Chapter 2. Properties and Characterization of Thin Films

This chapter includes the following characteristics:

A. Film Thickness
B. Roughness
C. Mechanical Properties
D. Electrical Properties
E. Optical Properties
F. Chemical Composition

The first feature:

A. Film Thickness

1. Gravimetric Methods

a. Weighing
b. Quartz Oscillator Method
c. Microbalance
d. Dosed Mass Supply

2. Optical Methods

a. Photometer Method
b. Tolansky Interferometer
c. FECO Method
d. Other Optical Methods

3. Direct Methods

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4. Film Thickness Measurement by Electrical or Magnetic Quantities

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b. Capacitance Method
c. Eddy Current Method
d. Magnetic Method

5. Thickness Measurement by Interaction with Particles

a. Evaporation Rate Monitor
b. Other Methods

A. Film Thickness

Thin film science has received tremendous attention in the recent years for their applications in diverse fields such as, electronic industries, military weapon systems space science, solar energy utilization etc.
Thin films are used as optical and super conducting film materials, high memory computer elements, sensors etc.
The film properties mainly depend upon the preparative conditions, film structures, presence of defects, impurities and film thickness. Various physical constants related to the bulk material properties may not often be the same for corresponding films prepared from the bulk However, with increasing film thickness these tend to assume corresponding bulk values. Numerous applications of films lead to intense studies of these especially to develop and prepare better films with specialized properties for newer compounds or composite materials.

A thin film may be defined as a solid layer having thickness varying from a few angstroms to about 10 micrometer or so. Further it may broadly be classified in three subdivisions according to its thickness as,
I) Ultra-thin (50- 100A°)
II) Thin (100- 1000A°)
III) Comparatively thick one (greater than 1000A°)
Thickness plays an important role in thin films it is an important parameter, which affects the optical, electrical, structural etc., properties of metals considerably. Reproducible characteristics can be obtained by choosing specific thickness and proper combination of deposition parameters for a particular material.

To make sure that coatings which were produced by a given process satisfy the specified technological demands a wide field of characterization, measurement and testing methods is available. The physical properties of a thin film are highly dependent on their thickness. The determination of the film thickness and of the deposition rate therefore is a fundamental task in thin film technology.

In many applications it is necessary to have a good knowledge about the current film thickness even during the deposition process, as e. g. in the case of optical coatings. Therefore one distinguishes between thickness measurement methods which are applied during deposition ("in situ") and methods by which the thickness can be determined after finishing a coating run ("ex situ").

1. Gravimetric Methods

These are methods which are based on the determination of a mass. The film thickness *d* can be calculated from the mass of the coating *m* if the density ρ and the area *A* on which the material is deposited is known:

$$d = m / (A \rho) \quad \ldots\ldots\ldots\ldots 1$$

For this method one has to bear in mind that the density of a coating may deviate significantly from that of the bulk (e. g. due to porosity or implanted interstitial atoms).

a. Weighing

The simplest method for film thickness determination is most probably the determination of the mass gain of a coated substrate with an exact balance. Although, together with the problem of film density mentioned above, also other obstacles exist (e. g. condensation of water vapor from the ambient) it is possible to determine film thickness with sufficient accuracy for several practical applications.

b. Quartz Oscillator Method

This set-up, which is commonly called "quartz oscillator microbalance (QMB)", is generally used for the in-situ determination and control of the film thickness and deposition rate in the case of PVD methods. In commercially available designs film thicknesses in the range from 0.1 nm - 100 µm and deposition rates in the range from 0.01 - 100 nms^{-1} are permanently displayed (see Fig. 1).

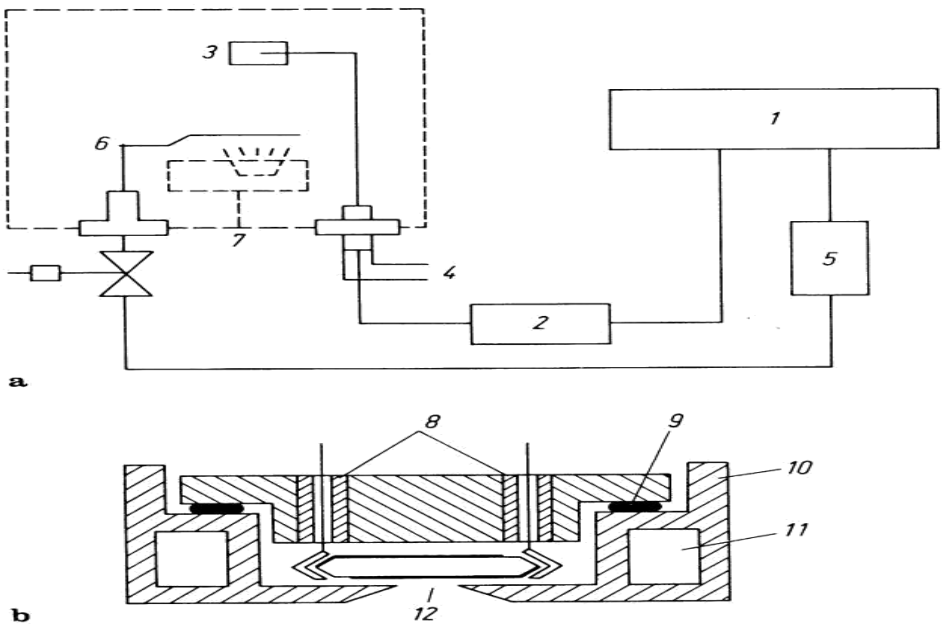

Fig. 1. Quartz oscillator microbalance and control of coating thickness and deposition rate:

a schematic of experimental set-up, **b** Oscillator head (schematic)

1 Quartz oscillator microbalance with D/A-converter; **2** oscillators; **3** measurement head with quartz oscillator; **4** water cooling of quartz crystal; **5** shutter control; **6** shutter; **7** vapor source; **8** electrical connects; **9** seal; **10** Cu block; **11** water cooling; **12** apertures

The method of mass determination was developed in 1959 by Sauerbrey and is based on the change of the resonance frequency of an oscillating quartz crystal

$$f = N / d_q \quad \text{……..2}$$

If the crystal is coated by a film with the mass

$$\Delta m = \rho A d \quad \text{……..3}$$

d_q is the thickness of the quartz crystal and *N* is the spring constant of the crystal, which amounts to (1.67mmMHz) in the case of the so-called AT cut (see Fig. 2, minimum temperature coefficient of the resonance frequency). *A* is the area, ρ the density and *d* the film thickness in the coated region of the quartz crystal.

The mass amount Δm acts similar to a thickness change of the quartz crystal by

$$\Delta d_q = \Delta m / \rho_q A_q \quad \ldots\ldots\ldots\ldots 4$$

Where A_q and ρ_q are the area and the density of the quartz plate, respectively. In this case the resonance frequency decreases proportionally to d if $\Delta f << f$ is valid.

With

$$\Delta f / \Delta d_q = - N / d_q^2 \ldots\ldots\ldots\ldots\ldots 5$$

One obtains

$$- \Delta f = N \Delta m / d_q^2 \rho_q A_q = A f^2 \Delta m / \rho_q A_q NA$$

$$- \Delta f = C \Delta m / A = C \rho d \quad \ldots\ldots\ldots 6$$

Where the constant $C = A f^2 / N \rho_q A_q$ is a measure for the weighing sensitivity.

A more exact calculation yields a function $F (A/ A_q)$ instead of (A/ A_q).

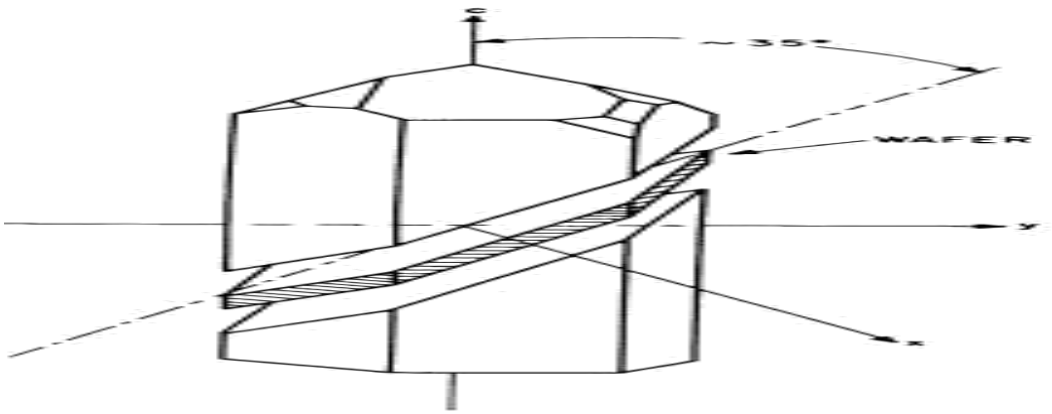

Fig.2: Quartz AT-cut

c. Microbalance

This very exact method is, unfortunately, not suitable for practical applications. It is therefore mostly used for calibrating other measurement processes. All microbalances used for film thickness measurement basically work by compensating of the coating weight by a counteracting force. The compensation can be accomplished by optical or electrical (turning coil) systems. It is possible to measure the mass thicknesses m / A as well as the coating rates $\dot{m} / A$ (see Fig. 3).

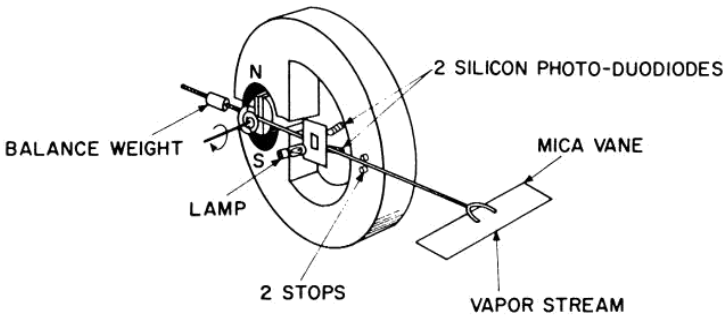

Fig. 3: Microbalance

d. Dosed Mass Supply

Many deposition processes are executed with dosed mass supply, i. e. by using a mass flow (given in kgs^{-1}) which is held constant due to defined geometry of the plant and due to temporarily unchanging process parameters. This method demands calibration e. g. by weighing or chemical microanalysis to find the connection between the mass thickness *m/A* at the substrate and the mass flow.

After calibration it is sufficient in most cases to keep the relevant process parameters constant to obtain the same thickness values in similar deposition times within certain margins.

If the mass supplied per unit time, *m*, or equally the increase of film thickness per unit time, *d*, is known and the deposition rate *a* is constant:

$$a = (dm / dt) / A = \rho\,(dD / dt) = \text{constant} \quad \ldots\ldots\ldots\ldots 7$$

Then the film thickness *D* grows as

$$D = a\,t / \rho \quad \ldots\ldots\ldots\ldots 8$$

i. e. proportionally to the coating time *t.*

Because of its simplicity the method of dosed mass supply is widely used: for thermal spraying, CVD processes, for galvanic and electroless deposition, for buildup welding and in many applications based on sputtering and ion plating.

2. Optical Methods

Optical coatings, unlike other applications, require the measurement of the film thickness as exactly as possible during deposition. Therefore film thickness monitors are used which, especially in the case of multi coated optics (interference filters etc.) are incorporated into closed loop controls by (in some cases quite complex) software components.

a. Photometer Method

This method is mostly used in PVD processes for the production of single layer and multiplayer coatings for optical applications. It measures the optical thickness *nd* so that it allows for a compensation of changes in the refractive index *n* by corresponding changes of the film thickness *d*.

With a photometer (see Fig. 4.) the intensity of light reflected on both interfaces of the sample or transmitted through the sample is measured. These intensities, related to the initial intensity, determine the reflectivity R and the transmittivity T of the film. The impinging light passes an interference filter which acts as a monocromator and is modulated by a chopper so that disturbances by stray light from the surrounding are avoided. The light ray is directed towards the substrate or a reference glass which is located in a test glass exchange unit.

The light intensities are measured by photomultipliers. Computers allow for the automated control of the coating process which is especially important for multiplayer coatings.

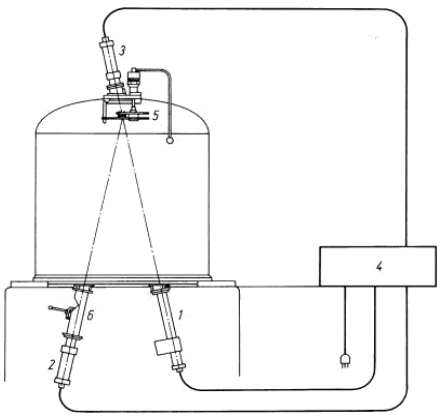

Fig. 4: Photometer-method for film thickness measurement:
1 modulated light source; **2** detector for light reflected at the coating;
3 detectors for light transmitted through the coating;
4 display unit; **5** test glass exchanger; **6** beam deflection

Although it is possible to calculate the film thickness *d* from *R* and *T* by using given values of the optical constants *n* and κ (i. e. real part and imaginary part of the refractive index, respectively) it is in most cases easier to deduce *d* from measured curves (see Fig. 5.)

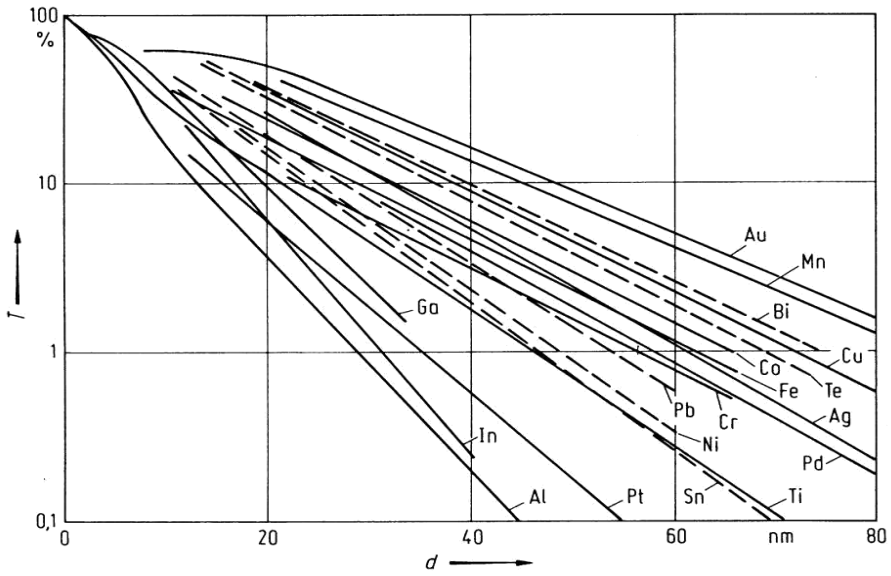

Fig. 5: Transmissivity *T* in dependence on the film thickness d, measured at 550 nm; substrate: glass.

b. Tolansky Interferometer

The basic principle of this multiple beam interferometer is as follows: a thin transparent glass slide is put onto a highly reflecting surface. The glass slide is tilted against the surface by an angle α. If this set-up is illuminated by monochromatic light, multiple beam interferences lead to the formation of equidistant interference lines. The more partial beams interfere, the sharper the lines. Their distance depends on α. A film thickness can be determined by this method as follows: First a scratch is made into the film which reaches down to the substrate (it is also possible to mask a part of the substrate during deposition which leads to the formation of a step). Then the sample is coated by a highly reflective layer. Because of the scratch the distance reflector/interference slide is changed, which leads to an offset of the interference lines relative to each other.

This situation is shown in Fig. 6. The film thickness *d* is given by:

$$d = \Delta N \lambda / 2 \quad \text{.....9}$$

Where ΔN is the number (or the part) of the lines by which the interference lines are shifted by the scratch or the step.

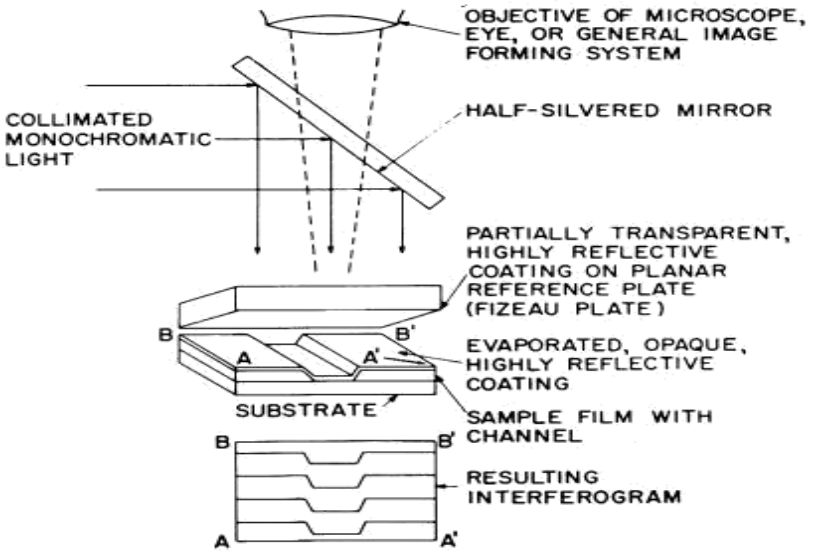

Fig. 6: Schematic of the Tolansky interferometer

Tolansky interferometer is commercially available as add ons for optical microscopes. The advantage of fast and easy use is counteracted by the disadvantage that a suitable scratch or step has to be present.

In addition the step (scratch) has to be covered by a highly reflective coating, mostly Ag. The resolution lies at approx. ± 1 nm if one works with strictly monochromatic light and highly reflective samples and interference slides.

c. FECO Method

The FECO (Fringes of Equal Chromatic Order) method has an even higher resolution than the Tolansky interferometer. Given a careful measurement a resolution of 0.1 nm can be achieved. The principle is displayed in Fig7. Parallel white light is illuminating the combination of sample and reference slide. The reflected light is focused into the entrance slit of a spectrograph via a semitransparent mirror. The image of the step has to be normal to the entrance slit.

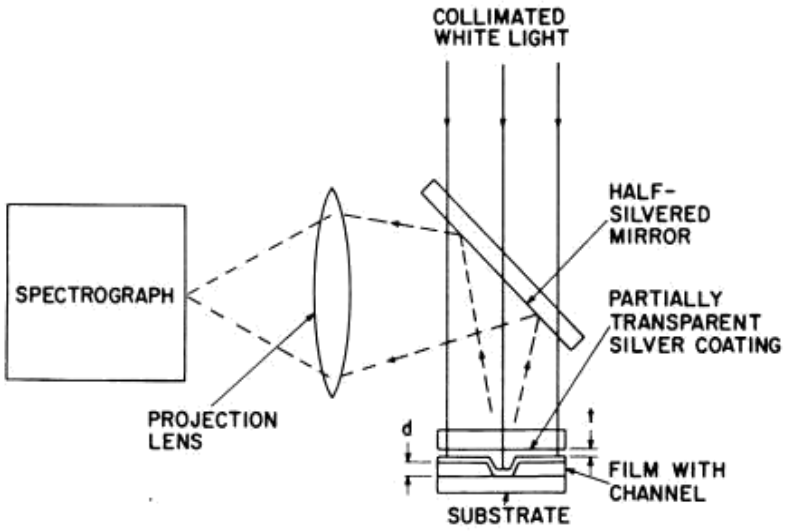

Fig. 7: Schematic of the FECO method

d. Other Optical Methods

Apart from the methods described previously the optical determination of film thickness can be done by various other techniques. Some examples are: The Nomarsky-interferometer, which is available as add on for optical microscopes; the VAMFO (Variable Angle Monochromatic Fringe Observation) method allows determining the film thickness and the refractive index in situ; the same is possible with Ellipsometry.

3. Direct Methods

Direct methods allow the determination of film thickness either by mechanical profiling or by observation in microscopes.

a. Stylus Method

The film has to exhibit a step on a plane substrate. A diamond stylus (tip curvature approx. 10 µm) is pulled along the surface at constant velocity. The step height is measured by a pick-up system. Prerequisite for an exact measurement are a suitable hardness of the film and a plane substrate. To prevent destruction of the sample the load on the tip can be reduced to approx. 10 µN.

The metering range ranges from some 5 nm to some 10 µm at a resolution of some Å in the most sensitive range. An additional application of these commercially available devices is the imaging of surface profiles and the acquisition of roughness values.

b. Optical and Electron Microscopy for Thickness Measurement

For the determination of the film thickness with the optical microscope e. g. metallographic cross sections are used. In the Transmission Electron Microscope (TEM) replica of a step in the film or cross sectional preparates can be investigated. In the Scanning Electron Microscope (SEM) the step itself or a fracture surface of the film can be imaged.

The resolution and the metric range depend on the instrument and on the magnification. In the optical microscope film thicknesses up to some mm with a resolution of 0.1 µm can be determined.

In the SEM a resolution of 5 nm can be achieved and in the High Resolution TEM (HRTEM) 0.1 nm are possible.

4. Film Thickness Measurement by Electrical or Magnetic Quantities

a. Resistance Method

This method is used in the case of PVD processes for the determination of the film thickness of metallic coatings. The monitoring element is an insulating plate with two parallel line contacts between which a film is deposited through a mask.

The resistance R as a measure of film thickness is controlled via a bridge circuit. The deposition rate is determined by electronic differentiation.

With the aid of a zero point indicator the deposition process is stopped if the set point of the film thickness is reached. The metric range lies between 1 nm and 10 µm. Applications are metal films for integrated circuits, resistance films made from NiCr, metallized foils etc.

b. Capacitance Method

In analogy to the previous method the film thickness of insulating coatings can be determined by a monitoring element consisting of comb shaped, interlocking plane electrodes which allow the measurement of the capacity change during deposition.

c. Eddy Current Method

The thickness of insulating coatings on non-ferrous metal or of non-ferrous coatings on insulating substrates can be measured by this method. The measurable quantity is e. g. the voltage applied to a RF coil which is modified by eddy currents in the non-ferrous metal. Since this quantity is also dependent on the conductivity of the non-ferrous metal a calibration is necessary. The method is mostly applied in polymer metallization.

d. Magnetic Method

This method is applied to films which are deposited on a substrate of plane ferritic steel. It is based on the measurement of the adhesive force of a magnet put on the coating (non- ferrous metal, lacquer, polymer) which depends on the film thickness. Since this force also depends on the permeability of the steel a calibration is necessary. Also Ni as coating material is accessible to thickness measurement after calibration.

5. Thickness Measurement by Interaction with Particles

a. Evaporation Rate Monitor

Film thickness or deposition rate monitors were developed especially for applications based on evaporation technology. To control the vapor density in the vicinity of the substrate the vapor is ionized at this position by collisions with electrons emitted from a glow filament. The ion current is measured. Some elder designs for these devices are displayed in Fig.8.

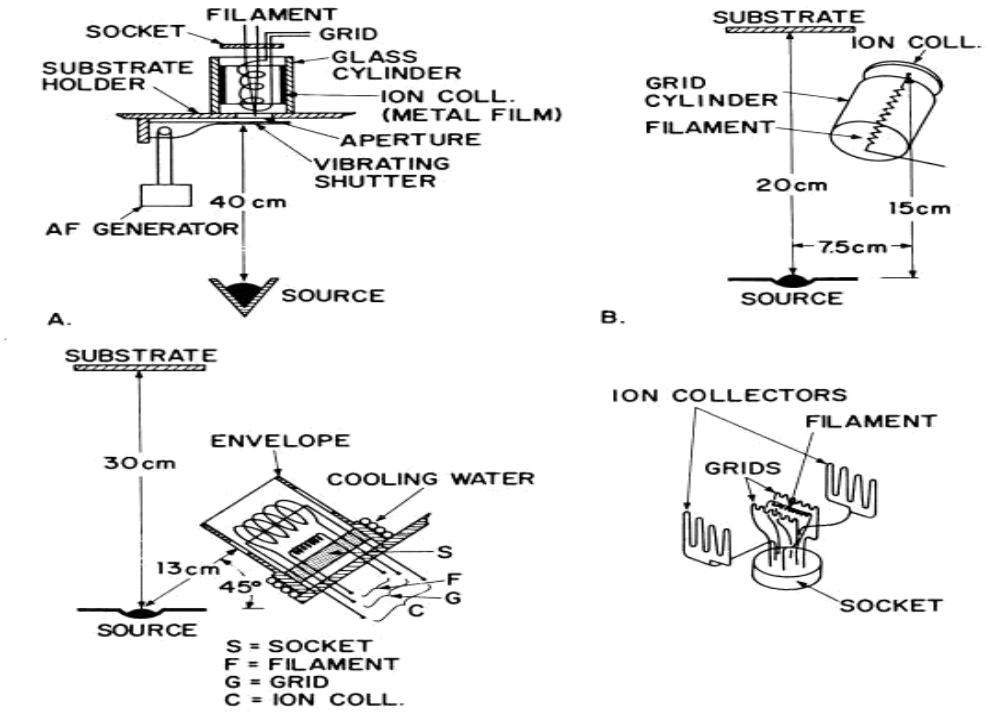

Fig. 8: Thickness and rate monitors based on the ionization principle

More recent devices analyze the ion current by a quadrupole mass spectrometer. By this method the evaporation rates of simultaneously evaporated materials can be determined.

b. Other Methods

... Beta (electron)-backscattering: especially suited for the film thickness determination of noble metal films of and of metal films on printed circuit boards.

... X-ray fluorescence: also the thickness of multilayer systems can be determined. Because the method is non-destructive and exhibits a high throughput it is used preferable in quality control e. g. for abrasion resistant coatings.

... Tracer-methods: either the coating or the substrate has to contain radioactive "tracer" atoms.