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Sol–Gel Synthesis of Titania Thin-Film-Stabilized Porous Silica Coating

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The sol–gel process has been widely used to prepare thin films with unique properties, such as tailored porosity, refractive index, and compositional homogeneity.[1,2] Titania-based thin films prepared by a sol–gel route, for example, have been used for the design of multilayer optical interference coatings.[3] For ultrathin films (<50 nm), crystalline anatase has been observed as the predominant phase after thermal treatment above 400 °C. Due to the presence of intergrain porosity, the refractive indexes of the crystalline titania films are lower than that of the bulk materials.[4,5] One strategy for designing multilayer optical coatings is to form alternate layers with indexes as widely spaced as possible, in order to achieve the desired properties using fewer numbers of layers. If one can introduce porosity into the low-index coatings and control the extent of composition interpenetration at the interface, it would be possible to deposit sequential layers with greater differences in the refractive index or with a controlled gradient index. Porous silica synthesized by a sol–gel process has been used as single layer or gradient index antireflective coatings.[6,7] However, mechanical and environmental instabilities are inherent in the porous coatings, a drawback which may limit their broad application. It has been noticed that during the formation of thin films on porous surfaces, intermixing of two materials may occur at the interface.[2,8] This interpenetration process may be aided in sol–gel coatings by the capillary pressure created by solvent flow into the porous media. If a silica coating has an initial porosity of 50%, and the pores are filled with materials having a refractive index of 2.20, a final index of 1.78 is expected as calculated from the Lorentz–Lorenz equation.[9] Stacked films[10,11] composed of porous layers have been exploited in optical designs and coatings. The intermixing process, however, has not been addressed in conjunction with film formation on the porous surfaces.

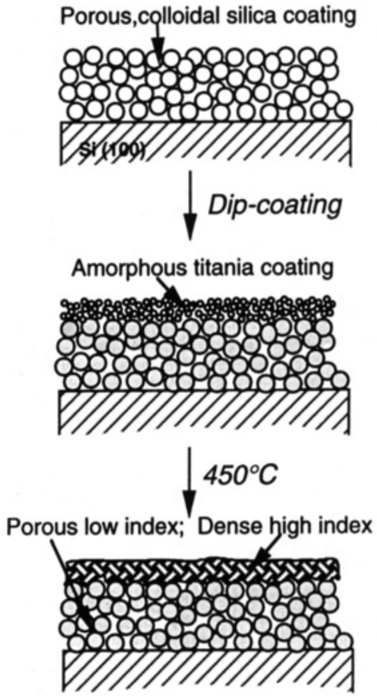

Figure 1. Deposition of titania film on porous surface by controlling the size of the condensed titania species in sol–gel solution and the microstructure of the deposited silica underlayer.

In this report we demonstrate that coatings consisting of stacked titania over silica can be prepared with a distinct difference in the indexes by incorporating high porosity in the silica underlayer. The intermixing of the two components and the filling of the underlayer porosity have been minimized by controlling the microstructure of the underlayer coating and by manipulating the size and structure of the condensed titania species in the coating solution prior to deposition. Figure 1 schematically depicts such an approach. This strategy may also allow for the design of asymmetric ceramic membranes,[8,12,13] chemical sensors,[14–17] and optical devices[1,3,18,19] with improved performance and enhanced stability.

The porous silica underlayer coatings were formed by dip-coating a Si wafer with a (100) orientation in a

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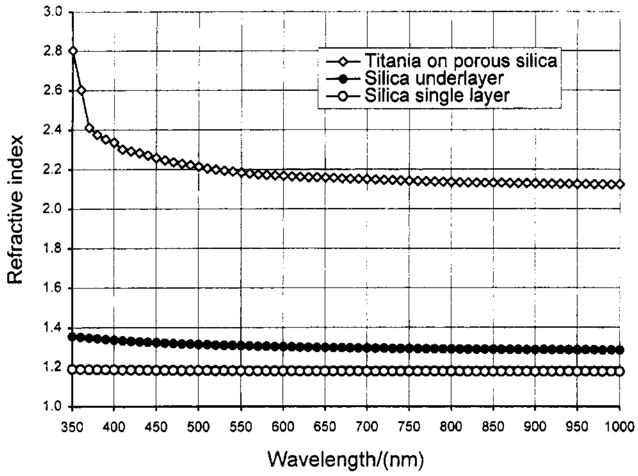

Figure 2. Dispersion curves of the refractive indices of the sol–gel thin films cured at 450 °C. (a) Colloidal, porous silica single film; (b) silica film coated with titania top layer; (c) titania coating on top of porous silica.

solution containing cross-linked colloidal silica. The film thickness after curing at 450 °C for 2 h is about 173 nm when it has been prepared at a substrate withdrawal speed of 0.4 cm/s. The coating solution was prepared by hydrolysis of tetraethyl orthosilicate (TEOS, Silbond Corp. Weston, MI) using ammonium hydroxide and hydrochloric acid as two-step catalysts. The colloidal silica nanoparticles were first synthesized by reaction of TEOS (0.7 mol) with water (2.45 mol) and ammonium hydroxide (0.04 mol) in an ethanol solvent (14 mol) at 70 °C for more than 15 h. This reaction was carried out in an autoclavable Teflon FEP bottle in a temperature-controlled water bath (*caution*: the boiling temperature of this solution is around 80 °C at 1 atm). After the ammonia in the solution has been evaporated at 60 °C and the solution has reached pH < 7, second doses of TEOS (0.07 mol), water (0.28 mol), and hydrochloric acid (0.01 mol) were added into the slightly opaque solution and further reacted for 4 h at room temperature. Under the acidic condition, the second dose of TEOS forms a polymeric sol and reacts with surface hydroxyl groups on the colloidal silica without destabilizing the colloidal phase.[7] Adding the siloxane binding phase increases the adhesion between individual silica particles and between the coating and the substrate. The silica coating (173 nm) derived from this solution has a refractive index of 1.18 at a wavelength of 510 nm after curing at 450 °C for 2 h. A spectroscopic ellipsometer (VASE, Woollam Co., Lincoln, NE) at three angles of incidence was used for measuring the optical constants and thickness of the film at relative humidity of 45 ± 5%. Figure 2 shows the dispersion curve of the refractive index. The low index of the silica coating correlates to a volume fraction porosity greater than 50%.[20] Atomic force microscopy (AFM, Nanoscope III, Digital Instruments, Santa Barbara, CA) images of the silica coating indicate that the porous silica is composed of randomly packed, nearly spherical particles about 40 nm in diameter.[21] However, the cured single-layer silica coatings can be easily scratched or peeled off by applying Scotch tape to the surface.

After the single-layer silica coating had been dried at 120 °C, the coating was further dip-coated to apply an amorphous titania layer. The titania precursor solution was synthesized by hydrolysis of chelated titanium alkoxide using hydrochloric acid as the catalyst. In a typical preparation, 0.2 mol each of titanium isopropoxide and the chelating agent, acetylacetone $CH_2(COCH_3)$ (acac, Aldrich, Milwaukee, WI), were first dissolved in 3.0 mol of 2-propanol at ambient temperature. To this solution 5 mol of ethanol containing 0.6 mol of water and 0.04 mol of HCl was subsequently added. Due to the endothermic reaction, the temperature of the solution may rise by 10 °C during the first hour of reaction (*caution*: the temperature may further increase if the amount of reactant is increased). The reaction mixture was aged for 15 h prior to being used for dip-coating for the formation of stacked films. A 31.3 nm titania coating can be obtained at a substrate withdrawal speed of 0.25 cm/s.

The acac-modified titanium top layers dried at 120 °C exhibit a smooth and continuous surface of significantly smaller interconnected colloidal particles (about 10 nm in diameter) according to the AFM.[21] The morphology of the coating is consistent with the observation that adding acac to the metal alkoxide promotes the formation of smaller particles, due to the presence of two kinds of hydrolyzyable ligands, namely, alkoxide and acac groups.[4,22,23] No surface cracks have been observed under 500 times magnification after the two-layer stacked films were cured at 450 °C for 2 h. The index of the top layer reaches 2.22, with a coating thickness of 31.3 nm.[24] A similar value of refractive index has been reported by others for sol–gel titania films formed on dense substrates and cured at a similar temperature.[2,5,25] The refractive index of the underlayer silica, however, is increased to 1.31 (Figure 2) after the 450 °C thermal treatment, compared to 1.18 for the silica layer without a titania top layer cured at the same temperature. The increase in the silica index indicates that about 13% of the void space in the silica layer has been filled by titania.[20] It is clear that the index of the underlayer coating is still substantially lower than that of dense silica ($n_d = 1.46$). The low extent of intermixing of the two components is primarily attributed to the difference between the pore sizes of the underlayer coating and the diameters of the condensed titania species. The interparticle porosity of the spherical silica could possibly construct "bottleneck" pores which consist of a narrow opening and a wide void space. The

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(20) The silica film exhibits a hydrophobic property after thermal treatment.[16] The sorption of vapor on this mesoporous film composed of interparticle porosity is characterized by type II BET isotherm. Under the measurement conditions (relative humidity of 45 ± 5%), about 1–2 layers of water molecule are adsorbed which contributes about 0.1–0.2% to the calculated porosity. For more detailed information on vapor sorption refer (a). Lowell, S.; Shields, J. E. *Powder Surface and Porosity*; Chapman and Hall: New York, 1984. (b) Yan Y.; Vansant, E. *J. Phys. Chem.*, in press. Thin-film porosity characterization: (a) Glaves, C. L.; Frye, G. C.; Smith, D. M.; Brinker, C. J.; Datye, A.; Ricco, A. J.; Martin, S. J. *Langmuir*, **1989**, *5*, 459. (b) Reference 19. (c) Fardad, M. A.; Yeatman, E. M.; Dawnay, E. J. C. *SPIE* **1994**, *2288*, 77.

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presence of the polymeric siloxane binding phase between the silica nanoparticles could further narrow the pore sizes and effectively prevent the relatively larger titania species from entering into the porous underlayer structure. It it not yet completely understood whether the titania diffused in the porous layer is present as a pure titania phase or forms a layer of titanium silicate on the colloidal silica surface. The intermixing process, however, does enhance the mechanical stability of the stacked film. The stacked films after curing consistently pass the Scotch tape adhesion tests at different peeling angles.

The validity of the refractive indexes and derived-intermixing information is further verified by comparison of the reflectances of the stacked films. The reflectances of the films are measured spectroscopically from 400 to 700 nm (Cary 4, Varian, Sunnyvale, CA) in the same humidity range and compared with those calculated from the above ellipsometric data (index and thickness) (Macleod thin film design programs, Thin Film Center Inc., Tucson, AZ). The results are depicted in Figure 3. The very close match of the two curves suggests that the refractive index and the derived intermixing model are reasonably reliable. On the basis of 31 data points across the wavelength range in 10 nm intervals, the average of the absolute relative deviations of the calculated data from the measurements is 1.50%. If a theoretical layer of film, for example, 30 nm composed of 50% titania and 50% silica is inserted between the actual two-layer stack and replaces 30 nm of the silica-based layer, the calculated reflectance is shifted far away from the actual measured one, and the average of the absolute relative deviations increases to 9.24%. We believe that the consistency between theoretical modeling and the actual measurement is an indication that the *titanium is homogeneously, rather than gradiently, mixed through the entire porous silica layer*, since a small change in refractive index or film thickness would show a larger difference between the reflectances. The presence of titanium in the silica layer is also confirmed with Auger electron spectroscopy.[21]

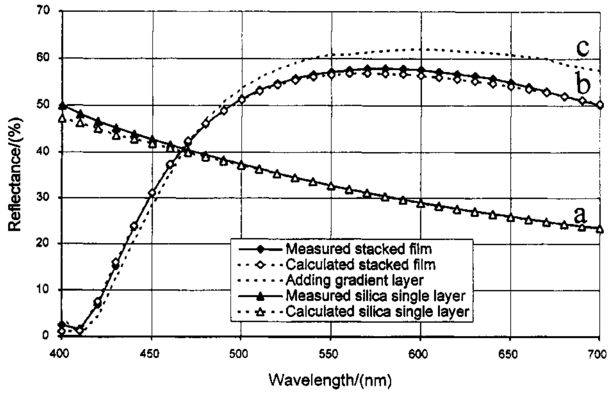

Figure 3. Comparison of the calculated reflectance with spectrophotometer measurement. (a) Colloidal, porous silica single layer (173.2 nm); (b) stacked films of titania (31.3 nm) on top of porous silica (157.3 nm); (c) assumed underlayers, composed of 30 nm of $n_d = 1.79$ and 127.3 nm of $n_d = 1.31$ gradient index layer, used for calculation of the reflectance of film (b).

In summary, we have reported that crack-free titania thin films can be deposited on porous silica layers by controlling the coating microstructure and size of sequential coating species. These stacked films represent the formation of titania layers on coatings with the lowest refractive index and highest porosity obtained by sol–gel synthesis. Theoretical modeling can also be used as an effective method to characterize the intermixing process and its extent. Optical designs using such materials also suggest that reflective or antireflective multilayer coatings can be theoretically prepared with much improved performance and/or enlarged bandwidth. The exploration of their novel applications are in progress.

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