Coating Materials

Martin Friz[1] and Friedrich Waibel[2]

[1]Merck KGaA, D-64579 Gernsheim, Germany
[2]Umicore Materials AG, FL-9496 Balzers, Liechtenstein

1 Coating Materials for Different Deposition Techniques

A large number of different deposition techniques are used for the production of thin films for optical applications, as outlined in chapter 'Thin Film Deposition Techniques' by H. K. Pulker. The two most important categories are physical vapour deposition (PVD), namely thermal vaporisation and sputtering, and chemical vapour deposition (CVD). It is obvious, that for each deposition technique suitable coating materials are required.

The PVD processes normally use inorganic elements or compounds and gases, whereas the CVD processes, dip coating and spinning, use liquid inorganic and organic compounds and gases.

Liquid compounds and gases are normally purchased directly from the producer, because they need no special preparation.

Solid materials have to be compact and in the appropriate form or shape, free of gas inclusions or even be prepared according to a special recipe. Targets must also fulfil structure requirements (grain size, texture, precipitation). These operations are the task of companies specialised in the production of coating materials and targets.

This chapter focuses on solid coating and sputtering materials. The requirements on these materials are discussed, their properties listed and their production described.

Earlier summary articles or chapters in monographs on coating materials have been written by H. A. Macleod (Macleod 1986) , H.K. Pulker (Pulker 1979, 1999) and E. Ritter (Ritter 1975).

2 Requirements for Coating Materials

2.1 Evaporation Materials

Apart from the elements only a relatively small number of inorganic compounds can be evaporated to produce a coating with the same composition as the starting material. Suitable compounds are found mostly among the chalcogenides and halides. In some cases it is necessary to change the evaporation process (e.g. reactive evaporation, evaporation from several sources or flash evaporation) in order to ensure that the resultant coating has the desired stoichiometry.

Evaporation materials have to fulfil a series of requirements in order to meet the demands of the coating process and to achieve the required film properties.

2.1.1 Chemical Purity

The chemical purity of vapour deposition materials influences not only the coating properties but also the way the material behaves during evaporation. As will be shown, a purity of least 99.99 %, normal in metallurgy and often specified by optical coating companies, is indeed a step in the right direction. However, it does not indicate whether the material will be suitable, nor how the material compares to materials of a different origin.

Even minute concentrations of transition elements can have a marked effect on the transmission properties of dielectric layers. Unfortunately, there are only few publications that address this topic. Nowhere is there a description, for instance, of the relationships between levels of contaminants and optical absorption in thin films. The most detailed articles containing quantitative accounts of impurity-specific losses can be found in the literature on optical waveguides made of silicon dioxide (SiO_2) (Newns et al. 1973; Schultz 1974). Particularly troublesome in the visible range are minute quantities of cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni) and vanadium (V). Cobalt, chromium and vanadium exhibit the greatest molar absorption or extinction coefficient k in the order of 100 litres·mol^{-1}·cm^{-1}. Using Beer's law of absorption

$$A = 1\text{-}e^{-k \cdot c \cdot d}$$

enables an absorptance A of 10^{-3} % to be estimated for a layer thickness d = 100 nm and an impurity level c = 100 ppm (equivalent to about 0.003 mol/litre). Compared to this value, other causes of optical losses in the layer, e.g. scattering or absorption caused by variations in stoichiometry, often have a much greater effect. This means the aforementioned purity of 99.99 % is almost invariably adequate. For many important applications (e.g. AR coatings for spectacles and photographic lenses, filters, cold-light mirrors) levels of impurities even totalling 1000 ppm may be tolerated.

Prerequisite is, of course, that the strongly absorbing impurities mentioned are actually detected during chemical analysis of the evaporation material. It is therefore necessary to define limits for the interfering impurities – usually the elements listed above. The methods of analysis most widely used nowadays for detecting impurities are flame atomic absorption spectrometry (FAAS) and optical emission spectrometry with plasma excitation (ICP-OES). For substances with light cations, e.g. for magnesium fluoride (MgF_2), aluminium oxide (Al_2O_3), silicon monoxide (SiO) and silicon dioxide (SiO_2), x-ray fluorescence may also be used with excellent limits of detection for heavier elements.

Chemical analysis must also be able to detect foreign substances, which, for instance, might have a detrimental effect on deposition behaviour or the structure of the coating. A well known effect is that of a high oxide content in fluorides, most noticeable perhaps in MgF_2, as it can result in splashing during evaporation. Many oxides have lower vapour pressure than the corresponding fluorides, and form an oxide layer over the melt during evaporation. This causes the melt to overheat and the oxide layer to tear, the actual cause of splashing. Determination of non-evaporable residue is one possible way of analysing the oxide content. Another option is inert gas extraction.

Evaporation behaviour and structure of the layer may be influenced by high residual gas content in the evaporation material. In such cases it is best to determine the residual gas content by heating the substance in a high-vacuum recipient while monitoring pressure versus time. A mass spectrometer should be used to test the liberated gases, to be able to find the precise cause.

2.1.2 Physical Properties

Testing of dimensions, particle sizes and weights is a vital part of quality control. For tablets it is quite easy to deduce their density, which in the case of substances with poor melting properties, e.g. zirconium oxide (ZrO_2), is a critical measure of the stability of the tablet. Extreme differences in temperature within a tablet during electron beam evaporation lead to significant heat stress. In such cases cracks in the tablet can not be completely avoided, and disintegration can only be prevented by keeping the porosity of the tablet sufficiently high; yet the porosity must not be so high as to make it impossible to maintain a low adsorbed gas content.

Some substances, e.g. some titanium suboxides, are relatively brittle and produce large amounts of abraded particles during storage and transport. The problem can be lessened by optimising the packaging with padding or vacuum wrapping. An abrasion test in a running wheel is needed to allow various production batches to be assessed and compared.

Various vapour deposition materials with favourable properties are prepared from substance mixtures, whereby new compounds are formed by solid state reactions during the production process. The melting and evaporation properties of these materials depend to a very large extent on the completeness of the chemical reaction. X-ray diffraction (powder diffraction) is used to check the phase purity of the end product. Also, differences in the stoichiometry of a compound may negatively affect evaporation characteristics and coating properties. A good example of this are the various titanium sub-oxides, where determination of stoichiometry may well be an appropriate part of quality control.

2.1.3 Process Suitability

Decades of experience in the manufacture and use of evaporation materials have shown that factors affecting process suitability are so complex that they do not allow quality to be defined simply by physical and chemical properties. Therefore, substance testing under actual conditions of use continues to be a major feature of quality control. The assessment criteria differ from substance to substance. Common criteria are, however, the way the material behaves during the heating or melting phase, the pressure profile for the system and the heating power needed for a given rate of evaporation. In the case of oxides, in particular during reactive evaporation, it is also necessary to record the evaporation data (pressure and rate fluctuations) over a prolonged period. In the case of mixed oxides, the reflectance of the coating is measured as it builds up, and the refractive index determined as an additional control for correct stoichiometry. In certain cases, such as when hafnium oxide (HfO_2) is used in UV applications, spectrophotometric measurements are taken to confirm the suitability of the material for this spectral range.

2.2 Sputtering Targets

Sputtering of metallic layers is straightforward. For the sputtering of dielectric layers there are two different approaches. The first is to use ceramic target materials of the desired layer composition. The second is a reactive sputtering process, where a metallic target is sputtered in a reactive atmosphere of oxygen or nitrogen. Most sputtering processes for interference coatings use metallic target materials. In reactive sputtering processes there is not only a reaction on the substrate but also on the surface of the metallic sputter target. A stable sputtering process needs optimised management of reactive gas and cathode power. Most processing problems (such as arcing) result from dielectric layers grown on the target surface.

Ceramic targets are seldom used because of two severe disadvantages. One disadvantage is that most of the ceramic materials are non-conductive and cannot be operated using Direct Current (DC) power. To install RF (Radio Frequency) power is expensive, it induces a low sputter rate and is complicated. The second disadvantage is the high production cost of ceramic target materials.

Ceramic targets are only used where an extremely precise stoichiometry of the dielectric layer is required . The best example is the production of ITO-layers with In_2O_3/SnO_2 targets. The use of conductive TiO_2 targets is also increasing (Weigert 2001).

Materials for sputtering targets have to fulfil specific requirements: The most important characteristics include:

- purity
- chemical homogeneity in case of alloys (stoichiometry)
- homogeneity of the structure (grain size, texture, precipitates, crystallinity)
- target density
- no oxide or other impurity inclusions (metals and alloys)
- no pores and voids

- good electrical conductivity (ceramics and semiconductors)
- no surface contamination
- dimension, target surface roughness
- mechanical stability of the compound target

The overall purity of sputtering targets for interference coating applications is 99.99%. It allows a sum of metallic impurities of 100 ppm. This is not very high compared with microelectronic applications (99.9999%, sum of impurities of 1 ppm in maximum).

Several of the most common analytical techniques to control impurity values and contents of alloying elements are XRF, ICP, GDS, GDMS, and CGHE. (Venzago and Weigert 1994; Wilhartitz et al.1990).

The optimised performance (purity, structure, homogeneity, etc.) for each target, from target-to-target, and from lot-to-lot is very important for good sputter results. The critical elements that influence the absorption levels are Co, Cr, Cu, Fe, Mn, Ni, V, etc.

Studies show a direct correlation between grain size and target performance. A small and homogeneous grain size induces a constant sputter rate over the entire target surface and produces consistent film thickness uniformity. It also affects the control of second phase precipitates (Marx and Murphy 1990). Precipitates larger than 10 µm cause particle generation during the sputtering process.

These quality factors are strongly influenced by the way the material is produced (see Chap. 4).

Nearly all modern sputtering processes are based on magnetically enhanced cathode processes. For the planar magnetron the sputtering target is just a sheet of metal or ceramic. Very often it is produced as a compound target bonded on a cooling or a special backing plate, to produce a mechanically stable system (weak or brittle materials) or to save costs of expensive target materials. Rotating cathodes are increasingly used for large area coatings (tube as target geometry).

The criteria for the choice of technology include target lifetime, target utilisation, material recycling and uptime of the sputtering process or stability of the process during target lifetime.

3 Survey on Materials, Properties and Applications

Properties of thin films including optical, mechanical, electrical, thermal, and chemical properties are influenced by deposition parameters. Therefore refractive indices and transmittance range given in this chapter are only meant as guidance values. Detailed information on the influence of deposition parameters on film properties is given in chapters ‘Some Fundamentals of Optical Thin Film Growth’ by N. Kaiser and ‘Film Deposition Methods’ by H.K. Pulker.

3.1 Dielectrics

3.1.1 Fluorides

Ultraviolet Spectral Range

The development of ultraviolet light sources, especially the Excimer laser, has had a significant impact on new applications in material processing and medicine (Stamm et al. 1997). Several fluorides with band gap energies around 10 eV are suitable for such applications in the wavelength range even below 200 nm. Extensive data on refractive index and extinction of fluoride films in the UV range using different coating techniques have been published between 1987 and 1991 (Lingg et al. 1987; Zukic et al. 1990; Kolbe et al. 1991).

Table 1. UV properties of fluoride films

Material	Transmittance Data	Refractive index
Aluminium fluoride (AlF_3)	k ~10^{-4} (λ=200 nm) k ~10^{-3} (λ=200 nm), IAD $T_{cut\text{-}off}$ = 120 nm	n = 1.4 (λ=200 nm) [a] n = 1.5 (λ=200 nm), IBS [a] n = 1.38 (λ=193 nm) [b]
Barium fluoride (BaF_2)	k ~10^{-2} (λ=140-230 nm)	n ~1.7 (λ=160-210 nm) [c]
Calcium fluoride (CaF_2)	k ~10^{-2} (λ≥180 nm)	n < 1.3 (λ≥180 nm) [c]
Cryolite (Na_3AlF_6)	$T_{cut\text{-}off}$ = 120 nm	n = 1.37 (λ=193 nm) [b] n = 1.42 (λ=193 nm) [d]
Dysprosium fluoride (DyF_3)	$T_{cut\text{-}off}$ < 190 nm	n = 1.55 (λ=193 nm) [b]
Gadolinium fluoride (GdF_3)	k ~10^{-3} (λ=200 nm) $T_{cut\text{-}off}$ =123 nm	n = 1.68 (λ=200 nm) [a] n = 1.58 (λ=193 nm) [b]
Lanthanum fluoride (LaF_3)	k ~10^{-3} (λ=200 nm) k ~10^{-3} (λ=200 nm), IAD k <2.2·10^{-2} (λ≥145 nm)	n = 1.7 (λ=193 nm) [a] n = 1.82 (λ=200 nm), IBS [a] n = 1.71 (λ=193 nm) [d] n ≥ 1.85 (λ=135-180 nm) [c]
Magnesium fluoride (MgF_2)	k ~10^{-4} (λ=200 nm) k ~10^{-3} (λ=200 nm), IAD k <10^{-4} (λ=140-230 nm)	n = 1.42 (λ=200 nm) [a] n = 1.46 (λ=200 nm), IBS [a] n ~ 1.5 (λ=140-220 nm) [c]
Neodymium fluoride (NdF_3)	k ~ 10^{-3} (λ=200 nm)	n = 1.75 (λ=200 nm) [b] n = 1.75 (λ=193 nm) [d]
Terbium fluoride (TbF_3)	T = 50% (λ=140 nm, d=100 nm) [e]	
Ytterbium fluoride (YbF_3)	T = 50% (λ=142 nm, d=100 nm) [e]	
Yttrium fluoride (YF_3)	k = 0.0025 (λ=193 nm)	n = 1.61 (λ=193 nm) [f]

[a] Kolbe et al. 1991
[b] Cowell 1996[d]
[c] Zukic et al. 1990
[d] Izawa et al. 1994
[e] Lingg et al. 1987
[f] Kolbe et al. 1990

Today research and development in ultraviolet coatings focuses on applications that meet the stringent requirements for optical components used in the new generations of wafer-steppers for the semiconductor industry working at 193 nm (ArF-Excimer) and 157 nm wavelength (F_2-Excimer).

The materials of choice for this application are magnesium fluoride (MgF_2) for the low refractive index layer and lanthanum fluoride (LaF_3) for the high refractive index layer (Bernitzki et al. 1999; Ristau et al. 2001). However, a series of problems still exists before the technological demands of chip production are met:

- small refractive index difference between the two materials used
- optical inhomogeneity of LaF_3 films
- optical losses
- laser induced damage thresholds
- mechanical stress of the thin films

Therefore alternative materials such as aluminium fluoride (AlF_3), cryolite (Na_3AlF_6) and various rare-earth fluorides are being evaluated. The influence of ion-assisted deposition (IAD) techniques on thin film properties is also being researched.

A detailled description on DUV/VUV coatings is given in chapter 'Optical Coatings for the DUV/VUV' by R. Thielsch.

Visible Spectral Range

Magnesium fluoride (MgF_2) is still the dielectric material with the highest consumption. This is based on a combination of material properties like low refractive index and film durability. A large area of applications is the refinement of mineral glass lenses with antireflection coatings for consumer optics (spectacle lenses, camera objectives, and binoculars). However this is by far outnumbered by the manufacture of the so-called optically variable pigment (OVP). This pigment is a multilayer coating made from metals and magnesium fluoride and was originally developed for optical document security. It is now applied to banknotes and valuable documents worldwide and also for a variety of decorative applications (Phillips and Bleikolm 1996; Phillips and Nofi 1999). Other fluorides still being used for applications in the visible range are cerium fluoride (CeF_3) for antireflection coatings and cryolite (Na_3AlF_6) respectively chiolite ($Na_5Al_3F_{14}$) for filters.

Infrared Spectral Range

Thanks to its outstanding mechanical properties for µm film thickness thorium fluoride (ThF_4) has been the material of choice for low index films in the infrared region up to wavelengths around 15 µm (Heitmann and Ritter 1968). ThF_4-films did not show the problem of cracking or peeling-off, encountered with other fluorides. But the main drawback of this material – its radioactivity – caused more and more users to look for a less hazardous replacement and ignoring it in new designs. Therefore, at the end of the 1980s an intense search for alternative materials and processes began for non-radioactive coatings with low losses and high damage thresholds especially for use with the CO_2-laser at 10.6 µm. The most promising candidates are barium fluoride (BaF_2), yttrium fluoride (YF_3) and ytterbium fluoride (YbF_3). It could be shown that films deposited with ion assistance (e.g. BaF_2 or YbF_3) show absorption data and damage thresholds comparable to those obtained from conventionally deposited ThF_4 (Rahe et al. 1990; Schnellbügel et al. 1994).

3.1.2 Oxides, Oxynitrides, Nitrides and Carbides

Film Preparation

Oxides are an important class of coating materials, because they generally form hard, abrasion resistant, chemically and environmentally stable films with a good variety of refractive indices and spectral ranges of high transmission.

Many oxides react at high temperatures with refractory metal boats. Therefore the electron beam evaporation with water-cooled copper crucibles or molybdenum liners is an adequate method for non-activated thermal evaporation.

Since quite a few oxides dissociate at high temperatures, at least to a certain degree, reactive evaporation in an oxygen atmosphere is advisable in most cases, but the level of oxygen has to be adjusted to the actual needs. Reactive evaporation of suboxides is in certain cases, like titanium oxide, a preferred choice.

The metal is used as starting material for the deposition of oxides by reactive arc evaporation and reactive DC-sputtering. If RF sputtering is applied, the oxide can be used as the starting material. For RLVIP the metal or a slightly reduced and hence conducting oxide is the starting material.

In general, all activated evaporation processes, such as IBAD, RLVIP, arc etc. increase and stabilise the refractive index and the transparency of most oxide films, especially the ones with high refractive index.

Nitride, oxynitride and carbide films are normally produced by reactive magnetron sputtering, ion beam sputtering, RLVIP, reactive arc evaporation or by ion-assisted reactive electron beam evaporation.

Important Materials

SiO_2: It can be deposited by electron beam evaporation with IAD (Alvisi et al. 1999) or without IAD (Scherer et al. 1996), by RLVIP (Lorenz et al. 1991), and by ion beam (Tabata et al. 1996), by reactive (Edlou et al. 1993) or RF sputtering. A summary of properties is given by Anderson and Ottermann (Anderson and Ottermann 1997).

SiO: Before the availability of electron beam evaporators for SiO_2 evaporation SiO_x films were prepared by the reactive evaporation of SiO (Ritter 1971). Their composition corresponds to Si_2O_3 and the refractive index is around 1.55. Today SiO is used mostly for multilayer coatings in the infrared range.

Al_2O_3: For optical applications it is mostly deposited by electron beam evaporation, although all the methods mentioned with SiO_2 can be applied (Edlou et al. 1993; Martin et al. 1999).

HfO_2: Used in the UV region and at certain laser wavelengths as a high index material. The films are produced by electron beam evaporation of HfO_2 (Reicher et al. 2000; Andre et al. 2000) or by reactive sputtering. (Edlou et al. 1993). Reactive evaporation of Hf reduces the number of film defects and enhances the laser-induced damage threshold at 1060 nm (Andre et al. 2000).

ZrO_2: Films of ZrO_2 prepared by electron beam evaporation show strong inhomogeneity of the refractive index (Klinger and Carniglia 1985). The refractive index at the film/air interface is smaller by about 0.1 than at the film-substrate interface, called negative inhomogeneity (Bennett et al.1989). This is due to the film structure and the lower packing density at the film-air interface. By using IAD the inhomogeneity changes to positive and under certain conditions homogeneous films can be obtained (Cho and Hwangbo 1996).

Ta_2O_5: Tantalum oxide shows a wide spectral range of high transparency, low losses and high stability. Besides TiO_2 it is probably the most used high index material. It is produced by ion assisted reactive electron beam evaporation (Zoeller et al. 1996), by ion plating, ion beam sputtering (Dods et al. 1999) and reactive DC magnetron (Edlou et al. 1993) or RF sputtering . A summary of properties is given by Bange (Bange 1997).

Nb_2O_5: Niobium oxide exhibits a somewhat higher refractive index than Ta_2O_5. But the UV transparency is not as good as with Ta_2O_5. Films can be produced by RLVIP (Edlinger et al.1989) and by reactive RF magnetron or dual AC magnetron sputtering (Sullivan et al. 2000)

TiO_2: Suboxides are often used for the production of TiO_2 films by evaporation (mostly electron beam), namely TiO, Ti_2O_3 and Ti_3O_5 (The paper by Selhofer et al. 2002 contains a large list of references). The use of TiO2 as starting material in reactive electron beam evaporation is also reported (Chen et al. 1997).

Other deposition methods are reactive arc evaporation (Bendavid et al. 2000), radical beam assisted reactive evaporation (Yamada et al. 1999), RLVIP, ion beam sputtering (Albertinetti and Minden 1996), reactive magnetron sputtering (Edlou et al. 1993) and helicon plasma sputtering (Wang et al. 1999).

A summary of properties is given by Bennett et al. (Bennett et al. 1989) and Anderson et al. (Anderson et al. 1997)

In_2O_3: Indium oxide doped with 5-10% Sn (ITO) is widely used as a transparent conductive film. It is deposited by reactive evaporation (Luff et al. 1997), by ion-assisted reactive evaporation, by DC magnetron sputtering (Lehan 1996), or RF sputtering (Kulkarni et al. 1998).

WO_3: Tungsten oxide films are prepared by thermal evaporation (Hussain 1999) or DC reactive magnetron sputtering. A summary of properties is given by Bange (Bange 1997).

SiON: Produced by dual ion beam sputtering (Brunet-Bruneau et al. 1996) or reactive magnetron sputtering of Si in an atmosphere of oxygen and nitrogen (Pinard and Mackowski 1997).

Si_3N_4: Produced by reactive magnetron sputtering in nitrogen (Martin et al. 1997), RLVIP (Lorenz et al. 1991) or ion-assisted electron beam evaporation of Si (Lee et al. 1999).

SiC: Produced by ion-beam sputtering from a SiC target (Larruquert and Keski-

Kuha 2000) or by ion-assisted electron beam evaporation of SiC.

B_4C: Produced by ion-beam sputtering from a B_4C target (Larruquert and Keski-Kuha 1999)

Table 2 summarises important properties of oxide, oxynitride, nitride and carbide films.

Table 2. Properties of oxide, oxynitride, nitride and carbide films

Coating material	Film composition	Deposition method	Range of transparency µm	Refractive index at 550 nm	Structure and packing density (p)	Mechanical properties
Si	SiO_2	R DC sputtering, RLVIP	0.2-9	1.45-1.5	A, p=0.98	Hard, CS
SiO_2	SiO_2	EB	0.2-9	1.45-1.46	A, p=0.9-0.98	Hard, CS
SiO	SiO	BE	0.7-9	2.0 (0.7 µm)	A	Hard, TS
Al_2O_3	Al_2O_3	EB	0.2-7	1.63 (T=300)	A, p=1	Hard, CS
HfO_2 or Hf	HfO_2	R EB	0.25-12	1.95 (T=250)	A/C	Hard
Y_2O_3	Y_2O_3	EB	0.25-12	1.87 (T=250)	A/C	Hard
ZrO_2	ZrO_2	EB	0.34-12	1.95-2.05 (T=200)	C, p=0.67-0.82	Hard, CS
Ta	Ta_2O_5	R DC sputtering, RLVIP	0.3-10	2.03-2.09	A	Hard, CS
Ta_2O_5	Ta_2O_5	R EB, RLVIP	0.3-10	2.1 (T=250)	A	Hard, CS
Nb	Nb_2O_5	R DC sputtering, RLVIP	0.38-8	2.35 –2.4	A	Hard, CS
Nb_2O_5	Nb_2O_5	R EB, RLVIP	0.38-8	2.2-2.4	A (T <200)	CS
Ti	TiO_2	R DC sputtering, RLVIP	0.4-3	2.2-2.4	A (T <200)	Hard, CS
TiO	TiO_2	R EB	0.4-3	2.2-2.4	A (T <200)	Hard, TS
Ti_2O_3	TiO_2	R EB	0.4-3	2.1-2.4	A (T <200)	Hard, TS
Ti_3O_5	TiO_2	R EB	0.4-3	2.1-2.4	A (T <200)	Hard, TS
In-Sn alloy or oxide	ITO	R DC sputtering	0.4-1.5	1.95-2.0	A (T <150)	
Zn, ZnO	ZnO	R DC sputtering		2.0		Not very stable
Si	SiO_xN_y	R magnetron or IBS	0.4-9	1.5-2.0		Hard
Si	Si_3N_4	R magnetron sputtering or IAD EB	0.25-9	2.0	A	Hard, CS
Si	SiC	IBS or IAD EB	1.5-11	2.95	Polycrystalline	

R reactive, A amorphous, CS compressive stress, EB electron beam evaporation, BE boat evaporation, TS tensile stress, C crystalline, T substrate temperature [°C], IBS ion beam sputtering

Mixtures of Oxides

Some refractive indices cannot be realized with pure evaporation materials. There is a gap between 1.63 (Al_2O_3) and 1.85 (Y_2O_3). There are also no pure oxides with indices of about 2.1, needed for three-layer AR coatings on glass. Some materials have disadvantages: ZrO_2 and HfO_2 do not melt and therefore form uneven surfaces during evaporation, which often causes inhomogeneous thickness distribution and poor thickness reproducibility. Ta_2O_5 normally needs postbaking to form transparent films if conventional electron beam evaporation without ion assistance is used. The grain structure, density, and stress of thin films can also be modified by using mixtures. Table 3 lists some of the commercially available mixtures.

Table 3: List of some commercially available mixtures

Substance	Supplier (Trade name)	Refractive index at ~ 550 nm	Transmittance range [µm]	Evaporation
SiO_2/Al_2O_3	Umicore (Lima) Merck (L5)	1.48-1.50	0.20-7	EB, 1600 °C
Al_2O_3/Pr_6O_{11}	Merck (M1), Umicore (Paso)	1.7-1.9	0.38-9	EB, 2100-2200°C
Al_2O_3/La_2O_3	Merck (M2), Merck (M3)	1.7-1.8	0.21-10	EB, ~2100°C
ZrO_2/Ta_2O_5	Umicore (Pisa)	2.05	0.35-10	EB, 2100°C
ZrO_2/TiO_2	Cerac, Merck (H1), Optron (OH-5)	2.1	0.40-7	EB, 2200-2400°C
ZrO_2/MgO	Cerac	2.1	0.35-10	EB, ~2200°C
ZrO_2/Al_2O_3	Optron (OM-4, OM-6)	1.68-1.75	0.35-10	EB, 1850-2200°C
TiO_2/Pr_6O_{11}	Merck (H2) Umicore (Ida)	2.1	0.40-7	EB, 2200-2400°C
TiO_2/Al_2O_3	Umicore (Dralo)	2.2	0.40-7	EB, 1700-1800°C
TiO_2/La_2O_3	Merck (H4)	2.1-2.2	0.40-7	EB, 2200-2300°C

Description of Mixed Materials in Detail

Electron beam evaporation is recommended for all of the materials described below. Oxygen partial pressure is about $2*10^{-4}$ mbar (except Lima), deposition rate 0.2 to 0.8 nm/s (if not otherwise noted). Substrate temperature 30 to 300°C (if not otherwise noted).

SiO_2/Al_2O_3: A mixture of SiO_2 and Al_2O_3 lowers the stress in SiO_2 films and enhances chemical stability (Selhofer and Müller 1999).

Al_2O_3/Pr_6O_{11} melts completely before evaporation starts. The melt forms an even surface during evaporation. Refilling of fresh material is possible. Durable films on glass and plastic substrates (Friz et al. 1992).

Al_2O_3/La_2O_3 melts partially before evaporation starts. Refilling possible. Durable films on glass and plastic substrates (Merck 1993, Koenig 1994, Friz et al. 1997). Application besides AR coatings are multilayer coatings, beamsplitters, and polarisers.

ZrO_2/Ta_2O_5: In contrast to pure ZrO_2 films this mixture has a homogeneous refractive index. In addition the ZrO_2 facilitates the oxidation of Ta_2O_5 (Wille 1974).

ZrO_2/TiO_2 forms homogeneous films with index 2.1. The material forms only a thin melted layer on top of the tablet or disc. Careful control of e-beam power distribution is needed to maintain an even surface, refilling not recommended. Deposition rate 0.2 to 1 nm/s. Very low absorption in transmittance range, hard and durable films on glass and plastic substrates. Application mainly AR coatings.

TiO_2/Pr_6O_{11} melts before evaporation starts. Even surface during evaporation, refilling of material possible. Boat evaporation also possible. Rate 0.2 to 1 nm/s. Stable index, absorption in NUV below 400 nm, very weak absorption band at about 450 nm. Application for AR-coatings on glass and plastic lenses (Kraus and Rheinberger 1962; Selhofer and Müller 1999).

TiO_2/Al_2O_3: The addition of Al_2O_3 lowers the stress and the refractive index.

TiO_2/La_2O_3 forms a melt before evaporation starts, refilling possible. Stable index, low absorption in transmittance range (Friz et al.1992, 1997; Merck 1993; Niederwald et al.1999). Application for AR coatings on glass and for multilayer coatings, substrate temperature 250 to 300°C. Also for coatings on plastic substrates at low substrate temperatures.

Ta_2O_5/Al_2O_3: Mixtures with different compositions can be used to deposit medium index films with refractive indices in the range of 1.66 to 1.9 and a range of transparency from 0.35-7 µm. Application for AR coatings on glass substrates with different refractive indices (Ganner 1986).

ZrO_2/Al_2O_3: Mixtures with different compositions can be used to deposit medium index films with refractive indices in the range of 1.63 to 1.75. Refractive index of films varies with composition of the mixture but is almost independent from evaporation temperature, evaporation temperature range 1850-2200°C. Application for three-layer AR coatings on glass substrates with different refractive indices (Canon 1976).

Applications of Oxide, Oxynitride, Nitride and Carbide Films

AR-Coatings

Oxides are used as high and medium refractive index films in most AR coatings. These include: titanium oxides, tantalum oxide, zirconium oxide, yttrium oxide, aluminium oxide and proprietary oxide mixtures, such as Pisa, Ida, Dralo, H1, H2, H4, OH-5, Paso, M1, M2, M3, OM-4, OM-6 etc. An alternative to high index oxide films are nitride films, e.g. silicon nitride.

SiO_2, Lima or Substance L5 is used as low index film in AR coatings, where MgF_2 cannot be used because of stability (soft due to low substrate temperature, e.g. on organic eyeglass lenses) or compatibility with the deposition technique used (large area coating by sputtering or dipping).

Multilayer Systems

Oxide films are also widely used in multilayer systems, such as cold light mirrors, heat reflecting filters, colour separators, narrow band interference filters, e.g. DWDM filters, and laser coatings.

Normally SiO_2 is the low index material. TiO_2-SiO_2 multilayers yield broad reflectance bands because of the large difference in refractive index. They are therefore applied for many mass products. TiO_2 is often replaced by tantalum oxide for multilayer systems with very high requirements in respect to accuracy, thermal stability and optical losses. Tantalum oxide is, like hafnium oxide, also a good high index material for multilayer systems used in the ultraviolet spectral region.

Transparent Conductive Coatings

A further important application of oxide films is the use as transparent conductive coatings in displays or in transparent heated windows. Transparent conductive coatings are formed by indium tin oxide (ITO), Al-doped zinc oxide (Gläser 1990) and F-doped tin oxide (Gläser 1990).

Films for Electrochromic Displays

Electrochromic displays use also oxide films such as tungsten or nickel oxide.

3.1.3 Sulfides, Selenides and Tellurides

Sulfides, selenides and tellurides used in vacuum evaporation include Sb_2S_3, Sb_2Se_3, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, and PbTe. All materials can be evaporated from resistively heated boats made of Ta or Mo. Indirect heated crucibles made from vitreous carbon or alumina are also recommended. Use of electron beam is recommended in literature especially for ZnS and ZnSe.

All of these materials sublime. Except Sb_2S_3 they all decompose during evaporation, but recombine on the substrate surface. Recombination is controlled by substrate temperature during deposition. Optimum substrate temperature is about 150-180°C.

Absorption of films depends strongly on stoichiometry and impurities. High purity 5N materials are recommended with impurity levels of about 1 ppm. Materials sintered or sublimed in vacuum are most suitable. Film stoichiometry has to be controlled very carefully by control of substrate temperature and deposition rate. Absorption can also be influenced by the oxygen partial pressure (Hawkins et al. 2000, Seeley et al. 1979, 1980, Bin et al. 1997).

Sb_2S_3 and **Sb_2Se_3** are mainly of historical interest. Recently Sb_2S_3 was used for making AR coatings on silver halide optical substrates (Matsushita Electric Ind. Co. Ltd. 1994).

ZnS in the past was a very important high index material because it can be evaporated easily from resistively heated boats. It was used e.g. for interference filters in the visible range (ZnS/Cryolite) and in large quantities for cold light mirrors (ZnS/SiO, ZnS/MgF_2). Since ZnS films are rather soft as compared with oxide films, ZnS was replaced by TiO_2 and other oxides in many applications. Today ZnS is used mainly for IR applications (e.g. AR coatings on Ge), for holographic applications and for decorative coatings. ZnS is also an interesting material for production of electroluminescent thin film devices.

Optimum substrate temperature is about 150-180°C. At this temperature the sticking coefficient at the substrate surface is zero for Zn and S atoms. Only ZnS molecules after recombination stick to the substrate (Goldfinger et al. 1963; Ritter and Hoffmann 1969).

ZnSe is used mainly for IR applications, e.g. for AR coatings on Ge or ZnSe (Rudisill et al. 1974; De et al. 1995).

ZnTe, CdS, CdSe, CdTe. These materials are of interest mainly for electrooptical applications (e.g. CdS, CdTe and CuInSe for solar cells or photoresistive films).

PbTe is used for filters in the 5 to 40 µm region in combination with ZnS. PbTe shows the highest refractive index of all evaporation materials (Hawkins et al. 2000; Seeley et al. 1979, 1980). Also (Ge,Pb)Te can be used (Zhang 1998).

Table 4. Properties of some sulfides, selenides and tellurides

Material	Density [g/cm³]	Refractive index	Transmittance range [µm]	Sublimation temperature [°C]
Sb_2S_3	4.12	3.2 at 550 nm	0.5 - 10	400 – 550
ZnS	3.98	2.3 at 550 nm 2 at 10 µm	0.4 - 15	1000 - 1100
ZnSe	5.42	2.6 at 633 nm 2.2 at 10 µm	0.6 - >15	800 - 1000
ZnTe	6.34	2.8 at 1 µm	0.7 - 20	1100
CdS	4.82	2.5 at 550 nm 2.26 at 10 µm	0.5 - >14	~680
CdSe	5.81	2.5 at 550 nm 2.4 at 10µm	0.7 - 25	600- 700
CdTe	5.85	3.1 at 3 µm 2.6 at 10µm	0.9 - 25	1000 - 1100
PbTe	8.16	5.6 at 5 µm	3.5 - >40	1100 - 1200

Toxicity

All of the materials mentioned are toxic, some are highly toxic, carcinogenic, mutagenic and dangerous for the environment. Therefore special precautions for handling and special disposal regulations have to be observed. It is recommended to carefully avoid any contact with the skin, to avoid inhalation of dust, and to remove gases (H_2S, H_2Se) which might exit the evaporation systems after opening.

3.2 Metals, Alloys, Semiconductors and Carbon

The evaporation and sputtering of metals, even of refractory metals, poses no big problems due to the development of high power e-beam and sputtering equipment. The metal can also be used as starting material in reactive processes, such as RLVIP, arc evaporation, reactive sputtering or IBS, for the production of oxide, nitride or carbide films.

For very pure metal films, attention has to be paid to the influence of the residual gas, since many metals react very easily with oxygen and water vapour and also with nitrogen or hydrocarbons. UHV technology may be necessary in certain cases.

Metal films show predominantly tensile stress. By doping with gases the stress can be lowered.

Silver, aluminum and gold films are soft. Chromium films are much harder, but still do not reach the hardness of oxide films.

Metal films are used as reflectors, as semitransparent beam splitters, as transparent conductive films, as absorbers, and in multilayer reflector stacks in the EUV/X-ray region.

Aluminum is widely used as reflector in the IR, visible and UV region (Méndez et al. 2000).

Protected silver films yield very high reflecting mirrors for the visible and near IR region. Semitransparent silver films can be used as transparent heat reflectors (Lee et al. 1996) and transparent conductive films. Semitransparent gold films serve also as transparent conductive films.

Figures with the reflectance of Ag, Al, and Au films from the UV to the IR can be found on pages 394-395 in Pulker's book (Pulker 1999).

The metals W, Mo, Cr, and Sc serve in combination with Si, C, or B_4C in reflector stacks for the EUV/X-ray region (Chapter 'Multilayer Coatings for EUV/X-ray Mirrors' by S. Yulin).

Flash evaporation and especially sputtering are the best deposition methods for alloys.

The semiconductors Si and Ge can be thermally evaporated (Rafla-Yuan et al. 1997) or sputtered and are used as high index films in the IR-region. Si is also used in multilayer stacks in the EUV/X-ray region. It readily forms oxide or nitride phases, so the background pressure has to be kept very low for very pure films.

Table 5 shows properties of Si- and Ge-films.

Table 5. Properties of silicon and germanium films

Coating material	Film composition	Deposition method	Range of transparency in µm	Refractive index at 2 µm	Structure	Mechanical properties
Si	Si	EB	1.0-9	3.4	A (T<300)	Hard
Ge	Ge	EB	1.7-25	4.4	A (T<300)	

EB electron beam evaporation, A amorphous, T substrate temperature [°C]

Carbon films, diamond like carbon films (DLC) and diamond films are deposited by various PECVD and PVD methods (Matthews and Bachmann 1991). They have found applications in optics as hard coatings in the infrared and as coatings in the EUV/X-ray range (Chapter 'Multilayer Coatings for EUV/X-ray Mirrors' by S. Yulin).

3.3 Cermets

Cermet films are combinations of metals and dielectric materials. Metal nanoparticles are embedded in a dielectric matrix. Typical examples are coatings that absorb light at a low reflectance level, e.g. for sunglasses.

A material used for this purpose is a mixture of SiO_2 and molybdenum (Balzers Patent- und Beteiligungs-AG 1967), which is evaporated by electron beam. It yields hard, environmentally stable coatings with a brown transmission color and moderate reflection.

3.4 Organic Materials

Although there are manifold examples of deposition methods and applications of organic thin film materials only a few are used for optical interference coatings.

The manufacture of multicolour interference coatings consisting of metallic layers and transparent acrylate polymer is described (Shaw et al. 1995). Acrylate monomer as starting material is evaporated in vacuum to form the dielectric film.

Enormous efforts in research of organic thin films for optoelectronic applications has been stimulated by C.W. Tang's observation of electroluminescence in a stack of low molecular weight organic semiconductors in 1987 (Tang and Van-Slyke 1987). Strictly speaking the conducting and light emitting films are no optical interference coatings but the final devices might well need such stacks for improved performance. The basic materials involved act as charge transporting layers (holes, electrons) and as emitter materials. Spin coating and evaporation in vacuum are the preferred processes to deposit the layers.

The section on optical interference coatings prepared from organic thin film materials would not be complete without mentioning multilayer films prepared by coextrusion of polymers to build stacks of up to 1000 individual layers (Schrenk et al. 1991). Various devices like polarizers, mirrors and filters have been demonstrated and are commercially available (Weber et al. 2000).

4 Industrial Production of High Quality Coating Materials

4.1 Evaporation Materials

High quality coating materials have to fulfil many requirements as outlined in Chap. 2.1. Industrial production of evaporation materials has to take into account all these demands by using optimised production steps. Raw materials and intermediates have to be controlled by several analytical methods. The finished products have to be analysed according to specifications including chemical analysis, weight and dimensions and stability. Also suitability for vacuum evaporation has to be tested (applications test). The most important production steps will be demonstrated in some examples below.

Production of Zirconium Oxide Discs

The raw materials are analysed for impurity levels. Grain size distribution is also analysed since it influences the sintering behaviour. Forming of discs needs organic binding materials to be added to the raw material, a technique commonly used in production of ceramic parts. In many cases the raw material is spray dried to form a free flowing granulate. Discs are then formed using hydraulic or mechanical presses. In this step it is very important to avoid contamination e.g. by tool abrasion. In the following step the discs are sintered in air to remove the organic additives, which is very important since even a very low carbon content causes spitting during heating and evaporation. In the last step the discs are sintered to reach the desired density and structure.

Similar processes are used to produce tablets of e.g. Al_2O_3, HfO_2, Nb_2O_5, Ta_2O_5, and TiO_2.

It is also necessary to control the density of the materials. In some cases high densities are required, but in general discs with too high densities are undesirable since they easily crack during heating up to the melting or evaporation temperature. Also spitting can occur during release of oxygen if densities are too high.

Some oxide materials, e.g. zirconium oxide, titanium oxide and hafnium oxide, are sintered in vacuum to produce oxygen deficiency. This step needs accurate control of pressure and temperature.

Production of Titanium(III)-Oxide

Ti_2O_3 is produced by sintering of discs or granules made from a mixture of TiO_2 and Ti. The raw materials are mixed and formed to discs or granules, which are then sintered in high vacuum to form Ti_2O_3. In this process the grain size distribution of raw materials is critical, as is homogeneity of the mixture and temperature profile during sintering. The reaction has to be complete since even a very low residue of TiO_2 causes degassing and spitting during melting and evaporation.

Other suboxides of titanium, namely TiO and Ti_3O_5 are produced in similar processes.

Production of Magnesium Fluoride Granules

MgF_2 granules are mainly produced by melting in vacuum. Oxygen content is very critical with MgF_2 because too high oxygen levels cause spitting during evaporation and absorption of the coatings in UV. Therefore the raw material and all production steps have to be optimised to maintain low oxide levels. The raw material is melted in vacuum furnaces to yield polycrystalline ingots. The ingots are crushed and the desired grain sizes are separated by sieving processes.

Similar processes are used to produce other fluoride materials like BaF_2, CaF_2, LaF_3, PbF_2, YbF_3, YF_3, etc. Sublimation in vacuum can be used to further reduce impurity levels, especially oxygen.

Production of Silicon Monoxide

Silicon monoxide is produced by synthesis in a vacuum sublimation process. A mixture of SiO_2 and Si powders is heated to about 1400°C in high vacuum. SiO is formed in gaseous state and is sublimed out of the crucible. The SiO vapour is condensed at surfaces at lower temperatures to form thick layers of black coke like SiO. The physical appearance of the material is controlled by the condensation rate and temperature. In this process very careful temperature control is absolutely necessary to get the desired quality. In a second step the material is crushed and separated into the desired grain sizes.

In case of SiO granules the density, form, grain size, gas content and the SiO_2 residue is critical for many applications.

Production of Mixtures – Substance H4 Patinal®

The raw materials TiO_2, Ti and La_2O_3 are mixed and formed to granules and sintered in high vacuum, where a solid state reaction takes place and a new chemical compound is formed. Therefore the temperature profile in the vacuum process has to be controlled very carefully. Otherwise spitting and even disintegration of granules may occur. The mixture homogeneity with respect to the constituents including oxygen is very important since refractive index and absorption depend on composition.

Similar processes are used for production of other materials, e.g. Substance H1, Substance H2, Ida, Dralo, and Pisa.

Silicon Dioxide Granules

Silicon dioxide granules are made from fused silica by crushing and sieving. For special applications in coating plants with automatic feeding systems it is necessary to avoid needle like particles which may block the feeding system. Therefore special equipment must be used to remove the needle like particles

Table 6. Typical specifications for evaporation materials

Material	Co [%]	Cr [%]	Cu [%]	Fe [%]	Ti [%]	V [%]	Zr [%]	Oxide [%]
ZrO_2 1)	≤ 0.0005	≤ 0.002	≤ 0.001	≤ 0.01	≤ 0.2	≤ 0.005		
HfO_2 2)	≤ 0.0005	≤ 0.005	≤ 0.0005	≤ 0.005	≤ 0.005	≤ 0.005	≤ 1	
MgF_2 3)	≤ 0.0005	≤ 0.0005	≤ 0.0005	≤ 0.001		≤ 0.001		≤ 0.15
SiO 4)	≤ 0.0005	≤ 0.001	≤ 0.002	≤ 0.005		≤ 0.0005		
Ti_2O_3 5)	≤ 0.0005	≤ 0.005	≤ 0.001	≤ 0.02		≤ 0.01		

1) Merck # 108904 Zirconium(IV) oxide discs about 6 g Patinal®.

2) Merck # 111626 Hafnium(IV) oxide UV granules (grey) about 1-4 mm Patinal®.

3) Merck # 108545 Magnesium fluoride granules about 1-4 mm Patinal®.

4) Merck # 107720 Silicon monoxide granules about 2-8 mm Patinal®.

5) Merck # 110203 Titanium(III) oxide tablets about 1 g Patinal®.

4.2 Sputtering Targets

Sputtering targets are produced by a melting and casting process or by powder metallurgy. Thermal spraying and electroplating are only used for special geometry and applications. The selection of the production process depends on desired material characteristics (metal or ceramic, melting point, kind of alloy, purity levels), target size and geometry, e.g. flat, tube, bonded, etc. Table 7 gives an overview of the production processes for sputtering targets.

Table 7. Production procedures for sputtering targets

Casting Metallurgy	**Powder Metallurgy**
	Powder Preparation
Vacuum Induction Melting (VIM) Continuous Casting Electron Beam Melting (EB)	Cold Isostatic Pressing (CIP) Sintering Hot Pressing (HP) Hot Isostatic Pressing (HIP)

Heat Treatment
Homogenisation, Recrystallization

Transformation Technique
Forging, Hot and Cold Rolling, Extrusion Pressing

Mechanical Tooling
Machining, Sizing

Bonding
Soldering, Diffusion Bonding, Roll Plating, Explosion Welding

Cleaning / Packing

Metallurgical melting processes are normally the most economic manufacturing methods. Metals such as Zn, Sn, In and their alloys can be melted in resistively heated open air furnaces. Materials with higher melting temperature up to 2000°C are melted in vacuum induction furnaces. The vacuum ensures high purity and low levels of volatile impurities (gases, Cl, P, K, Li, etc.). Any geometry of raw material and a recycling of used sputtering targets are possible. Chromium, titanium and niobium can be melted by electron beam melting. Most cast ingots are post-treated by forging, extrusion, rolling and high temperature annealing processes to improve the homogeneity and to reach a fine grain size structure. Also, special materials like silicon, germanium, SiAl alloys are produced as cast. Si and Ge single crystal targets are used when very accurate film distributions are required.

Melting processes are not applicable in the case of high melting temperatures (W, Ta, Mo, ceramics), of extremely brittle and stress loaded castings (ceramics), of sublimation before melting (Cr, ITO) and in the case of alloys with a miscibility gap in the liquid phase (Ag-Ni). In these cases powder metallurgical production techniques have to be used. After powder mixing and blending a press and heat treatment step is needed (cold pressing plus sintering, hot pressing or hot isostatic pressing). The advantages are adjustable target compositions, controlled microstructure, homogeneous grain size, adjustable amount of intermetallic phases and a possible near net shape production. The disadvantage is reduced density and a higher gas content in the finished product.

Another production method is thermal spraying, e.g. of silicon tube targets. The raw material is liquefied by a plasma and the molten droplets are directed towards the target.

Most targets have to be bonded on a backing or cooling plate to ensure good thermal contact to the cooling system of the cathode and to accommodate thermal and mechanical stresses. Common methods are: solder seal with indium, roll plating, diffusion bonding, explosion welding and epoxy gluing.

5 Summary and Outlook

The different deposition technologies for thin films for optical applications require a large number of evaporation materials and sputtering targets, which have to fulfil specific requirements. Their development and production is the task of specialised companies.

Coating materials for optical applications comprise dielectric materials, especially fluorides, oxides, nitrides and carbides, elementary and compound semiconductors, metals and their alloys.

Fluoride films are still a domain of classical evaporation technology. Ion assisted evaporation and sputtering are of increasing importance for oxide, nitride, carbide and compound semiconductor films. Ion assisted processes yield films of highest quality and sputter processes are well suited for mass production. The trend to these technologies will continue and pose new challenges for coating materials in future.

Acknowledgements

The preparation of this chapter within a relatively short period was only possible thanks to the cooperation of several people. The authors would like to thank their colleagues Friedrich Koenig, Klaus Leitner and Elmar Ritter for valuable contributions.

References

Albertinetti N, Minden HAT (1996) Granularity in ion-beam-sputtered TiO_2 films. Appl. Opt 35: 5620-5625

Alvisi M, De Nuncio G, Di Gulio M, Ferrara MC, Perrone MR, Protopapa L, Vasanelli L (1999) Deposition of SiO_2 films with high laser damage thresholds by ion-assisted electron-beam evaporation. Appl. Opt. 38: 1237-1243

Anderson O, Ottermann C (1997) Silicon oxides. In: Bach H, Krause D (eds) Thin films on glass. Springer, Berlin Heidelberg, pp 161-173

Anderson O, Bange K, Ottermann C (1997) Titanium oxide. In Bach H, Krause D (eds) Thin films on glass. Springer, Berlin Heidelberg, pp 137-161

Andre P, Poupinet L, Ravel G (2000) Evaporation and ion assisted deposition of HfO_2 coatings: Some key points for high power applications. J. Vac. Sci. Technol. A 18: 2372-2377

Balzers Patent- und Beteiligungs-AG (1967) Lichtabsorbierendes Sonnenbrillenglas. Schweizer Patent 447 476

Bange K (1997) Properties and characterisation of dielectric thin films. In: Bach H, Krause D (eds) Thin films on glass. Springer, Berlin Heidelberg, pp 101-225

Bendavid A, Martin PJ, Takikawa H (2000) Deposition and modification of titanium dioxide films by filtered arc deposition. Thin Solid films 360: 241-249

Bennett JM, Pelletier E, Albrand G, Borgogno JP, Lazarides B, Carniglia CK, Schmell RA, Allen TH, Tuttle-Hart T, Guenther KH, Saxer A (1989) Comparison of the properties of titanium dioxide films prepared by various techniques. Appl. Opt. 28: 3303-3317

Bernitzki H, Lauth H, Thielsch R, Blaschke H, Kaiser N, Mann K (1999) Current status of radiation resistance of dielectric mirrors in the DUV. SPIE 3578

Bin F, Zhang F (1997) Study on optical properties of PbTe and ZnSe at low temperature. J. of Shanghai Jiaotong Univ. 31: 69-71

Brunet-Bruneau A, Vuye G, Frigerio JM, Abelès F, Rivory J, Berger M, Chaton P (1996) Infrared ellipsometry investigation of SiO_xN_y thin films on silicon. Appl. Opt. 35: 4998-5004

Canon Kabushiki Kaisha (1976) Three layer antireflection film US Pat. 3 934 961

Chen JS, Chao S, Kao JS, Lai GR, Wang WH (1997) Substrate-dependent optical absorption characteristics of titanium dioxide thin films. Appl. Opt. 36: 4403-4408

Cho HJ, Hwangbo CK (1996) Optical inhomogeneity and microstructure of ZrO_2 thin films prepared by ion-assisted deposition. Appl. Opt. 35: 5545-5552

Cowell R (1996) Durable optical coatings for energetic UV laser sources. SPIE 2703:369-374

De CK, Misra NK, Gosh T B (1995) Preparation and structural characterisation of ZnSe thin films by x-ray diffraction technique. Indian J. Phys.,A 69A: 261-266

Dods SRA, Zhang Z, Ogura M (1999) Highly dispersive mirror in Ta_2O_5/SiO_2 for femtosecond lasers designed by inverse spectral theory. Appl. Opt. 38: 4711-4719

Edlinger J, Ramm J, Pulker HK (1989) Properties of ion-plated Nb_2O_5 films. Thin Solid Films175: 207-212

Edlou SM, Smajjkiewicz A, Al-Jumaily GA (1993) Optical properties and environmental stability of oxide coatings deposited by reactive sputtering. Appl. Opt. 32: 5601-5605

Friz M, Koenig F, and Feiman S. (1992) New materials for production of optical coatings. Proc. SVC 35th Ann. Techn. Conf 1992, 143-149

Friz M, Schallenberg UB, Laux S. (1997) Plasma ion assisted deposition of medium and high refractive index thin films. Proc. SVC 40th Ann. Techn. Conf. 1997: 280-292

Ganner P (1986) Medium-Index mixed-oxide layers for use in AR-coatings. Proc. SPIE 652: 69 –76

Gläser HJ (1990) Dünnfilmtechnologie auf Flachglas. Verlag Karl Hoffmann, Schorndorf

Goldfinger P, Jeunehomme M (1963) Mass spectrometric and Knudsen cell vaporization studies of 2B-6A compounds. Trans. Far. Soc. 59: 2851-2867

Hawkins GJ, Hunneman R, Sherwood R, Barrett BM (2000) Infrared filters and coatings for the High Resolution Dynamics Limb Sounder (6-18 µm) Appl. Optics 39: 5221-5230

Heitmann W, Ritter E (1968) Production and properties of vacuum evaporated films of Thorium fluoride. Appl. Optics 7:307-309

Hussain Z, (1999) Vacuum temperature-dependent ellipsometric studies on WO_3 thin films. Appl. Opt. 38: 7112-7127

Izawa T, Yamamura N, Uchimura R, Yakuoh T (1994) Damage thresholds and optical stabilities of fluoride HR coatings for 193 nm. SPIE 2114:297–308

Klinger RE, Carniglia CK (1985) Optical and crystalline inhomogeneity in evaporated zirconia films. Appl. Opt. 24: 3184-3187

Koenig F, Friz M (1994) Development of medium and high refractive index coating materials for the visible and UV spectral range. Proc. SVC 37th Ann. Techn. Conf. 1994: 118 -121

Kolbe J, Müller H, Schink H, Welling H, Ebert J (1990) Laser induced damage thresholds of dielectric coatings at 193 nm and correlations to optical constants and process parameters. NIST Spec. Publ. 801:404–416

Kolbe J, Kessler H, Hofmann T, Meyer F, Schink H, Ristau D (1991) Optical properties and damage thresholds of dielectric UV/VUV coatings deposited by conventional evaporation, IAD and IBS. SPIE 1624:221–235

Kraus T, Rheinberger P (1962) Use of rare earth metal in vaporizing metals and metal oxides. U.S. Patent 3 034 924

Kulkarni AK, Lim T, Khan M, Schulz KH, (1998) Electrical, optical and structural properties of indium-tin-oxide thin films deposited on polyethylene terephtalate substrates by rf sputtering. J. Vac. Sci. Technol. A 16: 1636-1640

Larruquert JI, Keski-Kuha RAM (1999) Multilayer coatings with high reflectance in the extreme-ultraviolet spectral range of 50 to 121.6 nm. Appl. Opt. 38: 1231-1236

Larruquert JI, Keski-Kuha RAM (2000) Reflectance measurements and optical constants in the extreme ultraviolet for thin films of ion-beam-deposited SiC, Mo, Mg_2Si, and InSb and of evaporated Cr. Appl. Opt. 39: 2772-2781

Lee CC, Chen SH, Jaing CC (1996) Optical monitoring of silver-based transparent heat mirrors. Appl. Opt. 35: 5698-5703

Lee CC, Chen HL, Hsu JC, Tien CL (1999) Interference coatings based on synthesized silicon nitride. Appl. Opt. 38: 2078-2082

Lehan JP (1996) Determination of grain size in indium tin oxide films from transmission measurements. Appl. Opt. 35: 5048-5051

Lingg LJ, Targove JD, Lehan JP, Macleod HA (1987) Ion-assisted deposition of lanthanide trifluorides for VUV applications. SPIE 818:86–92

Lorenz H, Eisele I, Ramm J, Edlinger J, Bühler M (1991) Characterization of low temperature SiO_2 and Si_3N_4 films deposited by plasma enhanced evaporation. J. Vac. Sci. Technol. B 9: 208-214

Luff BJ, Wilkinson JS, Perrone G (1997) Indium tin oxide overlayered waveguides for sensor applications. Appl. Opt. 36: 7066-7072

Macleod HA (1986) Thin-film optical filters. Second edn. Adam Hilger LTD, Bristol, pp 398, 504-511

Martin PJ, Bendavid A, Takikawa H (1999) Ionized plasma vapor deposition and filtered arc deposition; processes, properties and applications. J. Vac. Sci. Technol., A 17: 2351-2359

Martin PM, Stewart DC, Bennett WD, Affinito JD, Gross ME (1997) Multifunctional multilayer optical coatings. J. Vac. Sci. Technol. A 15: 1098-1102

Marx D, Murphy R (1990) Sputtering targets: Challenges for the 1990s. Solid State Technology, March: 11-14

Matsushita Electric Ind Co Ltd. (1994) Manufacture of optical parts. JP 05188204

Matthews A, Bachmann PK (eds) (1991) Diamond and diamond-like carbon coatings 1990. Elsevier Sequoia S.A., Lausanne

Méndez JA, Larruquert JI, Aznarez JA (2000) Preservation of far UV aluminum reflectance by means of overcoating with C_{60} films. Appl. Opt. 39: 149-156

Merck KGaA (1993) Process for producing evaporation material for preparation of medium refractive index optical films. EP 0 574 785

Merck KGaA (1993) Material for vapour deposition for the production of high refractive optical layers. EP 0 561 289

Newns GR, Pantelis P, Wilson JL, Uffen RWJ, Worthington R (1973) Absorption losses in glasses and glass fibre waveguides. Opto-electronics 5:289-296

Niederwald H, Laux S, Kennedy M, Schallenberg U, Duparré A, Mertin M, Kaiser N, Ristau D (1999) Ion-assisted deposition of oxide materials at room temperature by use of different ion sources. Appl. Opt. 38: 3610-3613

Phillips RW, Bleikolm AF (1996) Optical coatings for document security. Appl. Optics 35:5529-5534

Phillips RW, Nofi M (1999) Colors by chemistry or by physics. Proceedings SVC:494-499

Pinard L, Mackowski JM (1997) Synthesis and physicochemical characterization of silicon oxynitride thin films prepared by rf magnetron sputtering. Appl. Opt. 36: 5451-5459

Pulker HK (1979) Characterization of optical thin films. Appl. Opt. 18: 1969-1977

Pulker HK (1999) Coatings on Glass. Second, revised edn. Elsevier, Amsterdam, pp 219-223, 394-428

Rafla-Yuan H, Rancourt JD, Cumbo MJ (1997) Ellipsometric study of thermally evaporated germanium thin film. Appl. Opt. 36: 6360-6363

Rahe M, Oertel E, Reinhardt L, Ristau D, Welling H (1990) Absorption calorimetry and laser induced damage threshold measurements of AR-coated ZnSe and metal mirrors at 10.6 µm. SPIE 1441:113–126

Reicher D, Black P, Jungling K (2000) Defect formation in hafnium dioxide thin films. Appl. Opt. 39: 1589-1599

Ristau D, Günster S, Bosch S, Duparré A, Masetti E, Ferré-Borrull J, Kiriakidis G, Peiró F, Quesnel E, Tikhonravov A, (2001) UV-optical and microstructural properties of MgF_2- and LaF_3-coatings deposited by IBS and PVD processes. Optical Interference Coatings Banff, OSA Technical Digest: ThA5-1–ThA5-3

Ritter E, Hoffmann R (1969) Influence of substrate temperature on the condensation of vacuum evaporated films of MgF2 and ZnS. J. Vac. Sci. Technol. 6: 733-736

Ritter E (1971) Die Eigenschaften verschiedener Siliciumoxid-Phasen in dünnen Schichten. Vakuum-Technik 21: 42-48

Ritter E (1975) Dielectric film materials for optical applications. In: Hass G, Francombe MH, Hoffman RW (eds) Physics of thin films, vol 8. Academic Press, New York, pp 1-49

Rudisill, JE, Braunstein, M, Braunstein AI (1974) Optical coatings for high energy ZnSe laser windows. Appl. Optics 13: 2075-2080

Scherer K, Nouvelot L, Lacan P, Bosmans R (1996) Optical and mechanical characterization of evaporated SiO_2 layers. Long term evolution. Appl. Opt. 35: 5067-5072

Schnellbuegel A, Hagedorn H, Anton R (1994) Ion assisted deposition of non-toxic coatings for high power CO_2 laser optics. Proc. SPIE 2253: 839-848

Schrenk WJ, Wheatley JA, Lewis RA, Arends CB (1991) Nanolayer polymeric optical films. Tappi 1991 Polymers, laminations and coatings conference

Schultz PC (1974) Optical absorption of the transition elements in vitreous silica. J.Am.Ceram.Soc. 75:309-313

Seeley JS, Hunneman R, Whatley A (1979) Infrared multilayer interference filter manufacture: supposed longwave limit. Appl. Optics 18: 3368-3370

Seeley JS, Hunneman R, Whatley A (1980) Far infrared filters for the Galileo-Jupiter and other missions. Appl. Optics 20: 31-39

Selhofer H, Müller R (1999) Comparison of pure and mixed coating materials for AR coatings for use by reactive evaporation on glass and plastic lenses. Thin Solid Films 351: 180-183

Selhofer H, Ritter E, Linsbod R (2002) Properties of titanium dioxide films prepared by reactive electron beam evaporation from various starting materials. Appl. Opt. 41: 756-762

Shaw DG, Cline DS, Dawson EP, Langlois M (1995) Multicolor interference coating. US-Patent 5877895

Stamm U, Pätzel R, Bragin I, Kleinschmidt J, Voß F, Basting D (1997) Recent developments in industrial excimer laser technology. SPIE 3092:485–492

Sullivan BT, Clarke GA, Akiyama T, Osborne N, Ranger M, Dobrowolski JA, Howe L, Matsumoto A, Song Y, Kikuchi K (2000) High-rate automated deposition system for the manufacture of complex multilayer coatings. Appl. Opt. 39: 157-167

Tabata A, Matsuno N, Suzuoki Y, Mizutani T (1996) Optical properties and structure of SiO_2 films prepared by ion-beam sputtering. Thin Solid Films 289: 84-89

Tang CW, VanSlyke SA (1987) Organic electroluminescent diodes. Appl. Phys. Lett. 51:913-915

Venzago C, Weigert M. (1994) Application of the glow discharge mass spectrometry (GDMS) for the multi-element trace and ultratrace analysis of sputtering targets. Fresenius J Anal Chem 350: 303-309

Wang X, Masumoto H, Someno Y, Hirai T (1999) Design and experimental approach of optical reflection filters with graded refractive index profiles. J. Vac. Sci. Technol. A 17: 206-211

Weber MF, Stover CA, Gilbert LR, Nevitt TJ, Ouderkirk AJ (2000) Giant birefringent optics in multilayer polymer mirrors. Science 287:2451-2456

Weigert M (2001) New developments in materials for sputtering on glass. International Glass Review Issue 3: 72-76

Wilhartitz P, Ortner HM, Krismer R, Krabichler H (1990) Classical analysis including trace-matrix separation versus solid state mass spectrometry: A comparative study for the analysis of high purity Mo, W and Cr. Microchim. Acta (Wien) II: 259-271

Wille B (1974) Refracting light permeable oxide layer and method for its manufacture. U. S. Patent 3 783 010

Yamada Y, Uyama H, Watanabe S, Nozoye H (1999) Deposition at low substrate temperatures of high quality TiO_2 films by radical beam-assisted evaporation. Appl.Opt. 38: 6638-6641

Zhang, S et al (1998) The effects of processing conditions on PbGeTe film performances. Proc SPIE 3175: 429-432

Zöller A, Götzelmann R, Matl K, Cushing D (1996) Temperature-stable bandpass filters deposited with plasma ion-assisted deposition. Appl. Opt. 35: 5609-5619

Zukic M, Torr DG, Spann JF, Torr MR (1990) Vacuum ultraviolet thin films. 1: Optical constants of BaF_2, CaF_2, LaF_3, MgF_2, Al_2O_3, HfO_2, SiO_2 thin films. Appl. Opt. 29:4284–4292

Abbreviations

AC	Alternating Current
AR	Antireflection
CGHE	Carrier Gas Heat–Extraction
CIP	Cold Isostatic Pressing
CVD	Chemical Vapour Deposition
DC	Direct Current
DLC	Diamond Like Carbon
DUV	Deep Ultra-Violet
DWDM	Dense Wavelength Division Multiplexing
EB	Electron-Beam
EUV	Extreme Ultra-Violet
FAAS	Flame Atomic Absorption Spectrometry
GDMS	Glow Discharge Mass Spectroscopy
GDS	Glow Discharge Spectroscopy
HIP	Hot Isostatic Pressing
HP	Hot Pressing
IAD	Ion Assisted Deposition
IBS	Ion Beam Sputtering
IBAD	Ion Beam Assisted Deposition
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IR	Infrared
NUV	Near Ultra-Violet
OVP	Optically Variable Pigment
PECVD	Plasma Enhanced Chemical Vapour Deposition
PVD	Physical Vapour Deposition
R	Reactive
RF	Radio Frequency
RLVIP	Reactive Low Voltage Ion Plating
UHV	Ultra High Vacuum

UV	Ultra-Violet
VIM	Vacuum Induction Melting
VUV	Vacuum Ultra-Violet
XRF	X-Ray Fluorescence

Symbols

A	Absorptance
c	Concentration
d	Thickness
k	Extinction Coefficient
n	Refractive Index
λ	Wavelength
T	Transmittance