REACTIVE COATING TECHNOLOGIES FOR DIELECTRIC LAYERS

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Keywords: reactive coating, RPVD reactive physical vapour deposition, coating technologies, thin films, dielectric layers, planar waveguides, optoelectronic sensors, telecommunication systems, optical interference, reactive gases, discharge plasma, stoichiometry, PVD physical vapour deposition, film properties, film stability, gas discharge, IBS, Ion beam sputtering, IAD ion assisted deposition

Abstract: High quality dielectric films are required today for planar optical wave quides used in opto-electronic sensors and telecommunications. Many inorganic chemical compounds which were difficult to deposit by conventional techniques in form of well adherent, dense, hard and stable low-loss films are now routinly synthesized by reactive gas discharge plasma and energetic ion and/or coating material atom processes. The plasma provides an in-situ source of increased ionization and energetic deposition species. This is suitably used to enhance various chemical and physical processes that influence stoichiometry and growth properties of deposited films. A survey over such PVD coating technologies and on the resulting film properties is given. Among others Ta_2O_5, ZrO_2, TiO_2, SiO_2 and Si_3N_4 single films and multilayers were deposited in the new reactive low-voltage ion plating system Balzers BAP 800. The properties of the individual films and spectral filter characteristics of multilayers were investigated particularly with respect to time, humidity and temperature. The observed stability is correlated with film density, water vapour content and intrinsic film material properties.

Reaktivne tehnologije nanašanja dielektričnih tankih plasti

Ključne besede: nanašanje reaktivno, RPVD naparjevanje reaktivno fizično, tehnologije nanašanja, plasti tanke, plasti dielektrične, valovodi planarni, senzorji optoelektronski, sistemi telekomunikacijski, interferenca optična, plini reaktivni, plazma razelektrilna, stihiometrija, PVD nanašanje, lastnosti plasti, stabilnost plasti, razelektritev plinska, IBS naprševanje ionsko, IAD nanašanje

Povzetek: Tehnologija izdelave optičnih valovodov v optoelektronskih senzorjih in telekomunikacijskih sistemih, kakor tudi druge uporabe v interferenčni optiki zahtevajo nanašanje zelo kvalitetnih dielektričnih plasti. Mnoge anorganske kemične sestavine smo včasih s konvencionalnimi metodami nanašanja zelo tekčo nanašali v obliki trdih, gostih, stabilnih filmov brez izgub in z dobro adhezijo na podlago. Danes uspemo z uporabo nekaterih novih tehnik, kot so reaktivno plazemsko nanašanje in energijsko ionsko nanašanje atomov tarče, pospešiti razline kemične in fizikalne procese, ki vplivajo na rast, stohiometrijo in lastnosti tankih plasti.
V prispevku podajam pregled zgoraj omenjenih PVD tehnik nanosa, kakor tudi lastnosti tako dobljenih tankih plasti. Enojne in večplastne strukture Ta_2O_5, ZrO_2, TiO_2, SiO_2 in Si_3N_4 smo nanesli v novem sistemu za reaktivno nanašanje plasti Balzers BA 800. Zanimale so nas lastnosti posameznih plasti ter spektralne karakteristike večslojnih struktur zlasti časovna stabilnost ter občutljivost na temperaturo in relativno vlago. Stabilnost plasti smo korelirali z njihovimi notranjimi lastnostmi, vsebnostjo vlage in gostoto.

1. Introduction

The properties of thin oxide films deposited on glass substrates by evaporation and subsequent condensation or by sputtering under vacuum were generally found to be different from those of the bulk materials. Dissociation is a problem with many compound films. Even in evaporation, which is the gentlest physical vapour deposition process, chemical compounds are dissociated to a certain extent. Due to their low sticking coefficient, gaseous components can be pumped off, resulting in substoichiometric composition of the deposit. Optical films produced in processes without ion bombardment show properties associated with low mobility of the condensing atoms and molecules as consequence of their low energies of about 0,2eV. Most films evaporated conventionally have a columnar microstructure with large void volume. Silica films have a less dense spongy microstructure. This leads to deviations of the optical and mechanical properties from those of the bulk materials. The voids enlarge the internal surface of the coatings and encourage gas, particularly moisture adsorption. Anything filling the voids increases their refractive index so that the film index and consequently the optical thickness increase. Thus, whenever the environmental conditions change the films exhibit a shift in their properties. In view of the importance of dielectric films in optical coatings, it is not surprising that considerable work has been devoted to these materials. Attention has been paid how to make stoichiometric, low absorbing, stable and hard oxide, nitride and oxynitride films for various filter and mirror applications and for optical wave guides. Special reactive higher energetic deposition techniques have been developed to improve optical and mechanical properties of compound films. Among them, processes that retain as much of the traditional techiques as possible seem the most attractive ones. Work along these lines showed exciting results. The important reactions in plasma supported PVD processes are ionization, dissociation, radical formation, electron impact excitations and the ion energies involved. In this review most of these powerful ion or plasma supported techiques, particularly the new reactive low-voltage ion plating, will be discussed.

2. Reactive Evaporation Techniques

The loss of oxygen and nitrogen that usually occurs during evaporation or sputtering of transparent metal oxides and nitrides may cause optical absorption in the films. The effect could be appreciably corrected particularly in the case of oxides in the reactive deposition process [1,2] by adding oxygen to the residual gas: $MeO + 1/2O_2 \longrightarrow MeO_2$ I, $Me + O_2 \longrightarrow MeO_2$ II

The partial pressure of the reactive gas component is usually few 10^{-4} mbar. Reactive evaporation is applied in all cases where direct evaporation of a chemical compound is not possible because of degradation. In practice, oxide films are produced using suboxides as starting materials. Basically it is also possible to produce other compounds in this manner. The low reactivity of nitrogen (N_2), however, prevents the applicability of conventional reactive evaporation for metal nitride film synthesis.

When evaporating under reactive conditions, care must be taken that the gas components consumed during the chemical reaction are continuously replenished. This is frequently carried out through a pressure controlled gas inlet valve. The average mean free path at 10^{-4} mbar is still only 50 cm, which is somewhat less than the distance from boat to substrate. Reactions from collision in the gas space between gas molecules and metal atoms are only possible to a small percentage, although the collision probability is often more than 50 %. The reaction takes place to a far greater extent on the substrate surface.

Formation of a metal-oxide film by reactive evaporation takes place in the following stages:

1) The substrate surface is exposed to the coating material vapour atoms and gas molecules which impinge at a certain rate.

2) A portion of these atoms and molecules is adsorbed on the substrate surface, and another portion is either reflected or, after a short dwell on the surface, again desorbed. The ratio of the actually adsorbed quantity to the number of incident particles is given by the condensation coefficient. The condensation coefficients of metal vapours are frequently near to unity; large rates of incidence are chosen in the vacuum evaporation, so that they correspond to pressures which are much larger than the equilibrium pressures at the usual substrate temperatures.

3) In the adsorbed phase, in which the particles are mobile because of surface diffusion, the chemical reaction of the metal- oxide formation takes place via dissociative chemisorption of the oxygen. This means that, since the reaction takes place in the adsorption phase and the various reaction partners can have different condensation coefficients, the ratio of the rates of incidence is a

necessary but not adequate criterion. It is assumed [3], that the chemisorption rate of oxygen is the critical step for the completion of the reaction.

The need thus arises to select all parameters for the relevant process so that the film obtained fulfills the demand upon in the best possible way. For all that, however, oxide coatings produced in this way are often still slightly understoichiometric and slightly absorbing. Compound films approach asymptotically to stoichiometry and it should be considered that, for example, the composition of silica films correspond to SiO_{2-x} whereby x is between 10^{-3} and 10^{-6}.

Concerning structure, evaporated films are disordered polycrystalline, amorphous or polymeric. They show rough surfaces and have columnar or spongy microstructures with large void volume and great internal surface area [4]. Their adhesion to the substrate is poor and their abrasion resistance and hardness are low. As a consequence of the low density the film refractive indices are considerably lower than the values for the bulk oxides. They absorb water vapour on wet atmosphere and other gases which change their refractive index and other physical properties.

Heating the substrates to about 250 to 350°C during reactive evaporation improved a number of film properties including stoichiometry, purity, density, refractive index and adhesion. Therefore substrate heating became the standard procedure in this process, although it favours generally undesirable coarser film microstructure and surface roughness. Because of the high reactivity of oxygen and the low reactivity of nitrogen only oxide films have been successfully produced industrially by reactive evaporation.

3. Activated Reactive Deposition

Films for highly sophisticated optical applications, such as for special laser mirrors, should have extremly low absorption losses because these obviously decrease the reflectivity and lower the damage threshold for high power radiation. It is very important in the deposition of such films to achieve more complete oxidation, since traces of metal atoms or substoichiomietric species cause absorption. It has been found by various researchers that better stoichiometric films can be achieved with activated and ionized reactive gas. The process is shown schematically in the left branche of Fig.1.

Reactive evaporations performed under the above mentioned standard conditions, but with additional activation of the reactive gas, further improved film quality [5]. Better stoichiometry and rather low absorption values have been obtained when films were prepared by activated reactive evaporation (ARE) [8]. These coating experiments with ions and excited molecules clearly

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┌─────────────┐
│    IONS     │
└─────────────┘
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glow discharge   ion guns

low kinetic energy   higher kinetic energy
(more activated states
than ions)
          | |
     enhance: enhance:
chemical reactions   chemical reactions and
                                      packing density
          | |
     improve: improve:
   stoichiometry   stoichiometry,
                                      microstructure,
                                 adhesion hardness and
                                   abrasion resistance

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┌─────────────┐              ┌─────────────┐
│     ARE     │              │     IAD     │
└─────────────┘              └─────────────┘
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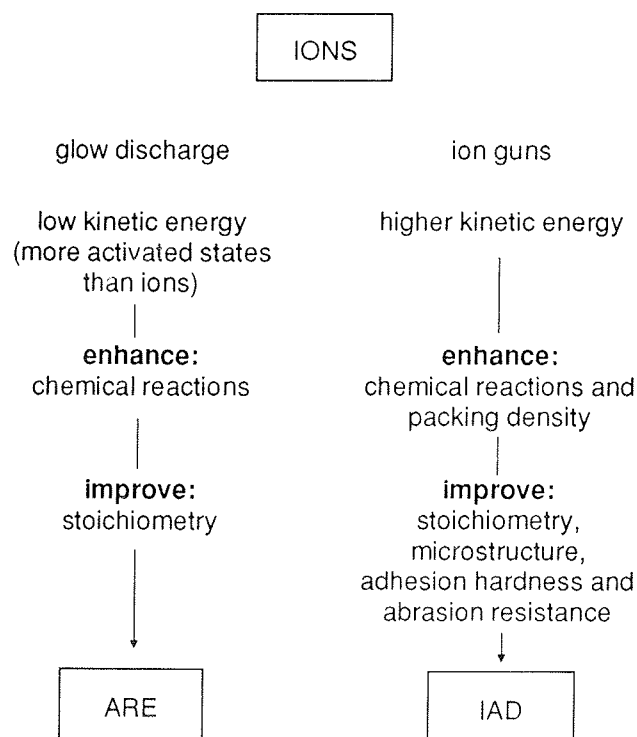
Fig. 1:   Schematic of plasma and ion supported
            reactive evaporations

showed that chemical reactivity is enhanced in the presence of a gas-discharge plasma. To generate oxygen ions for activated reactive evaporation cold gas discharge ion sources with a hollow cathode inside a quartz tube are used /6/. With this technique it became possible also to deposit metal oxynitride films.

In the case of TiO_2 films, the partial ionization of oxygen reduces the absorption by a factor of 10 for TiO starting material, or by factor of 100 for Ti_2O_3 or Ti_3O_5 starting materials compared with the values of films obtained with ordinary oxygen /7/. It was found that negative oxigene ions produced the best oxidizing effect /7/. They were therefore used to produce all the films.

4. Ion Assisted Deposition

Most properties of evaporated films are highly determined by the lack of mobility of the condensing atoms and molecules due to their low thermal energies between 0.1 and 0.2 eV. The activation energy necessary for physical and chemical processes is supplied by energetic ions, which replaces the requirement of elevated substrate temperature as discussed further above. This is shown schematically in the right branche of Fig.1. Controlled bombardment of a growing film by argon or/and oxygen ions with energies up to several hundred electron volts has been shown to improve density and stoichiometry and therefore optical properties of oxide coatings /8,9/. To make sure stoichiometry energy values below 100 eV are to prefere. Adding

energy to the film growth process also appears to improve adhesion /10/ and to modify stress /11/. Similar effects are observed when the ad- atoms of thin film materials have increased energy as is the case in sputtering. Ion beam techniques can be applied, however also before and after film deposition. Substrates can be ion beam cleaned with inert or reactive gas ions, depending upon substrate materials involved and freshly deposited films can be bombarded to further improve their properties.

Hot-cathode Kaufman-type /12/ ion guns are used usually in ion assisted deposition processes (IAD), but also other installations have been applied. It is impossible to discuss and compare here all the variants of this technique. Considerable efforts have been directed to the analysis of plasma conditions and their correlation with deposited film properties. The mechanism responsible for densification seems to be momentum transfer as was shown recently by molecular-dynamics calculation /13/.

5. Gas Discharge and Ion Beam Sputtering

In sputtering atoms or molecules from a target are ejected by momentum transfer processes caused by noble gas ion bombardment. Various possibilities are shown schematically in Fig.2. The initially relatively high energetic coating material atoms with energies between 1 and 40 eV pass through a more or less dense gas phase lose energy by collisions and condense at substrates which, in case of gas discharge sputtering, are arranged oposit the target at a small distance.

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┌─────────────────┐
│   SPUTTERING    │
└─────────────────┘
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gas discharges   ion beams

$p - 10^{-1} - 10^{-3}$ mbar $p \leq 10^{-4}$ mbar
non reactive, reactive   non reactive, reactive

normal cathodes   single beam sputtering
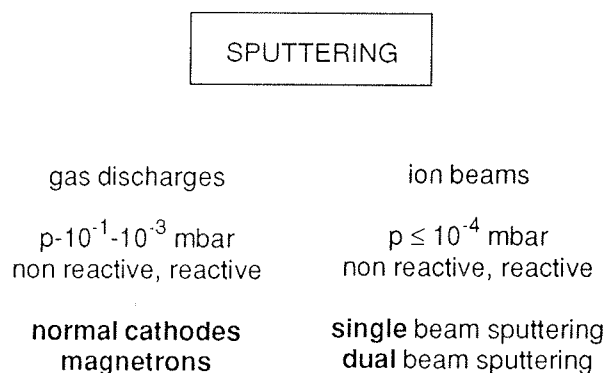magnetrons   dual beam sputtering

Fig. 2:   Schematic of sputtering

Ions stem from a dc of rf gas discharge or from special ion guns. In the first case the typical working gas pressure is in the 10^{-2} to 10^{-3} mbar range whereas with ion beam sputtering lower background pressures and there-

fore a larger distance target to substrate can be applied. Many variants of sputtering processes are known /14/. With all of them reactive gas processes can be performed. Conventional gas discharge sputtering is a rather slow process. The speed of deposition is increased, however, by magnetrons where, in addition to the electric field, a magnetic field enables, by keeping the electrons in trajectories close to the target surface, to increase the number of ionizing collisions in the bombardment-ion generation. Such devices are used for the deposition of large flat substrates, e.g. architectural glass and plastic foils /15,16/.

With reactive sputtering, one has to distinguish between a compound film synthesis under the actions of a diluted reactive gas atmosphere starting from pure metal, alloy or multi-element targets on the one hand, and the making up for the lost constituent when using compound targets on the other. The main difference is found in the dependence of the deposition rate on the partial pressure of the reactive gas. Generally the reactive gas component, which can be for example O_2, H_2O for the formation of oxides, N_2, NH_3 for nitrides, $O_2 + N_2$ for oxynitrides, H_2S for sulfides, C_2H_2, CH_4 or other hydrocarbons for carbides and CF_4 or HF for fluorides, is added to the sputtergas - mainly Ar^4 - in small amounts, between 10^{-5} and 10^{-4} mbar. In all gas discharge sputter arrangements, the added gas is in an activated state and therefore highly reactive.

Reactions in the gas phase, ignored in reactive evaporation, are here also generally negligible; the heat of reaction liberated cannot be dissipated in a two-body collision. Conservation of momentum and energy lead to heterogeneous reactions on the substrate surface but are unfortunately also possible on less eroding areas of the target surface. Reactions of the target surface are often called target poisoning when the reaction product, a chemical compound, is dielectric and leads to charging of the target surface. The compounds also frequently have a lower sputter rate. To overcome this disadvantage an interesting technical solution exists by alternating dc-magnetron sputtering of 2-3 monolayers metal film and subsequent oxidation in a separate reactive plasma zone /17/. A highly intense reactive plasma is present in a long narrow zone, isolated physically from the metal deposition zone by a region of relatively low pressure. A reactive ion source with a high intensity ion flux generates an intense reactive plasma of highly energetic oxygen adjacent to the periphery of the substrate, keeping the time required for the reaction very short. As a further advantage of this technique, compounds can be formed using a less reactive gas than oxygen, such as nitrogen and other, to form metal nitrides, or other compound films. The cyclic deposition/oxidation sputtering process seems to overcome all disadvantages of the prior art in reactive sputtering. The use of multiple stations affords a further advantage with a considerable increase of deposition speed. The possible film deposition rates are comparable with those in reactive evaporation. The elimination of the prior requirement of tight baffling allows for the coating of

curved substrates. It is, however, impossible to coat lager flat surfaces.

In ion beam sputtering (IBS) the target erosion is produced by a mono-energetic argon ion beam usualy from a Kaufman-type ion gun, but also high frequency ion sources should be considered /18/. In dual ion beam sputtering a second ion gun is used with the beam directed at the growing film similar to ion assisted deposition e.g. /19/. With the IB-sputtering techniques dense, well adherent and stoichiometric films of low optical absorption and with stable properties can be obtained. In all variants care must be taken to avoid unwanted sputtering of plant installations by high energetic neutral atoms what could cause film contamination. Unfortunately, the process has several practical limitations. It is relatively slow, and to deposit a thin film of one quarterwave optical thickness (visible range) takes 15 to 20 min. The area to be uniformly coated rarely exceeds a diameter of about 10 cm.

6. Reactive Ion Plating

In a conventional ion plating process /20/ evaporation is performed in the presence of an argon gas discharge. In collisions and electron impact reactions, coating material ions are formed and accelerated in the electric field of biased substrates so that condensation and film formation take place under the influence of ion bombardment. It can involve ions of the working gas, of the film-material vapour or of a mixture of both. In addition, the higher energetic neutral atoms of vapour and gas are also very important for the deposition process. This complex action is typically for ion plating. A large number of process variants is possible and different components can be combined to more complex triode and tetrode ion plating systems. It is furthermore remarkable that also high-speed sputtering cathodes are used as vapour sources in special ion plating arrangements. Bias sputtering and some types of plasma CVD also fall under the definition of ion plating. In conventional ion plating the degree of ionization is low and so the accelerating voltage must be rather high, generally between 3 and 5 kV, to supply the necessary energy for the formation of well adherent and dense films. The small number of ions, however, is also disadvantageous for a reactive gas process. Therefore, to overcome this problems a new form of reactive ion plating, shown schematically in Fig.3, has been developed in our laboratory /21/.

6.1. Reactive Low-Voltage Ion Plating

The new reactive ion plating process (RLVIP) /22/ performed in the specially designed automatic box type plating system BALZERS BAP 800, shown in Fig.4a and 4b, can be used for the deposition of single layer and multilayer oxide coatings onto unheated glass and other substrates. All evaporations are made by two special $270°$-type electron beam evaporators.
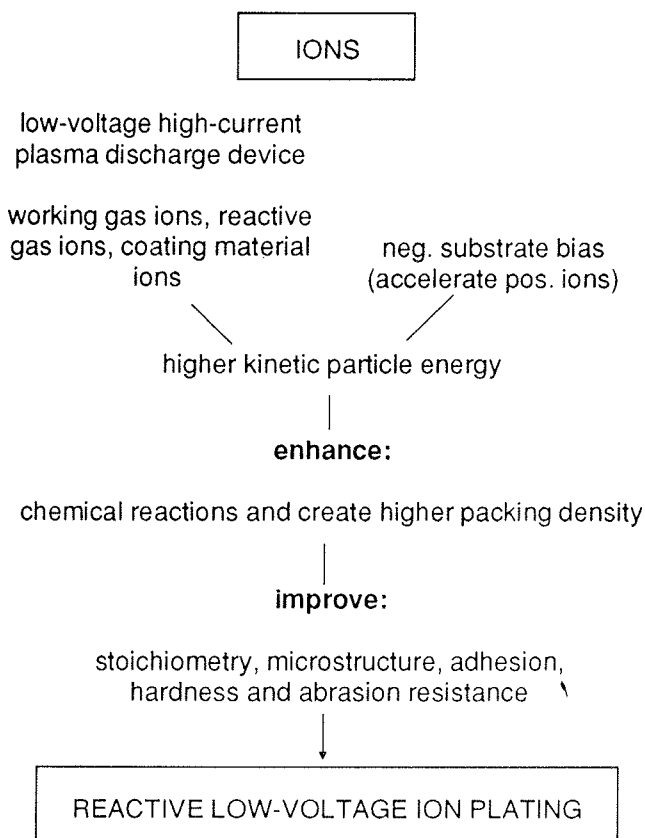
Fig. 3: Schematic of reactive low-voltage ion plating

Fig. 4a: Schematic of the reactive low voltage
high-current dc ion plating system Balzers
BAP 800

Fig. 4b: Front view of the BAP 800

The starting materials, metals or suboxides, form electrically conducting melts. Very effective ionisation and activation of the evaporating coating material atoms and the admitted reactive gas molecules occur by a low-voltage high-current argon plasma beam (hot cathode type) directed to the crucibles (anode). The substrate holder is electrically insulated. In contact with the formed plasma cloud the substrates receive a relatively high negative self-biasing potential of 15-20 V with respect to the plasma, which acts as accelerating voltage for positive ions. The repulsive force of the anode, gas phase collisions and the negative substrate bias determine the kinetic energy of the impinging positive ions. The total pressure in the plant is in the low 10^{-3} mbar range. Film deposition is started and stopped by opening or closing a moveable shutters in front of the electron beam evaporators. Film thickness and deposition rate are controlled by an oscillating quartz crystal monitor /23/. Optical thickness monitoring can be used too. Quarterwave films in the visible are deposited within 3 to 4 minutes. Uniformity in thickness distribution of $\pm$ 1 % over the whole substrate holder of 800 mm diameter can be achived by the use of a static correction shield. The BAP 800 can be tooled for both reactive ion plating and conventional reactive evaporation allowing alternating processes without requiring any changes in the plant.
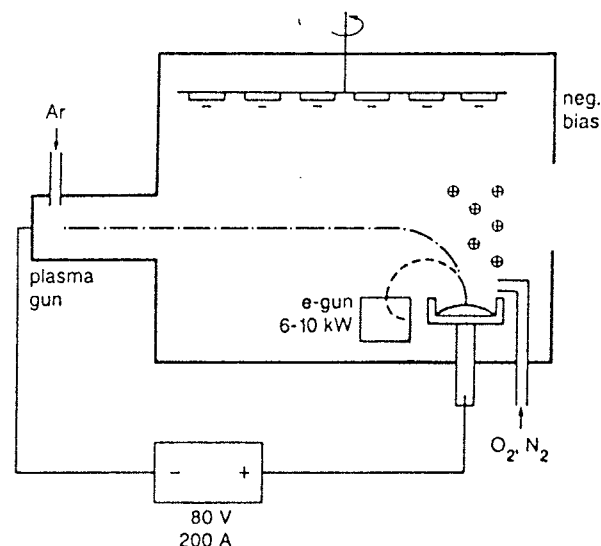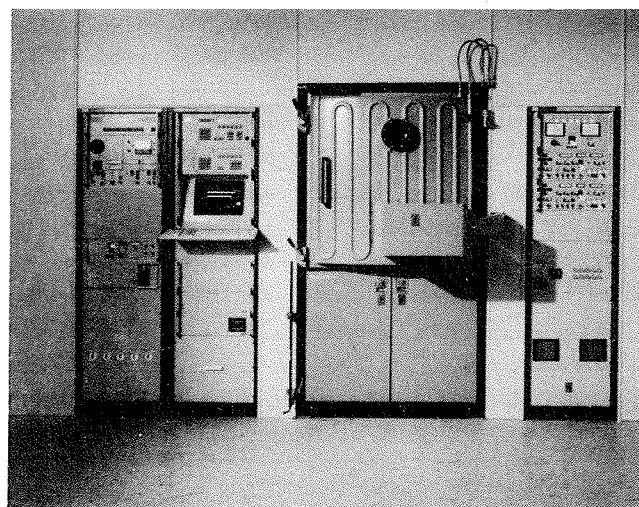
6.2. Structure, Microstructure, Non-Optical Properties

Electron optical investigations of plated oxide films onto unheated substrates showed amorphous and fine grained polycrystalline structures. Substrate temperatures of about 200° C seem not develope a coarser structure. All the films are very dense and generally without columnar microstructure. The surfaces were found to be very smooth compared with films deposited by conventional evaporation /24/.

Infrared, ultraviolet and Rutherford backscattering measurements of plated deposits showed stoichiometry and absence of incorporated water. The high density prevented water vapour sorption at humid atmosphere. The films are therefore also interesting as protective layers /25/.

Excellent adherence of single films and film systems on glass substrates was found in scratch adhesion test. And with the exception of TiO_2, film indentation hardness (Knoop) and abrasion resistance values (eraser test) of all other coatings were found to be very high. Ion plated films are generally under compressive intrinsic stress /26/. Their environmental stability according to US MIL-specifications shows a remarkable degree of quality. Some data are listed in Tab.1.

6.3. Optical Properties

Ion plated oxide films are very good oxidized. No absorption could be measured in the high transmittance range of well prepared single films with simple photometric

intensity methods. Photothermal deflection spectroscopy /27/ and loss measurments in optical waveguides /28/, showed very low values of k between 10^{-4} and 10^{-6}.

Film refractive index determinations from photometric and ellipsometric measurments showed values close to the bulk materials. In all cases measured indices were much higher than those of evaporated films. For comparision the various values are listed in Tab.2. The index values of single films could be reproduced within an accuracy of better than 1 %.

Homogeneity of the refractive index was good for films up to thicknesses of $7 \lambda/4$ (λ=550 nm). Thicker films were found to be slightly inhomogeneous. As a consequence of the intrinsic compressive stress the films showed

Film (deposited on unheated glass)	Structure (electr. diffr.)	Microstructure (SEM, TEM)	Water Vapour Sorption	Adhesion to Glass (Scratch Test)	Indentation Hardness / Abrasion Resistance	Intrinsic Mechan. Stress
TiO_2	amorphous	dense, homogeneous				
Nb_2O_5	amorphous	dense, homogeneous				
Ta_2O_5	amorphous	dense, homogeneous	in all films no measurable H_2O-sorption.	in all cases excellent, between 2.4 and 2.5 kgf (that is onset of strong glass substrate damage).	higher Knoop microhardness than glass / excellent abrasion resistance according to US MIL-C-675 C.	for all nd = $\lambda/4$ oxide films compressive in the 10^9 dyn.cm^{-2} range. No increase in thicker films and multilayers ---> stress relaxation.
ZrO_2	finest grained polycrystalline	dense, spheroidal				
HfO_2	amorphous	dense, homogeneous				
Y_2O_3	amorphous	dense, homogeneous				
Al_2O_3	amorphous	dense, homogeneous				
SiO_2	amorphous	dense, homogeneous				
SiO_xN_y	amorphous	dense, homogeneous				

Table 1: Non-Optical Properties of Ion Plated Oxide and Oxynitride Films

Film/(Starting Material) Glass Substrates $T_s \approx 50°C$	Refractive Index n_{550}	Homogeneity of n	Absorption Coefficient k_{546} PTDS (a) Photometric (b)		Stability on Wet Atmosphere	Stability at High Temperature
TiO_2 (Ti)	2.55	excellent up to nd = $7 \lambda/4$	1.77	$\cdot 10^{-4}$ (a)		
TiO_2 (TiO)	2.55	excellent up to nd = $7 \lambda/4$	7.0	$\cdot 10^{-5}$ (a)		
Nb_2O_5 (NbO_x)	2.40	excellent up to nd = $7 \lambda/4$	> 5	$\cdot 10^{-4}$ (b)		
Ta_2O_5 (TaO_x)	2.26	excellent up to nd = $7 \lambda/4$	4.0	$\cdot 10^{-6}$ (a)	no measurable changes on wet atmosphere	no degradation by baking up to and higher to 400°C
ZrO_2 (ZrO_x)	2.19	excellent up to nd = $4 \lambda/4$	2.3	$\cdot 10^{-5}$ (a)		
HfO_2 (Hf)	2.17	-		$< 10^{-4}$ (b)		
Y_2O_3 (Y)	1.95	-		$< 10^{-4}$ (b)		
Al_2O_3 (Al)	1.66	excellent up to nd = $7 \lambda/4$		$< 10^{-4}$ (b)		
SiO_2 (Si)	1.485	excellent up to nd = $7 \lambda/4$		$< 10^{-4}$ (b)		
SiO_xN_y (Si)	1.5 - 2.0	-		$< 10^{-4}$ (b)		

Table 2: Optical Properties of Ion Plated Oxide and Oxynitride Films

slight birefringence. Avoidance of water vapour sorption and desorption phenomena by the dense microstructure resulted in very stable film refractive indices. This is important for firm spectral system characteristics. The effect could be demonstrated with ion plated all-dielectric multilayer long-pass edge filters. Examples are shown in figures 5a and 5b. During controlled heating of such filters in a photometer to at least 130°C there occured either no measurable or only an extremly small shift in the position of the edge or of the transmittance band. The optical characteristics remained constant even during repeated heat treatment cycles. The marginal shift of 0.1 to 0.2 nm is not caused by water desorption/sorption phenomena but by the intrinsic material properties i.e. the change in refractive index with temperature dn/dT and the change in thickness by the expansion of the material with temperature dt/dT. Baking ZrO_2/SiO_2 and Ta_2O_5/SiO_2 multilayers on glass during a few hours at 400°C and subsequent storage tests in liquid water for three days produced no failure in optical and mechanical properties.
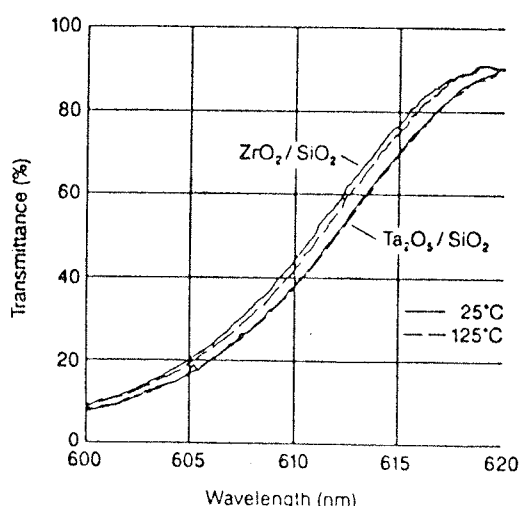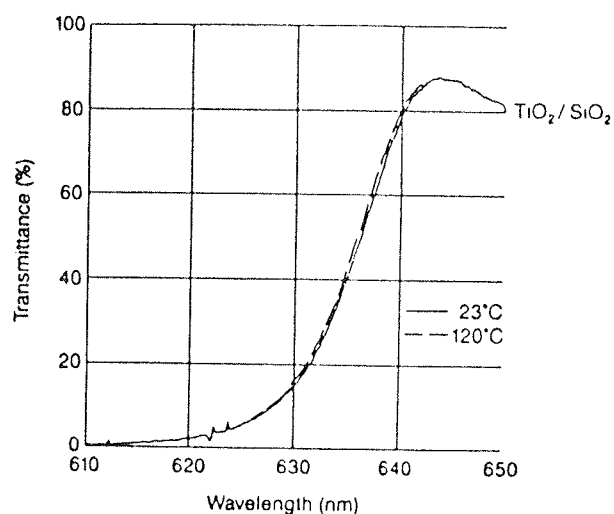
Figs. 5a and 5b:Transmittance versus wavelenght curve of the edge of ion plated long pass edge filters, each consisting of 23 layers of TiO_2/SiO_2, Ta_2O_5/SiO_2 or ZrO_2/SiO_2 including two matching layers. The dashed lines indicate the extremly small spectral edge shifts during heating to 125°C inside a photometer.

7. Discussion and Conclusion

The possibility to improve film performance in conventional reactive and even in activated reactive evaporation is rather limited. It is very effective, however, with the more recent developed higher energetic ion processes such as ion assisted deposition, sputtering, particularly ion beam sputtering and low- voltage reactive ion plating. Important features of coatings made by these techniques are: dense homogeneous microstructure resulting in relatively high refractive indices, low optical losses, insensitivity to changes in humid environment, high hardness and abrasion resistance and stability at high temperatures. A comparison of optical data is given in Tab.3.

Film	Conventional Reactive Evaporation	Reactive IAD	Reactive Sputtering	Reactive Ion Plating
SiO_2	1.46	1.485	1.48	1.485
Si_3N_4		1.93	1.95	2.05
Al_2O_3	1.63	1.68	1.67	1.66
ZrO_2	2.08	2.15	2.15	2.18
Ta_2O_5	2.10	2.30	2.15	2.26
TiO_2	2.30	2.43	2.51	2.52

Table 3   Refractive indices (λ=633 nm) of various compound films ($k << 10^{-4}$) obtained with different coating techniques

Bombardment of growing films with noble or reactive gas ions in ion assisted deposition and generation of energetic coating- material atoms in ion beam sputtering are powerful tools for basic parameter investigations in high energetic ion process developments and optimization studies.

The techniques are very effective for the deposition of low-loss oxide films on few small to medium size substrates.

Upscaling of directed ion beam processes for production purposes, however, is difficult and requires for IAD and IBS large size ion guns and highly efficient pumping systems. In film production the deposition time is important. Particularly with ion beam sputtering the low deposition rate of 15-20 minutes for a quarterwave thick film (visible range) is extremly time consuming in multilayer depositions. The new reactive low-voltage ion plating technology in the BAP 800 is an optimized and fast process for high volume production. Energetic conditions in the film formation are similar to those in IBS. The resulting film properties are similar with those obtained by ion assisted deposition. For comparison the typical energetic conditions of the mentioned processes are listed in Tab. 4. A slight deficit of the oxygen content in single films can occur /29,30/ depending on preparation conditions. The kinetic energy transferred to the atoms of the growing deposit should never exceed the

Technology	Gases Vapour Ions	Ion Current Density (Substrate)	Film Properties	Known Since	
Reactive Evaporation (RE)	O_2-neutral coating material		Columnar microstructure, close to stoichiometry	Aufwärter	1952
Activated Reactive Evaporation (ARE)	O_2-ions and activated states coating mat. atoms	$3 \cdot 10^{-4}$ mA/cm^2 < 100 eV	Reduction in opt. losses, improved stoichiometry	Heitmann Bunshah Ebert	1971 1972 1982
Ion Assisted Deposition (IAD)	Ar-and O_2-ions coating mat. atoms	$3 \cdot 10^{-1}$ mA/cm^2 50-500 eV	Densification by Ion bombardment, good adhesion	McNeil Macleod	1982 1983
Reactive Gas Discharge Sputtering (RGS)	Energetic activated neutral	Power density on target 2-15 W/cm^2	Dense microstructure, good stoichiometry and adhesion	Coleman Pawlewicz	1974 1978
Reactive Ion Beam Sputtering (RIBS)	Energetic atoms and ions	Target: $\approx$ 4 mA/cm^2 Substr.: 0.5-1 mA/cm^2 Beam energy: 500-2000 V		Wei	1979
Ion Plating (IP)	Coating material and Ar-ions	$\approx 1\text{-}5 \cdot 10^{-2}$ mA/cm^2 $\geq$ 1000 eV	Very dense microstruct. improved, adhesion	Berghaus Mattox	1937 1964
Reactive Low-Voltage Ion Plating (RLVIP)	Coating material Ar-, O_2- and N_2-ions	$\approx$ 1 mA/cm^2 5-50 eV	Very dense microstruct. smooth surface, improved stoichiometry and adhesion	Pulker Moll	1985

Table 4   Reactive PVD Coating Technologies

displacement energy to avoid chemical damage that produces optical absorption in the films. This effect is even more critical in multilayers. To lower particle energy of the condensing and bombarding species seems to be an important requirement /31/. RLVIP is not a cold technology. In multilayer production processes the substrate temperature rises from ambient values to approximately 200 ° mainly due to heat radiating from the large evaporation sources. There is, however, no influence on the film microstructure. It seems that RLVIP in the BAP 800 will become an extremly useful production technique for high quality optical coatings with many applications.

It is impossible to discuss and compare all the ion and plasma techniques currently used for optical film deposition. Plasma assisted CVD, plasma polymerization, plasma etching and the non- reactive energetic PVD techniques have been omitted intentionally. For the moment there is also little experience available about reactive ion beam deposited films produced by filtered arc evaporation /32/. Because of their importance, however, it should be mentioned here that some fluorides, particularly AlF$_3$, CeF$_3$ and LaF$_3$, have also been successfully deposited by ion assisted deposition and low-voltage ion plating. Many rare earth metal fluorides as those of Sm, Gd, Tb, Ho, Er and Y have been successfully processed by IAD /33/. MgF$_2$ is more critical because of slight impact dissociation. Only few results are available on plated sulfide films. ZnS-films on Ge substrates deposited by dc ion plating /34,35/ improved considerably humidity resistance and adhesion compared to films obtained by conventional evaporation. Clearly further work is required on this topic. Extensive literature on modern reactive and energetic coating technologies using gas discharge plasma or ions has been published in form of review papers by Holland /36/, Bunshah /37/, Macleod /38/, Moll at al. /39/ and Martin /40/.

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