Influences of Pulse Parameters on Properties of Optical Coatings Deposited by Reactive Pulsed Magnetron Sputtering

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ABSTRACT

Reactive pulsed magnetron sputtering incorporates a high potential for manufacturing optical multilayer systems (e.g., precision filter components). Only some investigations have been performed to describe the most important properties of such prepared films. A flexible magnetron sputter system using two planar metallic targets supplied with pulsed power equipment was used for reactive deposition of optical coatings. Single layers were investigated as an elementary stage for preparation of multilayer stacks. The pure metallic targets were sputtered in a strictly controlled reactive gas atmosphere. Layers with an optical thickness of $\lambda/4$ (for $\lambda = 1550$ nm) were deposited on Si wafers and glass substrates. The influence of total sputtering pressure and process temperature on optical and mechanical properties, surface topography and film structure were investigated. Special emphasis was put on detection of the influence of pulse mode and pulse parameters on layer properties. The samples were characterized by spectroscopic ellipsometry (SE), atomic force microscopy (AFM), X-ray diffraction (XRD) and nanoindentation techniques. It was possible to adjust the film properties by fine tuning of the process parameters.

INTRODUCTION

The industrial market forces the manufacturer of optical coatings to produce optical systems with steadily increasing quality. The high-quality optical components must be developed to provide the best combination of manufacturability, performance and price. Nowadays, there are telecommunication optical filters, such as narrow bandpass filters or gain flattening filters, on the imaginary top of technology investigation. Because of strict demands on accuracy and reliability it is necessary to control and more accurately investigate properties of basic single layers. The main properties that describe high-quality films are: very low absorption in the wavelength region of interest, smooth interface with low level of defects (e.g., low level of light scattering), no structural gradients in single layer and film densities approaching that of the bulk material. The deposition process itself should be reproducible because of manufacturing of components with exactly defined optical properties [1]. A standard deposition technique for preparation of precise optical systems used is ion beam sputtering. Many investigations were made to reduce the typically low deposition rate (deposition time of more than 30 hours) and low profit of this technology [2, 3]. Reactive magnetron sputtering in combination with appropriate design of an in-line coater can lead to reduced deposition time and, due to higher homogeneity, to improvement of the output profit.

The typical narrow bandpass filters are composed of $\lambda/4$ layers of high and low refractive index. In such a system a specific number of cavity layers is incorporated, which determines the characteristics of the filter. Tantalum oxide (Ta_2O_5) and silicon oxide (SiO_2) are frequently used for the high index and low index materials, respectively.

Tantalum oxide is a physically and chemically very stable material with relatively high crystallization temperature and a smooth interface. A significant disadvantage of this material is its enormous price. Another material, used in multilayer systems but not in such sensitive components, is TiO_2. The price for a Ti target is approximately 20 times lower than that of Ta one, today. The other advantage of TiO_2 is its higher refractive index, which allows one to deposit layers with lower physical thickness and so saves the deposition time of the whole system.

Titanium dioxide is one of the most important materials for optical and protective coatings and microelectronic devices [4, 5]. Besides the amorphous state three crystalline phases are known for TiO_2: tetragonal anatase, tetragonal rutile and orthorhombic brookite. All these phases have been detected in as deposited and annealed TiO_2 films, already. The occurrence of these phases in thin films strongly depends on substrate temperature [6]. Resulting crystalline structure and stoichiometry and optical properties, such as refractive index, extinction coefficient and scattering losses of TiO_2 films, are influenced by other deposition conditions, too. An appropriate choice of deposition parameters, such as partial pressure of oxygen, pulse mode and deposition rate, allows one to influence the resulting structure of growing TiO_2 layer [7, 8].

The present work focused our attention on the reactive magnetron sputtering of TiO_2 layers with new pulse generator UBS-C2 (FEP). The influence of the pulse mode, pulse frequency and duty cycle on the optical properties, surface roughness and phase formation in quarter-wave-thick (λ/4) TiO_2 layers were studied. To get a reliable point for comparison, some samples were prepared by a sine wave generator. From these experiments low total pressure, higher deposition power and reactive operating point near the transparency limit were evaluated as optimum parameters for deposition of TiO_2 layers with low surface roughness and high refractive index. These parameters were set constant for all runs made in the bipolar mode with UBS-C2. The main task was to reduce the surface roughness and to investigate the influence of pulse parameters (pulse form and pulse frequency) on structural gradients and optical properties.

EXPERIMENT

Titanium dioxide transparent films were deposited by reactive pulsed magnetron sputtering (PMS) in a vertical in-line sputter coater ILA S 750. This equipment consists of two separate chambers: load lock chamber and process chamber. For the powering the sine wave, a DC or pulse generator can be used. Accurate and reliable use of this equipment is ensured by the gas control loop and the full computer automation. The dual magnetron system (DMS), consisting of two metallic targets with a dimension of 750 mm x 120 mm arranged side by side, was used for deposition of TiO_2 in the reactive sputtering mode (Figure 1).

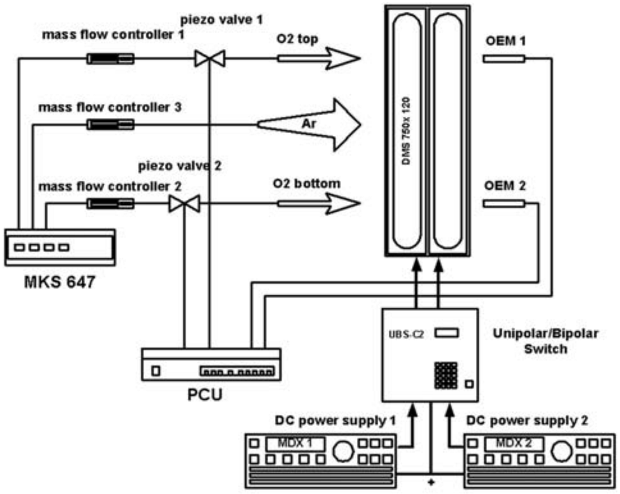

Figure 1: Schematic description of DMS system powered by two DC generators connected with UBS-C2 and controlled by PCU feed back loop

The system was powered with a sine wave generator, operating with a frequency of 28 kHz, and the deposition was carried out using a two channel pulse generator UBS-C2 in bipolar mode at different frequencies. In the bipolar pulse mode each of the targets of the DMS acts alternately as cathode and anode of the discharge. Beside the pulse mode, the duty cycle (DuCy) (i.e., the ratio of the power-on-time to the total cycle time of both of the targets) was modified. For all experiments with UBS-C2 powering in bipolar mode the discharge power was adjusted to 7.5 kW per target (i.e., 8.3 W/cm^2 target power density) taking the losses of the switching unit UBS-C2 of about ± 5 % into account [8].

A PID control loop stabilizes and controls the reactive sputtering process. The optical emission detector (OED) couples out a signal of characteristic wavelength of the plasma and transforms it into an electrical signal. The value of this signal is compared with the set value of plasma emission in the plasma control unit (PCU). The PCU is connected to a piezoelectric valve, which controls the flow of reactive gas [9].

The TiO_2 films were deposited on float glass (t = 3 mm), Si wafers (t = 0.375 mm) and on special glass slides (t = 0.15 mm) used for stress measurements. The process pressure of p = 0.16 Pa was kept constant for all deposition runs. The substrate-to-target distance TSD was 124 mm. All constant deposition parameters are listed in Table 1.

Table 1: Process parameters for deposition of TiO_2 films by reactive pulsed magnetron sputtering

Target material	Ti
Target size	2 x 750 mm x 120 mm
Substrates	float glass, Si wafers
Substrate temperature	20 … 250°C
Pulsed power	2 x 7.5 kW
Process pressure	0.16 Pa
TSD	124 mm
Layer thickness	172 nm (λ/4 for 1550 nm)
Substrate thickness	3 mm – float glass 0.15 mm – glass stripes 0.375 mm – Si wafers

The specific wavelength range used for data transmission in the telecommunication has a center at λ = 1550 nm. In this IR spectrum the typical refractive index of TiO_2 is n = 2.25, corresponding to a mechanical thickness of t = 172 nm.

CHARACTERIZATION

The layer thickness and the dispersion of optical parameters were calculated from ellipsometric measurements. A spectroscopic ellipsometer was used in the wavelength range of 250-1700 nm. For TiO_2 the Tauc-Lorenz-Oszillator model was applied [10]. In addition to the extinction coefficient k, refractive index n and optical thickness the modeling of ellipsometric results allows one to estimate the thickness of surface roughness layer by effective medium approximation (EMA). Atomic force microscopy (AFM) was applied to characterize the surface topography and the roughness of TiO_2 layers. Residual stress of the coatings was determined by measurement of the deflection of the thin glass stripes before and after the deposition. Hardness and Young's modulus were measured by nanoindentation technique. The crystalline structure of TiO_2 layers was investigated by grazing angle X - Ray diffraction using CuK_a radiation and an incidence angle of 1°.

RESULTS

Deposition rate

The curves obtained for the dynamic deposition rate of TiO_2 films calculated from the layer thickness are shown in Figure 2.

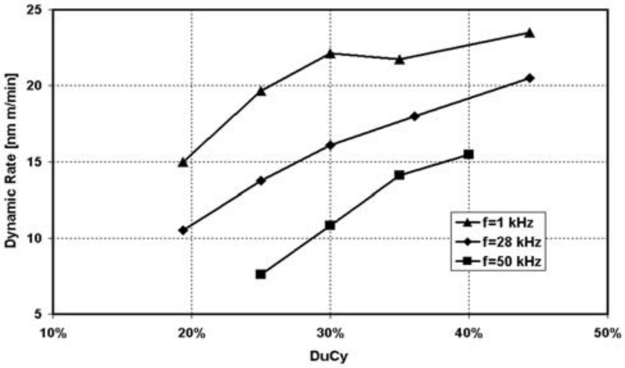

Figure 2: Dynamic deposition rate of the TiO_2 films as a function of DuCy at different frequencies prepared by reactive PMS (P = 2x7.5 kW)

A continuous decrease in deposition rate with decreasing DuCy was observed for all deposition frequencies. For frequencies f = 1 kHz and f = 28 kHz a difference between the highest and lowest value of deposition rate of approximately 10 nm m/min was recorded. This typical decrease of the deposition rate with the decreasing value of DuCy is connected with the energy distribution in pulsed plasma. More energy for plasma ignition is necessary and therefore there is less energy for the sputtering process for the lower values of DuCy at a constant middle energy input.

The higher value of dynamic deposition rate was achieved at the lowest frequency. The deposition process at low frequency needs fewer plasma ignitions, which means less energy losses, low substrate heat and therefore high deposition rates.

MECHANICAL PROPERTIES

Surface topography

Due to the variation of the pulse frequency and the form of pulses it was possible to influence the roughness of prepared TiO_2 films. Figure 3 shows the average roughness calculated from all different settings of DuCy for given frequency and the roughness for samples prepared at the same deposition rate.

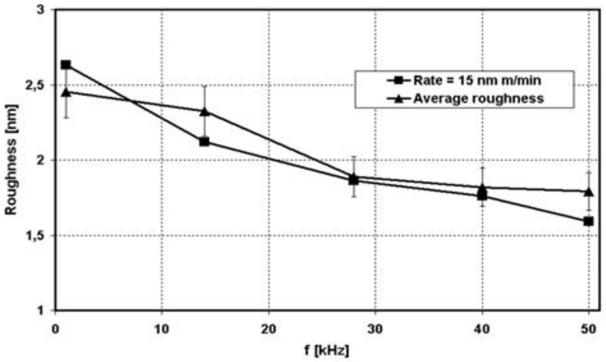

Figure 3: Surface roughness evaluated from ellipsometric measurements for TiO_2 layers deposited at different pulse frequencies (float glass)

From all measurements the average surface roughness for all different settings of DuCy and for each frequency was evaluated. The lowest investigated frequency of f =1 kHz leads to highest roughness. It can be reduced from 2.5 nm to 1.7 nm due to sputtering with higher frequencies. It is necessary to note that the deposition rate was in this case different. Therefore the samples with the same deposition rate (values of DuCy are growing from 20% at f = 1 kHz to 40% at f = 50 kHz) were chosen from all prepared films. The comparison shows the second curve (Rate = 15 nm m/min). The course of this function is very similar to the previous one. High frequencies in combination with relatively high DuCy create better conditions for particle movement onto the substrate surface. This leads to TiO_2 films with a lower value of surface roughness.

For better visualization and for comparison with ellipsometric measurements AFM investigations have been carried out. The decrease of surface roughness with increasing pulse frequency was observed. Figure 4 shows the surface topography of the layer deposited at low frequency. The relatively high value of average roughness R_a = 0.52 nm was measured. The topography looks grainy with some defects (max. height of 15 nm).

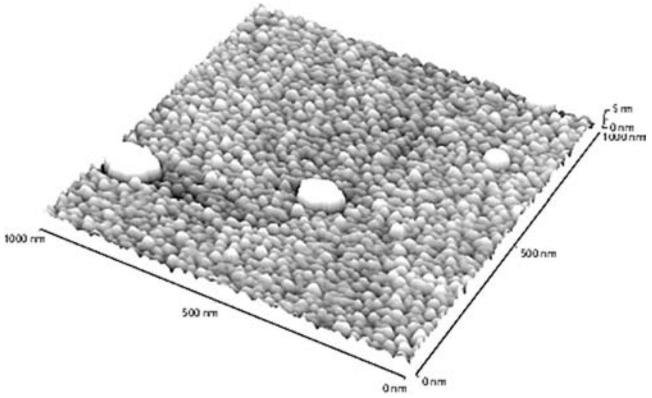

Figure 4: AFM image of TiO_2 layer deposited by reactive PMS at f = 1 kHz and DuCy = 30% (P = 2x7.5 kW, float glass)

The surface of TiO_2 layer prepared at high pulse frequency is shown in Figure 5. A smoother surface was observed. The corresponding R_a = 0.34 nm value is clearly lower than at 1 kHz. The surface looks dense and has a lower number of defects.

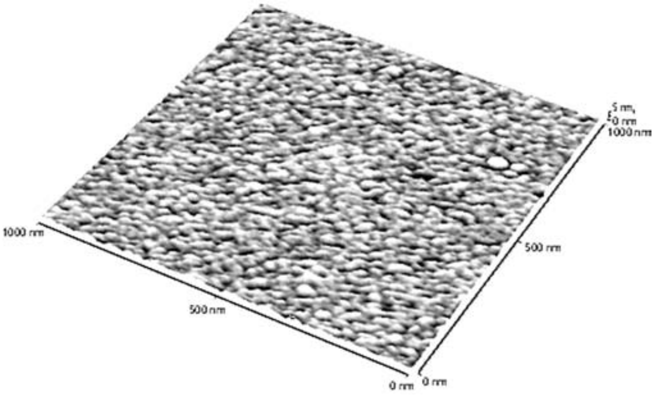

Figure 5: AFM image of TiO_2 layer deposited by reactive PMS at f = 50 kHz and DuCy = 30% (P = 2x7.5 kW, float glass)

Residual stress

Figure 6 shows the dependence of the residual stress of the TiO_2 on different values of DuCy. Compressive stress was observed for all films.

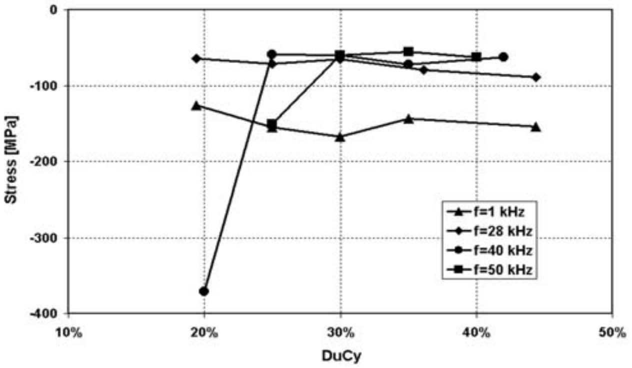

Figure 6: Residual stress of TiO_2 films deposited on glass slides as a function of DuCy at different frequencies (P = 2x7.5 kW)

Starting at higher pulse frequencies low compressive stresses of approximately 60…80 MPa are present. The stress values increase at lower frequencies. For frequencies f = 40 kHz and f = 50 kHz and for short pulse-on time two anomalous samples were registered. In these cases the thermal load of the substrate surface (due to higher ion density and higher self bias) is very high. The thin glass slides, used for stress measurement (t = 0.15 mm), have lower value of heat capacity than the float glass (t = 3 mm). This leads to higher substrate temperature and to a presumed transition from the amorphous to crystalline state. This phase transition is connected with a shift of intrinsic stress.

Starting crystallization in consecutive growing film caused an increase in the value of refractive index and incidence of structural gradients in prepared films. Corresponding dependencies in the refractive index are shown in Table 2.

Table 2: Values of n_{550nm} of TiO_2 layers prepared by reactive pulsed magnetron sputtering

f [kHz]	DuCy [%]	Float glass	Glass 0.15 mm	Si wafer 0.375 mm
1	20	2.49	2.42 – 2.51	2.52
40	20	2.45	2.42 – 2.68	2.42 – 2.69
50	25	2.45	2.42 – 2.56	2.42 – 2.51

Hardness

Changes in TiO_2 properties were detected by measurement of the layer hardness, too. The hardness of amorphous films was recorded between 6.8…7.0 GPa. Higher value of hardness (7.7 GPa), caused by starting crystallization, was observed for the high frequency (f = 40 kHz) and low DuCy (20%). This is in coincidence with the ellipsometric results and the shift in the intrinsic stress. Concerning the low thickness of the investigated coatings (~172 nm) all measured values are influenced by the substrate, and the calculation was done for indentation depths between 30…50 nm.

Structure

The XRD measurement proved that the structure of the films deposited on 3-mm thick float glass was amorphous in all cases. In the case of preheated float glass to 250°C exceptionally a very weak (110)-rutile diffraction peak was detected.

The low heat capacity of the Si wafers and the higher resulting process temperature caused other results. In the case of preheated Si-substrates to 250°C weak (110)-rutile peaks were recorded (Figure 7). The decreasing DuCy results in a significant enhancement of the (110)-peak intensity. That means that the portion of rutile related to their similar thickness of 172 nm is increased by lowering the DuCy. It is obvious that the thin glass strips for stress measurements will show the same behavior as Si wafers. Because of the low thickness of these substrates it can be expected that the crystallization starts already on unheated samples at high frequencies and low DuCy.

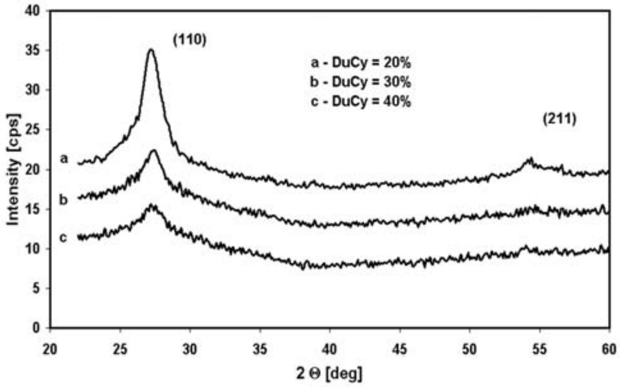

Figure 7: Increase of rutile phase of TiO_2 films prepared by reactive PMS with decreasing of the value of DuCy (P = 2x7.5 kW, T =250°C, Si wafers)

Optical properties

The results of ellipsometric measurements of TiO_2 layers prepared by reactive PMS and measured on float glass and Si wafers are shown in Figure 8. On float glass the refractive index n is not influenced by the pulse form. All values are in the typical range for amorphous titania. Refractive index n depends on the frequency and has the highest value at f = 1 kHz. It should be expected that low sputter frequency and the correlated higher deposition rate caused lower refractive index. In this case the behavior is dominated by the influence of the dynamic deposition rate and its corresponding condensation heat. On Si wafers a strong increase in values of refractive index for high frequencies combined with low DuCy was observed. This points out a rising of crystalline structure on these thin substrates, again.

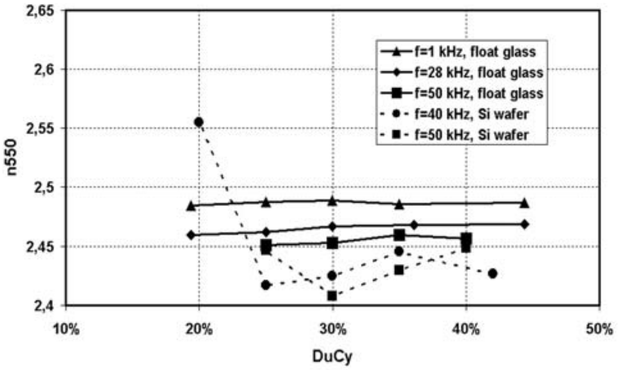

Figure 8: Refractive index n (at λ = 550 nm) of TiO_2 films prepared by reactive PMS acquired from ellipsometric measurements as a function of DuCy at different frequencies (P = 2x7.5 kW)

Because the extinction coefficient was approximately lower than 10^{-5} for all prepared samples, the layers can be regarded as absorption free.

CONCLUSION

With the new pulse generator UBS-C2 it is possible to prepare TiO_2 films with different properties. Due to various possibilities of setting of the pulse form and the sputter frequencies the plasma distribution and therefore the thermal load of substrate, the deposition rate and the structure of growing film can be controlled. It is evident that the resulting structure of TiO_2 strongly depends on the type of used substrate and on its thermal properties.

The resultant structure of TiO_2 layers prepared on float glass was amorphous. By selecting useful deposition parameters the surface roughness can be reduced to R_a = 0.3 nm. The refractive index shows only slight dependencies.

Measurements made on thin glass strips and Si wafers prepared at high frequencies and short pulse-on times show a shift to higher values of refractive index, which points to crystalline rutile structure. It is connected with an increase in residual stress and with higher layer hardness. Connected with the start of crystallization strong gradients of optical properties in these layers were observed.

Due to the appropriate choice of substrate material it was possible to influence and prevent the formation of structural gradients in TiO_2 layers.

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