Hollow glass waveguides with three-layer dielectric coating fabricated by chemical vapor deposition

Yuji Matsuura and James A. Harrington

Fiber Optic Materials Research Program, Rutgers University, P.O. Box 909, Piscataway, New Jersey 08855-0909

Received July 3, 1996; revised manuscript received October 30, 1996; accepted December 19, 1996

Hollow glass waveguides with three dielectric layers are fabricated with a chemical vapor deposition technique. The waveguides have an inner three-layer stack of aluminum oxide and titanium oxide, with the thickness optimized for the 3-μm wavelength of a Er:YAG laser. The measured attenuation spectra of the waveguides in the mid-infrared region show interference peaks that are due to the multiple dielectric layers and also exhibit a low-loss region at the design wavelength of 3 μm. The theoretical evaluation of the waveguide loss, including the inner surface roughness of the guide, shows that the roughness strongly affects the transmission losses of the multilayer-coated waveguides.
[S0740-3232(97)01206-4]

1. INTRODUCTION

A variety of medical and industrial applications involving mid-infrared (IR) laser radiation have been proposed and developed. An Er:YAG laser oscillating at a wavelength of 2.94 μm and a CO_2 laser operating in the 10-μm region are the most popular lasers for surgery, dentistry, and machine welding and cutting. Many applications of the these lasers, however, have been limited by the lack of robust and flexible fiber optic delivery systems because the silica-based, conventional optical fibers do not transmit mid-IR light beyond ~2 μm.

Hollow waveguides with internal metallic and dielectric layers are robust and have a broadband capability covering both the 3-μm Er:YAG and the 10-μm CO_2 laser light.[1,2] We have developed small-bore, hollow glass waveguides with bore sizes from 250 to 1000 μm, consisting of a metallic and a dielectric coating inside silica capillary tubing.[3] At 10.6 μm, the waveguides exhibit a low measured loss that is nearly equal to the loss calculated for the HE_{11} mode. However, the waveguides show a loss greater than expected at shorter wavelengths. One of the most effective methods to reduce the loss of dielectric-coated metal waveguides is to deposit multiple dielectric layers over the metal. Miyagi and Kawakami showed that a multiple stack of dielectric films could lower the attenuation by a factor of 10 or more.[4]

A variety of fabrication methods have been used for making dielectric-coated metal waveguides. Miyagi *et al.* developed a fabrication method that involves sputtering and electroplating coatings on leachable hollow mandrels.[5] They succeeded in fabricating hollow metallic waveguides with internal Ag and ZnS coatings with low attenuation losses at the CO_2 laser wavelength of 10.6 μm.[2] Another fabrication method employed by Croitoru *et al.* uses a liquid-phase process (conventional mirror plating followed by iodination) to form Ag and AgI films on the inner surface of hollow plastic waveguides.[6] These methods are not readily suitable, however, for depositing multiple dielectric layers. The sputter-plating method is too complex to be used effectively to form multilayers, and the liquid-phase method limits the number of dielectric materials that can be deposited to only a few metal halides. A promising technique for multilayer deposition is the chemical vapor deposition (CVD) method. In our previous work we have used CVD to deposit single-layer ZnS and Al_2O_3 films with good optical quality inside a silica capillary tubing.[7]

CVD is a well-established process for the deposition of many elements and compounds.[8] Many kinds of high purity and epitaxial films have been fabricated with CVD processing. Therefore the CVD technique is a suitable method for forming an effective multiple dielectric that has the correct alternating combination of high- and low-refractive-index layers. In this paper we use ray-optics theory to evaluate losses of the multilayer-coated hollow waveguides, taking the surface roughness of each layer into account. We also describe the fabrication method for forming a multiple dielectric film with the CVD process. Finally, we describe the results of our experiments in the preparation of multiple layers of Al_2O_3 and TiO_2 coatings inside 700-μm bore silica tubing.

2. THEORETICAL EVALUATIONS

The theory that we will use for the design of multiple-dielectric-coated metal waveguides is based on an electromagnetic waveguide theory proposed by Miyagi and Kawakami.[4] Their paper shows that transmission losses of the dielectric-coated metal waveguides are drastically reduced when a multiple dielectric layer is formed instead of a single dielectric layer. On the basis of this theory, the simplest and most efficient multilayer structure is a three-dielectric-layer stack deposited on a metal layer. The dielectric films would consist of two dielectric materials with different refractive indices. More specifically, the structure should be a stack of dielectric films with low/high/low refractive indices ($n_L/n_H/n_L$). The optimum thicknesses of the first dielectric layer d_1, which is adjacent to the metal; the center layer d_2; and the layer adjacent to the air, d_3 are expressed as

$$d_1 = \frac{\pi}{k_0 a \sqrt{{n_L}^2 - 1}},$$

$$d_2 = \frac{\pi}{k_0 a \sqrt{{n_H}^2 - 1}},$$

$$d_3 = \frac{2}{\sqrt{{n_L}^2 - 1}ak_0} \times \tan^{-1}\left[\frac{{n_L}^2}{({n_L}^2 - 1)^{1/4}}\left(\frac{n_L}{n_H}\right)\sqrt{\frac{{n_H}^2 - 1}{{n_L}^2 - 1}}\right], \tag{1}$$

where k_0 is the wave number in vacuum and a is the bore diameter of the waveguide.

The attenuation constants of the waveguides would normally now be derived from the electromagnetic wave theory. The actual waveguides, however, usually have imperfections, such as a surface roughness, that are difficult to take account of by using the wave theory. To overcome this deficiency, Matsuura *et al.* proposed a simple ray-optics theory.[9] In this theory, transmission losses of hollow waveguides are evaluated from the attenuation constants of meridional rays transmitting in the waveguide, because the attenuation of skew rays are equal to the meridional rays in the first-order approximation when the angle θ between the ray and the central axis of the guide is small enough.[10] The power attenuation constant 2α is calculated as

$$2\alpha(\theta) = \frac{1 - R(\theta)}{a \cot \theta}, \tag{2}$$

where $R(\theta)$ denotes the power reflection coefficient of the transmitting light at the boundary between the air core and the waveguide's inner surface. For the HE_{11} mode, $R(\theta)$ is the average for s and p polarization. The attenuation of the HE_{11} mode is calculated from the corresponding transmitting angle,

$$\theta_0 = \tan^{-1}\frac{2u_0}{k_0 a}, \tag{3}$$

where u_0 is the first zero point of the Bessel function J_0.

Surface roughness existing inside hollow waveguides affects the transmission losses by reducing the reflection $R(\theta)$ in Eq. (2). As seen in Fig. 1, the effect of roughness on the reflected light is evaluated by considering the phase offset that is due to the displacement $f(x)$ of the actual surface from the perfect flat surface. For simplicity, it is assumed that the inclination of the surface is very small ($|f'(x)| \ll 1$) and that the surface roughness is much smaller than 1. The phase offset of the reflected light $\phi_r(x)$ and the transmitting light $\phi_t(x)$ at the boundary $f(x)$ are expressed as

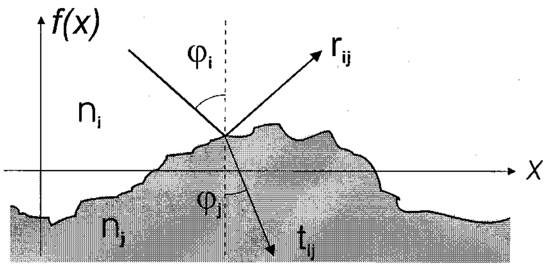

Fig. 1. Reflectance and transmittance of light incident on a rough boundary.

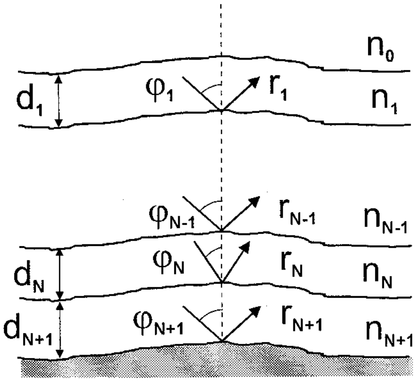

Fig. 2. Reflectance of a multilayer coating showing the key parameters used in our calculations.

$$\phi_r(x) = 2k_0 f(x) n_i \cos\varphi_i,$$

$$\phi_t(x) = k_0 f(x)(n_i \cos\varphi_i - n_j \cos\varphi_j), \tag{4}$$

where φ_i and φ_j are the angles of incidence and transmission, respectively, with respect to the normal to the surface. When the specular reflectance and transmittance coefficients r, t are expressed with use of the coefficients of the perfectly smooth surface ${r_{ij}}^0$, ${t_{ij}}^0$ (Ref. 11),

$$r_{ij} = {r_{ij}}^0 A_{ij},$$

$$t_{ij} = {t_{ij}}^0 B_{ij}. \tag{5}$$

A and B are

$$A_{ij} = \exp[-\tfrac{1}{2}(2k_0\sigma n_i \cos\varphi_i)^2],$$

$$B_{ij} = \exp\{-\tfrac{1}{2}[k_0\sigma(n_i\cos\varphi_i - n_j\cos\varphi_j)]^2\}, \tag{6}$$

where s is the RMS deviation of the surface from $f(x) = 0$, as shown in Fig. 1. To evaluate the power reflectance $R(\theta)$ of the multilayer structure shown in Fig. 2, we assumed that the roughness at the boundaries is the same as σ. The amplitude reflection coefficient at the $k{:}k + 1$ boundary is expressed as

$$r_k = r'_{k,k+1}A_{k,k+1} + \frac{(1 - r'^2_{k,k+1})B^2_{k,k+1}r_{k+1}\exp(-j\beta_{k+1})}{1 + r_{k,k+1}A_{k,k+1}r_{k+1}\exp(-j\beta_{k+1})},$$

$$\beta = 2k_0 n_k d_k \cos\varphi_k, \tag{7}$$

where d_k is the thickness of the kth layer. The reflectance R of an N-layer stack is calculated by using Eq. (7), with k set as $N, N - 1, \ldots, 0$.[12]

3. EXPERIMENT

The silica tubing used for the deposition of our CVD coatings has a bore size of 700 μm. First, a silver layer is deposited inside the silica tubing by use of our conventional, wet-chemistry, mirror-plating technology described in Ref. 3. This silver layer has a thickness of 0.3 μm, typical for the waveguides made entirely by the wet-chemistry methods.[4] Next, a three-layer dielectric stack is formed by using CVD methods to deposit Al_2O_3 and TiO_2. Al_2O_3 was chosen because we showed in a previous paper that CVD single-layer films of this material had good optical quality.[7] TiO_2 was selected as the other dielectric material because it has a higher refractive index (2.5) than Al_2O_3 (1.71). Because Al_2O_3 and TiO_2 are transparent at wavelengths shorter than 9 μm, they are suitable materials for the fabrication of waveguides transmitting 3-μm Er:YAG, 5-μm CO, and other mid-IR lasers.

The first layer of the dielectric stack is an Al_2O_3 film deposited on the Ag layer with use of the CVD setup shown in Fig. 3. As described in our previous paper, we used aluminum acetylacetonate (Al-acac) as the precursor.[13] A mixture of Ar carrier gas and water vapor are passed over the Al-acac, which is heated to 150 °C. The flow rates of the Ar carrier gas and the water vapor are 30 ml/min and 5 ml/min, respectively. The deposition pressure is 250 mmHg, which is controlled by a vacuum control system. The outer furnace is kept at 250 °C to prevent precipitation of the vapor, and the small internal furnace is heated to 420 °C for deposition of Al_2O_3. The internal heater is moved slowly over the glass tubing at a speed of 7.5 cm/min to ensure deposition of a film with uniform thickness. Our optimization calculations using Eq. (1) indicate that the thickness of the first Al_2O_3 layer should be 0.53 μm for operation at the 3-μm Er:YAG laser wavelength. To deposit this thickness requires ~1.5 hours for a 80-cm long silica tubing sample. This time was determined from a series of trial runs used to establish deposition rates and coating uniformity. The coating thickness had good reproducibility, with thickness fluctuations of less than 20%.

The second layer of TiO_2 is then deposited on the Al_2O_3 film with use of a metal-organic precursor, titanium isopropoxide (Ti-ipp), which is a liquid at room temperature. To produce a high deposition rate, the Ti-ipp is vaporized directly from a dilute liquid precursor. That is, the Ti-ipp solution is diluted with toluene to a concentration of 5%, because the higher concentrations cause a powdery nonadherent deposition.[14] The Ti-ipp solution is injected into a vaporizer by a peristaltic pump with a flow rate of 2–3 ml/min. The deposition pressure is controlled at 250 mmHg, and the flow rate of the Ar carrier gas is fixed at 30 ml/min. At a deposition temperature of 400 °C, a transparent and adherent TiO_2 film is deposited inside the glass tubing. The theoretical optimum thickness of the second layer for the 3-μm wavelength is 0.32 μm, and it takes around one hour to deposit this thickness.

Finally, an Al_2O_3 film with an optimum thickness of 0.33 μm is deposited as the third layer over the TiO_2. The combined three-layer dielectric stack exhibited an orange-to-red color as a result of interference effects. The adhesion of the films was checked by flowing dry air rapidly down the bore and also by repeated bending of the glass tube to a bending radius of 30 cm. We did not notice any peeling of the films during these simple tests, and therefore we found that the adhesion of the multiple-layered films appeared sufficient in the intended applications.

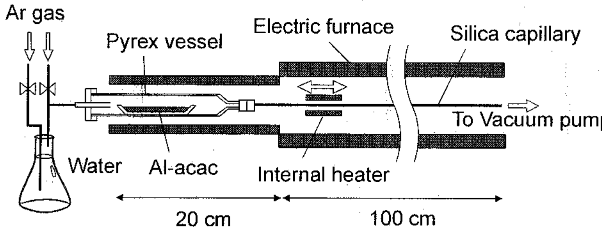

Fig. 3. CVD setup for the fabrication of Al_2O_3 films inside hollow glass waveguides.

4. RESULTS AND DISCUSSION

The transmission by the hollow glass waveguides with multiple dielectric layers is evaluated by using a Fourier transform IR spectrometer. In measuring the spectral losses, an incident beam with a large divergence angle (9.6° at FWHM) is used. This is in contrast to a laser measurement, in which the TEM_{00} mode is launched into the guides with a very small divergence angle (≈1° when a lens with $f/\# = 30$ is used). Therefore the losses obtained by using Fourier transform IR instrument are necessarily much higher than the losses that would be obtained if a laser were the source. This is because many higher-order modes are excited in the waveguides, owing to the large input angle. Using spectroscopic methods, we are also able to study the losses in short segments of waveguides that otherwise would be difficult to evaluate with a laser. The length of the waveguides measured in this work is limited, by the length of the furnace, to ~80 cm. Before measurement, 15-cm long pieces are cut from each end, because the film tends to be thinner at the ends than at the center.

Figure 4 shows the measured attenuation spectrum of the waveguide with the first layer, Al_2O_3. Theoretical losses calculated from Eqs. (2) and (7) are also shown. In the calculation, we assume that the absorption coefficient of the dielectric film is negligible; therefore the theoretical results shown in Fig. 4 are only for wavelengths shorter than 9 μm, where Al_2O_3 is transparent. We obtained the complex refractive index of Ag from Ref. 15 and used the bulk index of 1.71 for Al_2O_3. The coating thickness and surface roughness of the waveguide needed in the calculation are chosen so that the calculated data fit the measured values. The loss peak of the spectra at 3-μm wavelength is caused by the interference caused by the dielectric layer. From the peak wavelength of this band, the thickness of the Al_2O_3 layer is estimated to be 0.50 μm, which is close to the optimum value of 0.53 μm. The small loss peak at 7 μm is due to absorption of a carbon impurity that remains in the Al_2O_3 film, and the loss increase above 9 μm results from the anomalous dispersion of Al_2O_3. This means that the Al_2O_3 film is transparent at wavelengths shorter than 7 μm and that this material is suitable as a coating material for 3-μm Er:YAG laser energy. The surface roughness of the waveguides can be obtained from a fit of the theoretical spectrum to the measured spectrum. For the waveguide in Fig. 4 the RMS roughness σ is estimated to be 0.03 μm.

Figure 5 shows the measured and theoretical loss spectra after deposition of the second layer of TiO_2. The thickness of the TiO_2 layer is 0.31 μm, which is nearly equal to the optimum value of 0.32 μm. It was found that the surface roughness is the same as shown by the data shown in Fig. 4, or $\sigma = 0.03$ μm. The interference peak near 6 μm is shifted because of the difference of the thickness from the designed value. Though the deviation of the film thickness caused the slightly broad interference peaks, it did not affect the low-loss region near 4-μm wavelength.

In Fig. 6 we show the measured loss spectrum of the waveguide with all three dielectric layers. The thickness of the third layer, Al_2O_3, is estimated to be 0.32 μm. Because the measured spectrum shows the same overall behavior as that expected from the theoretical spectrum, we conclude that the newly developed CVD process provides an effective approach to depositing three dielectric layers rather uniformly within silica capillary tubing. It was also seen that the waveguide exhibits a low-loss region near the design wavelength of 3 μm. However, the loss at 3 μm is almost the same as the loss of the waveguides with only a single layer of Al_2O_3 (see Fig. 4). We conclude from this that the inner surface roughness of the waveguide affects the transmission loss more strongly in the multilayer-coated waveguides.

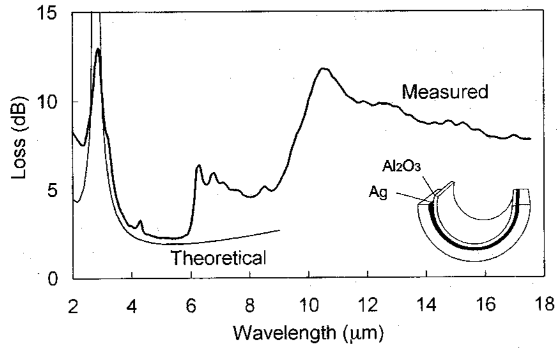

Fig. 4. Spectral losses of the hollow glass waveguide with a 700-μm bore and 50-cm length. The waveguide has an inner Al_2O_3 coating with an estimated thickness of 0.50 μm.

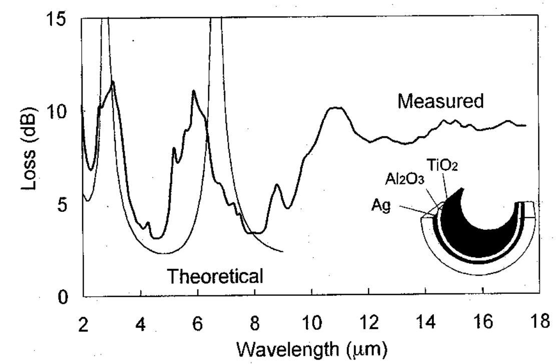

Fig. 5. Spectral losses of the Al_2O_3/TiO_2-coated waveguide. The estimated thickness of the films are 0.50 μm for Al_2O_3 and 0.31 μm for the TiO_2 layer.

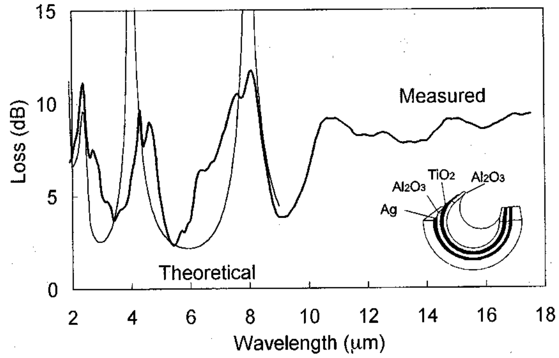

Fig. 6. Spectral losses of the hollow waveguide with three-layer, $Al_2O_3/TiO_2/Al_2O_3$, coating. The thickness of the third, Al_2O_3, layer is 0.32 μm.

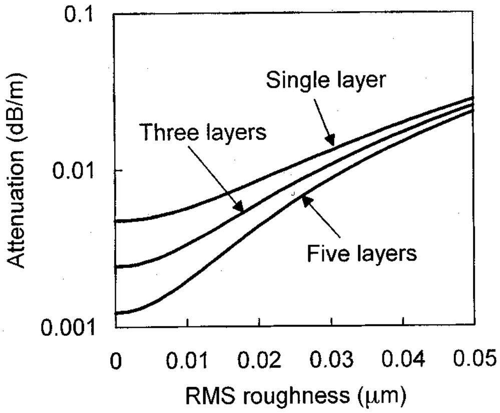

Fig. 7. Theoretical losses of the Al_2O_3/TiO_2 multilayer-coated waveguide and the Al_2O_3 single-layer-coated waveguide.

Figure 7 summarizes the theoretical attenuation for the HE_{11} mode at 2.94-μm wavelength in the hollow Ag waveguide with a $Al_2O_3/TiO_2/Al_2O_3$ three-layer coating, a five-layer coating, and an Al_2O_3 monolayer coating calculated with use of Eqs. (2) and (3). From this data we see that the loss predicted for the multilayer coating is substantially less than for the monolayer structure when the inner surface is smooth, i.e., when the RMS roughness is 0. However, in practice, the loss difference between the multilayer and the monolayer structures becomes less as the surface roughness increases. In fact, at our estimated surface roughness of 0.03, the loss difference can be seen from Fig. 7 to be rather small. Therefore, to realize the potential small loss for a multiple-dielectric-film hollow waveguide, it is essential to reduce the inner surface roughness. At present, the surface of the Ag film is somewhat rough, and it does not appear as shiny as a mirror. We are now working on the preparation of smoother Ag films deposited by the liquid-phase method. In some preliminary experiments we have been able to reduce the surface roughness by modifying the deposition conditions.

5. CONCLUSIONS

We have fabricated hollow glass waveguides with inner multiple dielectric layers, using CVD techniques. The waveguide is composed of a three-layer stack consisting of Al_2O_3 and TiO_2 layers with the thickness optimized for the 3-μm-wavelength of a Er:YAG laser. The measured loss spectra of the waveguide show a low-loss region near 3 μm, as expected. The losses for this three-layer structure, however, are much higher than our theory predicts. The reason for this is the surface roughness of the films. If this roughness could be lessened, then the losses could be lowered by as much as a factor of 2. We have shown that CVD methods can be successfully used to fabricate IR transmissive waveguides, but there are still some problems to overcome if we are to achieve the low loss predicted. Nevertheless, CVD offers a wide selection of potential coating material with good optical quality, and, furthermore, it is possible to fabricate much longer waveguides by applying this fabrication method simultaneously in a fiber drawing process. Therefore CVD presents great promise as a method of making the next generation of hollow glass waveguides with losses well below the current 0.1 dB/m for single-layer structures.

The corresponding author, James A. Harrington, can be reached by tel: 908-445-3932; fax: 908-445-4545; e-mail: jaharrin@rci.rutgers.edu.

REFERENCES

1. T. Abel, J. Hirsch, and J. A. Harrington, "Hollow glass waveguides for broadband infrared transmission," Opt. Lett. **19**, 1034–1036 (1994).
2. Y. Matsuura and M. Miyagi, "Er:YAG, CO, and CO_2 laser delivery by ZnS-coated Ag hollow waveguides," Appl. Opt. **32**, 6598–6601 (1993).
3. Y. Matsuura, T. Abel, and J. A. Harrington, "Optical properties of small-bore hollow glass waveguides," Appl. Opt. **34**, 6842–6847 (1995).
4. M. Miyagi and S. Kawakami, "Design theory of dielectric-coated circular metallic waveguides for infrared transmission," J. Lightwave Technol. **LT-2**, 116–126 (1984).
5. M. Miyagi, A. Hongo, Y. Aizawa, and S. Kawakami, "Fabrication of germanium-coated nickel hollow waveguides for infrared transmission," Appl. Phys. Lett. **43**, 430–432 (1983).
6. N. Croitoru, J. Dror, and I. Gannot, "Characterization of hollow fibers for the transmission of infrared radiation," Appl. Opt. **29**, 1805–1809 (1990).
7. Y. Matsuura and J. A. Harrington, "Infrared hollow glass waveguides fabricated by chemical vapor deposition," Opt. Lett. **20**, 2078–2080 (1995).
8. H. O. Pierson, *Handbook of Chemical Vapor Deposition* (Noyes, Park Ridge, Ill., 1992).
9. Y. Matsuura, M. Saito, M. Miyagi, and A. Hongo, "Loss characteristics of circular hollow waveguides for incoherent infrared light," J. Opt. Soc. Am. A **6**, 423–427 (1989).
10. M. Miyagi, "Waveguide loss evaluation in circular hollow waveguides and its ray optical treatment," J. Lightwave Technol. **LT-3**, 303–307 (1985).
11. H. E. Bennett, "Specular reflectance of aluminized ground glass and the height distribution of surface irregularities," J. Opt. Soc. Am. **53**, 1389–1394 (1963).
12. M. Born and E. Wolf, *Principles of Optics* (Pergamon, New York, 1985).
13. T. Maruyama and S. Arai, "Aluminum oxide thin films prepared by chemical vapor deposition from aluminum acetylacetonate," Appl. Phys. Lett. **60**, 322–323 (1992).
14. Jian-Ping Lin, Jenqdaw Wang, and Rishi Raj, "Solution precursor chemical vapor deposition of titanium oxide thin films," Thin Solid Films **204**, L13–17 (1991).
15. E. D. Palik, ed., *Handbook of Optical Constants of Solids* (Academic, New York, 1985).