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Infrared Refractive Index and Extinction Coefficient of Polyimide Films[1]

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We have measured the transmittance of several polyimide ($C_{22}H_{10}N_2O_4$) films at wave numbers from 6000 to 500 cm^{-1} (wavelengths from 1.67 to 20 μm) using a Fourier-transform infrared (FT-IR) spectrometer. The free-standing polyimide films are made by spin coating and thermal curing processes. The thickness of the films ranges from 0.1 to 4 μm. In the nonabsorbing region from 6000 to 4000 cm^{-1}, the minimum transmittance caused by interference is used to obtain the refractive index for film thicknesses greater than 1 μm. The film thicknesses are determined by fitting the spectral transmittance using the refractive index. Molecular absorption strongly reduces the transmittance at wave numbers from 2000 to 500 cm^{-1}. The optical constants, i.e., the refractive index and the extinction coefficient, are determined from the measured transmittance for several films of different thickness using a least-squares method. A Lorentzian oscillator model is also developed, which in general agrees well with the measured transmittance at wave numbers from 6000 to 500 cm^{-1}. This study will facilitate the application of polyimide films in the fabrication of infrared filters and other optoelectronic applications. The methods presented in this paper can be used to determine the optical constants of other types of thin-film materials.

KEY WORDS: Fourier transform infrared spectrometer (FT-IR); infrared filters; optical constants; polyimide films; radiative properties; refractive index; transmittance.

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1. INTRODUCTION

Polyimide films have received much attention due to their mechanical strength, low thermal expansion coefficient, and low dielectric constant [1, 2]. The applications of polyimide range from optoelectronics to X-ray astronomy [1–10]. The standard fabrication method includes a spin coating from solution followed by a thermal curing to induce imidization [3, 4]. Molecular beam deposition and ionized beam deposition have also been used to produce polyimide films [5, 6].

Frenkel and Zhang [11] reported the development of neutral-density infrared filters using metallic coatings on polycarbonate thin films (≈ 100 nm thick) to eliminate transmittance variation caused by interference effects in the conventional dielectric substrates of thickness on the order of 1 mm. Because polyimide possesses larger tensile strength and can withstand higher temperatures than polycarbonate, it may be a better candidate for fabrication of neutral-density infrared filters [4]. Knowledge of the optical constants (i.e., refractive index and extinction coefficient) is essential for the design of infrared filters. Fourier-transform infrared (FT-IR) spectrometers have been widely used to study the infrared absorption of polyimides. Most studies, however, have dealt with the locations of the absorption peaks rather than the magnitudes of the refractive index and the extinction coefficient [5–7]. Saito et al. [8] obtained the optical constants of several polymer coatings from the measured transmittance, with a limited wavelength range from 2 to 12 μm.

This paper presents the infrared transmittance measurements of five polyimide films using an FT-IR spectrometer. Different methods are used to determine the optical constants and thickness of these films for infrared applications.

2. MEASUREMENTS

The polyimide ($C_{22}H_{10}N_2O_4$) films were made from a solution by spin coating and were cured with optimized time and temperature parameters to provide the best combination of strength and ductility [4]. The polyimide film was peeled from the substrate and mounted on a ring with an opening 15 mm in diameter, which defines the clear aperture for optical applications. The film thickness was measured with a surface profilometer. Table I lists the thicknesses of the five specimens used in the present study. The method of determining the film thickness from the transmittance spectrum is discussed in the following section.

A Bomem MB100 Fourier-transform infrared (FT-IR) spectrometer was employed to measure the transmittance from 6000 to 500 cm^{-1}. The

Table I. Thickness of the Polyimide Films Used in the Present Study, Where the ± Values Indicate Uncertainties

	Specimen No.				
	1	2	3	4	5
Measured with a profilometer (μm)	0.105 ± 0.01	0.198 ± 0.02	0.97 ± 0.10	2.34 ± 0.23	3.77 ± 0.38
Determined from transmittance (μm)	0.11 ± 0.01	0.20 ± 0.01	0.98 ± 0.01	2.45 ± 0.02	3.93 ± 0.03

spectrometer is equipped with an external SiC infrared source, a KBr-on-Ge beamsplitter, and a DTGS pyroelectric detector. The interferometer is sealed with ZnSe windows. No purge gases are used in the sample, detector, and source chambers. Therefore, H_2O and CO_2 absorption lines become visible in the response spectra. The effect is not significant for the transmittance (i.e., the ratio of the sample spectrum to the reference spectrum) since the specimens are thin and the time span between the sample and reference measurements is no more than a few minutes. Calibrations were made to eliminate the effects of detector nonlinearity and non-equivalent responsivity on the measurement accuracy [12, 13]. A sample holder with a 6-mm-diameter hole was used to limit the beam spot on the sample. The specimen was placed normal to the beam axis. The maximum beam divergence is ≈9.6° (f/3 optics). Calibration using a single-crystal optical-quality Si wafer showed that the uncertainty in transmittance is

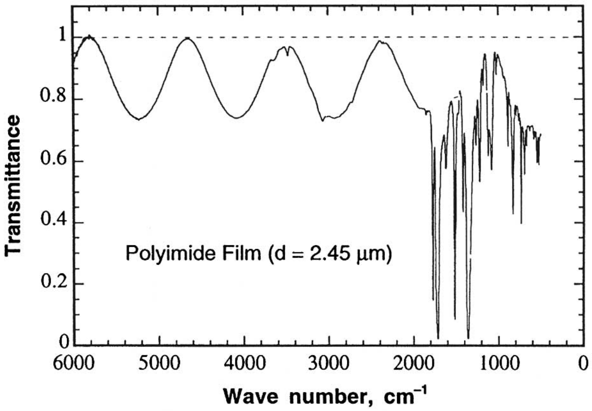

Fig. 1. Transmittance spectrum of a 2.45-μm-thick polyimide film.

0.01 (a coverage factor of 2, i.e., 95% confidence, is used in this paper). A spectral resolution of 2 cm^{-1} was used, and it took approximately 1 min to collect 10 scans.

The wave number accuracy was calibrated using a polystyrene film, certified by the National Institute of Standards and Technology [14]. The agreement of the peak wave numbers for the four absorption bands that are less sensitive to the peak-finding method is within 1 cm^{-1} by observing the wave numbers near the transmittance minima (absorption peaks). Figure 1 shows a typical transmittance spectrum for a 2.45-μm-thick polyimide film. At wave numbers greater than 2000 cm^{-1} the interference between the multiple reflected waves results in a periodic variation in the transmittance. The maximum transmittance is 1 between 6000 and 4000 cm^{-1}, indicating little absorption in this region. Both the interference effects and the absorption caused by molecular vibrations influence the transmittance at wave numbers less than 2000 cm^{-1}.

3. ANALYSIS

Consider a thin film of thickness d with optically smooth, parallel surfaces. The complex refractive index is $\bar{n} = n + i\kappa$, where the real part n is called the refractive index and the imaginary part κ is called the extinction coefficient. The optical constants, n and κ, are wavelength dependent. If the film thickness is much less than the coherence length of the incident radiation, the spectral transmittance is [15, 16]

$$T = \left| \frac{(1-r)(1+r)\,e^{i\delta}}{1 - r^2 e^{i2\delta}} \right|^2 \tag{1}$$

where r is the complex Fresnel's reflection coefficient at the air–film interface and δ is the complex phase change inside the film. At normal incidence, $r = (1-\bar{n})/(1+\bar{n})$ and $\delta = 2\pi\bar{n}\nu d$, where ν is the wave number of the incident radiation.

In the nonabsorbing region, $\kappa = 0$. Let $\rho = r^2 = [(1-n)/(1+n)]^2$, then

$$T = \frac{(1-\rho)^2}{1 + \rho^2 - 2\rho\cos(4\pi n\nu d)} \tag{2}$$

For a given material and film thickness, the transmittance oscillates as the wave number changes because of interference effects, as shown in Fig. 2. The wave numbers corresponding to the transmittance maximum and minimum are $\nu_{\text{max},m} = m/(2nd)$ and $\nu_{\text{min},m} = (m + \frac{1}{2})/(2nd)$, respectively, where the integer $m = 0, 1, 2, \ldots$ [16]. The free spectral range is the spacing

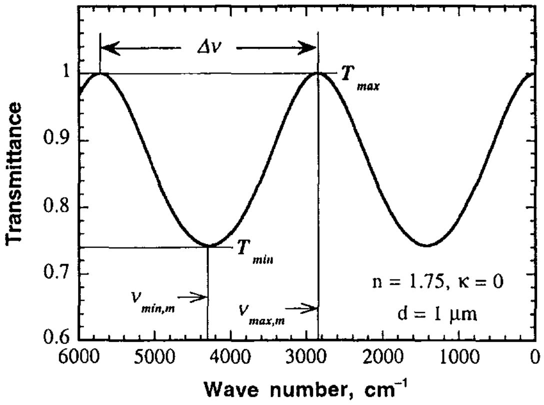

Fig. 2. Predicted transmittance for a 1-μm-thick film with $n = 1.75$ and $\kappa = 0$.

between two wave numbers at the adjacent transmittance maxima, i.e., $\Delta\nu = (2nd)^{-1}$. Note that $T_{\max} = 1$ and $T_{\min} = [2n/(1 + n^2)]^2$. The measured $T_{\min}$ can be used to determine the refractive index n, and the measured $\Delta\nu$ can then be used to determine the film thickness d. The refractive index changes little for $6000 \text{ cm}^{-1} > \nu > 4000 \text{ cm}^{-1}$. A curve fit of the transmittance in this spectral region to Eq. (2) determines both n and d. The curve-fitting method takes advantage of the numerous data points in the transmittance spectrum and, therefore, reduces the uncertainty caused by the measurement. The free spectral range increases as the film thickness decreases. For a film thickness equal to or less than ± 0.2 μm, the wave number corresponding to the first transmittance minimum is greater than 6000 cm^{-1}. For the three thicker specimens, the resulting refractive index is 1.75 ± 0.01 at wave numbers between 6000 and 4000 cm^{-1}, within the uncertainty of the measured transmittance. Note that a change of 0.01 in n results in a change of ≈ 0.005 in $T_{\min}$ for $n \approx 2$. The thicknesses of the two thinner specimens are determined by fitting the transmittance spectra using the average refractive index obtained from the thicker specimens. The thicknesses of the five specimens obtained from the transmittance are listed in Table I, which agree with the data measured with a surface profilometer within the overall uncertainties of the two methods. For films thicker than 1 μm, the spectroscopic method is more accurate than the direct measurement with the surface profilometer.

In the absorbing region ($\nu < 2000 \text{ cm}^{-1}$), the wavelength-dependent n and κ can be determined from Eq. (1) using the spectral transmittance of two films (of different thicknesses). Due to the experimental uncertainty, the solution does not always exist, especially in the strongly absorbing bands. Therefore, a multiple-parameter least-squares fitting program is employed [17]. It determines the best fitting parameters by minimizing the quantity chi-square defined as

$$\chi^2(\nu) \equiv \sum_{j=1}^{M} \left(\frac{T_{\mathrm{m}}(\nu, d_j) - T_{\mathrm{c}}(\nu, d_j; n, \kappa)}{\sigma_{\mathrm{m}}} \right)^2 \tag{3}$$

where T_{m} and σ_{m} are the measured transmittance and its standard deviation, M is the total number of specimens (five in the present study), and T_{c} is the transmittance calculated from Eq. (1). The computer program determines the n and κ values that minimize χ^2 for each wave number from an initial guess. Detailed discussions about the numerical algorithm can be found in Ref. 17. The standard deviation between the fitted and the measured transmittance is calculated by

$$\sigma_{\mathrm{st}} = \sim \sigma_{\mathrm{m}}[\chi^2/(M-1)]^{1/2} \tag{4}$$

For $M=5$ and $\sigma_{\mathrm{m}}=0.01$, $\sigma_{\mathrm{st}}=0.005$ for $\chi^2=1$ and $\sigma_{\mathrm{st}} \approx 0.03$ for $\chi^2=30$. The fitted and the measured transmittances agree extremely well for $4000\ \mathrm{cm}^{-1} > \nu > 500\ \mathrm{cm}^{-1}$, with an average χ^2 of 1.2 and a maximum χ^2 of 30.

The dielectric function is the square of the complex refractive index and can be modeled by a superposition of many Lorentzian oscillators, *viz.* [18],

$$\varepsilon(\nu) = [n(\nu) + i\kappa(\nu)]^2 = \varepsilon_\infty + \sum_{j=1}^{N} \frac{S_j \nu_j^2}{\nu_j^2 - \nu^2 - i\gamma_j \nu} \tag{5}$$

where ε_∞ is a real constant, N is the number of oscillators, and S_j, γ_j, and ν_j are the strength, the width, and the center wave number of the jth oscillator, respectively. Each oscillator corresponds to an absorption band, with its center wave number located at the absorption peak (transmittance minimum). By comparing the measured transmittance with that calculated from the Lorentz model for all specimens, the best-fitting parameters (i.e., ε_∞, S_j's, γ_j's, and ν_j's) can be obtained. Note that ε_∞ is almost equal to the square of the refractive index at $6000\ \mathrm{cm}^{-1}$, ν_j's are obtained directly from the measured transmittance minima, and S_j's and γ_j's are estimated using the n and κ values obtained from the least-squares method [19]. The large number of the Lorentzian oscillators makes a least-squares fit impractical. Hence, the fit-by-eyes method is used to improve the agreement between the calculated and measured transmittance, which requires a large amount of time and fine adjustments to obtain the best-fitting parameters. Because S_j and γ_j are directly related to the width and height of each individual band, the resulting parameters are unambiguous. The Lorentz model is in good agreement with the experimental results, except for a few nonsymmetric absorption bands.

4. RESULTS AND DISCUSSION

The measured transmittance and that calculated from the Lorentz model with 31 oscillators are shown in Fig. 3 for $6000\ \mathrm{cm}^{-1} > \nu > 2000\ \mathrm{cm}^{-1}$ and Fig. 4 for $2000\ \mathrm{cm}^{-1} > \nu > 500\ \mathrm{cm}^{-1}$. The fitted parameters for the Lorentz model are listed in Table II. The transmittance calculated using the optical constants obtained from the least-squares method is not shown since it is almost the same as the measured value.

As shown in Fig. 3, absorption by CO_2 (near $2350\ \mathrm{cm}^{-1}$) and by H_2O (in the region $3900\ \mathrm{cm}^{-1} > \nu > 3600\ \mathrm{cm}^{-1}$) is discernible. A nitrogen gas or a CO_2-free dry air may be used to reduce the H_2O and CO_2 structures in the future. The data become noisier approaching $6000\ \mathrm{cm}^{-1}$ because of the rapid decrease in the signal near the cuttoff wave number. The difference between the measured and the calculated transmittances for the 0.98-μm-thick film near $4400\ \mathrm{cm}^{-1}$ is slightly greater than 0.01. This is because the same Lorentzian parameters are used for all films. The refractive index calculated from the Lorentz model is 1.75 at $6000\ \mathrm{cm}^{-1}$ and reduces to 1.73 at $2500\ \mathrm{cm}^{-1}$. The extinction coefficient is less than 0.001 for $6000\ \mathrm{cm}^{-1} > \nu > 2500\ \mathrm{cm}^{-1}$, except near the center wave numbers. The extinction coefficients at the center wave numbers are $\kappa(\nu_{28}) = 0.004$, $\kappa(\nu_{29}) = 0.006$, $\kappa(\nu_{30}) = 0.005$, and $\kappa(\nu_{31}) = 0.003$. The refractive index

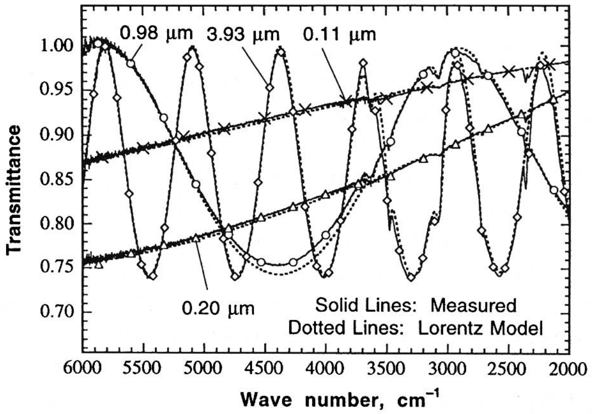

Fig. 3. Measured and calculated transmittance for $2000\ \mathrm{cm}^{-1} < \nu < 6000\ \mathrm{cm}^{-1}$. Note that the markers are used for identification and the actual data intervals are $\approx 1\ \mathrm{cm}^{-1}$.

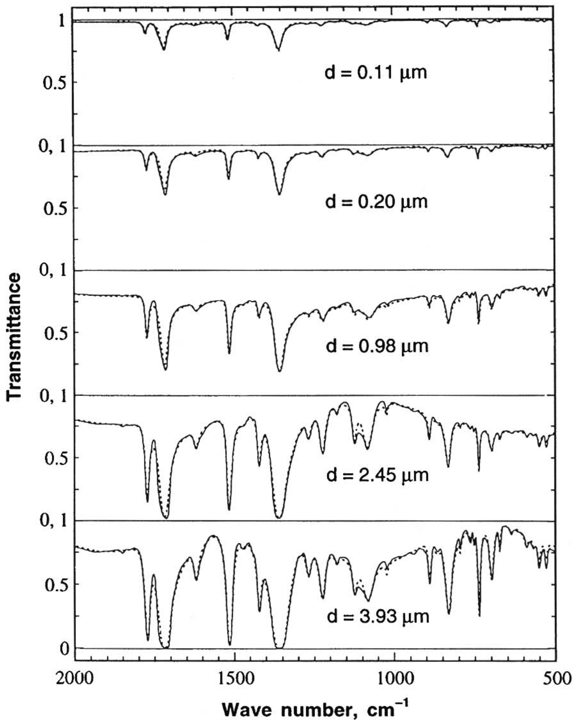

Fig. 4. Transmittance of all five samples for 500 cm^{-1} < ν < 2000 cm^{-1}. Solid lines are measured and dotted lines are calculated from the Lorentz model.

obtained by Saito et al. [8] is 1.59 for a polyimide coating 2.12 μm thick, which is 10% lower than the value obtained in the present study. Whether this difference is caused by the different processing conditions or measurement methods needs further investigation. Goeschel et al. [10] measured the refractive index of several polyimide samples at 0.633-μm using a He–Ne lasers and observed a large anisotropy between the in-plane and the out-of-plane refractive indices. The average refractive index is 1.76, which compares well with the present study. The radiation in the FT-IR spectrometer is assumed to be randomly polarized [10]. The issue of polarization dependence of the optical constants merits further investigation.

The transmittance spectra in the absorbing region are stacked in Fig. 4. The agreement between the Lorentz model and the experimental data is quite good, except for several asymmetric absorption bands near 1700 and 1100 cm^{-1}. The model overpredicts the transmittance for the 3.93-μm-thick film near 500 cm^{-1}, indicating that additional oscillators

Table II. Fitted Parameters for the Lorentzian Oscillator Model ($\varepsilon_\infty = 3.075 \pm 0.03$), Where the Uncertainties are Estimated to be 1 cm^{-1} for ν_j and 10 % for S_j and γ_j

j	ν_j (cm^{-1})	γ_j (cm^{-1})	S_j
1	529.5	8	0.004
2	551	10	0.0065
3	568	10	0.002
4	590	14	0.0035
5	636.5	10.5	0.001
6	673	5.5	0.0018
7	698.5	12.5	0.01
8	736.5	6.5	0.0106
9	752	3	0.00035
10	763.5	8	0.0008
11	795.5	5	0.0007
12	832	17	0.02
13	865.5	18	0.0016
14	890	8.5	0.0035
15	1023	9	0.001
16	1082.5	35	0.016
17	1123	14	0.004
18	1177.5	10	0.00065
19	1224	19	0.0068
20	1267	17	0.0025
21	1356	25	0.06
22	1421	11	0.0032
23	1472	15	0.0004
24	1515	10	0.011
25	1620	19	0.002
26	1717	20	0.026
27	1773	10.5	0.0054
28	2718	40	0.00018
29	3070	80	0.00055
30	3476	40	0.00017
31	3630	80	0.00025

exist below 500 cm^{-1}. The center wave numbers of the Lorentzian oscillators correspond to the absorption peaks due to molecular vibration. The identification and assignment of the vibration modes are beyond the scope of the present study. A detailed discussion can be found in the work of Ishida and Huang [7]. Many of the absorption peaks reported by Ishida and Huang [7] agree with the present study.

Figure 5 compares n and κ obtained from the least-squares method and the Lorentz model for 2000 $\mathrm{cm}^{-1} < \nu < 500$ cm^{-1}. The extinction coefficients obtained from the two methods agree very well, whereas there

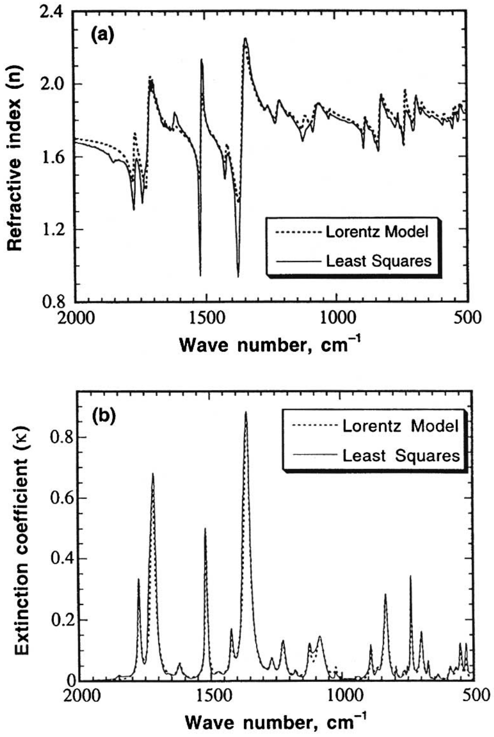

Fig. 5. Optical constants obtained from the least-squares method and from the Lorentz model: (a) refractive index n; (b) extinction coefficient κ.

appears to be a larger discrepancy in the refractive index near 1515 cm^{-1} and 1356 cm^{-1}. The transmittance predicted by the Lorentz model agrees fairly well with the experiments, suggesting that the transmittance is much more sensitive to κ than to n. Reflectance measurement may improve the accuracy in the determination of the n values within these spectral bands. The dielectric function of Eq. (5) can easily be programmed using the parameters listed in Table II for infrared design applications.

5. CONCLUSION

The optical constants of polyimide films are determined based on the transmittance measured by an FT-IR spectrometer at wave numbers from 6000 to 500 cm^{-1}. Several methods are used to infer the wavelength-dependent refractive index and extinction coefficient. The interference effects are used to determine the refractive index and film thickness in the weakly absorbing region (6000 to 4000 cm^{-1}). A least-squares method is used to determine n and κ in the absorbing region (2000 to 500 cm^{-1}). A Lorentzian oscillator model is developed by fitting the transmittance between 6000 and 500 cm^{-1}. The results show that the refractive index and extinction coefficient are thickness independent for specimen thicknesses from 0.11 to 4 μm. The optical constants obtained from this study can be applied to design infrared filters and other optoelectronics devices. The methods presented in this paper can be used to determine the optical constants of other types of thin-film materials.

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REFERENCES

1. A. M. Wilson, in *Polyimides: Synthesis, Characterization and Applications*, K. L. Mittal, ed. (Plenum, New York, 1984), Vol. 2, p. 715.
2. T. Verbiest, D. M. Burland, M. C. Jurich, V. Y. Lee, R. D. Miller, and W. Volksen, *Science* **268**:1604 (1995).
3. R. Wolf, H.-G. Birken, and C. Kunz, *Appl. Opt.* **31**:7313 (1992).
4. F. R. Powell, R. A. M. Keski-Kuha, M. V. Zombeck, R. E. Goddard, G. Chartas, L. K. Townsley, E. Möbius, J. M. Davis, and G. M. Mason, in *Grazing Incidence and Multilayer X-Ray Optical Systems*, Vol. 3113, R. B. Hoover and A. B. Walker, eds. (SPIE, Bellingham, WA, 1997), pp. 432-440.
5. K. W. Kim, C. E. Hong, S. C. Choi, S. J. Cho, C. N. Whang, T. E. Shim, and D. H. Lee, *J. Vac. Sci. Technol.* **A12**:3180 (1994).
6. C. D. Dimitrakopoulos, S. P. Kowalczyk, and K.-W. Lee, *Polymer* **36**:4983 (1995).
7. H. Ishida and M. T. Huang, *Mikrochim. Acta* **51A**:319 (1995).
8. M. Saito, T. Gojo, Y. Kato, and M. Miyagi, *Infrared Phys. Technol.* **36**:1125 (1995).
9. T. C. Kowalczyk, T. Z. Kosc, K. D. Singer, A. J. Beuhler, D. A. Wargowski, P. A. Cahill, C. H. Seager, M. B. Meinhardt, and S. Ermer, *J. Appl. Phys.* **78**:5876 (1995).
10. U. Goeschel, H. Lee, D. Y. Yoon, R. L. Siemens, B. A. Smith, and W. Volksen, *Colloid Polymer Sci.* **272**:1388 (1994).
11. A. Frenkel and Z. M. Zhang, *Opt. Lett.* **19**:1495 (1994).
12. Z. M. Zhang, L. M. Hanssen, J. J. Hsia, R. U. Datla, C. Zhu, and P. R. Griffiths, *Mikrochim. Acta Suppl.* **14**:315 (1997).
13. M. I. Flik and Z. M. Zhang, *J. Quant. Spectrosc. Radiat. Transfer* **47**:293 (1992).
14. D. Gupta, L. Wang, L. M. Hanssen, J. J. Hsia, and R. U. Datla, *Polystyrene Films for Calibrating the Wavelength Scale of Infrared Spectrophotometers—SRM 1921*, NIST SP 260-122 (U.S. Government Printing Office, Washington DC, 1995).
15. Z. M. Zhang, *J. Heat Transfer* **119**:645 (1997).

16. M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, Oxford, 1980), Chaps. 1, 13.
17. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran*, 2nd ed. (Cambridge University Press, Cambridge, 1992), Chap. 15.
18. C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983), Chap. 9.
19. Z. M. Zhang, B. I. Choi, M. I. Flik, and A. C. Anderson, *J. Opt. Soc. Am.* **B11**:2252 (1994).
20. Z. M. Zhang, L. M. Hanssen, and R. U. Datla, *Infrared Phys. Technol.* **37**:539 (1996).