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Characterization of thin films of a-SiO_x ($1.1 < x < 2.0$) prepared by reactive evaporation of SiO

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Abstract
Thin films of a-SiO_x with values of x ranging from 1.13 to 1.89 were prepared by reactive evaporation of SiO in a controlled oxygen environment. The oxygen pressure in the deposition chamber was varied so as to obtain films with different values of x. The films were studied by x-ray photoelectron spectroscopy and optical spectrophotometry. An attempt was made to analyse the Si 2p core-level spectra in terms of five chemically shifted components corresponding to basic Si bonding units Si–($Si_{4-n}O_n$) with $n = 0, 1, \ldots, 4$. The concentration of these bonding units as a function of oxygen concentration was in reasonable agreement with the random-bonding model, with the exception that the Si–(Si_3O) component was almost completely suppressed for all stoichiometries. Films with $x < 1.65$ consisted of elemental Si and oxides of silicon, while those with $x \geqslant 1.65$ were almost free of Si. Films containing Si have higher refractive indices and degrees of absorption in the visible region compared with those which were free of Si.

The optical properties of the films approach those of fused silica (SiO_2) as the values of x increase. For the films with the largest value of x (=1.89), the refractive index is smaller than that of fused silica. The density of these films was estimated to be smaller than that of fused silica by about 13%.

1. Introduction

Thin films of semi-insulating silicon suboxides deposited by the well-known method of reactive evaporation of SiO in an O_2 ambient are frequently used in semiconductor surface passivation and can be deposited at relatively low process temperatures [1]. The low process temperatures during the preparation of semiconductor films are needed to reduce problems such as substrate

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warpage, dopant redistribution and defect generation and migration caused by high-temperature processing [2].

The optical properties of silicon oxide films have been the subject of several articles [3–7]. It is not unusual to observe a wide disparity in the values of the optical constants (refractive, n, and absorption, k, indices). Only the influence of the deposition conditions (i.e. substrate temperature, deposition rate, oxygen pressure) as well as the method of producing the film can account for these widely divergent values [3–7]. Optical properties of oxide films are dependent on chemical composition and microstructure. Films prepared by physical vapour deposition under different pressures of oxygen in a vacuum chamber can lead to films of different compositions and thus with different optical properties. Moreover, distinct preparation methods lead to different SiO_x structures which can be described with the help of a macroscopic mixture model (MM) and a microscopic random-bonding model (RBM) [8–16]. The MM assumes a simple mixture of Si and SiO_2, whereas the RBM is based on a statistical distribution of Si–Si and Si–O bonds. Therefore, careful measurement of the optical and structural properties of SiO_x films are very important.

The aim of this work was to study the possible variation in the optical and structural properties for a-SiO_x oxide films prepared by thermal evaporation under an oxygen atmosphere at different pressures. Films with different values of x (lying in the range of 1.0–2.0) were prepared under these conditions. A spectrophotometer was used to determine the optical constants. Chemical analysis of the films was performed using x-ray photoelectron spectroscopy (XPS).

2. Experimental details

Thin films of a-SiO_x of thickness 100–300 nm were prepared simultaneously on fused silica and tantalum substrates in a Leybold model L560 box coater pumped by a turbomolecular pump. The silica substrates were in the form of wedges of 3° angle. The coating chamber was pumped to a base pressure of 1×10^{-6} mbar. The source material, SiO, of purity 99.95%, was evaporated from a tantalum boat. The base pressure increased to about 8×10^{-6} mbar during deposition of the film. Substrates were rotated during the deposition. For all the samples, a fixed rate of evaporation of 0.5 nm s^{-1} was controlled and monitored using a quartz crystal thickness monitor. The source-to-substrate distance was 40 cm. Silicon oxide films deposited on unheated substrates are known to be amorphous [3].

Thin films of a-SiO_x with different values of x (in a range of 1–2) were prepared by varying the pressure of intentionally introduced oxygen in the deposition chamber. Initially the chamber was pumped to a base pressure of 1×10^{-6} mbar and then oxygen was readmitted to raise the pressure of the chamber to a certain fixed value that lay in the range 2.0×10^{-5}–7.2×10^{-4} mbar. During deposition the pressure was maintained at this value by controlling a needle valve. Some films were prepared without the introduction of oxygen into the coating chamber. In the coating chamber, the substrates were maintained at ambient temperature. After the films were deposited, they were removed from the coating chamber and exposed to the ambient atmosphere, prior to measurement of their optical properties and XPS.

Normal incidence transmittance of the films on fused silica wedges was measured over the 200–850 nm wavelength range using a double-beam Bausch and Lomb spectrophotometer, model Spectronic 2000. The use of a wedge substrate ensured that reflections from the back of the substrate were deflected from the optical path of the instrument so that multiple reflections in the substrate did not affect the measurements. However, the wedge angle was small enough for transmission across the back face to be given accurately enough by the transmittance formula for normal incidence. The optical constants (refractive, n, and absorption, k, indices) were determined from the transmittance measurements [17].

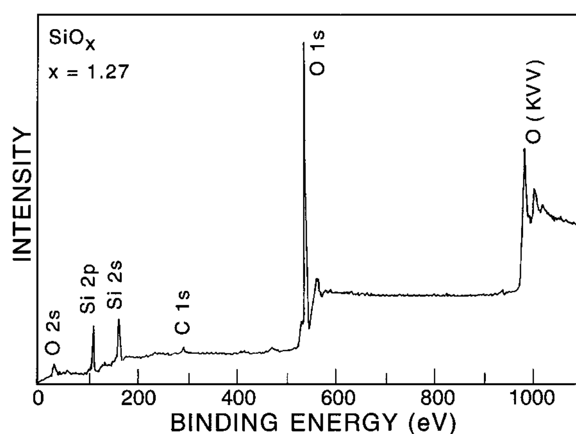

Figure 1. A typical wide scan XPS spectrum for an a-SiO_x film with $x = 1.27$.

The XPS was performed in a VG Scientific ESCALAB MKII spectrometer. The system has been described elsewhere [18]. XPS spectra were obtained using Al Kα (1486.6 eV) radiation. Films deposited on tantalum substrates were used for XPS analysis so that the charging of nonconducting samples could be reduced. In order to avoid any shift in spectra due to charging and to bring energies to the same reference point, all energies are stated with reference to the C 1s line at a binding energy of 284.6 eV [19]. This is a fortuitous peak which arises due to hydrocarbon contaminants in the vacuum and is generally accepted to be independent of the chemical state of the sample under investigation.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

Thin films of a-SiO_x with different values of x were prepared by controlling the oxygen pressure in the deposition chamber. A wide scan XPS spectrum for a film prepared in an oxygen atmosphere at 2×10^{-5} mbar is shown in figure 1. Similar spectra were obtained for other films that were prepared under different oxygen pressures. Apart from the photoelectrons and Auger transitions of the film constituents (Si and O), C 1s was observed. The C 1s at a binding energy of 284.6 eV is the usual peak associated with hydrocarbon contamination, nearly always present on samples introduced from the laboratory environment or from a glove box [19]. This peak is used as an energy reference in the present work.

The average chemical composition x was determined from the O 1s/Si 2p intensity ratio (figure 1) with an accuracy of approximately 10% [11]. Variations in the values of x from sample to sample, prepared under a given oxygen pressure, were less than 10%. Figure 2 shows a plot of x versus oxygen pressure. The points in figure 2 represent the data, while the broken curve indicates the trend followed by the results. The rise in the values of x with oxygen pressure is much larger for lower pressures ($<1 \times 10^{-4}$ mbar) than that for higher pressures. The values of x found in the present work (figure 2) fall in a range from 1.13 to 1.89. O'Leary and Thomas [3] obtained their values in a range of 1.18–1.91 for SiO_x films prepared under conditions different from the ones used in the present work. They were able to vary x by evaporating SiO at different rates, in an environment in which a constant flow of oxygen was maintained.

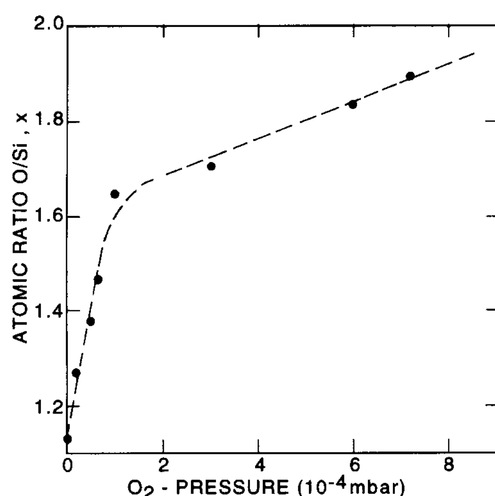

Figure 2. Dependence of x in a-SiO_x films on oxygen pressure. Points represent the data while the broken curve was drawn so as to indicate the trend followed by the results. x was determined with an accuracy of about 10%.

The Si 2p core level spectra for SiO_x films with different values of x are shown in figure 3. These spectra closely resemble the spectra reported in [11–14] for films of SiO_x. For films with $x < 1.65$, the Si 2p spectra show some shoulder and structures, while for films with $x \geqslant 1.65$ such a shoulder was not observed (figure 3). The peak positions of the Si 2p determined [1, 12–14, 19] for individual samples of elemental Si and SiO_2 are indicated in figure 3. This suggests that such a shoulder may have a contribution that is coming from the presence of elemental Si in the samples with $x < 1.65$.

In the case of SiO_x, two models [8, 10–16] have been suggested for the structure based on fourfold-bonded Si and twofold-bonded O. The first model for the network is the MM, in which the film is expected to be composed of randomly arranged clusters of Si and SiO_2 of varying sizes. The second is the RBM, in which there is a statistical distribution of five basic bonding units, Si–Si_nO_{4-n} ($n = 0, 1, \ldots, 4$). It follows from above that the spectra of Si 2p for SiO_x films could have contributions coming from two (in the case of the MM model) or five (in the RBM model case) chemically inequivalent Si atoms that may be present in the films. These inequivalent states are Si^0 (corresponding to Si) and Si^{4+} (SiO_2) in the MM model and Si^0 (Si–Si_4), Si^{1+} (Si–Si_3O), Si^{2+} (Si–Si_2O_2), Si^{3+} (Si–SiO_3) and Si^{4+} (Si–O_4) in the RBM model.

A curve-fitting procedure of the main Si 2p core level line was adopted in order to identify the inequivalent states of Si and to estimate the relative amount of Si that may be present in each of the states. The photoelectron core level (Si 2p) lines from the Si^0 (Si–Si_4), Si^{1+} (Si–Si_3O), Si^{2+} (Si–Si_2O_2), Si^{3+} (Si–SiO_3) and Si^{4+} (Si–O_4) are expected to occur at binding energies of 99.6, 100.5, 101.4, 102.7 and 103.8 eV, respectively, all within ± 0.3 [12–14] and each with a full width at half-maximum (FWHM) in the vicinity of about 2 eV [12, 13]. Based on the above parameters the least-squares method was used to obtain the intensities of the five individual components by minimizing the χ^2 for each sample. In figure 4, we report the results of these fits for some of the spectra shown in figure 3. The Si^{1+} (Si–Si_3O) component (not shown in figure 4) is almost completely suppressed for all stoichiometries (i.e. $x = 1.13$–1.89). In some previous studies [12–14] made on SiO_x films, with values of x

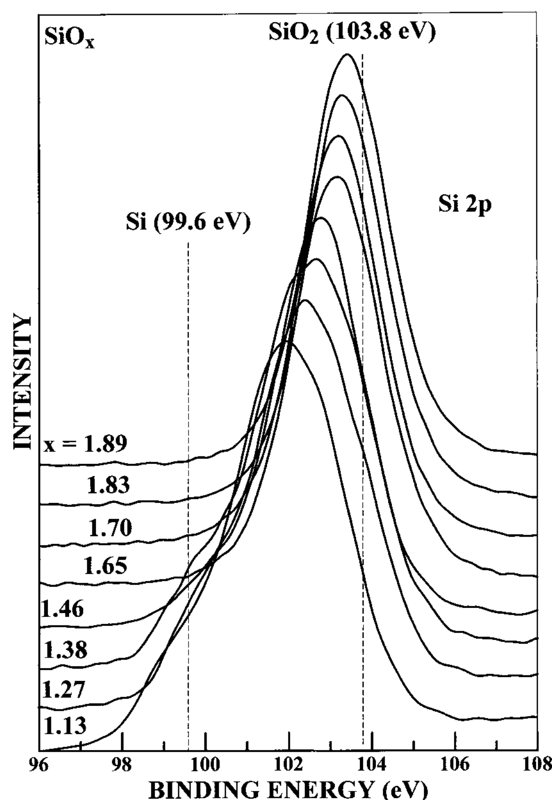

Figure 3. The Si 2p spectra of a-SiO_x films with different values of x. Peak positions of the Si 2p reported [1, 12–14, 19] for individual samples of elemental Si (99.6 ± 0.2 eV) and SiO_2 (103.8 ± 0.2 eV) are indicated by vertical broken lines.

that are comparable to those of the present work, an absence of the Si^{1+} ($Si–Si_3O$) component was reported. In [15, 16] contributions corresponding to Si^{1+}, Si^{3+} and Si^{4+} were observed while those corresponding to Si^0 and Si^{2+} were absent. However, film preparation conditions used in [15, 16] were much different to those used in the present work, for example, their rate of evaporation was 0.2 nm min^{-1} (the present rate was 30 nm min^{-1}) and they used an ultrahigh vacuum of 10^{-9} mbar (10^{-6} mbar range in the present work). It may be mentioned that the film preparation conditions used in [13, 14] were closer to those used in the present work.

In figure 5, we show the component intensities as calculated in the RBM (equation (1) in [12]) and those obtained from the fits (such as in figure 4). From the plots of figure 5 it can be seen that the component intensities from the fit agree better with the RBM than with the MM (only two components are required in the MM). Results shown in figure 5 are in close agreement with those of [12]. For samples with $x < 1.65$, four components corresponding to Si^0 ($Si–Si_4$), Si^{2+} ($Si–Si_2O_2$), Si^{3+} ($Si–SiO_3$) and Si^{4+} ($Si–O_4$) are observed while for the samples with $x \geqslant 1.65$ two components corresponding to Si^{3+} ($Si–SiO_3$) and Si^{4+} ($Si–O_4$) have been observed (figures 4 and 5). Another check on the network structure is obtained from a second method to determine the oxygen concentration. Here the oxygen concentration (x_{fit}) is obtained from the relative concentrations of the Si^{2+} ($Si–Si_2O_2$), Si^{3+} ($Si–SiO_3$) and

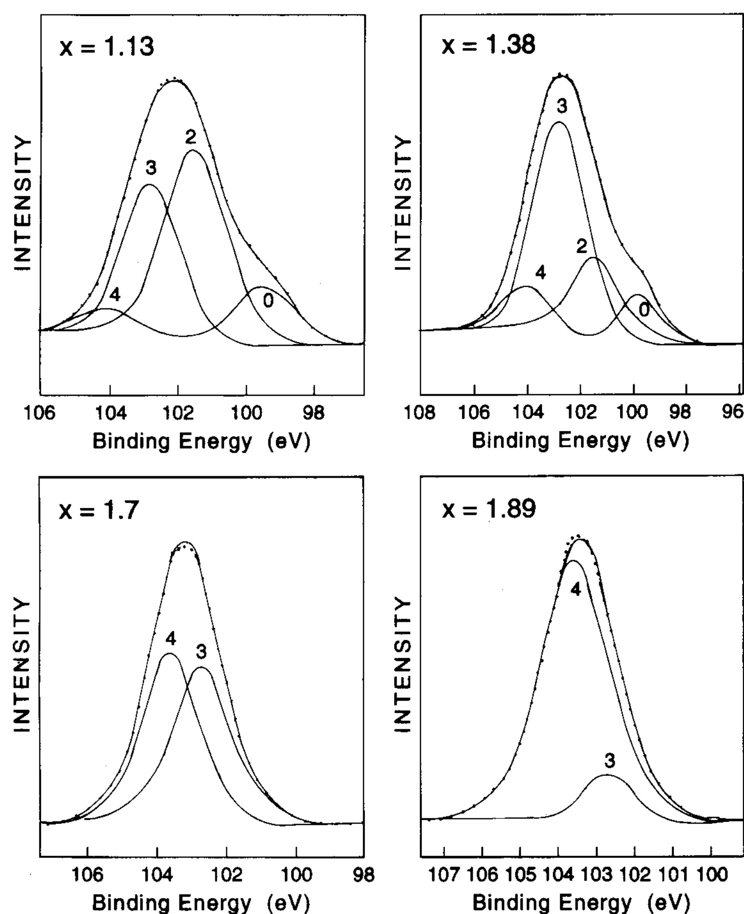

Figure 4. Si 2p core-level spectra in SiO_x films for selected oxygen concentration x. Dots are the measured data and the full curve is the result of a least-squares fit. Individual peaks in the fits are designated by integers corresponding to the number of Si–O bonds.

Table 1. Comparison of oxygen concentration in SiO_x films, obtained by two different methods: (1) using the ratio of the intensities of the O 1s and Si 2p core level peaks (say, x) and (2) from the components of Si 2p (figure 5) using the equation (say, x_{fit}).

x	1.13	1.27	1.38	1.46	1.65	1.70	1.83	1.89
x_{fit}	1.09	1.25	1.31	1.40	1.70	1.75	1.86	1.93

Si^{4+} (Si–O_4) components (figure 5) using the relation

$$x_{fit} = \frac{1}{2}(2R_{Si^{2+}} + 3R_{Si^{3+}} + 4R_{Si^{4+}})$$

where the R are the relative concentrations of the three components (since $R_{Si^{1+}}$ is nearly zero), given in figure 5. The factor of $\frac{1}{2}$ is included since each oxygen atom is shared by two Si atoms. The values of x_{fit} thus obtained are compared with those obtained from the ratio of the intensities of the O 1s and Si 2p core level peaks (x) in table 1. These two measures of the concentration are in good agreement (within about 5%).

The above findings are based on XPS measurements, which is a surface-sensitive technique looking into specimen depths of less than 4 nm. The question arises as to whether the above

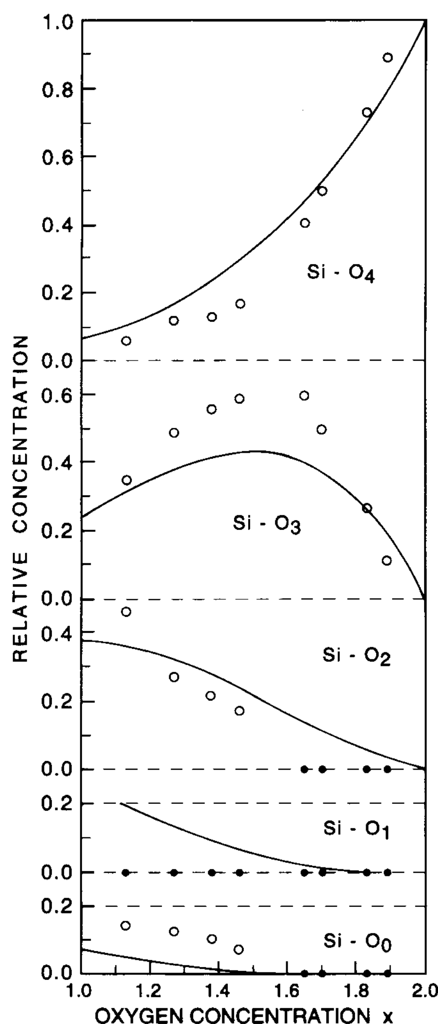

Figure 5. Full curves are relative concentrations of the basic bonding units in the RBM and the open circles represent the data obtained from the least-squares fits (such as figure 4). The full circles indicate points at which no significant contribution of the given component was detected.

findings hold true for the bulk of the sample. To answer this question we have carried out optical measurements of the transmittance through the sample, as discussed in the next section.

3.2. Optical properties

A comparison of spectral transmittance measured at normal incidence from films with different x is made in figure 6. The spectral transmittance of an uncoated fused silica substrate is also shown. During the measurement of the transmittance using a double-beam spectrophotometer, air was the medium in the reference beam. Results shown in figure 6 are for films prepared at a fixed value of thickness fed into a quartz crystal thickness monitor. The actual thickness of each of the films was measured by an optical method [17] as will be discussed later. It was found that the thickness increased from about 125–143 nm in going from $x = 1.13$ to 1.89.

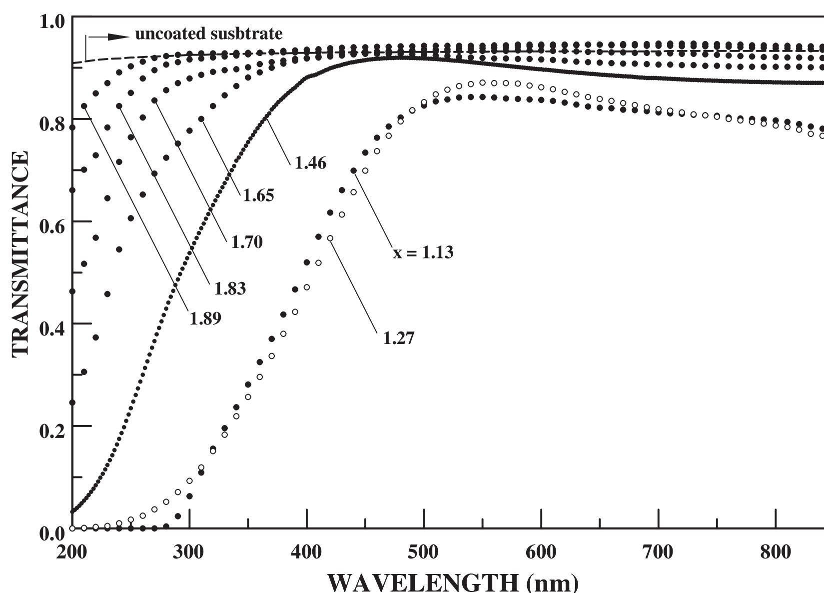

Figure 6. Transmittance spectra of an uncoated fused silica substrate and SiO_x films with different values of x.

This suggests that the densities of the films decrease in going from $x = 1.13$ to 1.89. The transmittance curve for the films with $x = 1.38$, not shown in figure 6, lay close to the curves for $x = 1.13$ and 1.27.

A method for the determination of the refractive (n) and absorption (k) indices and thicknesses of thin dielectric films on transparent substrates was reported earlier [17]. It requires the measurement at normal incidence of the transmittance (using the relation given in [20]) from two films of a given dielectric of different thicknesses as a function of wavelength (λ). The method has been applied successfully to films of different dielectrics [17, 21, 22]. The results (n and k), discussed below, were obtained by the use of this method. The results for different specimens (sets of two films of different thicknesses) of a given type of film were reproducible to within 2% for the values of n and within 5% for the values of k, for k larger than about 0.1. For values of k lower than this, the uncertainty was much larger. The results for the a-SiO_x films with different values of x are shown in figures 7 and 8. In figure 7, the results for films with $x = 1.13$, 1.38, 1.70 and 1.83 are not included, because the refractive indices for $x = 1.13$ are slightly higher, and for $x = 1.38$ are slightly lower, than that for $x = 1.27$ shown in figure 7 (both within 3%). Similarly, the refractive indices' curves for $x = 1.70$ and 1.83 lie in between the curves for $x = 1.65$ and 1.89 shown in figure 7. In general, the refractive indices of the films decreased with increasing values of x and fell below even that of fused silica. The absorption edge shifts to lower wavelengths (figures 6 and 8), moving closer to that of fused silica as x is increased.

In the low absorption region that we are concerned with in the visible part of the spectra the absorption data are not reliable since these samples were not thick enough for the measurement of absorption indices of low value. In order to overcome this difficulty, the transmittance spectra of figure 6 are expanded in scale in figure 9 so as to highlight the differences in the spectra. It may be worth noting the following two points.

(1) For a system of a transparent film on a transparent substrate, a transmittance spectrum of the system lying above the transmittance spectrum of the uncoated substrate (figure 9)

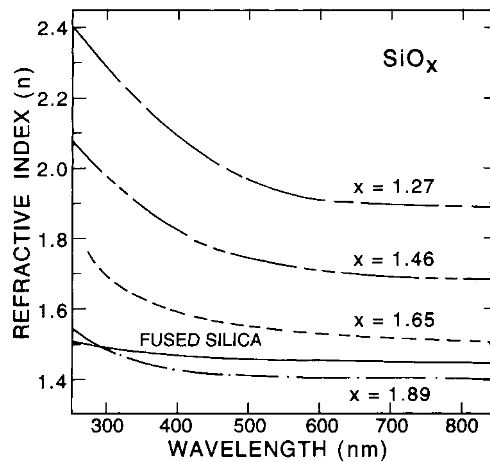

Figure 7. Plots of refractive index versus wavelength for SiO_x films with different x.

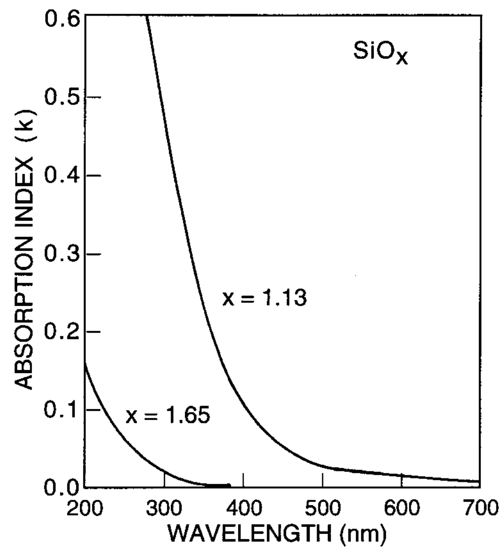

Figure 8. Plots of absorption index versus wavelength for SiO_x films with different x.

suggests [20] that the index of refraction of the film is smaller than that of the substrate. The spectrum of a system lying lower than that of the uncoated substrate (figure 9) suggests the opposite. Thus, it follows from figure 9 that films with $x \geqslant 1.83$ and those with $x < 1.83$ should have refractive indices that are smaller and larger, respectively, than that of the substrate. Indeed, this is what is observed (figure 7).

(2) For a transparent film on a transparent substrate [20] with refractive index of the film larger than that of the substrate, the maximum in transmittance (T_{max}) should be equal to the transmittance of the uncoated substrate (T_s).

The fact that T_{max} is less than T_s for some of the films (figure 9) suggests that these films show some absorption for and around the wavelength at which the T_{max} occurs. The absorption index is expected to increase with ΔT ($=T_{max} - T_s$). In the case of transparent films

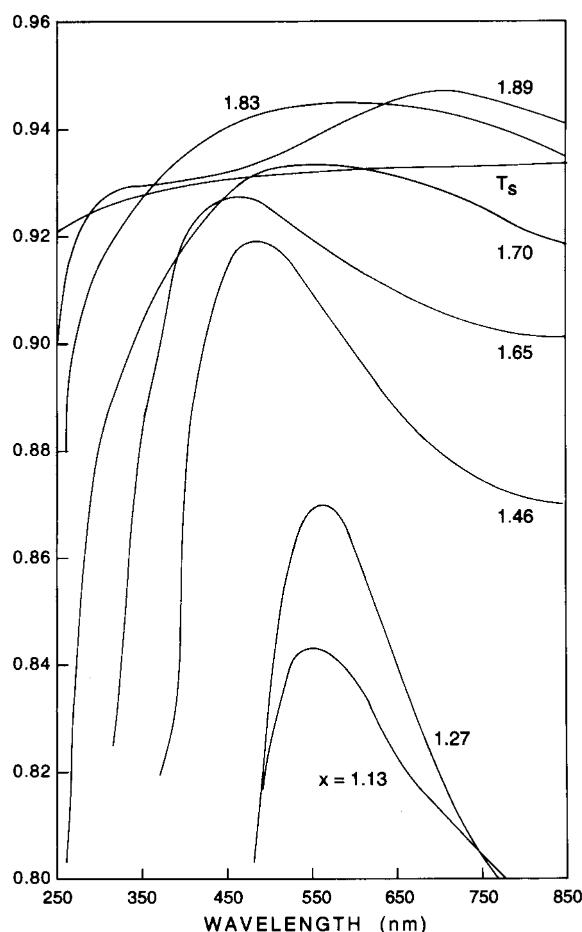

Figure 9. The transmittance spectra shown in figure 6 are expanded in scale here. T_s is the transmittance of an uncoated fused silica substrate.

with refractive indices smaller than that of the substrate, the minimum in transmittance should be equal to the transmittance of the uncoated substrate [20]. Thus, it follows from figure 9 that absorption in the films in the wavelength region of about 450–550 nm (photon energy of 2.2–2.8 eV) decreases as x increases and is insignificantly small for films with $x \geqslant 1.65$. According to Philipp [8] the absorption in this particular spectral region has a major contribution that is coming from Si, and the various other oxides of Si have insignificantly small contributions. Therefore, the absorption discussed above may be associated with the presence of elemental Si in some of the samples. If this holds true, then Si concentration in the film is expected to decrease with x until it approaches a near-zero value for films with $x \geqslant 1.65$. This is supported by the XPS results (figure 5). In an earlier study [1] it was reported that SiO_x films became SiO_2-like at oxygen pressures greater than 1.33×10^{-4} mbar (1.33×10^{-2} Pa). At this pressure the value of x was found to be larger than 1.65 (figure 2). The present results do support this view to some extent as it follows from the above.

Again, the high index of refraction of films with $x < 1.65$ (figure 7) may be due to the presence of elemental Si in these films because Si is known to have a much higher refractive index ($n \sim 3.9$), at least as compared with SiO_2 ($n \sim 1.45$). The refractive indices of the other

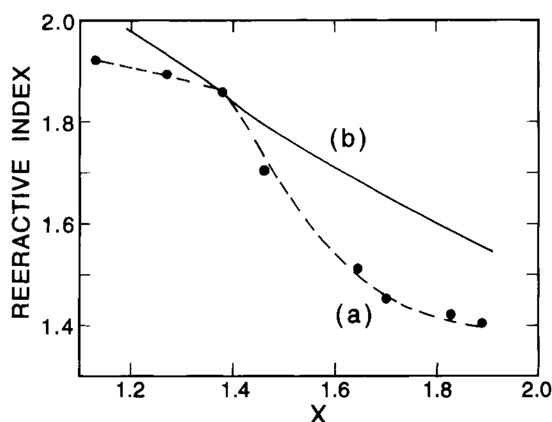

Figure 10. Plots of refractive index (at a wavelength of 630 nm) versus x: (a) dots represent the data and the broken curve is drawn to indicate the trend followed by the data, and (b) data from [3].

oxides of Si (section 3.1), which may be present in the films, are not known. In figure 10, the refractive indices measured at a wavelength of 630 nm are plotted as a function of x. For comparison, the corresponding data from [3] are included in figure 10. For lower values of x, the agreement between the present data and those of [3] seems to be reasonably good. However, at higher values of x, the present values are lower than those of [3]. As the value of x increases, the composition of the film approaches that of fused silica (SiO_2). Generally, the density of a film is lower than that of the corresponding bulk material [23]. Therefore, the refractive index of films being less than that of fused silica for films with $x > 1.8$ may be due to the lower density of these films when compared with fused silica. In the appendix, the density of these films has been estimated from the transmittance measurement using the Lorentz–Lorenz law. It was found that the densities of such films are about 13% smaller than those of fused silica. For a-SiO_x with $x = 1.91$, O'Leary and Thomas [3] reported a value of the density (1.83 g cm^{-3}) that is at least 17% smaller than that of the bulk value of SiO (2.2 g cm^{-3}) or SiO_2 (2.27 g cm^{-3}).

4. Conclusions

Thin films of a-SiO_x with values of x in a range from 1.13 to 1.89 were prepared by controlling the oxygen pressure in the deposition chamber. The films were studied by XPS and optical spectrophotometry. The XPS agree with the RBM rather than with the MM. The XPS and optical measurements suggest that the films can be divided into two groups: group I films with $x < 1.65$ and group II films with $x \geqslant 1.65$. Films in group I consisted of Si and oxides of silicon, while those in group II were almost free of Si. The presence of Si in the films of group I makes them absorbent in the visible spectrum while such absorption is absent in the films of group II. The higher refractive index of group I compared to that of group II may be associated with the presence and absence of Si, respectively.

The refractive index of the group II films is close to that of fused silica (SiO_2). The absorption edge of films in group II shifts towards lower wavelengths in the ultraviolet, closer to the absorption edge of fused silica with increasing x (i.e. as the composition of the films approaches that of fused silica).

Acknowledgment

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Appendix. Estimation of the density of a transparent film

Generally, the density of a film is smaller than that of the bulk material from which it is prepared. For the estimation of small changes in the density of a transparent film on a transparent substrate, it seems to be helpful (as outlined below) to have a substrate that is of the same material as the film itself. Then, the most obvious indication of the presence of a small change in the density of a thin film with respect to that of a substrate is usually seen in the changes that occur in the transmittance maxima.

Consider a transparent film of refractive index n_1 on a wedge-shaped transparent substrate of refractive index n_2. A wedge-shaped substrate is suggested so that the effects of reflections from the back face of the substrate on the transmittance measurements are eliminated. Then the maximum transmittance (T_{max}) measured just across the back face of the substrate is [20], assuming that $n_1 < n_2$:

$$T_{max} = \frac{4n_1^2 n_0 n_2}{(n_1^2 + n_0 n_2)^2} \frac{4n_0 n_2}{(n_0 + n_2)^2}$$

where n_0 is the refractive index of air ($\sim$1). Similarly, the transmittance (T_s) of the uncoated substrate across the back face is

$$T_s = \left[\frac{4n_0 n_2}{(n_0 + n_2)^2}\right]^2.$$

Then the difference between the two transmittances is

$$\Delta T = T_{max} - T_s = \left[\frac{16n_2^2}{(1 + n_2)^2}\right]\left[\frac{n_1^2}{(n_1^2 + n_2)^2} - \frac{1}{(1 + n_2)^2}\right]. \tag{A.1}$$

In a case when the film and the substrate are both of the same material, one can assume that $n_2 = n$ and $n_1 = n_2 - \Delta n = n - \Delta n$. This is because, generally, the film's refractive index is known [14] to be smaller than that of the bulk material. Thus, (A.1) may be written as

$$\Delta T = \left[\frac{16n^2}{(1 + n)^2}\right]\left[\frac{(n - \Delta n)^2}{\{(n - \Delta n)^2 + n\}^2} - \frac{1}{(1 + n)^2}\right]. \tag{A.2}$$

It is expected that, when $\Delta n = 0$, ΔT should be zero and indeed this is the case.

On expansion of (A.2), while retaining first-order terms in Δn, as Δn is much smaller than n, we get

$$\Delta T = \frac{32n^2(n - 1)}{(1 + n)^5} \frac{\Delta n}{n}. \tag{A.3}$$

The refractive index and the density (ρ) of a transparent material are related to each other through the Lorentz–Lorenz law, such that

$$\frac{n^2 - 1}{n^2 + 2} \propto \rho$$

which in turn gives

$$\frac{6n^2}{(n^2 - 1)(n^2 + 2)} \frac{\Delta n}{n} = \frac{\Delta \rho}{\rho}. \tag{A.4}$$

Eliminating $(\Delta n/n)$ between (A.3) and (A.4), we have

$$\frac{\Delta\rho}{\rho} = \frac{3(1+n)^4}{16(n^2+2)(n-1)^2}\Delta T. \tag{A.5}$$

The refractive index, n, of a bulk material such as fused silica is readily available and ΔT can be measured from transmittance plots such as those shown in figure 5. In the present work the films with the largest value of x, i.e. $SiO_{1.89}$, have transmittance spectra that are close to those for fused silica (figure 4). For such films, $\Delta T = 0.015$ (figure 5) and n at $\lambda \sim 700$ nm for the fused silica is 1.46. Using these values in (A.5), we obtain

$$\frac{\Delta\rho}{\rho} = 0.12.$$

This means that the density of the films with $x = 1.89$ may be smaller by about 12% than that of the bulk fused silica.

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