Original Paper

Composition of titania coatings deposited by different techniques

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Quantitative element concentrations in titania films produced by different deposition techniques (evaporation, sputtering, ion-assisted deposition, ion plating and dip coating) have been determined by means of Rutherford Backscattering Spectrometry and Nuclear Reaction Analysis with the reaction $^{1}H(^{15}N, \alpha\gamma)^{12}C$. Large differences of the hydrogen content are found for the various production techniques and the related deposition parameters, which correlate with the refractive index of the respective film. In dependence on the deposition conditions the oxygen/titanium ratio of the investigated titania films varies between 1.95 and 2.09. The impurities detected in the films (tantalum, molybdenum, silicon, argon, carbon, sodium) can be related to specific deposition conditions. Three multilayer interference systems containing TiO_2 and SiO_2 show large variations in hydrogen content resembling those found for single TiO_2 films.

Zusammensetzung von Titanoxidschichten in Abhängigkeit von den Herstellungsbedingungen

Quantitative Elementkonzentrationen in Titanoxidfilmen, die durch verschiedene Herstellungsverfahren (Aufdampfen, Sputtern, ionenunterstütztes Aufdampfen, Ion Plating und Dip Coating) erzeugt waren, wurden mit Hilfe der Rutherford-Rückstreu-Spektrometrie und der Kernreaktionsanalyse mit der Reaktion $^{1}H(^{15}N, \alpha\gamma)^{12}C$ bestimmt. In Abhängigkeit von den verschiedenen Herstellungsverfahren und den entsprechenden Verfahrensparametern werden große Unterschiede im Wasserstoffgehalt gefunden, die mit dem Brechungsindex des entsprechenden Films korrelieren. Das Sauerstoff/Titan-Verhältnis der untersuchten Titanoxidschichten liegt je nach Herstellungsbedingung zwischen 1,95 und 2,09. Die in den Filmen nachgewiesenen Verunreinigungen (Tantal, Molybdän, Silicium, Argon, Kohlenstoff, Natrium) können mit den spezifischen Bedingungen bei der Filmherstellung in Verbindung gebracht werden. Drei Vielschicht-Interferenzsysteme, die TiO_2 und SiO_2 enthalten, weisen große Unterschiede im Wasserstoffgehalt auf, die den bei TiO_2-Einzelfilmen gefundenen ähneln.

1. Introduction

Several applications involving low-loss optical coatings on glass have stimulated a considerable amount of activity in preparation techniques of oxide films with high refractive index and low absorption. The increased interest in such dielectric layers on glass results also from possible improvement of commercially available products, for instance in antireflecting coatings for shop windows, reflecting layers for architectural glass or interference filters. Various deposition techniques have been developed for the production of coatings with desirable optical, mechanical and chemical properties. Up to now most of the employed deposition techniques are in practice selected on an empirical basis with respect to the specially desired film properties.

One of the most extensively used coating materials with a high refractive index is titania. For this material it is well known that different types of deposition techniques create films with very different properties [1 to 4]. It is reported that those coatings possess differences in the refractive index [2 and 3], in the film density [5], in the stress [6], crystal structure [2 and 6], etc., which depend on the actual deposition conditions. However, detailed studies of the composition of TiO_2 layers, especially of the hydrogen content in dependence on the deposition conditions, have so far been lacking to the authors' knowledge.

In this paper it is therefore reported on a quantitative analysis of chemical elements in TiO_2 single films prepared by reactive evaporation, sputtering, ion-assisted deposition, ion plating and dip coating. Using high-energy ion beam analysis techniques, the oxygen and hydrogen contents were determined as well as the amount of impurities of other elements. In addition, optical measurements were performed. Furthermore, three multilayer systems consisting of TiO_2 and SiO_2 alternating layers were analyzed for the hydrogen content.

2. Experimental

2.1. Sample preparation and film deposition

TiO_2 films were produced by four Physical Vapour Deposition (PVD) techniques, which were reactive e^--beam

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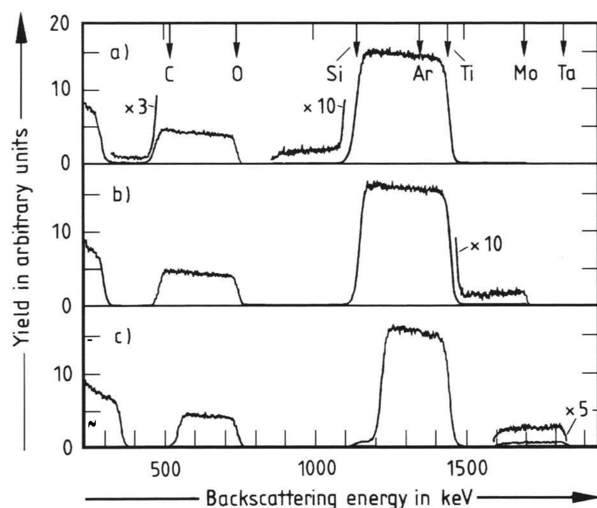
Table 1. Comparison of relevant deposition parameters for titania single films produced with different coating techniques

deposition technique	thickness in nm	deposition rate in nm s^{-1}	substrate temperature in °C	substrates	p_{O_2} in Pa
EV	400	0.5	380	BK 7 glass; carbon	10^{-2}
IP	400	0.4	<100	carbon	≈0.1
IAD	300; 600	0.2	250	BK 7 glass; carbon	10^{-2}
SP	300	0.2	room temperature	BK 7 glass; carbon	10^{-2}
DC	45; 215	–	170; 500	soda–lime–silica glass	–



Figures 1a to c. RBS spectra of three TiO_2 films, deposited on carbon substrates by PVD techniques (IP: figure a; EV: figure b; SP: figure c) showing the specific contaminations. The arrows in figure a) indicate the energies which correspond to backscattering from atoms at the surface.

evaporation (EV), reactive low-voltage ion plating (IP), reactive ion beam sputtering (SP) and reactive ion-assisted deposition (IAD), and by the sol-gel technique dip coating (DC). TiO_2/SiO_2 multilayer systems were deposited by DC, EV and reactive SP.

The substrates used were soda–lime–silica glass (SLG), BK 7 glass and carbon. Before coating, the glass substrates were treated by a standardized cleaning procedure and the carbon plates were rinsed with acetone to remove surface contaminations.

For comparison some relevant deposition parameters for single films are given in table 1. Starting material for the PVD processes was TiO_2. A Balzers BAK 760 coater (Balzers AG, Balzers (Liechtenstein)) was used for the reactive e^--beam evaporation, whereas IP was performed in a Balzers BAP 800 system. For IAD the titania starting material was evaporated by an e^--beam source, with an additional oxygen ion beam directed onto the substrates. An Oxford Instruments coating unit is used for SP film deposition. The sputtering was performed with a 1 keV argon beam. More details on the PVD techniques are given elsewhere [2 and 3]. Sol-gel films were deposited on soda–lime–silica glass by DC. The films were drawn from a titanium alkoxide solution and hydrolyzed in moistened air. For film formation and densification the layers were heated to 500 °C in an oven. More information on the DC technique can be found in [7]. Some films were heated only to 170 °C in order to obtain information on the composition at an intermediate state.

2.2. Analysis techniques

The oxygen content of the TiO_2 single films was determined by Rutherford Backscattering Spectrometry (RBS), using a 2 MeV ^4He beam and a 160° scattering geometry. The RBS measurements yielded also information on impurities with mass number > 4. The RBS spectra were evaluated using the computer simulation program RUMP [8]. The hydrogen contents of the single films and of the multilayer systems were determined with the ^{15}N Nuclear Reaction Analysis (NRA) technique which is based on the nuclear reaction $^1H(^{15}N,\alpha\gamma)^{12}C$. More details on these two ion beam analysis techniques and the experimental environment at the 7 MeV Van de Graaff accelerator of the Institut für Kernphysik can be found in [9]. It is worth mentioning that the hydrogen content of the films was not influenced by the ^{15}N ion beam, as was checked by repeating some profiling measurements.

The single films, which were deposited on glass substrates, were also examined optically with respect to transmittance and reflectance in the 400 to 1000 nm wavelength range using a Hitachi spectrometer. From these data the spectral refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ were deduced, using a recently developed fitting routine [10] assuming homogeneous films with smooth behaviour of $n(\lambda)$ and $k(\lambda)$.

3. Results and discussion

3.1. Single films

The results obtained from RBS measurements will be described first. This will be followed by the results on hydrogen from NRA.

RBS spectra of three TiO_2 films, deposited on carbon substrates by EV, IP and SP are shown in figures 1a to c. The main features in each spectrum are the signals arising from titanium and oxygen and from the carbon substrate. Furthermore, signals from various impurities can be seen, which are different for each film. It should be recalled that the ^4He ions scattered on heavy elements have higher energies after scattering than the ions scattered on light elements. If the scattering process does not

Table 2. Composition of titania films normalized to titania

deposition technique	titanium	oxygen	hydrogen	other elements
EV	1	2.08±0.03	0.1	Si: 0.25±0.05; C: 0.25±0.08
IP	1	1.99±0.03	0.001	Mo: 0.0025±0.0005
SP	1	2.04±0.03	0.05 to 0.1	Ar: 0.05±0.007; Ta: 0.004±0.0005
IAD	1	2.03±0.04	0.23	C: 0.09±0.05
DC	1	1.95±0.15	0.1; 0.65	C: not detectable due to interfering signals

occur at the surface but in a certain depth of the sample, the energy of the detected ^4He ion is shifted to lower energies because of the energy loss along the incoming and outgoing paths. The number of ions scattered on a specific element (creating a certain spectrum height) is mainly determined by the (known) scattering cross-section and the atomic concentration [11]. The RBS spectrum of the IAD film (not shown) did not possess signals arising from impurities.

The RBS spectra of two DC films on float glass, which had been heated to two different temperatures, are shown in figure 2. The spectra show beside the signal from titanium also signals from the substrate (calcium, silicon, sodium, and oxygen); the oxygen signal from the TiO_2 film is adjoining the oxygen signal from the glass. The two spectra differ only in the position of the sodium edge. In the spectrum of the film annealed at the lower temperature, the sodium edge appears at an energy corresponding to the substrate/film interface. For the film annealed at 500 °C the sodium edge appears at an energy corresponding to the surface of the TiO_2 film, showing that the film contains sodium. The sodium concentration is found to be 15 at.%.

The concentration values for oxygen and for impurity elements derived from the RBS spectra are reported in table 2. These values have a systematic error of 5 % arising from the uncertainty of the RBS stopping power which enters into the evaluation of the RBS spectra. The precision of the concentration values is limited by statistical fluctuations in the spectra and in some cases by the interfering signals of another element. This leads to different uncertainties for the various analyzed elements (table 2). Note that the oxygen/titanium atomic ratios are all close to 2, as expected for completely oxidized films. The small differences between films deposited by different techniques are not fully understood. They may be partly connected with the hydrogen content of the films (OH, H_2O), but also the impurities of other elements may affect the oxygen content.

Most of the contaminations by heavy impurities in the PVD films can be understood by considering the specific way of production. The evaporation chamber in which the EV film was produced is also used for production of SiO_2 films (multilayer systems), so that the silicon in the film might originate from contaminations of previous runs which remained in the chamber. The sputtering was done using an argon beam; consequently,

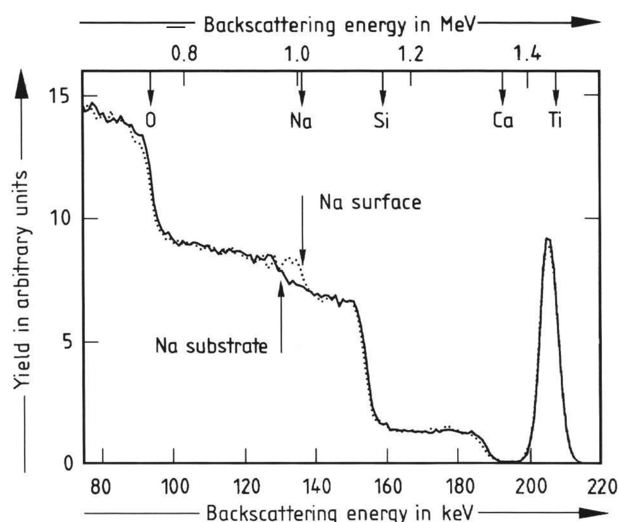


Figure 2. RBS spectra of two TiO_2 films on soda–lime–silica glass produced by dip coating using baking temperatures of 170 °C (full line) and 500 °C (dotted line).

scattered argon ions are incorporated into the TiO_2 layer. Some parts of the sputtering coating unit are made of tantalum. If these parts have been hit, even by a small fraction of the ion beam, sputtered tantalum ions could create a tantalum contamination in the film. The molybdenum content of the IP film could possibly be caused by interactions (sputtering) of the plasma ions with parts of the coating chamber made of molybdenum. The high carbon content in the EV films is surprising. The most likely explanation would be that carbon has diffused from the carbon substrate into the film; EV films have a rather high porosity. Another source may be parts of the production chamber, especially the crucible. Concerning the sodium found in the DC films, this can readily be explained as arising from diffusional transport from the glass substrate. This process has been observed before [3]. From the present result it can be concluded that sodium diffusion is unimportant at temperatures up to 170 °C.

The ^{15}N profiling measurements show that all investigated films contain hydrogen. The hydrogen concentration varies strongly depending on the deposition technique used (see table 2). Figure 3 displays four hydrogen profiles taken from films produced by EV, SP, IP and IAD. In the profiles of this figure and in all of the following hydrogen profiles, the hydrogen/titanium ratio is

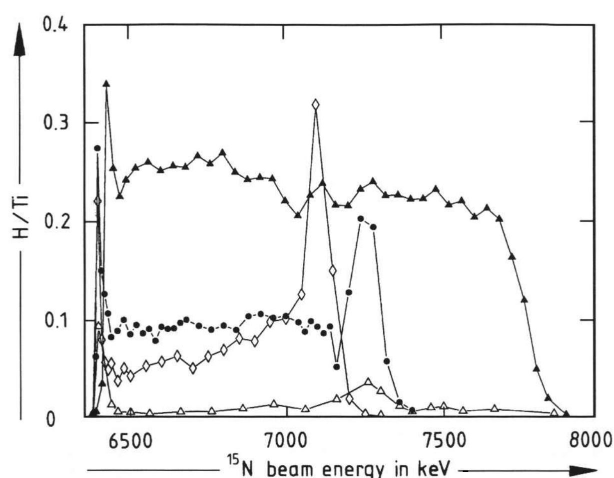


Figure 3. Hydrogen depth profiles of TiO_2 films produced by PVD techniques; IP: △, SP: ◇, EV: •, IAD: ▲.

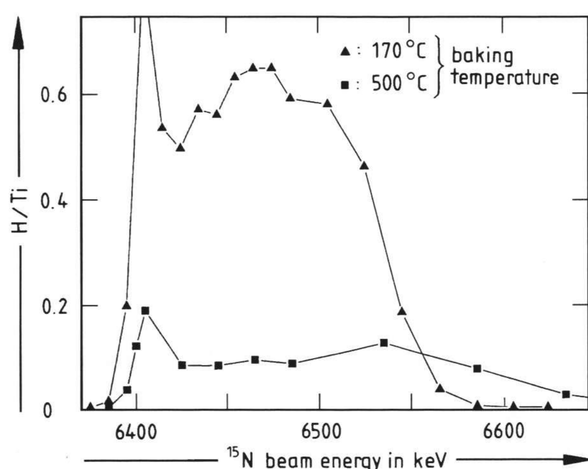


Figure 4. Hydrogen depth profiles of TiO_2 films produced by dip coating at different temperatures.

plotted versus the ^{15}N beam energy because for a transformation into a depth scale the film density has to be known. However, the density depends on the used deposition technique and the coating conditions [5] and is unknown in general. The resonance energy of 6.4 MeV corresponds to the sample surface. (The peak structure in the hydrogen profiles at this energy is due to water or hydrocarbon molecules adsorbed at the surface of the samples.)

As can be seen from figure 3, the IAD film has the highest hydrogen concentration, with an average hydrogen/titanium ratio of 0.23. The IP film shows the smallest hydrogen/titanium ratio of 0.01. The two other films have intermediate hydrogen/titanium ratios. The high hydrogen concentration found at the film/substrate interface of the SP and EV films (at 7100 keV (SP) and at 7300 keV (EV)) are caused by hydrated surface layers of the glass substrate. The IP film was deposited on a carbon substrate, therefore, only a small interface peak is visible. Also in the profile of the IAD layer (substrate BK 7) no additional increase in hydrogen concentration at the film/substrate interface can be seen because for this sample, the value of the hydrogen concentration in the film itself and in the hydrated glass surface are about the same. The comparison of the hydrogen profiles of the two DC films (figure 4) shows that the hydrogen content depends strongly on the temperature used for film formation. The rather high value for the hydrogen/titanium ratio of about 0.6 found for the 170 °C film is reduced to ≈ 0.1 when the film is annealed at 500 °C. Since the DC process uses alkoxide solution as starting material and moistened air for the hydrolysis, it is not surprising that the DC films themselves contain hydrogen.

The situation is not so clear in the case of the PVD films. The hydrogen found in these films could have been incorporated during the deposition process (from water in the residual gas) or have been taken up later from the environment. Water uptake on a time scale of a few hours has been observed for other oxidic thin film materials [12]. (All the hydrogen profiles shown have been measured several days after production.) However, for SP films the observations on a multilayer system (section 3.2.) give evidence for hydrogen incorporation during production.

A comparison of the hydrogen concentrations of the different films with their optical data is very instructive. Although all films show low absorption ($k < 10^{-3}$) and the spectral shape of the refractive index $n(\lambda)$ of all films is similar, the absolute value of $n(\lambda)$ is different, depending on the deposition technique. When $n(\lambda)$ is plotted against the hydrogen/titanium ratio (figure 5), a distinct correlation is found: Films with low hydrogen contents possess a high refractive index. IP films show the highest refractive index and are known to exhibit also high density [5, 13 and 14]. Therefore, one possible explanation for the differences in the refractive index is a variation of the densities of the films. The different hydrogen concentrations can then be interpreted by a different porosity of the film structure with different internal surface areas on which water molecules or hydrogen-bearing species are adsorbed. It should be mentioned that the analyzing technique used (NRA) does not give any information on the chemical state of binding of hydrogen because the technique is only sensitive to the absolute number of atoms. However, it can be guessed that hydrogen is bound in OH groups or water molecules, as it was found for other oxidic film materials [12].

3.2. Multilayer systems

Three multilayer systems, produced by EV, SP and DC, were analyzed for their hydrogen content. Figure 6 displays the hydrogen depth profiles of samples of a three-layer system ($TiO_2/SiO_2/TiO_2$) produced by DC. As in the case of the single DC films discussed in section 3.1., baking temperatures of 170 and 500 °C were used. For a third sample the temperature was raised to 700 °C. At the lowest temperature the hydrogen/titanium ratio is

about 0.65, very similar to that of a single film. The hydrogen content in the SiO_2 film is distinctly smaller. Heating to 500 °C reduces the hydrogen/titanium ratio strongly which is qualitatively very similar to the case of a single TiO_2 film. In contrast the hydrogen content of the SiO_2 film is almost unchanged. Only at a temperature of 700 °C the SiO_2 film shows a strong reduction of the hydrogen content.

It should be noted that several days had passed between film production and analysis. Therefore, the hydrogen content of the SiO_2 layer for the 500 °C treatment could have been lower directly after the production process, and then the measured hydrogen/silicon ratio would be due to a later hydrogen uptake. This would imply that baking at 700 °C causes modifications in film structure which changes the velocity of hydrogen uptake. For clarifying this question, in-situ analysis of samples at elevated temperatures is needed.

The hydrogen profiles of a system composed of 30 alternating TiO_2 and SiO_2 layers produced by SP and of a system consisting of 23 layers produced by EV are shown in figure 7. The two profiles have in common that the hydrogen content of the SiO_2 is higher than that of the TiO_2 layers. The general shapes of the two profiles are quite different: When averaged over TiO_2 and SiO_2 films, the hydrogen concentration is almost constant throughout the EV system, while it decreases towards the surface in the SP system. This decrease seems to be typical for the SP films because it can be seen also in the profile of the sputtered single film. It can be understood from the variation of the H_2O partial pressure in the SP coating unit which had been registered for part of the multilayer system deposition (figure 8). On the average, p_{H_2O} decreases with time, which indicates that the residual water molecules in the coating unit are consumed by gettering during film deposition. Moreover, figure 8 shows that p_{H_2O} is lower each time a SiO_2 film is deposited, indicating stronger gettering by SiO_2 than by TiO_2. This explains the observed variations in the hydrogen concentration within the SP multilayer system. It can be assumed that the different gettering behaviour of SiO_2 and TiO_2 is also the reason for the hydrogen concentration variations in the EV multilayer system.

4. Summary

A full quantitative analysis of TiO_2 films deposited by different techniques was obtained by the combination of NRA and RBS (table 2). Hydrogen depth profiles of TiO_2 coatings were determined by NRA and have been compared with the optical data of the coatings. The hydrogen content of the films varies strongly, depending on the used deposition technique. A close correlation between the hydrogen content and the refractive index is found, i.e., films with a high refractive index have a low hydrogen/titanium ratio. The hydrogen concentration of films produced by dip coating was found to be very sensitive to formation and densification temperature. Also the hydrogen content of dip-coated multilayer systems shows a strong dependence on the temperature.

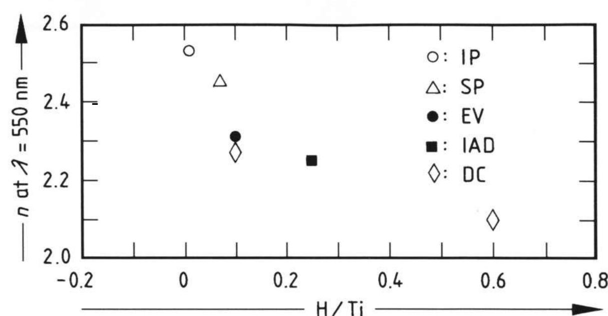


Figure 5. Refractive index n (at 550 nm) versus hydrogen/titanium ratio for films produced by different deposition techniques.

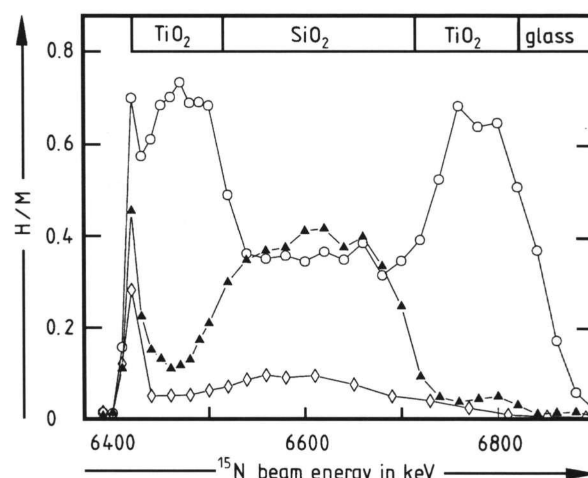


Figure 6. Hydrogen depth profiles of $TiO_2/SiO_2/TiO_2$ multilayer samples (thickness: 45/90/45 nm) produced by dip coating at temperatures of 170 °C (○), 500 °C (▲), 700 °C (◇). (M = silicon, titanium.)

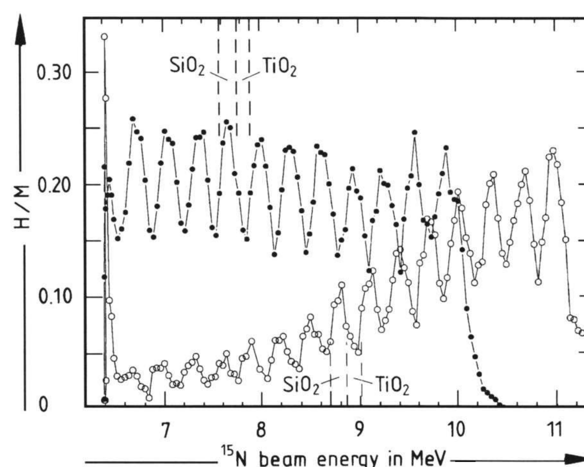


Figure 7. Hydrogen depth profiles of SiO_2/TiO_2 multilayer systems produced by PVD techniques EV (•) and SP (○).

By RBS analysis oxygen/titanium ratios and the contamination concentrations of various elements (tantalum, molybdenum, silicon, argon, carbon, sodium, depending on the deposition method) were determined.

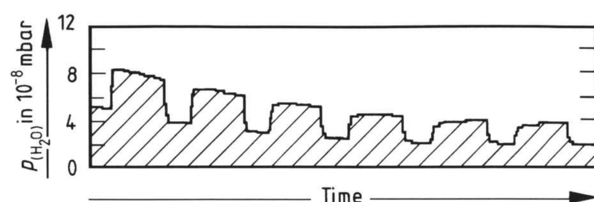


Figure 8. H_2O partial pressure during deposition of the multilayer system from figure 7 by the SP technique.

Sodium diffusion from the glass substrate into dip-coated films was observed when high substrate temperatures were used.

In sputtered and evaporated TiO_2/SiO_2 multilayer systems, the hydrogen concentration of SiO_2 layers was higher than that of titania layers. Analogously to the results for single films, the EV system contained more hydrogen than the SP system. Results for absolute amounts and for dependence on production parameters of hydrogen content obtained on titania single films describe qualitatively the behaviour of TiO_2 films as part of multilayer systems.

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