Tensile stress in hard metal films

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Thin films on substrates are usually in a stressed state. An important, but trivial, contribution to that stress stems from the difference in thermal expansion coefficient of substrate and film. The resulting stress is called extrinsic stress. This stress may either be tensile or compressive. Intrinsic stress is the name for stress due to defects, microstructure, or lattice mismatch between film and substrate. Intrinsic compressive stress is caused by ion peening, forcefully introducing defects in the growing film. Intrinsic tensile stress in fcc metal films has been interpreted successfully by Doljack and Hoffman in 1972. Those relatively soft films exhibit grain growth during deposition. This leads to films with a microstructure consisting of more or less equiaxed grains with grain size about equal to the film thickness (h). Doljack and Hoffman explained the tensile stress by realizing that tensile stress is generated at the grain boundaries. The grain boundaries shrink over a distance Δ, a fraction of the atomic spacing. This gives rise to an elastic strain Δ/h and thus to a stress of ΔEY/(1-ν)h, with EY as Young’s modulus and ν as Poisson’s ratio. Doljack and Hoffman found for nickel a grain boundary shrinkage of 0.3 times the interatomic distance. They explicitly state that the film is recrystallized; the growth history is not reflected in the stress. Only the final structure is responsible for the stress.

This great result for deformable fcc metals, however, did not proliferate in understanding stress development in hard bcc films like chromium or tungsten. Here phenomenological Hall–Petch type models, based on film thickness and plastic deformation erroneously predicted square root dependence of stress on thickness. By combining the 30 year old grain boundary shrinkage model, modern grain growth models for nonrecrystallizing films and accurate stress gradient measurements we show that stress and grainsize codevelop in hard polycrystalline metal films.

Intrinsic tensile stress in bcc polycrystalline films until now defied a satisfactory explanation. It was, however, noted that both for bcc metals as well as for fcc metals the stress in thicker films is less than the stress in thinner films, all other things being equal. For bcc polycrystalline films we assume that at each height in the film stress is generated at the moment of deposition and that the stress at that height in the film is preserved during further growth of the film. In order to test this hypothesis we deposited a 1.1 μm Cr film on a Si wafer and etched the Cr film back in a number of steps.

We employ the wafer curvature method to measure the stress in the thin film. Two parallel HeNe laser beams 40 mm apart fall on the Si wafer. After traveling 10 m the distance between the two beams is measured. The measuring accuracy is 0.1 mm. Each measurement is preceded by a measurement on an optical flat mirror to correct for thermal induced nonparralelism of the laser beams. All wafers have been measured before and after deposition. In wafer curvature measurements the moment exerted by the film on the wafer is determined.

\[ \int_0^{t_f} \sigma_j(z)dz = \frac{E_s t_s^2}{6(1-\nu)R}. \]  

In Eq. (1), the Stoney equation for a film with a stress gradient over the thickness of the film, the subscript f indicates the film and subscript s indicates the substrate. R is the radius of the curved wafer. From a wafer curvature measurement on a single film a stress gradient cannot be determined. Such a measurement will yield an average stress

\[ \sigma_f^{av} = \frac{1}{t_f} \int_0^{t_f} \sigma_j(z)dz. \]  

However, from a series of measurements on films with increasing thickness a gradient will be clear. Wafer curvature has the advantage over x ray for measurements on films with a gradient in the stress over the thickness of the film since the stress is integrated over the thickness. X-ray diffraction...
stress measurements on films with a stress gradient will lead to broadened peaks and not only to shifted peaks, making the interpretation very difficult.

An initial deposition was done in a Hauzer HC 750 sputter deposition machine laid out to coat three-dimensional objects, rather than planar substrates, such as Si wafers. The deposition pressure was 0.3 Pa, the distance from target to substrate was 25 cm. We etched this wafer back in steps in order to observe the stress evolution over the thickness of the film. The etching was done in a 50% diluted Merck selectipur chromium etch solution. Grain boundary grooving while etching was prevented by not stirring the solution. We measured the film thickness by weight loss and the stress by wafer curvature. In Fig. 1 the results are presented. The data presented here are the average stress at each thickness as follows from Eqs. (1) and (2). Both the deposition as well as the etchback resulted in some nonuniformity over the wafer. The data in Fig. 1 therefore will contain some systematic error but the trend is clear. By etching back the film the average stress in the film increases. This experiment proves the existence of a stress gradient in the film.

In order to attain optimal control over the deposition process, we took recourse to a parallel plate reactor, designed for wafer processing for further experiments: Leybold Heraeus Z 550. Deposition pressure was 2 Pa, target to substrate distance was 4 cm. 100 mm Si (111) wafers were used as substrate. In Fig. 2 the stress measurements on a series of Cr films with thickness ranging from 40 nm to 6 μm are presented. Again the average stress is plotted. The thickness of the films was 10% larger in the center than at the edges. At each thickness the average stress was measured. The stress exhibits a powerlaw dependence on the thickness of the film. From a fit to the data we find a power $p = -0.57$ and an intercept with the Y axis of 4.99.

The microstructure of bcc metal films does reflect the growth history, opposed to the fcc films treated by Doljack and Hoffman. In Fig. 3 a transmission electron microscopy (TEM) cross section of a 0.8-μm-thick Cr film is shown. The film exhibits columnar grains. The width of the grains increases over the thickness of the film. In Fig. 4 the number of grains per unit length as a function of height is presented. The data points are taken from the sample shown in Fig. 3. Since we want to compare the intercepts in Figs. 2 and 4 a constrained fit to datapoints of Fig. 4 has been made with the

![FIG. 1. Average stress in a Cr film as function of thickness. The measurements were performed by etching the film back. Finding a higher stress for thinner films demonstrates the existence of a stress gradient.](image1)

![FIG. 2. Dependence of the average stress on film thickness for a series of depositions done in a parallel plate sputter deposition system. The error in the measurements is on the order of the size of the symbols. The measured stress obeys a power law dependence on film thickness. The line is a linear unconstrained fit to the data points. The slope of the line is $-0.57$.](image2)

![FIG. 3. TEM cross section of a 0.8-μm-thick Cr film. The development of the microstructure with thickness is clear. With increasing thickness the width of the columns increases.](image3)

![FIG. 4. Dependence of the number of surviving grains on height in the film. The data were taken from the sample shown in Fig. 1. The line is a constrained fit to datapoints of Fig. 4 has been made with the](image4)
slope prescribed to $-0.57$. The intercept of the $Y$ axis then is 3.97.

The stress and number of grains per unit length obey a power law with the same exponent. This leads us to conclude that for bcc polycrystalline films tensile stress is generated at the grain boundaries during deposition. All atoms that condense on a grain end up in a lattice position. At grain boundaries atoms will be slightly too far apart. The attractive force they experience over the grain boundary leads to a displacement and thus to a strain in each atomic plane of deposited atoms. At each height in the film stress will be generated inversely proportional to the number of grains per unit length at that height. Moreover from the intercept of the $Y$ axis we can calculate the shrinkage of the grain boundaries.

For the development of amorphous and polycrystalline films numerical and analytical models exist.\textsuperscript{9–13} After an initial stage the number of surviving grains or domains per unit length at height $z$ in the film is given by

$$N(z) = A \cdot z^{-p}. \quad (3)$$

Indeed for our sputter deposited polycrystalline films we observe a power law dependence of the number of surviving grains on the height in the film (Fig. 4). In line with the reasoning given earlier the stress at height $z$ in the film will be

$$\sigma(z) = \Delta N(z) \frac{E_Y}{(1-\nu)} , \quad (4)$$

with $\Delta$ as the shrinkage of the grain boundary. The measured average stress in a film of thickness $h$ is

$$\sigma_{av}(h) = \frac{1}{h} \int_0^h \sigma(z) dz . \quad (5)$$

Inserting Eqs. (3) and (4) in Eq. (5) gives

$$\log[\sigma_{av}(h)] = \log\left[ \frac{\Delta E_Y A}{(1-p)(1-\nu)} \right] - p \log(h). \quad (6)$$

Using $E_Y/(1-\nu) = 352$ GPa (Ref. 14) we arrive at a value for $\Delta = 0.013$ nm. The interatomic distance in Cr is 0.249 nm. The measured grain boundary shrinkage is 5% of the interatomic distance. A number on the order of a few percent to 50% of the interatomic distance was expected without shrinkage atoms on opposite sides of a grain boundary would on average be 1.5 atomic distances apart. When the grain boundary shrinks some atoms will be forced closer than the equilibrium spacing. This leads to large repulsive forces balancing the attractive forces of the atoms further apart than the equilibrium spacing.

To discuss the importance of the actual value of the exponent $p$ we note that preliminary stress data obtained at various pressures in the industrial PVD equipment show power law behavior with the power $p$ ranging from 0.25 to 0.75. Misra et al.\textsuperscript{7} presented data on stress and grain growth in Cr films deposited in a parallel plate reactor. We can describe both the stress and the grain size development in their experiments with a power $p = 0.39$ and a grain boundary shrinkage $\Delta = 0.006$ nm. More work is needed to correlate the growth exponent $p$ and the amount of grain boundary shrinkage $\Delta$ to the processes occurring at the surface of the growing film. For bcc Chromium we find a relative shrinkage six times smaller than Doljack and Hoffman reported for fcc nickel. This may well have to do with the better deformability of fcc crystals.

In conclusion we have shown that the tensile stress in bcc polycrystalline films is generated at the grain boundaries. By realizing that the growth history of the film is preserved, one can describe the stress evolution for hard, non recrystallizing films by the same mechanism as proposed 30 years ago for films that do recrystallize.

4 E. S. Machlin, Materials Science in Microelectronics (Giro, Croton-on-Hudson, NY, 1995).