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Reactive high-rate deposition of titanium oxide coatings using electron beam evaporation, spotless arc and dual crucible

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A B S T R A C T

Results of investigations on thin films of titanium oxide are presented in which the layers were deposited at a very high deposition rate of approximately 50–100 nm/s. The high-performance coating process is based upon electron beam evaporation, a dual crucible, and a spotless arc that burns in the metal vapor and reactive gas between the evaporating titanium electrodes that are heated by the electron beam. Electron beam power, arc current and oxygen flow rate were varied and the resulting coatings investigated with regard to their composition, optical properties, and microstructure. Even at such high deposition rates, transparent and dense layers with a high refractive index (2.4) could be produced. Amorphous TiO_2 coatings were obtained at a substrate temperature below 150 °C while crystalline layers of the anatase form could be deposited at a substrate temperature in the range of 200 to 300 °C. The data regarding the chemical composition of the titanium oxide layers are compared with a mathematical model of reactive vapor deposition. An estimate based on the model shows that the incorporation coefficient of oxygen, which gives its deposit probability in the coating, is approximately 0.25 for stoichiometric TiO_2 layers. Possible applications of the PVD process presented are foreseen for large-area optical coating systems and large-scale application of photo-induced effects.

1. Introduction

Thin layers of titanium dioxide are employed for optical coating of surfaces, making use of titanium dioxide's special property of relatively high refractive index. Depending on the structural form of the layer material (amorphous or crystalline) and the method by which the layers are produced, the refractive index of titanium dioxide layers (measured at about 500 nm) lies between 2.1 and 2.6 [1,2]. Effects of reflection, anti-reflection, or optical filtering are achieved by coating stacks with alternating low and high refractive index. Today optical coating systems in which the effect of titanium dioxide's high refractive index is utilized are applied to aluminum strips with large surface areas (many millions of square meters annually) [3]. Moreover, the crystalline forms of titanium dioxide (anatase and rutile) are of particular technical interest due to their photo-induced catalytic properties and photo-induced superhydrophilic surface effects [4]. The demand for high-productivity TiO_2 deposition is well-served by electron beam evaporation using axial electron guns. High deposition rates can be achieved with this process. However, a high deposition rate and high pressure have a negative effect on the density and the refractive index of reactive vapor-deposited TiO_2 layers due to the increasing collision rate in the gaseous phase, as was shown in [5] for deposition rates up to 2×10^{-7} g/(cm^{2}s) and pressures to 5×10^{-4} mbar, for example. The microstructure of these types of vapor-deposited amorphous layers produced at a high deposition rate is porous and the refractive index at a wavelength of 550 nm is below 2.3 [5].

As was variously demonstrated, the microstructure of layers can be made more dense by means of plasma-assisted vapor deposition and the refractive index of amorphous layers can be increased up to a value of 2.5 [6]. Spotless-arc activated deposition (SAD process) has succeeded in achieving very high static TiO_2 deposition rates in the range of 40 to 70 nm/s [7]. The crucible and the evaporation material (titanium) serve as the cathode of an arc in the SAD process. If the temperature of the evaporating titanium is high enough that sufficiently intense thermionic emission occurs [8,9,10], the footpoint of the discharge develops in a diffuse manner over the liquid and evaporating titanium. Due to the relatively low current density in the spotless arc, no droplets are emitted. Advanced development of the SAD process is based on a dual crucible, where one of the two crucibles is connected as the cathode and the other as the anode of an arc. This variant of SAD process is advantageous for TiO_2 coating and is described in detail in [11,12]. The hot, evaporating material in the crucibles forms the electrodes for the arc, whereby the stability of the process over longer operating periods was able to be greatly improved. However it was not clear whether and under what conditions high-refractive index and low absorbing optical TiO_2 coatings can be produced using a dual crucible and hot

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evaporating arc electrodes. The main objective of this study was to investigate the influence of oxygen supply on the optical properties of layers deposited at a deposition rate above 50 nm/s. Knowledge about oxygen incorporation, the necessary oxygen flow rate for stoichiometric TiO_2 coatings, and the resulting pressure in the vacuum chamber should be generated and might help in sizing of vacuum pumping system in industrial application. Therefore in this paper a simple mathematical model of reactive vapor deposition is presented which gives an estimate for the incorporation coefficient of oxygen. Moreover the study should show whether and under what conditions crystalline forms of TiO_2 can be obtained. The results of the investigations into reactive deposition of titanium oxide coatings by means of electron beam evaporation, spotless arc, and a dual crucible will be presented in this article, and the dependencies between the deposition parameters and the coating properties will be detailed in particular.

2. Experimental setup

A "MAXI" inline unit for coating plates and metallic strips was utilized for the experiments as described in detail in [13]. A metal strip up to 300 mm wide and plates that are secured in specialized frames can be moved in horizontal position through a total of eight vacuum chambers in the unit at a speed of approximately 0.01 to 1 m/s. One of these chambers, which is fitted with an electron gun, was used for the coating experiments. A schematic of the experimental setup within one of the coating chambers is shown in Fig. 1. The dual crucible, as it is referred to, consists of two water-cooled copper crucibles arranged beside one another that are electrically insulated from each other and from the frame ground they are attached to. The crucibles are furnished with two independent motor-driven material supply systems with which the cylindrical 65 mm diameter titanium rods can be pushed from below vertically into the crucible and the molten titanium. The center-to-center distance between the crucibles' was set at 190 mm during assembly. The crucibles were connected to a current source (DC, maximum current 500 A) using vacuum feedthroughs and high-current copper cables, with the crucible nearest the electron gun connected to the positive pole of the power supply and the crucible further away to the negative pole. An axial electron gun with a tungsten cathode heated by electron-bombardment ("ERIC" series from FEP, maximum 160 kW, 60 kV) [14] was used as the energy source for evaporation with its accelerating voltage set to 40 kV. The electron gun is pointed toward the evaporation chamber at an angle of 30° from the horizontal. The electron beam is bended toward the evaporation crucibles with a steady-state magnetic field. The magnetic bending field is created with four electromagnets that are positioned within the vacuum chamber. The inhomogeneous magnetic field attains a field strength of 1.6 kA/m at the surface of the crucible. Moreover the electron beam is deflected very quickly with the magnetic beam deflection system integrated within the electron gun so that the evaporation material is alternatingly heated in both crucibles (jumping-beam method). Simultaneously, the power of the electron beam is distributed over the surface of the evaporation material using a computer-generated deflection pattern. The deflection period for the beam pattern and for the jumps back and forth between crucibles is 12 ms.

A medium-frequency power supply that delivers a sinusoidal output voltage at 25 kHz was used as the bias current supply. The output voltage was rectified with what is known as a Villard circuit using a capacitor and a rectifying diode. A 25 kHz pulsed DC voltage was created in this manner with amplitude set at 250 V. The crucible connected as the anode of the arc was connected to the positive pole of the pulsed bias voltage while the equipment ground was connected to the negative pole. In this fashion, the plasma electrodes formed from the crucibles and evaporation material as well as the plasma itself that is electrically coupled to the electrodes is periodically raised to a positive potential

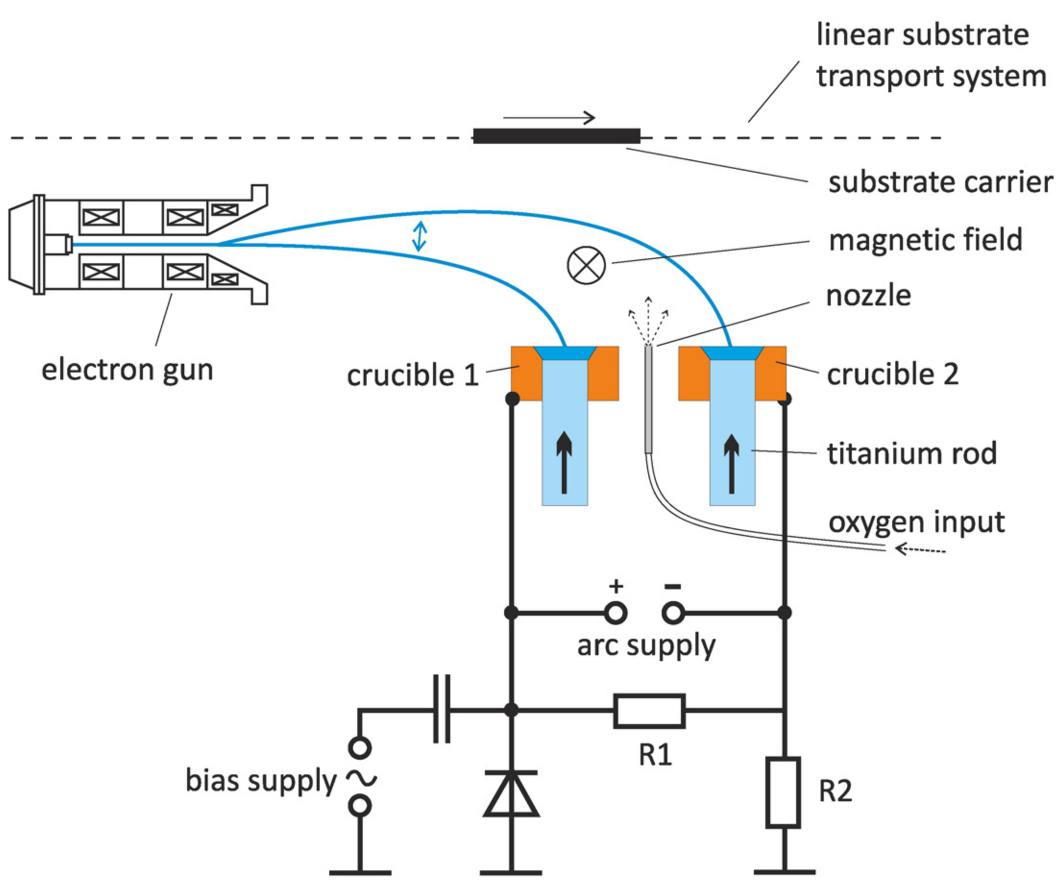

Fig. 1. Schematic diagram of the SAD process with dual crucible and electrical circuitry for reactive deposition of TiO_x coatings.