Indentation measurements on thin films

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Thin films have an important part to play in modern technology. It is difficult to characterize the mechanical properties of thin films because the films cannot usually be investigated separately from the substrate. One of the few methods that can be used for such investigations consists in making an indentation in the film by applying an extremely small and accurately controlled force while at the same time measuring the depth of indentation. The indentation-test machine that has been designed at Philips Research Laboratories in Eindhoven is capable of applying forces between 10 μN and 50 mN. It can be used for measuring the ultramicro-hardness of thin metal films and also for determining the visco-elastic properties of polymer films. Both quasi-static and dynamic measurements can be performed.

Introduction

Thin films are used today to an increasing extent in high-technology products. Thin metal films are used for example to improve the wearing properties or corrosion resistance of metal components. Thin polymer films are used as protective coatings for optical fibres for data transmission. In applications of this kind the mechanical properties are crucial, and the mechanical characterization of the film by measurements is therefore essential.

Tensile tests and hardness measurements, the classical methods of materials testing \cite{1}, are inadequate for determining the mechanical properties of films only a few microns thick or less. Where it is possible to separate the film from the substrate, handling and clamping problems add to the difficulties of making reliable measurements. When the film and substrate are measured together, the result of the measurement is usually affected by the properties of the substrate.

One of the few methods suitable for the mechanical characterization of thin films consists in measuring the depth of an indentation produced by a lightly loaded pointed object. The effect of the substrate is negligible if the depth of the indentation is no more than 10 to 20% of the film thickness, and the substrate is not much softer than the film. The object, usually called an indenter, must have a well-defined shape and the applied force must be very low. In practice this means that, depending on the deformability of the film, the force must lie in the range from 10 μN to 50 mN. The mechanical properties then follow from the depth of the indentation as a function of time or load. For the characterization of films about one micron thick it is necessary to be able to observe displacements of 10 nm or less. Measurements of the indentation depth in thin metal films are referred to as ultramicrohardness tests. Various ultramicrohardness testers have been described in the literature \cite{2}.

Results of hardness measurements made with different instruments are not usually comparable because they depend so much on the test conditions, such as the shape of the indenter and the applied force. They are certainly not comparable with the results of ‘conventional’ hardness tests, such as Vickers hardness measurements.

We have designed an ultramicroindentation-test machine that not only measures the ultramicrohardness of thin metal films, but can also determine the mechanical properties of other types of films, such as polymer coatings. These coatings generally have a visco-elastic behaviour, which means that the response

\begin{itemize}
\item \cite{1} M. M. Eisenstadt, Introduction to mechanical properties of materials, Macmillan, New York 1971.
\item J. B. Pethica, Microhardness tests with penetration depths less than ion implanted layer thickness, in: V. Ashworth, W. A. Grant and R. P. M. Proctor (eds), Ion implantation into metals, Pergamon, Oxford 1982, pp. 147-156.
\end{itemize}
of the indentation to a step-function change in the load is not instantaneous but gradual. Our machine can be used to measure this step-function response. The visco-elastic properties can also be characterized by the complex modulus of elasticity. This quantity is particularly important in processes with a short characteristic time. The complex modulus of elasticity can be determined in our machine by measuring the indentation dynamically instead of quasi-statically. This is done by superimposing a sinusoidally alternating force on the force for the quasi-static indentation. The required complex modulus of elasticity can then be obtained from the amplitude ratio and phase shift of the alternating indentation relative to the alternating load. The machine is also suitable for surface-scratch experiments, for example to quantify the adhesion of films to their substrates, and it can be used for measuring the roughness of soft materials. These two applications will not be dealt with in this article.

A photograph of our ultramicroindentation machine for the mechanical characterization of thin films is shown in fig. 1. In developing the machine we used several special techniques that have been initiated and refined over the years at Philips Research Laboratories. These techniques have provided sharp diamond indenters with a tip radius smaller than 0.1 μm, a precision air-bearing to carry the indenter holder, and a hysteresis-free friction-wheel drive mechanism for the slow uniform motion of the indenter holder.

We shall next describe the operation of the machine. Then we shall look at a number of applications, dealing in particular with quasi-static indentation measurements on protective coatings for glass optical fibres and on binary metal-alloy films. Finally we shall discuss dynamic indentation measurements on pigmented polymer films on magnetic tape.

**The ultramicroindentation machine**

The ultramicroindentation machine is shown schematically in fig. 2a. The sample is held by suction to a sample holder, which can be moved vertically and horizontally. The indenter holder, supported by an air bearing, has virtually frictionless movement along a horizontal shaft. The shaft itself can be moved very slowly towards the sample by friction wheels and guide wheels; the principle of a friction-wheel transmission is illustrated in fig. 2b. A coil fixed to the indenter holder is located in the air gap of an electromagnet, which is mounted on the shaft. When the coil is energized with direct current, a force is exerted on the indenter; this force can be varied from 10 μN to 50 mN. Two inductive displacement transducers measure the displacement of the indenter with respect to the shaft and the displacement of the shaft with respect to the surroundings. Two stops attached to the...
shaft limit the movement of the indenter holder. Isolation from building vibrations is provided by mounting the entire machine on a table top supported on air springs. The resonant frequency of the sprung table

Fig. 2a) is adjusted to give a zero signal when the indenter holder is somewhere between the two stops. A small current is then passed through the coil, so that the holder is gently pushed against the front stop (St1),

top is about 2 Hz. A pneumatic control system for the air springs keeps the table top horizontal to within 0.001°. To minimize the effect of air currents the measuring system is enclosed in a box of transparent polymethyl methacrylate.

An indentation experiment proceeds as follows. The displacement transducer that measures the position of the indenter holder relative to the shaft (T1 in

with a force of say 10 μN. The motor of the linear drive mechanism is now switched on, causing the shaft to move slowly in the direction of the sample. After some time the indenter touches the sample. A control system stops the movement of the shaft when the signal from the displacement transducer T1 falls to zero. The indenter then presses against the sample with a force of 10 μN, leaving a slight indentation in it. To
provide a 'virgin' surface the sample is moved a short distance sideways at the same small force between indenter and sample, and then the force is increased. At the same time the control system makes the shaft move so that the signal from the displacement transducer \( T_1 \) remains equal to zero. The indentation depth of the indenter in the sample is then given by the displacement measured by transducer \( T_2 \). The smallest observable displacement is 1 nm. The signal from \( T_2 \) is automatically corrected for changes in the ambient temperature during the measurement. The temperature-sensing element is a platinum resistor, mounted around the displacement transducer \( T_2 \). The degree of correction is determined by calibration.

Fig. 2c shows an example of the track made by the indenter during the sideways movement with the minimum indenter force of 10 \( \mu \)N. The actual indentation produced by a force of 0.5 mN can also be seen. The figure relates to indentation measurements on a soft gold film vacuum-evaporated on silicon; in harder films the track produced by the sideways movement is far less deep. The imprint is that of a triangular pyramidal diamond, ground with an angle of 97° between the edges. The radius of the tip is less than 0.1 \( \mu \)m. This is the indenter we use in our ultramicrohardness measurements \([6]\). The projected area of the indentation can be calculated from the measured penetration depth at a given load. The ratio of the applied force to this area is then the ultramicrohardness as in our definition. The measurement information is digitally processed and stored in a microcomputer.

Applications

**Quasi-static indentation measurements on protective coatings for optical fibres**

Protective coatings for optical fibres have to satisfy a number of optical and mechanical requirements. First of all the refractive index of the transparent material of the coating must be higher than that of the glass cladding of the fibre. Another requirement is that the fibre must be 'embedded' in the protective coating in such a way that the fibre cannot 'kink' if the fibre-optic cable is bent, which would make the radius of curvature of the fibre too small. (Deformation of the optical fibre with an unduly small radius of curvature is called 'microbending'.) This requirement can be met by using two polymer layers: a relatively hard outer layer and a soft inner layer, the buffer layer. Both layers should give little creep, i.e. they should keep their shape under permanent load and not become further deformed. Finally the layers must protect the fibre from external mechanical and chemical effects, to prevent damage and the penetration of water. The coating must retain all these properties over a long period of time, without the material becoming cracked or otherwise degraded.

The indentation machine described here is particularly suitable for measuring the mechanical properties of protective polymer coatings in situ. The tip radius of the indenter is much smaller than the outer radius of the protective film, which can therefore be regarded as a planar layer and no correction is necessary. As the depth of the indentation is small compared with the thickness of the film, the result of the measurement is not affected by the mechanical properties of the intermediate layer or the glass.

If at time \( t = 0 \) an indenter of radius \( R \) is pressed with force \( F \) into the plane surface of a visco-elastic material occupying a semi-infinite space, the depth \( e \) of the indentation follows from a generalized form \([7]\) of Hertz's equation \([8]\):

\[
\{e(t)\}^{3/2} = \frac{3(1 - v)}{8v^2} J(t) FH(t). \tag{1}
\]

Here \( v \) is the lateral contraction coefficient (Poisson's ratio) and \( J(t) \) is the (time-dependent) creep-compliance function (in \( m^2/N \)), characterizing the mechanical properties of the visco-elastic material. \( H(t) \) is the unit-step function (or Heaviside function): \( H(t) = 1 \) for \( t \geq 0 \) and \( H(t) = 0 \) for \( t < 0 \).

The creep compliance of a perfectly elastic material (i.e. one with no viscous properties) is not time-dependent, and is then equal to the reciprocal of the shear modulus of elasticity \( G \). On applying the well-known relation

\[
G = \frac{E}{2(1 + v)},
\]

where \( E \) is the modulus of elasticity, equation (1) reduces to:

\[
e^{3/2} = \frac{3(1 - v^2)}{4E} \frac{F}{R}. \tag{2}
\]

This is Hertz's equation for an infinitely rigid sphere of radius \( R \) pressed into the plane surface of an elastic material with modulus of elasticity \( E \) occupying a semi-infinite space.

For relatively soft materials it is not permissible to neglect the indentation at the minimum load \( F_0 \) (equal to 10 \( \mu \)N in our case). The modulus of elasticity is then given by an expression derived from equation (2):

\[
E = \frac{3(1 - v^2)}{4} \left( \frac{F^{3/2} - F_0^{3/2}}{\Delta e} \right)^{2/3}, \tag{3}
\]

where \( \Delta e \) is the difference between the indentations at normal load \( F \) and minimum load \( F_0 \).

In selecting polymers for protective coatings on glass fibres certain conditions must be taken into account: the modulus of elasticity of the buffer layer must be small compared with that of the outer layer, and the creep and plastic deformation of both layers must be small. We shall now describe a number of measurements on protective coating materials in which these aspects are important \([9]\).
First of all we studied the effect of the UV curing time on a commercially available polymerizable acrylate, to be applied as a hard outer layer. Fig. 3a shows the effect of the curing time on the degree of polymerization of this material. It was determined by means of a differential scanning calorimeter, which measures the heat liberated during the polymerization of the as yet uncombined oligomers — the ‘building blocks’ of the acrylic resin. Next we measured indentation curves of samples of the same acrylic resin that had been exposed for 2.4, 4.8 and 24 seconds to ultraviolet irradiation at a wavelength of 365 nm and an intensity of 0.6 W/cm². In these measurements we used an indenter with a radius of 7 µm and a ‘jig’ with a V-groove in which the fibre with the protective coating is held by suction. Fig. 3b shows the curves of indentation depth as a function of time; the numbers on the curves correspond to the numbers in fig. 3a. It can be seen that as the exposure increases, and hence the degree of polymerization, the initial deformation decreases and with it the creep. Our indentation machine can thus also be used for monitoring the curing conditions during the production process.

Fig. 3c illustrates some measurements on soft materials for buffer layers, where the difference $\Delta e$ between the depth of penetration at normal load and minimum load is plotted as a function of time. The radius of the indenter used for these measurements was 4 µm. Curve 4 relates to a commercially available thermohardening silicone rubber. The material is per-

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This indenter differs from the four-sided pyramidal indenter used for Vickers hardness measurements. It is simpler, however, to give a sharp point to a diamond indenter shaped like a triangular pyramid than to one shaped like a four-sided pyramid.


fectly elastic in its behaviour: there are no creep effects, and after removal of the load the residual deformation is virtually zero. Curve 5 relates to a commercially available UV-polymerizable polyurethane acrylate. As can be seen, this material does show creep effects, and after removal of the load some plastic deformation remains.

A polyurethane acrylate for buffer layers, which has better mechanical properties than the material of curve 5, has been developed in our own laboratory. In the indentation measurement the layer behaves in virtually the same way mechanically as the silicone rubber of curve 4. Advantages of polyurethane acrylate compared with silicone rubber are that it has a higher refractive index and is easier to apply as a protective coating on the glass fibre. The modulus of elasticity of our polyurethane acrylate is calculated from the measurements as 1.7 MPa; for the silicone rubber the value is 1.6 MPa. (In the calculations Poisson’s ratio was taken as 0.5.)

Ultramicrohardness measurements on thin metal films

It is important to measure the hardness of thin metal films primarily because there is usually a correlation between hardness and resistance to wear. The mechanical properties of vacuum-evaporated binary metal-alloy films have been investigated at our Laboratories [10]. The ultramicrohardness of the films was measured with our indentation machine with the triangular pyramidal indenter whose imprint is shown in fig. 2c. The force applied to the indenter was 0.5 mN; the indentation depths were only read off if they had not changed for 10 seconds. Some results of measurements were checked with a scanning electron microscope.

Many thin metal films were investigated; we shall only discuss here the measurements on cobalt/nickel and silver/gold films. At room temperature silver and gold are completely soluble in one another; evaporated silver/gold films are therefore found to be single-phase in practice. Cobalt and nickel are only partly soluble in one another, and for this reason cobalt/nickel films are two-phase in a large range of miscibility. The phases consist of mixed crystals with more than 95% cobalt and mixed crystals with more than 70% nickel. The silver/gold mixed crystals and the cobalt/nickel mixed crystals consisting mostly of nickel are both face-centred cubic (fcc), that is to say the atoms form a cubic close packing. The cobalt/nickel mixed crystals that are largely cobalt form a hexagonal close packing (hcp).

We have evaporated metal films about 1 µm thick on to silicon substrates, successively increasing the relative proportions of the elements from 0% to 100% in steps of 10%. We then determined the phase diagrams (metastable for Co₁₋ₓNiₓ) of the films at room temperature by X-ray diffraction and transmission electron microscopy. The results for the two alloys are shown in the top row of fig. 4. The two-phase region of the cobalt/nickel alloys is indicated by the horizontal hatching.

The second row in fig. 4 gives the results of the ultramicrohardness measurements. In general the hardness of metals increases when the propagation of dislocations encounters obstacles, such as foreign atoms in the crystal structure. This effect increases with the difference in size between the foreign atoms and the atoms of the metal itself. There is not much difference, however, between the radii of cobalt and nickel atoms and those of silver and gold atoms. The increase in the hardness of silver films alloyed with gold or of gold films alloyed with silver must clearly be due to some other effect.

The propagation of dislocations in the crystal structure is also obstructed by grain boundaries. A fine-grained metal is therefore in general harder than a similar coarse-grained metal. The TEM micrographs in the bottom two rows, made with a Philips transmission electron microscope, demonstrate that this effect is the cause of the increased hardness. The micrographs of the Co₁₋ₓNiₓ films with x = 0.4 and 0.9 show an almost identical grain size. The micrographs of the Ag₁₋ₓAuₓ films with x = 0 and x = 0.4 show a distinctly different grain size. The difference in grain structure also appears from the corresponding electron-diffraction patterns, made with the same electron microscope. In the diffraction pattern of the pure silver film there are breaks in the rings. This points to the presence of texture (preferred orientation of the crystallites), presumably due to recrystallization after vacuum evaporation. The regularity of the rings in the other diffraction patterns indicates random orientation of a large number of crystallites.

Dynamic indentation measurements on magnetic tape

The methods of measurement we have been discussing are quasi-static, i.e. the sample is subjected for some time to the load exerted by the indenter during the measurement. Quasi-static measurements are appropriate when the processes to which the material of the sample is subjected in its application have


a long characteristic time. This is the case with fibre-optic telecommunication cables, which are wound on reels during manufacture, so that the fibres in the cable are bent to a certain radius of curvature.

At Philips Research Laboratories the running characteristics of magnetic tape for video and audio cassette recorders are also a topic of investigation. Magnetic tape consists of carrier material 10 μm thick and a coating of about 5 μm of visco-elastic polymer containing the magnetic particles $^{[11]}$. Since the friction is associated with the actual contact surface between the tape and the magnetic heads and guide pins, we expect that the coefficient of friction will depend on the deformability of the magnetic coating. Clearly, the characteristic times associated with the friction that occurs as the magnetic layer passes along the heads and pins will be short. A quasi-static measurement of the visco-elastic properties is therefore not suitable for determining the deformability of the polymer layer.

We have recently started experiments with magnetic tape in which the visco-elastic properties of the magnetic layer are measured with our indentation machine in a dynamic method. In the configuration shown schematically in fig. 5 a diamond indenter with a
radius of about 5 \mu m is pressed against the magnetic tape with a well-defined force. The tape is stretched tight over a smooth cylinder of hardened steel. The magnetic layer on the tape is subjected to a static indentation, which must not be greater than about 0.2 \mu m or the results would be distorted by the carrier material. Next a sinusoidally alternating force at a frequency of up to 100 Hz is superimposed on the static force. The static force and the dynamic force are produced by a direct current and an alternating current in coil C (see fig. 2). The sum of the static and dynamic indentations is measured by displacement transducer $T_1$ (fig. 2). During the dynamic measurements the control system for the linear drive mechanism is switched off. The temperature in the magnetic tape can be made locally higher or lower than the ambient temperature by the Peltier element shown in fig. 5.

The microcomputer determines the amplitude ratio of the alternating force to the dynamic indentation during the measurement. The corresponding phase difference is measured as well. The values for the real and imaginary parts of the complex (frequency-dependent) modulus of elasticity $E^*$ can now easily be derived from the amplitude ratio and phase angle, provided that the amplitude of the dynamic indentation does not exceed about 20 nm. The complex modulus of elasticity is defined as

$$E^* = E' + iE''$$

where $E'$ is a measure of the elastic properties and $E''$ is a measure of the damping properties of the material. $E'/E''$ represents the loss factor of the material, and the corresponding arc tangent is indicated as the loss angle. For the visco-elastic polymer coating on magnetic tape typical values for $E'$ are in the range from 2.5 to 4 GPa and the loss factor is in the range from 0.02 to 0.10.

We intend to carry out a series of measurements of the complex modulus of elasticity for tapes of simplified composition in the near future, to gain a better understanding of the running characteristics of magnetic tape.

In the design and building of the ultramicroindentation machine important contributions were made by R. M. van Bree, K. W. de Graaf, F. G. A. Homburg and A. C. Jacobs. The studies on protective coatings for optical fibres were made in cooperation with D. J. Broer, and the investigations of metal films were carried out in cooperation with J. J. van den Broek and A. G. Dirks.

**Summary.** In an ultramicroindentation machine very low forces - 10 \mu N to 50 mN - are exerted on a diamond indenter to produce small indentations in thin films. For thin metal films the ratio of the applied force to the projected area of the indentation is a measure of the ultramicrohardness. The indenter used in these measurements is shaped like a triangular pyramid with a tip radius of less than 0.1 \mu m. The visco-elastic properties of protective polymer coatings on optical fibres for data transmission are measured with an indenter of radius about 5 \mu m. When the force is suddenly increased the curve of the depth of indentation as a function of time gives information about the creep and other deformation properties of the polymer film. For short characteristic times the visco-elastic properties can be characterized by the complex modulus of elasticity. This can be determined by superimposing an alternating force on a constant indentation force and then measuring the phase and amplitude ratio of the dynamic force and the dynamic indentation depth.