Structure, Properties and Applications for PVD Al_2O_3 Layers - A Comparison of Deposition Technologies

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ABSTRACT

Because of its variety of properties aluminum oxide is widely used as coating material for different kinds of applications. Optical, insulating and barrier layers as well as protective coatings against abrasion, wear and chemical attack are examples. Owing to the special properties and with respect to reasonable coating cost aluminum oxide layers are produced by various technologies. A report will be given on coatings, which were deposited by plasma activated reactive evaporation and reactive pulse magnetron sputtering. The structure of the coatings was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Depending on the deposition technology layers with amorphous and crystalline structure were obtained. With increasing density and crystallinity of the coatings the hardness rises up to values of corundum, i.e. to 22 GPa. In the same manner a marked improvement of other properties such as abrasion and chemical resistance is observed. It can be shown, that various PVD technologies allow the deposition of layers within a wide range of properties. The spectrum covers a span of applications from barrier layers for packaging up to wear resistant layers.

INTRODUCTION

Because of its various properties, aluminum oxide (Al_2O_3) is a very interesting coating material. In particular, we can point to its outstanding mechanical, chemical, optical and dielectric features [1]. The extent to which these properties are formed depends on various factors such as the chemical composition, the structure and the microstructure of the layers obtained. As to the chemical composition it is aimed at the stoichiometric compound Al_2O_3. In this case the atomic ratio amounts to Al/O = 0.66. A substoichiometric (surplus of aluminum, Al/O > 0.66) or hyperstoichiometric (surplus of oxygen, Al/O < 0.66) composition of the layers is, in general, linked up with a loss in properties. The surplus aluminum is incorporated in the layers in a finely dispersed form and, for instance, causes a loss in transparency. The surplus oxygen collects in submicroscopic cavities and the layer becomes porous; an effect which, for instance, affects the gas permeability [2]. In regard of the structure of the layer material it should be taken into account that aluminum oxide occurs in various modifications [3-6]. Aside from amorphous Al_2O_3, metastable crystalline phases exist that are termed γ–, δ–, θ-and κ-phases. The thermodynamically stable crystalline α-phase is generally known as corundum. The formation of these phases depends on the coating technology employed. Here the substrate temperature has the greatest influence. Linked up with an increase in substrate temperature and the occurrence of crystalline phases is a considerable improvement of mechanical and chemical layer properties (Fig. 1).

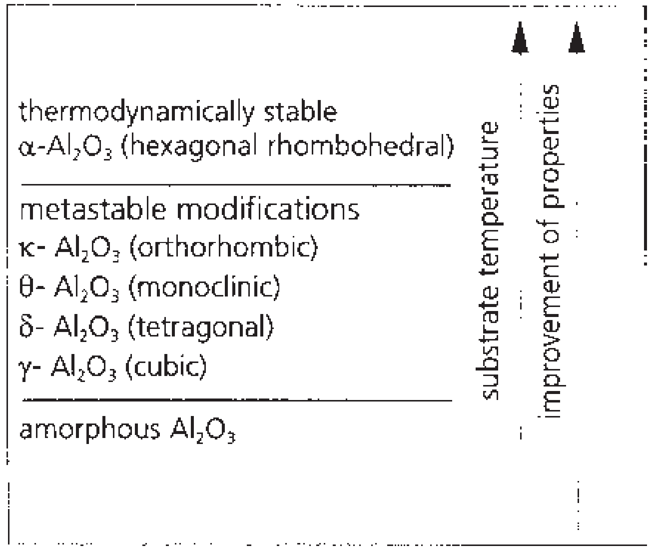

Figure 1. Influence of substrate temperature on the structure and properties of aluminum oxide

In addition to the type of phases formed, the properties of the deposited layers also depend on the macroscopic features of the microstructure; *i.e.* porosity and cracks *etc.* An improvement of the properties takes place with increasing density and crystallinity of the layers. Through variation of the coating technology it is possible to adjust layer properties matched to the corresponding application. In this context we can point to wear-resisting layers on magnetic heads and tools, just to cite some examples. In the first case an amorphous, compact aluminum oxide layer of medium hardness is needed; a hardness that must be matched to that of the frictional partner (disk). In the second case a very hard crystalline layer made of corun-

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dum becomes a must in order to process the workpieces.

The coatings are produced by means of CVD (Chemical Vapor Deposition) and PVD (Physical Vapor Deposition) techniques. CVD techniques are preferably employed to deposit hard, crystalline layers on high-speed cutting tools (*e.g.* cemented carbide inserts). Here substrate temperatures of 1000 °C and more become a must [7]. In the case of cemented carbide inserts these high temperatures already damage the substrate. In addition, volume changes occur in connection with the deposition of the metastable, crystalline κ-phase that cause cracks in the layer during the use of the tool and therefore result in a premature failure [8]. Because of the high substrate temperature of 1000 °C the choice of substrates being suitable for CVD techniques is very restricted.

Today, PVD techniques are preferably used for the production of amorphous compact layers. In recent papers it is further outlined that hard, crystalline layers can also be deposited at lower substrate temperatures [9,10]. Among other things, this allows to circumvent the deficits and drawbacks of the CVD techniques.

In the following a brief report is given about coating technologies for aluminum oxide that were developed by FEP. Here we point to layer properties that can be attained by means of the various technologies and indicate for which application these coatings seem to be particularly useful. Aside from plasma activation, this contribution deals with the influence of the substrate temperature. Investigations into the structure and microstructure were conducted by XRD, TEM and SEM techniques. The measurement of the Vickers hardness was carried out via nanoindentation. A Taber abraser was used to determine the abrasion resistance of the coatings.

TECHNOLOGIES

For reasons of economy, Al_2O_3 coatings are produced by magnetron sputtering or evaporation of aluminum in an oxygen atmosphere. The advantages of this reactive technique are its greater practicability and high deposition rates. The highest rates can be obtained by electron beam evaporation. But high coating rates are often linked up with inadequate layer properties. Here a plasma activation of the coating process has a positive bearing on the layer growth. On the one hand, plasma activation causes an increase in reactivity of the partners participating in the layer formation. On the other hand, it enhances the energy of the condensing vapor particles. The resulting increase in mobility of the particles may cause a changed structure in the sense of the previously mentioned phases as well as in an improved microstructure of the coating and therefore in better properties.

In the case of sputtering a process-dependent plasma exists already. For evaporation, however, a suitable plasma source must be integrated into the process. To obtain a corresponding activation, the plasma density has to be matched to the evaporation rate. To this end, FEP often uses the plasma of a hollow-cathode discharge. Processes based on this activation are termed HAD processes (Hollow-Cathode Activated Deposition) [11]. If the activation takes place via a magnetron discharge, one speaks of an MAD process (Magnetron Activated Deposition) [12].

Reactive HAD Process

Electron Beam Evaporation

With this technique the Al_2O_3 layers are produced by the electron beam evaporation of aluminum in an oxygen atmosphere (Fig. 2). Plasma activation of the coating process is carried out with the aid of a low-voltage electron beam (LVEB) of a hollow-cathode discharge. Figure 2 gives a schematic illustration of the coating of plate-type substrates. By means of this technique it is of course possible to coat plastic films or metal strips as well [13].

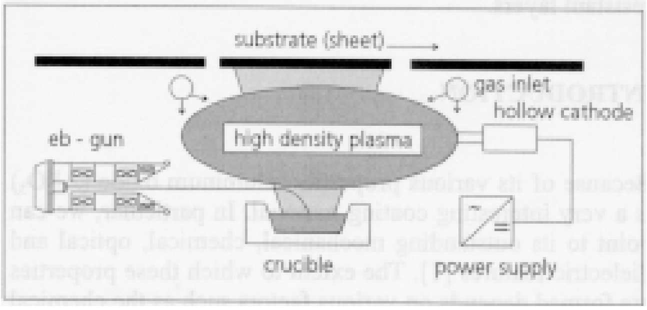

Figure 2. Schematic arrangement of HAD process with eb evaporator for coating of sheets

Boat Evaporation

The evaporation of aluminum may also be performed from a wire-fed boat evaporator that is heated by a direct current flow (Fig. 3). Again, oxygen is used as reactive gas. Same as with the electron beam evaporation, plasma activation takes place by means of a LVEB [14].

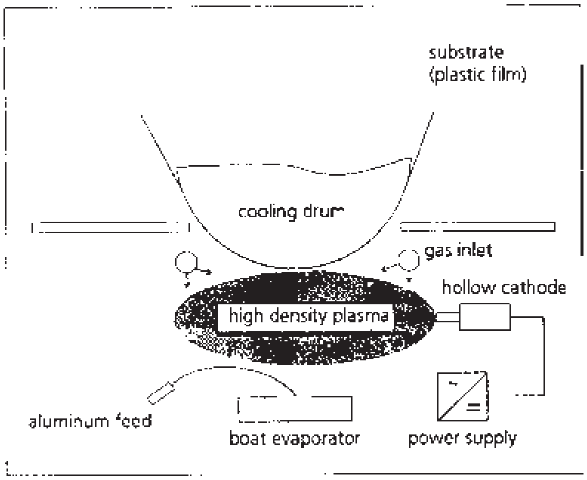

Figure 3. Schematic arrangement of HAD process with boat evaporator for coating of plastic films

Reactive MAD Process

Aluminum is evaporated from a boat evaporator in an argon-oxygen mixture. Plasma activation takes place by a magnetron discharge of two electrodes that are connected to a bipolar pulse generator in such a manner that the electrodes alternately act as cathode and anode (Fig. 4). In each sputtering phase, some deposited material is sputtered away from the electrodes. In this way the functionality of the electrodes is maintained in full [2].

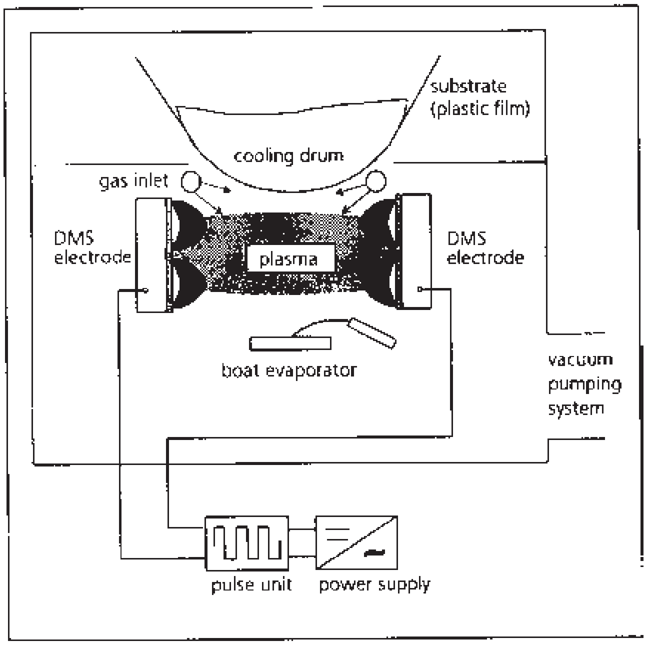

Figure 4. Schematic arrangement of MAD process with boat evaporator for coating of plastic films

Reactive Pulsed Magnetron Sputtering (PMS)

With this technique, the deposition of Al_2O_3 layers takes place through sputtering from the aluminum targets of a Dual Magnetron System (DMS) in a reactive argon-oxygen mixture. The DMS consists of two magnetron sources with planar targets arranged side by side. The targets are connected to a bipolar pulse generator so that they alternately act as cathode and anode of a magnetron discharge (Fig. 5). Each sputtering phase of some microseconds duration is followed by a phase in which the insulating layers are discharged. Such a pulsed mode prevents the complete coverage of the targets with insulating layers. In addition, it prevents arcing which would cause the splashing of target material and therefore defects in the coating. In this way, long-term stable operation becomes possible without difficulty [15, 16]. Figure 6 gives a schematic illustration of a sputtering system devised for three-dimensional coating [17].

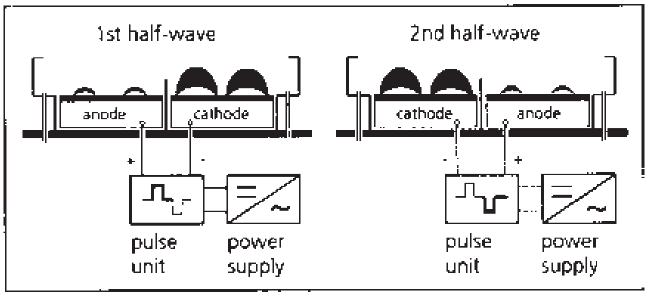

Figure 5. Schematic arrangement and time behavior of bipolar pulsed sputtering with DMS system

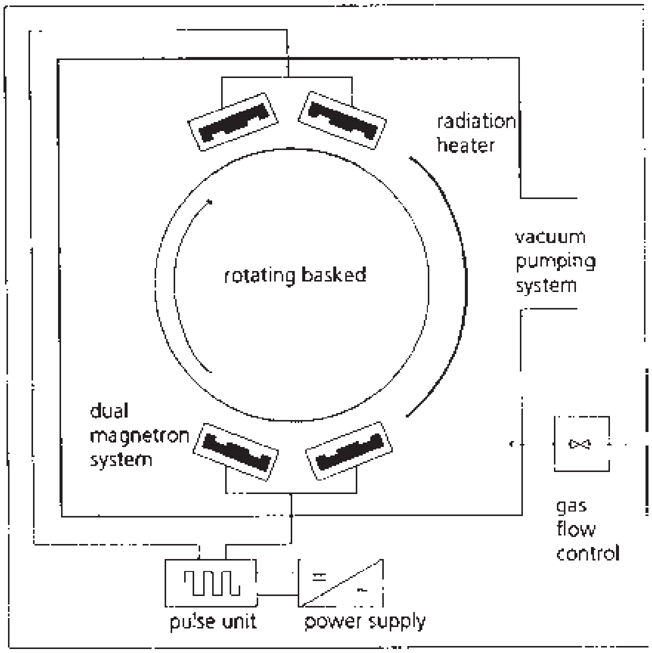

Figure 6. Schematic top view of an arrangement for three-dimensional hard coating with PMS

MICROSTRUCTURE, STRUCTURE AND PROPERTIES

Reactive Evaporation without Plasma Activation

First let us explain the influence the substrate temperature exerts on the formation of the layer structure. Shown in Fig. 7 is the microstructure without plasma activation as a schematic representation. The homologous temperatures T_S/T_M (T_S = substrate temperature and T_M = melting temperature of layer material) were used to follow the known structure-zone models [18,19]. At low substrate temperatures the layers are strongly porous and cracky. With increasing substrate temperatures the layers become more dense and the cracks finer. At a temperature of T_S = 600 °C (T_S/T_M = 0.38) the SEM micrographs showed no more cracks. From TEM micrographs it is further evident that, at this temperature, tiny cavities still exist in the layers. The layers exhibit a columnar fracture that extends throughout the investigated temperature interval of T_S = 20 - 700 °C (T_S/T_M = 0.13 - 0.42). The layers consist of amorphous

aluminum oxide in which nanocrystallites of the γ-phase will be incorporated at T_S = 700 °C (T_S/T_M = 0.42).
The constitution of the layer microstructure is also reflected in the properties stated on behalf of the hardness (Fig. 9). The latter increases with the substrate temperature monotonous from about 3 GPa at room temperature to a maximum of 7 GPa at 700 °C. This rise represents the increase in density of the coating. The inclusion of the nanocrystallites of the γ-phase into the amorphous aluminum oxide practically causes no increase in hardness.

Reactive HAD Process

Quite different conditions are obtained in the layer deposition under simultaneous plasma action. Even at a lower substrate temperature the layers are comparatively dense and exhibit a hardness of about 12 GPa (Figs. 8, 9). With the HAD process and temperatures of up to T_S = 600 °C (T_S/T_M = 0.38) the layer consists of amorphous aluminum oxide and, at a higher temperature, crystalline, metastable γ-phase will be formed. This transition goes along with a pronounced increase in hardness to 19 GPa. The effect of plasma activation on the layer properties becomes also clearly evident from the abrasive behavior of coated films. Layers with a hardness of 6 - 7 GPa can be deposited on plastic films at substrate temperatures of less than 100 °C (see table II). Depicted in Fig. 10 is the relative gloss of coated and uncoated films after abrasive treatment with the Taber abraser. Whereas an Al_2O_3 coating deposited without plasma activation exhibits a drop in brightness to 60% of the initial value, a layer with plasma activation practically shows no gloss loss.

Reactive MAD Process

This coating process has been developed especially for the deposition of barrier layers on packaging films. Plasma activation results in a substantial improvement which becomes manifest in a pronounced reduction of the permeability of the layers to water vapor and oxygen. Compared to uncoated films this reduction is greater than one order of magnitude. At the interesting thickness of the layers of 10 - 60 nm, however, structure investigations are very expensive and have not been carried out up to now.

Reactive Pulsed Magnetron Sputtering (PMS)

The influence of the substrate temperature on the structure and microstructure of the layers has been investigated for this technology, too. Details about the deposition conditions are given in [9]. A detailed representation of the results is given in a structure model shown in Fig. 11. The investigated range of substrate temperatures covers a span of about 20 - 770 °C. Expressed in homologous temperatures T_S/T_M this corresponds to a range of approximately 0.13 to 0.45. As indicated in Fig. 11, amorphous aluminum oxide occurs up to 350 °C (T_S/T_M = 0.27).

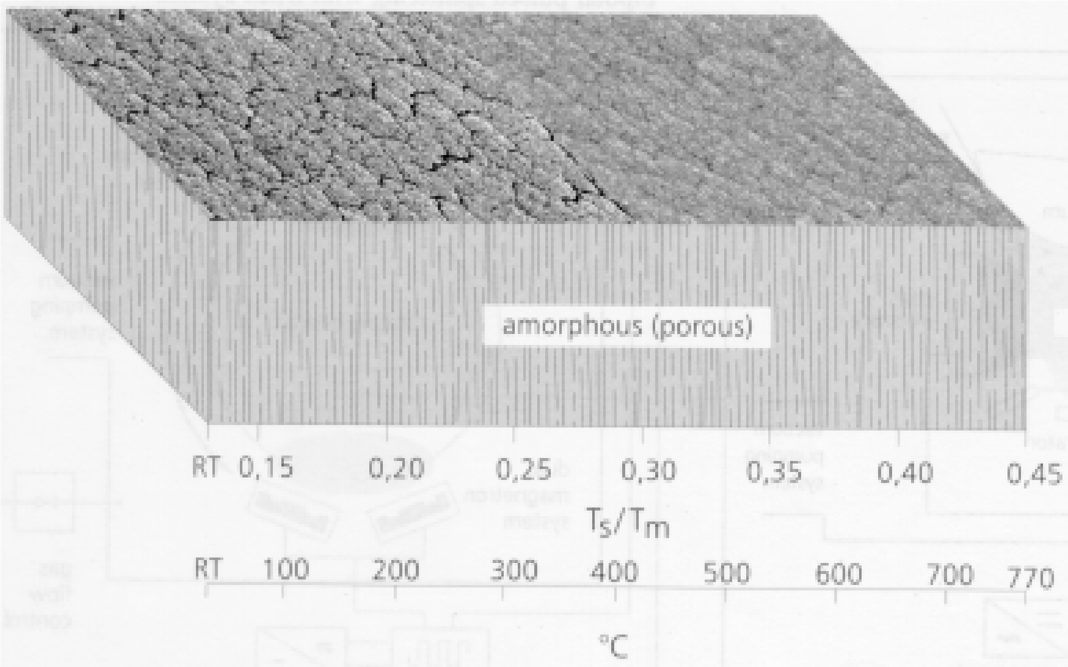

Figure 7. Structure model of aluminum oxide coatings deposited by reactive evaporation without plasma activation (RT= room temperature)

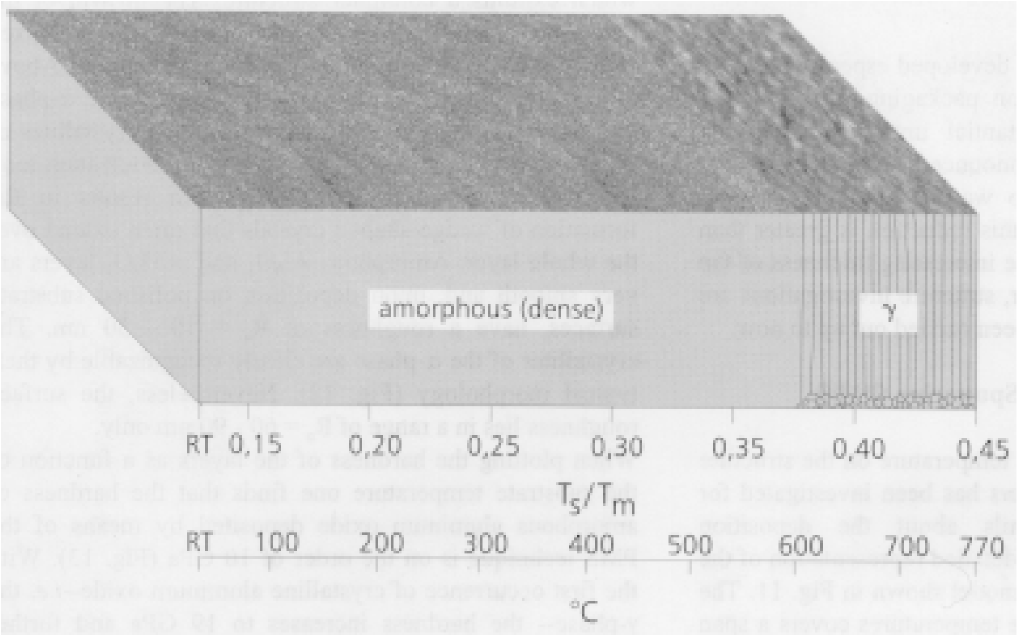

Figure 8. Structure model of aluminum oxide coatings deposited through reactive HAD process (RT = room temperature)

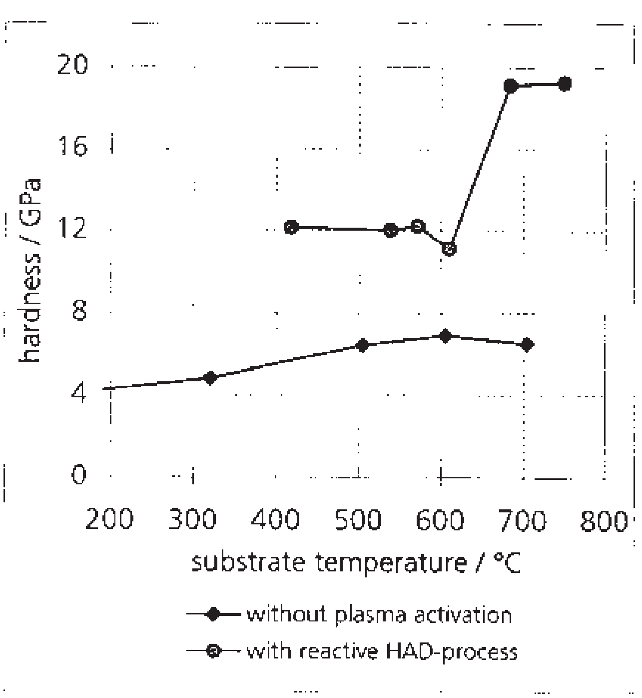

Figure 9. Influence of the substrate temperature and the plasma activation on the hardness of aluminum oxide

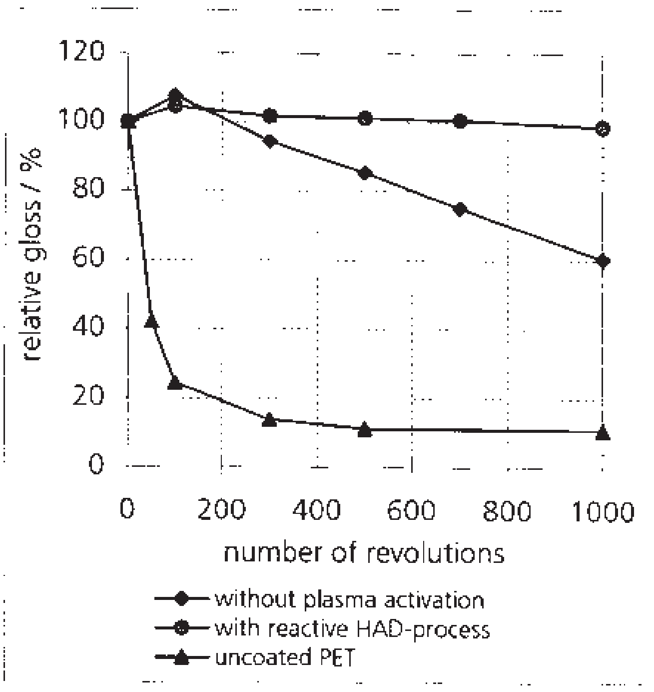

Figure 10. Influence of the plasma activation on the abrasion resistance of aluminum oxide coatings on plastic films measured via relative gloss after a testing with the Taber abraser (abrasion wheels CS10F)

The layer material is practically free from pores and has a glassy character. Above this temperature the layer consists of crystalline aluminum oxide. Up to 680 °C ($T_S/T_M = 0.41$) the metastable γ-phase has been observed which exhibits a columnar structure. The growth of the latter takes place from a narrow area of equiaxed nanocrystallites near the layer-substrate interface. Above 680 °C one obtains the thermodynamically stable α-phase the nucleation of which is likely to start on crystallites of the γ-phase that was deposited first. When nucleation took place in the α-phase a lateral growth results in the formation of wedge-shaped crystals that often extend over the whole layer. Amorphous Al_2O_3 and γ-Al_2O_3 layers are very smooth and, upon deposition on polished substrate surfaces, have a roughness of R_a = 10 - 50 nm. The crystallites of the α-phase are clearly recognizable by their typical morphology (Fig. 12). Nevertheless, the surface roughness lies in a range of R_a = 60 - 90 nm only.

When plotting the hardness of the layers as a function of the substrate temperature one finds that the hardness of amorphous aluminum oxide deposited by means of the PMS technique is on the order of 10 GPa (Fig. 13). With the first occurrence of crystalline aluminum oxide—*i.e.* the γ-phase—the hardness increases to 19 GPa and further rises to 22 GPa with the formation of the α-phase. This value corresponds to the hardness of the monocrystalline α-aluminum oxide; *i.e.* of corundum.

The most striking result of this investigation is the possibility to deposit α-aluminum oxide at substrate temperatures of 680 °C. Hence the use of the PMS technique permits to utilize the good mechanical and chemical properties of γ-Al_2O_3 even for temperature-sensitive substrates.

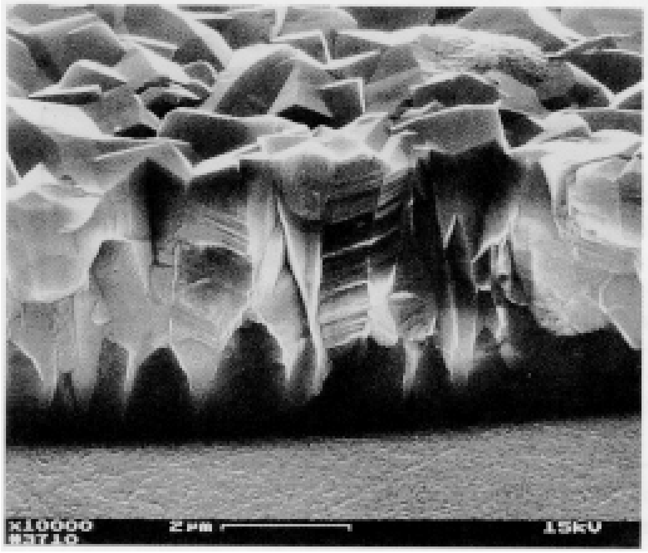

Fig. 12 Typical topography of cross fracture and surface of crystalline α-Al_2O_3

APPLICATIONS

The technologies specified herein are particularly useful for the coating of large areas. This includes plastic films, plastic plates, metal strips, metal sheets and glass panes. Aside from the coating of large-area substrates the PMS technique further allows the coating of small parts such as tools, disks *etc.* The choice of the technology to be used depends on the product

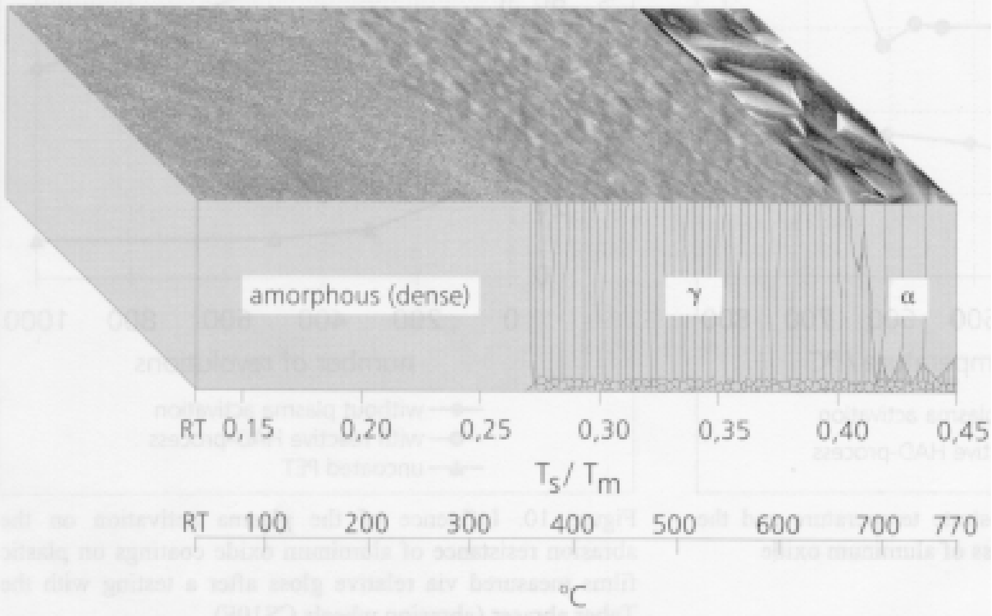

Figure 11. Structure model of aluminum oxide coatings deposited through reactive PMS process (RT = room temperature)

to be coated, on the layer properties and on the coating costs. The latter substantially depend on the coating rate. Here the rule of thumb applies: The higher the rate the lower are the costs [20].

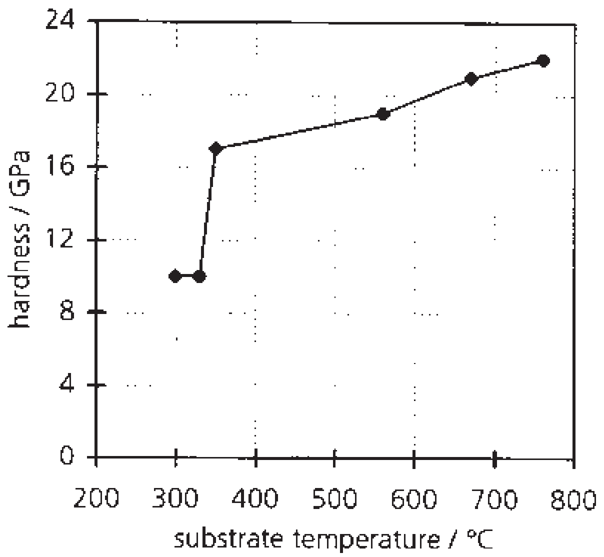

Fig. 13 Influence of the substrate temperature on the hardness of aluminum oxide coatings deposited with reactive PMS process

The highest rates are obtained with HAD and MAD processes. Characteristic parameters have been compiled in Table I.

Another very important selective criterion is the substrate temperature. Detailed data about the ranges of substrate temperatures and attainable properties are given in Tables II to IV.

In this way it will be clearly evident that the various technologies allow to use the whole property spectrum of aluminum oxide to deposit tailor-made coatings.

SUMMARY

Presented are chosen technologies for the deposition of aluminum oxide layers that were developed by FEP. Available for plasma-activated coating are the HAD and MAD processes. The coating rates cover a span of 50 to 200 nm/s and the uniformity of thickness distribution amounts about ± 10 %.

HAD layers excel in their outstanding mechanical and chemical properties. Wear and corrosion protection are possible applications.

MAD layers are best suited as barrier layers to reduce the permeability to gas and water vapor of packaging films. With the aid of the PMS technique a wide range of properties can be covered. Particularly useful is this technology for the deposition of hard, crystalline coatings, however, at much lower rates. In this special case the substrate temperatures are as low as 350-770 °C. For comparison, CVD techniques require temperatures of at least 1000 °C. Here the enormous capability of the PMS technique becomes clearly evident. The uniformity of the thickness distribution obtained with this method is about ± 2 % and the coating rates lie in a range of 1-5 nm/s.

The development of these techniques allows for a widespread utilization of the various structure-dependent properties of aluminum oxide.

Table I
Characteristic Parameters for Coating Large-Area Substrates by Means of Pulsed Magnetron Sputtering and Plasma-Activated Evaporation (HAD and MAD Processes, Respectively)

	Pulsed Magnetron Sputtering	**Plasma-Activated Evaporation**
deposition rate	1 - 5 nm/s	50 - 200 nm/s
coating costs, normalized for 100 nm layer thickness	2 - 10 $\$/\text{m}^2$	0.05 - 0.2 $\$/\text{m}^2$
thickness uniformity	± 1 % to ± 2 %	± 5 % to ± 10 %

Table II

Structures, Properties and Applications of HAD Al_2O_3 Layers

Substrate Temp. Interval[1]	**Structure**	**Property**	**Application**
RT - 600 °C[2]	amorphous	• hardness of 6 - 7 GPa (plastic film) • hardness of 10 - 12 GPa (metal substrates, glass)	• antiabrasive coatings for metal substrates, plastic films, plastic plates and glass panes
> 600 °C	γ, crystalline	• hardness of 17 - 19 GPa • resistant to 60 % phosphoric acid at 60 °C	• wear protection at medium load • corrosion-protective coatings

[1] substrate temperature interval within which the specified structure occurs

[2] to maintain lower temperatures the substrate has to be cooled (RT = room temperature)

Table III

Structure, Properties and Applications of MAD Al_2O_3 Layers

Substrate Temp.	**Structure**	**Property**	**Application**
RT[1]	amorphous, medium density	gas and vapor barrier	barrier layers for packaging film (on PET, OPP)

[1] RT = room temperature

Table IV

Structures, Properties and Applications of PMS Al_2O_3 Layers

Substrate Temp. Interval[1]	**Structure**	**Property**	**Application**
RT - 350 °C[2]	amorphous	variation of technology permits adjustment of • variable hardness 7 - 10 GPa • variable chemical etchability in 60 % phosphoric acid at 60 °C	• wear protection at moderate load, e.g. magnetic heads; • antiabrasive coatings for metal substrates, plastic films, plastic plates and glass panes • dielectric layers
350 - 680 °C	γ, crystalline	• hardness 17 - 19 GPa • resistant to 60% phosphoric acid at 60 °C	• wear protection at medium load, e.g. slides, tools • corrosion-protective coatings
680 - 770 °C (cf. CVD at 1000 °C)	α, crystalline	• hardness to 22 GPa • resistant to acids • stable at high temperatures	• wear protection at high load, e.g. cutting tools • corrosion-protective coatings

[1] substrate temperature interval within which the specified structure occurs

[2] to maintain lower temperatures the substrate has to be cooled (RT = room temperature)

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