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Infrared spectra of mixed oxide thin films containing Group IV oxides with CeO_2 – a comparative study

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The infrared spectra of a series of vacuum co-evaporated SnO_2–CeO_2 thin amorphous films are presented and compared with those of similar series of SiO–CeO_2 and GeO_2–CeO_2 films reported earlier. It is noted that although they are chemically similar, each series of spectra contains unique features. The differences are attributed to structural variations related to the size and mass differences among the Group IV cations. The picture of a modified random network is invoked to explain the possible structure of the films. Some preliminary extended X-ray absorption fine structure results are quoted to support the idea that Ce^{4+} exists as six-fold coordinated modified cations amongst the silicate-like anions formed by the network-forming Si^{4+} ions.

1. Introduction

This paper is the final in a series of studies of the infrared (IR) characteristics of vacuum-evaporated films containing a Group IV oxide co-evaporated with CeO_2. Such films first gained interest because of the possible utilization of their dielectric properties in metal–insulator–metal (MIM) micro-electronic devices. CeO_2 was chosen as a common component because of its unique optical absorption edge, which is sharp even in the amorphous phase. By varying the compositions of the films, it was found that their optical band-gaps could be tuned to any desired value within the range set by the pure films.

The current investigations were initiated by the earlier electrical and optical measurements on the same three series by Hogarth, Al-Dhhan and Riddleston [1–5]. Singh and Hogarth followed this work with the first of the IR studies [6] on the SiO–CeO_2 series, and later on the GeO_2–CeO_2 series of thin films [7].

This paper first reports the extension of this IR study to the SnO_2–CeO_2 system. It then compares the results of all three systems. Finally, it discusses qualitatively the possible structures of these films and briefly quotes the preliminary results of an extended X-ray absorption fine structure (EXAFS) analysis of the structure of the first of these series in support of the ideas presented.

2. Experimental procedure

The SnO_2–CeO_2 thin films were deposited by a co-evaporation technique described by Hogarth and Wright [8], on to silicon substrates held at a temperature of 100° C. Film thicknesses were monitored using quartz crystal monitors and measured using multiple beam interferometry [9]. IR spectra were run on a Perkin–Elmer model 1710 FTIR spectrophotometer over the 400 to 2000 cm^{-1} range of frequencies.

Samples for the EXAFS measurements were prepared by r.f. sputtering in a Nordiko sputtering unit on to mylar substrates. The measurements were carried out on the LIII X-ray absorption edge of cerium at Station 7.1, SERC Daresbury Laboratory, Warrington, UK. The results were analysed using the EXCALIB, EXBACK V and EXCURV 88 software packages available at the same laboratory.

3. IR spectra of vacuum-evaporated SnO_2–CeO_2 thin films

Fig. 1 shows the IR spectra of six different compositions of the films (ranging from 100 mol % SnO_2/0 mol % CeO_2 to 25 mol % SnO_2/75 mol % CeO_2) over the frequency range 400 to 2000 cm^{-1}. The individual spectra are labelled in the figure by their mol % SnO_2 content. The pure SnO_2 film is seen to exhibit a sharp peak at 800 cm^{-1} with a shoulder on the high-energy side, and a broad peak centred at 500 cm^{-1}. This spectrum is distorted somewhat by the presence of the large "symmetric bend" absorption peak of the water molecule at 1595 cm^{-1} (not shown in the figure). This peak was included inadvertently in the spectrum and arose from the single-beam nature of the spectrometer used.

The peak at 800 cm^{-1} is almost certainly due to the stretching vibrations of the Sn–O–Sn linkages. It must be noted here that the octahedral units of the rutile structure of crystalline SnO_2 should be retained in the amorphous state. Because this unit possesses two non-equivalent bond lengths, with a mean value of 0.205 nm [10] one may expect to see two peaks corresponding to the different lengths. However, the small difference in

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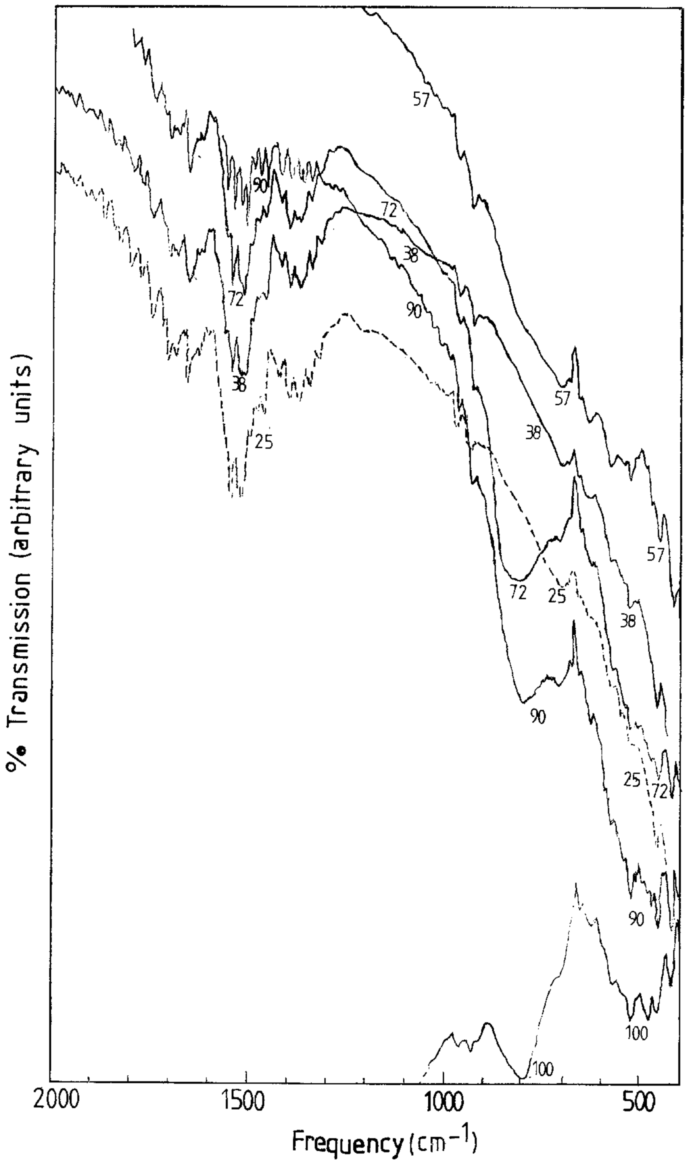


Figure 1 Infrared spectra of SnO_2-CeO_2 thin films of various compositions. The numbers indicate film composition in mol % SnO_2.

these lengths probably means that the peaks remain unresolved.

As seen in Fig. 1 the 800 cm^{-1} peak reduces rapidly in strength as CeO_2 is added to the films, and new peaks appear at 1340 cm^{-1}. These new peaks, as well as the sharp rise in absorption at the lowest frequencies, as seen in the 25 mol % SnO_2/75 mol % CeO_2 spectrum, are known to be due to CeO_2, which has been observed [6] to have peaks at 290, 1340 and 1540 cm^{-1}.

4. Comparisons with previous Group IV oxide series

4.1. Summary of results

In the SiO-CeO_2 series of IR spectra [6] the pure SiO film possessed a prominent peak at 1050 cm^{-1} arising from the stretching vibrations of the Si-O-Si linkage, a broad medium band at ~ 440 cm^{-1} produced by the rocking motion of the same bending, and a weak peak at 876 cm^{-1} identified as originating from the stretching vibrations of the non-bridging oxygen atoms. As CeO_2 was added to the films the O-stretch peak of the bridging oxygen shifted towards lower frequencies, while that of the non-bridging oxygen atom at 876 cm^{-1} steadily weakened, disappearing altogether beyond the 44 mol % SiO/56 mol % CeO_2 composition. Both of these changes were explained as being produced by the Ce^{4+} ions co-ordinating to non-bridging oxygen ions.

Electron spin resonance (ESR) results for a similar series of films [11] supported the above picture by showing that the number of dangling bonds on oxygen atoms reduces as the Ce^{4+} concentration is increased.

The GeO_2-CeO_2 series of films [7] showed a strong absorption band in the 830 to 730 cm^{-1} region, another centred at 500 cm^{-1} and a third at 350 cm^{-1}. The first band arises partly from the stretching vibrations of the Ge-O-Ge linkage, and partly from the O_1^- defect structure. The band at 500 cm^{-1} could not be attributed to the bending vibrations of the bridging oxygens. Also, there was no systematic shift in the bridging O-stretch bond frequency, and only a very gradual weakening of its strength. The band at 500 cm^{-1}, however, weakened dramatically with only a small proportion of Ce^{4+} ions.

The SnO_2-CeO_2 results reported here show bands at 800 cm^{-1} (due to O-stretch vibrations of the Sn-O-Sn linkage) and another band at 500 cm^{-1}, the former band reducing rapidly with CeO_2 addition but not shifting in position. Table I lists the important IR bands of all three series.

TABLE I Important IR bands for the three series of films (M represents either Si or Ge or Sn)

Film series	M–O–M linkage related bands			Other bands (cm^{-1})
	O-stretch (cm^{-1})	O-bend (cm^{-1})	O-rock (cm^{-1})	
Si–CeO_2	1050–950	800 (very weak)	440	876 (non-bridging O-stretch)
GeO_2–CeO_2	825–730	–	350	500
SnO_2–CeO_2	800	–	–	500

4.2. Comparison of features

Although one would expect all three series of films, containing chemically similar cations, to exhibit similar IR characteristics, the results of these investigations show each series to possess unique features. Most notable is the shift in the Si–O–Si O-stretch frequency with change in composition. The absence of similar shifts in the latter two series is intriguing in view of the identical electronegativities of all the Group IV elements (see Table II). Possible explanations can, therefore, be related only to differing sizes and masses of these cations. In particular, the relatively small size of the Si^{4+} cation enables it to occupy tetrahedral sites amongst close-packed oxygen anions while the larger Ge^{4+} cations are sometimes found in octahedral holes. The still larger Sn^{4+} ions are found exclusively in the latter sites. In addition, the larger masses of the latter two cations will have a direct bearing on the O-stretch frequencies. With increasing masses the cationic contribution to the vibrational energy of the "O-stretch" mode of motion of the Si–O–Si unit will decrease (as demonstrated quantitatively by Bell *et al.* [12]) leading to an overall decrease in frequency of the associated peak.

The possibility that the difference in oxygen stoichiometry between the first series and the following two could have some bearing on the IR results, cannot be allowed to go overlooked. Specifically, it may be argued that the different behaviour of the O-stretch frequency in the first series would be linked to the oxygen deficiency in these films. Arguments against such a case have been presented earlier [6]. Recently, measurements have been made on r.f. sputtered films of the SiO/CeO_2 and SiO_2/CeO_2 systems [13] which show explicitly that the O-stretch frequency shifts with CeO_2 addition regardless of the oxygen stoichiometry of the films. Table III shows the O-stretch peak positions in relation to the composition for both series. It is seen that although the initial peak position is lower for the SiO/CeO_2 series, both show a clear reduction in frequency with CeO_2 addition.

The feature unique to the GeO_2–CeO_2 series was the rapid disappearance of the peak at 500 cm^{-1} with CeO_2 addition. The source of this peak could not be identified, although it was ascertained that it could not be attributed either to the O_1^0 or the O_1^- centre (i.e. uncharged or charged non-bridging oxygen) stretch vibrations. The likely cause appeared to be a reactive centre present in GeO_2 thin films but absent in both SiO and SnO_2 films. More interestingly, such a centre also appears to be absent in vitreous GeO_2 [14].

TABLE II Useful atomic parameters [19]

Element	Atomic mass	Radius of cation (nm)	Electronegativity
Si	28.09	0.041	1.8
Ge	72.59	0.053	1.8
Sn	118.69	0.071	1.8
Ce	140.12	0.101	1.1
O	16.00	0.141	3.5

TABLE III Shift in Si–O–Si O-stretch peak position with film composition for SiO/CeO_2 and SiO_2/CeO_2 sputtered films

Film composition (at %)				O-stretch peak position (cm^{-1})
Si	Ce	O	Ar	
SiO/CeO_2 films				
29.7	10.7	51.1	8.6	1025
24.5	15.2	55.0	5.3	1000
17.9	19.8	57.5	4.8	970
16.5	21.1	58.7	3.7	950
SiO_2/CeO_2 films				
30.7	2.5	66.5	0.2	1070
23.6	9.5	66.2	0.69	1060
18.4	14.9	66.6	0.61	1050
7.7	25.5	66.4	0.38	960
6.3	27.1	66.7	0	950

In marked contrast to the above, the SnO_2–CeO_2 series neither exhibits the O-stretch frequency shifts nor a disappearing band. However, the Sn–O–Sn O-stretch peak reduces in strength much more rapidly with CeO_2 addition than in the other series.

These varied results for chemically similar series of films suggests that their infrared responses are influenced to a great extent by their ionic packing and the presence of defect centres in some films.

5. Possible structure of films

An important aim of these investigations has been to elucidate the structure of the series of the films with formula $Ce_xM_yO_z$ (where M represents one of the Group IV elements Si, Ge, Sn). A rigorous determination would only be possible if a more detailed local atomic structure study by a technique such as EXAFS were coupled with the present IR investigations. Such a complementary study is under way for the first of the series. It is instructive in the meantime to reflect on the most probable nature of the structure of these films.

Crystalline ternary oxides may acquire the relatively simple structures of binary oxides if the cations are similar in size. This is possible because the similarity in size implies that one cation may substitute for the other in its oxide structure in either an irregular or a regular way, giving rise to random structures or superstructures, respectively ([10], p. 575 ff.). But if, as in the present case, cations are quite dissimilar in size (see Table II), then these oxides acquire the less simple "complex oxide" structures. A unit cell description of all such structures would entail the enumeration of a formidable range of possibilities. The task is simplified, however, by the large electro-negativity difference between cerium and the Group IV elements. It implies that the Group IV atoms would be found covalently bonded to oxygen atoms in the form of complex anions similar to those found in the silicates, with Ce^{4+} cations co-ordinating ionically to their singly

TABLE IV Variation of silicate anion structure with Si : O ratio (from West [15])

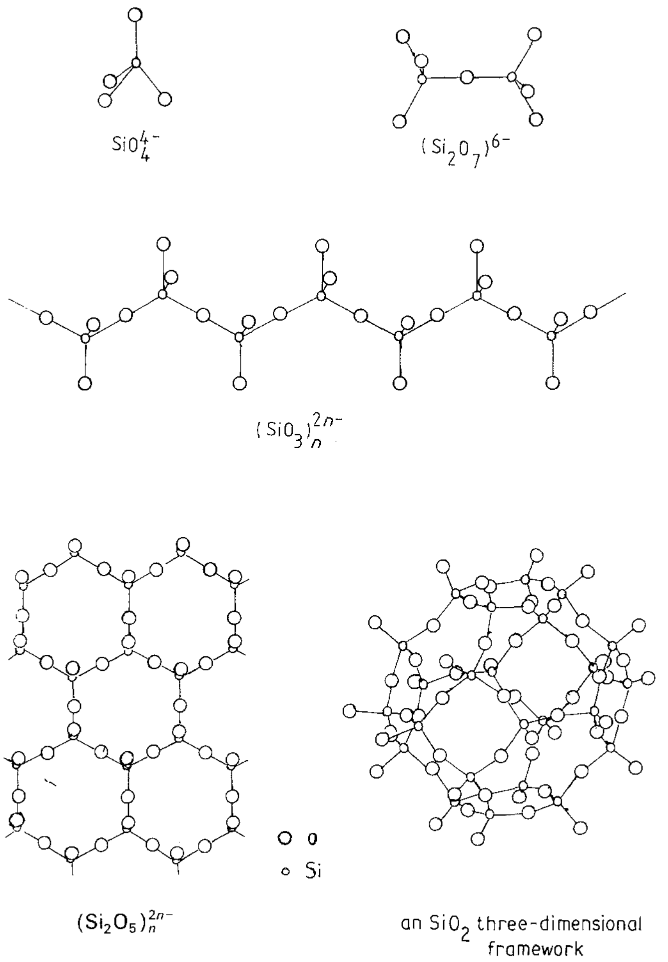
Si : O ratio	No. of O per Si		Type of silicate	Examples
	Non-anion bridging	Bridging		
1 : 4	0	4	isolated SiO_4 units	Mg_2SiO_4 (olivine)
1 : 3.5	1	3	dimer Si_2O_7	$Ca_3Si_2O_7$
1 : 3	2	2	chains $(SiO_3)^{2n-}$ rings, e.g. Si_3O_9	Na_2SiO_3, $MgSiO_3$ $CaSiO_3$
1 : 2.5	3	1	infinite sheets $(Si_2O_5)n^{2n-}$	$Na_2Si_2O_5$
1 : 2	4	0	three-dimensional framework	SiO_2

charged non-bridging oxygen atoms in a manner dependent on the compositions of the films. The task then is to decide the nature of the possible complex anions, and the co-ordination of the Ce^{4+} cations.

In the case of $Ce_xSi_yO_{2x+y}$, the complex anions in the crystalline state should be similar to the silicate anions themselves. Thus their nature would be determined by their Si : O ratio. As illustrated by West [15], the anionic structures would range from single SiO_4^{4-} tetrahedra towards the three-dimensional network configuration of SiO_2 as the SiO ratio is varied from 1 : 4 to 1 : 2. This is depicted in Table IV and Fig. 2.

In the present situation this ratio is given by $y/(2x + y)$. We see that as x approaches zero, the ratio tends towards unity, whereas for large values of x it becomes diminishingly small. In the former case the anionic structure would approach a three-dimensional framework with an increasing percentage of Si–Si bonds as the ratio approaches unity. In the latter case the structure should tend towards that of the fluorite structure of CeO_2. We thus see that for low or medium values of x the crystalline structure of $Ce_xSi_yO_{2x+y}$ should be viewed as consisting of a host matrix of silicate-like anions arranged periodically, with Ce^{4+} ions occupying the regions between them and co-ordinated by singly-charged non-bridging oxygens. The nature of the host matrix will range from an array of individual SiO_4^{4-} tetrahedra on the one hand, to three-dimensional networks comprising either linked SiO_4 tetrahedra, or structures containing Si–Si bonds, on the other.

The structure of the thin films of this study should be some amorphous derivative of the above. In films where the anions are constrained by the Si : O ratio to be individual SiO_4^{4-} tetrahedra, these would be expected to be randomly oriented. Where they form three-dimensional matrices in the crystalline state, they will be replaced by a three-dimensional continuous random network (CRN). Such amorphous structures have been described as modified random networks



SiO_4^{4-}

$(Si_2O_7)^{6-}$

$(SiO_3)_n^{2n-}$

$(Si_2O_5)_n^{2n-}$

an SiO_2 three-dimensional framework

Figure 2 Representative structures of silicate anions/framework (see Table III). Adapted from Bragg and Claringbull [20].

(MRN) by Greaves *et al.* [16, 17] who comment on their probable morphology in some detail [18].

The $Ce_xGe_yO_{2x+2y}$ series of films is expected to have structures similar to those elucidated above except for differences caused by the larger size of the Ge^{4+} cations. Wells ([10], p. 150) shows that for an array of hexagonal close-packed spheres of unit radius, the radii of the tetrahedral and octahedral holes are 0.0225 and 0.0414 nm, respectively. For such an array of O^{2-} anions, the two radii are 0.032 and 0.058 nm, indicating that the Ge^{4+} ions may be both tetrahedrally and octahedrally co-ordinated by oxygen. The structure of the host matrices in the films would therefore be expected to be somewhat different from that in the former series.

Because of the even larger size of the Sn^{4+} cations, the anions of the $Ce_xSn_yO_{2x+2y}$ series should be formed almost exclusively from SnO_6 octahedra. This will produce overall structures which may be in marked contrast to those found in the above two series.

6. Preliminary EXAFS results for $Ce_xSi_yO_7$

EXAFS measurements have so far been made on the cerium edge of a selected range of the first series of films. These results seem to support the picture outlined above of an MRN structure. It has been found that for low/medium values of x, the cerium atoms are invariably coordinated by six oxygens at a distance of 0.24 nm. This is in keeping with the view that Ce^{4+} ions act as modifiers in the silicate networks formed by Si^{4+} cations. This coordination reduces to four for very high values of x, where the structure is expected to become more like that of CeO_2.

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