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Refractive Index Dispersion in Semiconductor-related Thin Films

Abstract: A technique is described for determining refractive index dispersion throughout the uv-visible spectrum in semiconductor-related transparent thin films. The dispersion constants that have been measured can be used in the design of optical systems and in photolithography. Measurements were made with the LASER-VAMFO interferometer. Calculations and analyses are also described which show the accuracy and repeatability of the technique. Data were taken for 28 different thin-film materials, and representative refractive index dispersion curves are shown for some of them. The dispersion constants for each material evaluated are also presented.

Introduction

In the design and fabrication of semiconductor devices, it is frequently important to know (or be able to obtain) the optical constants for a number of transparent thin-film materials. Some such films are used, for example, in device passivation, where optical thickness measurements are critical. Others are used in photolithographic processes, for which the design and control of processing systems depends on a knowledge of optical properties.

This paper describes an investigation of one such property, refractive index dispersion, in which the change in refractive index as a function of incident-light wavelength has been determined for twenty-eight different materials throughout the ultraviolet-visible spectrum.

An optical interference technique [1] employing the LASER-VAMFO (Variable-Angle Monochromatic Fringe Observation) [2,3] was used to calculate specific refractive indices at various light wavelengths for each film. With these data, refractive index dispersion constants were calculated by means of the Sellmeier dispersion equation [4].

Instrumentation

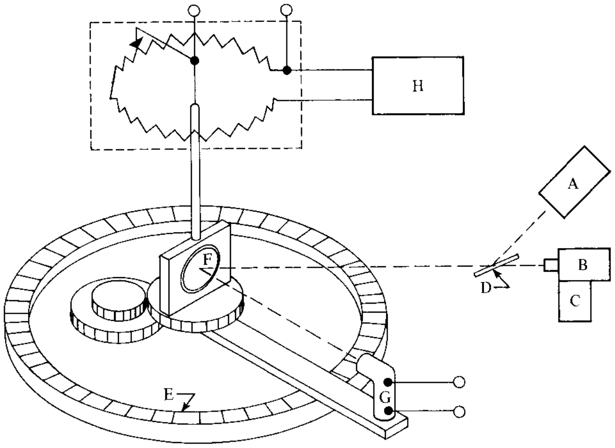
The LASER-VAMFO was used for these refractive index measurements; a schematic of the instrument is shown in Fig. 1. All films measured on that instrument, for this study, were on blank silicon-wafer substrates. Similar films were also coated on transparent quartz discs; optical transmission was determined with a uv-visible spectrophotometer. As an independent check on film thickness, a multiple-beam interference microscope was used on one of the LASER-VAMFO samples to confirm the reflected light order.

Film preparation

Films were prepared under conditions closely approximating those actually used in the photolithographic manufacturing process. Thermal oxides were grown at about 1000°C using dry oxygen and steam. Sputtered materials were deposited by both rf and dc reactive sputtering techniques [5,6]. Commercially available materials such as photoresists were coated as closely to the manufacturers' specifications as possible. Solvents used for other organic materials were conducive to the production of transparent thin films.

Since experience had shown that reflectance minima, as measured with the LASER-VAMFO, had the sharpest peaks and best resolution when they occurred at roughly 30 and 60 degrees of sample deflection (angle of light

Figure 1 Laser-VAMFO schematic. (A, He-Ne laser; B, monochromator; C, xenon lamp; D, removable mirror; E, goniometer; F, sample; G, detector; H, power supply.)



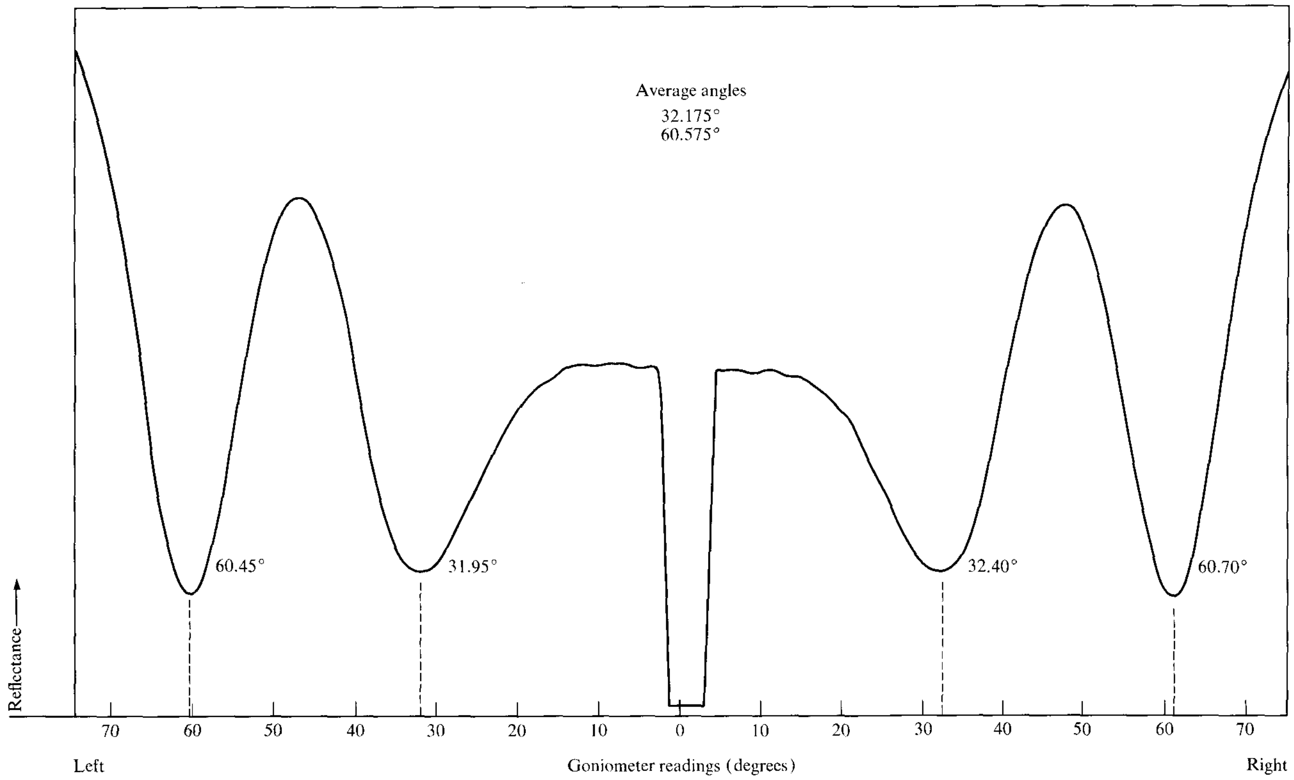


Figure 2 Typical reflectance trace.

incidence) on the goniometer, preparation conditions for each sample were adjusted to produce this optimum reflectance profile. However, the only parameter that was intentionally varied during preparation was film thickness, the variations being only a few thousand angstroms in most cases.

Measurement technique

All films were measured at room temperature, using the standard VAMFO [1] measurement technique. First, the LASER-VAMFO interferometer was checked to ensure correlation between its two light sources, the He-Ne gas laser and the Xe lamp monochromator. This was done simply by making a reflectance trace (of any sample) using the laser, then remeasuring that sample with the monochromator. The monochromator dial was set at 6328 Å when the traces were identical. All other necessary calibrations were inherent in the interferometer [3].

As previously stated, each film to be measured was prepared to a thickness such that a minimum reflectance would be observed at an angle of incidence of about 30° and another at about 60°, using the 6328.17 Å line from the He-Ne gas laser. A typical trace is shown in Fig. 2. With this trace, the exact thickness of the transparent film as well as the refractive index at the 6328-Å wavelength could be calculated according to the following equation:

$$d=\frac{N\lambda}{2(\mu^2-\sin^2 i)^{\frac{1}{2}}}, \tag{1}$$

where d is the film thickness in angstroms, N is the reflected light order, λ is the light wavelength in angstroms, μ is the refactive index of the film, and i is the angle of incidence with respect to the perpendicular. The effect of optical correction factors in this equation is not inherently negligible. However, at the film thickness and wavelengths used, the RMS error magnitude without optical correction in the computation was never greater than the calculated experimental error.

It should also be noted that in Fig. 2 each trace was checked for x-axis (angle) linearity. Over an entire scan linearity is ±0.05%, but when a given angle is read directly from the goniometer, the error in angle reading is improved by about an order of magnitude over the average error for a complete trace. With these angle readings and the self-calibrating angle technique of the LASER-VAMFO [3], the refractive index measurement was quite accurate, as will be demonstrated in the data section.

Table 1 Calculation of refractive index-thickness pairs at the laser wavelength (6328.173 Å).

Angle (degrees)	*Order*	*Refractive index*	*Thickness (Å)*
42.475	10.5	1.5820	23223.
65.450	9.5		
42.475	9.5	1.5230	22018.
65.450	8.5		
42.475	8.5	*1.4600*	20778.
65.450	7.5		
42.475	7.5	1.3960	19422.
65.450	6.5		
42.475	6.5	1.3280	17986.
65.450	5.5		

Table 2 Calculation of refractive index from next lower wavelength (5600 Å).

Angle (degrees)	*Order*	*Refractive index*	*Thickness (Å)*
65.025	10.5	1.5571	23223
65.025	9.5	1.5104	22018
65.025	8.5	*1.4607*	20778
65.025	7.5	1.4110	19422
65.025	6.5	1.3586	17986

Table 3 Measured refractive index vs wavelength for three samples of thermal oxide on silicon.*

		Refractive index	
Wavelength (Å)	1	2	3
6328	1.4602	1.4588	1.4585
5600	1.4610	1.4609	1.4601
5000	1.4645	1.4634	1.4619
4600	1.4665	1.4653	1.4646
4200	1.4694	1.4684	1.4678
3900	1.4726	1.4721	1.4715
3600	1.4776	1.4769	1.4768
3400	1.4816	1.4802	1.4796
3200	1.4849	1.4847	1.4831
3000	1.4898	1.4880	1.4879
2800	1.4964	1.4951	1.4959
2700	1.4992	1.4999	1.5001
2600	1.5039	1.5040	1.5038
2500	1.5091	1.5088	1.5104
2400	1.5147	1.5158	1.5153
2300	1.5216	1.5211	1.5197
2200	1.5280	1.5295	1.5290

*Silicon (111) wafers.
Film thickness: 20742 Å.
Preparation conditions:
15 minutes dry oxygen at 1100°C
8 hours, 5 minutes steam at 1100°C
5 minutes dry oxygen at 1100°C.

After the trace was drawn using the laser light (actually, five separate traces were made and the average used), a shorter wavelength from the Xe lamp monochromator made a similar trace of the same sample. Instrument sensitivity limited measurements to between 2100 and 6400 Å. The next lower wavelength used yielded a minimum reflectance at about a 60° incidence angle, which is one order higher than the same angle read from the laser trace. For example, the order at the 60° minimum for a 6328.17 Å laser trace is 7.5; the wavelength for the next trace was adjusted so the order at the 60° minimum was 8.5. The exact wavelength and angle were used for calculation after each trace was drawn.

The third lower wavelength used for measurement was determined by comparison to the previous trace. Again, it is that wavelength which yields a minimum reflectance at about 60°, which is one order higher than the previous trace. By this technique, the wavelength was reduced in varying steps until the film absorbed the incident light radiation, or until a wavelength of 2100 Å was reached.

Calculation

First, a calculation of thickness and refractive index was made for a number of orders within a refractive index range at the laser wavelength. An example is shown in Table 1. For each pair of minima a number of possible refractive index-thickness pairs was calculated.

To determine which pair was correct for the film that had been measured, we then used the next lower wavelength trace for the same sample. As described above, the monochromator trace was drawn so that order at the 60° angle was exactly 1.0 higher than the laser trace. Taking the thickness data shown in Table 1, a new refractive index calculation was made at the lower wavelength. These values are listed in Table 2. The correct value is that which *first* exceeds the corresponding refractive index value shown in Table 1, since these values will satisfy the Sellmeier dispersion equation [4]. (Care must be taken with this technique to ensure that the film will absorb neither the laser wavelength nor the next lower wavelength of light chosen for calculation.) As an additional check on the technique's validity, film thickness was measured independently with the multiple-beam interference microscope over a step placed in the film. The sloping step was metallized to make the measurement independent of refractive index and the order was observed. The accuracy of this technique was sufficient to select the correct thickness from Table 1. Now, along with the film thickness, the refractive index was also known for the first two wavelengths. The refractive index could then be calculated for each of the other measured wavelengths by rearranging Eq. (1) and solving for μ as a single un-

Table 4 Dispersion equation constants for measured films

Film	λ *Range* (*Å*)	*RMS calc. refractive index error*	A_1	A_2	L_1^2	L_2^2
Thermal oxide on silicon	2200-6328	0.0008	-2.0780×10^{12}	1.1012	3.5785×10^{14}	0.0085769
Oxidized boron-doped silicon	2250-6328	0.0012	1.1781×10^{13}	1.0994	-2.2057×10^{15}	0.0087831
Oxidized phosphorus-doped silicon	2250-6328	0.0010	-2.1145×10^{11}	1.0939	1.8876×10^{13}	0.0089495
Sputtered silica	2200-6328	0.0014	2.9699×10^{11}	1.1267	-4.5615×10^{14}	0.0085074
Sputtered aluminum oxide	2400-6328	0.0051	5.1372×10^{46}	1.4056	-1.3691×10^{48}	0.011570
Sputtered silicon nitride	2850-6328	0.0022	-1.0223×10^{11}	2.4513	6.9262×10^{11}	0.020236
Polyvinyl pyrrolidone	2900-6328	0.0041	6.0448×10^{37}	1.2415	-1.0193×10^{39}	0.012967
Polystyrene	3000-6328	0.0010	1.6212×10^{20}	1.3678	-1.2962×10^{21}	0.023755
Polyvinyl chloride	2150-6328	0.0014	4.3126×10^{10}	1.3025	-9.5994×10^{11}	0.012964
Polyvinyl chloride-polyvinyl acetate copolymer	2180-6328	0.0011	-1.9596×10^{12}	1.2938	4.8882×10^{13}	0.012809
Polyvinyl acetate	2150-6328	0.0060	-2.8112×10^{12}	1.0892	6.7540×10^{13}	0.011833
Polytrifluorostyrene	3050-6328	0.0017	1.8486×10^{24}	1.1861	-1.7096×10^{25}	0.021298
Neoprene rubber	2900-6328	0.0015	-5.0948×10^{12}	1.3001	6.2378×10^{13}	0.018678
S-5B pliolite rubber	3350-6328	0.0013	-5.6063×10^{11}	1.3683	5.8135×10^{12}	0.022297
Cyclized polyisoprene	2850-6328	0.0009	5.0723×10^{18}	1.2575	-6.6945×10^{19}	0.016258
Polyvinyl cinnamate	4100-6328	0.0016	3.0307×10^{16}	1.4044	-2.0679×10^{17}	0.037579
Phenol formaldehyde Resin	4000-6328	0.0034	-1.2404×10^{11}	1.4762	1.6929×10^{12}	0.025015
Polyvinyl alcohol	2180-6328	0.0210	1.0047×10^{12}	1.2964	-1.4645×10^{13}	0.011605
Kodak KTFR photoresist	4000-6328	0.0008	9.8742×10^{43}	1.2516	-9.5924×10^{44}	0.020935
Centrifuged Kodak KMER photoresist	4100-6328	0.0009	2.8425×10^{18}	1.2911	-3.3701×10^{19}	0.018892
Kodak KPR-4 photoresist	4400-6328	0.0014	-1.2344×10^{11}	1.3568	5.4527×10^{11}	0.041268
Kodak KOR photoresist	4650-6328	0.0014	-1.0369×10^{15}	1.4852	-7.9352×10^{16}	0.041197
Kodak KAR-3 photoresist	4700-6328	0.0006	-1.4334×10^{11}	1.4034	5.7082×10^{11}	0.035607
Waycoat IC photoresist	4000-6328	0.0007	9.2453×10^{11}	1.2513	-7.4577×10^{12}	0.020708
AGFA copyrex D photoresist	3800-6328	0.0012	1.3715×10^{19}	1.2721	-1.6338×10^{20}	0.018290
Shipley AZ-1350H photoresist	4700-6328	0.0012	-1.4993×10^{11}	1.4005	5.9629×10^{11}	0.040679
Fast AZ-1350H photoresist	4700-6328	0.0015	3.8332×10^{14}	1.4193	-1.6955×10^{15}	0.040087
Shipley AZ-111 photoresist	4100-6328	0.0009	2.5747×10^{42}	1.3318	-1.4516×10^{43}	0.030805

known, since the order was increased by 1.0 for each succeeding calculation.

Thus, beginning with the laser trace, d, N, and μ are unknown. All three variables can be determined by calculation from and comparison to the analytical data taken at the laser wavelength and at least one other wavelength.

Data

An example of this technique's accuracy can be shown (Table 3) by comparing the calculated refractive index of thermal oxide on silicon with previously published data [7]. Accuracy is generally to the fourth decimal place. A total of 28 different semiconductor-related thin film systems were evaluated in the same manner as shown in Table 3. Three different samples were prepared and measured separately for each thin-film material. Five general classes of semiconductor-related thin films were analyzed:

1. Thermal oxides
2. RF-sputtered materials
3. Organic polymers
4. Basic photoresist polymers
5. Commercial and modified commercial photoresists

From data similar to that shown in Table 3 for each of the other thin films analyzed, the nonlinear plot was calculated by means of the Sellmeier dispersion equation [5-7]:

$$\mu = \left[1 + \frac{(A_1)(\lambda'^2)}{\lambda'^2 - L_1^2} + \frac{(A_2)(\lambda'^2)}{\lambda'^2 - L_2^2}\right]^{1/2}, \tag{2}$$

where A_1, A_2, L_1 and L_2 are constants to be determined, and $\lambda' = \lambda \times 10^{-4}$. These constants are listed in Table 4 for each of the thin films measured in the wavelength range specified. (Table 5 gives the relevant properties and preparation conditions for each material listed in Table 4.) Outside this range Eq. (2) fails, usually because the film absorbs the shorter wavelengths. The accuracy figure quoted for each material is the root mean square (rms) error from the three samples prepared. Figure 3 is a least-squares plot of refractive index dispersion. This curve follows the normal dispersion equation [Eq. (2)], while that in Fig. 4 does not, due to the absorbing characteristics of the sensitizer in the photoresist.

In some cases the thin film material properties described in Table 5 may not define all the criteria affecting refractive index. Therefore, Table 4 should be con-

Table 5 Film preparation conditions and thicknesses.*

Film	Thickness (Å)	Conditions
Oxidized boron-doped silicon	14943	Monsanto 100 silicon wafers Boron doped, P type, resisitivity 10-20 ohm centimeters 15 minutes dry oxygen at 1100°C 4 hours, 15 minutes steam at 1100°C 5 minutes dry oxygen at 1100°C
Oxidized phosphorus-doped silicon	15127	Monsanto 100 silicon wafers Phosphorus doped, N type, resistivity 1.0-2.0 ohm centimeters 15 minutes dry oxygen at 1100°C 5 hours steam at 1100°C 5 minutes dry oxygen at 1100°C
Sputtered silica	21681	Power 1.8 kW 2 μm pressure argon Deposition rate 260 angstroms per minute
Sputtered aluminum oxide	16402	Power 1.0 kW, bias 100 volts Gallium backed, preheat temperature of anode 150°C Run time 85 minutes
Sputtered silicon nitride	24789	Power 1.0 kW, 25 volts bias 4 μm pressure nitrogen Gallium backed run temperature 200°C Run time 3 hours
Polyvinyl pyrrolidone	16817	Molecular weight approximately 700,000 Bulk polymer dissolved in isopropyl alcohol Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 3300 rpm for 30 seconds Baked horizontally in 85°C air oven for 30 minutes
Polystyrene	18107	Molecular weight approximately 230,000 Bulk polymer dissolved in xylene Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 5000 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Polyvinyl chloride-polyvinyl acetate copolymer	15982	Approximately 6% polyvinyl acetate Bulk polymer dissolved in 1-1 tetrahydrofuran-cyclohexanone Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 3300 rmp for 30 seconds Baked 10 minutes on 100°C hot plate
Polyvinyl acetate	17426	Bulk polymer dissolved in 1-1 tetrahydrofuran-cyclohexanone Solution filtered through 5.0 μm Silicon wafer flooded, static start Spin coated at 5200 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Polytrifluorostyrene	16640†	Bulk polymer dissolved in 1-1 tetrahydrofuran-cyclohexanone Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 4000 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Neoprene rubber	16020	Bulk polymer dissolved in xylene Solution filtered through 10 μm Silicon wafer flooded, static start Spin coated at 5800 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
S-5B pliolite rubber	18388	Bulk polymer dissolved in xylene Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 5000 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Cyclized polyisoprene	16661	Polymer extracted from KTFR lot #6911-77 Bulk polymer dissolved in xylene Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 3300 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Polyvinyl cinnamate	17516	Bulk polymer dissolved in KOR thinner Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 3900 rpm for 30 seconds Baked 5 minutes on 100°C hot plate
Phenol formaldahyde resin	17874	Bulk polymer dissolved in AZ thinner Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 4700 rpm for 30 seconds Baked 30 minutes in air oven at 85°C
Polyvinyl alcohol	21047	Bulk polymer dissolved in water Solution centrifuged at 2500 rpm for one hour Silicon wafer flooded, static start Spin coated at 2000 rpm for 30 seconds Baked in 85°C air oven for 30 minutes
Centrifuged Kodak KMER photoresist	16324	Stock resist (lot #6911-157) centrifuged at 20,000 rpm for 90 minutes Resist diluted 2-1 in xylene, unfiltered Silicon wafer flooded, static start Spin coated at 4100 rpm for 30 seconds Baked 30 minutes on 100°C hot plate
Kodak KPR-4 photoresist	17613	Resist lot #7001-16 diluted 10-1 in KPR-4 thinner Solution not filtered Silicon wafer flooded, static start Spin coated at 5300 rpm for 30 seconds Baked 5 minutes on 100°C hot plate
Kodak KOR photoresist	17074	Stock resist, lot #38 Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 900 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Kodak KAR-3 photoresist	17335	Stock resist (MX 740-1), lot #3 Solution filtered through one μm Silicon wafer, flooded, static start Spin coated at 1350 rpm for 30 seconds Baked 30 minutes in 85°C air oven
Waycoat IC photoresist	16315	Stock resist lot #70211, unfiltred Silicon wafer flooded, static start Spin coated at 3000 rpm for 30 seconds Baked 30 minutes on 100°C hot plate
AGFA copyrex D photoresist	16374	Stock resist, experimental lot #1543, unfiltered Silicon wafer flooded, static start Spin coated at 3300 rpm for 30 seconds Baked 10 minutes on 100°C hot plate
Shipley AZ-1350H photoresist	17514	Stock resist lot #13034H Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 3500 rpm for 30 seconds Baked 30 minutes in 85°C air oven
Fast AZ-1350H photoresist	17382	Viscosity similar to AZ1350H Solution filtered through 0.8 μm Silicon wafer flooded, static start Spin coated at 3600 rpm for 30 seconds Baked 30 minutes in 85°C air oven
Shipley AZ-111 photoresist	15705	Stock resist lot #A11106 Solution filtered through one μm Silicon wafer flooded, static start Spin coated at 1800 rpm for 30 seconds Baked 30 minutes in 85°C air oven

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*Data for thermal oxide, polyvinyl chloride, and Kodak KTFR photoresist are given in Table 3, Fig. 3, and Fig. 4 respectively.
†One measurement also taken at 13983.

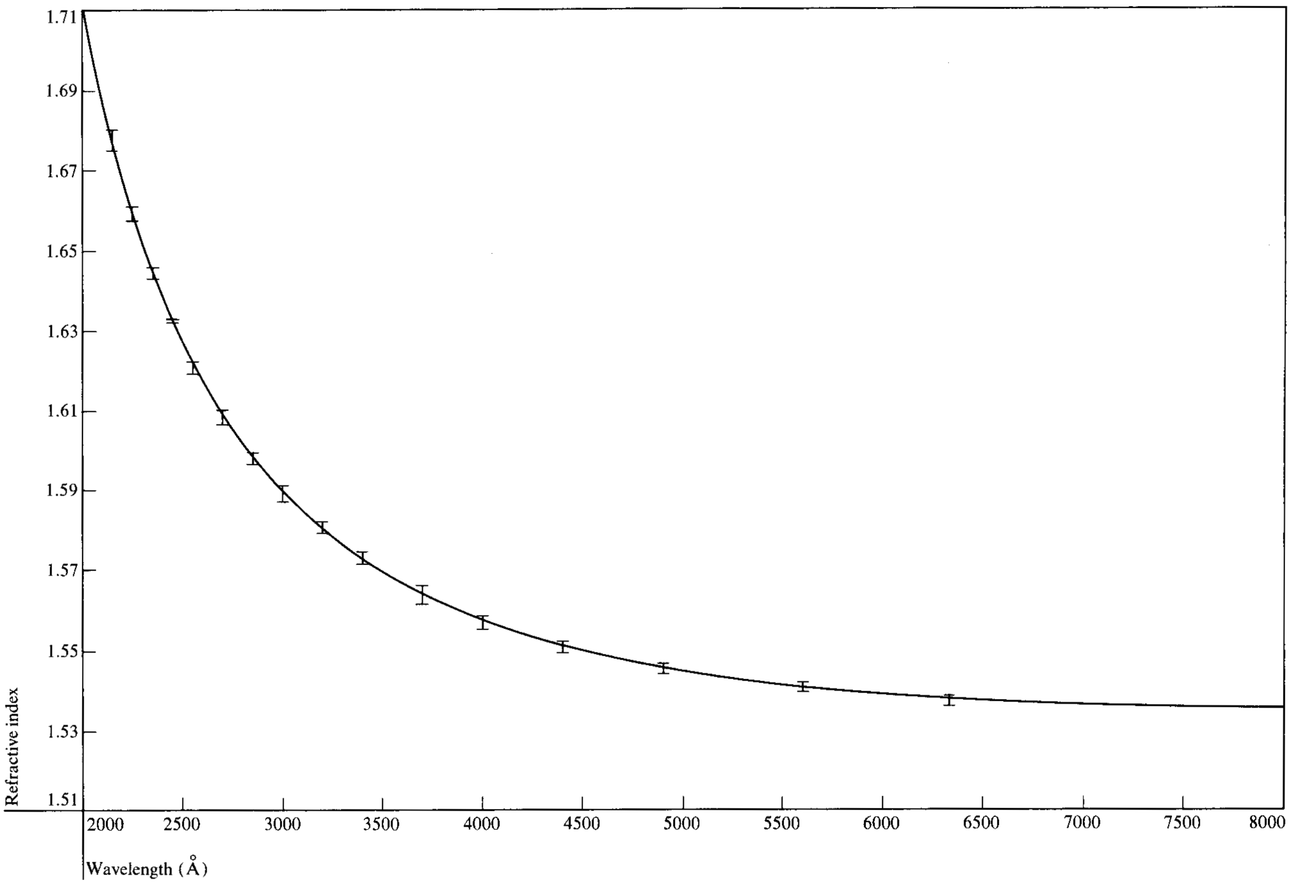

Figure 3 Refractive index vs wavelength for polyvinyl chloride. (Film thickness 16360 Å. Bulk polymer dissolved in 1-1 tetrahydrofuran-cyclohexanone; solution filtered through 5.0 μm; silicon wafer flooded, static start; wafer spin-coated at 4400 rpm for 30 seconds, then baked 10 minutes on 100°C hot plate.)

sidered an illustration of the technique and a guide to expected values, but the refractive index dispersion of individual films may vary by small amounts.

Conclusions

A technique has been described for the measurement and calculation of refractive index for semiconductor-related thin films. Measurements were made, nondestructively, throughout the uv-visible spectrum. From experimental data a calculation technique has been developed to accurately determine refractive index dispersion over this spectrum for 28 different films. With the indices determined from Eq. (1), dispersion constants have been calculated using Eq. (2).

The refractive index dispersion data presented here have been used effectively in photolithography, film thickness measurement, and the design of other optical systems related to the manufacture of semiconductor devices.

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References

1. W. A. Pliskin and E. E. Conrad, *IBM J. Res. Develop.* **8**, 43 (1964).
2. J. M. Harvilchuck, W. M. Moreau, and A. J. Warnecke, "Nondestructive Single or Dual Film Thickness and Refractive Index Measurements, "*IBM Tech. Disclosure Bull.*, Vol. 11, No. 9, pp. 1075–1076, Feb. 1969.
3. A. J. Warnecke, "An Optical Interferometer for Thin Film Measurement," *Proc. Kodak Photoresist Seminar*, May 19–20, 1969. (Also available as *IBM Technical Report TR 22.780.*)
4. R. W. Ditchburn, *Light*, 2nd Ed., Interscience Publishers, New York 1963, p. 567.

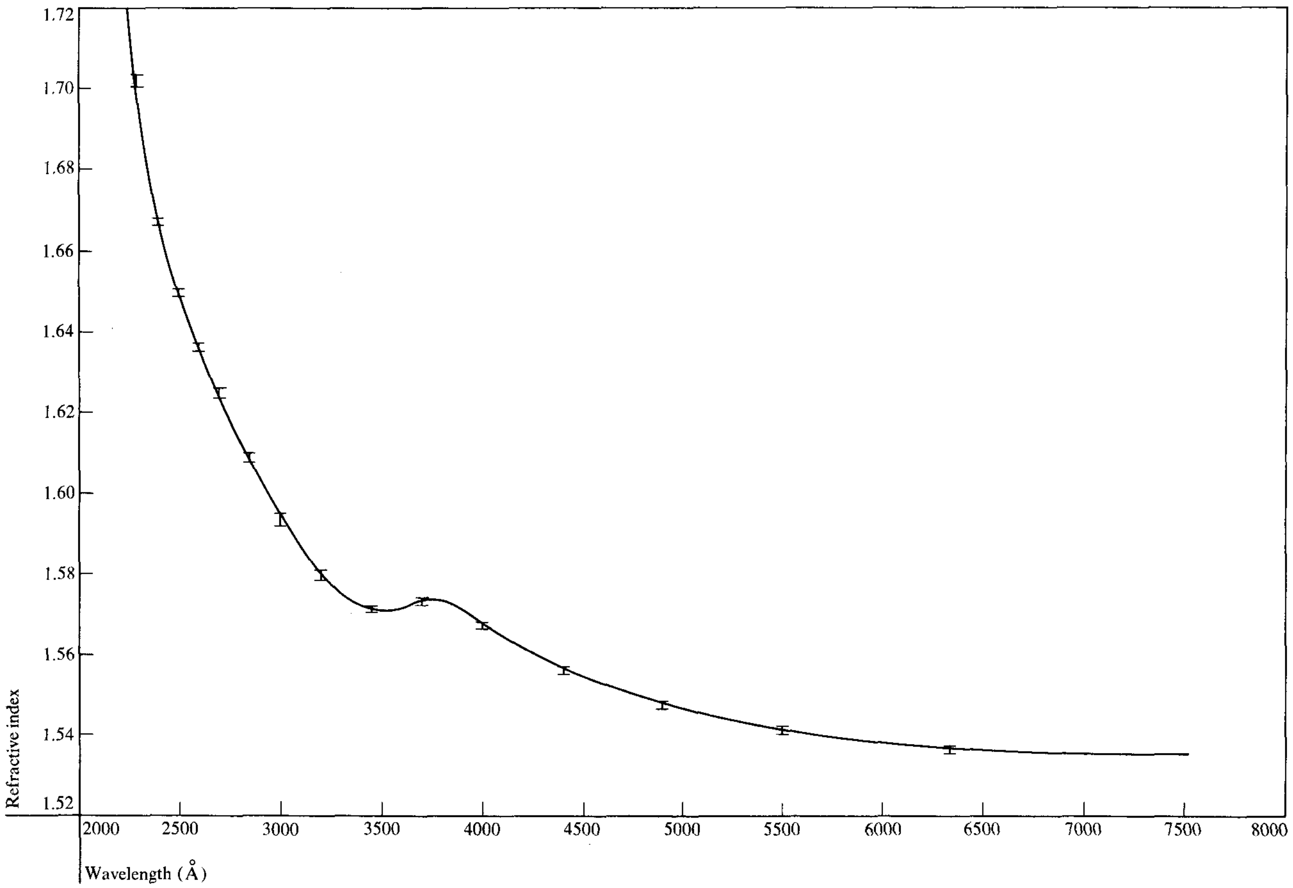

Figure 4 Refractive index vs wavelength for Kodak KTFR photoresist. (Film thickness 16714 Å. Resist lot No. 6911-77 diluted 3:2 in xylene; solution filtered through 1.0 μm; silicon wafer flooded, static start; wafer spin-coated at 4100 rpm for 30 seconds, then baked 10 minutes on 100°C hot plate.)

5. G. K. Wehner and G. S. Anderson, *Handbook of Thin Film Technology*, McGraw-Hill Publishing Co. Inc., New York 1970, Ch. 3.
6. L. I. Maissel, *Handbook of Thin Film Technology*, McGraw-Hill Publishing Co. Inc., New York 1970, Ch. 4.
7. W. A. Pliskin and R. P. Esch, *J. Appl. Phys.* **36**, 2011 (1965).
8. I. H. Malitson, *J. Opt. Soc. Am.* **55**, 1205 (1965).
9. O. N. Stavroudis and L. E. Sutton, *J. Opt. Soc. Am.* **51**, 368 (1961).
10. L. E. Sutton and O. N. Stavroudis, *J. Opt. Soc. Am.* **51**, 901 (1961).

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