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Use of zirconium dioxide multilayer dielectric coatings for the ultraviolet and visible spectrum

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The index of refraction of thin films of zirconium dioxide was determined in wavelength range of 250-1200 nm. Multilayer dielectric mirrors were prepared using zirconium dioxide and silicon dioxide. The radiant reflectance exceeded 97.9% at a wavelength of 337 nm and 98.7% at a wavelength of 600 nm on fused silica — Tetrasil A substrate.

Introduction

This study was undertaken to determine the best condition of evaporation of zirconium dioxide films for production of multilayer ZrO_2/SiO_2 coatings. The indices of refraction are strongly dependent upon the evaporation condition. Although, some useful information about the mentioned film materials have been reported by the authors [1-4] little information was published about the use of these materials for preparing optical interferences coatings.

Experimental

Deposition of the films

The ZrO_2 and SiO_2 films were deposited in a vacuum chamber with an electron beam gun from a water-cooled hearths. The zirconium dioxide was prepared by the Cerac (in the cone form) or by the Merck (in tablet form) especially for vacuum evaporation by hot pressing. The silicon dioxide films and the substrates were prepared from fused silica — Tetrasil A. The accelerating voltage was 10 kV, the beam current 0.1-0.2 A and the beam spot about 0.5-1 cm². The substrates were rotated while deposition took place and the hearth-to-substrate distance was 70 cm. The evaporation rates were 0.5 nm/sec for ZrO_2 and 1.5 nm/sec for SiO_2. The measurement and control of the evaporated films were provided by the quartz-crystal mass-thickness monitor and by the optical-thickness monitor.

Before evaporation the base pressure in the chamber was about 0.67 mPa. As suggested by other investigators of rare earth oxides, the both film materials were reactively evaporated in oxygen residual atmosphere. Oxygen was guided by pipe nearby the substrate — the pressure of flowing oxygen in the pipe was about 0.67 Pa.

Halogen lamps heated the substrates to 673 K during deposition. It is easy to notice from fig. 1 that the characteristics of the 673 K-heated

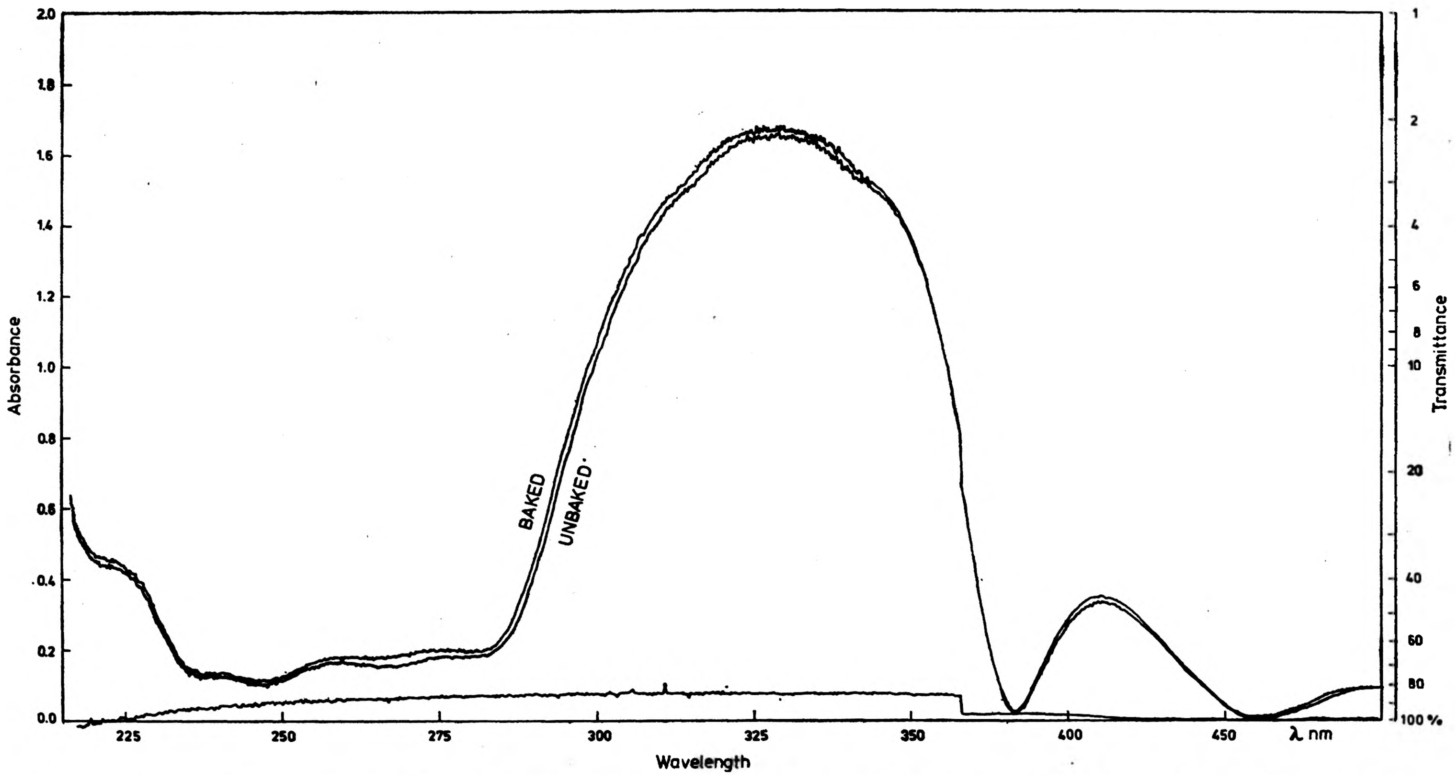

Fig. 1. The measured transmittance T_m of a quartewave stack consisting of thirteen alternate layers of zirconium and silicon dioxides. The zirconium dioxide layer is the first one on the fused silica substrate. The measured physical thickness of the stack was 593.3 nm, and after postbacking — 608.5 nm

oxide multilayers are nearly the same if the samples are respectively, subject to no baking or postbaking at the 673 K air atmosphere for ca 6 h.

Measurement

After the films were deposited, they were removed from the coating chamber and set in air for at least 24 h. The transmittance T_m was measured with an identical fused silica substrate in the reference beam of the spectrophotometer — Beckman model ACTA M (fig. 2). The transmittance of the film T_f is [5]:

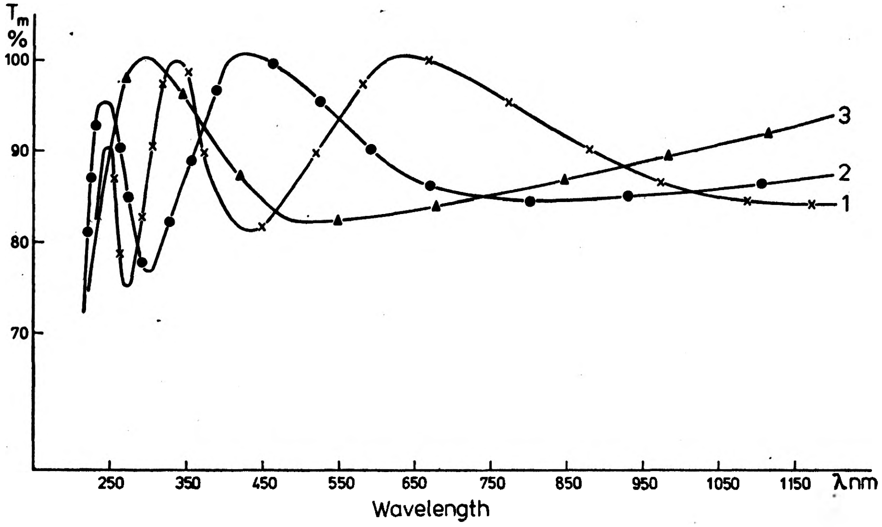

Fig. 2. The measured transmittance T_m of the ZrO_2 films deposited on the fused silica substrate and kept in the air atmosphere for at least 24 h after removal from the coating chamber. The substrates were heated up to 673 K. The numbers 1, 2, 3 of the curves correspond to optical thickness: 1 of 300 nm, 2 — 206 nm, 3 — 127 nm, respectively

$$T_f = T_m \frac{(1-R)}{1+R(1-T_m)},$$

where R is the radiant reflectance at the air-substrate interface.

The indices of refraction of the films were calculated from the minima of transmittance T_f [6]. These values were used as first approximation.

Physical thickness of the layers was measured with a multiple beam Fizeau-Tolansky interferometer — Sloan model M-100 Angstrometer. The physical thickness of the layers, the wavelengths corresponding to the maxima in the spectrophotometric curves, and dispersion data for the substrate [7] being known, the Sellmeier type dispersion equation for the index of refraction was assumed in the form

$$n^2 = A + B \cdot s^2,$$

where s is the wavenumber. The index of refraction was found by a trial and error process.

The large specular reflectance R_s of multilayer ZrO_2/SiO_2 coatings was measured via a reflectance attachment on the spectrophotometer — Hilger-Watts [8]. Assuming that rms of the surface roughness of substrate-coating δ is substantially less than λ, specular reflectance (in normal incidence) is [9]:

$$R_s = R_0 \exp\left[-\left(\frac{4\pi\delta}{\lambda}\right)^2\right],$$

where R_0 is the reflectance of smooth boundaries of substrate and individual layers.

Data

The measured refraction index of ZrO_2-films is shown in fig. 3. The coefficients for the Sellmeier equation fit of the dispersion of the index are:

$$A = 3.6032, \quad B = 0.0818.$$

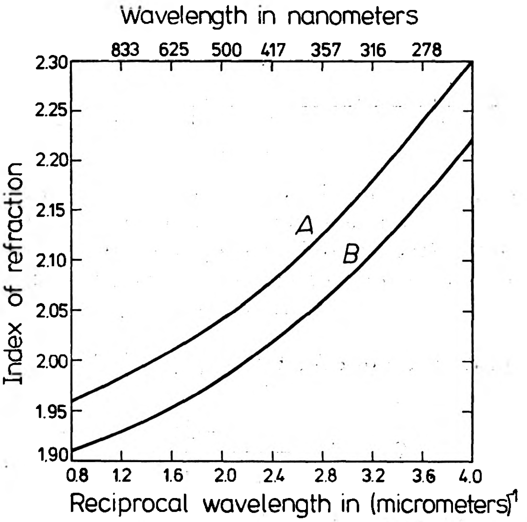

Fig. 3. The refractive index of ZrO_2-films computed from $n^2 = A + B s^2$, s is wavenumber in (micrometers)$^{-1}$. The curve 1 corresponds to the constants given in [11] (EB-gun voltage — 5 kV, temperature during deposition — 523 K, postbacking temperature — 673 K); the curve 2 corresponds to the constants described in the experimental (EB-gun voltage — 10 kV, temperature during deposition — 673 K)

Zirconium dioxide films start absorbing at 250 nm, i.e. for the wavelength at which the absorption exceeds about 5 % [10]. The transmittance of the silicon dioxide film (deposited under the described evaporation conditions) on fused silica substrate is practically identical with that of fused silica substrate in wavelength range 250-1200 nm. The refraction index of SiO_2-films is evidently that of fused silica [7].

Multilayer mirrors

As long as losses due to absorption and scattering do not prevail, the maximum specular reflectance R_s of quartz-wave stock increases with the number of layer. The maximum reflectance R_0 is expressed in terms of standing wave ratio V

$$R_0 = \left[\frac{1-V}{1+V}\right]^2.$$

When each layer has a quarter-wave thickness, V reduces to:

$$GV = \frac{n_H}{n_H n_s}\left[\frac{n_H}{n_L}\right]^{2m},$$

where n_H, n_L, n_S, and n_A are the indices of ZrO_2-layer, SiO_2-layer, substrate and air, respectively, and m is number of periods in a design:

$$A-(HL)^m H-S.$$

The calculated V of multilayer mirrors from optical constants of ZrO_2/SiO_2 films and from the measured reflectance values R_s are shown in fig. 4.

The ultimate 97.9 % reflectance corresponds to stock of 17 (15) layers — for wavelength near 337 nm. For the wavelength of 600 nm the reflectance

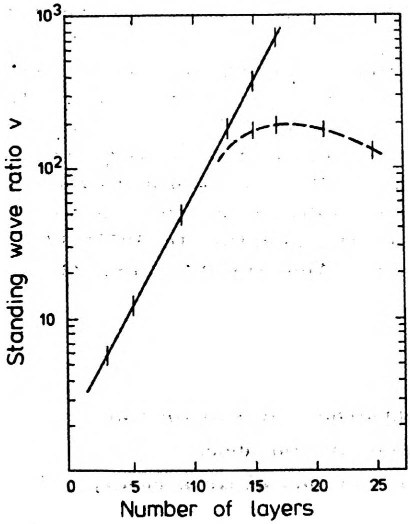

Fig. 4. Standing wave ratio V (the measured reflectance R_s) of stacks composed of alternate zirconium dioxide and silicon dioxide layers vs. the number of layers (dashed curve). Solid line corresponds to the values of V computed by using the measured optical constants, for the wavelength 337 nm

of stock consisting of alternating 25 ZrO_2/SiO_2 layers exceeded 98.7 %.

The multilayer coatings were deposited on ordinary optical polished surfaces of fused silica substrates. The *rms* of the substrate roughness was about 4.6 nm.

Conclusions

Under the above described conditions of evaporation (substrate temperature) — the multilayer coatings of ZrO_2/SiO_2 films can be produced without postbaking. There is evidence that for higher ultimate reflectance, especially for UV, the multilayer coatings must be deposited on smoother substrate surfaces than these described in the experimental part.

The determined indices of ZrO_2/SiO_2 films have lower values than those given in the literature [10, 11]. This discrepancy can be attributed to the different accelerating voltage of electron beam gun and the temperature of substrate during deposition.

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Применение двуокиси циркония для изготовления многослойных диэлектрических оболочек для ультрафиолетовой и видимой области спектра

Определён коэффициент преломления слоёв из двуокиси циркония в спектральной области от 250 до 1200 нм. Были выполнены различные диэлектрические зеркала, применяя для их изготовления слои из двуокиси циркония и слоя из двуокиси кремния. Полученные значения зеркального отражения от зеркальных оболочек, осаждённых на основе из расплавленного кварца — тетрасил А, достигли 97,9% для волны 337 нм, а также 98,7 для волны 600 нм.