

# Ion assisted deposition of oxide-materials

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## Abstract

A gridless end-hall ion source is used for the ion assisted deposition of titanium dioxide and zirconium dioxide on unheated glass substrates. The deposited thin films have near bulk properties. The optical properties are compared with those of corresponding thin films deposited with conventional electron gun deposition on substrates preheated to about 300°C.

## Introduction

Optical coatings are produced by deposition of highly pure starting materials in vacuum systems that reach base pressures of less than  $5 \times 10^{-6}$  mbar. It is possible to use different starting materials and different types of deposition systems depending on the application. The development of new ion assisted deposition techniques has made it possible to stabilize properties like the packing density, extinction ratio, thermal sensitivity and resistance against moisture penetration, which in turn reduces the number of thin film materials necessary to apply in the production. Furthermore, theoretical considerations have revealed that using thin-film materials having the highest possible refractive index contrast and only two materials are preferential in most cases<sup>1</sup>. It appears that this understanding was not apparent to most experts in the field prior to the last decade or two<sup>2</sup>. Today the choice of materials and type of deposition technique mainly is a question of a weighing out costs against the needed quality<sup>2,3</sup>.

In the visible spectral range the highest possible refractive index is around 2.5 whereas the lowest is about 1.3. The easiest way to obtain a large refractive index contrast is to soft-coat filters from the high index material Zinc Sulphide, ZnS ( $n_H \approx 2.35$ ), and a low indexed Fluoride-material like Chiolite ( $n_L \approx 1.30$ )<sup>4,5,6</sup>. These materials are easily evaporated from aluminium-oxide crucibles applying heat from tungsten filaments. Furthermore the packing density in the layers is quite high even when the substrates are unheated. This enables the deposition of complex multi-layers affording precise refractive indices<sup>5</sup>. The coatings typically shift 1 - 2 nm when the temperature is changed 100°C, which means that the spectral characteristics are relatively insensitive to temperature shifts. Further densification of the films by application of ion assisted deposition is not realistic because of the preferential depletion of fluorine by the ion beam<sup>6</sup>. The disadvantages of this industrially successful type of coatings are mainly that they are relatively soft and sensitive to moisture penetration, which means that they must be protected by a cover glass, and that the ZnS starts absorbing in the spectral range below 400nm.

Hard durable surface coatings can be obtained by deposition of hard oxide materials like titanium dioxide, TiO<sub>2</sub>, zirconium dioxide, ZrO<sub>2</sub>, hafnium dioxide, HfO<sub>2</sub>, and quartz, SiO<sub>2</sub>. The

refractive index of the high indexed materials ranges from 1.95 to 2.5 depending on the type of material. The highest index is obtained with TiO<sub>2</sub> that starts absorbing below 400nm whereas the lowest index is obtained with the HfO<sub>2</sub> that extends to below 240nm. The refractive index of the low indexed quartz is around 1.5, which is not nearly as low as the refractive index of the fluoride materials. This means that the refractive index contrast is less than that of the soft coatings.

The starting materials are hard to evaporate, and use of an electron gun for this purpose is necessary. Furthermore it is necessary to deposit the thin films in a reactive oxygen atmosphere to compensate for tendency of the oxides to dissociate as they go from the solid to the gas phase<sup>7</sup>. Unfortunately the presence of a gas during the deposition is detrimental to a dense microstructure<sup>2,6</sup>, and although the coatings are hard, the layers tend to be relatively porous. The substrates are normally preheated to a temperature of about 300°C to obtain an acceptable packing density in the high indexed layers. However, the temperatures to which optical components can be heated prior to the deposition are limited, and it is not possible to obtain as stable conditions during the deposition as in the case of soft-coatings. Furthermore moisture penetration makes the coatings shift towards longer wavelengths when the vacuum chamber is vented. A shift of 15nm is common and makes the production of precision coatings difficult. Although we manage to produce relatively advanced hard coatings today (1996) we intend to move forward towards more complex coatings. The ultimate goal is the production of hard coated gradient index coatings that can be cut into pieces, shaped and applied on different surfaces. This is only obtainable if the thin films are densified.

Ion assisted deposition (AID) has become established for making optical coatings denser to stabilize their optical parameters<sup>2,6,8,9,10,11,12,13,14</sup>. In the autumn of 1995 the thin film department installed a gridless Mark II ion gun and a hollow cathode electron source HCES5000 (from Common Wealth Scientific, CSC) to be used with two electron guns in a Balzers BAK640 box-coater. In the following we will present some of the results obtained with the system within the first year.

## What is a gridless ion source and what is it used for?

A ion gun is a device which bombards the growing thin film with energetic ions during the deposition<sup>2,6,14,15</sup>. The impinging ions that have energies of tens or hundreds of electron volts are much more energetic than the deposited atoms that have energies which lie in the meV range. The energy of the deposited atoms and the temperature of the substrates determine the time the atoms have to find an optimal position in the atomic structure<sup>6</sup>. Without the application of an ion-gun it is necessary to preheat the substrates to a temperature of around 300°C to obtain reasonable packing densities in the high-indexed metal-oxide-

layers<sup>6</sup>. When the ion-gun is used, the deposition of thin films with higher packing densities on non-preheated substrates is possible. In case of no IAD the strong dependence of micro-structure on substrate temperature has been illustrated by an important three zone model which was first introduced by Movchan and Demchishin<sup>16</sup>. At temperatures that are low compared with the melting temperature of the thin film material, mobility is low, and growth is therefore controlled by the shadowing of vacancies from incoming vapour by already deposited material. As a result the film consists of tapered crystallites with a domed structure (zone 1). At intermediate temperatures, adatom surface diffusion overcomes the shadowing and dominates the growth process. As a result the surface gets smooth and the film has well defined grain boundary zones, and columnar grains (zone 2). At higher temperatures, bulk diffusion is high, and larger crystallites are formed with rearrangement. The surface gets bright and the grains equiaxed (zone 3). Oxides are zone 1 materials, and the surface mobility required to produce a dense structure is higher than what can be achieved by substrate temperatures compatible with optical requirements<sup>6</sup>. The major effect of IAD is to increase the packing density by forward recoil of adsorbed species into open pores and by incorporation of ions in the film<sup>17</sup>.

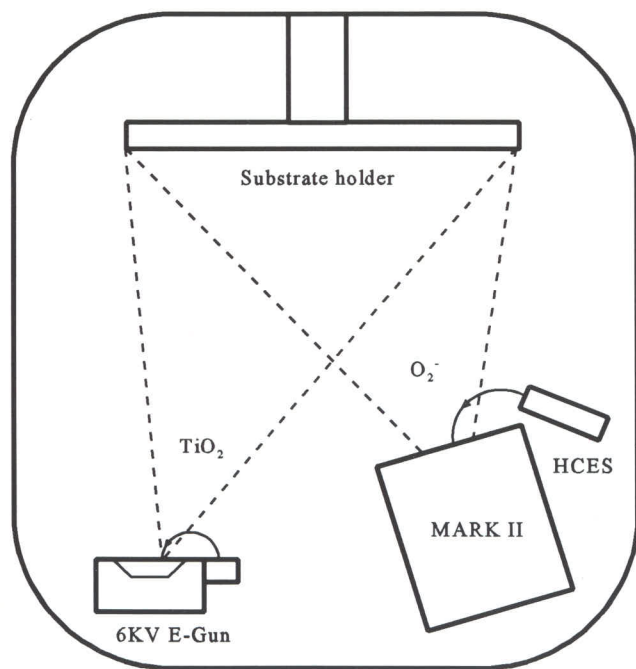


Figure 1. Illustration of the vacuum chamber with the Mark II gun, the hollow cathode electron source and the electron gun. The substances are placed in a rotating plane holder.

Figure 1 shows a schematic illustration of the system we use. The substrates are placed in a rotating plane substrate-holder. The starting materials are evaporated from two electron guns placed in the bottom end of the vacuum-chamber baseplate. The vertical distance between the electron guns and the substrate holder that is around 44cm was optimized to obtain a good thickness distribution. The ion gun is placed in the front end of the baseplate and directed towards the centre of the substrate

holder. Until recently, most research with ion guns was done with gridded Kaufmann-type sources<sup>6,8,9,10</sup>. This type of ion source is characterized by a relatively collimated beam and a high particle energy<sup>18</sup>. However, lately better results were obtained with gridless end-Hall ion sources<sup>10,11,12,13,14,15</sup>. The end-Hall ion source was described by Kaufmann et al.<sup>18</sup> It produces a broad beam with a 30 degrees half angle that is well suited to cover large substrate holders as used in a production environment. Figure 2 shows a picture of the Mark II ion gun we installed. The gas to be ionized is admitted through the anode at a controlled flow rate. When depositing oxides the gas is pure oxygen. Electrons from an electron source bombard the gas as a high voltage is applied to the anode and an ionization of the gas occurs. A primarily axial magnetic field in the anode region enhances the affectivity of the electrons. The ion gun produces a low-energy (40 - 120eV) ion beam with a high current density. The electrons from the cathode also serve as the neutralization for the ion beam. The neutralization is needed to avoid arcing in the vacuum chamber. Arcing between substrates and holder may damage the coatings. Too many electrons are not experienced to be any problem<sup>14</sup>.

### Choice of cathode system

An important feature of the IAD process is the possibility to deposit hard metal-oxide coatings on objects that do not stand to be preheated to several hundred degrees. Typical objects could be fibre optics, plastics and special types of coloured glass. When the coating is deposited on a non-preheated substrate, the temperature raises during the coating process due to the emission of heat from the electron guns, the ion gun and the cathode system. Keeping the maximum substrate temperature below 100°C is possible, if the conventional hot cathode filament is replaced by a hollow cathode electron source and if the conventional anode is replaced by a water cooled type developed by Commonwealth Scientific Corporation in 1995<sup>13</sup>. The system we use is equipped with these parts. However, the water cooled anode was not installed until the experiments described in this paper were made.

The unit at the top of the ion gun in Figure 2 is the hollow cathode electron source, HCES5000, from CSC that is able to deliver a neutralization current of 5000mA. It functions like a small sputtering chamber where the electron beam is drawn from a hole in the keeper. The process gas is pure argon. The lifetime of the cathode tip is several hundred hours which should be compared with a lifetime of about five hours in case of the conventional hot filament. This means that the HCES is much better suited for the deposition of complex coatings like the gradient index coatings than the hot filament. Furthermore the contamination from the hot tungsten filament is avoided.

### Experience with the installation and the use of the ion-gun system

The Mark II ion gun and the HCES5000 cathode are rigid components suited for a production environment. The sensible parts seem to be the magnet in the ion-gun that could be depolarized by too high temperatures (another reason for the water cooling of the anode) and the inside of the HCES5000 that should be flossed by argon when hot to prevent an oxidation of the DC-driven system. The source has limits of: 5000mA of

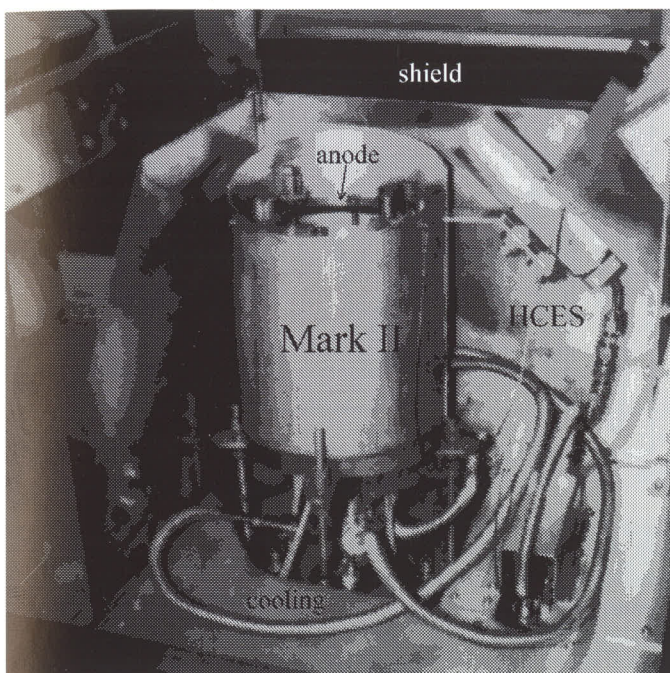


Figure 2. The ion-gun system installed in a Balzers BAK640 box-coater. The Mark II ion-gun is connected to an oxygen gasline whereas the hollow cathode electron source is supplied with argon. The anode is water-cooled and the ion-gun is shielded from the electron-guns by mu-metal shields.

drive current, 175 anode or drive volts and 50sccm gas flow. We did obtain the best results with: 4000mA drive current, 120 anode volts, 20sccm oxygen gas for the ion gun and -4600mA neutralization current and 15sccm argon flow for the hollow cathode electron source. It is not advisable to use higher currents because of the power supplies for the units.

The power units are problematic parts that are easily damaged. Both were burned within the first year and this is no outstanding story. Other groups of researchers did experience the same thing<sup>14,15</sup>. The Power supply for the ion gun is triac based, and it is easily disturbed by EMC<sup>14</sup>. The system did not function when the power unit was placed next to the power supply for the electron guns, and we had to make careful shields of mu-metal in the vacuum chamber. The power unit contains several servo loops that try to keep the voltage and the current stable. However, this may be at the cost of a stable gas flow through the ion gun, which is found to be a very important parameter. It seems as if the power supply tries to protect itself because it is inadequately proportioned<sup>15</sup>. We had to replace the triac board during the first year.

The power supply for the HCES5000 is transistor based and mostly it functions very well. However, it is a good idea to turn the supply on before everything else because transistors are easily damaged by high voltages. Several power transistors and a driver transistor were burned during the first year. However, the circuit is relatively easily repaired.

The gas-supply for the flow controller that comes with the ion gun must be very stable. It is easily disturbed by other equipment that consumes oxygen from the line.

## Determination of the refractive index, dispersion and packing density of a thin film

Characterising the deposited thin films in different manners is possible. The refractive index, packing density and dispersion of the thin film can be revealed from transmission measurements. The microstructure can be investigated with X-ray diffraction and Scanning electron microscopy (SEM) and the stress level can be determined by measuring the bending of the carrying substrate in an interferometer. In this paper we will deal with the information that can be obtained from SEM pictures and measurements with the most common instrument in a thin film coating laboratory - the spectrometer.

### Preparing the coatings for SEM

The SEM pictures presented in this paper were obtained using the method of microfractography<sup>19</sup>. The rear of the glass substrate was scratched with a diamond glass cutter. Breaking the glass, the coated layer on top of the substrate preferentially cleaves at places of little strength like grain boundaries and interfaces that then can be observed in a scanning electron microscope. Considering the insulating properties of the dielectric thin-film, coating the sample with a thin conductive over layer of gold to prevent electrically charging by the electron beam is necessary. The thin gold layer is sputtered on the sample. The SEM pictures were prepared by DELTA's test division - DELTA Materials and Components Technology.

### Measurements with the spectrometer

The optical performance of a homogeneous layer can be described by the refractive index,  $n$ , and the coefficient of extinction,  $k$ , related to the dielectric constant by  $\sqrt{\epsilon} = n + ik$ . In case of weakly absorbing and dispersive thin films  $n$  and  $k$  can be determined from a single transmission curve measured with a spectrometer at normal incidence. The amplitude modulation renders the refractive index  $n(\lambda)$ . The spacing of the fringes, the dispersion and the amplitude decay at short wavelengths provide a good value for the extinction coefficient  $k^{2,11}$ . There has been a myriad of papers in Applied Optics and other journals on the determination of the index of refraction<sup>2,20</sup>. However, from a practical point of view, we find that it is sufficient to apply the following procedure which is simple compared with the more refined and sophisticated ones published, but adequate for our practical applications.

The experiment is performed as follows: The vacuum system is prepared for the experiment and a single layer of the selected thin film material is deposited on top of a glass substrate. In our case the optical thickness of the layer was 2.5 wavelengths at 706nm. After the deposition the films were left for settling in ambient atmosphere for at least 15 hours. This allowed water vapour to diffuse into the lattice. The transmission through the coated substrate was measured from 250 nm to 1200 nm with a Perkin Elmer Lambda 900 spectrophotometer. At the long wavelength, where the dispersion and the extinction are low, it is possible to calculate the refractive index by

$$n = \frac{1}{2} \left( A + \sqrt{A^2 - 4n_s} \right) \quad (1)$$

where  $n_s$  is the refractive index of the substrate and where

$$\left. \begin{aligned} A &= (1+n_s) \frac{B+1}{B-1} & \text{for } n > n_s \\ A &= (1+n_s) \frac{B-1}{B+1} & \text{for } n < n_s \end{aligned} \right\} \quad (2)$$

$B$  is connected to the measured transmission values as expressed by

$$B = 1 + \frac{2}{\sqrt{\left(\frac{1}{T_{\min}} - \frac{1+n_s}{4n_s} + 1\right) / \left(\frac{1}{T_{\max}} - \frac{1+n_s}{4n_s} + 1\right)} - 1} \quad (3)$$

Eqs. (3) takes into account the multiple inter reflections between the backside of the substrate and the thin-film.

When the refractive index is calculated, calculating the physical thickness of the single layer is possible, as the optical thickness is precisely known at the turning points at the transmission curve. The optical thickness increases by one quarter of a wavelength each time we move to the next turning point placed at a lower wavelength (not totally correct in the presence of some absorption). This means that calculating the refractive index at all turning points, when the physical thickness of the thin film is known, is easy. The dispersion relation is extracted from a mathematical fit on the data derived in this manner.

Given the bulk index  $n_B$  of the starting material, calculating the packing density of the thin film by the following equation<sup>5</sup> is possible

$$P = \frac{n_B^2 + 2}{n_B^2 - 1} \frac{n^2 - 1}{n^2 + 2} \quad (4)$$

### Experiments with TiO<sub>2</sub> films

Our first experiments were carried out with titanium dioxide which is characterized by an attractive high refractive index in the visible and the near infrared. It is not one of the materials we prefer to use. It starts absorbing at too long wavelengths for most of our applications (below 400nm). However, titania was one of the first materials studied using various ion beam processes offering some good possibilities to compare the obtained results with the literature<sup>2,6,8,10,11,12,13</sup>.

The problem with titania is that a large number of suboxides exists, and that TiO<sub>2</sub> is known to exist in several crystalline structures: Anatase, brookite (very rare), rutile (highest index) and amorphous. The starting material we used was the new Titanium oxide S granules Patinal from Merck that has the composition TiO<sub>x</sub> with  $x=1.7$ . According to Pulker et al. this composition is stable and suited for the deposition of homogeneous thin films with a reproducible index<sup>7</sup>. Furthermore, the Titanium oxide S starting material is prefused to minimize spitting and to enhance reproducibility. The oxide was evaporated using an electron beam evaporator and the substrates were made of amorphous glass.

The thin solid curve in Figure 3 shows the transmission through an 802 nm thick titania film deposited on a glass substrate preheated to a temperature of 300 °C. The oxygen partial pressure was  $2 \times 10^{-4}$  mbar and the rate was 0.6 nm sec<sup>-1</sup>.

T in % Titanium-dioxide (IAD: thick curve)

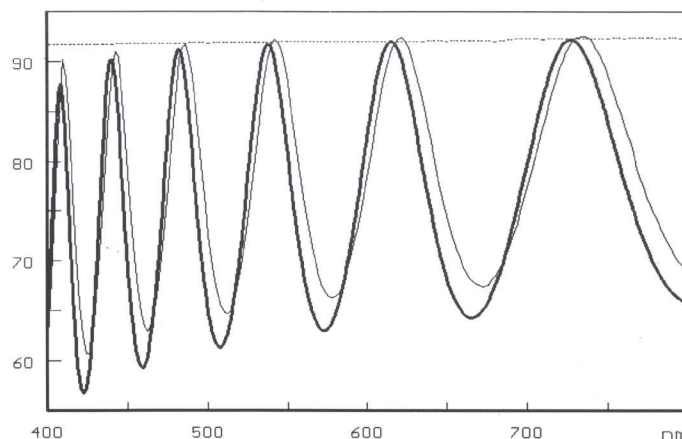


Figure 3. Thin solid curve shows the transmission through a TiO<sub>2</sub> film deposited by normal electron gun deposition on glass-substrates preheated to 300°C. The thick solid curve shows the corresponding transmission of a titania film that was ion assist deposited on an unheated glass-substrate. The refractive index in this case increased to 2.45 at 550nm.

According to the dispersion curve the refractive index was 2.36 at a wavelength of 550 nm. This value is remarkably higher than the 2.2 which is usually reported<sup>2,7,11</sup>, but consistent with the value mentioned in the sales data for Titanium oxide S. The thick solid curve in Figure 5 shows the corresponding transmission through a 762 nm thick titania film deposited by IAD on a non-preheated glass substrate bombarded by energetic oxygen ions from the Mark II ion gun. In this case the refractive index increases further to a value of 2.45 at 550 nm. This value is comparable to what was reported by other groups<sup>8,11,12</sup>. The rate was 0.35 nm sec<sup>-1</sup> and the settings for the ion gun and the electron source were: 4000 mA drive current, 120 anode volts, 20 sccm oxygen gas for the ion gun and -4600 mA neutralization current and 15 sccm argon flow for the hollow cathode electron source. The argon contribution to the pressure reading was  $1.6 \times 10^{-4}$  mbar of a total of  $2.8 \times 10^{-4}$  mbar.

The transmission of the first sample is slightly higher than the transmission of the uncoated substrate (dotted curve) at the highest wavelength, indicating that the thin film deposited without any ion assist is slightly inhomogeneous. On the other hand sample 2 is slightly more absorbing at the low wavelength. According to Martin et al.<sup>8</sup> the absorption in the ion assisted TiO<sub>2</sub> films can be higher or lower than in the non-ion assisted films depending on the strength of the ion bombardment leaving room for further improvements of our processing of this material.

### ZrO<sub>2</sub> films

Zirconium dioxide is another important high indexed optical thin film material with good mechanical properties. The spectral range for the thin films covers at least 340 nm to 7000 nm<sup>2,4,6</sup>, but the ZrO<sub>2</sub> films are transparent enough to be used in multi layered mirror coatings for excimer lasers at 230 nm<sup>21,22</sup>. The transmission in the ultraviolet makes it a good candidate for our applications. One disadvantage is that the bulk refractive index of cubic ZrO<sub>2</sub> is only 2.17<sup>23,24</sup> and 2.1 in case of the monoclinic state. Furthermore the thin films exhibit a columnar structure and can

T in % Zirconium-dioxide (IAD: thick curve)

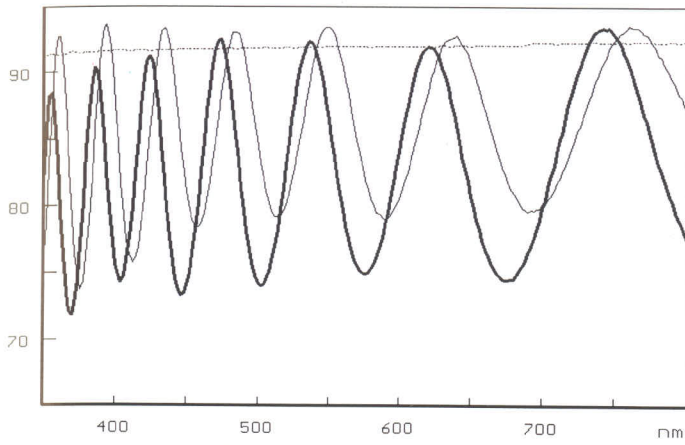


Figure 4. Thin solid curve shows the transmission of a  $ZrO_2$  thin film deposited by conventional electron gun deposition on glass-substrates preheated to  $275^\circ C$ . The thick solid curve shows the corresponding transmission of a  $ZrO_2$  film that was ion assist deposited on an unheated substrate. The refractive index in this case increased from 1.99 to 2.14. The transmission through the coated substrates sometimes exceeds the transmission of the glass substrate implying inhomogeneity. Furthermore, some absorption might be present.

be quite porous when deposited by normal electron gun evaporation. The packing density is known to depend critically on the oxygen pressure, substrate temperature, and rate of deposition<sup>21</sup>.  $ZrO_2$  films were very difficult to deposit until the electron gun was developed, but inhomogeneity is still the classic problem with this material.

The thin solid curve in Figure 4 shows the transmission through a 971 nm thick  $ZrO_2$  film that was electron beam deposited on a glass substrate preheated to  $275^\circ C$ . The starting material was  $ZrO_2$ , the rate of deposition was  $2 \text{ nm sec}^{-1}$  as proposed by Dobrowolski et al.<sup>21</sup>, and the partial oxygen pressure was  $2 \times 10^{-4}$

T in % Zirconium-dioxide (IAD-Zr: thick curve)

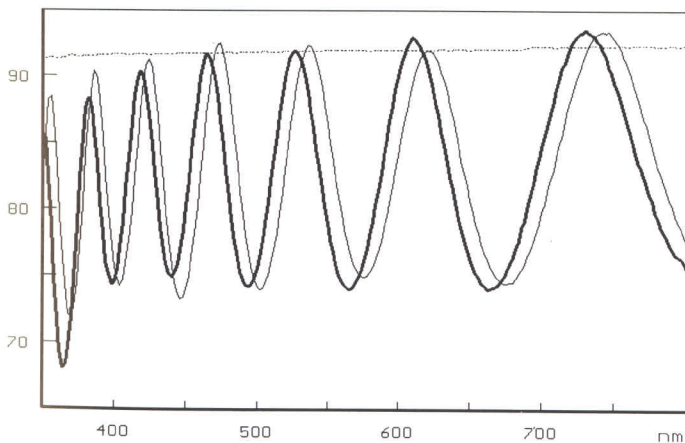


Figure 5. Thick solid curve shows the transmission of a  $ZrO_2$  film IAD-deposited from the starting material zirconium. The thin solid shows the corresponding transmission curve of a film that was IAD-deposited from the starting material  $ZrO_2$ . A slightly higher loss of transmission at low wavelengths is observed in the first case.

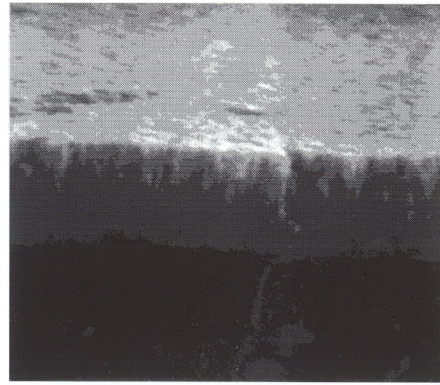


Figure 6a. SEM of a  $ZrO_2$  thin-film deposited by electron gun deposition on a glass substrate preheated to  $275^\circ C$  (starting material was  $ZrO_2$ ). The physical thickness of the thin-film is 971nm. The thin-film consist of tapered crystallites with a domed structure (typical zone 1 structure). The diametre of the grains is approximately 50nm.

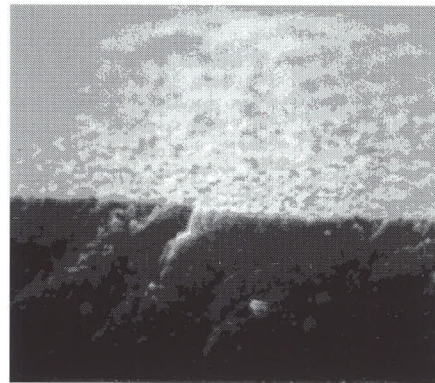


Figure 6b. SEM of  $ZrO_2$  thin-film of the type shown in figure 6a. In this case the thin film was cleaved imperfectly and the interface is charcterized by broken crystallites with diametres of 50 - 60nm.

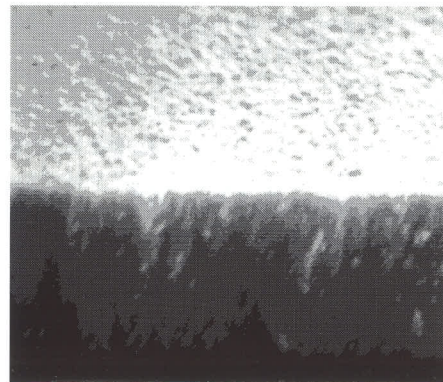


Figure 6c. SEM of  $ZrO_2$  film prepared by IAD on unheated glass substrates (Starting material was Zirconium). The physical thickness of the thin-film is 888nm. The thin-film is composed of closely packed columnar grains with diametres of 100 to 150nm. The major effect of IAD is to increase the packing density by forward recoil of adsorped species into open pores and by incorporation of ions in the film.

mbar. The refractive index is 1.99 at a wavelength of 550 nm indicating a relatively low packing density. The transmission maxima exceeds the transmission of the glass substrate itself indicated by the dotted curve. This reveals that the thin film is inhomogeneous. Klinger et al. did show that this is partly due to a crystallographic shift from cubic to monoclinic orientation within the first part of the thin film<sup>23</sup>. Furthermore, Dobrowolski et al. showed that the porosity depends strongly on the oxygen partial pressure during the deposition and they obtained the best results with an oxygen partial pressure of only  $2 \times 10^{-5}$  mbar<sup>21</sup>. A stable partial pressure that low is not realistic in our system.

The thick solid curve in Figure 4 shows the transmission of an 888 nm thick zirconium dioxide film that was electron beam and ion assist deposited from the starting material  $ZrO_2$ . In this case the rate was 0.25 nm/s corresponding to the rates applied by other groups for IAD of  $ZrO_2$ . The settings for the ion gun and the electron source were as listed for the titania. It is clearly seen that the refractive index has increased as a result of a densification of the thin film. The refractive index is 2.14, which is close to the bulk index of the cubic high temperature version of  $ZrO_2$ . However, we note that some inhomogeneity remains and that we may have a problem with a loss of transmission at the low wavelength. Similar results were obtained when applying zirconium as the starting material (see the thick solid curve in Figure 5). But in this case the loss of transmission at the low wavelength was more pronounced. According to the literature depositing thin films with absorption properties similar to those obtained by evaporation on heated substrates should be possible<sup>11</sup>. However, lately Uhlig et al.<sup>25</sup> presented test results on coatings for the UV-B region implying that losses in non ion assisted coatings may be less at low wavelengths<sup>3</sup>. We would not ourselves describe our AID of  $ZrO_2$  as optimized at the moment of writing (September 96). We expect to improve the quality of the coatings further within the next month. Nevertheless the results presented give a good impression of the near bulk properties that can be obtained in the thin films deposited on unheated substrates by IAD with a gridless end-Hall source.

Figure 6 shows SEM pictures of the deposited  $ZrO_2$  thin films. Figures 6a and 6b show SEM-pictures of the thin film deposited with conventional electron gun deposition on the preheated substrate (275 °C). The thin films have a typical zone 1 structure with grain diameters of 50-60 nm. Figure 6c shows the corresponding SEM picture of the ion assisted thin film that consist of larger grains with a less domed structure (typical diameters of 100-150 nm). This thin film was deposited on a non-preheated substrate.

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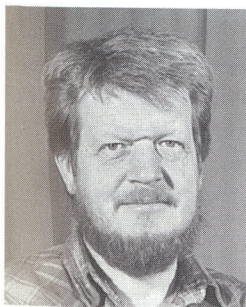
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