Mechanical properties of solid bulk materials and thin films

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Chapter 4. Mechanics of thin films

4. Mechanics of thin films

4.1. Introduction

Thin films are solids, however, they are peculiar in several respect. The most important peculiarities are:

- geometry („thin film"),

- structure,

- stresses,

- film edges, flaws and other defects.

We will discuss shortly these issues in the following:

Geometry

In general, a film (synonyms: layer, coating) is a region at the surface of a body which has different composition and properties. Usually, the film is formed by **deposition** of a certain material on top of a different one. The body coated by the film is called substrate.

In some cases, films are formed not by deposition but by **modification** of a surface region of the substrate. Modification can, for instance, be carried out by

- ion implantation,

- diffusion of gas atoms into the substrate followed by chemical reaction (e.g. nitration of steel; oxidation),

- plasma treatment (for example of polymers).

In one direction, the dimension of a film is much smaller than in the other ones. In particular we call a film *thin* if this restricted dimension has an effect on the properties of this film. Examples for such thickness effects are

- a thickness dependent electrical conductivity due to scattering of charge carriers at film surface and film-substrate interface, resp.,

- optical interference effects,

- a dependence of the mechanical behaviour of the film on the mechanical properties of the substrate.

This is usually the case for a film thickness < 1 μm, the thinnest films which are intentionally formed are as thin as about 1 nm. Considering this, thickness of a thin film is both << its lateral extension and << substrate thickness.

In most cases, thin films are formed atom-by-atom - in contrast to methods like plasma spraying where large droplets are deposited.

Example for the influence of film thickness on the measured hardness value (from N. G. Chechenin et al., Thin Solid Films, 261 (1995), 219-227):
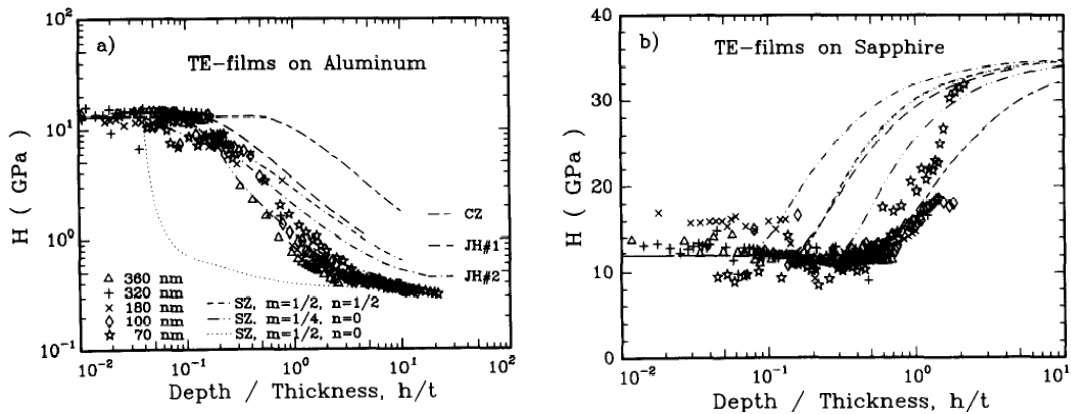
Measured hardness of organic so-called TE films in dependence on the ratio h/t (h – maximum indentation depth, t – film thickness) for a soft (aluminium, left) and a hard substrate (sapphire, right).

When h/t is varied, a transition in the measured effective hardness value is found from H_{film} (obtained for small h/t) to $H_{substrate}$ which is received for large h/t. In order to get the true value of the film material one must not exceed a certain critical h/t. If the film is harder than the substrate (e.g. TE on aluminium, left picture) maintaining h/t < 0.1 is sufficient. In case of a soft film on a hard substrate things are even less critical and h/t = 0.5 or more can be tolerated (right picture).

Therefore, when using the well-known **10% rule**, one is always on the safe side!

It should be mentioned that for the measurement of Young´s modulus by indentation methods the influence of the substrate is much higher (cf. sect. 6.1.).

The examples discussed so far can be understood considering the material as a continuum.

The figure[+)] right shows the increase of yield strength for $t_f \rightarrow 0$.

Explanation: constraint of dislocation motion in the film (e. g. by interaction with misfit dislocations).

[+)] taken from W.D.Nix, Metallurg. Trans. A, Vol. 20A, Nov. 1989, pp. 2217-2245.
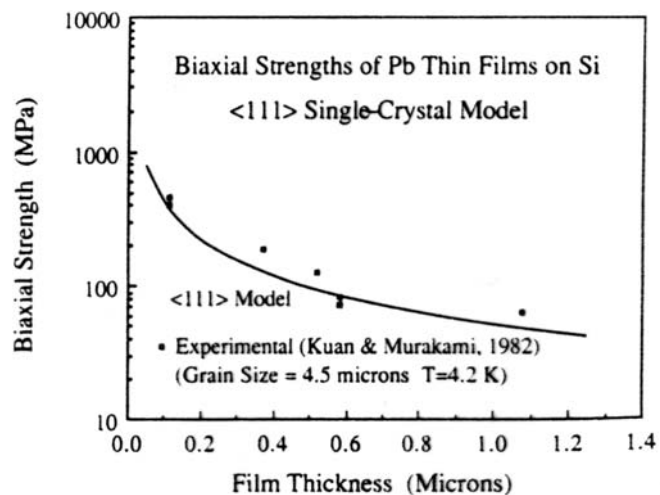

Fig. 25 — Biaxial strengths of Pb thin films on Si substrates as a function of film thickness.[28] Predictions of the misfit dislocation model for film strength are shown for comparison.

Structure

Thin films usually show an anisotropy of their structure which is due to the fact
that the growth direction is very particular. In case of polycrystalline films,
mostly *evolutionary selection* takes place as certain grains having highest growth velocity (indicated by the arrows) overgrow the others (picture from A. van de Drift, Philips Res. Reports, Vol. 22 (1967) 267-288):
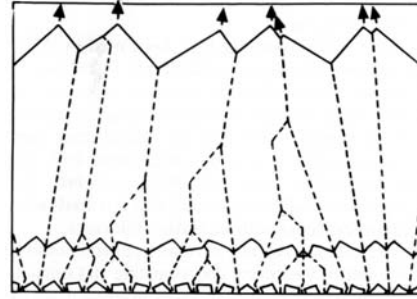
The dependence of the growth velocity on the grain orientation depends on many factors, including

-   the properties of the growing crystal itself,
-   the interaction at the growing surface (kind of adatoms, surface chemistry,...)
-   special overall conditions like temperature or <u>ion bombardment</u>.

An example for the latter is shown in the next figure (from I. PETROV et al., JVST A21, No. 5, Sept/Oct. 2003, pp. S117 – S128.)

δ-TaN films are grown by magnetron sputtering at 350 °C under a bombardment by 20 eV Ar^+ ions.

Controlling flux and energy of the ions independently, the authors varied the flux ratio of Ar^+ ions and Ta atoms, J_i/J_{Ta}, between 1.3 and 10.7, thereby leaving the ion energy unchanged.

While the ion energy was not high enough to form distinct film stress, the ion-to-neutral ratio proved to have a dramatic influence on film texture:

Films grown with high ion impact ($J_i/J_{Ta} \geq 7.4$) have a complete <002> texture, while for lower ion impact ($J_i/J_{Ta} < 6.3$) films exhibit a strong <111> texture with small volume fractions of grains having <002>, <022> and <113> orientation.
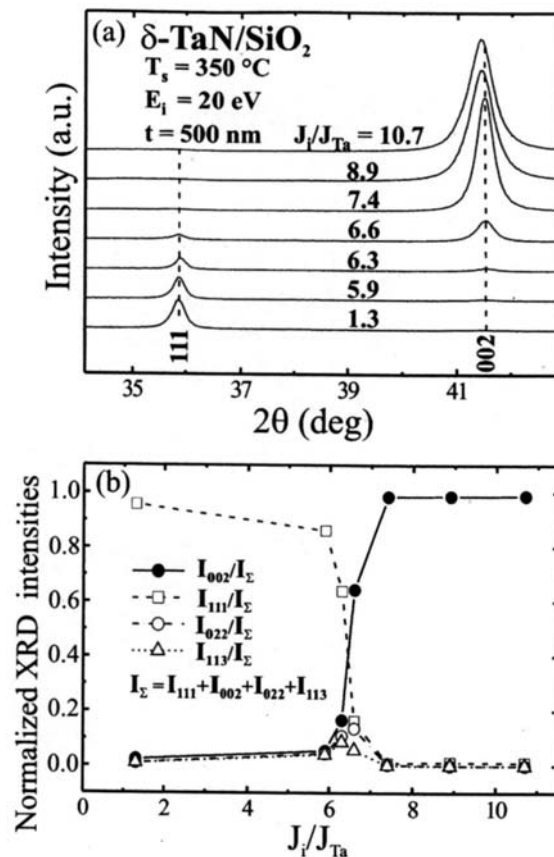
It is obvious that such an anisotropy of thin film structure (which is in fact in most cases is a transverse isotropy) has distinct influence on the mechanical behaviour of the films.

Measurement of elastic parameters using the BRILLOUIN light scattering method (cf. section 5.2.) may reveal this type of anisotropy. Then, results may be quantitatively analysed by fitting to a hexagonal model (cf. section 2.3.).

Stresses

Most thin films are under mechanical stress. Because in the direction perpendicular to the surface the material can move freely, only stresses in lateral directions occur. This is the so-called **biaxial stress state** existing in a thin film which will be discussed in more detail in section 4.2..

There are several possible **sources of stresses** in thin films, including

- cooling down from elevated deposition temperature to room temperature together with a difference in thermal expansion coefficient between film and substrate ("thermal misfit"),

- ion bombardment of the growing film,

- a film having a certain lattice constant is matched ("by force") to a somewhat different substrate lattice ("epitaxial misfit stresses"),

- volume shrinkage or expansion due to recrystallisation, phase transformation, precipitation of other phases, or similar.

Some of those sources of stress may – under appropriate conditions - also provide stress relieve. However, the most important mechanisms of stress reduction is plastic deformation.

The reasons for stress formation in thin films will be treated in section 4.4..

Effects of stresses: Stresses in thin films may

- cause elastic deformation (substrate bending, cf. section 4.2.),

- impair mechanical stability and adherence of the film, in particular when connected with edges and defects (cf. section 4.3.),

- modify film properties, or

- influence the measurement of thin films.

An example for the latter is the determination of yield strength by nanoindentation where the measured value may be largely influenced by intrinsic[1] stresses in the sample. This is explained in section 6.3..

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[1] Here we mean stresses existing in the sample without any indentation.

Film edges, flaws and other defects

Consider a homogeneous thin film that is indefinitely extended on a flat substrate. Here, indefinitely means *lateral extension >> film thickness*, so this case is realised already for usual samples with a size in the cm range. Under these circumstances, even for very high compressive or tensile stresses in the film, no shear stress components between film and substrate exist. So, the adhesion strength of this film is not challenged!

This situation is changed very much at the edge of a film, where shear stresses appear particularly at the film/substrate interface. Similarly, geometrical imperfections like little humps or depressions cause shear stresses and can give rise to detachment of the film. These problems are dealt with in some detail in section 4.3..

Moreover, due to the geometric restrictions and the usually existing stresses, any kind of defect or flaw can cause more severe effects as in bulk materials. This is shown in section 5.4. using the investigation of fracture toughness of thin films by spherical indentation as an example.

In general, the influence of geometrical restrictions (film edges) as well as flaws and other defects on the mechanical behaviour of thin films must be investigated considering the special case as general rules do not exist.

4.2. The biaxial stress state

Stress and strain in 3D[2]

A strain in a certain direction can occur

- because a stress in this direction acts, or

- because a stress acts perpendicular to that direction (negative lateral strain corr. to POISSON´s ratio).

Considering an isotropic material (E and υ having the same values in all directions), a simple derivation delivers for ε_x as an example

$$\varepsilon_x = 1/E \,[\sigma_x - \upsilon(\sigma_y + \sigma_z)], \tag{1a}$$

and analogue expressions for y and z.

Now, we apply formulas (1) to the case of a thin film lying on a flat substrate with the surface normal being the z axis. Since the material can move freely in z direction,

$$\sigma_z = 0. \tag{2a}$$

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[2] Note: The complete derivation is given at the blackboard as well as in provisional from in Appendix 4

The biaxial stress state be isotropic in the x-y plane (so-called *equal-biaxial* state), i.e.

$$\sigma_x = \sigma_y \equiv \sigma. \tag{2b}$$

From eqs. (1) and (2) we get

$$\varepsilon_x = \varepsilon_y = (1-\upsilon)/E \cdot \sigma \tag{3a}$$

and

$$\varepsilon_z = -2\upsilon/E \cdot \sigma. \tag{3b}$$

We see, that the deformation parallel to the stress direction is smaller and the strain perpendicular to the stress direction (i.e. ε_z) is bigger than in the uniaxial case (cf. eqs. (2.1.-3) and (2.1-4), resp.).

Thin film on a plate-like substrate

The derivation above applies to given stress in the film, corresponding to a film on a rigid substrate. Now, we consider a film on a non-rigid, plate-like substrate which to a certain extent follows the films stress. The behaviour of film and substrate is visualised in the figure (taken from [N]):

a.   b.

FILM UNDER RESIDUAL TENSILE STRESS   FILM UNDER RESIDUAL COMPRESSIVE STRESS
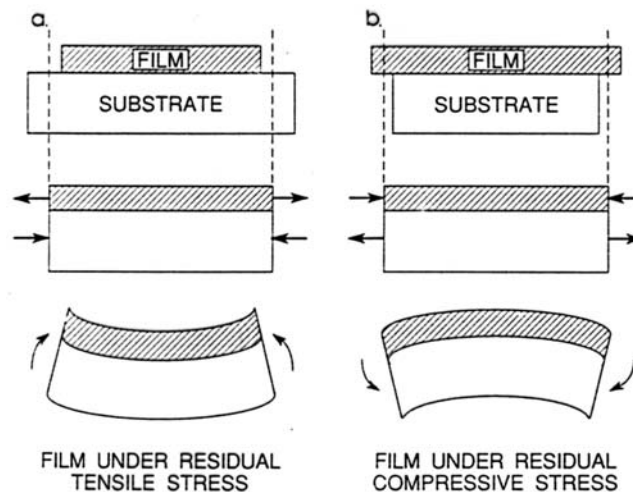
The equilibrium state of the film-substrate system is characterised by the fact that both total force and total torque be zero. Doing the simple derivation completely for

film thickness .... $t_f \ll t_s$ ... substrate thickness

one finally gets for the film stress σ_f in dependence on the radius of curvature:

$$\sigma_f = \left(\frac{E_s}{1-v_s}\right)\frac{t_s^2}{6t_f R} \tag{9}$$

This equation was published by G. G. STONEY already in 1909[3] however with YOUNG´s modulus E instead of the biaxial modulus E/(1-υ). This is because STONEY´s derivation was for a beam (1D) and not for a plate (2D).

The effect of using the biaxial modulus instead of YOUNG´s modulus is that – at a given σ_f - the deformation is smaller (i.e. R is larger) than in the 1D case because the deformation is additionally hampered by the negative lateral strain. This is the same issue as in eq. (3) where already the biaxial modulus was obtained.

STONEY´s equation is a useful tool for determination of film stresses by measuring the bending of thin flexible substrates (Si wafers or glass strips).

Important information from the derivation of STONEY´s equation includes:

- The neutral fibre of the substrate is situated at a distance of 1/3 t_s from the back-side of the substrate.

- The maximum stress σ_{max} in the substrate - which exists at the forefront of the substrate, i.e. at the interface to the film - is given by

$$\sigma_{max} = -4 \, (t_f/t_s) \, \sigma_f. \tag{*}$$

This lets one conclude that always $\sigma_{max} \ll \sigma_f$. Therefore, trying to measure film stress by analysing strain and stress in the bent substrate is not a good idea!

Another conclusion from eq. (*) is that the relief of film stress due to the substrate bending is negligible.

Bending of a an arbitrarily shaped substrate:

It was assumed in the literature that a small stripe-like substrate with

width ... b ≪ a ... length

rather curls in a cylindrical shape instead of a bowl or sphere-like deformation. Theoretical modelling[4] showed that as long as b ≫ t_s, the shape of the bent substrate again fits the surface of a sphere. This can be generalised: A substrate of constant thickness exposed to (laterally constant) film stress always deforms into a part of a sphere surface as long as its smallest dimension is large in comparison to the substrate thickness.

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[3] G. G. STONEY, Proc. Royal Soc. London, A82, 172 (1909)
[4] N. Schwarzer, F. R., Electronic Archive TU Chemnitz MONARCH, document 2006/011

Hydrostatic component of a biaxial stress state

We have seen before, that the hydrostatic stress is 1/3 of the sum of the normal stresses in any three rectangular directions:

$$\sigma_{hyd} = \sigma_{okt} = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} \qquad (3\text{-}8)$$

This is of course also true for a thin film under biaxial stress. Therefore, the film considered above (eqs. (2a), (2b)) has a hydrostatic pressure

$$\sigma_{hyd} = 2/3\ \sigma. \qquad (10)$$

Since biaxial stresses in thin films can be very big (up to about 10 GPa depending on the special case), also quite high hydrostatic stresses can occur in these films. A nice example was given by D. R. MCKENZIE[5] concerning the formation of cubic boron nitride (c-BN) thin films. It is well known that c-BN thin films are only formed when a strong bombardment by energetic ions is applied during growth. Since energetic ions cause compressive stresses (cf. section 4.4.2) it is not surprising that c-BN films always have very high stresses. On the other hand, small crystals of c-BN can be formed from hexagonal BN in a high-temperature high-pressure vessel applying a hydrostatic pressure of about 5 GPa and a temperature > 1000 °C (HPHT method). MCKENZIE et al. now drew the attention to the fact that the hydrostatic stress who is accompanying - corresponding to eq. (10) - the biaxial stress in the c-BN films is of the same magnitude as the stress in the HPHT vessel. They found that the percentage of c-BN in the films showed a sudden increase at about 4 – 5 GPa which is in good agreement with the pressure applied in the HPHT technique:
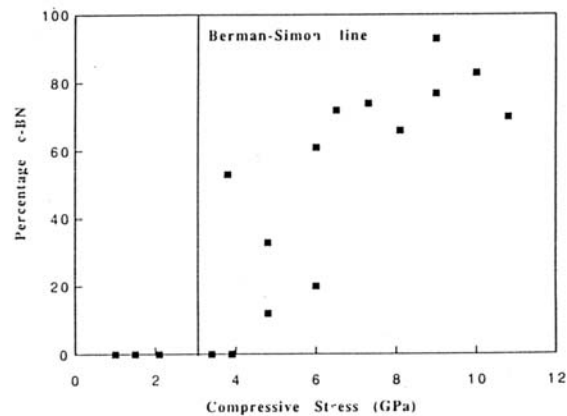
The much lower temperature in the "thin film case" is not a strong argument against their reasoning since it is known that energetic ions, excited plasma parti-

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[5] D. R. MCKENZIE et al., Diamond Rel. Mater. 2 (21993) pp. 970

cles or similar can activate reactions in a non-thermal way at low temperatures where those reactions would never occur under pure thermal activation.

## 4.3. Manifestations of film stresses

In this chapter we will give an overview of stresses in thin films, how they appear and what effects they have under certain circumstances. First, we have to consider that the homogeneous stress considered so far is an idealisation. Most materials are not homogeneous – they consist, for instance, of individual crystal grains – and therefore also the stress is not homogeneous. Three types of intrinsic stresses are to be discriminated:

-   macroscopic stresses (*Spannungen 1. Art*),

-   stresses acting with single grains (*Spannungen 2. Art*),

-   stresses acting at minor defects within a grain (*Spannungen 3. Art*).

This is illustrated in the picture form the PhD thesis of ANDREAS EHRLICH:
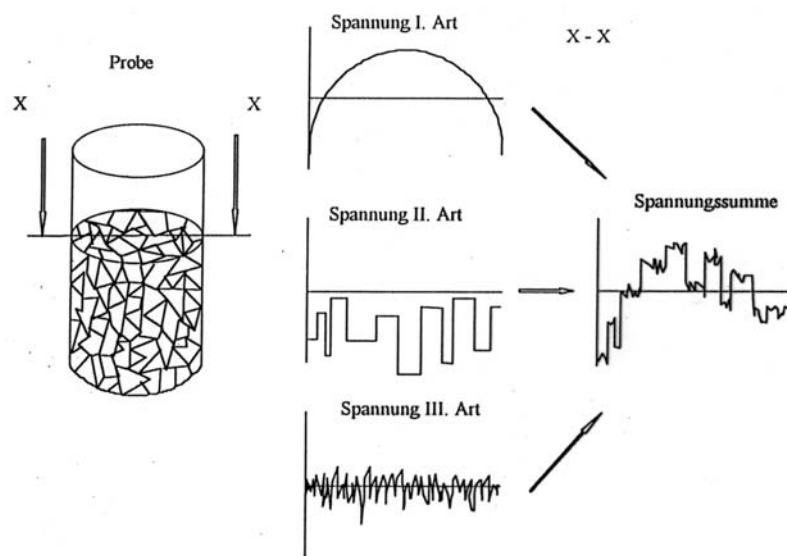
What we have discussed so far are macroscopic stresses. The following picture (from J. MICHLER et al., J. Appl. Phys. 83(1998) pp. 193) shows *Spannungen 2. Art* in a diamond film. Please pay attention to the fact that even the character of the stress (tensile vs. compressive) is changing from one grain to another!
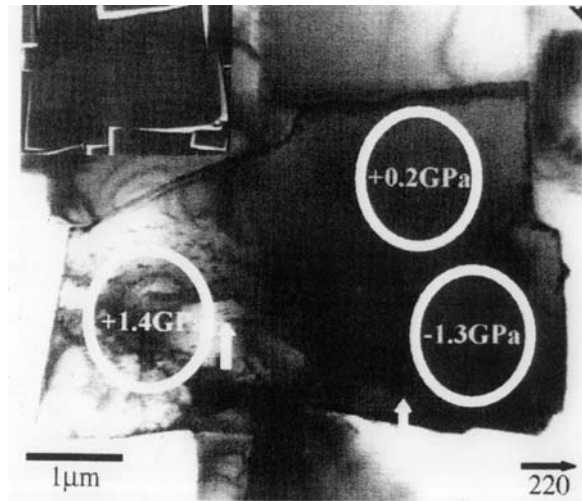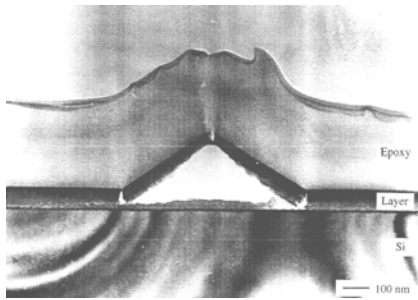
One of the most remarkable effect of stresses is debonding of films or – in more severe cases – cracking of film and/or substrate. Debonding is illustrated in the following graph (from [A]):
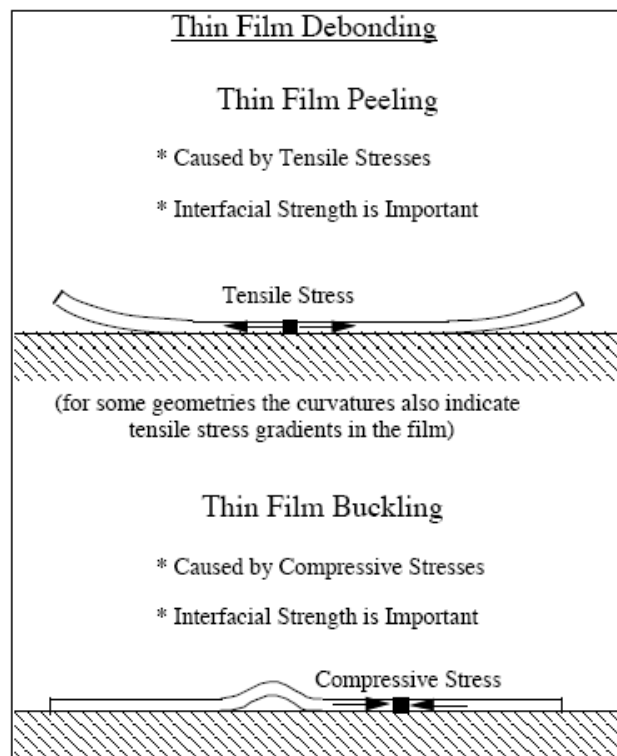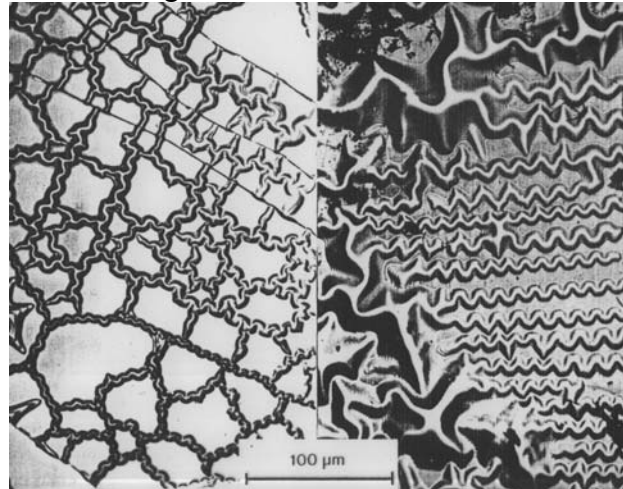
In the next figures one example from our work for either effect is given:

| debonding of a c-BN film	stress relief pattern in a-C:H films
on silicon	on glass on silicon

(cross-section TEM from M. RÖDER)

As already mentioned, in case of a *perfect film on a perfect substrate* even very high biaxial stresses would <u>not</u> cause delamination. Biaxial stresses is only a necessary but not a sufficient condition for that. Debonding necessitates also the existence of inhomogeneities in the stress field. A few examples are shown in the following picture (from S. HOGMARK, TU BAF #287, p. 38):
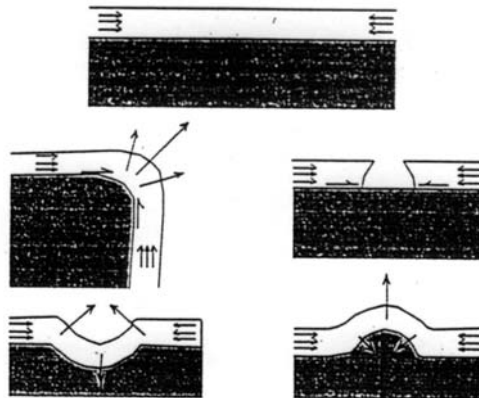
Stresses may also be utilized for certain purposes. As an example, the next pictures show a micro spring formed using intentionally stressed metal films (from D. L. SMITH et al., Proc. 1996 Electr. Comp. and Technol. Conf., pp. 1069 (p.t.o.).
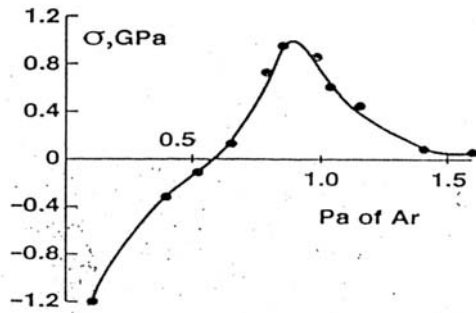
Fig. 1. Intrinsic stress vs Ar pressure for DC magnetron sputtering of 80-20 Mo-Cr alloy (by weight). The exact shape of the curve changes with sputtering conditions and material, but this general behavior is characteristic of metal sputtering. [1, 2]
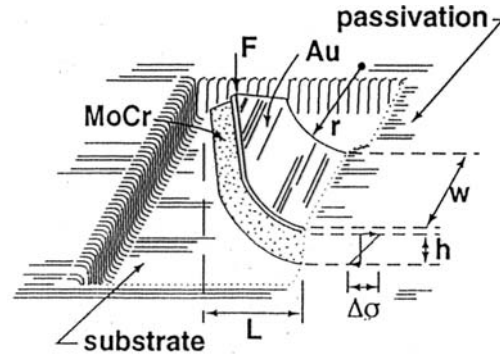

Fig. 2. Perspective view of spring finger, showing released and stress-relaxed cantilever portion within passivation window area and showing anchored portion to the right.

A most important role for stresses play the edges of a film. In the following an FEM calculation[6] of a structure is shown with the following data:

A film 1 μm thick lies on a 7 μm thick substrate. The width of both is 20 μm. In the third direction (y direction) the structure is infinite, i.e. the calculation was a 2D. The backside of the substrate is fixed and the cell size was 1/8 μm in each direction.

Both film and substrate have a YOUNG´s modulus of 500 GPa and a POISSON´s ratio of 0.3. In the flat starting state the film was given a compressive strain of 0.01 both in x and z direction and then allowed to relax.

After relaxation, the film surface is bowed out and the left and right boundaries (at about ± 10 μm) show a nonlinear shape.
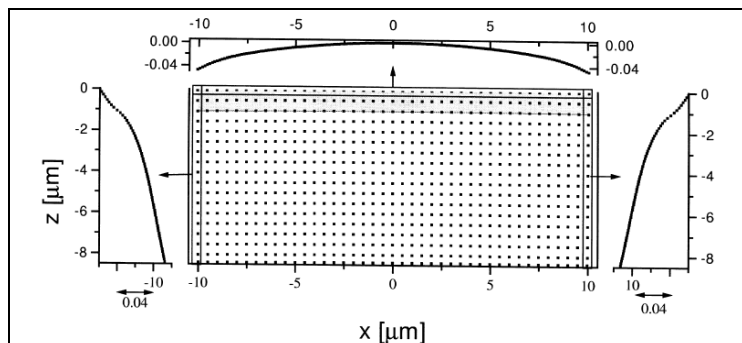

After relaxation shear stress exists in the sample. The maximum shear stress is situated in the film-substrate interface close to the edges (cf. left fig. below) and has a magnitude of about 1 GPa.

In another calculation, a gradient layer beneath the film was considered which was approximated by two layers each 0.5 μm thick. The substrate was again 7.5 μm thick so the whole structure was 1 μm thicker. The two layers was given a stress

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[6] C. SPAETH, M. KÜHN, T. CHUDOBA, F. RICHTER, Surf. Coat. Technol. 112(1999) pp. 140

which provided a stepwise transition from the film stress in the starting state to the zero substrate stress. This measure yields a remarkable reduction of the shear stress maxima to about one half (cf. right figure):
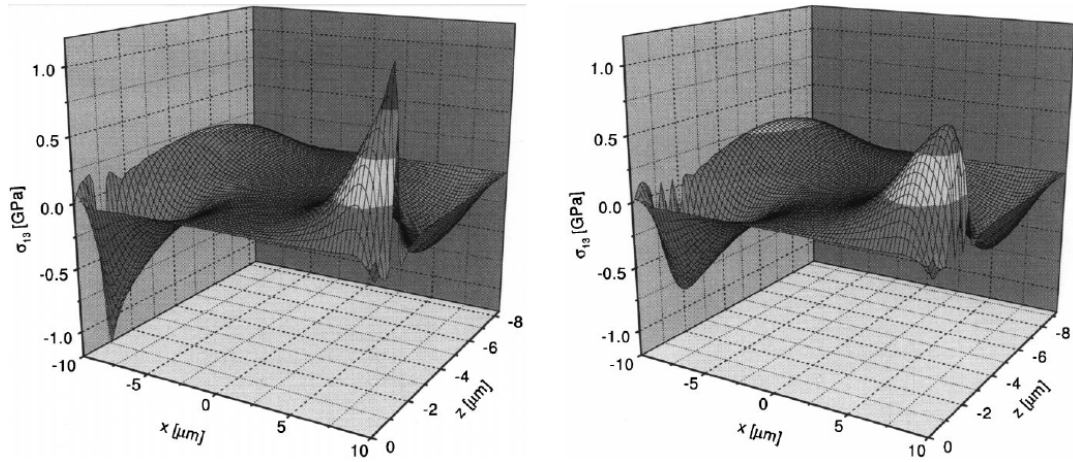
Another important effect of stresses is influencing film properties.

Example: Dependence of the IR-TO peak (so called *Reststahlenbande*) at about 1055 cm^{-1} on the film stress. This can be used to estimate the stress according to

ω_{TO} =1054.7+3.39 p_{hyd}/GPa.
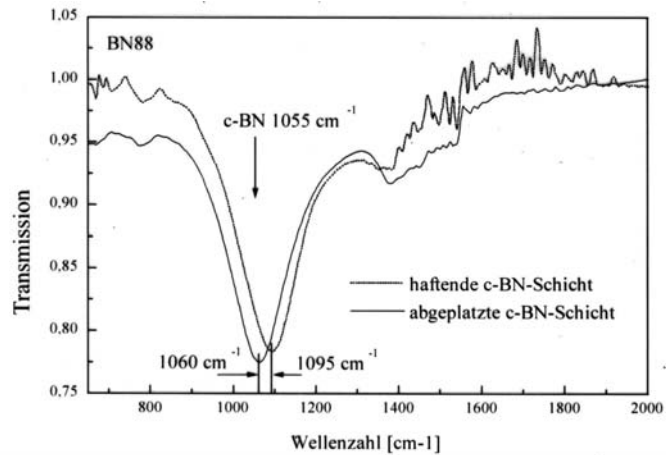
4.4. Sources of film stresses

We start with a wise statement given by M. F. DOERNER and W. D. NIX in 1998:

"Stresses in thin films on substrates are produced by processes
which would cause the dimension of the film to change
if it were not attached to the substrate"

All these stresses we will call intrinsic stresses, in contrast to stresses applied from outside, for instance by external bending of the substrate or by application of an indenter.
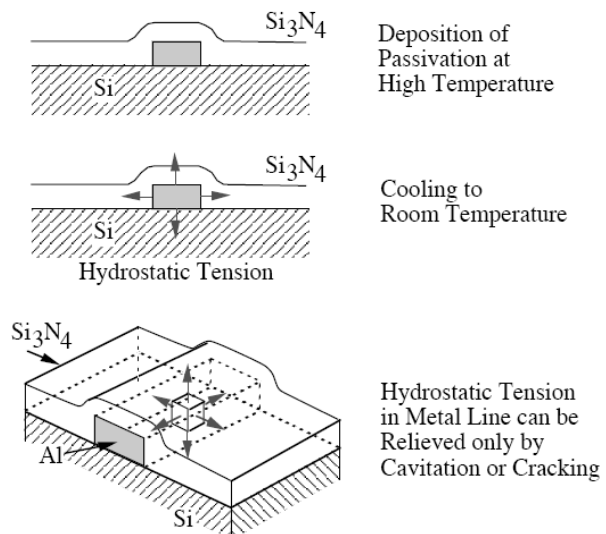
Thermal stresses

Thermal stress occur due to cooling the film down from growth temperature to room temperature. The thermal misfit strain formed this way is

$$\varepsilon_{tm} = (\alpha_f - \alpha_s) \cdot \Delta T \tag{12}$$

Estimation of the magnitude of thermal stresses: Linear thermal expansion coefficients vary a lot (cf. table in script 1+2, p.20): While many metals have a coefficient of $(10\text{-}20) \cdot 10^{-6} K^{-1}$ or more (Al: $23{,}1 \cdot 10^{-6} K^{-1}$), non-metals including semiconductors and insulators have frequently only a few times $10^{-6} K^{-1}$ (Si: $2{,}6 \cdot 10^{-6} K^{-1}$). So, a difference $\Delta\alpha = 10 \cdot 10^{-6} K^{-1}$ can readily exist. The temperature for film growth and treatment is usually several 100 °C, hence we get a ε_{tm} of several 10^{-3}. Considering a YOUNG´s modulus in the order of magnitude of 100 GPa we obtain a **thermal stress of several 100 MPa!**

NIX shows in [A] how in this manner hydrostatic tension can be formed in metal lines of an integrated circuit.

The hydrostatic tension gives rise to processes which weaken the metal line and make it sensitive to electromigration.

Deposition of Passivation at High Temperature

Cooling to Room Temperature

Hydrostatic Tension in Metal Line can be Relieved only by Cavitation or Cracking

Thermal stresses are usually connected with plastic deformation, which is shown in the next figure:
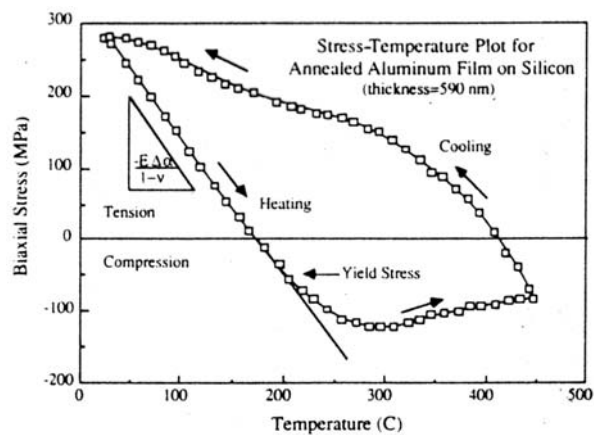
We see the following stages during the T(t) cycle:

a) Reduction of the tensile stress in the Al due to the thermal misfit,
b) onset of plastic deformation at a certain level of tensile stress. Be aware that the yield stress marked in the figure is σ_0 @ 200 °C!
c) After that point, thermal misfit tries to increase the tensile stress while the steadily reducing yield stress acts towards reduction of stress by plastic deformation.
d) During cooling down from 450°C, $\Delta\sigma/\Delta T$ is at first constant (corresponding to elastic behaviour), then decreases steadily corresponding to the increasing yield strength.

Epitaxial stresses

We speak about heteroepitaxy, i.e. the growth of a material B on a different material A. If there is a certain similarity (in terms of crystal symmetry, lattice constant and chemical bonds), nevertheless epitaxial growth is possible. Usually, at the beginning the film is forced to grow in the lattice of the substrate (pseudomorphic growth) which is connected with the formation of stresses in the film:
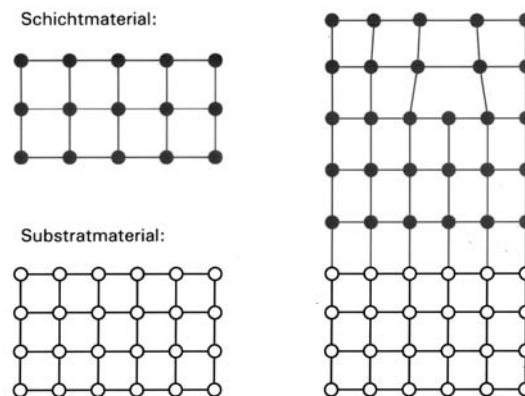
After a certain critical thickness value has been reached, a further increase of the elastic strain energy is prevented by the formation of edge dislocations (called misfit dislocations).

Stresses due to surface energies

These stresses are also called *intrinsic stresses in the narrower sense* or *growth stresses*. They are due to the fact that every surface or interface represents an additional energy per unit area.

Usually, this kind of problems is explained taking the surface of a liquid as an example (cf. the phenomenon of capillarity). However, the same acts for solids. Not only in a small droplet but also in a small crystal the pressure is increased!

It comes out (cf. [A]) that in a spherical solid of radius r having the surface stress f_s the inner pressure is

$$p = \frac{2f_s}{r} \tag{13}$$

If the solid is a crystal this causes a reduction of the lattice constant, a. It comes out that

$$\frac{\Delta a}{a} = -\left(\frac{2K}{3}\right)\frac{f_s}{r} \tag{14}$$

(Here, K is not the bulk modulus but it reciprocal, the compressibility of the particle!) - This effect was investigated by J.S. VERMAAK et al. who measured the lattice constant of tiny gold crystals in dependence on their size and found indeed a 1/r dependence on the crystal radius:
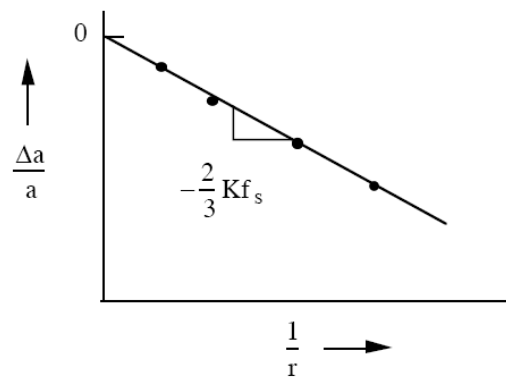
From the measurement they got for the surface tension of gold f_s = 1,175 N/m.

Another effect of the surfaces and interfaces is that – due to the surface tension – any surface wants to contract. If surface tensions f_0, f_1 and f_2 are similar, the coated substrate will be bent concavely because $f_1 + f_2 > f_0$:
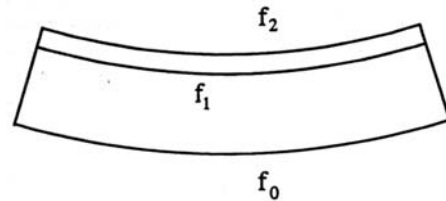
Of course, this effect is very weak and will usually be superimposed by others. However, in case of a multilayer with very thin single layers this effect may become important.

In [A] an example is given: In a multilayer consisting of single layers with thickness h and interface tension f, an *effective biaxial stress* σ is formed corresponding to

$$|\sigma| = f / h \tag{15}$$

Taking f = 1 N/m = 1 J/m^2 (similar to the gold value above!) one gets for

$$h = 1\ \mu m \qquad \rightarrow \qquad |\sigma| = 1\ \text{MPa}$$
$$h = 100\text{Å} = 10^{-2}\ \mu m \qquad \rightarrow \qquad |\sigma| = 100\ \text{MPa}.$$

The latter is a quite remarkable stress!

The multilayer will be bent concavely which looks like tensile stress in the film. However, the bending is due to the interfaces only, and the material in the multi-layer is under biaxial compression!

Stresses related to film growth conditions

First, we have to consider how thin films grow.

"Ordinary" thin films (which do not grow under perfect conditions on a perfect single crystal substrate) exhibit

- 3D nucleation, followed by

- island growth, followed by

- coalescence of islands.

The example shows the growth of a Ag film on (111) NaCl (picture from R. W. VOOK, Int. Metals Rev. 27, 209(1982)). The nominal film thickness is given together with ED diffraction and plan view EM picture.
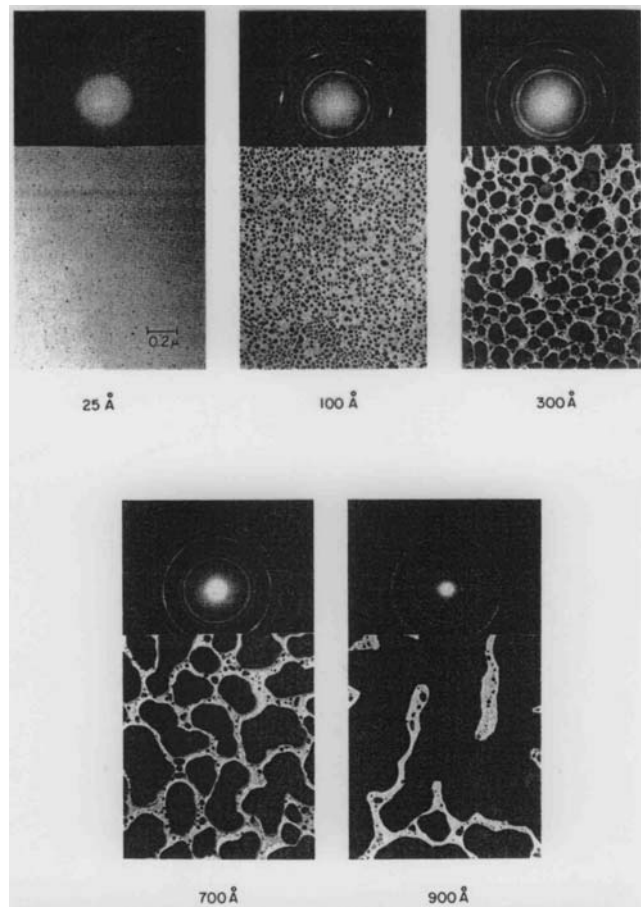
Each film growth is a complicated interplay of material properties, process conditions (particle fluxes, particle energies, impurities, etc.), and temperature. Therefore, only few quite **general statements** can be made.

**First rule:** Coalescence of islands tends to cause tensile stress which then gradually reduces with increasing film thickness.

explanation by W. D. NIX ([A]):	experiment by M. JANDA et al.[7]
For energetic reasons the crystallites snap together as soon as they get in contact. Since they are already "anchored" at the substrate, tensile stress is formed.	
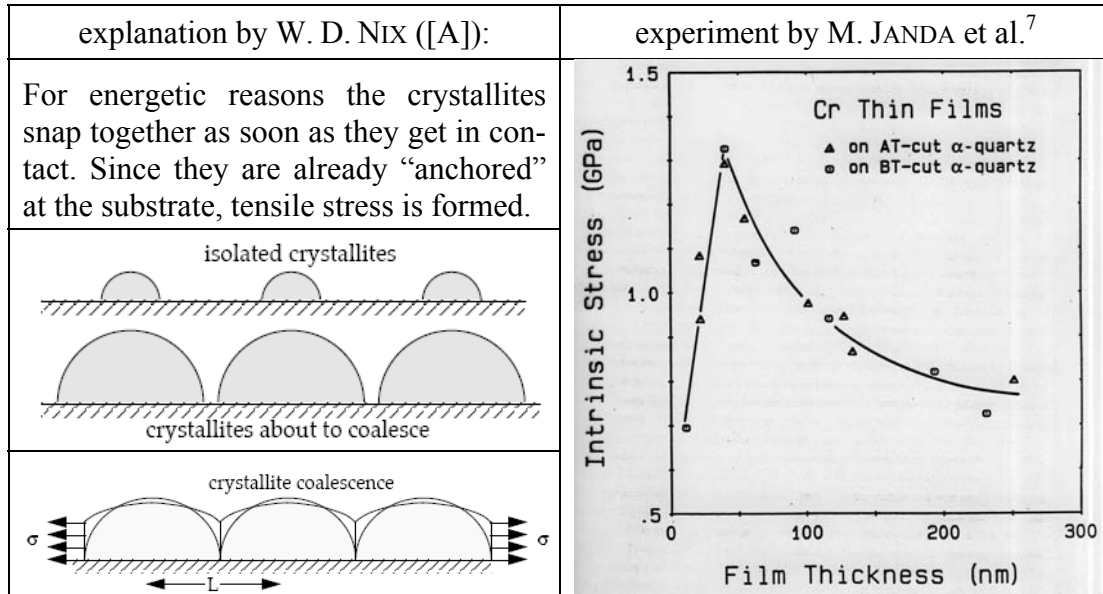
The stress in thicker films depends on film structure which on its part depends on the deposition conditions as shown in the famous THORNTON diagram:
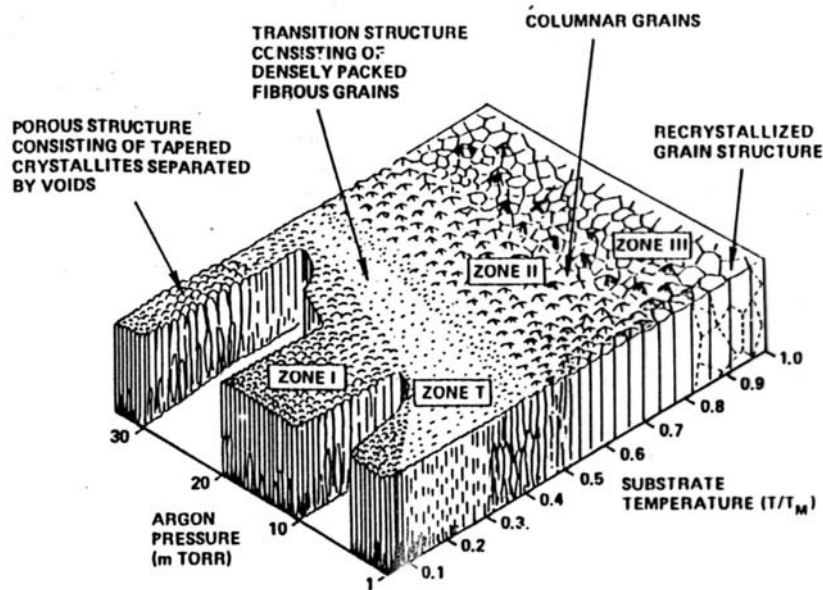
The THORNTON diagram[8] is represents a very universal picture of the structure of vapour grown films in dependence on gas pressure and substrate temperature. The

[7] M. JANDA and O. STEFAN, Thin Solid Films 112 (1984) 127
[8] J. A. THORNTON, J. Vac. Sci. Technol. A11 (1974) pp. 666

temperature is given as the so-called homologous temperature, T/T_m, with T_m being the melting temperature. The gas pressure represents the energy of the particles hitting the growing film: the lower the pressure the higher the particle energy.

The THORNTON diagram proved to be adequate for many different film materials, including reactive and non reactive processes.

THORNTON discriminates four structure zones:

Zone 1:   tapered crystals, separated by voids,

Zone T: tightly packed fibrous grains which generally do not extent through the coating thickness,

Zone 2:   columnar grains which extent through the coating thickness,

Zone 3:   grains are more or less equiaxed (rather than columnar) due to re-cristallisation.

When a deposition process is performed at several tenths of T_m, the film structure changes form Zone 1 into Zone T with increasing particle energy. Zone 1 consists of grains separated by small voids. The grains attract each other by VAN DER WAALS forces, therefore these films have tensile stresses. Zone T films are already quite dense and get increasing compressive stress with increasing particle energy and reduced pressure, resp..
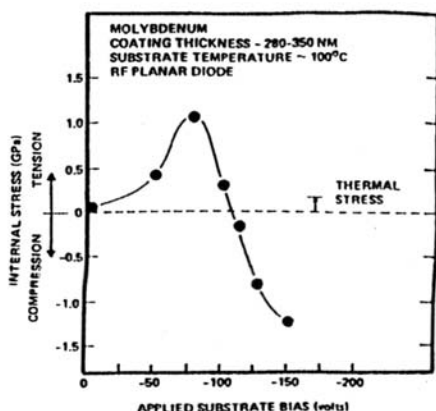

Figure 6.8. Variation of intrinsic stress with substrate bias. From J.A. Thornton, Semiconductor Materials and Process Technology Handbook, Noyes, Park Ridge, NJ, 1988, 329. ©1988. Noyes Publications. With permission.
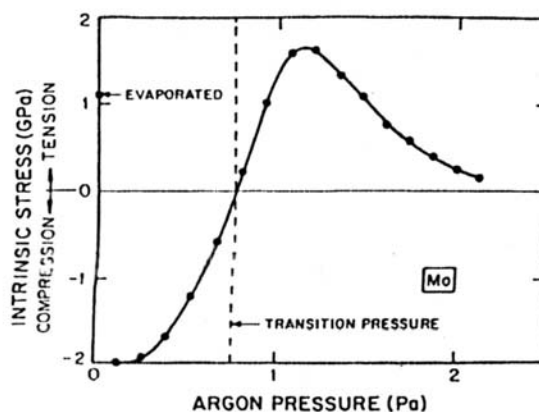
Figure 6.9. Intrinsic stress dependence on Argon pressure. From D.W. Hoffman and R.C. McCune, Handbook of Plasma Processing Technology, Noyes, Park Ridge, NJ, 1990, 483. ©1990. Noyes Publications. With permission.

So we have a **second rule:** Films grown at low particle energy have tensile stress while under high energy particle impact films with compressive stress are formed.

This is illustrated by the two figures above. Both of them show that at low particle energy tensile stressed films (Zone 1) and with higher energy films with compres-

sive stress (Zone T structure) are formed. The only difference is that in the left picture the particle energy is characterised by the substrate bias voltage while in the right figure the gas pressure is given at the abscissa. One can say that the two figures have mirror symmetry.

Third rule: <u>When the particle energy is increased further, films get even more dense.</u> At particle energies above few dozens eV, atomic cascades are formed which drive excess material into the film. This causes the mass density to increase but also some incorporation of gas atoms:

Increase of the mass density of sputtered Ta films with increasing substrate bias voltage:
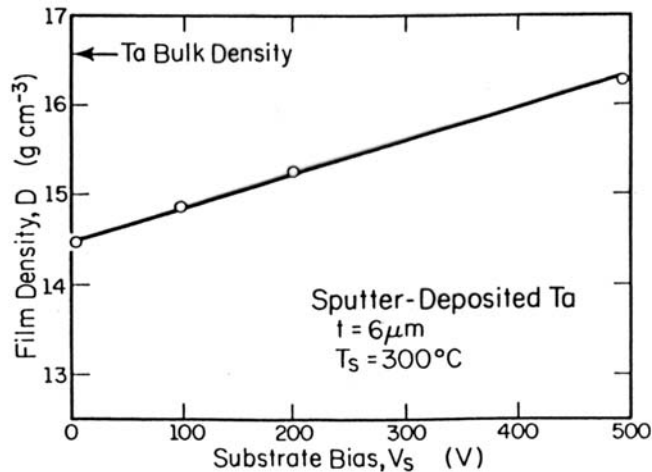
Incorporation of Ar atoms can be as high as a few at.-percent, however does not show a correlation with the measured strain in the film:
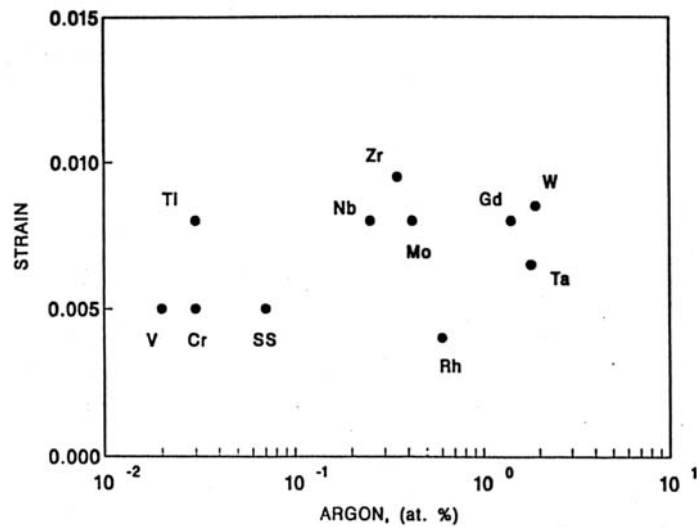
Compressive stress and high mass density are an advantage for many applications. In particular the reader should remember the fact that compressive stresses may prevent brittle fracture. This is particularly important for hard coatings.
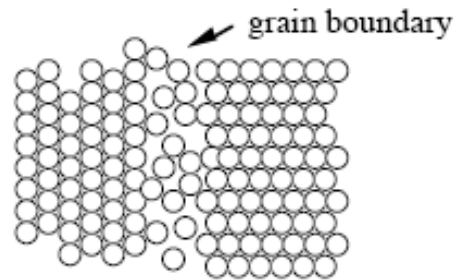
Equilibrium vs. non-equilibrium:

Usually, thin films grow far from equilibrium. Therefore, many structural features appear which would be absent under equilibrium conditions. Examples for that are amorphous phases, mixed crystals, grain boundaries, or excess point defects. This non equilibrium structure is more or less "frozen-in" when the film is cooled down from growth temperature.

However, it may happen that the film changes its structure towards the equilibrium state. This can be due to heat treatment after the growth process, but also due to annealing during the growth, particularly of those parts of the film which have been grown first.

This structural transition (coalescence of grains, out-diffusion of excess vacancies, etc.) leads to a densification of the film which is insofar similar to the densification due to energetic particle impact. However, this time the densification is not driven by material coming from outside but takes place via rearrangement of existing material. Therefore, the effect is different: The rearrangement makes the film locally denser, but at the same time tensile stress is formed because there is not enough material to fill the original volume with the dense, equilibrium-like structure.

The issue is illustrated with the figure at the right (from [A]) showing that a grain boundary – when compared to the perfect crystal lattice – corresponds to approximately one missing monolayer of atoms.

grain boundary

This brings us to the **forth rule:** <u>During transition from non equilibrium to equilibrium structure, usually tensile stresses are formed.</u>

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[B] MELVIN M. EISENSTADT, Introduction to Mechanical Properties of Materials, Macmillan, New York and London, 1971.

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[F] H.G. HAHN, Elastizitätstheorie, B.G. Teubner, Stuttgart 1985.

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[H] Cd from http://www.doitpoms.ac.uk/tlplib/miller_indices/images/cadmium%20slip.jpg
Al from http://www.univie.ac.at/hochleistungsmaterialien/mikrokrist/characterization.htm

[I] Cu from http://www.tms.org/Meetings/Annual-08/images/AM08educ_clip_image002.jpg
Au from http://www.imechanica.org/node/679

[J] http://www.fiu.edu/~thompsop/liberty/photos/fractures.html

[K] http://chaos.ph.utexas.edu/%7Emarder/fracture/phystoday/how_things_break/how_things_break.html

[L] G. Gottstein, Physikalische Grundlagen der Materialkunde, Springer Vlg., 2001.

[M] Yip-Wah Chung, Introduction to Materials Science and Engineering, CRC Press, Boca Raton, FL, USA, 2007.

[N] M. Ohring, The Material Science of Thin Films, Academic Press, 1992

Appendix 4: Complete derivation from section 4.2.

(1) Simple derivation for thermal strain in 3D:

- We consider an isotropic material, i.e. E and ν the same for all directions.

- The co-ordinate system used is the principal axes system.[+)]

- A strain ε in a certain direction may occur
  - because a stress in this direction acts, or
  - because a stress acts perpendicular to this direction (negative lateral strain, Poisson's ratio!)

$$\sigma_x \nearrow \quad \varepsilon_x^{(1)} = \frac{\sigma_x}{E} \quad AND \quad \varepsilon_y^{(1)} = \varepsilon_z^{(1)} = -\nu\,\varepsilon_x^{(1)} = -\nu\,\frac{\sigma_x}{E}$$
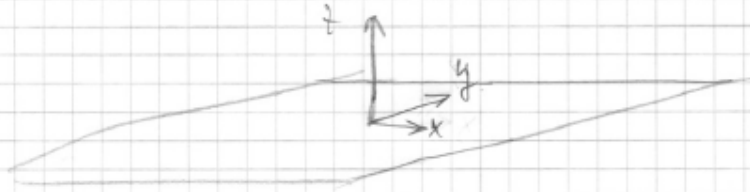
$$\sigma_y \nearrow \quad \varepsilon_y^{(2)} = \frac{\sigma_y}{E} \quad AND \quad \varepsilon_x^{(2)} = \varepsilon_z^{(2)} = -\nu\,\varepsilon_y^{(2)} = -\nu\cdot\frac{\sigma_y}{E}$$

$$\sigma_z \nearrow \quad \varepsilon_z^{(3)} = \frac{\sigma_z}{E} \quad AND \quad \varepsilon_x^{(3)} = \varepsilon_y^{(3)} = -\nu\,\varepsilon_z^{(3)} = -\nu\,\frac{\sigma_z}{E}$$

Because of the superposition of strains, $\varepsilon_x = \varepsilon_x^{(1)} + \varepsilon_x^{(2)} + \varepsilon_x^{(3)}$, etc.

$$\varepsilon_x = \frac{1}{E}\left[\sigma_x - \nu(\sigma_y + \sigma_z)\right]$$

$$\varepsilon_y = \frac{1}{E}\left[\sigma_y - \nu(\sigma_x + \sigma_z)\right] \qquad (1)$$

$$\varepsilon_z = \frac{1}{E}\left[\sigma_z - \nu(\sigma_x + \sigma_y)\right]$$

+) This doesn't bring any restrictions in the considered case
(In the biaxial stress state one principal axis is $\perp$ to the plane!)

— Now, we consider a thin film lying in the x–y–plane.

• because the material can freely move in z direction, $\sigma_z = 0$

• The stress state be isotropic in the x–y–plane (equal–biaxial state), i.e.

$$\sigma_x = \sigma_y \equiv \sigma \qquad (2)$$

From (1) and (2) we get

$$\left. \begin{array}{l} \varepsilon_x = \varepsilon_y = \dfrac{1-\nu}{E} \cdot \sigma \\[4mm] \varepsilon_z = -\dfrac{2\nu}{E} \cdot \sigma \end{array} \right\} \qquad (3)$$

Comments:

— Deformation $\parallel \sigma$ is smaller than in the uniaxial case (influence of $1-\nu$!)

— Material is "side stepping" in z direction, e.g. gets thicker in case of compressive stress.
The lateral strain is bigger than in the uniaxial case (2ν) !

(2) Thin film on a plate - like substrate:

The derivation so far was for given stresses. Now we consider a non rigid, plate - like substrate which — to a certain extent — follows the film stress:

FILM UNDER RESIDUAL
TENSILE STRESS

FILM UNDER RESIDUAL
COMPRESSIVE STRESS
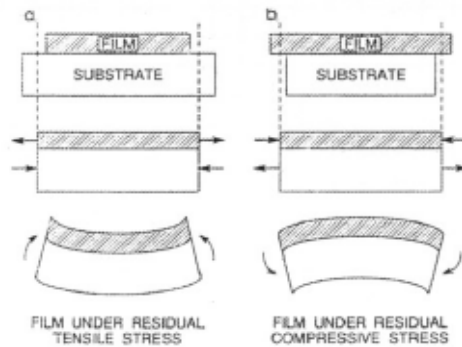
stress in the film $\longrightarrow$ stress in the substrate

bending of substrate + film

The equilibrium is characterised by

cross-section area
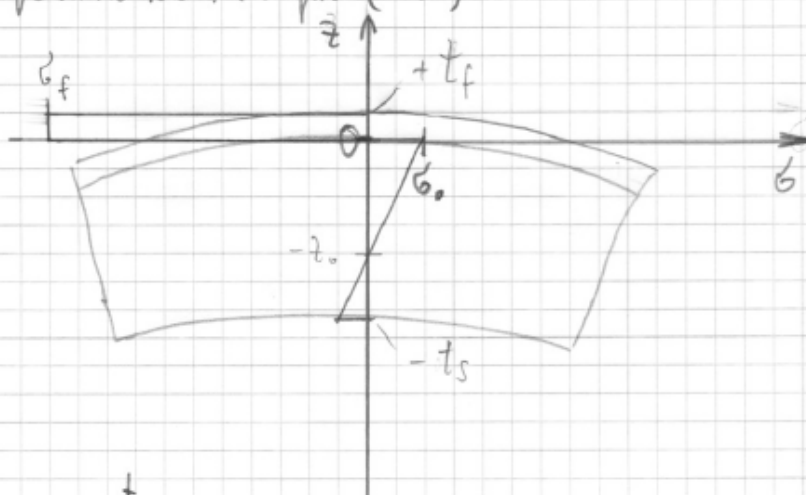
total force ... $F = \int \sigma \, dA = 0$, and $\qquad$ (4)

$\sigma(z)$ in film and substrate, resp.

total torque ... $M = \int \sigma \cdot z \cdot dA = 0$ $\qquad$ (5)

length of lever

quantitative analysis (10):

– since $t_f \ll t_s$ we set $\sigma_f = const \neq f(t)$

we set further

$$\sigma_s(t) = \frac{t + t_0}{z_0} \cdot \sigma_0$$

width

$$F = b \int_{-t_s}^{+t_f} \sigma(t)\, dt = 0 \tag{4'}$$

apostrophe or „dash"

$$M = b \int_{-t_s}^{t_f} z \cdot \sigma(t)\, dt = 0 \tag{5'}$$

Solutions for $t_f \ll t_s$: $\quad t_0 = \frac{2}{3} t_s \tag{6}$

$$\sigma_0 = -\frac{4\, t_f}{t_s} \sigma_f \tag{7}$$

Discussion:

(6) $\curvearrowright$ neutral fiber at $\frac{1}{3} \big| \frac{2}{3}$

(7) $\curvearrowright$ because of $t_f \ll t_s$, $|\sigma_0| \ll |\sigma_f|$! $\Rightarrow$ (weak prop)

→ it follows: • $E_{substrate}$ very small even at the interface

(No σ_f measurement thus $E_{substrate}$ analysis possible)

• relaxation ($=\sigma_f$ reduction due to substrate bending)
can be neglected.

Interrelation of σ_f and radius of curvature, R:

$S \ldots$ arc length

$z_0 = \frac{2}{3} t_s$
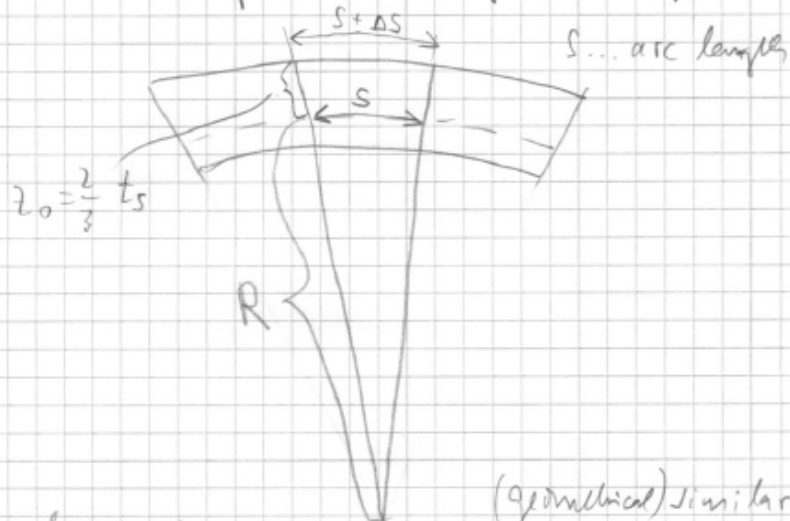
Simple geometry:

$$\frac{S}{R} = \frac{S + \Delta S}{R + \frac{2}{3} t_s}$$

(geometrical) Similarity

Strain at the substrate

$$\Delta S = S \cdot (\varepsilon_0) = S \cdot \frac{\sigma_0}{E_s}$$

$$\frac{S}{R} = \frac{S\left(1 + \frac{\sigma_0}{E_s}\right)}{R + \frac{2}{3} t_s}$$

because of

$\longleftarrow$ (7)

$$\sigma_f = \frac{t_s^2 \cdot E_s}{6 R \cdot t_f} \qquad (8)$$

Stoney's equation

- Stoney's equation (G.G. STONEY, Proc. Royal Soc. London A 82, 172 (1909)) _Radius_

was derived in form of eq. (8) for a (beam).

- To generalize it for a plate, we have to replace E_s

by $\dfrac{E_s}{1 - \nu_s}$ ... plate modulus

→ Stoney's eq. as it is used today

$$\sigma_f = \frac{1}{6R} \frac{E_s \cdot t_s^2}{(1 - \nu_s)\, t_f} \qquad (9)$$

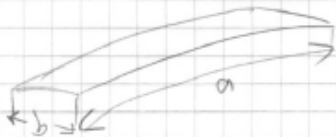Comment: Using $\dfrac{E_s}{1 - \nu_s}$ instead of E_s means that the deformation

(which is proportional to the curvature which is equal to $\frac{1}{R}$) is reduced: $\dfrac{1}{R}$ = bending (Krümmung)

$$\text{deformation} \propto \frac{1}{R} \propto \frac{1 - \nu_s}{E_s} \cdot \sigma_f \quad !$$

This is physically the same as we have already found in eq. (3). (= additional hampering of elastic deformation due to the negative lateral strain)

Bending of a small stripe ($b \ll a$): As long as $b \gg t_s$,

the shape of the substrate fits again to the surface of a sphere.

$(NS + F.Si, Monarch, 2006/011)$