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The dielectric properties of glass-ceramic-on-metal substrates for microelectronics packaging

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The dielectric properties of some glass-ceramic-on-metal substrates have been determined over the frequency range 500 Hz to 5 MHz using a.c. bridge techniques. The substrates consisted of cordierite-based glass-ceramics screen printed on molybdenum. For glass layers of thickness greater than 100 μm both the permittivity, ε' and the dielectric loss, ε'', are frequency independent over this frequency range at room temperature giving the value of $\varepsilon' = 6.5$ and $\tan\delta = 8\times10^{-3}$; the room-temperature data are consistent with the universal law of dielectric response. The variation of permittivity with temperature has also been examined and, below 120 °C, the temperature coefficient $[(\varepsilon'-1)(\varepsilon'+2)]^{-1}(\partial\varepsilon'/\partial T)_p$, was found to be 1.3×10^{-5} K^{-1}. The results are compared with those previously reported for Al_2O_3 and AlN substrates.

1. Introduction

As silicon microelectronic devices become more complex and are required to operate at steadily rising frequencies, the type of package used to house the silicon chip increasingly affects the performance of the device. With these large high-speed devices, one of the major problems encountered is that of heat dissipation. Conventional cofired ceramic packages generally have poor thermal performance in this respect. To improve the thermal conductivity several solutions have been suggested, such as the use of aluminium nitride substrates or copper–tungsten inserts, but although these materials have adequately high thermal conductivities they seem unlikely to provide a cheap, easily produced alternative to alumina and they have not yet achieved widespread acceptance in high-performance microelectronics packaging. As a result there is still a requirement for a substrate which can combine high electrical and thermal performance with relatively low cost and conventional processing routes. Glass-ceramic-on-metal substrates [1] appear to be ideal candidates for filling these requirements. The metal base provides the high thermal conductivity whilst the glass-ceramic coating forms a dense dielectric layer upon which conductor tracks can be printed. The whole structure is easily produced via standard thick film and enamelling techniques. One of the main benefits of using such substrates is that very close thermal expansion matching between package and device can be achieved by judicious selection of materials. The thermal coefficient of expansion (TCE) of a silicon chip is typically about 3 m K^{-1}. It is possible to choose a metal with a similar TCE, for example tungsten or molybdenum which have TCEs of 4.4 and 5.5 m K^{-1}, respectively, then "design" a glass-ceramic material which has a matching TCE. It is this ability to tailor accurately the thermal expansions of glass-ceramics by careful control of heat treatment and crystallization which make them ideal for many microelectronic substrate applications [2].

The most suitable glass-ceramic systems for microelectronic substrates are those based on $MgO–Al_2O_3–SiO_2$, $Li_2O–Al_2O_3–SiO_2$ and $ZnO–Al_2O_3–SiO_2$, each of which can be formed as a glass and then heat treated to give largely crystalline material. The overall thermal expansion of the materials is controlled by the relative proportions of high and low thermal expansion phases.

In this work, an $MgO–Al_2O_3–SiO_2$ type glass-ceramic was used as a coating on a molybdenum base. The principal crystalline phase formed in this glass-ceramic was cordierite, with a TCE of 2.6 m K^{-1} and similar materials have been used to give a very close thermal expansion match to silicon [3]. The work reported here is concerned with the dielectric properties of a series of these glass-ceramic on molybdenum substrates. Data are presented for both the permittivity, ε', and dielectric loss, ε'', at frequencies over the range 500 Hz to 5 MHz; at room temperature both ε' and ε'' are frequency independent, and for glass-ceramic thicknesses exceeding about 100 μm, $\varepsilon' = 6.5$ with $\tan\delta \sim 8\times10^{-3}$. These data are compared with those recently reported for two alternative microelectronic package substrate materials, namely aluminium oxide (alumina) [4] which, at the present time, is the material in most widespread use, and aluminium nitride [5]. The temperature variation of permittivity has also been examined over the temperature range 20–350 °C.

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A comparison is made between the dielectric behaviour of these glass-ceramic-on-metal systems and the behaviour reported previously in similar dielectric studies of bulk oxide and oxynitride glasses [6, 7].

2. Sample preparation and characterization

The glass-ceramic material was prepared by melting together the constituent oxides to form a glass, which was then milled to give a powder with particle sizes in the range 1–10 μm. The powder was applied to the clean metal surface by screen printing, using a commercially available screen printing medium, and the samples were fired in a belt furnace under nitrogen at temperatures between 900 and 1000 °C. During firing, crystalline phases nucleate and grow within the glass and the proportions of these phases are determined by the temperature/time profile. The optimum firing schedule was determined by differential thermal analysis of the glass powder which indicated the temperatures at which sintering and crystallization occurred. This allowed a profile to be established which gave maximum densification of the material during sintering, followed by nucleation and crystallization of the required phases. During firing, a small amount of air was let into the furnace at the start of the hot zone. This allowed the organic materials present in the screen printing medium to be burnt out and was necessary because retained organic matter gives a porous glass-ceramic with large amounts of residual carbon. The small amount of air also caused some preoxidation of the molybdenum base. This thin oxide layer helps the adhesion of the coating to the metal by allowing continuous chemical bonding across the interface between the metal and the oxide glass. During this process some diffusion of metal oxide into the glass-ceramic occurs, the extent of which is strongly dependent upon the type of metal and glass-ceramic system used.

The samples detailed in this work were produced in the glass-ceramic form, i.e. crystalline phases in a residual glass; however, some samples were processed so as to give a layer of uncrystallized glass. This allowed direct comparisons between the bulk glass and the glass coating and between glass and glass-ceramic coatings to be made allowing for the influence both of the metal base and of grain-boundary effects in the polycrystalline material.

Evaluation of the samples was carried out using a variety of techniques. Determination of the crystal phases in the glass-ceramic materials was performed using X-ray diffraction and showed the principal phases to be cordierite (in both α and β forms) and enstatite in a residual glass matrix. The microstructure of the glass-ceramics and the interfacial regions between the metal and glass-ceramic coatings were examined by scanning electron microscopy coupled with energy dispersive X-ray analysis to determine compositions and distributions of elements. No diffusion of molybdenum oxide into the glass-ceramic could be detected by this method but a cross-section, bevelled at an angle of 3° to exaggerate the interface, showed a distinct purple discoloration in the glass-ceramic adjacent to the metal (Fig. 1). This indicates that very small amounts of molybdenum ions, perhaps only of the order of a few parts per million, had diffused into the glass-ceramic and measurements of this purple band showed that it extended approximately 10 μm into the glass-ceramic layer.

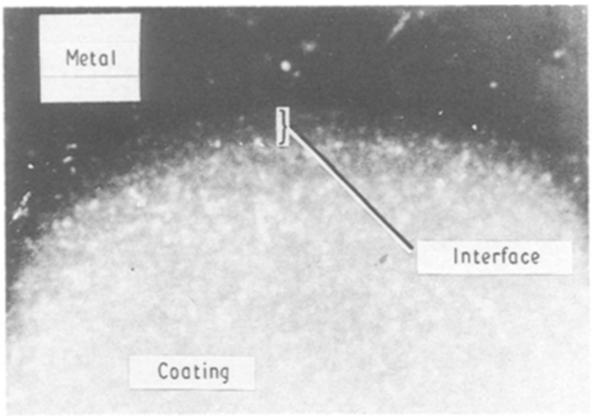

Figure 1 Bevelled section through a glass-ceramic coating on molybdenum showing an interfacial diffusion zone of approximately 10–20 μm thickness.

Measurements of coating thickness were carried out using both micrometer measurements and scanning electron microscopy of cross-sections.

3. Dielectric measurement techniques

The dielectric measurements were made using adaptations of the a.c. bridge technique utilized in earlier studies of dielectric materials [8]. The major difference arose from the specimen geometry. The substrates as supplied were normally in the form of 5.0 cm × 5.0 cm square sheets of molybdenum with the glass-ceramic coating on one surface. The early measurement methods were developed for bulk single-crystal specimens and used evaporated gold electrodes on each side of a thin disc-shaped sample to define the electric field region. Here, however, one side of the dielectric is bonded to an extended metal base and consequently it was necessary to gold-evaporate not only a central electrode but also a circular guard ring on the glass-ceramic surface to achieve good definition of the field configuration; this had the additional advantage of reducing edge field effects. The molybdenum base then served as the second electrode. Given such a sample the conductance and capacitance could then be measured directly with an a.c. bridge. The permittivity, ε', is obtained from

$$\varepsilon' = \frac{C}{C_0} \tag{1}$$

where C is the measured capacitance with the specimen in position and C_0 is the capacitance at the same jig electrode spacing without the specimen. The conductance, G, of the specimen is given by

$$G = \sigma\frac{A}{d} \tag{2}$$

where A is the electrode area, d is the thickness of the glass and σ is the a.c. conductivity. The dielectric loss, ε'', is obtained from σ, because

$$\sigma = \omega_0\varepsilon_0\varepsilon'' \quad (3)$$

where ω is the angular frequency, and $\tan\delta$ is given as usual by the ratio

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (4)$$

In these measurements the main source of error lay in the uncertainty of the glass-ceramic layer's thickness and in some cases of some non-uniformity of thickness across the specimen diameter. The accuracy of the permittivity measurements was estimated to be ± 5% and of the dielectric loss measurements ± 10%.

The temperature variation of permittivity was measured over a temperature range 20–300 °C by suspending the specimen in a vertical furnace (cf. [9]) through which oxidizing or inert gases could be passed; the electrical contact to the glass-ceramic face was made by a platinum paste/platinum wire combination which also acted as one of the specimen supports.

4. Room-temperature permittivity and dielectric loss

Data for substrates having thicknesses of glass-ceramic in the 100–140 μm range are presented in Fig. 2 which also shows, for comparison, the results obtained over the same frequency range (500 Hz to 5 MHz) for a 0.46 mm thick sample of pure bulk cordierite glass. It can be seen that both ε' and ε'' are substantially independent of frequency over this range. For the glass-ceramic-on-metal the average value obtained for the permittivity was $\varepsilon' = 6.5$ at 1 kHz which is very similar to that of the glass-on-metal sample and compares well with that of $\varepsilon' = 6.8$ for bulk cordierite glass, bearing in mind the difficulties of obtaining precise values for glass-ceramic thickness. This tends to indicate both that the effect of changing from a glassy to a polycrystalline layer with residual glass matrix is small and that at these coating thicknesses the metal base has very little effect. It is noticeable that whereas the ε' value of the two glass-ceramic-on-molybdenum substrates are very similar, there is a more noticeable difference in their losses. However, the average loss of $\varepsilon'' \sim 7 \times 10^{-2}$ is not much greater than that of the bulk cordierite glass, giving $\tan\delta$ values in the region of 8×10^{-3}, compared with 3×10^{-3} for the bulk glass.

Measurements were also made on a series of substrates having successively thicker glass-ceramic coatings. These substrates were made by repeated printing, then fired using identical furnace processing conditions, a procedure which should therefore give increasing thickness of the same composition of glass-ceramic. The number of successive prints ranged from 1–6, corresponding to glass thicknesses of 14–128 μm. The actual layer thicknesses were measured directly using a precision micrometer and taking the average of values obtained at many different points over the whole sample. These results were confirmed by using scanning electron microscopy to measure sample cross-sections. The variation of thickness with the number of prints is shown in Fig. 3, the linearity of

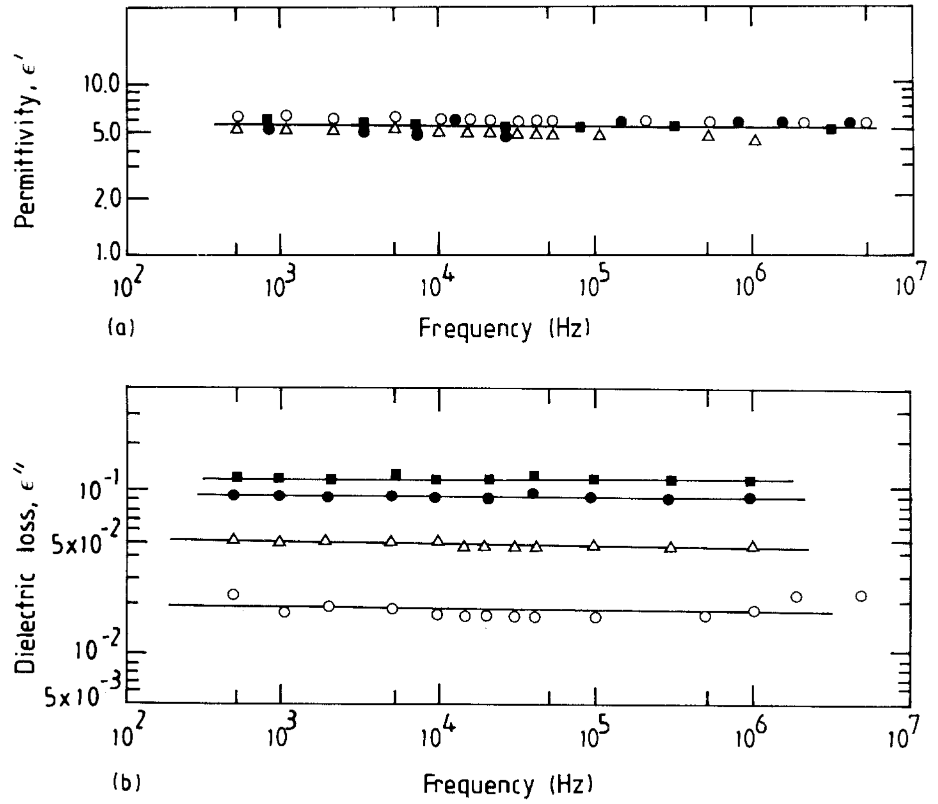

Figure 2 Frequency dependencies of (a) permittivity, ε', and (b) dielectric loss, ε'', for (●) 100 μm glass-on-molybdenum, (■) 100 μm glass-ceramic-on-molybdenum, (△) 128 μm glass-ceramic-on-molybdenum, (○) bulk cordierite glass.

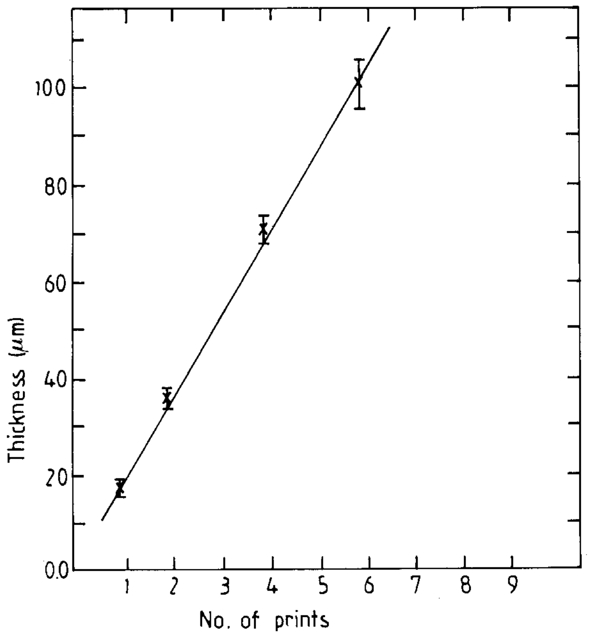

Figure 3 Variation of thickness of over-printed glass-ceramic-on-molybdenum substrates.

TABLE I Comparison of permittivity data (1 kHz) for glass substrates of different thickness with those of other bulk glasses

	Thickness (μm)	Permittivity
Glass-on-metal substrate	14	6.7
	52	5.9
	60	6.0
	100	6.8
	128	7.3
Glass detached from metal base	74	7.2
	82	7.3
Bulk cordierite glass ($MgO \cdot Al_2O_3 \cdot SiO_2$, 20:20:60 wt%)	0.46	6.5
Bulk magnesium sialon glass (Mg–Si–Al–O–N) (0% N ref. 6 and 7)	0.33	6.7

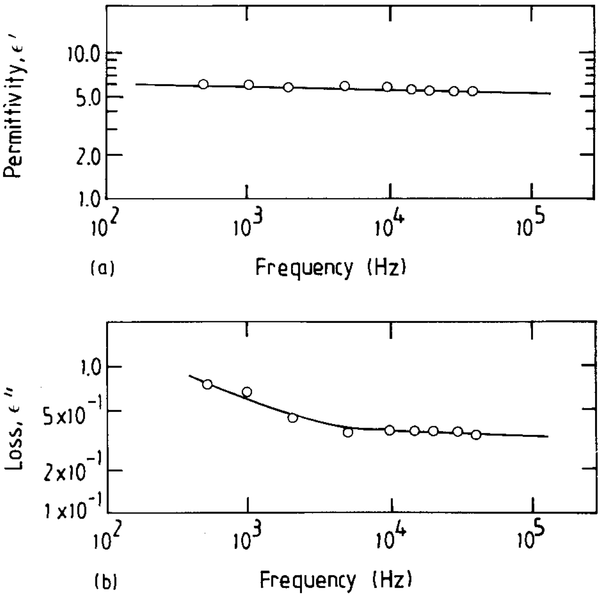

Figure 4 (a) Permittivity–frequency and (b) loss–frequency plots for 60 μm glass-ceramic thickness.

which indicates the reliability of the over-printing technique. The permittivity values were fairly consistent, averaging at $\varepsilon' \approx 6.5$; they are detailed in Table I which also includes for comparison data taken from previous studies of bulk samples of both cordierite glass and magnesium sialon glass of similar composition [6]. There was, however, a much more marked variation of dielectric loss with glass-ceramic thickness. This is illustrated by Figs 4 and 5 which show the frequency variation of ε' and ε'' for substrates having thicknesses of 60 and 14 μm, respectively. The main feature is the non-linearity of the ε'' versus frequency characteristics; this is reflected, though to a smaller extent, in the variations of ε' versus frequency where in each case there is small reduction in ε' as frequency increases. The $\tan\delta$ values are quite high for the thinner layers at low frequencies being for example 7.14×10^{-1} at 500 Hz for the thinnest (14 μm) layer and 1.2×10^{-1} (at 500 Hz) for the 60 μm thick layer as compared with the frequency independent value of $\tan\delta = 8 \times 10^{-3}$ obtained for the thickest layer (i.e. 128 μm, thick). It is likely that the reason for both the curvature of the ε'' versus frequency plots for the thinner layers and these high values of $\tan\delta$ is the contamination, by metal oxide, of the 10 μm layer of glass-ceramic adjacent to the glass/metal interface as shown in Fig. 1. The behaviour observed is typical of increased polarization due to defects in structure and impurities at grain boundaries which is most pronounced at low frequency.

Returning to consider the data obtained for the thicker samples, the frequency independence of both ε' and ε'' (Fig. 1) suggests that the Universal law of dielectric response [10, 11] applies. Taking numerical data from the plots and assuming a value of $\varepsilon'_\infty = 2.46$ [6], which was obtained from the optical refractive index and is appropriate for the composition of the cordierite glass used for the glass-ceramic-on-metal substrate, we obtain a value of the exponent n in the relation

$$(\varepsilon' - \varepsilon_\infty) \propto \omega^{n-1} \tag{5}$$

of $n = 0.98 \pm 0.02$; the corresponding value obtained from the ε'' versus frequency plot assuming

$$\varepsilon'' \propto \omega^{n-1} \tag{6}$$

gives $n = 0.98 \pm 0.02$.

The close agreement between these two values shows that the Universal law can be applied with some confidence at least up to frequencies of 10 MHz. This general behaviour agrees very well with that reported by Kenmuir *et al.* [6], and Thorp *et al.* [7], who studied the dielectric behaviour of Mg–Al–Si, Ca–Al–Si, Y–Al–Si and Nd–Al–Si oxynitride glasses over a similar frequency range at room temperature. In these measurements bulk specimens were used whose dimensions were typically 1.0 cm diameter and 0.054 cm thickness. For the pure oxide Mg–Al–Si glass similar to that used here for the glass-ceramic-on-molybdenum substrate, Kenmuir *et al.* [6] found

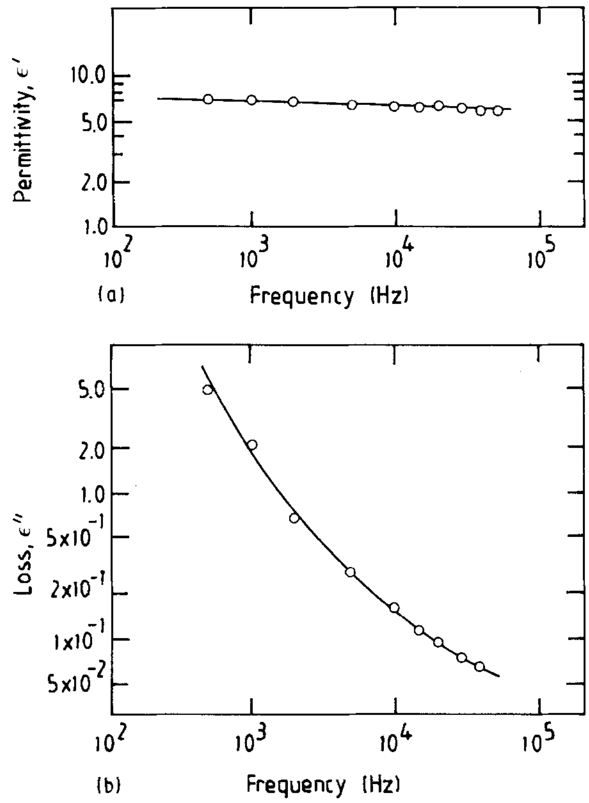

Figure 5 (a) Permittivity–frequency and (b) loss–frequency plots for 14 μm glass-ceramic thickness.

that $\varepsilon' = 6.8$ and both ε' and ε'' were frequency independent, giving from both the permittivity and loss variations the value $n = 1.0 \pm 0.1$. They also state that the value found for $\tan\delta = 2 \times 10^{-3}$. All these values are in fairly close agreement with the data reported here for the glass-ceramic-on-molybdenum substrates. It is interesting to note that bulk tape-cast material gives the same results as layers of thickness greater than about 100 μm.

5. Temperature coefficient of permittivity

The temperature variations of permittivity for several of the glass-ceramic-on-metal substrates were also examined in the temperature range 20–300 °C over the frequency range 500 Hz to 20 kHz (for the glass composition used the softening temperature was greater than 800 °C and so unlikely to have any effect in the temperature range used). The data for a 100 μm thick glass-ceramic layer on molybdenum are shown in Fig. 6. The first feature revealed is that, at each frequency, the variation is approximately linear from 20 °C to about 120 °C and thereafter becomes non-linear with ε' increasing rapidly as T increases; the second feature is that the frequency dispersion becomes very pronounced at the higher temperatures. It is important to note that the non-linearity begins at a lower temperature for the lower frequencies and at a relatively higher temperature for the higher frequencies. Over the linear regions the temperature coefficient of permittivity at constant pressure, $[(\varepsilon' - 1)(\varepsilon' + 2)]^{-1} (\partial\varepsilon'/\partial T)_p$ was calculated [12]. Even between 20 and 120 °C there is a small but noticeable variation of the coefficient with frequency. The values of temperature coefficient vary from $1.73 \times 10^{-5}\,\mathrm{K}^{-1}$ at 500 Hz to $1.0 \times 10^{-5}\,\mathrm{K}^{-1}$ at 20 kHz but because the variation is relatively small the average may be taken as $\approx 1.3 \times 10^{-5}\,\mathrm{K}^{-1}$.

This figure is rather higher than those for aluminium nitride substrates ($1.05 \times 10^{-5}\,\mathrm{K}^{-1}$) and for aluminium oxide substrates ($9.3 \times 10^{-6}\,\mathrm{K}^{-1}$) recently reported [4, 5]. Neither pure alumina nor pure aluminium nitride sintered polycrystalline substrates show any frequency dispersion in this temperature range.

Above about 120°, Fig. 6 shows that the temperature coefficient for each individual frequency increases with increasing temperature much more rapidly than would be expected if the Bosman and Havinga model applied. Plots of log ε' versus temperature for the range 120–300 °C give good straight lines (though with slightly different slopes for different frequencies) indicating an exponential variation. This type of behaviour has been observed in many materials at sufficiently high temperatures. It is apparent in the ε'–T variations of the pure and impure Al_2O_3 and AlN sintered polycrystalline substrate materials recently discussed [4, 5] and in several bulk oxide and nitride ceramics; in the case of pure and iron-doped magnesium oxide [9] this has been analysed in terms of a contribution to the measured permittivity arising from temperature-enhanced conductivity. It is important to note, however, that the temperature at which the ε' versus T relation changes from a linear to a non-linear variation depends markedly on the materials. For the present glass-ceramic-on-molybdenum substrates it is about 120 °C, for pure aluminium nitride substrates about 150 °C, for pure alumina substrates 270 °C and for pure single-crystal magnesium oxide about 200 °C. The lower value for glass-ceramic-on-metal is not unexpected on the quasi-conductivity approach because it would be expected that in a soft, random network glassy materials (as found in the residual glass phase of the glass-ceramic) conductivity mechanisms will come into play at lower temperatures than in the well-defined, rigid structures of the oxide and nitride ceramics.

Turning to the effect of temperature on the frequency dependence of permittivity it has been found that for glass-ceramic thicknesses exceeding 100 μm at room temperature, ε' is consistent with the Universal law of dielectric response in that $[\varepsilon'(\omega) - \varepsilon_\infty] \propto \omega^{n-1}$ where ω is the angular frequency and $n = 0.98 \pm 0.02$. This corresponds to the limiting form of lattice loss [13] in which most dipolar processes have been eliminated. This situation is also found in the rigid ceramics (Al_2O_3, AlN MgO) [4, 5, 9] already noted, in the ternary oxide and oxynitride glasses formed from the Mg–Al–Si, Ca–Al–Si, Y–Al–Si and Nd–Al–Si glass-forming systems [6] and in some binary glasses such as molybdenum-phosphate glass [14] and praseodymium phosphate glass [15]. Replotting the high-temperature data for the glass-ceramic-on-molybdenum substrates to illustrate the variation of permittivity with frequency at different temperatures, gives the result shown in Fig. 7. This shows that ε' falls progressively faster with increasing frequency from a

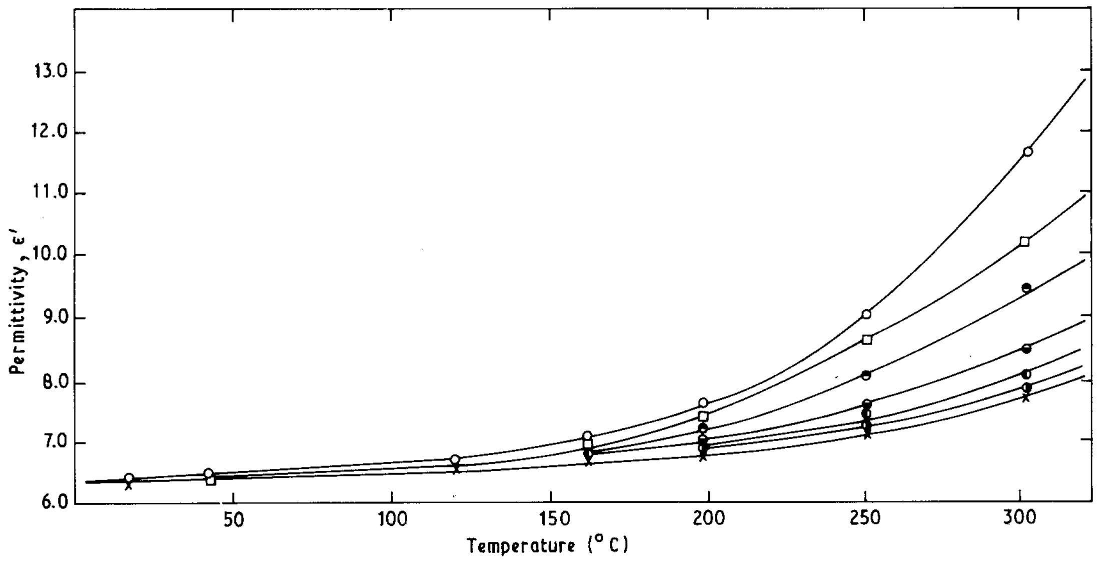

Figure 6 Variation of permittivity with temperature for 100 μm thick glass-ceramic-on-molybdenum substrate. (○) 500 Hz, (□) 1 kHz, (◓) 2 kHz, (◒) 5 kHz, (◐) 10 kHz, (◑) 15 kHz, (×) 20 kHz.

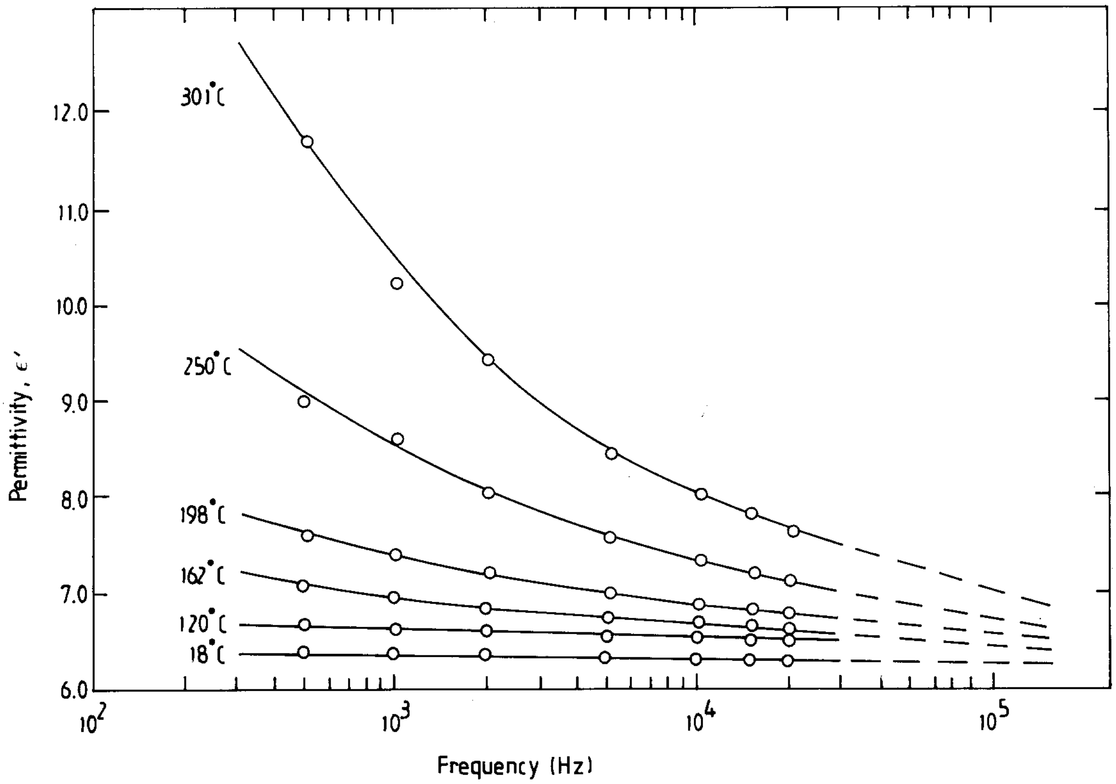

Figure 7 Variation of permittivity with frequency for different temperatures: 100 μm thick glass-ceramic-on-molybdenum substrate.

higher starting value as the temperature is increased. An interesting point is illustrated by the dashed extrapolations in Fig. 7. Assuming that the increase of ε' with temperature is due to a quasi-conductive process [16, 17], the extrapolations suggest that the contributions due to the conductivity become negligible at some frequency rather higher than the upper value used in the present experiments, probably in the region 10–100 MHz. Similar behaviour has previously been reported in MgO, and is apparent in the high-temperature permittivity data for Al_2O_3 and AlN substrates recently given [4, 5]. The implication is that if packages are used at higher frequency, e.g. approaching the microwave region, the temperature variation of permittivity will be of much less importance than in the kilohertz frequency range, though this hypothesis has yet to be proved.

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