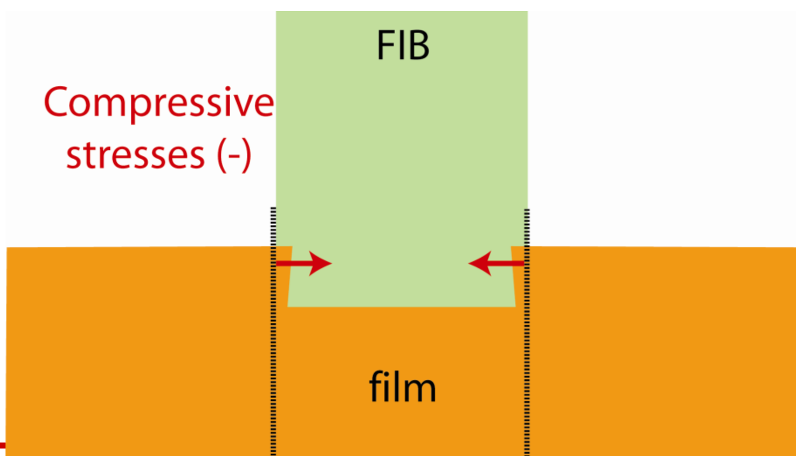
- Scan with AFM before & after milling with FIB
- Digital Image Correlation (DIC) used on both AFM and SEM images to measure stress relaxation wrt marked pattern

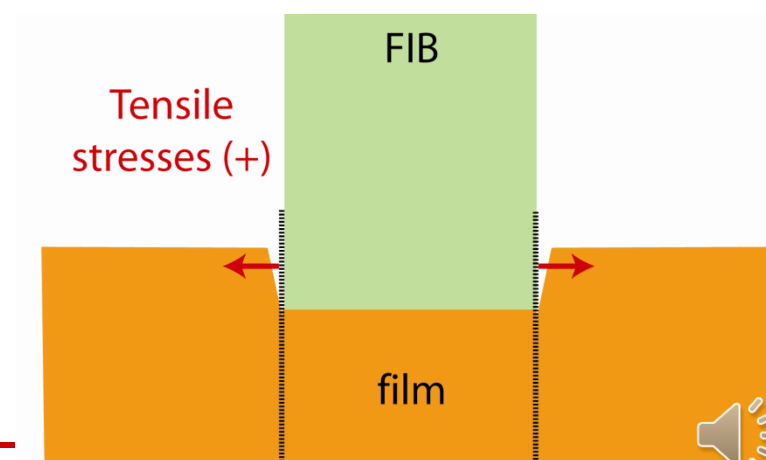
Residual stress at interface





Incremental hole milling

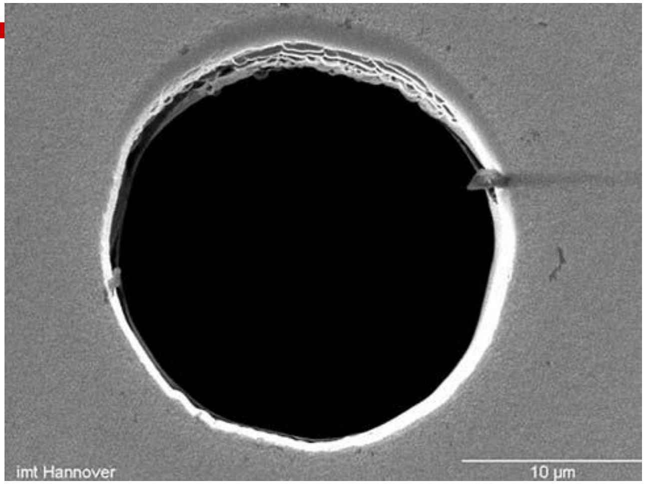




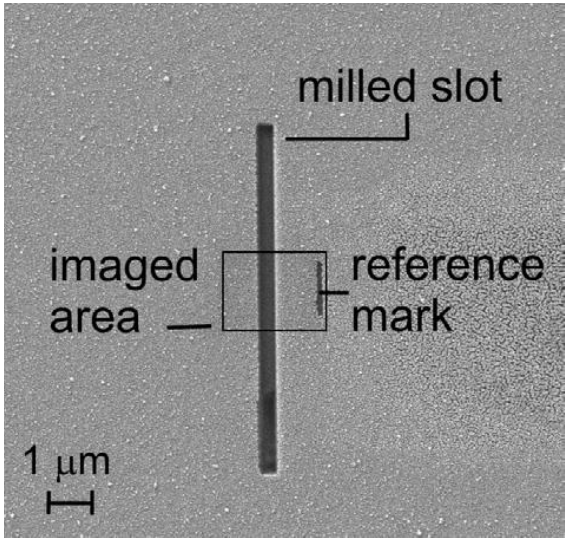
Surface will relax depending on sign of stress

Residual Stress: Milling Geometries

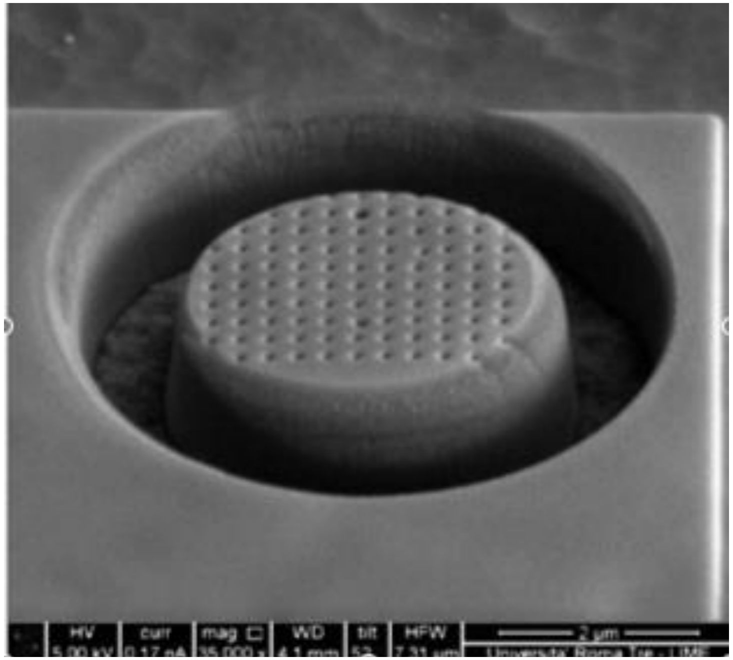
- Incremental slot, hole or annular milling
- Monitor surface relaxation with depth
- Fiducial markers used as reference points during imaging and analysis
- Uniaxial and Biaxial stress distributions of site-specific features measurable



Gerdes & Gatzen, Microsyst. Technol., **15** (2009)

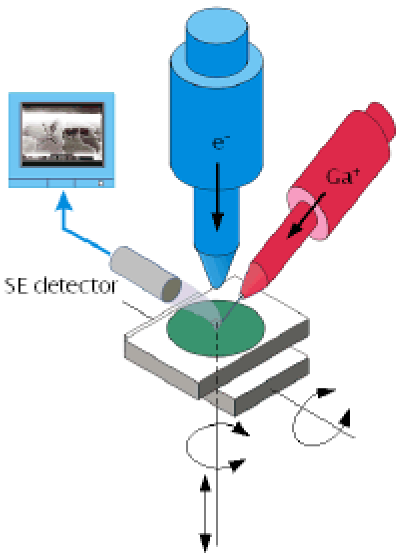


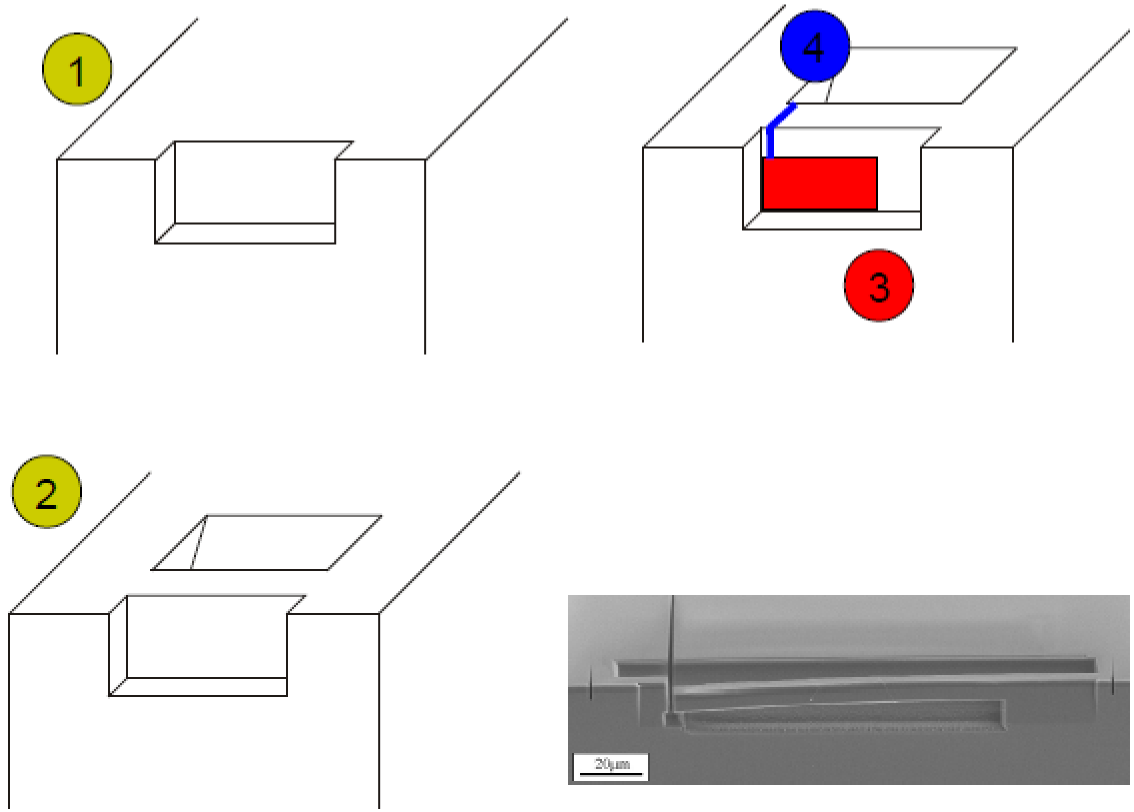
Sabaté, *et al*, Nanotechnology., **17** (2006)



Korsunsky, *et al*, Mater. Lett., **63** (2009)

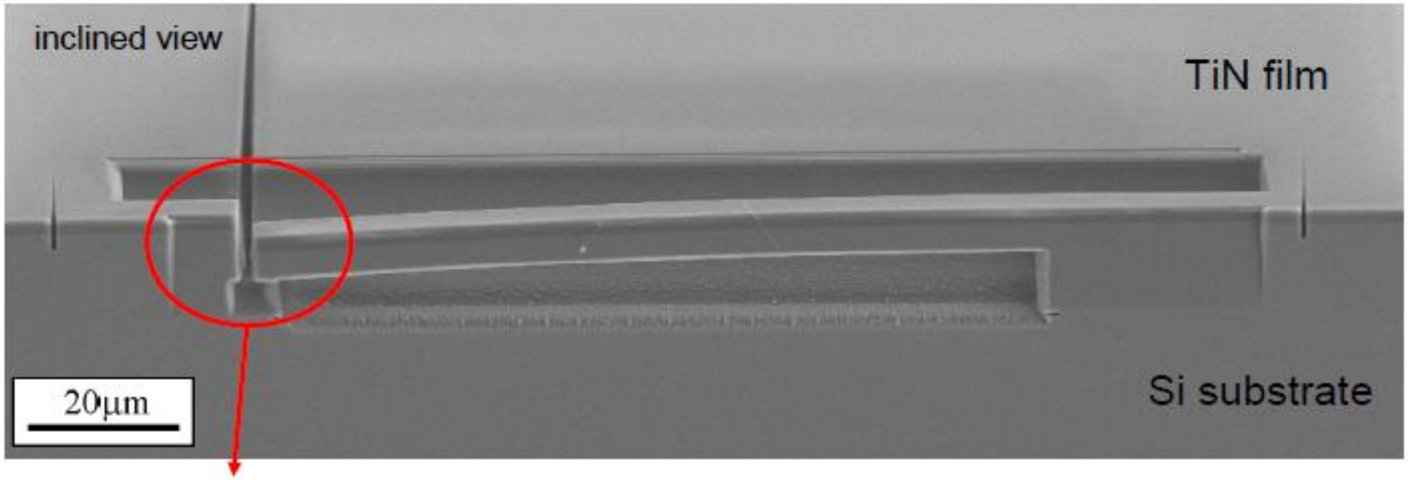
Cantilever beam methods

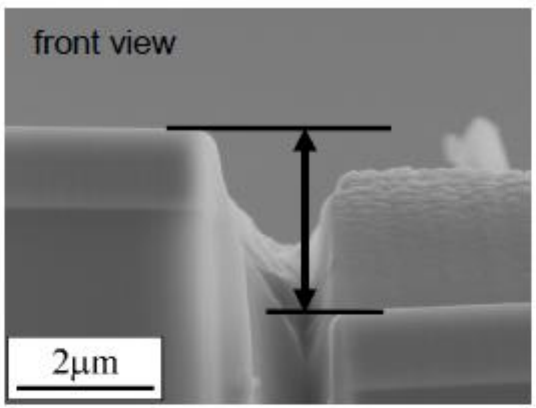




Cantilever beam methods

- fabrication of a micro cantilever by means of a FIB workstation

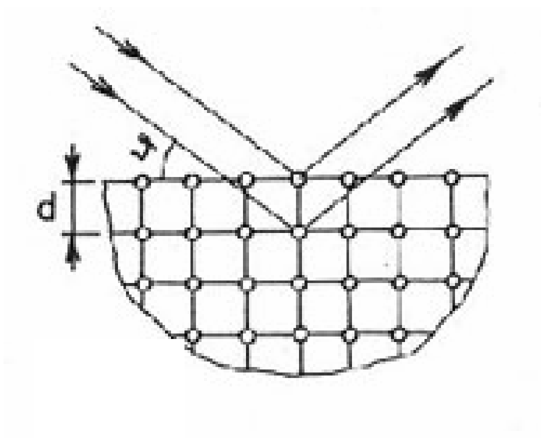




- deflection depends on the residual stresses

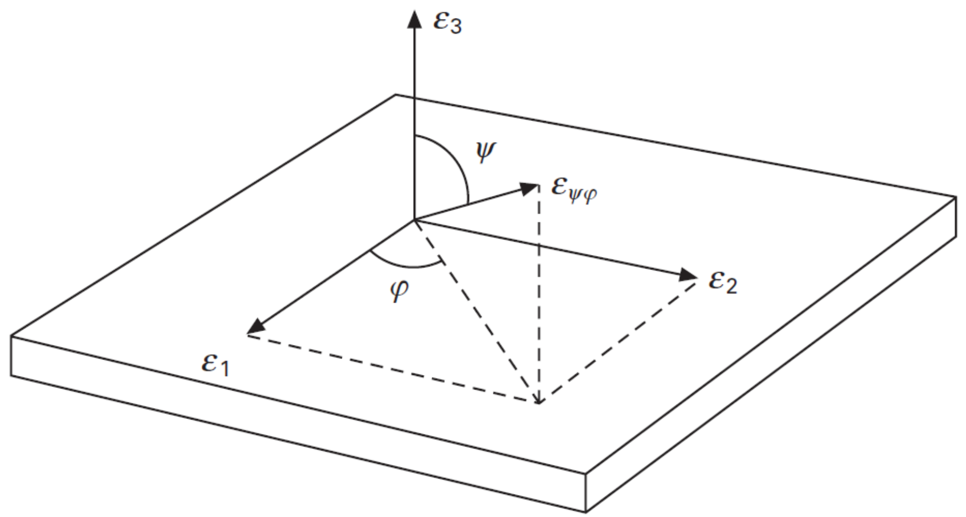
X-ray diffraction

Bragg equation



$$2d \sin \vartheta = n\lambda$$

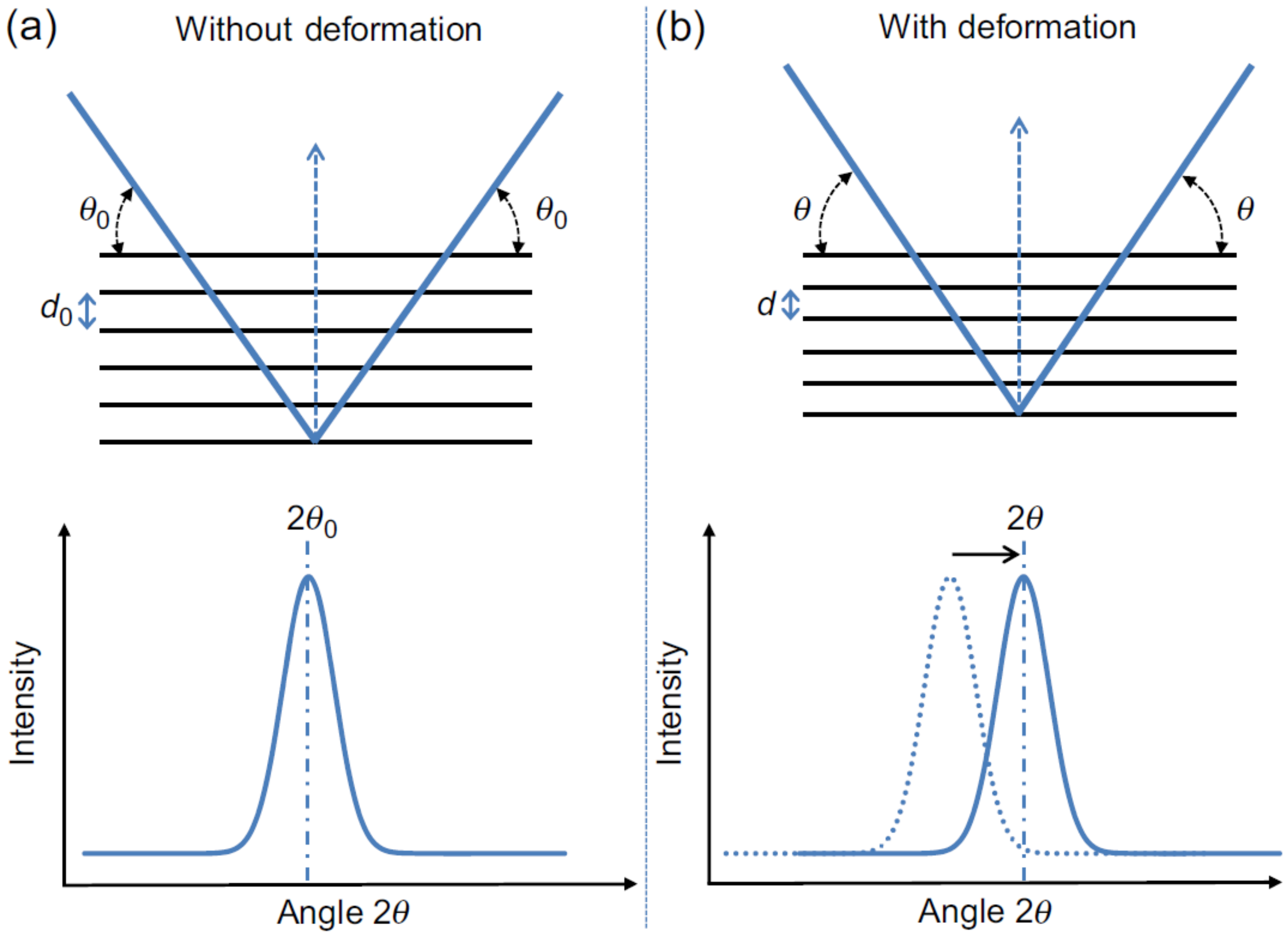
$$\varepsilon_{\varphi\Psi} = \frac{\Delta d}{d}$$



1: Normal to sample
2: Normal to lattice plane (measurement direction)

Any state of strain can be described in terms of the principal strains, the axial strains in the principal coordinate system. In this coordinate system all of the shear stress components are zero. The thin film geometry requires the principal coordinates to lie parallel and perpendicular to the plane of the film. In the coordinate system shown the shear strains ε_{13} and ε_{23} must be zero

Peak shift due to strain



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X-ray diffraction

Thus the axial strain, $\varepsilon_{\psi\varphi}$, in any arbitrary direction in the film, $\psi\varphi$ the strain that could be measured by X-ray diffraction, can be related to the principal strains through a coordinate transformation as follows:

$$\varepsilon_{\psi\varphi} = \varepsilon_1 \sin^2\psi \cos^2\varphi + \varepsilon_2 \sin^2\psi \sin^2\varphi + \varepsilon_3 \cos^2\psi$$

We assume the stress state to be biaxial, which reduces to

$$\varepsilon_{\psi} = \varepsilon_1 \sin^2\psi + \varepsilon_3 \cos^2\psi$$

Under these conditions the measured strain depends only on the angle between the film normal and the scattering vector. Using Hook's law

$$\varepsilon_1 = \varepsilon_2 = \frac{1}{E}\left(\sigma_1 - \nu(\sigma_2 + \sigma_3)\right)$$

$$\varepsilon_3 = \frac{1}{E}\left(\sigma_3 - \nu(\sigma_1 + \sigma_2)\right)$$

Leads to $\varepsilon_1 = \varepsilon_2 = \frac{1-\nu}{2\nu}\varepsilon_3$ as $\sigma_1=\sigma_2$ and $\sigma_3=0$

We see from this that the strains and biaxial stress in the film can be determined by measuring the out-of-plane strain, ε_3, by X-ray diffraction.

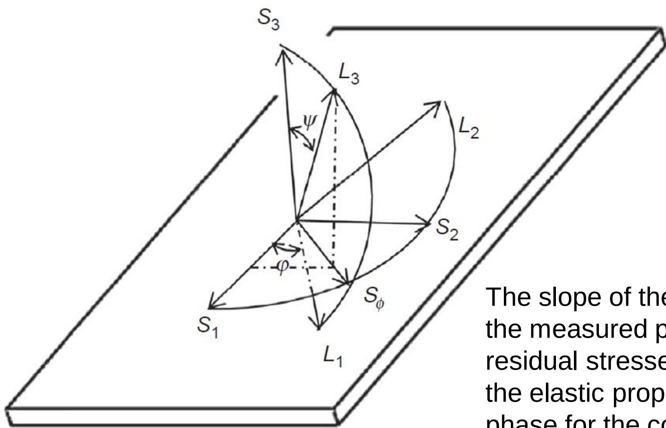
$$\frac{d_{hkl} - d^o_{hkl}}{d^o_{hkl}} = \varepsilon_\psi = \frac{(1+\nu)}{E}\sigma \sin^2\psi - \frac{2\nu}{E}\sigma$$

This relation provides the basis for the so-called 'sin$^2\psi$' method for measuring stresses $\sigma_1=\sigma_2=\sigma$ in thin films. For $\psi=0$ we see

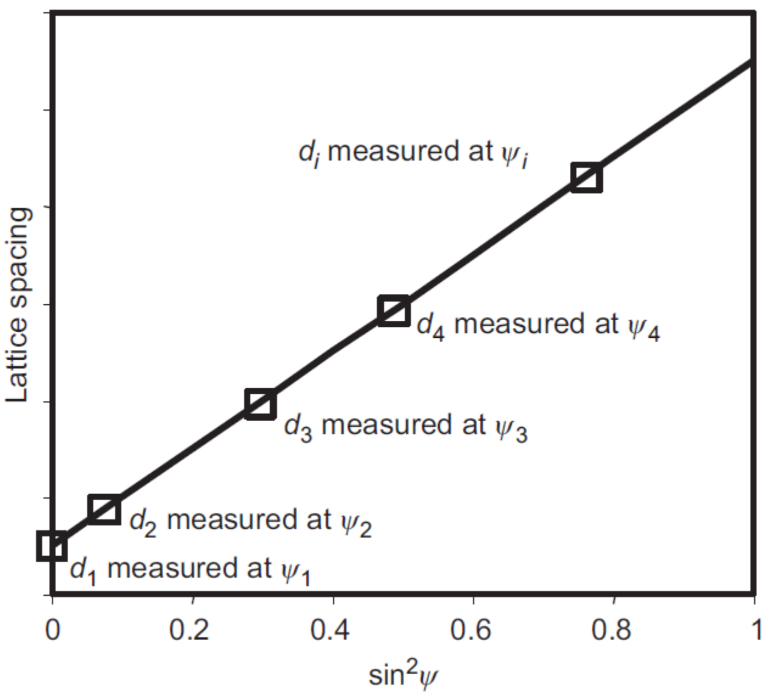
$$\sigma = -\frac{E}{2\nu}\varepsilon_3$$

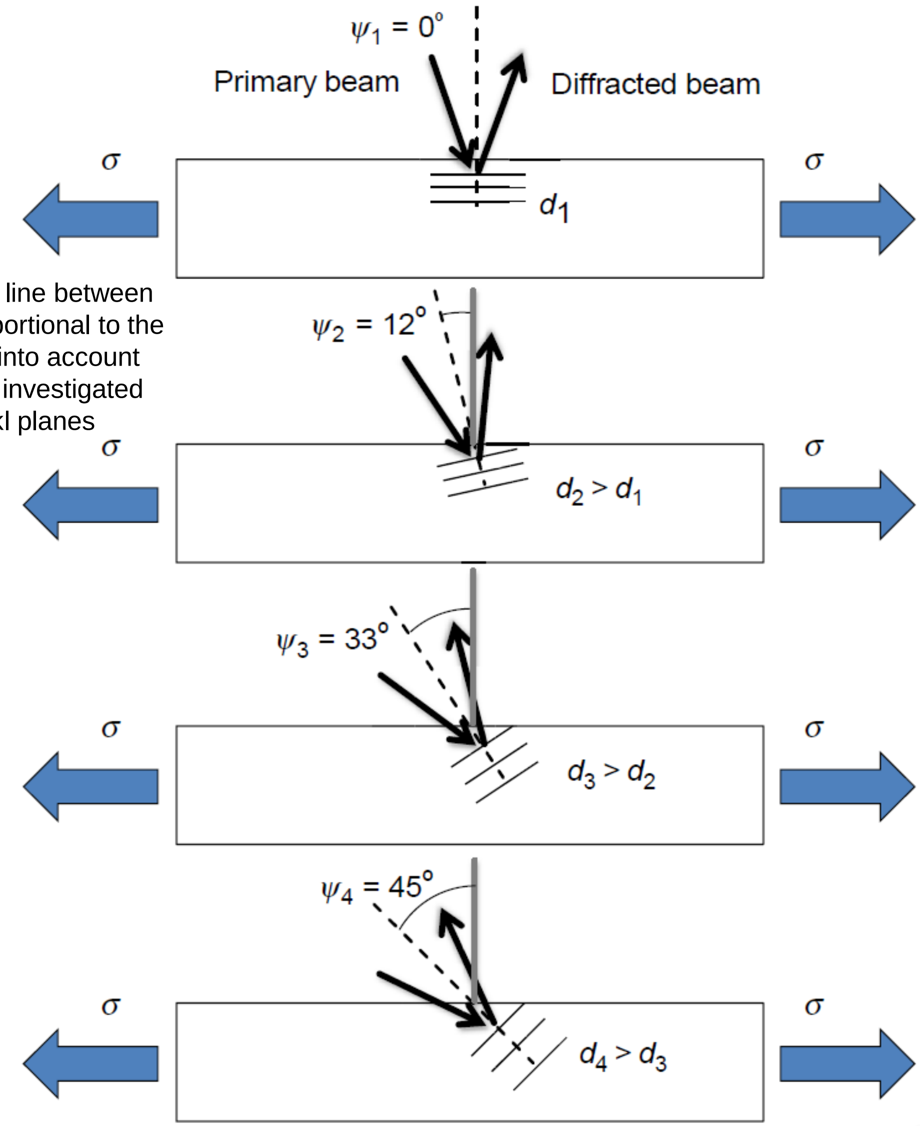
Thus, measurement of the out of plane strain by X-ray diffraction gives the biaxial stress in the plane

Stress with XRD: $\sin^2 \Psi$ Method



The slope of the regression line between the measured points is proportional to the residual stresses by taking into account the elastic properties of the investigated phase for the considered hkl planes





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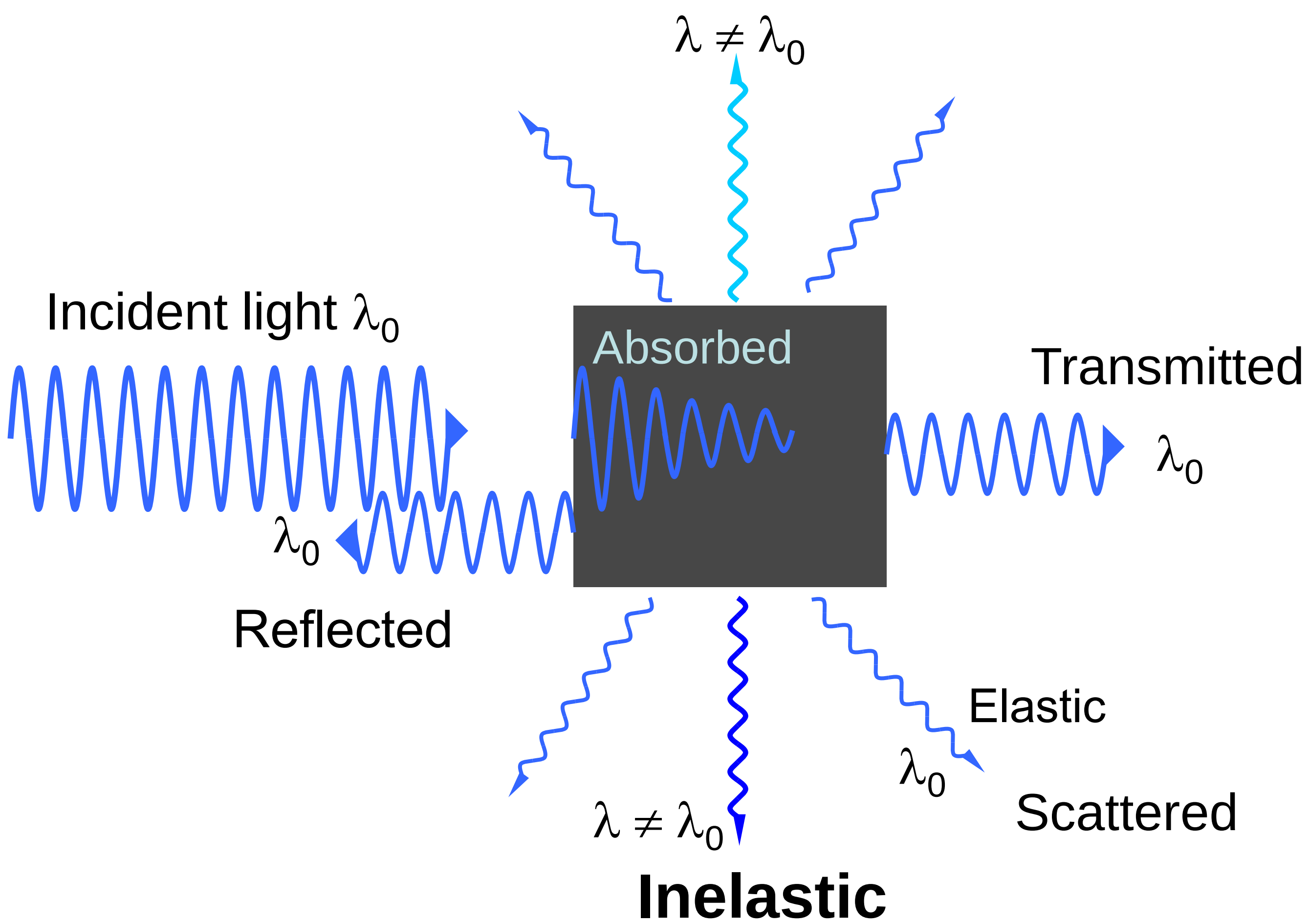
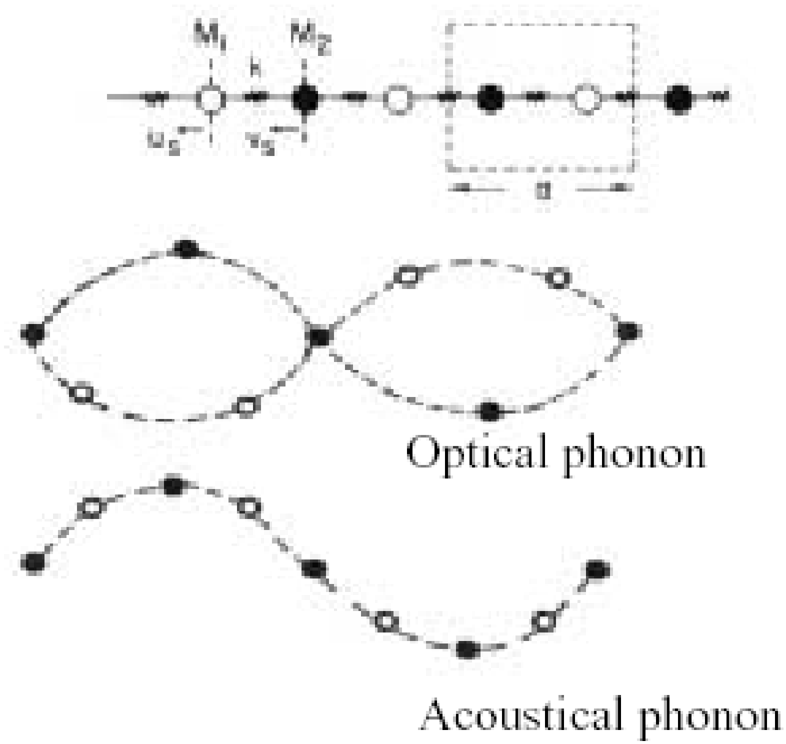
Raman spectroscopy: Light scattering



Raman scattering: **Inelastic** light scattering

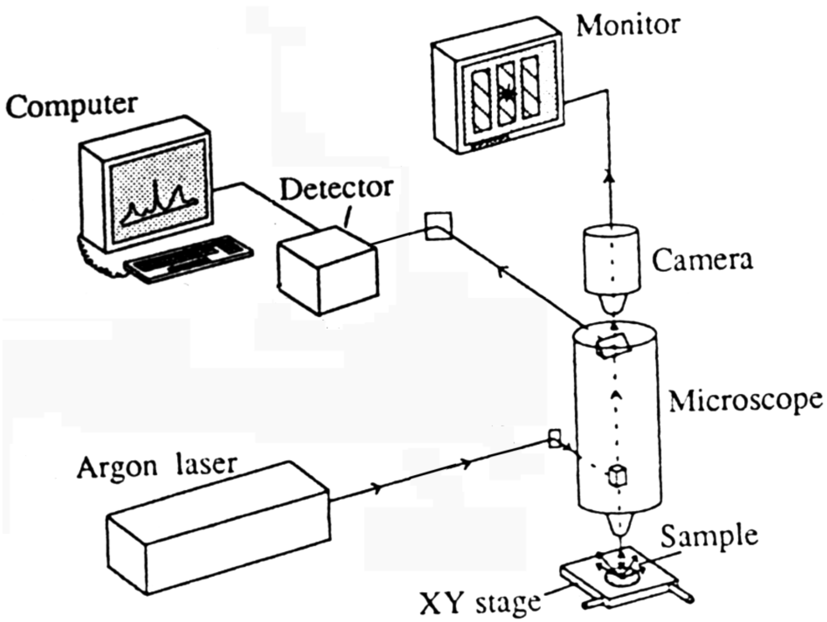
Residual stresses via Raman spectroscopy

optical phonons

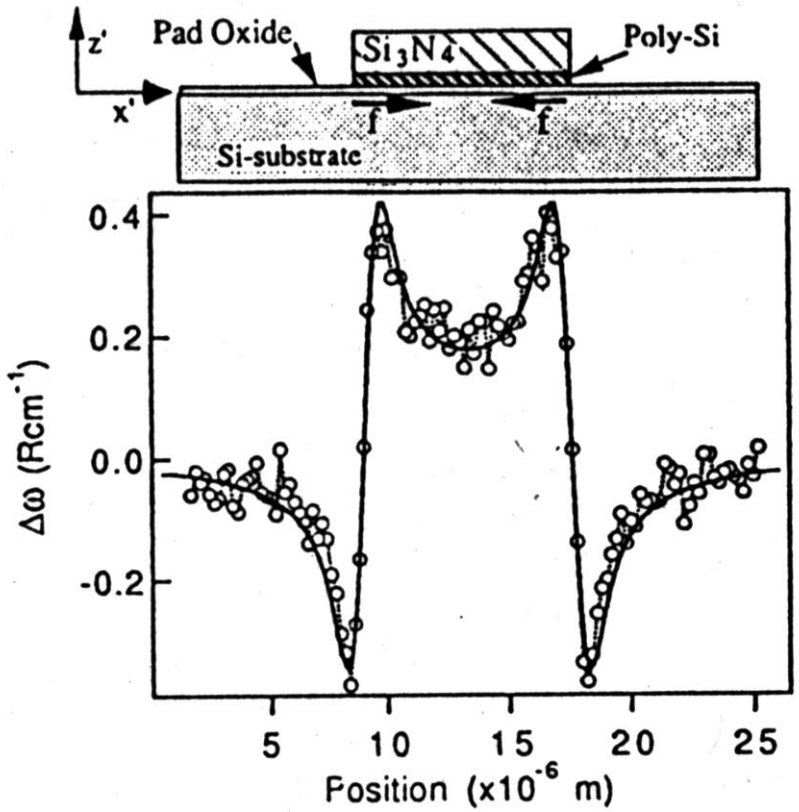


Micro-Raman sprectroscopy

instrument

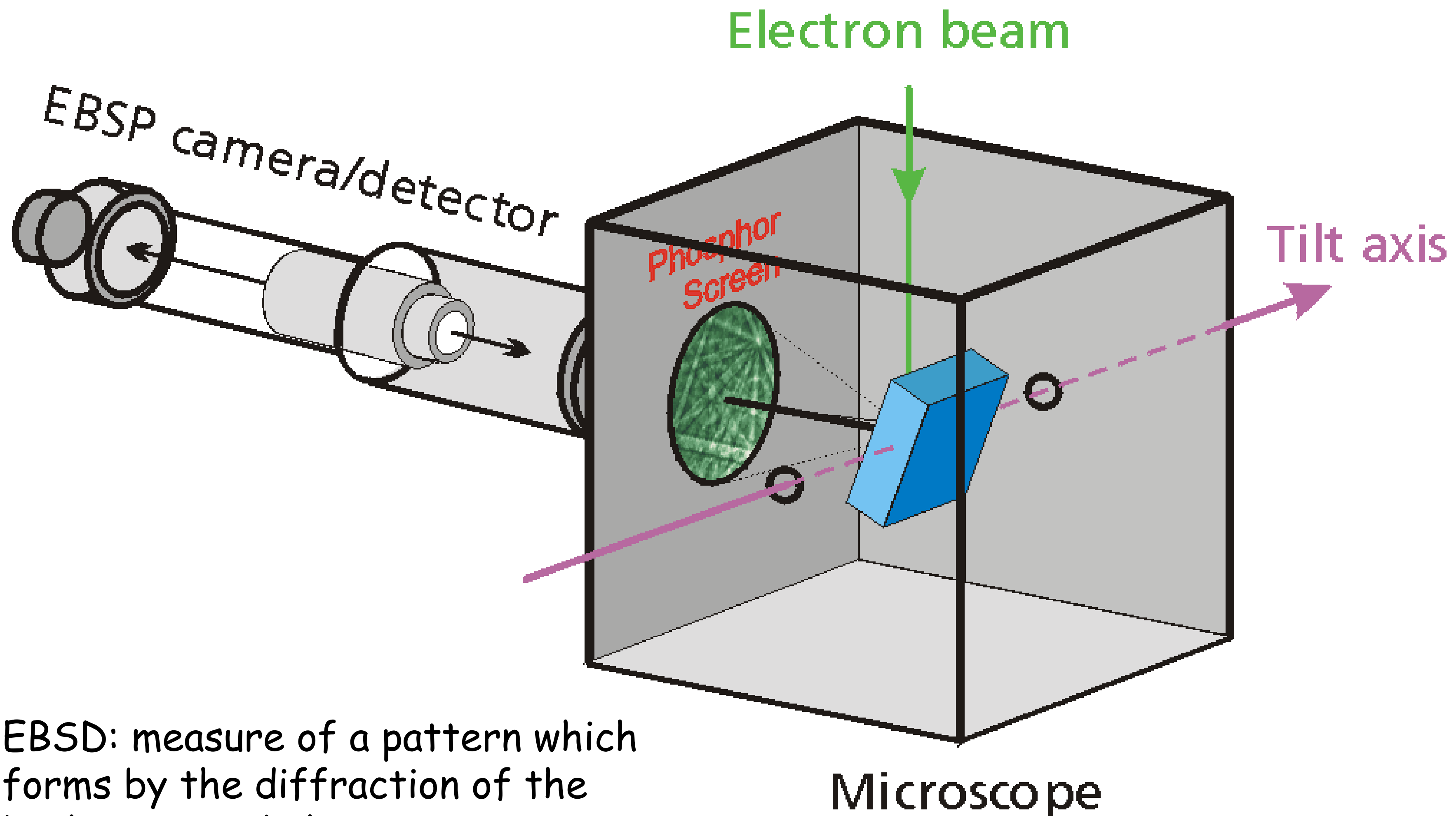


example



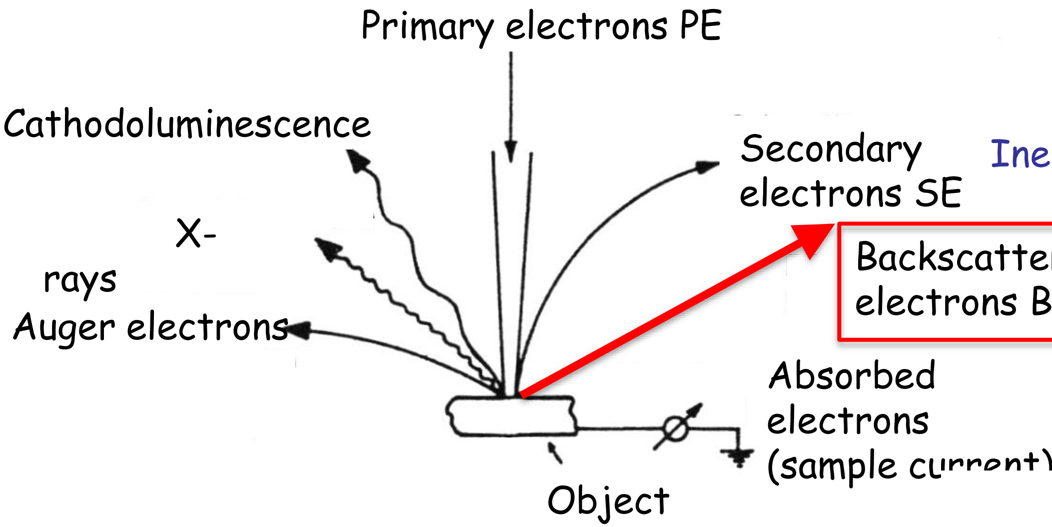
De Wolf 1996, Semicond. Sci Technol. **11**, 139

EBSD: Electron Backscatter Diffraction



EBSD: measure of a pattern which forms by the diffraction of the backscattered electrons

EBSD Pattern Formation



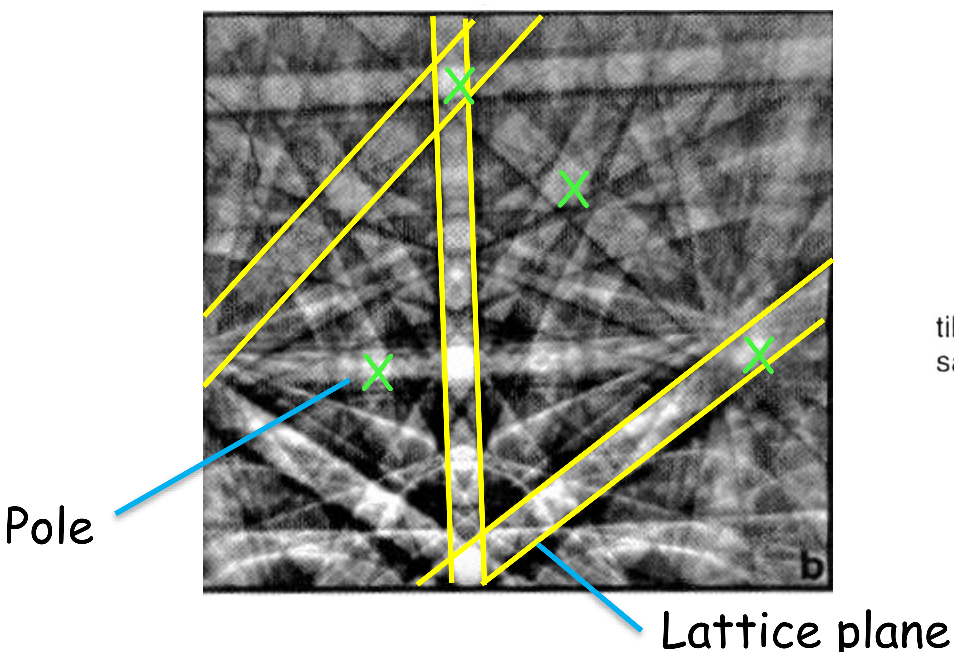
Inelastic scattering

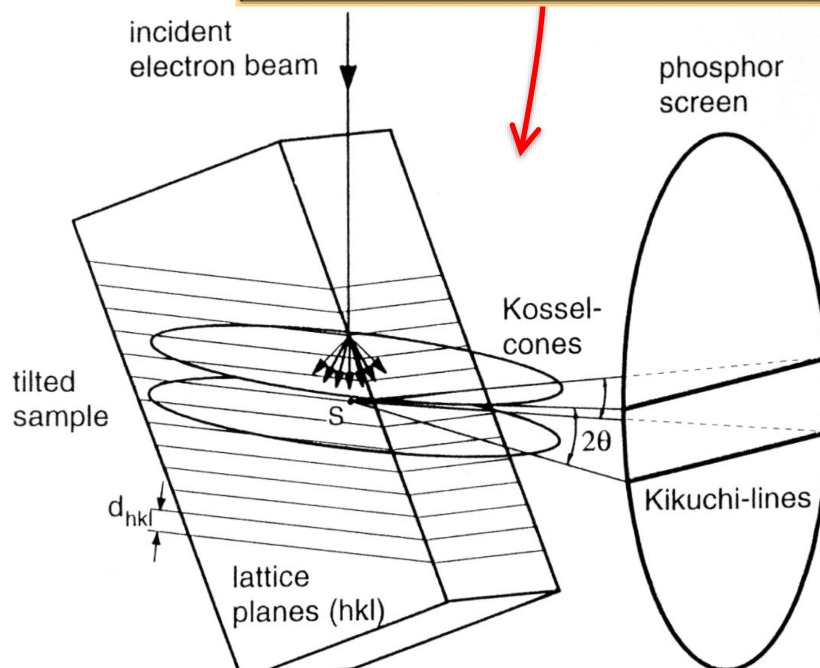
Backscattered electrons BSE — Elastic scattering

Diffraction on the lattice plane according to the Bragg law

Bragg : $2\, d_{hkl} \sin\theta = n\,\lambda$

20 keV $\rightarrow \lambda \approx 7\ 10^{-3}$ nm $\rightarrow \theta \approx 0.5°$





Large scale, multicrystalline thin film silicon

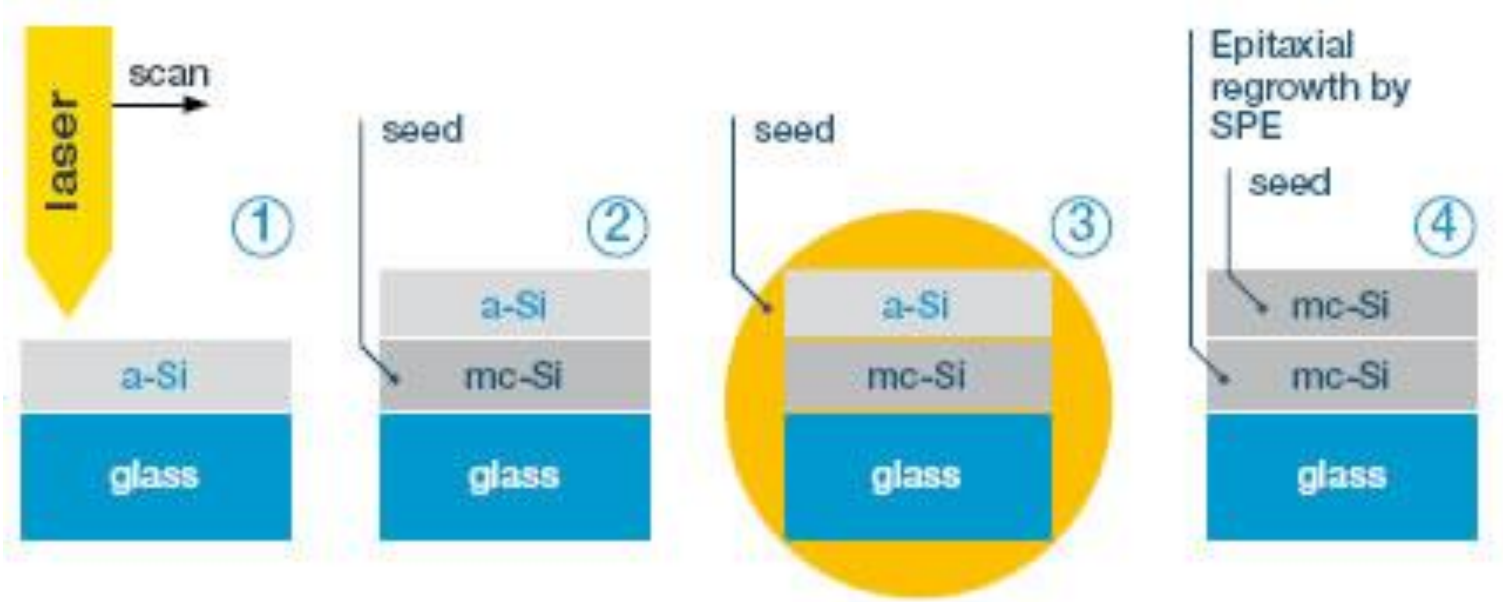
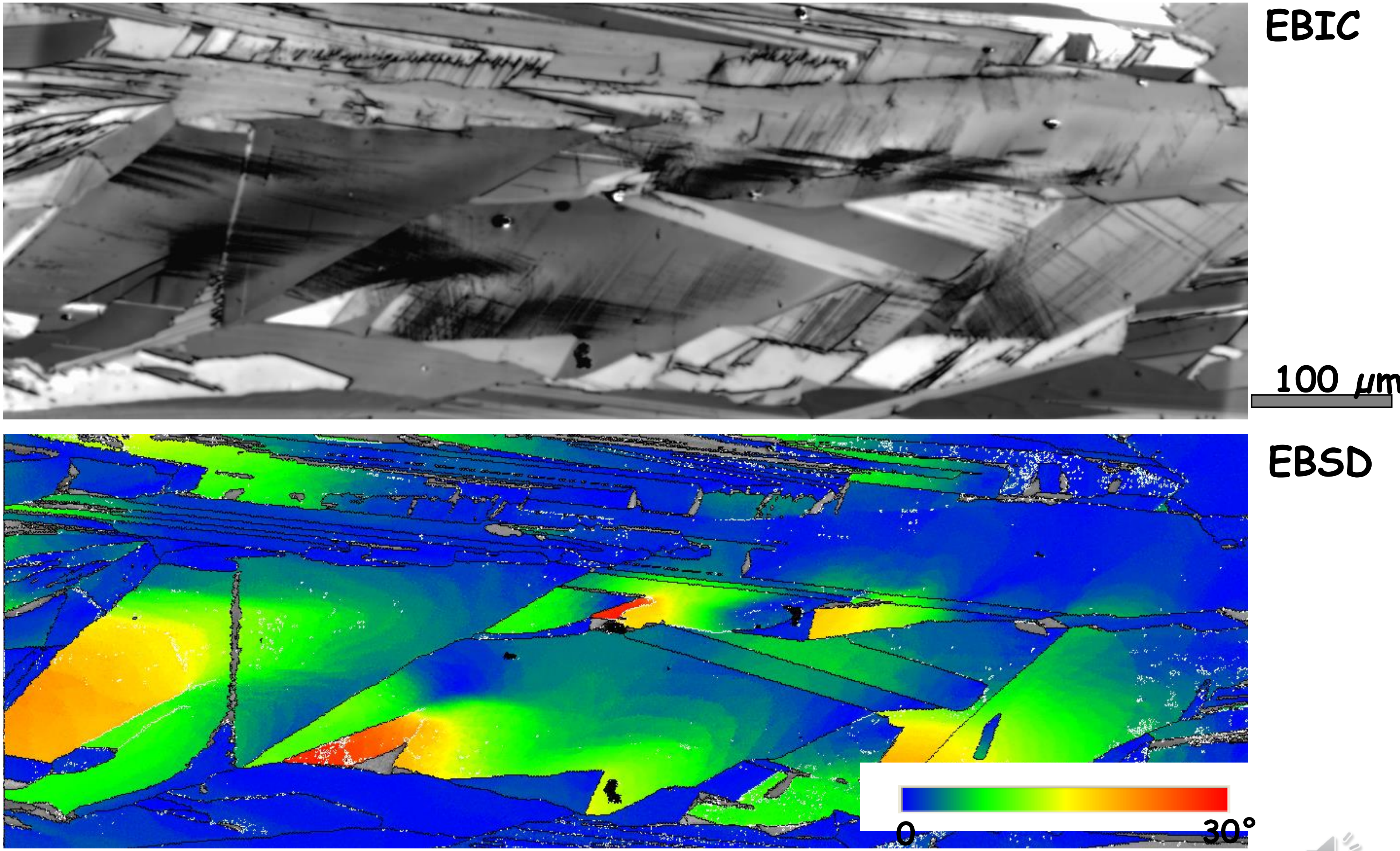


Figure 1:
Schematic of the laser-SPE process which will be established to realize large grained, low defective silicon layers on glass that have the potential for >10% efficiencies.

dislocation distribution: EBIC and OIM



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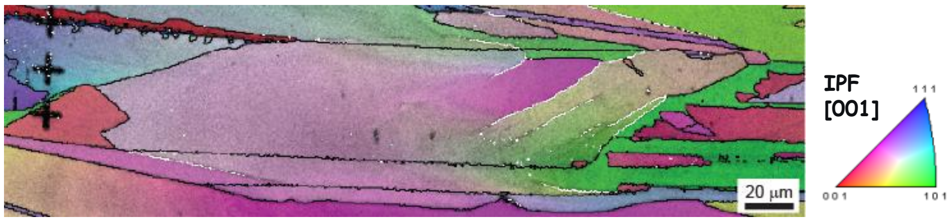
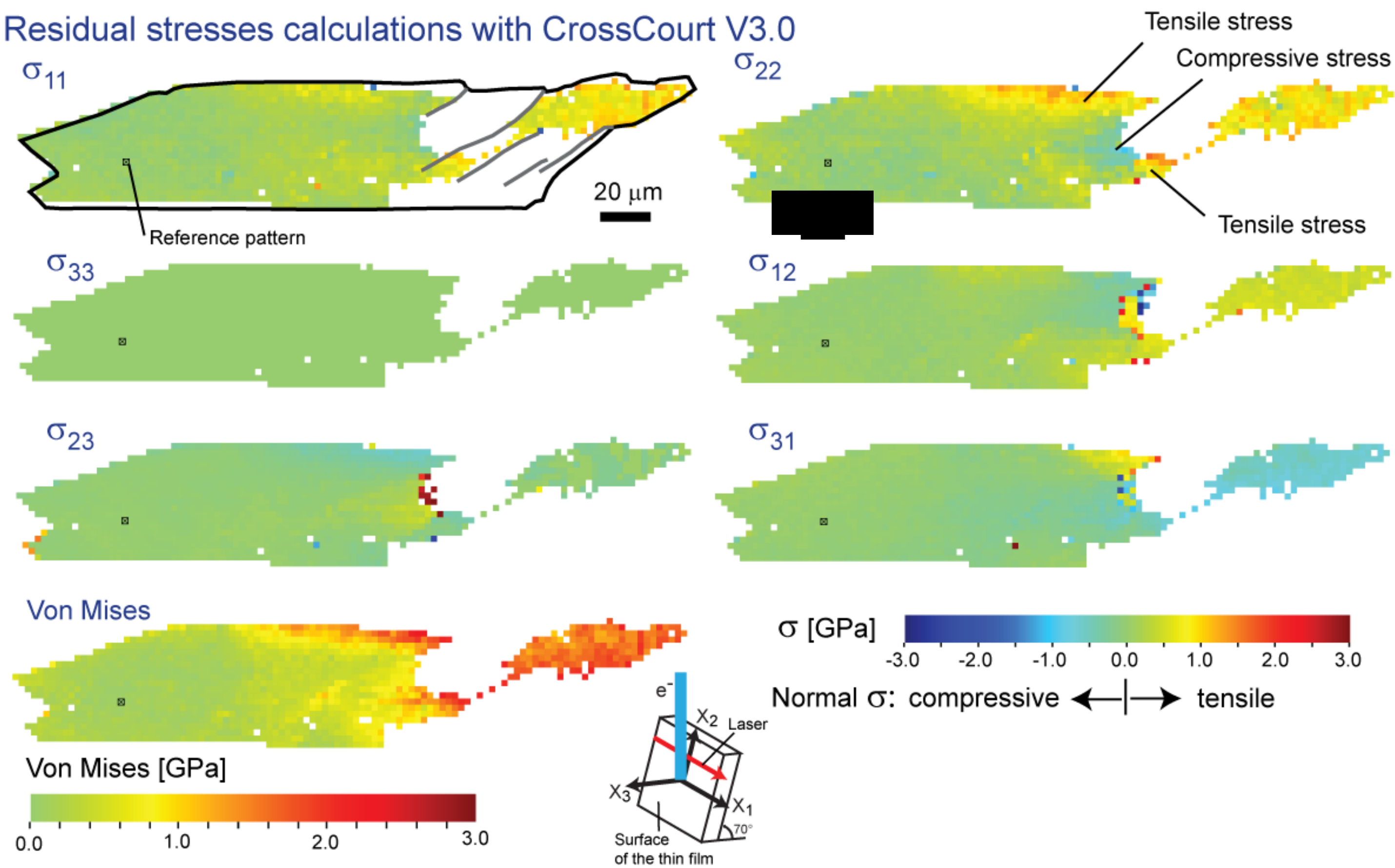
stress concentrations: EBSD





others

- Neutron diffraction
- CBED
- Ultrasonic measurements
- Magnetic methods

comparison

Method	Penetration	Spatial resolution	Accuracy
Hole drilling (distortion caused by stress relaxation)	~1·2 × hole diameter	50 μm depth	±50 MPa, limited by reduced sensitivity with increasing depth
Curvature (distortion as stresses arise or relax)	0·1–0·5 of thickness	0·05 of thickness; no lateral resolution	Limited by minimum measurable curvature
X-ray diffraction (atomic strain gauge)	<50 μm (Al); <5 μm (Ti); <1 mm (with layer removal)	1 mm laterally; 20 μm depth	±20 MPa, limited by non-linearities in $\sin^2 \psi$ or surface condition
Hard X-rays (atomic strain gauge)	150–50 mm (Al)	20 μm lateral to incident beam; 1 mm parallel to beam	$\pm 10 \times 10^{-6}$ strain, limited by grain sampling statistics
Neutrons (atomic strain gauge)	200 mm (Al); 25 mm (Fe); 4 mm (Ti)	500 μm	$\pm 50 \times 10^{-6}$ strain, limited by counting statistics and reliability of stress free references
Ultrasonics (stress related changes in elastic wave velocity)	>10 cm	5 mm	10%
Magnetic (variations in magnetic domains with stress)	10 mm	1 mm	10%
Raman	<1 μm	<1 μm approx.	$\Delta\lambda \approx 0{\cdot}1\ \text{cm}^{-1} \equiv 50$ MPa

Origins of residual stress

stresses in thin films are associated with the elastic accommodation of misfit strains that can arise from various sources:
- thermal,
- epitaxial
- transformational/intrinsic/growth stress.

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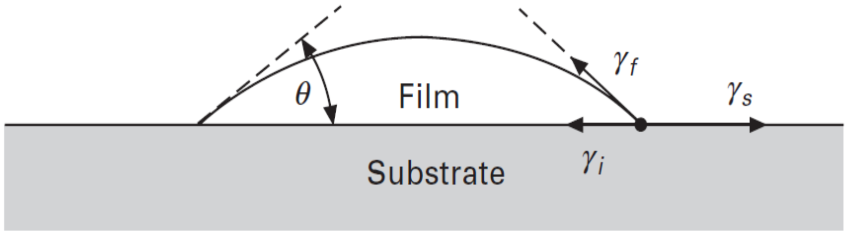
Capillary stresses

Capillary stresses are well known in small particles that show an internal pressure according to the **Laplace-Young equation $p=2\gamma_s/r$.**

Capillarity stresses in thin films arise because there **are biaxial stresses acting in the plane of the surfaces and interfaces** in these structures.
During nucleation of a thin film for atoms taking the form of a hemispherical cap the Young's equation holds:

$$\cos\theta = \left(\frac{\gamma_s - \gamma_i}{\gamma_f}\right)$$



Three interfaces are present in this structure:

- the top surface of the film, with surface stress, f_f,
- the interface between the film and substrate, with interface stress, f_i,
- and the bottom surface of the substrate, with the surface stress, f_s.

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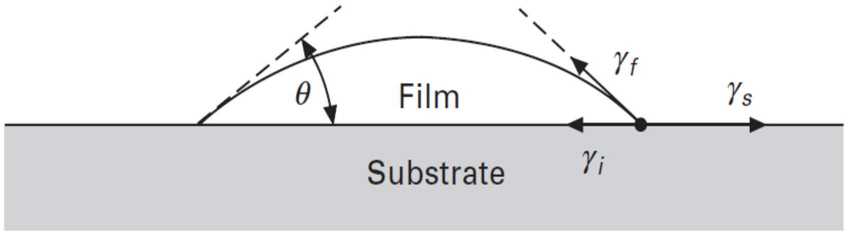
Capillary stresses

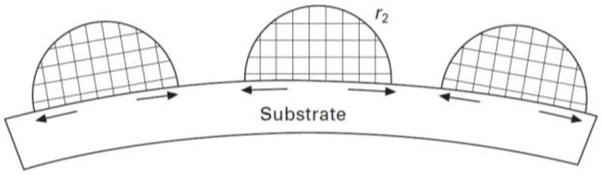
The **interface stresses act to elastically bend the substrate**, much like a stressed thin film would do. According to the Stoney relation, these interface stresses would cause the curvature of the substrate to change as

$$\Delta\kappa = \left(\frac{1-\nu_s}{E_s}\right)\frac{6}{t_s^2}(f_f + f_i - f_s)$$



With this relation we see that the **biaxial stress in the film can be found by measuring the curvature**. To be more precise we take into account the curvature the substrate might had before film deposition:

Unless a large number of interfaces are present, such as in the case of **a metal multilayer with a very small bilayer period**, these effects are **usually much smaller than those that arise from thermal or epitaxial stresses**



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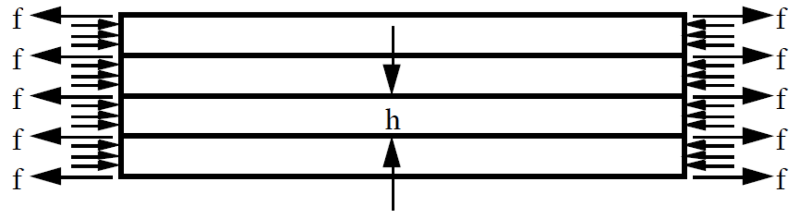
Capillary stresses in multilayers

Consider a free-standing multilayer with interfaces having an interfacial stress f.



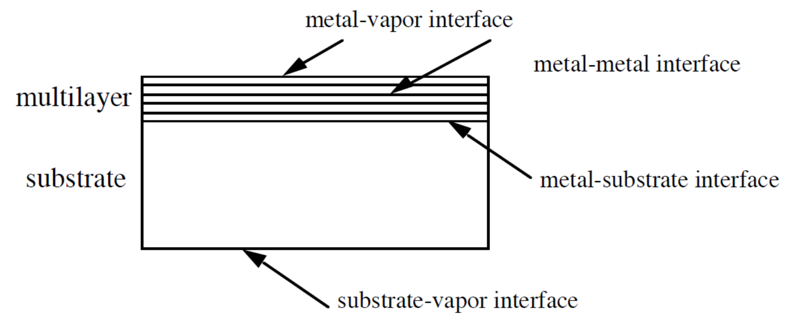
The biaxial stress induced in the multilayer is

$$\sigma = \frac{f}{h}$$

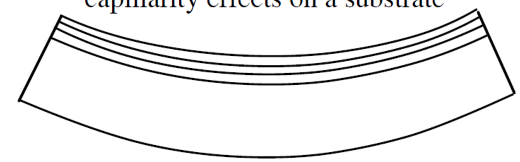
<u>Example:</u>
Using **h = 100Å** = 10^{-2} μm =10^{-8}m and f=1 J/m^2 we have **σ=100MPa**, which is a significant stress!

Using **h=1μm**, we have **1MPa**, which is small!

Now consider a multilayered film deposited onto a solid substrate. Each of the interfaces in the sample will have an interfacial stress and each will exert forces on the entire composite with a resulting curvature.



capillarity effects on a substrate



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thermal stresses

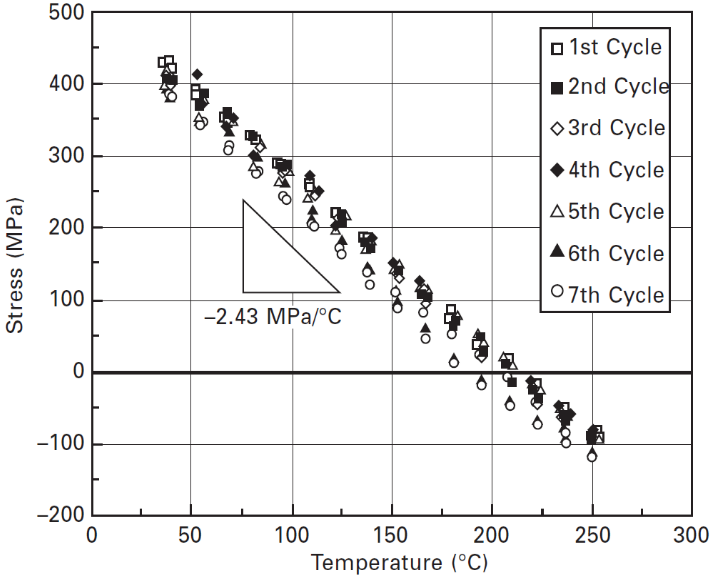
For any continuous film with a **thermal expansion coefficient** that **differs from that of the substrate**, a thermal stress will be generated whenever the temperature is changed.

If α_f is the linear thermal expansion coefficient of the film and as that of the substrate, then the thermal misfi t strain for a temperature change ΔT would be:

$$\varepsilon^{\Delta T}_{misfit} = (\alpha_f - \alpha_s)\,\Delta T$$

and the resulting biaxial stress would be

$$\sigma = \left(\frac{E}{1-\nu}\right)_f \varepsilon = -\left(\frac{E}{1-\nu}\right)_f (\alpha_f - \alpha_s)\,\Delta T$$



The Figure shows the measured stress in a 0.4 μm thick thin film of Al-1%Si-0.5%Cu on a silicon substrate during several thermal cycles from room temperature to 250°C.

Using the properties of pure Al and Si the slope of the stress–temperature plot might be expected to be −2.37 MPa/°C. As shown in the figure, the actual slope is about −2.43 MPa/°C, probably because the alloyed film is a little stiffer than pure Al would be.

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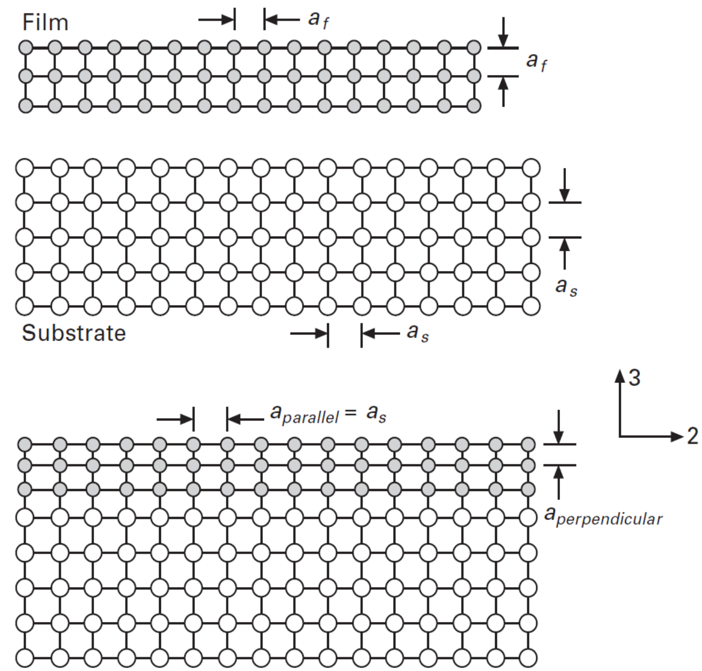
Anisotropic epitaxial stresses



We assume an <001> oriented substrate. For the in-plane elastic strain:

$\varepsilon_1 = \varepsilon_2 = -\varepsilon_{misfit} = -(a_f - a_s)/a_s \cong (a_f - a_s)/a_f$

and the resulting biaxial stress is

$$\sigma_1 = \sigma_2 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}\right)\varepsilon_1 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}\right)\left(\frac{a_s - a_f}{a_s}\right)$$

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Intrinsic stresses in vapor deposited polycrystalline films

For **polycrystalline metal films** that grow in the **Volmer–Weber mode**, there are a **variety of microstructural and kinetic processes that cause residual stresses** to be created during the course of growth.

These are **called intrinsic or "growth" stresses** because they **cannot be attributed to stresses associated with thermal or epitaxial misfit**.

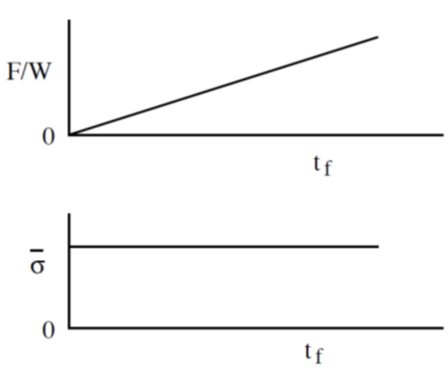
By measuring the **curvature of a substrate during the film deposition** process, the bending force (per unit length) F/W, can be directly monitored.

Here, using the Stoney equation,

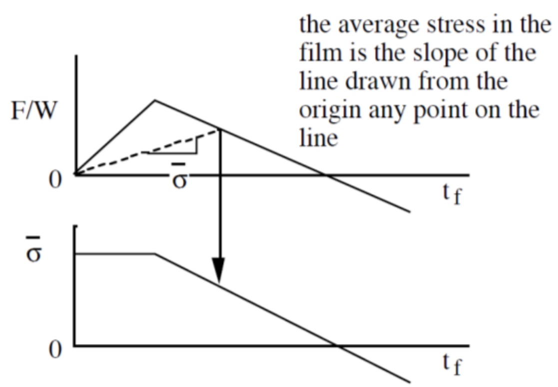
$F/W = \sigma_f t_f = B_s t_s^2 \Delta\kappa/6$,

where σ_f is the average biaxial stress in the film and t_f is the film thickness.

Force-thickness curve for constant stress



Force-thickness curve for position dependent stress



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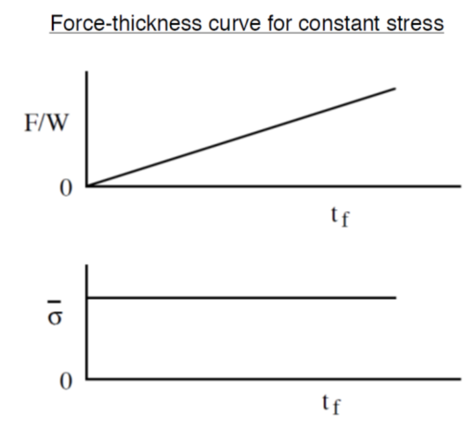
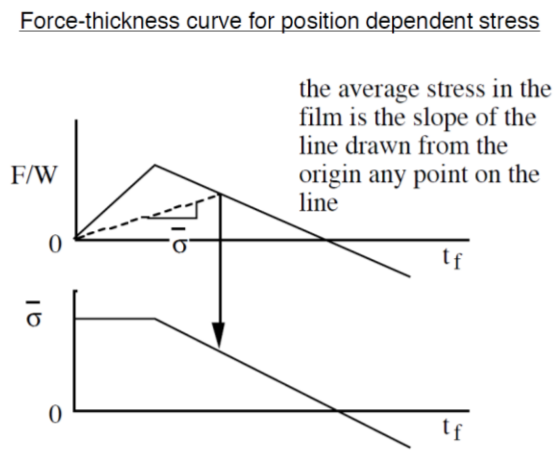
Intrinsic stresses in vapor deposited polycrystalline films

If the **stress in the film is uniform and independent of the thickness**, then the **bending force (per unit width) would vary linearly with film thickness.**



More commonly, the **stress in the film is not uniform and varies through the thickness of the deposited film.**

The **slope of line drawn from origin to the curve gives the average stress in the film at that thickness.**



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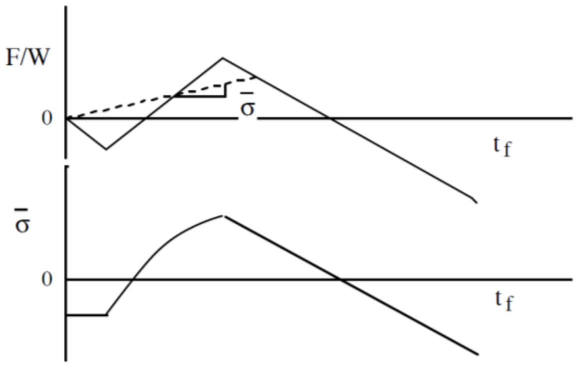
Intrinsic stresses in vapor deposited polycrystalline films

As a third example consider a film in which the **stress changes sign during growth**.
In that case the measured force (per unit width) can be expressed as

$$\frac{F}{W} = \int_0^{t_f} \sigma_f dz = B_s \frac{t_s^2}{6} \Delta\kappa$$



It follows that if the stresses in the film are frozen in and do not change as the film thickens, then the biaxial stress in the last layer of film to be deposited is.

$$\sigma_f(t_f) = \frac{d(F/W)}{dt_f} = B_s \frac{t_s^2}{6} \frac{d\Delta\kappa}{dt_f}$$

Thus the **local stress in the film is simply the slope of F/W vs. t_f.**

At **any point in the growth process** both the
- average stress in the film to that point and
- the local stress at that point

can be determined from the slopes shown in the figure.

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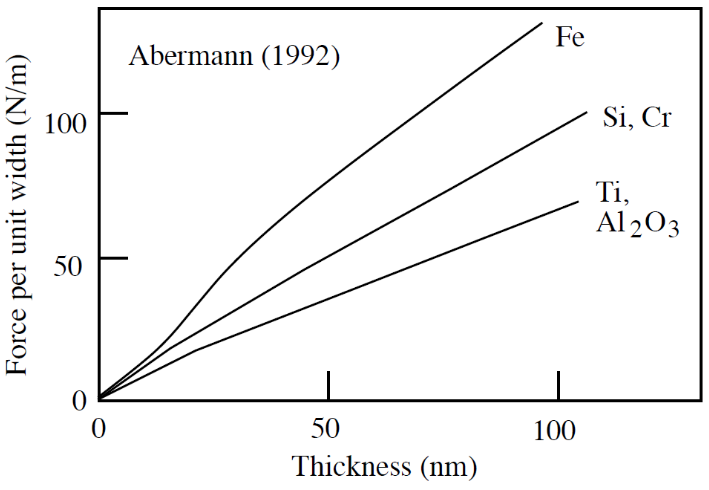
typical results from in-situ curvature measurements

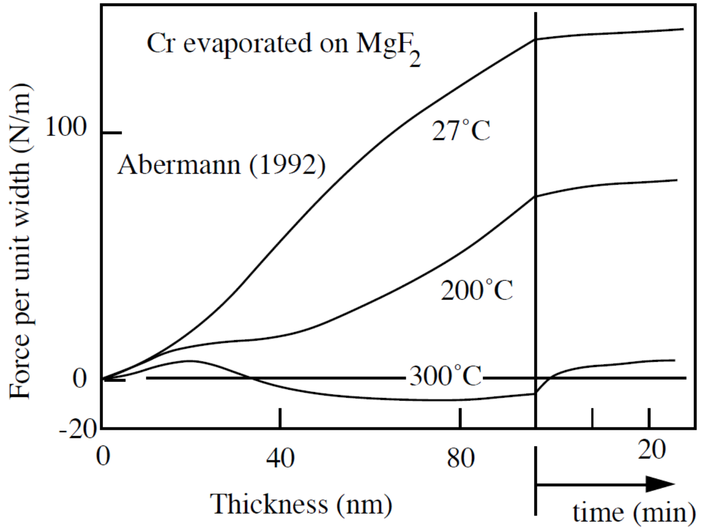
Abermann and Koch found that the force (per unit width) varies **about linearly for (refractory) materials with low adatom mobility**,

suggesting that the **stress developed in these materials is essentially constant** and independent of position through the thickness.



Abermann has shown that the **stress generation in metal films is very much less if the temperature is raised**.

This is shown for the evaporation of Cr as a function of temperature.



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typical results from in-situ curvature measurements

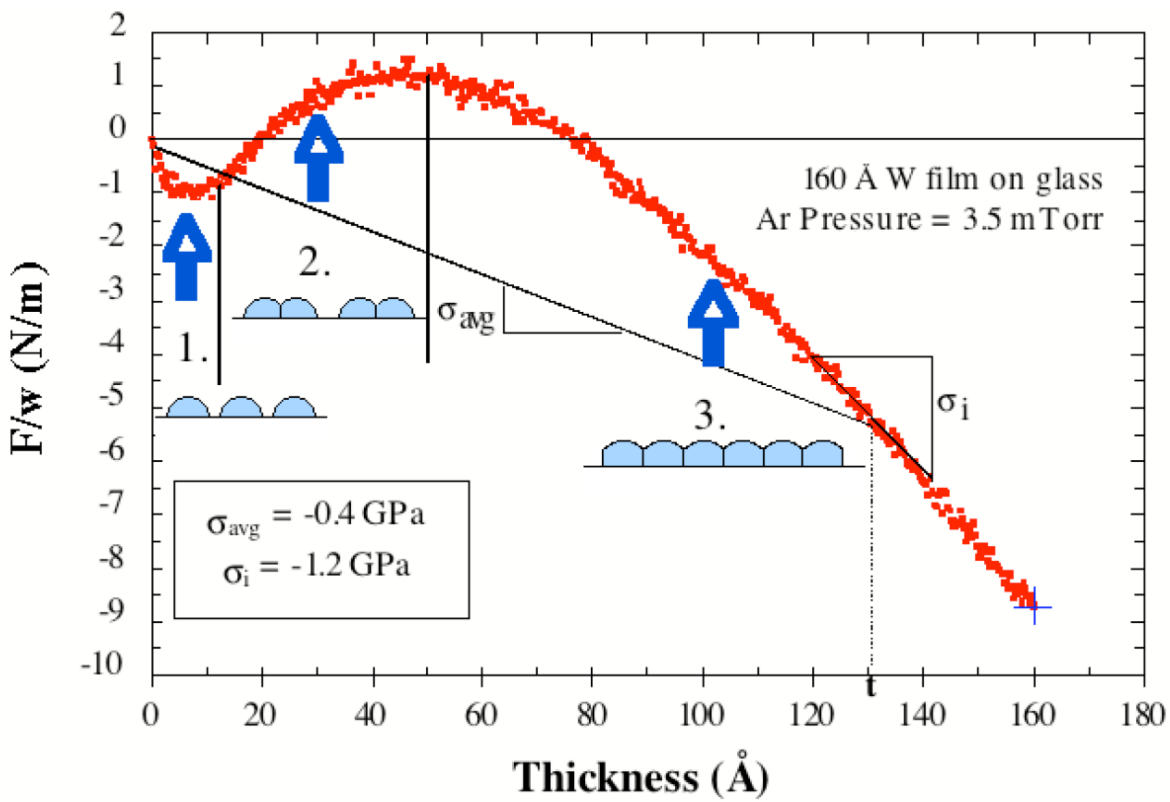
The data show that the measured F/W oscillates during the course of growth,

- **being negative at the start of growth** and
- **then becoming positive**
- Before again being **negative in the later stage of growth**.

The slopes at different points in the curve indicate that the stress in the film is

- **initially compressive**
- **then becomes tensile**
- and is **compressive again** in the later stages of growth.

This oscillatory behavior is widely observed for many metallic films.



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Stage I: isolated crystals

For **very small crystallites the surface stress would be expected to compress the crystal lattice**, much like it would if the crystallites were isolated spherical particles.

For an isolated spherical particle of radius R the **Laplace pressure** in the particle due to the surface stress is

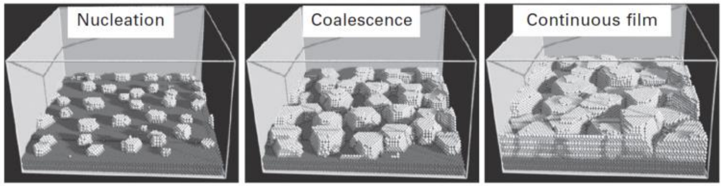
p = 2fs/R,

where fs is the surface stress.

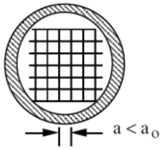
The pressure would compress the crystal lattice and cause the lattice parameter, a, to be smaller than the lattice constant of the stressfree crystal, a_o:

$$\frac{a}{a_o} = 1 - \frac{p}{K} = 1 - \frac{2f_s}{KR}$$

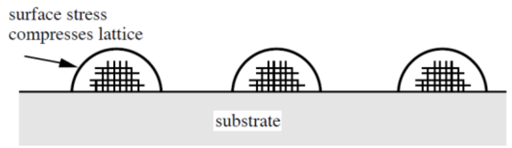
where K is the bulk elastic modulus of the crystal.



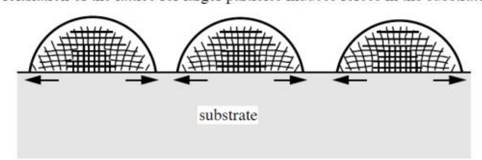
Atomistic modeling of Volmer–Weber film growth showing crystallite growth and coalescence leading to a continuous film



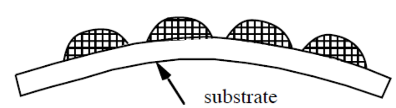
Compression of a small particle by surface stress



relaxation of the lattice for larger particles induces forces in the substrate



The effect on substrate is to induce a curvature.



Attachment to the substrate restrains lattice expansion and this leads to compressive stresses in the film.

Stage II: crystallite coalescence

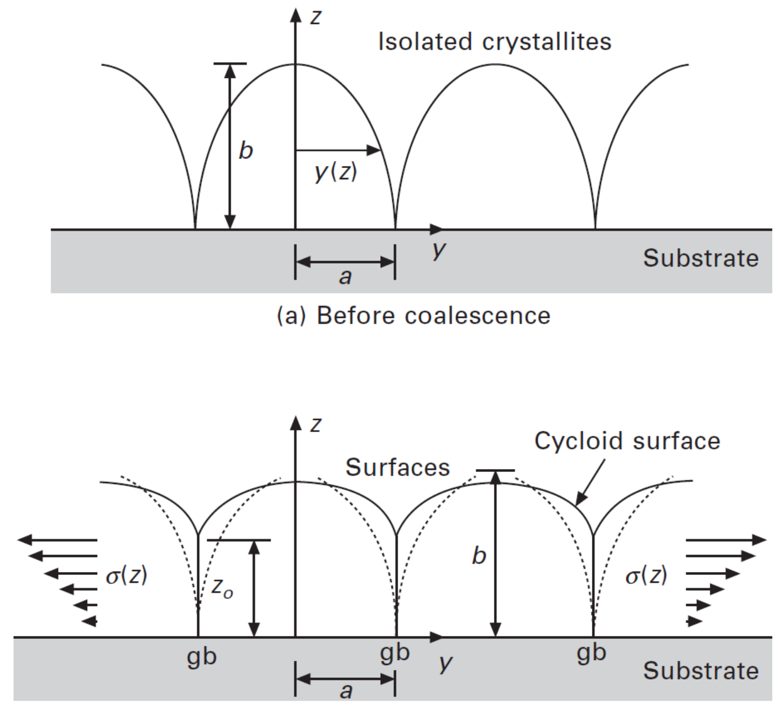
It has been shown that **tension stresses develop in a growing film when the crystallites begin to grow together.**

As soon as crystals come into **touching contact**, we can predict that the **two free surfaces will snap together**.

The reason for this is that when they snap together they form a **single grain boundary in place of two surfaces**, and since the energy of that one boundary is much less than the energy of the two surfaces, this is a spontaneous process.

Eventually, the **zipping process** stops because the stress in the film causing the crack-like feature to grow is just balanced by the interfacial energy differences causing the crack to heal. The stress car be estimated to

$$\sigma \approx \left[2E \frac{(2\gamma_s - \gamma_{gb})}{a} \right]^{1/2}$$



(a) Before coalescence

(b) After coalescence

Taking $2\gamma_s - \gamma_{gb}$ **≅1.5 J/m², E = 100 GPa and ν = 1/3**, we find stresses of **several GPa for crystalline sizes** in the **range of a few nanometers**.

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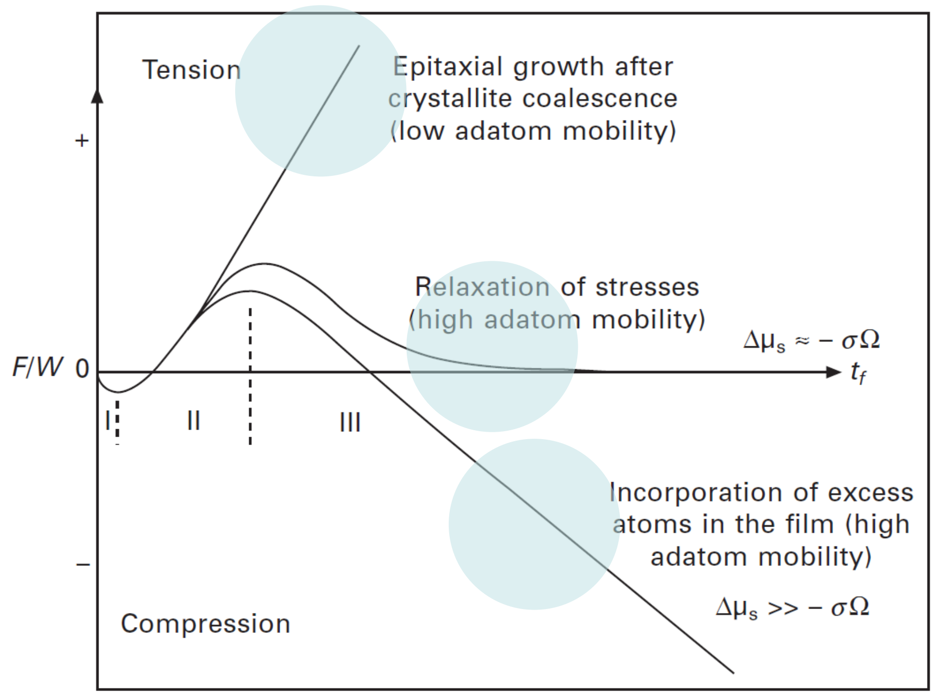
Stage III: stress evolution following coalescence

How the stresses in the film evolve after the crystallites have grown together to form a continuous film **depends on the driving forces and mobilities of the arriving atoms**.

1) the **tensile stresses** generated by crystallite coalescence are propagated into the growing film as the **arriving atoms simply grow epitaxially onto the already strained film**.

2) For metals with high adatom mobilities, such as many fcc metals grown at relatively high homologous temperatures, the **tensile excursions** associated with crystallite coalescence are soon **relaxed** because the arriving **atoms have sufficient mobility to diffuse into the grain boundaries** and gradually relax the tensile stresses as the film grows thicker.



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Stage III: stress evolution following coalescence

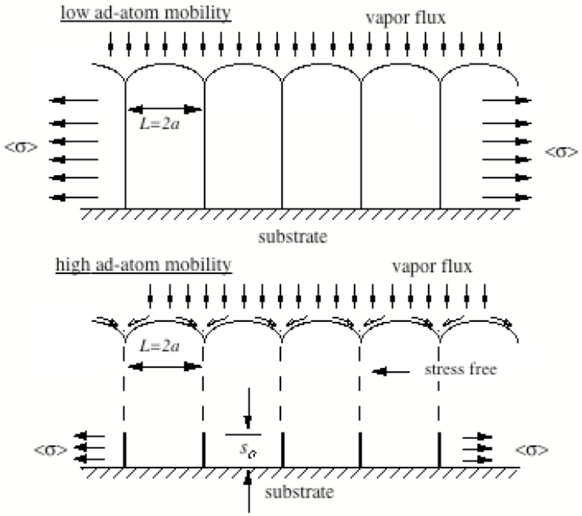
We consider now a more general description of the kinetic processes leading to biaxial tensile stresses in deposited films.

The basic idea is that the film is deposited in a non-equilibrium, non-dense state. Densification after the film material is attached to the substrate leads to tension stress in the film.

Consider atoms arriving from the vapor and depositing on a growing film. Two rates are of importance and will be compared:

- Rate of arrival of depositing atoms (growth rate)
- Rate of atomic rearrangement on the surface of the growing film by surface diffusion (R surface rearrangement).

If the rate of surface rearrangement is much greater than rate of arrival, then an equilibrium structure is produced and there is no potential for film stress (discounting epitaxy and thermal stresses in this discussion).



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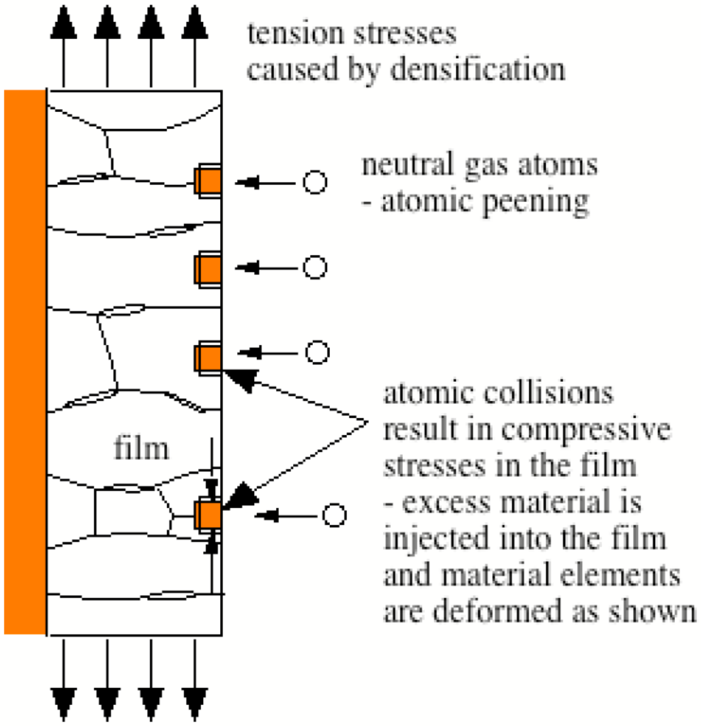
Stage III: stress evolution in sputtered thin films

Another explanaton is related to the **incorporation of neutral gas species such as Ar** during deposition.

Therefore, the conclusions are:

1. Low argon pressure – The neutral argon atoms reflected from the target suffer few collisions with other gas atoms on their way to the growing film, with the consequence that many energetic argon atoms arrive at the growing film and produce high compressive stresses by "atomic peening".
2. High argon pressure – Many collisions in the gas prevent energetic argon atoms from arriving at growing film - so natural processes leading to tension prevail.



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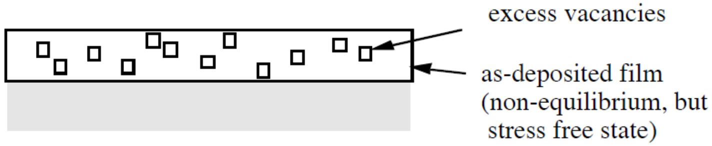
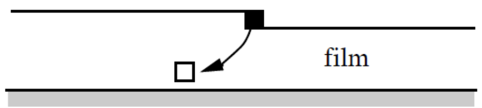
vacancy annihilation

3) When crystalline films are formed by deposition onto cold substrates, the conditions are far from equilibrium and it is reasonable to expect a nonequilibrium, excess vacancy concentration to be established in the film. As these vacancies annihilate, the associated volume changes cause a stress to develop within the film.

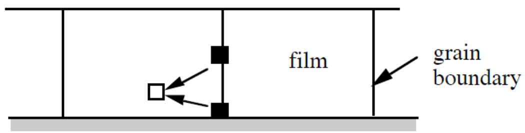
These vacancies annihilate at the surface, interface, internal voids or dislocation core which leads to tensile stresses.



Vacancy annihilation at a free surface



Annihilation at grain boundaries perpendicular to the film



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stresses in films during processing – plastic deformation

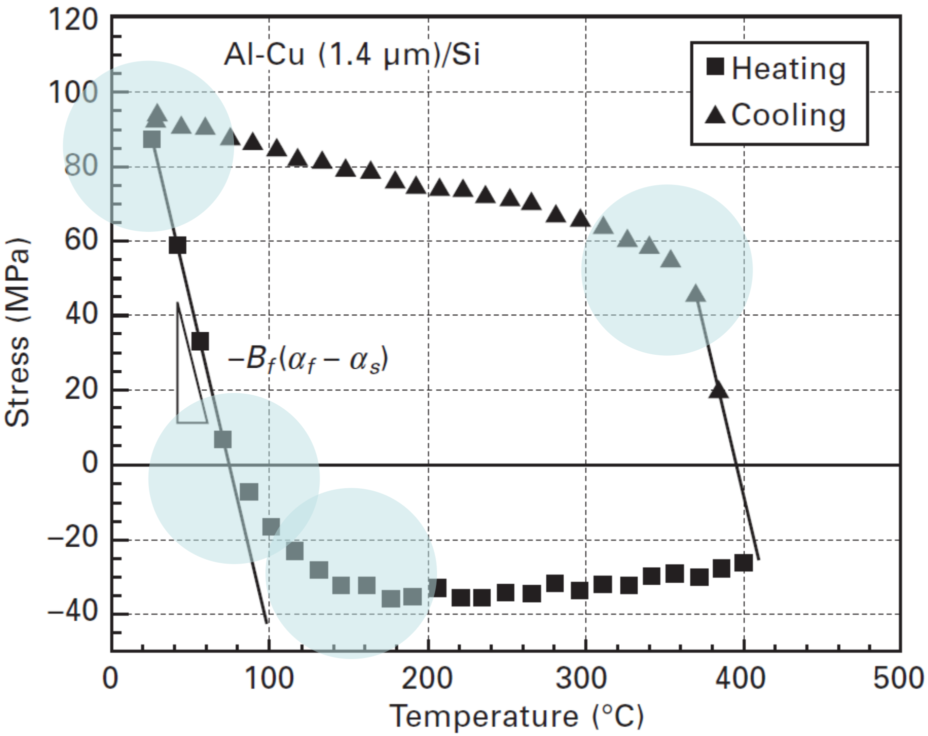
the thermal misfit changes with temperature due to **difference in thermal expansion**, but there are additional mechanisms such as **plastic deformation, grain growth** and **phase changes**.

1) **Plastic deformation**:
At room temperature the stress in Al-Cu/Si is about 90 MPa (tension).

On **heating** the **tensile stress declines** as the film expands thermally more than the substrate, but the stress deviates from linear expansion relationship at a temperature of about 80°C, as the film begins to deform plastically in compression.

With **continued heating past 150°C**, the stress hardly changes at all.

On **cooling the film shrinks thermally relative to the substrate**, causing the film to be subjected to a **tensile stress**. Again, below about 350°C, the stress does not change much because of plastic extension of the film.



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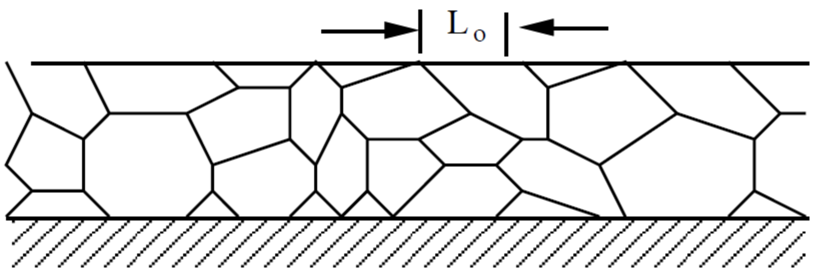
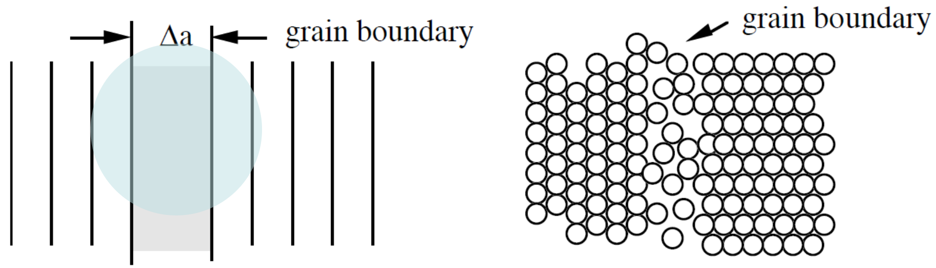
stresses in films during processing – grain growth



2) **Grain growth**
The **excess volume per unit area, Δa** is expected to be of order of the atomic dimension and the **grain boundary is equivalent to a gap Δa between the adjacent crystals**.



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stresses in films during processing – grain growth

Consider a **reference crystal volume Vref of the film** (Here, Vref is the crystal volume not including excess volume associated with the grain boundaries) with grain diameter L.

Using the model of spherical grains, the **grain boundary area per unit volume** is

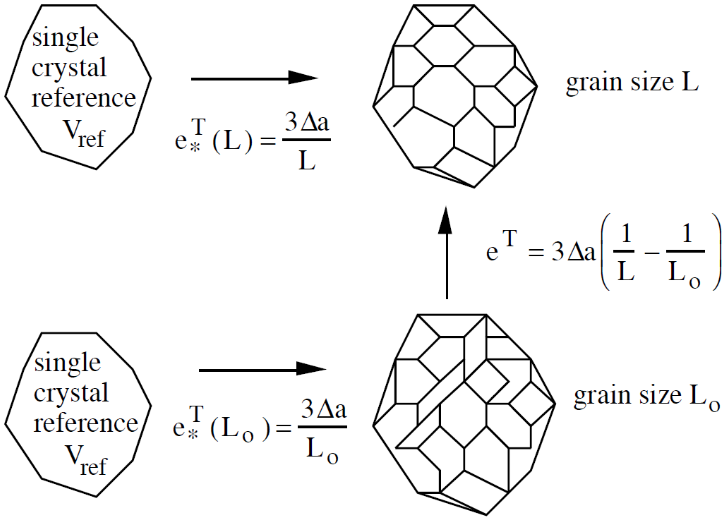
$$\frac{A}{V} = \frac{1}{2}\frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{2R} = \frac{3}{L},$$

Excess volume in the reference volume Vref is

$$V_{gb}^{xs} = V_{ref}\frac{3}{L}\Delta a \,.$$

The total volume of the polycrystalline aggregate is then

$$V_T = V_{ref} + V_{gb}^{xs} = V_{ref}\left(1 + \frac{3\Delta a}{L}\right).$$



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stresses in films during processing – grain growth

Thus the polycrystalline solid **is dilated relative to single crystal reference by**

$$e_*^T = \frac{V_T - V_{ref}}{V_{ref}} = \frac{V_T}{V_{ref}} - 1 = \frac{3\Delta a}{L}.$$

Suppose the film is deposited in stress free state with grain size L_0. Then after grain growth to grain size L, the transformation strain relative to the as deposited state is

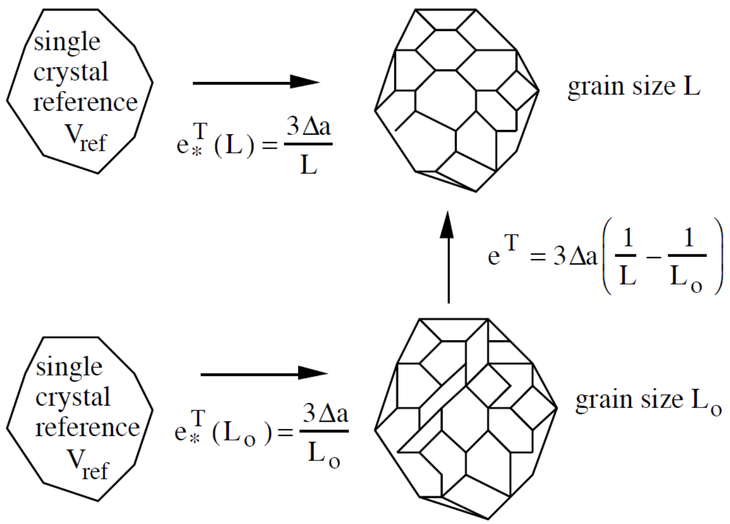
$$e^T = 3\Delta a\left(\frac{1}{L} - \frac{1}{L_o}\right).$$

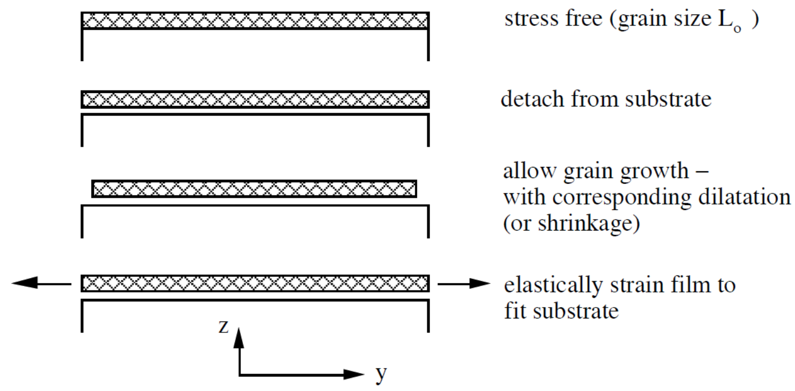
For

1/L -> 0 (infinite grain growth),
Lo = **100Å = 10 nm,**
Δa= 1Å = **0.1 nm,**
$(E/1-v)_{film}$ = **100GPa,**

We find

σ=1GPa





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stresses in films during processing – grain growth

During grain growth, **the elastic strain energy increases** as the stresses and strains in the film develop.

$$W_{el} = \frac{1}{2}\sigma_{xx}\varepsilon_{xx}^{el} + \frac{1}{2}\sigma_{yy}\varepsilon_{yy}^{el},$$

which, with the equations above becomes

$$W_{el} = \left(\frac{E}{1-\nu}\right)_{film} (\Delta a)^2 \left(\frac{1}{L_o} - \frac{1}{L}\right)^2$$

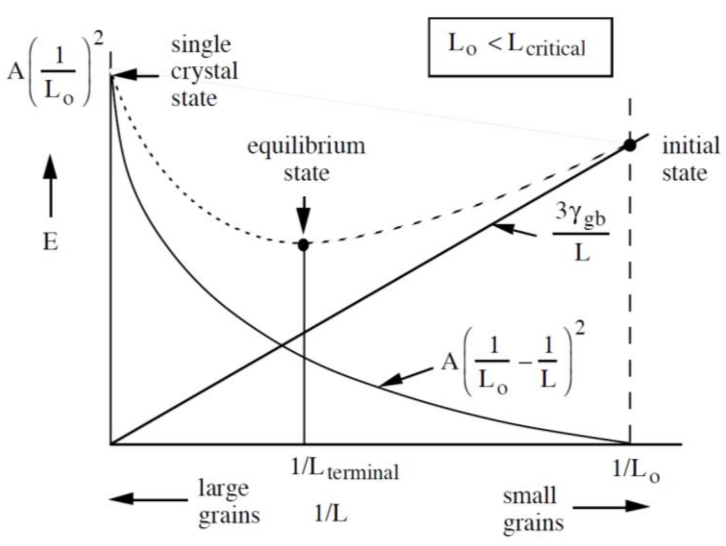
So **W_{el} increases with grain growth** - This can **stop grain growth**!

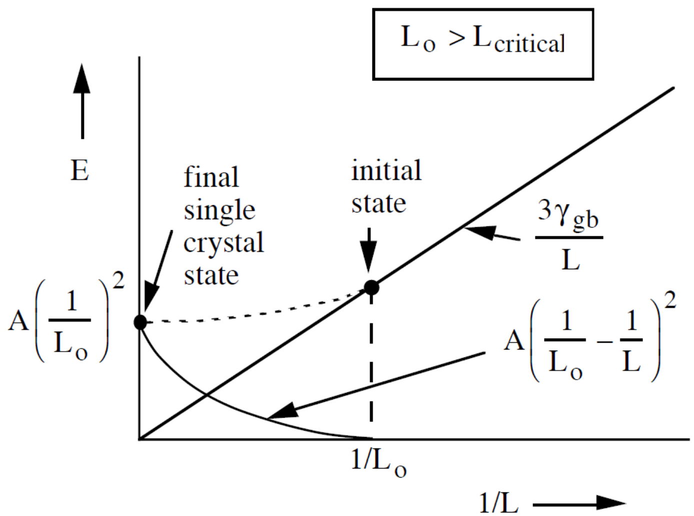
We can calculate the total energy

$$E = \frac{3\gamma_{gb}}{L} + \left(\frac{E}{1-\nu}\right)_{film} (\Delta a)^2 \left(\frac{1}{L_o} - \frac{1}{L}\right)^2,$$

If **the initial grain size is greater than the critical value, $L_o > L_{critical}$,** then **the grains will grow** in an unbounded manner **until a single crystal state** is reached.

In this case the strain energy that develops in the film is not great enough to stop the grain growth.





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stress. in films during processing – crystallizat. & phase change

A **major source of stress in alloy thin films involves volume changes** that may occur when **phase changes** occur after the films are deposited.

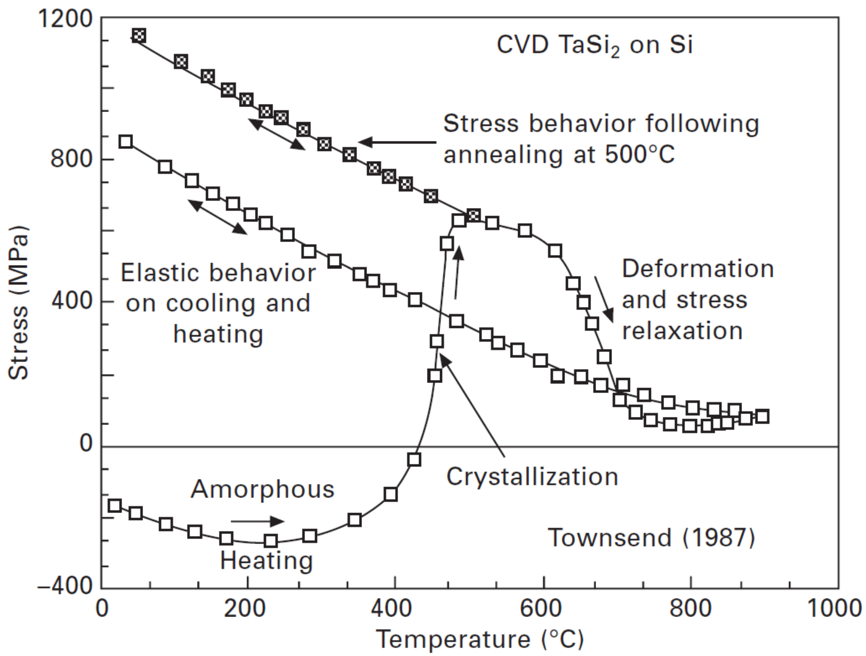
Alloy films are often **deposited in an amorphous state**. On **heating, the film can crystallize** to form stable crystalline phases.

A **stress develops** if the more stable phases that are created **have a different volume or density** (compared to the initial amorphous state).

Example: Ta-Si films deposited at room temperature by CVD.

The amorphous-to-crystalline transition at 450°C creates a negative misfit strain that leads to a tensile stress in the film.

On **cooling below 600°C**, the crystalline $TaSi_2$ film deforms elastically down to room temperature, leaving the film with a tensile stress of over 800 MPa.



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stress. in films during processing – deposition techniques

In evaporated metal films the stress is invariably tensile with a typical magnitude of ~ 1 GPa.

The stress in sputtered metal films appears to be 2 - 3 times higher than for evaporated metals. Such stress values considerably exceed those for the yield stress in bulk metals.

There is no apparent strong dependence of stress on the nature of the substrate.

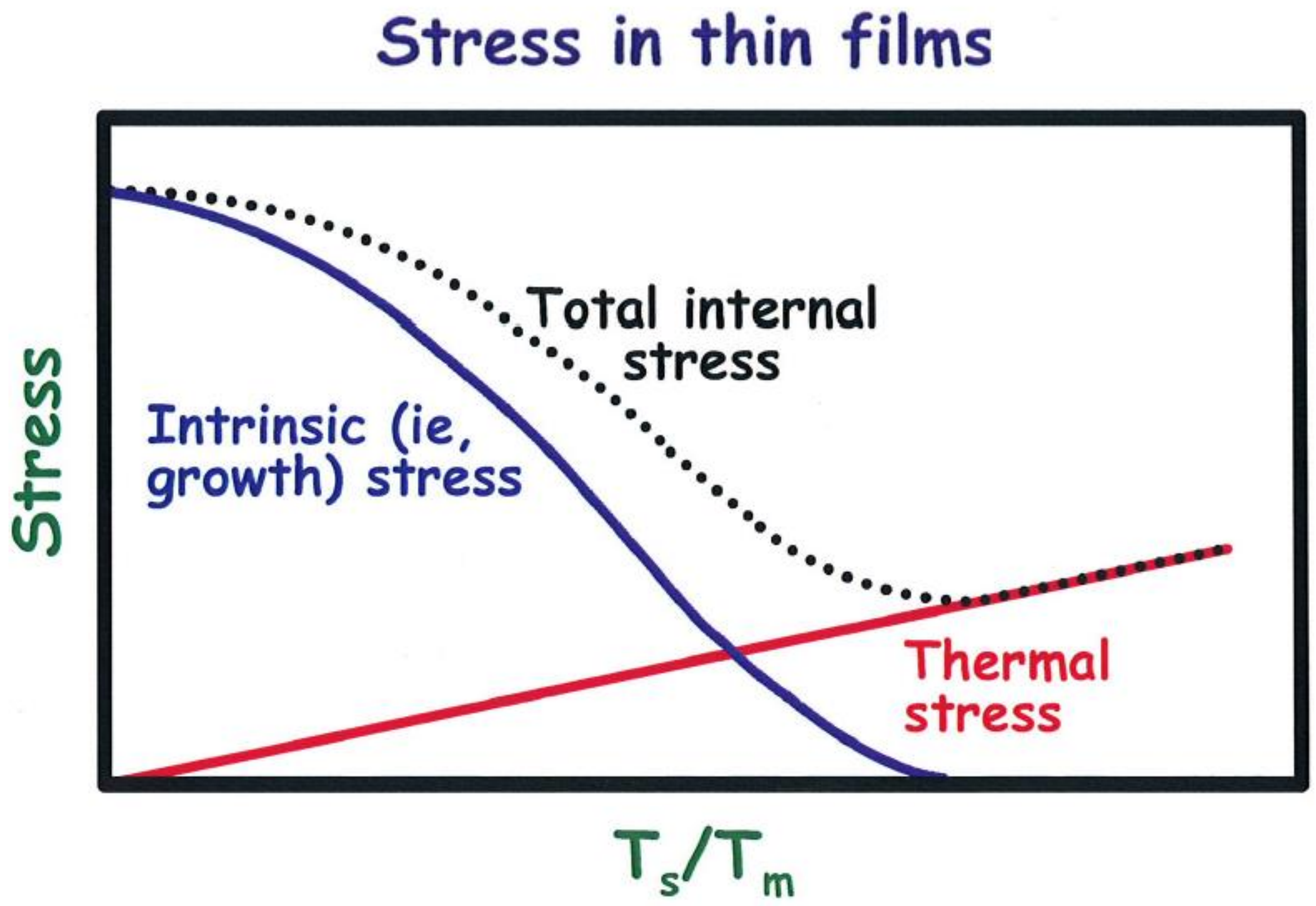
The magnitude of the stress in nonmetallic films is typically 100- 300 MPa.

Both compressive and tensile stresses arise in dielectric films.

Film	Process	Conditions	Stress (GPa)
SiO_2	Thermal	900–1200°C	−0.2 to −0.3
SiO_2	CVD 400°C	40 nm/min	+0.13
SiO_2	$SiH_4 + O_2$	400 nm/min	+0.38
SiO_2	CVD	450°C	+0.15
	TEOS	725°C	+0.02
SiO_2	TEOS	685°C	+0.38
	TEOS + 25% B, P		−0.02
SiO_2	Sputtered		−0.15
Si_3N_4	CVD	450–900°C	+0.7 to +1.2
Si_3N_4	Plasma	400°C	−0.7
		700°C	+0.6
Si_3N_4	Plasma 13.56 MHz	150°C	−0.3
		300°C	+0.02
Si_3N_4	Plasma 50 kHz	350°C	−1.1
Poly Si	LPCVD	560–670°C	−0.1 to −0.3
$TiSi_2$	PECVD	As-deposited	+0.4
		Annealed	+1.2
$TiSi_2$	Sputtered		+2.3
$CoSi_2$	Sputtered		+1.3
$TaSi_2$	Sputtered	800°C anneal	+3.0
$TaSi_2$	Sputtered		+1.2
W	Sputtered	200 to 400 W power	+2 to −2
W	Sputtered	5 to 15 mtorr Ar pressure	−3 to +3
Al			+0.5 to ~ +1

Ohring 2003

The stress dilemma



Courtousy, Joe Greene. Univ. Illinois

Summary

Stress in thin films

- Film exerts bending moment on substrate plate which leads to curvature=1/R
- Stoney equation is independent of film properties:

$$\sigma_f = \left(\frac{E_s}{1-\nu_s}\right)\frac{t_s^2}{6t_f}(\kappa - \kappa_o)$$

- In textured films biaxial film modulus for <111> and <001> textures used, <110> more complicated
- In plane Young's modulus depends on grain size (10%less for <10nm), texture (up to 2x), porosity (~ porevolume^2)
- Stress of 1st, 2nd, 3rd order
- methods for residual stress
    - Mechanical methods: Substrate curvature via laser deflection, bending of FIB bi-metal beam
    - (Fib-)Hole drilling & edge relaxation,
    - XRD (sin2 Ψ - method measures out of plane strain and converted to in-plane stress, epi-layers and reciprocal space map,
    - Raman spectroscopy stress dependence of opt phonon frequency,
    - EBSD cross.correlation method
    - Cantilver beam methods
    - Method comparison: spatial (lateral & depth), and spectral resolution
- Types of stresses (thermal, instrinsic, epitaxial)

$$\sigma = \left(\frac{E}{1-\nu}\right)_f \varepsilon = -\left(\frac{E}{1-\nu}\right)_f (\alpha_f - \alpha_s)\,\Delta T$$

$$\sigma_1 = \sigma_2 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}\right)\varepsilon_1 = \left(c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}\right)\left(\frac{a_s - a_f}{a_s}\right)$$

- Intrinsic: Capillary, Laplace pressure of islands, Zip stress during coalescence
- Stress evolution after coalescence, Impurities, vacancies, ion bombardment
- Evolution during growth: Capillary stress: Laplace-Young equation $p=2\gamma_s/r$. ; Zip stress like healing crack, following coalescence either compressive due to epitaxy, relaxed due to adatom mobility or compressive due to incorporation of excess atoms (at GB, or bigger Ar atoms)
- Evolution during or after: vacancy annihilation, densification, crystallization, grain growth
- The stress dilemma: intrinsic stress relaxes at high deposition T, thermal increases

questions

- Name 3 industrial problems related to residual stresses
- Write down the Stoney equation, why is the equation independent from the film materials properties? How would you measure stress based on this relationship?
- You are dealing with a textured film. Explain the term bi-axial modulus and give the equation for a <001> surface.
- Name 3 factors influencing the in-plane Young's modulus of a crystalline thin film on an amorphous substrate.
- Which are the 3 principal sources of residual stress in thin films? How do you calculate the stress?
- Explain the measurement principle of residual stresses by X-ray's
- Suggest 3 methods to measure residual stress of a 5 micrometer thick amorphous thin film on silicon wafers.
- You want to measure residual stresses in an epitaxial SiGe Film on Silicon. Compare Raman, spectroscopy, EBSD and X-Ray methods in terms of spatial and spectral resolution
- What are the origins of residual stresses during film growth starting from nucleation of islands to thick films. Draw a typical force-thickness vs layer thickness curve from in-situ wafer curvature measurements and label different mechanisms.
- Through which processes can residual stresses be relaxed?