Thin Solid Films, 191 (1990) 13–19
ELECTRONICS AND OPTICS

REFRACTIVE INDEX OF VACUUM-EVAPORATED SiO THIN FILMS: DEPENDENCE ON SUBSTRATE TEMPERATURE

F. LÓPEZ
Departamento de Fisica Aplicada, Universidad Politecnica, EUIT Telecomunicación, Cra Valencia Km.7, 28031 Madrid (Spain)
E. BERNABÉU
Départamento de Optica, Universidad Complutense, Facultad CC, Físicas, Cuidad Universitaria, 28040 Madrid (Spain)
(Received August 7, 1989; revised March 6, 1990; accepted April 4, 1990)

The substrate temperature dependence of the IR refractive index of vacuum-evaporated silicon monoxide thin films is reported. This process parameter can control the refractive index of the samples provided that the other parameters (pressure, deposition rate, source temperature etc.) are maintained under reasonably constant conditions during the evaporation process. Our results demonstrate the possibility of obtaining SiO thin films with different and controlled refractive indices by controlling the substrate temperature. Also, a process temperature has been obtained at which no dispersion of the refractive index in the IR 1–5 μm range occurs.

1. INTRODUCTION

Silicon monoxide thin films are extensively used both as protective layers in mirrors[1,2] because of their good mechanical properties and as low index layers in the medium IR range of the electromagnetic spectrum because of their low absorption and compatibility with other materials with higher refractive indices (germanium, silicon etc.)[3]. For these reasons SiO is commonly used in multilayers for interference filters.

Although these and other applications (microelectronics) are important, not very much information is available on SiO's optical properties[4]. The most important data in the IR are those from Hass and Salzberg[5], compiled by Philipp[4]. It is very common for various researchers[6,7] to accept a marked influence of substrate temperature on the refractive index of the layers but no data are available reporting this influence on the optical properties of SiO.

It is well known[8] that the optical properties of thin films are strongly dependent on the so-called "process parameters" that exert a strong influence on a large number of variables concerning thin film properties: mechanical (adherence, abrasion resistance), optical (refractive index and absorption coefficient) and environmental (operating temperature, humidity resistance). This influence is exerted by varying the microstructures of the layers through, among other properties, crystal size, internal stresses, packing density and sticking coefficient.

0040-6090/90/$3.50 © Elsevier Sequoia/Printed in The Netherlands

SAMSUNG EX. 1023 - 1/7

There are a lot of process parameters affecting significantly the optical and mechanical resistance properties of evaporated layers[8,9]; nevertheless, most of them, such as substrate cleaning, source type and temperature, deposition rate or residual pressure, are relatively easy to control. However, substrate temperature is a process parameter with two main characteristics. The first is the difficulty in measuring it directly over the substrate during the process because of rotation of the substrate holder, which is necessary to obtain good uniformity. The second is the strong dependence of the optical properties of vacuum-evaporated thin films on the substrate temperature. This is probably the most pronounced influence[10].

In the work reported in this paper we have obtained an experimental relation between the refractive index of evaporated SiO layers and substrate temperature, in the medium IR (1–5 μm). This relation allows for the control, under certain limits, of the refractive index of layers. Further, we have found a substrate temperature at which there is no significative dispersion in the refractive index of the samples with wavelength in the 1–5 μm region. This result is of practical interest in applications requiring a constant refractive index over this spectral region, for example in automatic processes for optical multilayer manufacture.

2. SAMPLE PREPARATION

Samples have been prepared in a high vacuum evaporation system (Leybold A700-QE) with a 12 000 l s^{-1} diffusion pump speed and liquid N_2 trap. The process parameters common to all samples are as follows:

deposition rate	15 Å s^{-1}
evaporation source	Mo boat
substrate–source distance (mean)	50 cm
substrate holder speed	20 rev. min^{-1}
residual pressure	$< 5 \times 10^{-6}$ Torr
source temperature	$\approx$ 1473 K

Keeping these parameters fixed, we made five samples in five different runs changing only the substrate temperature from one run to another. The temperature of the samples was controlled at 373 K, 423 K, 473 K, 523 K and 573 K. The maximum error in the measured temperature has been evaluated to be ± 5 K.

The sample thickness was measured with a Sloan Dektak 3030 profiler, ranging in all five samples from 2.5 to 3.0 μm.

3. REFRACTIVE INDEX DETERMINATION

The simplest method of obtaining the refractive index of materials in thin film form in a wide wavelength range (1–5 μm) is to derive it from spectrophotometric transmittance curve extrema (minima and maxima). This method was initially proposed by Manifacier *et al.*[11] for low absorption films and was subsequently improved by Swanepoel[12] for films with both absorbing and transmitting regions. The method yields errors of less than 1% in the refractive index determination. This upper limit to the error can be assigned also to sample thicknesses determined by

SAMSUNG EX. 1023 - 2/7

this method in the low absorption wavelength region. The adequacy of the Swanepoel method has recently[13] been tested and improved to take into account slit width and surface roughness, but both reflectance and transmittance spectrophotometric curves are then used.

4. EXPERIMENTAL RESULTS

Refractive indices of SiO samples obtained using the Swanepoel method have been adjusted in the 1–5 μm region to a Cauchy-type expression

$$n = A/\lambda^2 + B$$

where A and B have been determined for each of the five samples. Values of A and B for each of the samples are shown in Table I.

TABLE I

COEFFICIENTS A AND B IN THE CAUCHY EXPRESSION $n = A/\lambda^2 + B$ FOR DIFFERENT SUBSTRATE TEMPERATURES AND REFRACTIVE INDICES OF SAMPLES AT FIVE DIFFERENT WAVELENGTHS

T_S (K)	A (μm^2)	B	n(1 μm)	n(2 μm)	n(3 μm)	n(4 μm)	n(5 μm)
373	0.1186	1.809	1.928	1.839	1.822	1.816	1.814
423	0.0870	1.820	1.907	1.842	1.830	1.825	1.824
473	0.0481	1.830	1.878	1.842	1.835	1.833	1.832
523	0.0013	1.837	1.838	1.837	1.837	1.837	1.837
573	0.0065	1.850	1.857	1.853	1.851	1.850	1.850

T_S, substrate temperature.

In order to evaluate the accuracy of this refractive index fitted through the coefficients A and B, we have obtained a computer-simulated transmittance curve of one of the layers described previously, corresponding to a substrate temperature of 473 K, a 2.75 μm thickness, and a refractive index

$$n = 0.0481/\lambda^2 + 1.830$$

The Swanepoel method has been used to obtain the thickness of the layer. The value so obtained was in good agreement with that obtained from the profiler (2.78 μm). The thickness error for this sample has been evaluated to be less than 2%.

In order to achieve an adequate simulation of the whole sample (layer and substrate), the refractive index of the substrate (sapphire) was also adjusted. This was again carried out in accordance with the Swanepoel method and yields for sapphire substrates the expression

$$n_Z^2 = 0.0845/\lambda^2 + 2.8989$$

which is a type of expansion of the Sellmeier equation, very similar to the Cauchy expression. Nevertheless, this expression with a square index, fits better for bulk sapphire than that used before. A computer simulation of the transmittance curve of this sample can be seen in Fig. 1. To obtain a more realistic simulation curve, in order

SAMSUNG EX. 1023 - 3/7

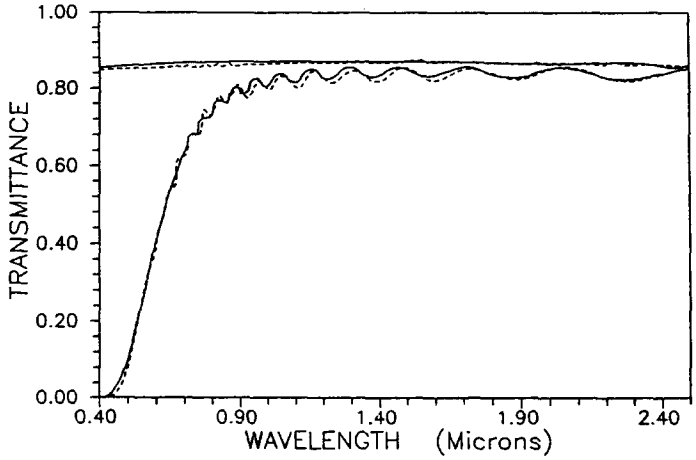

Fig. 1. Transmittance of a 2.75 μm thick SiO film on a sapphire substrate held at 473 K during deposition. The quasi-horizontal lines represent the transmittance curves of uncoated sapphire, - - -, experimental curves obtained with a spectrophotometer; ——, computer simulation. See text for process parameters and fitting constants.

to compare with the experimental curve, we have derived an expression for the absorption coefficient α.

The absorption coefficient for this sample was obtained by fitting, using the least-squares method, the transmittance values in the high absorption region, following Swanepoel's recommendations for the accurate obtention of the α coefficient. The results for this sample have been determined to be

$$\log \alpha = 9.588\lambda^{-1/4} - 11.517$$

where λ is expressed in micrometres and α is obtained in reciprocal micrometres.

The phenomenological exponent $-1/4$ is the most significant result of the above expression and can be explained by an appropriate combination of different absorption mechanisms, varying from intrinsic absorption (Urbach tail), to extrinsic and Rayleigh scattering losses. The absorption coefficients obtained for the rest of the samples and one possible explanation of the exponent will be studied elsewhere[14].

The values for n, α and n_Z, defined before, have been used to obtain, by computer simulation, the full curves in Fig. 1. The accuracy of this fit can be tested by comparison with the broken curves in the same figure. The latter represent the spectrophotometric transmittance of a silicon monoxide layer 2.75 μm thick, deposited onto a sapphire substrate, maintained during the deposition at a temperature of 473 K. The bare sapphire substrate is also represented by a quasi-horizontal curve. Comparison of both experimental and simulation curves reveals a very accurate fitting of the simulation parameters.

From Table I we can derive the following consequences for the refractive index between 1 and 5 μm.

(1) The refractive index of evaporated SiO layers depends strongly on the substrate temperature T_S, mainly at shorter wavelengths (about 1 μm).

SAMSUNG EX. 1023 - 4/7

(2) At low T_S (373–473 K), the refractive index depends strongly on wavelength.

(3) As T_S increases, the refractive index tends to stabilize, becoming more constant with wavelength (less dispersive).

(4) At $T_S = 523$ K, the refractive index becomes fairly constant with wavelength in the 1–5 μm region.

(5) As T_S increases further (573 K), the refractive index also remains nearly constant with wavelength, but at higher values.

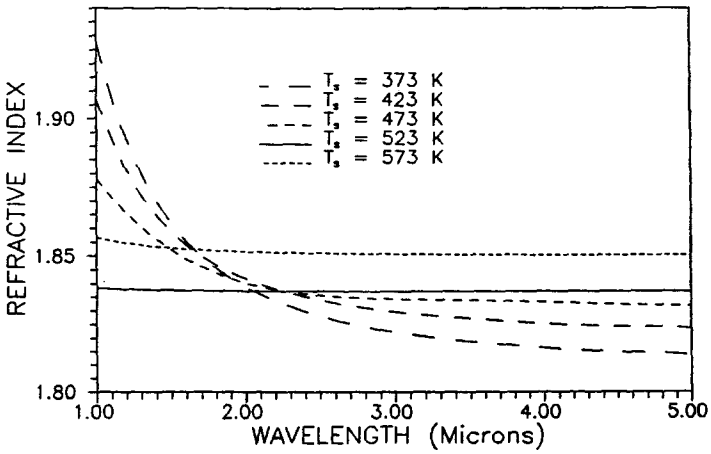

Fig. 2. Plots of refractive index of silicon monoxide layers *vs.* wavelength. The substrate temperature T_S is the parameter.

Figure 2 shows a plot of the refractive index of silicon monoxide layers *vs.* wavelength in the 1–5 μm range. The plot has been built up out of the data of Table I. The full curve represents the dispersion of the refractive index for sample obtained at a substrate temperature of 523 K, which represents a quasi-stable refractive index. If we consider the 3–5 μm wavelength region, which is of interest in many applications because of the atmospheric window, an increment in the refractive index with substrate temperature can be observed. This fact contrasts with that observed in the low wavelength region (below 1.5 μm), where the refractive index decreases with substrate temperature, except for the sample with the highest (573 K) substrate temperature.

In Fig. 3 different curves of the variation in refractive index with substrate temperature during deposition can be seen. Each curve is a parametric representation, wavelength being the parameter. The most remarkable event in this figure is that all curves, corresponding to different wavelengths, cross at a substrate temperature of 523 K. This behaviour must correspond to a structural change in the microstructure of the samples. Observation of the refractive index of the sample evaporated at 573 K reveals a sharp index increase at all wavelengths, relative to the sample evaporated at $T_S = 523$ K, and also a low dispersion. A higher refractive index means a higher packing density.

SAMSUNG EX. 1023 - 5/7

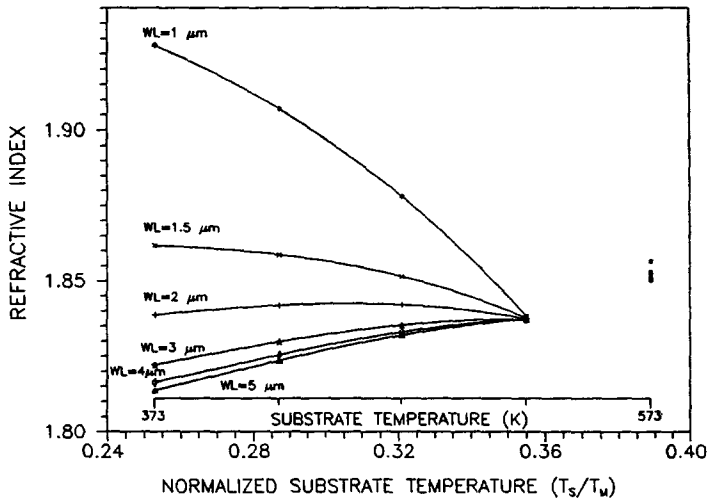

Fig. 3. Refractive index of silicon monoxide layers *vs.* normalized substrate temperature T_S—T_M. All curves cross at $T_S = 523$ K (T_S/T_M) = 0.355) (non-dispersive layer). Values for $T_S = 573$ K correspond to a different layer structure.

The Movchan model, modified by Thornton[15], proposes for condensed layers a strong dependence of microstructure on substrate temperature T_S. Depending on T_S, four different microstructures, defined by "zones" resulting from different surface mobilities of the adatoms, have been observed. At low T_S (below $0.22T_M$, where T_M (K) is the melting point) a porous structure, consisting of tapered crystallites separated by voids, is observed, the so-called zone 1. A higher T_S produces a transition structure (zone T) consisting of densely packed fibrous grains. The zone T structure can appear for different T_S ranges. A higher T_S produces a new structure (zone 2) consisting of a full density columnar morphology. This structure can appear up to T_S values from $0.5T_M$ to $0.71T_M$. A zone 3, consisting of a recrystallized grain structure, can occur at higher T_S.

From the observation of the refractive index of our samples for different T_S, we can conclude that all of them have values sufficiently high to be considered as being of high packing density. Hence we can say that the first four samples deposited at 373, 423, 473 and 523 K present the same zone T type of structure in the Movchan–Thornton model. Nevertheless, it is necessary to accept that between 523 and 573 K the beginning of the zone-2 type structure occurs, as revealed by the sharp increase in refractive index for the sample with $T_S = 573$ K and also by its loss of smoothness as observed in Fig. 3. The discontinuity in the curves for $T_S = 523$ K in this figure means that a new dependence appears for higher substrate temperatures which must correspond to a change in the microstructure of the samples as described previously. It should be noted also that, as SiO sublimes, using the source (boat) temperature (about 1473–1523 K) analogously to T_M, the ratio T_S/T_M would be between 0.34 and 0.38, which is an acceptable value for a zone 2 type of structure in Thornton model.

SAMSUNG EX. 1023 - 6/7

Moreover, it has been observed by Vincett *et al.*[16] than an optimum in the structure-sensitive properties occurs when T_S/T_B is within a few per cent of 1/3, where T_B is the boiling point of the material. If we use again the source temperature T_M, but now as T_B, a good structure may be obtained with T_S at about 500 K. This is consistent with our results that give a very low dispersion of the refractive index with wavelength in the 1–5 μm region for $T_S = 523$ K. Figure 3 shows how the 523 K abscissa value corresponds to a non-dispersive layer since all curves cross in it. Nevertheless, it would be necessary to study the values of the absorption coefficient at different temperatures in order to be sure of what the optimum substrate temperature is from this point of view. This work is now in progress and will be the subject of a future paper[14].

5. CONCLUSIONS

The dependence of refractive index on wavelength for different substrate temperatures in thin evaporated films of SiO has been determined. By studying the refractive index behaviour with wavelength at different substrate temperatures, we have shown that, for a substrate temperature of 523 K, layers with no appreciable dispersion of the refractive index with wavelength, between 1 and 5 μm, have been obtained. Controlled refractive index of SiO thin films can be obtained by controlling the substrate temperature during the evaporation process.

ACKNOWLEDGMENT

The authors would like to thank Dr. L. L. Sánchez-Soto for helpful discussions on the content of this article.

REFERENCES

1 L. F. Drummeter, Jr., and G. Hass, in G. Hass and R. E. Thun (eds.), *Physics of Thin Films*, Vol. II, Academic Press, New York, 1964, p. 305.
2 G. Hass, *J. Opt. Soc. Am.*, *72* (1982) 27.
3 J. T. Cox and G. Hass, in G. Hass and E. Thun (eds.), *Physics of Thin Films*, Vol. II, Academic Press, New York, 1964, p. 239.
4 H. R. Phillipp, in E. D. Parlik (ed.), *Handbook of Optical Properties of Solids*, Academic Press, Orlando, FL, 1985, p. 765.
5 G. Hass and C. D. Salzberg, *J. Opt. Soc. Am.*, *44* (1954) 181.
6 E. Ritter, *Opt. Acta*, *9* (1962) 197.
7 K. H. Guenther, *Proc. Soc. Photo-Opt. Instrum. Eng.*, *401* (1983) 31.
8 E. Ritter, *Appl. Opt.*, *20* (1981) 21.
9 W. P. Thoeni, *Thin Solid Films*, *88* (1982) 385.
10 H. K. Pulker, *Appl. Opt.*, *18* (1979) 1969.
11 J. C. Manifacier, J. Gasiot and J. P. Fillard, *J. Phys. E*, *9* (1976) 1002.
12 R. Swanepoel, *J. Phys. E*, *16* (1983) 1214.
13 K. A. Epstein, D. K. Misemer and G. D. Vernstron, *Appl. Opt.*, *26* (1987) 294.
14 F. López and E. Bernabéu, in preparation.
15 J. A. Thornton, in R. F. Bunshah (ed.), *Deposition Technologies for Films and Coatings*, Noyes, Park Ridge, NJ, 1982, p. 214.
16 P. S. Vincett, W. A. Barlow and G. G. Roberts, *J. Appl. Phys.*, *48* (1977) 3800.

SAMSUNG EX. 1023 - 7/7