

OPTICAL COATINGS: STATUS OF  
THE ART AND RECENT DEVELOPMENTS

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An attempt will be made to review optical coatings, including their present scientific and industrial applications, recent developments and possible future requirements. The following six points will be considered. i) the applications for thin films in optics , ii) methods used for their production, iii) kind of substrates used, iv) kind of films deposited, v) required film properties, vi) future trends.

Optical Coatings, Thin Films

1. APPLICATIONS OF THIN FILMS IN OPTICS

Thin films are used in following applications:

- i) to decrease the reflectance of an air/solid interface with antireflection (AR) coatings. At present, single layer AR coatings are being replaced more and more by broad band multilayer antireflection coatings; ii) to enhance the reflection of a solid surface with mirror coatings. (Of primary importance are front-surface mirrors of metals with and without protective films; and all dielectric mirror coatings.); iii) to split light uniformly, such as across the whole visible range with neutral beam splitters or into its spectral characteristics with colour separators to obtain long wave pass and short wave pass; iv) to filter light with broad band filters, narrow band filters (monochr. f.) and polarizing filters; v) to guide light, such as in planar wave guides or channel wave guides; vi) to absorb

and to scatter light such as in absorption filters, screens; vii) to emit and to detect light as in lasers and detectors. Some examples of these important applications are shown schematically in Fig. 1.

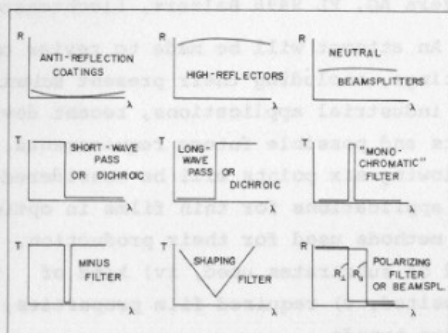


Fig. 1 Typical applications of optical coatings

## 2. THE METHODS USED FOR THEIR PRODUCTION

A distinction is made between two different groups of processes:

a) subtractive methods: e.g. surface leaching by acids and bases to produce AR coatings. These older techniques have been replaced by the b) additive methods: which can be divided into chemical and physical processes, with an exception of AR coatings for fusion lasers. Typical methods in the group (b) are i) dip and spray coating: chemical processes used to coat large areas of complex shape; ii) chemical vapour deposition (CVD) processes, plasma polymerisation: protective coatings; iii) physical vapour deposition (PVD) processes: evaporation/condensation in vacuum, sputtering, ion plating, and the corresponding reactive gas processes to produce stoichiometric compound films by PVD (mainly oxides, nitrides or oxynitrides).

The various additive film production methods are shown

in the block diagram in Fig. 2.

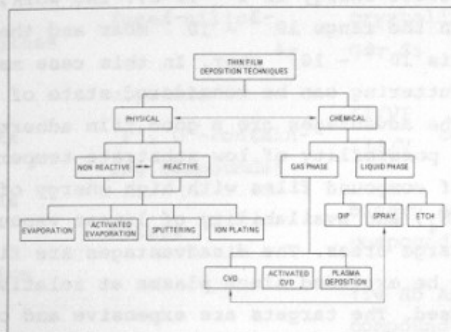


Fig. 2 Various deposition techniques for optical coatings

### 3. CHARACTERISTICS, ADVANTAGES AND DISADVANTAGES OF PVD PROCESSES.

#### i) Evaporation/condensation:

The mechanism consists of melting or subliming a material to form a vapour. The techniques used are resistance heating, electron beam heating, plasma beam heating, ion beam heating, laser beam heating.

The energy of vapour particles is 0.1 - 0.2 eV (1000 - 2000°C). The residual gas pressure range is  $10^{-6}$  -  $10^{-4}$  mbar. Electron beam guns can be qualified as state of the art PVD process. The advantages are versatility (materials, substrates), high deposition rates possible, very pure films and that standard configuration covers most applications. The disadvantages are film adherence and density are critical. Substrate heating is often required. The compound films with high free energy of formation (e.g.  $\text{TiN}$ ,  $\text{Si}_3\text{N}_4$ ) cannot be obtained.

#### ii) Sputtering:

The mechanism is based on ejection of target atoms by

momentum transfer from impinging atoms/ions. The techniques employed are plasma (dc, rf), electrons, microwave and ion beam. The particle energy is 1 - 10 eV. The working gas pressure is in the range  $10^{-3}$  -  $10^{-1}$  mbar and the residual gas pressure is  $10^{-6}$  -  $10^{-4}$  mbar. In this case magnetron and plasmatron sputtering can be considered state of the art techniques. The advantages are a good film adherence, high film density, possibility of low substrate temperatures preparation of compound films with high energy of formation e.g.  $\text{TiN}$ ,  $\text{Si}_3\text{N}_4$ , and availability of linear vapour source for coating large areas. The disadvantages are film contamination cannot be excluded since plasma at relatively high pressure is used. The targets are expensive and only plane substrates can be coated.

### iii) Ion Plating:

In this mechanism substrates are subjected to a flux of energetic particles which may cause sputtering during film formation. The techniques are ionization and acceleration of atoms using evaporation or sputtering sources; and ion bombardment (high energy neutral atom bombardment) of the substrate before and during film formation by separate ion beam guns. The particle energy is 10 - 100 eV. The advantages are the possibility of sputter cleaning, wide choice of different evaporation sources, highest ionization efficiencies and ion energies compared to all other deposition techniques, excellent coating adherence, high film density and three dimensional coverage for complex substrates. The disadvantages are highly diversified equipment configurations and complex process with a large number of parameters.

## 4. KIND OF SUBSTRATES

Different substrate materials are used. These can be classified into inorganic materials (mineral glass, metals) organic glass, plastics and crystalline materials.

Typical substrates for the various spectral ranges are described in Table I.

Table I

<u>visible range:</u>	<u>ultra violet:</u>	<u>infrared:</u>
inorganic and organic glass	fused silica	crystalline materials Ge, Si
	crystals	II/VI III/V compounds
plastic parts	(F', O"-containing compounds)	
plastic foils	metals	binary and ternary compounds
glass ceramics		(Te Sb As) Ox or Sx
metals		compound glass spinel metals

The substrates must be cleaned carefully before coating. Special wet and/or dry processes have been developed to perform this operation.

#### 5. KIND OF FILMS DEPOSITED

The following types of thin films can be deposited.

i) metals: Al, Cr, Ag, NiCr, Au, Rh, alloys; ii) semiconductors: elements, compounds (e.g. (Si, Ge, ITO) fluorides (e.g. of Li, Mg, Ca, Ba, Al); iii) compounds: sulfides, selenides, tellurides (e.g. of Zn, Cd) oxides (e.g. of Si, Ti, Zr, TaAl, Hf, Sn, In), oxynitrides, nitrides and carbides; iv) cermetes: SiO/Cr, TiO<sub>2</sub>/Au, Ag, Cu, SiO<sub>2</sub>/Au, Ag, Cu.

The films are used as single films or in more or less complex multilayer structures.

Most multilayer structures are all-dielectric film systems composed of nonabsorbing films. The quality of the whole thin film product depends to a high degree on the properties of the individual films.

## 6. THE REQUIRED FILM PROPERTIES

The properties of thin films are primarily determined by the type of chemical element or compound they are made of and by the film thickness. Their optical, electro-optical, electrical, chemical and mechanical behaviour is also determined by structure, microstructure, surface and interface morphology, and chemical composition. These are strongly influenced by the film preparation method, the chosen parameters, and by the post-deposition treatment. To answer this question we have to consider optical properties, chemical stability, mechanical stability and electrical properties.

i) Optical properties - Concerning optical properties the following characteristics are important: homogeneity, isotropy, reproducible refractive index, absorption/transparency relation and optical losses by scattering and absorption.

Many investigations have been performed to determine the optical properties of thin films. Published data can be found in the literature cited at the end of this paper.

ii) Chemical stability - In this case following points should be considered: environmental stability effects of climatic conditions such as in tropical and arctic regions and of humidity, stability against attack by sea water and stability against deterioration produced by sudden changes in temperature and humidity. There are many different methods and procedures, i.e. various military specifications and government acceptance requirements which can be used to check these.

iii) Mechanical stability - The important mechanical properties are adhesion, hardness, abrasion resistance, density, fewer pinholes and low mechanical stress (possibilities to influence stress in sign and magnitude). The mechanical properties of thin films produced by the various deposition techniques are strongly dependent on structure, microstructure, chemical composition and in particular incorporated

impurities. They can thus be influenced by the production technology used and the parameters chosen. The published data concerning mechanical properties are not as extensive as those concerning other film properties.

iv) Electrical properties - The films can be insulating, semiconducting or conducting. These properties are best studied, for instance with transparent conducting electrode films and electrochromic layer structures.

## 7. FUTURE TRENDS

Scanning through the film literature, certain trends can be recognized:

i) films and film systems with lower optical losses for ringlasers (Gyrolasers), high energy laser applications e.g. nuclear fusion experiments.

To obtain such films requires purest materials (careful material preparation to avoid contamination), stoichiometry (activated reactive deposition), clean pumping systems (diffusion pumps are replaced by turbomolecular and cryopumps) and change in deposition technique (trend to ion assisted deposition techniques, e.g. sputtering and ion plating).

ii) films with refractive indices very near or equal to the bulk material. Such films are obtained with a suitable deposition technology (such as ion plating) as a consequence of dense microstructure, fewer or no grain boundaries, high degree of homogeneity and low roughness.

These requirements are important not only for an extension in application, but also for better economy in production. Optical thin film products suffer on close bargaining!



Further trends are:

iii) extension of the application in electrooptics as in transparent electrodes for liquid crystal displays (LCD) plasma-, and electroluminescence-displays, electrodes and colour filters for flat LCD-TV-display panels neutral filters also for black and white television panels, AR-coatings on cathode ray tube panels for data reading devices, electrodes and AR coatings for display sets in automobile instrumentation, darkening/brightening systems consisting of electrochromic layers.

iv) reliable film thickness and rate control using photometric (reliability, termination point, wide band monitoring), quartz crystal (reliability, extension of range) and improvements in automation (fully automatic coating plants of highest reliability).

v) increase in the number of suitable film materials for UV and IR for example:  $\text{HfO}_2$  ( $0.22 \mu\text{m}$ ),  $\text{Y}_2\text{O}_3$  ( $0.3 \mu\text{m}$ ),  $\text{Ge}_{30}\text{As}_{17}\text{Te}_{30}\text{Se}_{23}$  ( $n = 3.1$  at  $10.6 \mu\text{m}$ ).

vi) films for digital optical data recording and optical audio and video recording using compact disk, programmable optical disk and erasable and reusable optical disk.

vii) in integrated optics applications such as glass fiber optical wave guides, e.g. (InGa)(AsP) Laser  $1.3 \mu\text{m}$ , monomode  $0.38 \text{ dB/km}$ , active thin film components e.g. lasers and modulators and passive components e.g. planar and channel wave guides.

viii) in energy related coatings a) films for laser fusion experiments such as AR coatings, mirrors and polarizing beam splitters e.g. (Nova-project Lawrence Livermore, large dimension  $\varnothing = 50 \text{ cm} \rightarrow 120 \text{ cm!}$ ). b) transparent, conducting coatings to reflect inefficient IR radiation and prevent photovoltaic cell overheating, to diminish sheet resistance



typical of thick Si cells, to increase solar collector panel transparency and energy conversion efficiency, for window coatings which reduce room heat loss without light transmission reduction and coating on low pressure Na lamps which allow higher operation temperature and yields more light output. c) architectural coatings - Such coatings are used both for decorative and functional purposes such as: colour effects (e.g. decorative windows), summer window (short wave pass,  $\text{TiO}_2/\text{Me}/\text{TiO}_2$ , Coating designs are adjusted to lower visual transmission and enhance IR rejection) and winter window (short-wave pass, ITO, Coating designs with longer spectral cut-off to admit a maximum amount of visible light while maintaining high for infrared reflection). d) interference optics used for the production of X-ray and neutron mirrors.

ix) soft X-ray mirrors  $\lambda = 45 - 200 \text{ \AA}$  (radiation obtained from synchrotrons). About 200 alternating layers with planarity of  $1/20 \lambda$  consisting of: C or B (transparent) and ReW or AuPb alloy (opaque) result in a mirror reflectance of about  $R \sim 30\%$  at normal incidence.

x) super mirrors for neutrons  $\lambda = 4 - 8 \text{ \AA}$ . Using a multilayer structure of the following bilayers Fe/Ag, Co/Ti and Fe/Co a high reflectance at  $\alpha = 0.2 - 1.5^\circ$  is obtained. Such devices can be used as polarizers or monochromators.

This review, does not pretend to be more than a rough survey on the topic. However, the examples given on applications and possible application should illustrate the broad spectrum of possibilities offered by optical coatings for progress in science and technology.

#### LITERATURE:

- H. Anders, Dünne Schichten für die Optik, Wiss. Verlagsges. mbH. Stuttgart (1965).

- H.A. MacLeod, Thin Film Optical Filters, Adam Hilger, London (1969).
- H.K. Pulker, Coatings on Glass, Elsevier, Amsterdam (1984).
- R. Puyan  (Ed.), Proc. Battelle Seminar on Coatings on Glass, Geneva, 1980, Thin Solid Films, 77 No. 1/2/3, (March 1981).
- S. Musikant (Ed.), Proc. SPIE, 297, Emerging Optical Materials, San Diego (1981).
- D. Brandon (Ed.), Proc. 5 ITFC, I and II, Herzlia on Sea, (1981), Thin Solid Films, 89 (1982), 90 (1982).
- R.I. Seddon (Ed.), Proc. SPIE, 325, Optical Thin Films, Los Angeles (1982).
- J.R. Jacobsson (Ed.), Proc. SPIE, 401, Thin Film Technologies, Geneva (1983).
- ISSN 0091-3286, Optical Engineering, 23, No. 3 (May/June 1984).