

Mechanical characterisation of very thin films

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Abstract

The objective of this paper is to introduce mechanical properties of thin films, measurement of the mechanical properties of very thin coatings and creep performance of coatings. Thin film mechanical properties can be measured by tensile testing of freestanding films and by the microbeam cantilever deflection technique, but the easiest way is by means of nanoindentation. The design of reliable and functional micro/nano electro mechanical systems (MEMS/NEMS) relies on the knowledge and understanding of the mechanical behavior of thin film. The tensile properties, optical properties, creep performance and also the Oliver-Pharr Analysis of thin films are also given.

1. Introduction

The first evaporated thin films were probably the deposits which Faraday obtained in 1857 when he exploded metal wires in an inert atmosphere. In the following decades, evaporated thin films remained in the domain of academic research but were developed to permit large-scale application and control of film properties. During the last 25 years, evaporated films have found industrial usage for an increasing number of purposes. Examples are antireflection coatings, sunglasses, decorative coatings on plastic and textiles, in the manufacture of cathode-ray tubes, and most recently in electronic circuits. [1]

Thin films are extremely thermally stable and reasonably hard, but they are fragile. On the other hand organic materials have reasonable thermal stability and are tough, but are soft. For mechanical device stability four material properties of the device components are important: elastic modulus, yield strength, interfacial adhesion, and film fracture toughness. Mechanical properties of thin films often differ from those of the bulk materials. This can be partially explained by the nanostructure of thin films and the fact that these films are attached to a substrate. Due to typically high yield strengths, thin films can support very high residual stresses. This residual stress can be relieved later during processing or in the actual device operation through plastic deformation, thin film fracture, or interfacial delamination. Both elastic and plastic properties are important for thin film characterization. Thin film mechanical properties can be measured by tensile testing of freestanding films and by the microbeam cantilever deflection technique, but the easiest way is by means of nanoindentation, since no special sample preparation is required and tests can be performed quickly and inexpensively. Nanoindentation is a versatile technique for

measuring films mechanical properties (elastic modulus, hardness, interfacial adhesion, and film fracture toughness). During the measurement a sharp diamond indenter is forced into the tested material while continuously recording both the force and the indentation depth.

Mechanical and structural properties of fine scale materials are the subject of intense investigations. [9] Both fundamental and applied problems arise with the decrease of the internal microstructural length scale to several nanometers. Influence of length scale on a variety of physical processes such as mechanical strength, work hardening is still not well understood. Moreover, because an in-depth knowledge of the microstructure is required, little detailed experimental studies exist

One role very important in thin films have grain size. Hardness and strength increase as the grain size is reduced. The Hall-Petch equation was derived to explain this

$$\sigma = \sigma_0 + kd^{-1/2}$$

Derivation depends on considering the stress necessary to operate dislocation sources in neighbouring grains.

Hall-Petch behaviour observed for many coatings:

- deviation when grains smaller than source size (<100nm)
- ion bombardment changes transition

Flow stresses of thin metal films (less than 1 micron) deposited on rigid substrates are significantly higher than those observed in the corresponding bulk metal. Furthermore, the flow stresses increase with decreasing film thicknesses. This phenomenon has been attributed to geometrical constraints on the films, which alter the energetic of the dislocation motion. Fundamental information regarding plasticity mechanisms in thin metal films on substrates can be obtained by using in-situ transmission electron microscopy (TEM).[9] In-situ TEM experiments revealed that the film-substrate interface influences thin film plasticity. For crystalline-crystalline interfaces the film-substrate interface acted mainly as a dislocation source, and dislocations advancing through the epitaxial metal films frequently deposited dislocation segments near the film-substrate interface. In contrast, for crystalline-amorphous interfaces the film-substrate interfaces acted as dislocation sink. The interfacial dislocation mechanisms observed in thin metal films constrained by a substrate are expected to be of similar importance in lamellar and dispersion strengthened alloys. While the mechanical reliability of these complex devices often represents a critical limitation for new technologies, they also provide a unique opportunity to study the underlying physics and fundamental mechanisms of deformation and fracture with unprecedented control of composition and length scale. Despite the technical and methodical progress in nanoindentation technique it is still very difficult to obtain accurate values for mechanical properties of coatings below 2 μm thickness. To obtain pure film properties the measurement conditions have to be chosen in a way that a substrate influence can be minimized. The natural tip rounding of sharp indenters generates a physical thickness limit, where comparable hardness measurements are impossible. Alternatives are measurements with spherical indenters, which can be combined with elastic stress and deformation modelling. Modulus measurements down to 5 nm film thickness became possible. Using pyramidal indenters only the hardness and Young's modulus of bulk materials can be investigated from indentation experiments. Polymer thin films and surfaces play a major role in the functionality of many components in the microelectronic and automotive industries. The characterization of their mechanical properties at a nanometre scale remains a technological challenge. Instrumented indentation testing

with frequency-specific dynamic analysis provides access to viscoelastic measurement of near surface properties of polymeric materials. The flow stresses of polycrystalline thin metal films are much higher than flow stresses for the corresponding bulk material and scale approximately with the inverse film thickness. Discrete dislocation simulations are well suited to investigate dislocation glide in a thin film because configurations can be treated which are not tractable analytically and the number of dislocations is still relatively small due to the confined geometry.

Both elastic modulus and hardness can be readily extracted directly from the nanoindentation curve. Since the depth resolution is on the order of nanometers, it is possible to indent even very thin (100 nm) films. Indentation has been also used to measure thin film adhesion, where the mechanical energy release rate, or practical work of adhesion is calculated based on the delamination size. Similar fracture properties such as fracture toughness or adhesion strength are derived from the continuous load-displacement profile and an independently measured geometrical scale parameter, which results from indentation, such as crack length or delamination radius.

Indentation techniques could also be used for measuring fracture toughness. When a sharp tip such as Vickers, Berkovich or a cube corner diamond is indented into bulk brittle materials, radial cracking usually occurs after a critical load has been reached, which allows ones to calculate fracture toughness based on the maximum indentation load and the crack length. This method of analysis is complicated in the case of thin film radial fracture because of the half penny crack shape perturbation by the substrate, film densification, and residual stresses in the film. Current studies have yielded promising developments in this area however.

2. Measurement of the Mechanical Properties of very thin coatings

For measurement of the mechanical properties of very thin coatings we use direct measurements and indirect measurements. [2]

In direct measurements we use:

- a) MEMS-based mechanical test systems. Generally limited to silicon and some metals.
- b) Indentation tests. Limited by thickness of coatings and available indenters.

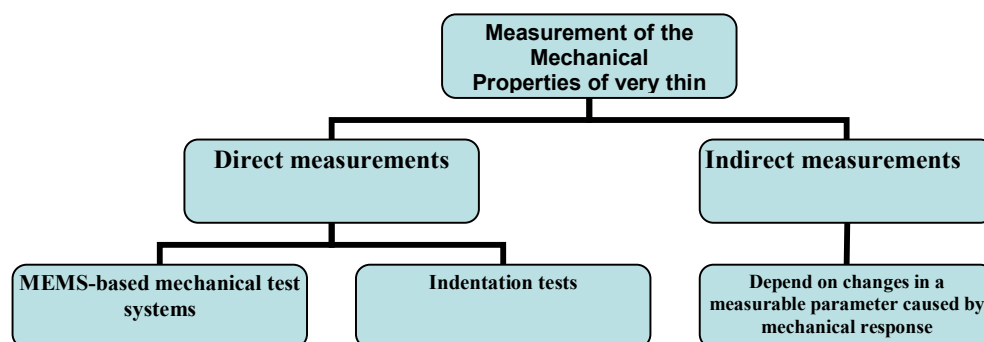


Figure 1. Schematic showing the Measurement of the Mechanical Properties of very thin films.

In indirect measurements depend on changes in a measurable parameter caused by mechanical response e.g. Raman shifts due to strain.

The mechanical properties of a coating/substrate system depend on the microstructure of the coating/substrate and interface region. Composition, phases present, porosity, grain size, grain shape, defect types and density.

Time-independent properties are:

- Elasticity (Young's Modulus)
- Plasticity (Yield stress, work hardening exponent)
- Fracture (Toughness, crack driving force)

Time-dependent properties are:

- Viscoelasticity
- Creep/viscoplasticity
- Slow crack growth (Fatigue strength)[2]

3. Nanoindentation

The measurement of mechanical properties of microelectronic thin films and coatings are necessary in many electronic and mechanical systems such as integrated circuits, microprocessors, data storage technologies, and Micro Electro Mechanical Systems (MEMS).

Measuring mechanical properties like hardness and modulus of elasticity can help to evaluate the reliability of the materials in part and components and to understand the strengthening and deformation mechanisms in small scales [10-11]

Indentation tests, sometimes called hardness tests, are perhaps the most commonly applied means of testing the mechanical properties of materials. The technique has its origins in the Mohs scale of mineral hardness, in which materials are ranked according to what they can scratch and are, in turn, scratched by. The characterization of solids in this way takes place on an essentially discrete scale, so much effort has been expended in order to develop techniques for evaluating material hardness over a continuous range. Hence, the adoption of the Meyer, Knoop, Brinell, Rockwell, and Vickers hardness tests. More recently (ca.1980), the nanoindentation technique has been established as the primary tool for investigating the hardness of small volumes of material. The test is usually performed with a sharp indenter (Berkovich) but other indenters are available modulus conical and spherical geometry. Spherical indentations can be used to determine elastic property but is not applicable to very thin coating with no depth. [8]

In a traditional indentation test (macro or micro indentation), a hard tip whose mechanical properties are known (frequently made of a very hard material like diamond which can have tip geometry, tip radius, tip end-shape) is pressed into a sample whose properties are unknown. The load placed on the indenter tip is increased as the tip penetrates further into the specimen and soon reaches a user-defined value. At this point, the load may be held constant for a period or removed. The area of the residual indentation in the sample is measured and the hardness, H , is defined as the maximum load, P_{max} , divided by the residual indentation area, A_r , or

$$H = \frac{P_{max}}{A_r} \quad (1)$$

For traditional hardness techniques, the projected area may be measured directly using light microscopy. As can be seen from equation, are given load will make a smaller indent in a "hard" material than a "soft" one.

This technique is limited due to large and varied tip shapes, with indenter rigs which do not have very good spatial resolution (the location of the area to be indented is very hard to specify accurately). Comparison across experiments, typically done in different laboratories, is difficult and often meaningless. Nanoindentation improves on these macro and micro indentation tests by indenting on the nanoscale with a very precise tip shape, high spatial resolutions to place the indents, and by providing real-time load-displacement (into the surface) data while the indentation is in progress.

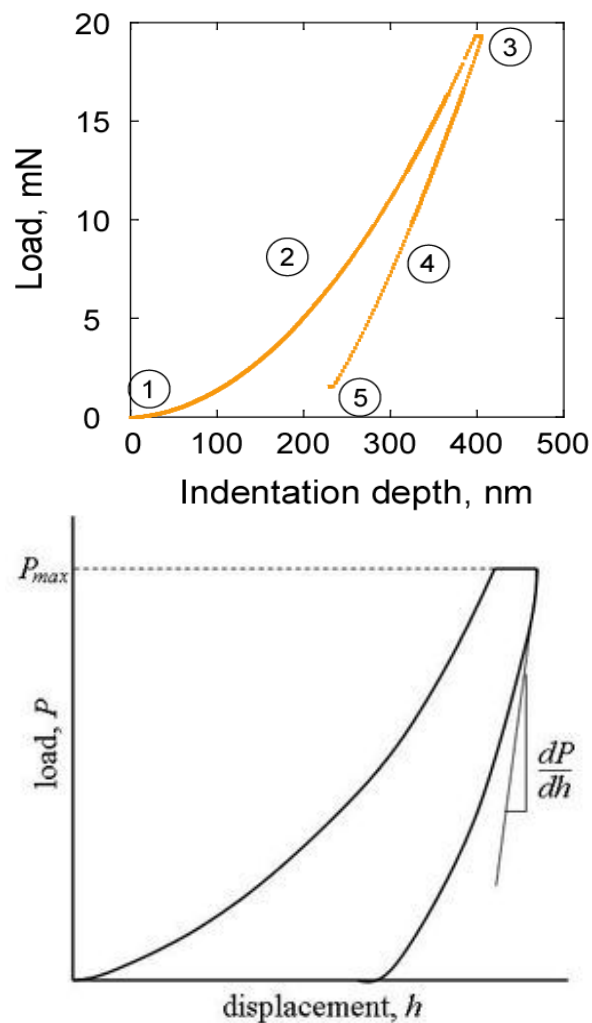


Figure 2. Schematic of load-displacement curve for an instrumented nanoindentation test.

Nanoindentation of film/substrate system Probe begins to move towards surface. Contact (1) occurs when stiffness increases. Load (2) to a prescribed displacement. Hold (3) at maximum load to assess creep behavior. Unload (4) 90% of the way. Hold (5) at 90% unload to assess thermal drift [2-8].

In nanoindentation small loads and tip sizes are used, so the indentation area may only be a few square micrometres or even nanometres. This presents problems in determining the hardness, as the contact area is not easily found.

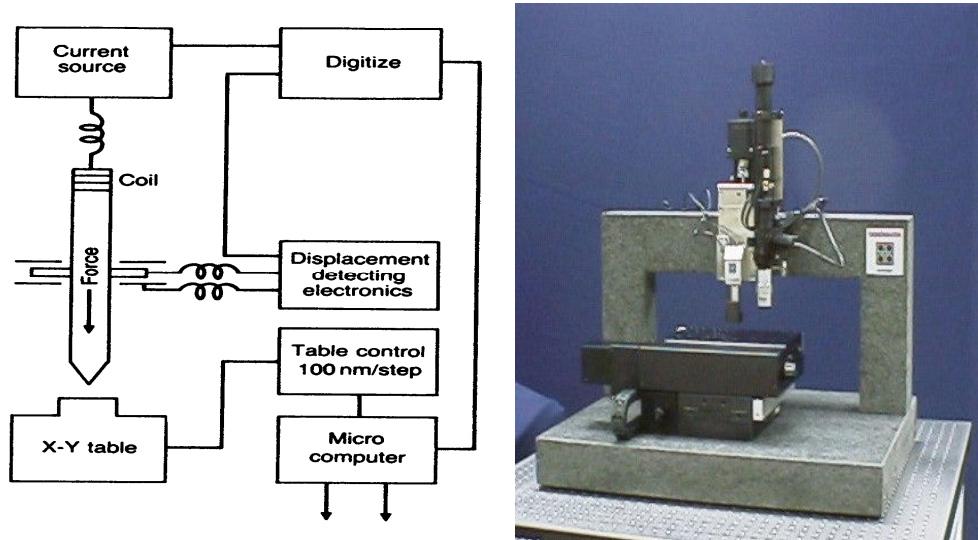


Figure 3. Schematic is shown a machine of nanoindentation test [2]

Atomic force microscopy or scanning electron microscopy techniques may be utilized to image the indentation, but can be quite cumbersome. Instead, an indenter with a geometry known to high precision (usually a Berkovich tip, which has a three-sided pyramid geometry) is employed. During the course of the instrumented indentation process, a record of the *depth* of penetration is made, and then the area of the indent is determined using the known geometry of the indentation tip. At the same time, various parameters, such as load and depth of penetration, can be measured. A record of these values can be plotted on a graph to create a *load-displacement curve* (such as the one shown in Figure 1). These curves can be used to extract mechanical properties of the material using the method of Oliver and Pharr [12].

- Modulus of elasticity: The slope of the curve, dP / dh , upon unloading is indicative of the stiffness S of the contact. This value generally includes a contribution from both the material being tested *and* the response of the test device itself. The stiffness of the contact can be used to calculate the *reduced modulus of elasticity* E_r as

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A(h_c)}} \quad (2)$$

where $A(h_c)$ is the area of the indentation at the contact depth h_c (the depth of the residual indentation prior to elastic recovery of its shape), and β is a geometrical constant on the order of unity. The reduced modulus E_r is related to the modulus of elasticity E_s of the test specimen through the following relationship from contact mechanics:

$$1/E_r = (1-\nu_i^2)/E_i + (1-\nu_s^2)/E_s \quad (3)$$

Here, the subscript i indicates a property of the indenter material and ν is Poisson's ratio. For a diamond indenter tip, E_i is 1140 GPa and ν_i is 0.07. Poisson's ratio varies between 0 and 0.5 for most materials (though it can be negative) and is typically around 0.3.

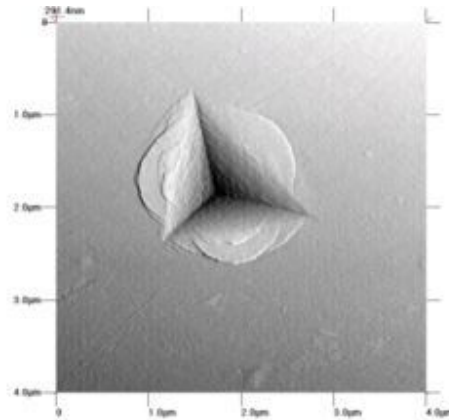


Figure 4. An AFM image of an indent left by a Berkovich tip in a Zr-Cu-Al metallic glass; the plastic flow of the material around the indenter is apparent.

- Hardness: There are two different types of hardness that can be obtained from a nanoindenter: one is as in traditional macroindentation tests where one attains a single hardness value per experiment; the other is based on the hardness as the material is being indented resulting in hardness as a function of depth. (This is only available in MTS indenters, the so called "continuous stiffness" option on older models [such as the Nano Indenter II].)

$$H = \frac{P_{\text{max}}}{A_r} \quad (4)$$

The hardness is given by the equation above, relating the maximum load to the indentation area. The area can be measured after the indentation by in-situ atomic force microscopy, 'after-the event' optical (or electron) microscopy. An example indent image, from which the area may be determined, is shown at right.

Some nanoindenters use an area function based on the geometry of the tip. Use of this area function provides a method of gaining real-time nanohardness values from a load-displacement graph. However, there is some controversy over the use of area functions to estimate the residual areas versus direct measurement. An area function $A(h)$ typically describes the projected area of an indent as a 2nd-order polynomial function of the indenter depth h . Exclusive application of an area function in the absence of adequate knowledge of material response can lead to misinterpretation of resulting data. Cross-checking of areas microscopically is to be encouraged.

- Strain-rate sensitivity: The strain-rate sensitivity of the flow stress m is defined as

$$m = \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}} \quad (5)$$

where $\sigma = \sigma(\dot{\epsilon})$ is the flow stress and $\dot{\epsilon}$ is the strain rate produced under the indenter. For nanoindentation experiments which include a holding period at constant load (i.e. the flat, top area of the load-displacement curve), m can be determined from

$$d \ln H = m d \ln \dot{\epsilon}_p + n d \ln h_p \quad (6)$$

The subscript p indicates that these values are to be determined from the plastic components *only*.

- Activation volume: Interpreted loosely as the volume swept out by dislocations during thermal activation, the activation volume V^* is

$$V^* = 9k_B T \frac{\partial \ln \dot{\epsilon}}{\partial H} \quad (7)$$

where T is the temperature and k_B is Boltzmann's constant. From the definition of m , it is easy to see that

$$V^* \propto (Hm)^{-1} \quad (8)$$

As an example, nanoindentation experiments have been conducted using three different indenters (Berkovich, Cubecorner, and Conical) on Nickel thin film of different thickness (38nm, 95nm, 110nm, 194nm, and 230nm) on copper substrates. Results indicate that the indentation size effect is independent of indenter tip geometry. [10] Some other conclusions for nanoindentation are:

- Substrate effects can be dramatically reduced if elastic mismatch is minimized.
- A tip calibration can be accurate for depths greater than ~ 5 nm.
- Scale effects indicate that elementary processes of deformation occur at depths less than ~ 200 nm.

4. Tensile properties

In this section, we will therefore attempt only to summarize the available information. The most important feature that is found when one examines the tensile properties to explain this, and these will be discussed in the appropriate contexts.

a. Methods of measurements

Various types of apparatus have been used for examining the mechanical properties of thin film, and some of these have already been considered in the section on stress. Hoffman has summarized the various methods in a useful table. A brief review is given here.

(1) Microtensile Apparatus

Different machines have been built for measuring tensile properties by observations of the elongations by small loads.

(2) Bulge Techniques

To eliminate the mounting problem Beams has developed a method for measuring stress-strain characteristic.

(3) Centrifugal Methods

The use of spinning rotor for measuring adhesion of films deposited on the rotor. Such an apparatus is useful for measuring the ultimate strength of the film, although the method is applicable only to films with low adhesion so that they are removed by spinning.

(4) X-ray and Electron-diffraction Techniques, in combination with applied load

Changes in lattice spacing can be measured by these techniques, and therefore stress-strain characteristics can be measured.

5. Creep Exponent

When designing any system there are a number of mechanical behaviour of materials questions that must be answered. Among them are fracture, yield, fatigue, stress corrosion cracking, and creep, just to scratch the surface. Some of these considerations, like fracture and yield, are well recognized mechanical behaviour problems. The other phenomena are more subtle and happen over longer time periods. Creep is a form of mechanical degradation that occurs at an accelerated rate at high temperatures where thermally activated diffusion more important. A material under a constant tensile stress at high T will undergo plastic deformation resulting in an increase in length. Creep deformation occurs by the activated movement of dislocations or directly by the diffusion of atoms to change the shape of individual grains and thus the macroscopic material (diffusion creep).[5]

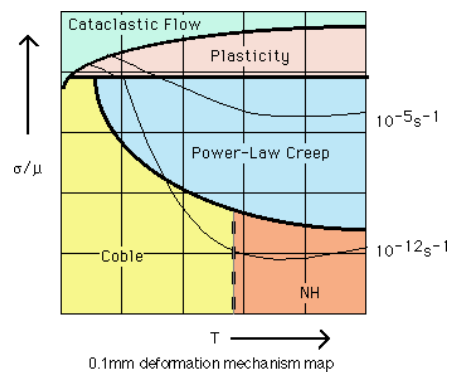


Figure 5. Ashby map for pure nickel of grain size 0,1mm
[Deformation –Mechanism Maps, copyright 1982, Pergamon Press PLC.]

The effects from those mechanisms are:

- **The transition to**
- Diffusional creep dominates to higher stresses in the small-grained material.
- The vertical line between diffusion creep occurring by lattice diffusion and by boundary diffusion moves to the right for the smaller-grained material.

Secondary creep rate for a particular metal or alloy depends on several variables, the most important of which are stress and temperature. The most commonly used expression for relating secondary creep rate $\dot{\epsilon}$ to stress σ and absolute temperature T has the form

$$\dot{\epsilon} = A_1 \exp\left(-\frac{Q}{RT}\right)\sigma^n$$

where A and n are constants, Q (kJ·mol⁻¹) is the activation energy for creep in the metal, R is the universal gas constant (8.31 J/mol K) and T is absolute temperatures in degree Kelvin.

This is consistent with Norton's law.

In indentation experiments creep can also be observed. Creep is best assessed under load control. Generally indentation testing at room temperature shows only primary creep unless the melting temperature as the material is low.

At high temperatures, where grain-boundary sliding is an important creep mechanism. Samples with larger grain size usually exhibit a lower creep rate than do fine-grained samples. On the other hand, the flow stress at low temperatures increases with a decrease in grain size according to the Hall- Petch relationship [Petch, 1953]. The best grain size for a given material therefore depends on the conditions under which it is to be used [Whittenberger, 1986].

6. Conclusions

- ✓ Thin film mechanical properties are different from bulk.
- ✓ Microtensile or indentation tests can provide useful information or mechanical properties.
- ✓ Films < 200 nm thick require modeller to extract good mechanical properties.

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