

An infrared spectroscopic study of vacuum-evaporated SiO–CeO₂ thin films

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Infrared spectra of vacuum-evaporated SiO–CeO₂ thin films are reported for a series of thin films of varying compositions. They show a systematic shift of the SiO "O stretch" frequency from a value of 1040 cm⁻¹ in the pure (100 mol%) SiO film to 950 cm⁻¹ in the 16 mol% SiO–84 mol% CeO₂ film, as well as a gradual diminishing of the band at 876 cm⁻¹ with increasing CeO₂ concentration. After introducing the general perspective for the analysis of the infrared spectra of amorphous solids, and tetrahedrally bonded compounds in particular, it is proposed that the first two features of the spectra result from a chemical association between non-bridging oxygen atoms of the SiO network and cerium atoms. This entails the interpretation of the band at 876 cm⁻¹ as being due to the stretching vibrations of the non-bridging oxygen atoms. The effect of annealing on the spectra is also presented and explained in terms of creation of new Si–O–Si linkages.

1. Introduction

Over the years we have published from this laboratory a significant number of papers concerning the properties of thin dielectric films made by the co-evaporation of two oxides, at least one of which is a glass-former. Such films are generally of high resistance, possess an amorphous and fairly open structure, and have shown promise as insulating films and as elements in metal–insulator–metal (MIM) active devices. We have become more concerned about the detailed structures and composition of these films, and the similarities and differences between the same system of elements prepared as a glass by melting and as a thin amorphous film by co-evaporation. We have published briefly some comparative results on the SiO–B₂O₃ and TeO₂ systems. We have also investigated glasses of which a major constituent is CeO₂ or its equivalent, and Hogarth and Al-Dhhan [1] have recently described the nature of the optical absorption edge in thin films of CeO₂–SiO, as well as the derived values of the optical energy gap E_{opt} .

The role of lanthanide elements in glasses is known to be rather different from the role of the more usual transition metal ions, since although the bonding is via the outermost 5p and possibly 5s electrons, the electrons in the incompletely filled 4f shell are the ones more likely to be involved in processes such as optical absorption and the conduction of electricity. Thus when the optical absorption edge of thin CeO₂ films is studied it is found to be sharp, more like that of a non-metallic crystal than that of a glass. A considerable amount of SiO needs to be added to the CeO₂, up to 60 mol% in fact, before a significant change in the value of E_{opt} is measured. The nature of the bonding in the thin films is therefore of interest, particularly since it has recently been observed that the spin density measured by electron paramagnetic resonance

(e.p.r.) is drastically reduced as the CeO₂ content of a series of CeO₂–SiO thin films is increased. The spin density is believed to be a measure of the concentration of unsatisfied electrons on dangling bonds in the open thin film structure, and thus the reduction indicates the development of a more closed structure as the CeO₂ concentration is increased. One means of studying structure and bonding in films is the use of infrared absorption spectroscopy. This is particularly of concern in the present instance, since the optical edge in CeO₂ resembles that of a crystal whereas the edge of SiO is much more like that of a glass in which the absorption is due to indirect transitions.

The only report of infrared absorption in thin CeO₂ films is by Mochizuki [2] who studied his samples in the region 200 to 1000 cm⁻¹ and found a band at 285 cm⁻¹ together with a shoulder at 585 cm⁻¹, both of which he attributed to crystal lattice modes of vibration.

Thin films of SiO, on the other hand, have been extensively studied, largely on account of their use in microelectronic and optical devices. Thus Pliskin [3] reported absorption at 1000 and 1060 cm⁻¹ for SiO and SiO₂, respectively, and suggested that the composition of SiO would depend on the evaporation parameters of rate and residual pressure in the vacuum system. The parameter normally used to characterize the process is R/p where R is the evaporation rate and p is the system pressure. Timson and Hogarth [4] showed how the concentration of dangling bonds in SiO determined by electron spin resonance varied as a function of R/p . For high values the spin density was $\approx 10^{20}$ cm⁻³, corresponding to an open SiO structure, whereas for low values the spin density was $\approx 10^{18}$ cm⁻³ corresponding to SiO₂. Thus in the literature, evaporated silicon oxide is often referred to as SiO_x. Philipp [5] elucidated the structures of SiO_x

samples by the use of optical techniques and proposed that they are built from randomly oriented $\text{Si}_y\text{O}_{4-y}$ tetrahedra where y may vary from 0 to 4. Hübner [6] made use of high-resolution scattering experiments to show that SiO films prepared by vacuum evaporation must be described by random bonding statistics employing the tetrahedra of Philipp, while the SiO films prepared by chemical vapour deposition of SiO_x at elevated temperatures could be considered as simple mixtures of silicon and SiO_2 . The problem is related by Hübner to his own work on the $\text{Si}-\text{SiO}_x-\text{SiO}_2$ structures occurring in microelectronic devices.

The chemical shift in the Si–O stretch frequency of SiO_x as x is varied has been studied by several workers. Schumann *et al.* [7] described the measured spectra of SiO_x films prepared by reactive sputtering for x values between 0.20 and 1.95, and showed that the theoretical absorption frequencies were 1085 cm^{-1} for SiO_2 and 1019 cm^{-1} for SiO. They also showed that the bond angles of the Si–O–Si bridges must lie between 118 and 146° . Lucovsky *et al.* [8] have recently investigated SiO_x films prepared by plasma-enhanced chemical vapour deposition using infrared spectroscopy, X-ray photoelectron spectroscopy and Auger electron spectroscopic techniques and have given a table of infrared absorption frequencies ranging from 940 cm^{-1} for oxygen-doped silicon to 1075 cm^{-1} for SiO_2 . Using their figures the value for stoichiometric SiO would be 1004 cm^{-1} . Pai *et al.* [9] have related the absorption frequency to the value of x in SiO_x which yields the same value for SiO as given above.

The theoretical basis for predicting the form of the infrared spectra of SiO_x is well established. Bell and co-workers [10–12] in a series of papers between 1968 and 1971 have used the structural models of Bell and Dean [13] and the mathematical method of Dean and Bacon [14] to calculate the vibrational frequency spectra of vitreous SiO_2 , GeO_2 and BeF_2 as a means of investigating the spatial extension of these vibrational modes in the solid, and to assign the prominent spectral frequencies to the normal modes associated with cation motions and with bond stretching, bending and rocking motions of the anions in the Si–O–Si linkages. They obtained 1040 , 730 and 410 cm^{-1} for the theoretical frequencies of the Si–O bond stretching, bending and rocking vibrations, respectively, and 850 cm^{-1} for the stretching frequency of the non-bridging oxygen atoms.

Laughlin and Joannopoulos [15] have reported the use of the newer Cluster Bethe Lattice Model (CBLM)

for analysing amorphous materials so as to derive the densities of vibrational states and the infrared and Raman spectra for amorphous SiO_2 , and the results are in good agreement with those of Bell and colleagues. Lucovsky *et al.* [16] have refined the lattice model to include effects of intermediate-range order and a more appropriate Hamiltonian incorporating a valency force-field instead of the Born Hamiltonian used earlier.

The objects of the present investigation were to determine whether the prepared films of SiO– CeO_2 composites constituted a new chemical species, rather than a simple mixture of the two oxides, and to elucidate the nature of any species formed. Such a change would probably manifest itself in the development of new infrared bands and/or the disappearance of some of the existing bands in the original materials.

2. Experimental procedure

The thin films were evaporated on to silicon wafers by a vacuum co-evaporation technique described by Hogarth and Wright [17]. Open tungsten boats and covered molybdenum boats were used for the heating of the CeO_2 and SiO sources, respectively. Although the high melting point of CeO_2 (2500°C) posed some difficulties in maintaining low pressures, they were generally kept at better than 4×10^{-5} torr. The substrate was maintained at a temperature of $100 \pm 10^\circ\text{C}$ throughout all evaporations.

The approximate relative amounts of the components in each specimen were calculated prior to evaporation and replicated as well as possible by manually adjusting the current supply heating the sources, while using calibrated quartz crystal monitors to monitor the deposition rates. Exact values of the thicknesses of three of the films (including the two pure SiO and CeO_2 films) were determined using multiple-beam interferometry [18]. Evaporation rates and film thicknesses were typically of the order of 0.7 nm sec^{-1} and 500 nm , respectively. Table I summarizes the preparation conditions and film parameters for the series.

The spectra were run on a Perkin Elmer SP2000 spectrophotometer (having a resolution of 2 cm^{-1}) to investigate the region between 200 and 400 cm^{-1} . The region above the latter value was measured on a Model 1710 FTIR spectrometer (with a resolution of 4 cm^{-1} and excellent spectral reproducibility) supplied by the same company.

The annealing of the films was performed for a

TABLE I Composition and preparation data for SiO– CeO_2 films

SiO content (mol % SiO)	Film thickness (nm)	Deposition rate (nm sec ⁻¹)	R/p (sec ⁻¹ torr ⁻¹)
100	600.0	2.6	1.3×10^5
77	521.5	1.3	7×10^4
62	445.5	0.7	1×10^4
51	420.5	0.7	1×10^4
44	648.5	0.3	3×10^4
30	1005	1.0	3×10^4
25	907.0	0.6	3×10^4
16	427.5	0.9	2×10^4
0 (i.e. pure CeO_2)	735.0	0.5	3×10^4

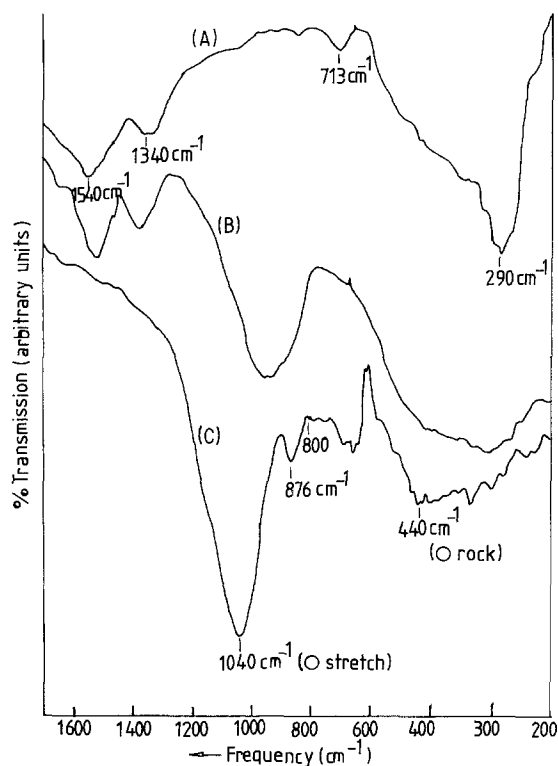


Figure 1 Infrared spectra of (A) 0 mol % SiO–100 mol % CeO₂, (B) 16 mol % SiO–84 mol % and (C) 100 mol % SiO–0 mol % CeO₂ thin films showing the positions of important bands. Note the change of scale at 400 cm⁻¹.

duration of two hours at a temperature of 200°C under a vacuum of 1×10^{-5} torr in the same unit as that used for their preparation.

3. Experimental results

Fig. 1 shows the spectra of films of SiO and CeO₂ and also that for the 16 mol % SiO–84 mol % CeO₂ film. The absorption bands of SiO are labelled in a traditional manner as “O stretch” for the 1040 cm⁻¹ band, and “O rock” for the band at approximately 440 cm⁻¹, the term O referring to the bridging oxygen atoms in the Si–O–Si linkage. The significance of the band at 876 cm⁻¹ is elucidated in the discussions that follow. The notable features of the CeO₂ spectrum are the strong absorption at 290 cm⁻¹ and the weaker bands at 1540, 1340 and 713 cm⁻¹. The pronounced broadening of the first band in going from the pure CeO₂ film to the 16 mol % SiO–84 mol % CeO₂ sample is noted.

Fig. 2 shows the spectra of films containing varying molar percentages of SiO and CeO₂, revealing a clear shift in the “O stretch” frequency with changing film composition. These shifts are shown graphically in Fig. 3. Equally significant is the gradual decrease resulting in the eventual disappearance of the band at 876 cm⁻¹ with the reduction of SiO concentration. The sudden loss of the SiO feature centred at 670 cm⁻¹ after the SiO concentration is reduced below 30 mol % should also be noted.

4. Discussion of results

4.1. Preamble

Although the results show a gradual disappearance of the band at 876 cm⁻¹ in SiO, no obviously new bands are observed in the range of frequencies investigated.

Thus the systematic shift in the SiO stretch frequency, together with the weakening band at 876 cm⁻¹ with increasing CeO₂ concentration, becomes the most interesting feature of the spectra. Before looking for chemical explanations for these, one must first consider all physical reasons.

With reference to the shifts, one such reason that suggests itself immediately is that they are due to some stoichiometric change in the SiO_x content of the films brought about by the preparation conditions. That this is an unlikely explanation for the shifts observed in this work is evidenced firstly in the nature of Curve A in Fig. 3, whose monotonicity and general form seems to indicate otherwise. Secondly, at the slow rates of evaporation used one would expect that if anything, the frequencies should shift to higher values. This is all the more so since the films with higher CeO₂ concentrations were prepared at lower SiO evaporation rates. Therefore a reason based on simple stoichiometry seems highly unlikely, and a chemical explanation must be sought.

An obvious way of analysing the chemical nature of the film is to conjecture the presence of possible “molecular-like” groupings of atoms within the solid and to use their vibrational spectra as a first approximation for the infrared spectra of the film. In the present case one could for instance consider species containing Ce–Si–O groupings and calculate the associated vibrational frequencies. In the simplest approximation, these bonds could be represented by completely uncoupled simple harmonic oscillators representing independently vibrating bonds. Such vibrational frequencies can be estimated quite easily. For instance, assuming that only the central interactions are important and using Saksena’s [19] central force constant of 5×10^2 N m⁻¹ for the Si–O bond, and Mochizuki’s [2] force constant of 2×10^7 N m⁻¹ for the Ce–O bond, one easily obtains a Ce–O stretch frequency of 570 cm⁻¹. Also, using the electronegativity differences for Si–O and Ce–Si bonds as a measure of their relative central force constants, an estimated stretch frequency of 443 cm⁻¹ for Ce–Si vibrations is obtained.

Whether such approximation techniques have any validity becomes clear only after one considers the subject of the vibrational spectra of amorphous solids in its entirety. This may be done by starting with the spectra of crystalline solids, and examining the changes that occur as the amorphous state is approached.

4.2. Infrared spectra of amorphous solids

Compound crystals consist of basic structural groups arranged periodically. The modes of vibration of the crystal may be divided into those confined within these groups, called internal modes, and those of the groups relative to each other, known as external or lattice modes. The features of the infrared spectrum of the crystal are determined by the absorption of radiation by those modes capable of exhibiting changing dipole moments. If the bonding within these groups or parts of these groups is strong enough so that they resemble molecules (as for example in molecular crystals), then the crystal spectrum will include a set of bands

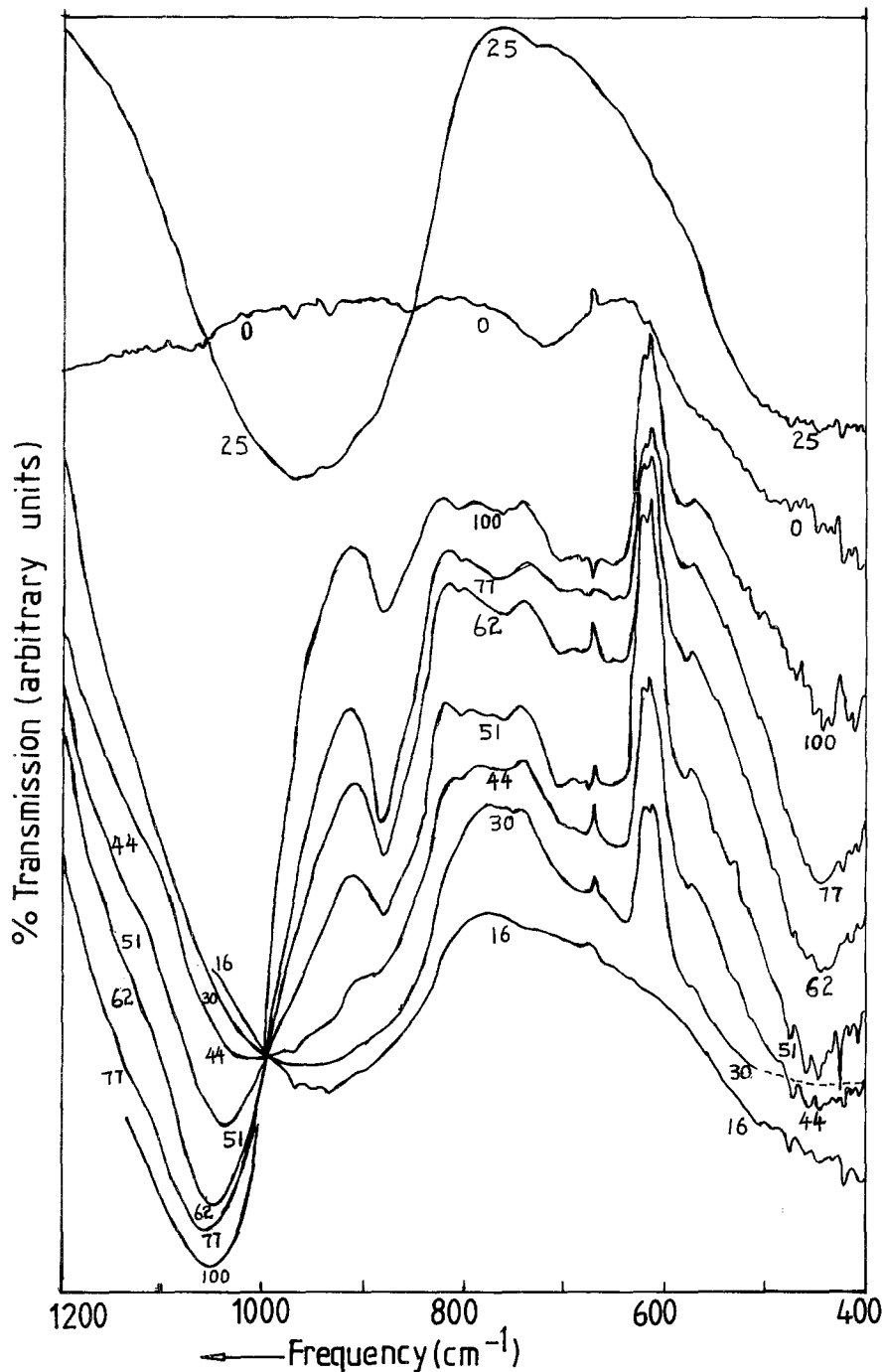


Figure 2 Infrared spectra of SiO-CeO₂ thin films of various compositions. The numbers show values of (mol % SiO).

corresponding to the molecular spectrum of such a molecule, as well as other bands.

As pointed out by Mitra [20], for such "molecular-like" crystals, the spectra will be different from the corresponding molecular spectra in the following respects:

- (i) There will be the appearance of entirely new bands in the low-frequency region (below $\approx 800 \text{ cm}^{-1}$). These will be due to the lattice vibrational modes.
- (ii) The positions of the molecular bands will be shifted from their values in the gaseous state.
- (iii) The molecular bands may split into multiplets.

He explains the origins of these differences by considering the perturbative effects of the crystal environment on the vibrational levels of the molecule. In terms of potentials, the molecule embedded within the crystal is subjected to a different vibrational potential

than in the isolated situation, leading to a new set of vibrational levels and resulting in the observed shift in the positions of the infrared bands. The band splittings may be associated with a lifting of degeneracies of the vibrational states. In the isolated molecule, several modes may possess the same vibrational frequency due to the high symmetry of the molecule and its environment. The new environment within the crystal will introduce asymmetries via the new potential seen by the molecule, leading to a lifting of some degeneracies and introducing splittings in the bands.

If we accept the continuous random network (CRN) model of the amorphous state proposed by Zachariasen [21, 22], then we should expect that in this state the average vibrational potential seen by the molecular units is the same (within an additive constant) as that in the crystalline state. This is best seen by representing the vibrational potential energy V of

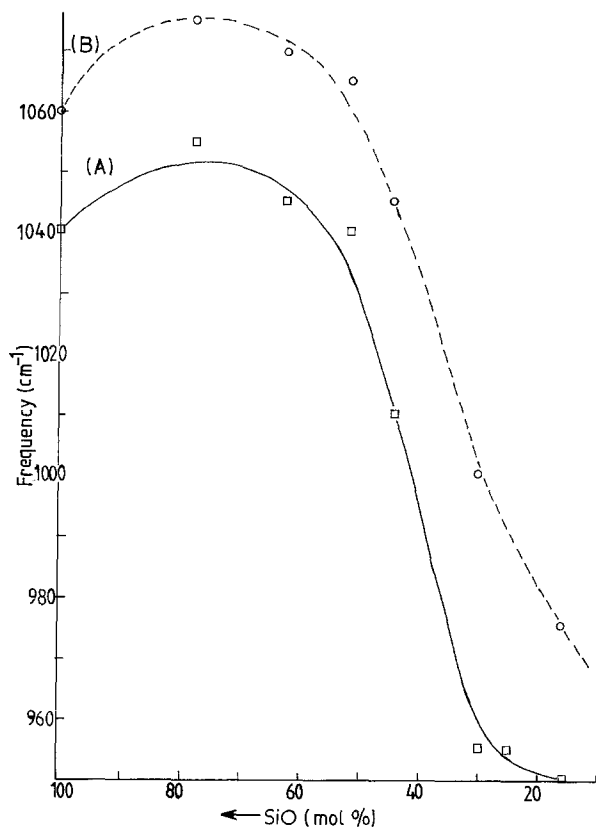


Figure 3 "Si-O stretch" frequency against film composition curves for the whole series of films (A) before annealing and (B) after annealing.

the molecule after Horning [23] as

$$V = \sum_n V_n + \sum_n \sum_k V_{nk} + V_l + V_{ln}$$

where V_n is the potential energy of the molecule due to all the internal coordinates of the n th molecular group, V_{nk} is the potential energy of the n th molecule due to the k th molecule, V_l the potential arising from the external coordinates and V_{ln} the potential energy of the n th molecule due to the lattice coordinates.

In going to the amorphous state, the introduction of disorder will change the individual values of the V_n and V_{nk} terms. The summations however ensure that the net changes due to these variations will be zero, and the only conceivable change will be due to constant changes in V_l and V_{ln} . As a result the vibrational energy eigenvalues of the associated Schrodinger equation will change at most by the same additive constant, and the positions of bands in the vibrational spectrum, which depend on the differences between such eigenvalues, will remain fixed at their crystalline values. However the increase in disorder, manifest especially in the relative orientations of the molecules, will mean a considerable decrease in the local symmetry of the potential. This should lead to a pronounced increase in degeneracy lifting and consequent splitting of the molecular bands. The net result should be a broadening of these molecular bands.

It is seen from the above discussion that the analysis of the infrared spectra of solids is greatly simplified if the solid could be perceived as composed of molecular groups bound together weakly. In the case of SiO_2 , the SiO_4 tetrahedra may provide such units. Lucovsky

et al. [24] have shown that in the case of glassy GeS_2 , a solid composed of GeS_4 tetrahedra, such an analysis is indeed possible. Criteria for deciding when such a partitioning of modes is possible for the general case of tetrahedrally bonded A-X-A systems, where A is beryllium or a Group IV element, and X is either oxygen or sulphur, are provided by Sen and Thorpe [25]. They show that if the A-X-A bond angle is close to 90° , the effective coupling between the AX_4 tetrahedra is zero, and they may be treated as independent molecular units. As the bond angle approaches 180° , however, the coupling increases and the character of the spectra is decided more by the A-X-A bonds than by the tetrahedra. Such is the case with SiO_2 and GeO_2 . However, because of the continuum of vibrational energy states now present due to the strong coupling between the tetrahedra and the consequent perturbation of their energy levels, the analysis is not easy, even in terms of these linkages. This is seen in the work of Bell and co-workers, which will be described here in some detail because of its relevance to the interpretation of the present spectra.

4.3. The spectrum of a- SiO_2

Bell *et al.* [11, 12] adopt the CRN model for a- SiO_2 and build two physical models of the network with SiO_4 tetrahedra as basic building blocks. Randomization is brought about by varying the bridging bond angle as well as the relative orientations of the tetrahedra. The X-ray radial distribution function and infrared spectra are calculated under both fixed-end (surface oxygen atoms fixed) and free-end (surface oxygen atoms free) boundary conditions. The latter are more appropriate here since the relatively open structure of thin films with greater surface/volume ratio implies higher concentrations of non-bridging oxygen atoms at the surfaces. These workers resolve the normal vibrational modes of the bridging unit (Fig. 4) into

- (i) motion of the bridging oxygen atom in the S direction (called asymmetric stretch or S vibration),
- (ii) motion of the oxygen atom in the B direction (called the "O bending" or B vibration),
- (iii) motion of the oxygen atom in the R direction (called the "O rock" or R vibration).
- (iv) all motions of the silicon atom (called cation, or C motions),
- (v) motion of the non-bridging oxygen atoms along the direction of their bond (called non-bridging stretch, or NS vibration),
- (vi) motion of the non-bridging oxygen atoms perpendicular to their bonds (called non-bridging bend or NB vibrations).

Their calculated spectra show bands at 1040, 850, 730 and 410 cm^{-1} , which are close to the observed bands for a- SiO_x . The complexity of these bands is revealed when vibrational modes are assigned to them. These assignment patterns clearly show that although the major contributions to the above bands are from the S , NS, B and R vibrations, respectively, these modes are by no means the only ones contributing to these bands. Thus they show for example that only 65% of

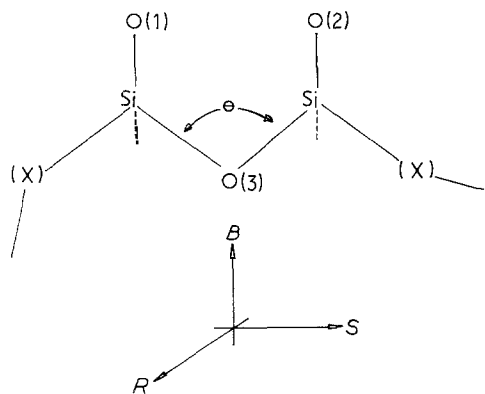


Figure 4 Vibrational modes of the Si–O–Si linkage. The figure shows two SiO_4 -type tetrahedra linked by a bridging oxygen atom O(3). O(1), O(2) non-bridging (e.g. surface) oxygen atoms; (X) further bridging oxygen atoms or other oxygen atoms; (B,S) vibrational coordinates in the plane of the Si–O–Si linkage; (R) vibrational coordinate perpendicular to the above plane.

the energy in the *S* band comes from *S*-type vibrations, while the remaining 35% is mostly due to cation motion.

These workers also investigate the degree of localization of the normal modes of vibrations in a- SiO_2 [11]. Of significance is their result that the NS band at 850 cm^{-1} is highly localized, and that localization generally increases with frequency.

Theoretically more rigorous methods of calculations elucidated more recently involve the use of Cluster Bethe Lattices to model the CRN (e.g. Laughlin and Joannopoulos [15]). Here the infrared adsorption is expressed by the quantum-mechanical relation

$$n\alpha(\nu) = \pi^2 \left(4\pi N \frac{e^2}{M} \right) f(\nu)g(\nu)$$

where $\alpha(\nu)$ is the absorption coefficient, $g(\nu)$ is the density of vibrational states function, $f(\nu)$ is the oscillator strength which includes the matrix element and the other terms are constants with their usual meanings (Lucovsky and Hayes [26]). Usually the matrix element is found to be only a slowly-varying function of the frequency, which means that $g(\nu)$ itself resembles the frequency spectrum closely. The results gained using these more sophisticated techniques are very similar to those of Bell and co-workers.

4.4. Interpretation of current spectra

To make a plausible interpretation of the spectral trends noted in this work and recorded in Fig. 2, one must begin with an examination of the spectrum of “pure” SiO_2 . The strong absorption at 1040 cm^{-1} exhibited by the 100 mol % SiO_2 spectrum is clearly due to the well-known “O stretch” or *S* vibration of the Si–O–Si linkage, its frequency value of 1040 cm^{-1} indicating that this film is not composed of stoichiometric SiO_2 but that some small degree of inadvertent oxidation has taken place, presumably in the preparation process. Similarly the broad medium band at 440 cm^{-1} is without doubt the “O rock” or *R* band due to the rocking motion of the bridging oxygen atom. But the expected *B* band at 800 cm^{-1} due to the bending motion of the same oxygen atom is absent

(although one can just make out the rudiments of this band in the region 750 to 800 cm^{-1} on careful examination). Instead, a new band appears at 876 cm^{-1} . A similar band occurs in the spectra of Pliskin [3]. For very fast evaporation rates (37.5 nm sec^{-1}) and medium vacuum (1×10^{-4} torr) he obtains a band at 1000 cm^{-1} and a weak shoulder at just below 800 cm^{-1} . On the other hand, he obtains bands at 1085 , 870 and 800 cm^{-1} for slow rates (less than 0.5 nm sec^{-1}) and low vacuum (2×10^{-4} torr or higher). He attributes the new band to the formation of the Si_2O_3 species.

If we adopt the alternative view that SiO_x thin films are composed of tetrahedra of the type proposed by Philipp (instead of a mixture of SiO_2 , Si_2O_3 and SiO species as suggested by Pliskin) then both Pliskin’s results and the current work can be viewed directly in terms of the calculations of Bell and co-workers. Then the only explanation that can be assigned to the band near 870 cm^{-1} is that it is due to the stretching vibrations of the non-bridging oxygen atoms (i.e. the NS vibrations of Bell and co-workers). Such an assignment is supported by the observation of the workers cited that although this band is not normally present in vitreous silica (which is known to have a relatively closed structure), it does become evident in the same material after it is exposed to heavy neutron irradiation. According to Simon [27] this disrupts the SiO_2 network, producing non-bridging oxygen atoms in the structure. Since thin films are known for their relatively open structure as compared to the glassy state, it is not unreasonable to expect that they contain a high degree of non-bridging oxygen atoms, giving rise to the NS band near 870 cm^{-1} . An independent endorsement of this assignment of the 870 cm^{-1} band is contained in the results of annealing the films, to be discussed later. (A possible reason for the non-appearance of this NS band in the rapidly deposited film of Pliskin may be that the film was oxygen deficient, since SiO_2 decomposes into silicon and O_2 above 1250°C .)

Having accepted the view that the new band is due to oxygen atoms with dangling bonds, both the disappearance of this band with increasing CeO_2 concentration and the shift of the “O stretch” band may be explained in the same process. As CeO_2 is added, the highly electropositive cerium atoms must readily attach themselves to these oxygen atoms with unsatisfied valencies, thereby reducing the density of non-bridging oxygen atoms and consequently weakening the NS band. At the same time the more electropositive environment now seen by the bridging oxygen atoms within a radius of a few bond lengths would act so as to reduce the *S* vibrational frequency via an electron induction effect similar to that proposed by Lucovsky [28] for the chemical shift observed in SiO_x . According to this proposal the *S* band shifts to lower frequencies in SiO_x when the concentration of silicon atoms (which are less electronegative than oxygen atoms) in the oxygen environment is increased. In the present case a similar but more pronounced effect should be created by the addition of the even less electronegative cerium atoms to the oxygen vicinity.

A positive confirmation of this explanation is



Figure 5 Spectra of a 77 mol% SiO₂-23 mol% CeO₂ thin film (—) before and (---) after annealing.

accorded by the recent e.p.r. investigations of the same series of films by Razzaq *et al.* [29]. They show that the spin density of the films reduces dramatically with the addition of CeO₂. Since the unpaired electrons resident on the non-bridging oxygen atoms would be expected to contribute significantly to the total measured spin density, a reduction in their quantity would imply a similar reduction in the number of non-bridging oxygen atoms, evidently due to the presence of cerium atoms.

4.5. Effect of annealing

One last consideration that cannot be left unattended is the possibility that the conditions under which the films were prepared had themselves somehow affected the shifts in the *S* band. In particular, since CeO₂ with its high melting point (2500°C) was more difficult to evaporate than SiO₂, the films having relatively lower concentrations of SiO₂ took longer to prepare. Thus it may be possible that the shifts arose out of an accidental "annealing" effect to which the latter specimens of the series were subjected as a result of their longer preparation times. If this were the case, then it is to be expected that a similar heat treatment of the specimen richer in SiO₂ should also produce a lowering of their *S* band frequencies. To test this possibility, it was decided to anneal the whole series of films. The temperature of 200°C and annealing period of two hours were chosen to be well above the conditions prevailing during the evaporations. This should have reduced the frequency difference between the two ends of the series, or at least lowered the frequencies of the films richer in SiO₂ content.

The results of the annealing are contained in Fig. 5 as well as in Curve B of Fig. 3. It is seen that there is a general shift of all frequencies towards higher values. Moreover it is found that the hitherto almost non-existent "O-bend" spectral band at 800 cm⁻¹ becomes clearly apparent in the typical annealed spectrum (see

Figure 5). In addition a perceptible increase in the intensities of the "O stretch" and "O rock" bands and a similar decrease in the NS band is noticed. These changes clearly indicate an increase in the number of Si-O-Si linkages at the expense of non-bridging oxygen atoms. Thus annealing evidently converts some of the non-bridging oxygen atoms to bridging ones, thereby shifting the oxygen stretch frequencies to higher values. Conversely, since the above transformation to a more closed structure with annealing was only to be expected, this provides a reaffirmation of the identification of the band near 870 cm⁻¹ as the NS band.

Since annealing increases rather than decreases the frequencies, the lowering of frequency with SiO₂ concentration cannot be assigned to any accidental heat treatment of the samples during preparation. The chemical reasons for the shifts presented above therefore become even more plausible, and it can be said in conclusion that the observed spectral features are very probably due to the attachment of cerium atoms to available non-bridging oxygen atoms in the SiO₂ CRN.

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