Microstructure of SiO_2/TiO_2 Coatings and Their Use in Graded-Index Optical Filters

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ABSTRACT

In the present work, we study the microstructural properties of SiO_2/TiO_2 mixtures deposited by plasma-enhanced chemical vapor deposition using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and X-ray diffraction. We found that the chemical and physical properties of the mixtures are consistent with a single-phase material. These materials, with an adjustable refractive index, are then applied for the fabrication of rugate filters. For monitoring their deposition, we propose a new technique that analyzes the ellipsometric spectra outside of the rejection band in order to determine, in real-time, the optical thickness of the growing filter. An example is shown for a single-band rugate filter centered at 550 nm.

INTRODUCTION

Graded-index optical filters offer interesting characteristics difficult to obtain with traditional multilayer coatings; this includes elimination of harmonics and sidelobes [1] and improved mechanical performance [2]. Plasma-enhanced chemical vapor deposition (PECVD) [3] appears very suitable to fabricate graded-index filters as the index profile can be controlled by continuously varying the concentration of precursors by an appropriate adjustment of the working gas mixture.

In our previous work, we have demonstrated the ability to deposit SiO_2/TiO_2 mixtures with refractive index, n, between 1.50 and 2.35, and the possibility to fabricate graded-index filters using these materials [4]. We have also analyzed real-time spectroscopic ellipsometry data with the generalized virtual interface (GVI) method [5] and determined, in real-time, the instantaneous value of n of a graded-index filter [6]. This technique can determine n and the deposition rate of the top material (approx. 5 nm) regardless of the underlying structure. However, the GVI approach alone is not well suited for monitoring graded-index filters. It does not provide information about the whole structure of the filter and, therefore, does not allow one to correct errors committed during the previous steps of the filter fabrication.

In the present work, we first study the microstructure of SiO_2/TiO_2 mixtures exhibiting different n values. We then present a new monitoring technique for the fabrication of rugate filters based on the analysis of the ellipsometric spectra outside the principal band region.

EXPERIMENTAL METHODOLOGY

Deposition System

The coatings were prepared in a PECVD reactor described in more detail in a previous paper from our laboratory [7]. Glass substrates were placed on an RF (13.56 MHz) powered electrode where a negative bias, V_B, develops. SiO_2/TiO_2 mixtures of different n values were obtained by varying the flow of precursors, $SiCl_4$ and $TiCl_4$, in the gas phase. The flow of O_2 and Ar was kept constant. The working pressure was 25 mTorr. The gas flow and V_B were controlled by computer using a homemade software.

Microstructural Characterization

The chemical structure of the coatings was determined by X-ray photoelectron spectroscopy (XPS) using a VG Escalab 3 MK II spectrometer. The peaks were deconvoluted using the Surfsoft software, and the peak position, full width at half-maximum (FWHM) and the gaussian-lorentzian ratio were fitted.

Complementary information about the chemical structure was obtained by Fourier transform infrared spectrometry (FTIR) using a Bio-Rad Excalibur spectrometer. The spectra were deconvoluted using the Bomem Grams/32 software; the peak position, FWHM and gaussian-lorentzian ratio were fitted.

The crystallinity of the samples was evaluated by X-ray diffraction (XRD) using a Philips X'Pert diffractometer and Cu K_α radiation. The spectra were acquired in grazing incidence mode.

Monitoring Approach

The fabrication of the films and filters was monitored *in situ* using the M-2000 spectroscopic ellipsometer and the EASE software from the J. A. Woollam Co., Inc.

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We propose here a new monitoring technique for rugate filters using the ripples outside of the rejection band. Figure 1 shows an example of the index profile of a rugate filter with apodization. The transmission spectrum at normal incidence of such filter contains a rejection band at a wavelength λ_0, but no sidelobes and no harmonics (see Figure 2a). The ripples, outside of the band, are caused by the reflections at the substrate/filter and filter/air interfaces. The ripples can be modeled by a single homogeneous layer of the same thickness with the same index value as the mean index of the rugate filter (see Figure 2a). The ellipsometric spectrum of the filter, except for the rejection band, can also be modeled using the same single homogeneous layer (see Figure 2b). Since the ellipsometric data are acquired at non-normal incidence, the band is shifted to a lower wavelength. This allows one to use the ripples around λ_0 to determine the mean index of refraction and the thickness at the design wavelength λ_0.

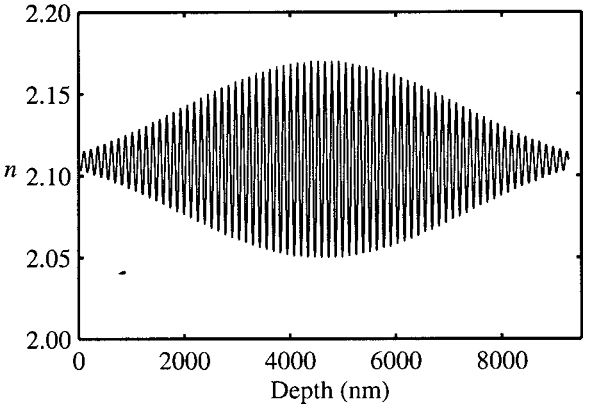

Figure 1: Index profile of an apodized rugate filter.

During the actual deposition, the filter was modeled using a single homogeneous layer, and only the ripples were fitted. To avoid instability, the index of refraction was fixed and only the thickness was considered in the fit. The deposition control software retrieved the optical thickness from EASE using a network connection (TCP/IP), and the process speed was adjusted in real-time to obtain the desired index profile.

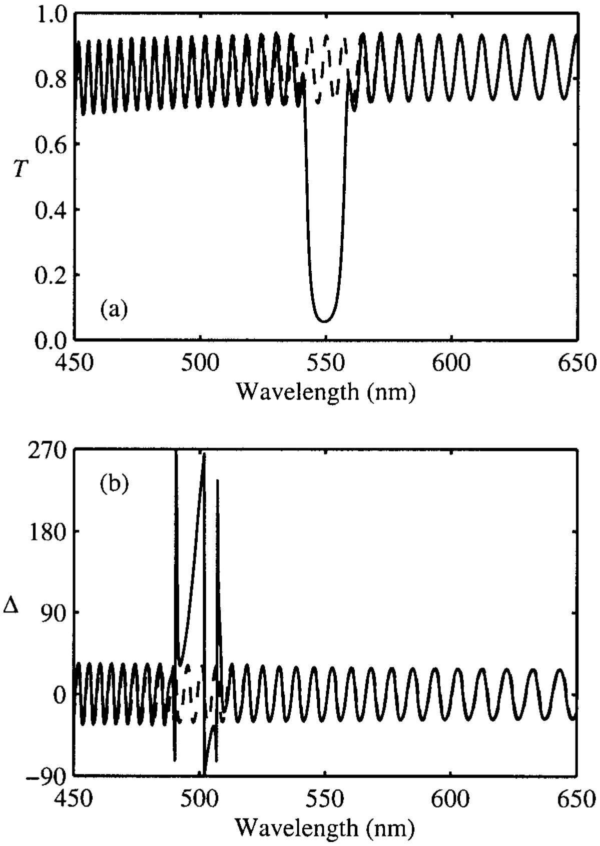

Figure 2: Transmission spectra (a) and ellipsometric angle Δ at an incidence angle of 75° (b) of a rugate filter (full line) and a single homogeneous layer with the same thickness and mean index (dashed line).

RESULTS AND DISCUSSION

Microstructure

In the first part, we study the microstructure of the SiO_2/TiO_2 mixtures. Figure 3 shows the FTIR spectra; all the peaks in the spectra of SiO_2 and TiO_2 can be assigned using the literature data [8,9]. In the mixtures, an additional peak appears that can be assigned to Si-O-Ti bonds [10]. This peak clearly indicates the presence of a phase containing both Si-O and Ti-O bonds. In addition, there is a progressive shift in the position of the Si-O-Si stretching peaks, indicating a change in the chemical structure of the material. This suggests that SiO_2/TiO_2 mixtures form a single phase. This conclusion is supported by the evaluation of the optical properties using the effective medium approximation (EMA). In fact, EMA models (Bruggeman, Maxwell-Garnett) representing mixtures of two phases did not fit the experimental data.

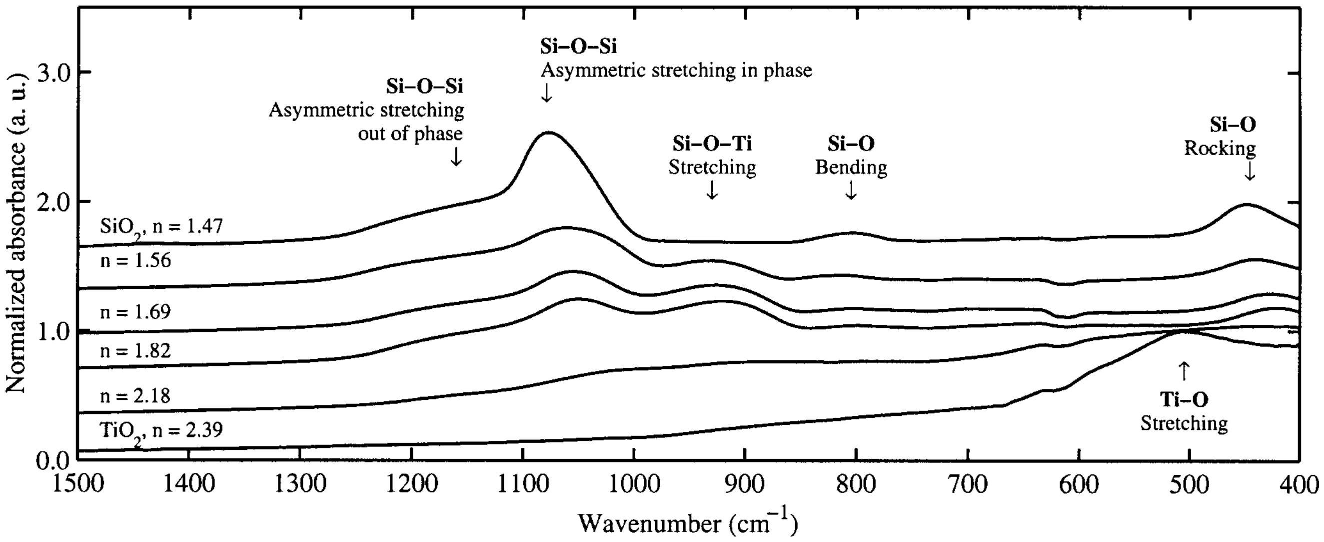

Figure 3: FTIR spectra of SiO_2/TiO_2 mixtures.

Figure 4 shows the XPS spectra of SiO_2/TiO_2 mixtures. The O(1s) peak shifts from 532.5 eV for SiO_2 to 529.8 eV for TiO_2, in good agreement with the published values [11]. The presence of only one peak in the case of mixtures indicates the absence of two separate SiO_2 and TiO_2 phases, but rather one single phase. The oxygen bonding shifts from a more covalent bond in SiO_2 to a more ionic bond in TiO_2 [12]. The second peak in the TiO_2 spectra can be assigned to the presence of water or hydroxyl groups at the surface of the coating, as often reported in the literature [9,13].

XRD measurements confirm that all as-deposited samples are amorphous. After annealing for 4 hours at 400 °C, XRD spectra of SiO_2/TiO_2 mixtures, shown in Figure 5, indicate that only TiO_2 crystallizes and that rutile and anatase phases are present. In high index mixtures, TiO_2 precipitates. The size of anatase particles, calculated from the broadening of the peaks, is 39 nm for pure TiO_2, 37 nm for the highest index mixture, and 13 nm for the mixture with n = 2.08. When annealing, the TiO_2 groups diffuse to form a crystal, leaving behind a TiO_2-poor region. When the SiO_2 content in the mixture is higher, the supply of TiO_2 is exhausted more rapidly, explaining formation of smaller particles. In SiO_2-rich mixtures, there is no precipitation of TiO_2; this suggests that there is no region containing only TiO_2 to initiate crystallization, confirming that SiO_2/TiO_2 mixtures consist of a single phase.

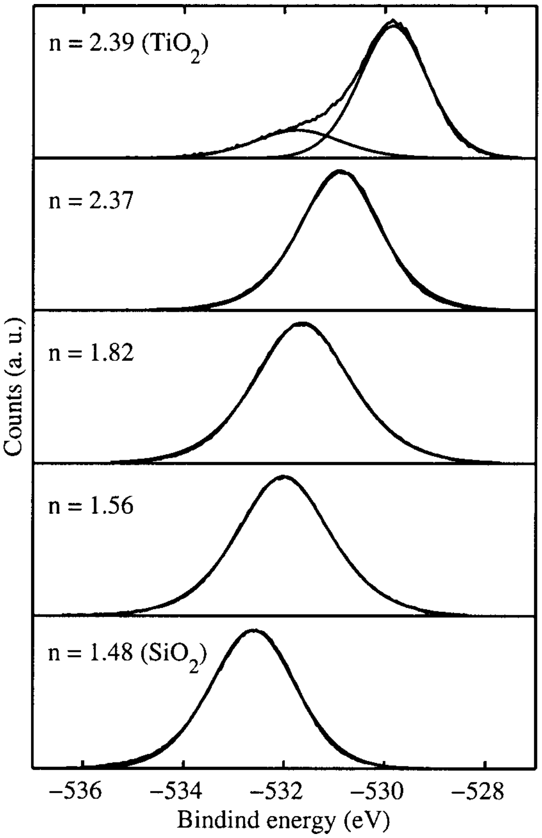

Figure 4: O(1s) XPS spectra of SiO_2/TiO_2 mixtures.

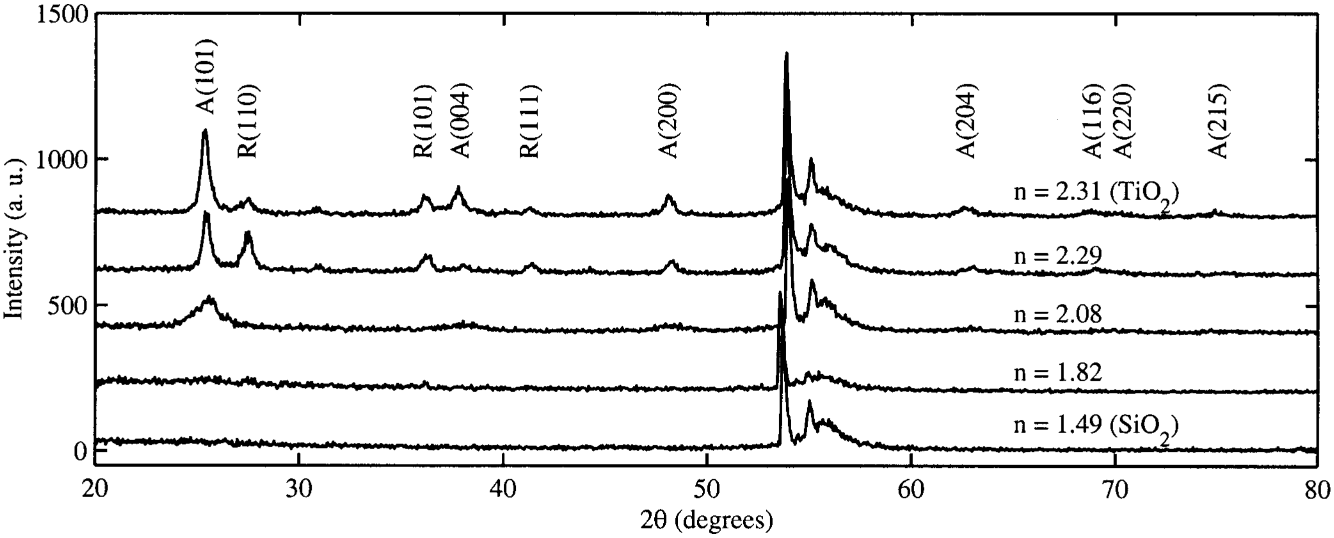

Figure 5: XRD spectra of SiO_2/TiO_2 mixtures after annealing for 4 hours at 400 °C. Anatase (A) and rutile (R) planes are indicated. Peaks between 50° and 60° are due to the crystalline Si substrate.

Monitoring

In the second part, we describe results illustrating the monitoring technique explained above. Example is shown for three attempts to fabricate the rugate filter shown in Figure 1 using the materials described above. The transmission spectra of the obtained filters are shown in Figure 6. In the three cases, the rejection band minimum was obtained between 550 nm and 560 nm, close to the design value of 550 nm. Differences between the expected and obtained spectra can be explained in terms of (1) local and (2) global errors.

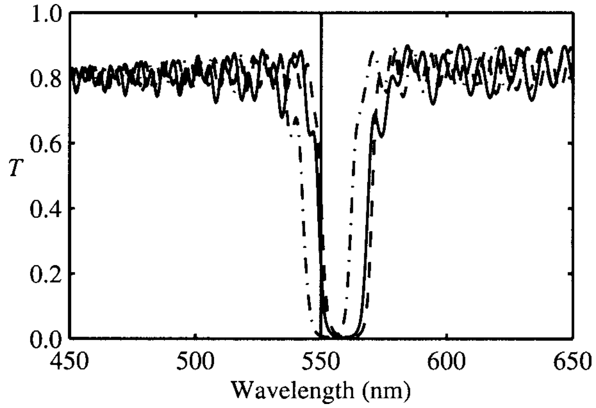

Figure 6: Transmission spectra of the three rugate filters deposited using the new monitoring technique.

(1) Local errors cause deviations of the index profile at a given moment during the deposition, but do not affect the overall optical thickness. They can change the shape of the index profile, affecting the shape of the rejection band or its reflective power, but not its position. Local errors are expected to arise when depositing high or low index mixtures. At those moments, the approximation using a single homogeneous layer is apparently very coarse.

In the present case, we observed a small underestimation of the optical thickness in the low index regions, and a small overestimation of the optical thickness in the high index regions. Those errors probably affected the sinusoidal shape of the index profile and, therefore, appropriate elimination of harmonics, a typical property of the rugate filter.

(2) Global errors can affect the overall optical thickness of the filter. They can, therefore, change the position of the rejection band. Two possible global error sources can be:
   a) The uniformity of the sample. If the uniformity is not sufficient, the band might be shifted between the position where the monitoring is done, and the position where the transmission measurement is performed.
   b) An error in the calibration of the incidence angle used during the monitoring. At an angle of incidence of 75°, an error of 1° would cause a change of 0.2 % on the optical thickness of the filter.

In the present case, a 2 % global error is necessary to explain the 10-nm shift observed in the position of the rejection band. During our experiment the uniformity was better than 1.5 % in a 1-inch radius around the monitoring position and cannot explain the shift in the position of the band. Also, although it is difficult to calibrate the incidence angle on a transparent substrate, a precision better than 0.5 ° can easily be obtained and the calibration of the angle of incidence cannot explain the experimental error.

At this moment, we cannot easily explain the differences between the expected and the experimental spectra of the rugate filters. However, we plan to study in more detail the capabilities and limitations of the new monitoring technique.

CONCLUSIONS

We have shown that FTIR and XPS spectra of SiO_2/TiO_2 mixtures indicate a single-phase material. The behavior of those mixtures upon annealing is also consistent with a single-phase material. These properties make SiO_2/TiO_2 mixtures deposited by PECVD suitable for the fabrication of optical filters for which uniform and isotropic microstructure is necessary.

We have proposed a new monitoring technique for the fabrication of rugate filters. This technique, based on the fitting of ripples outside of the band does not provide any information about the index profile, but it provides a control of the optical thickness. A good opportunity appears to combine this monitoring technique with the GVI approach to obtain information about both the index profile and the optical thickness.

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