Thin Solid Films 558 (2014) 86–92

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Density dependence of refractive index of nanoparticle-derived titania films on glass

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ARTICLE INFO

Article history:
Received 18 October 2013
Received in revised form 20 February 2014
Accepted 24 February 2014
Available online 28 February 2014

Keywords:
Titania
Nanoparticle sol
Density to refractive index relationship
Mixture models
Porosity

ABSTRACT

In order to test the relationship of refractive index to mass density within a wide range, porous titania films up to 800 nm thickness were prepared on silica glass by repetitive dip-coating and thermal curing of anatase sols having primary particle sizes below 7 nm. Profilometry showed a decrease in film thickness and an increase in the index of refraction of up to 50%, if the curing temperature was increased from 100 °C to 1000 °C. The decrease in film thickness was related to an increase in mass density, which directly acts on the optical polarizability and thus the (effective) refractive index of the film. In particular, mass density–refractive index calculations were performed using linear (Arago–Biot, Gladstone–Dale) and nonlinear mixture models (Drude, Lorentz–Lorenz), assuming either air- or water-filled pores, while anatase and rutile fractions were determined by X-ray diffraction. These investigations were verified using refractive index and mass density data from literature. For each model noticeable deviations from the expected trend were evident. We show that an empirical power law expression holds for the Lorentz–Lorenz theory and permits to calculate effective density and porosity of titania thin films from effective refractive index with high accuracy.

1. Introduction

Titania (TiO_2) is one of the most interesting and widely studied semiconductors with a large band gap. Deposited as thin films, TiO_2 is of great interest for a large range of applications like gas sensors [1,2], solar cells [3,4], photocatalyst [5–7], anti-reflection [8,9] and self-cleaning coatings [10]. The refractive index $n(\lambda)$ and optical dispersion of titania thin films were found to depend strongly on deposition methods and conditions. Values for $n(\lambda = 550\ nm)$ of 2.23–2.35 [11], 2.0–2.3 [12], 2.3–2.52 [13] for electron beam evaporation, 2.42–2.56 [11], 2.45–2.73 [14] 2.31–2.37 [15], 1.53–1.54 [16] for magnetron sputtering, 2.56–2.72 [17] for chemical vapor deposition, 2.32–2.49 [18] for atomic layer deposition and 1.93–2.12 (at $\lambda =$ 600 nm) [19], 2.18 [20], 2.26–2.31 [21], 2.20–2.43 [22], 2.02–2.11 [23], 2.34 [24] for sol–gel spin- and dip-coating were reported. In these films titania is present as amorphous material, possessing brookite, anatase, and rutile phases as well as mixtures of these modifications. In most works a deviation from the refractive index of the pure TiO_2 polymorphs (mean refractive index n_d at wavelength 550 nm is 2.566 for anatase [25], 2.654 for brookite [25] and 2.742 for rutile [26]) was related to a heterogeneous film structure. In particular, $n(550\ nm) < 2.45$ (dense amorphous titania [11]) was assigned to pore-bearing films. The properties of these nanocomposites were mostly treated by effective media approximations. Different mixing models were used to predict porosity, densification and pore-filling media (air and water) from effective optical properties. For sol–gel derived titania films Hu et al. [27], San Vincente et al. [19], Ahn et al. [22] and Mathews et al. [23] applied the Drude (also referred as Yoldas) model, while Hostetler et al. [20] and Vitala et al. [28] used a Lorentz–Lorenz relation, while Taylor et al. [29] calculated porosity from the Maxwell–Garnet equation.

In most of these studies the microstructure of porous films was predicted without comparison between theory and experiment. Furthermore, changes in the deposition conditions used in these studies resulted in similar optical properties, i.e., the differences in the effective refractive index were relatively small ($\Delta n_{eff} \approx 0.1$–$0.3$), which makes it difficult to test the above mixture models by analyzing trends in the density dependence of n_{eff} [30,12]. Thus, the present study aims in providing a relatively broad range of refractive indices by using a single preparation method. For this, low- and high-index TiO_2 films ranging from $n_{eff} = 1.75$ to $n_{eff} = 2.62$ were prepared using anatase sols with primary particle size below 7 nm and applying simple variations (temperature, time) in the curing conditions. In order to make theoretical predictions of porosity to allow for a comparison with experimental data, independent determinations of the film density are necessary, which were collected from gravimetric, Rutherford backscattering and X-ray absorption data reported in the literature. This compilation of densities covers a large range of the effective refractive index ($\Delta n_{eff} \approx 1.5$) for titania structures and thin films.

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http://dx.doi.org/10.1016/j.tsf.2014.02.078
0040-6090/

2. Characterization of microstructure using effective optical properties

2.1. Mixture models

Effective medium approximations of nanocomposite and mesoporous thin films are derived from calculation and are based on relative volume fractions of their components. For ideal mixing of a dispersed pore volume (refractive index n_P) in a dense titania film (refractive index n_D) the effective refractive index n_{eff} of the porous film is given by

$$f\left(n_{eff}\right) = (1-P)f(n_D) + Pf(n_P), \tag{1}$$

where $f(n_i)$ is the specific refractive index of a certain model, P is the volume fraction of pores (porosity), and $(1-P)$ is the volume fraction of pore-free titania (i.e. packing density or filling factor). Numerous mixture models have been reported to treat a heterogeneous thin film as homogeneous with an effective refractive index. Among these Arago–Biot, Gladstone–Dale, Drude (or Yoldas), Lorentz–Lorenz, Heller, Wiener, Maxwell–Garnett, volume averaging theory and Bruggeman are most frequently employed [31,32]. The use of these principal mixture rules results in either a linear refractive index-porosity dependence or in a negative or positive deviation from a linear additivity of n_{eff} vs. P. Representatives of the former are Arago–Biot [$f(n_i) = n_i$] and Gladstone–Dale [$f(n_i) = (n_i - 1)$], while members of the latter are Drude [$f(n_i) = (n_i^2 - 1)$] and Lorentz–Lorenz [$f(n_i) = (n_i^2 - 1)/(n_i^2 + 2)$] models. Compilations of these models are given in [31–33]. Using Eq. (1) for volume conservation the Arago–Biot and Gladstone–Dale models lead to a porosity

$$P = \frac{n_{eff} - n_D}{n_P - n_D}. \tag{2}$$

Application of the Drude model results in

$$P = \frac{{n_{eff}}^2 - {n_D}^2}{{n_P}^2 - {n_D}^2}, \tag{3}$$

while the porosity obtained from Lorentz–Lorenz model is

$$P = \frac{\left({n_{\mathrm{eff}}}^2 - {n_D}^2\right)}{\left({n_{\mathrm{eff}}}^2 + 2\right)} \frac{\left({n_P}^2 + 2\right)}{\left({n_P}^2 - {n_D}^2\right)}. \tag{4}$$

The dimensionless Eq. (1) can be formulated in an alternative way by introducing the mass density of pure components, which is referred as specific refraction R (in units of volume per mass)

$$f\left(n_{eff}\right)/\rho_{eff} = (1-P)f(n_D)/\rho_D + Pf(n_P)/\rho_P = (1-P)R_D + PR_P \tag{5}$$

with ρ_{eff}, ρ_D and ρ_P being the mass density of the porous film, pore-free titania, and pores, respectively. For $f(n_i) = n_i - 1$ and water-filled pores, Eq. (5) is equal to the Gladstone–Dale equation in its widely used form:

$$\frac{n_{eff} - 1}{\rho_{eff}} = R_{eff} = (1-P)R_{TiO_2} + PR_{H_2O}, \tag{6}$$

which is used to calculate mass density from refractive index of titania-bearing minerals. In optical mineralogy values of $R_{TiO_2} = 0.397\ \mathrm{cm^3\ g^{-1}}$ and $R_{H_2O} = 0.34\ \mathrm{cm^3\ g^{-1}}$ at 598 nm are employed [34].

Assuming a polycrystalline random structure in the titania film, n_D of Eqs. (1)–(5) can be derived from single crystal data by

$$n_D(\lambda) = \frac{(2n_o + n_e)}{3}, \tag{7}$$

where n_o and n_e are the ordinary (2.5915 and 2.6433 at 550 nm) and the extraordinary (2.5138 and 2.9387 at 550 nm) refractive indices of anatase [25] and rutile [26], respectively. For mixed anatase–rutile films a mean value based on their relative volume fractions is widely accepted.

In general these mixture models do not account for the actual polarization of the incident light, or for the local size, shape and spatial distribution of the pores in the thin film. Hence, refractive index predictions for given pore morphologies can differ considerably from numerical solutions [35,36]. Consequently, calculation of ρ_{eff} from effective refractive index using mixture models requires information on the true mass density or on the specific microstructure of the film.

2.2. True mass density of titania thin films and structures

In the case of titania thin films true mass density ρ has been determined independent of effective optical theory by combining metric (thickness) with gravimetric experiments [30,13], using Rutherford backscattering intensities [11,17] and X-ray absorption [37]. Together with the corresponding effective refractive indices n_{eff}, which were determined in these studies using ellipsometry and optical transmittance spectra, the data permit to verify the underlying mixing models. These tests will provide the basis for estimates on the effective density of nanoparticle derived films within this study. Specific volumes of natural (anatase [38], brookite [39] and rutile [40]) and modeled (density functional simulations of columbite, rutile, brookite, anatase, ramsdellite, bronze and hollandite [41]) titania structures, as determined from their unit cell parameters, were included as well for the data compilation shown in Fig. 1. For these pure titania materials the refractive indices n_D from Refs. [25,26] and [42] were applied. Fig. 1 reveals that the dependence of the refractive index [effective (n_{eff}) and bulk (n_D)] on

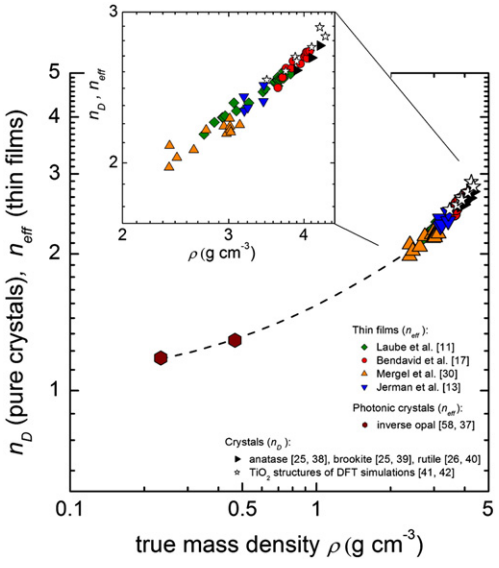

Fig. 1. Dependence of the index of refraction n ($\lambda = 550$ nm) on true mass density ρ of titania thin films and crystal structures in double logarithmic scales. Thin film data as prepared by: sputtering and ion plating (anatase) [11], filtered arc deposition (amorphous, anatase, rutile) [17] and electron beam evaporation and post heating (amorphous, anatase) [30,12,11,13]. Crystal data: anatase [38,25], rutile [41,26], brookite [39,25], modeled TiO_2 structures: columbite, rutile, brookite, anatase, ramsdellite, bronze and hollandite (density functional simulation (DFT) for 2.1 eV) [41,42]. Photonic crystal data: Inverse OPAL structures (anatase) at 14,900 cm^{-1} [58,37]. Inset shows details for $\rho > 2$ g cm^{-3}. The dashed line is intended as a visual guide.