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The permittivity and dielectric loss of reaction-bonded silicon nitride

J. S. THORP, A. B. AHMAD, B. L. J. KULESZA, T. G. BUSHELL
Department of Applied Physics and Electronics, University of Durham, Durham, UK

Using recently developed coaxial line methods values of permittivity and dielectric loss have been determined over the frequency range 0.5 to 7 GHz for a series of reaction-bonded silicon nitride specimens in which the degree of nitridation has been varied. For fully nitrided material (having a weight gain of 62% and a volume porosity of 19%) the measured permittivity was 4.60 and was almost independent of frequency; fitting both the permittivity and loss data to the Universal Law of dielectric response confirmed that the limiting condition of lattice loss applied with $n = 0.98 \pm 0.02$. Reduction of the degree of nitridation caused progressive increases in permittivity and loss, both of which closely approached the quoted values for pure silicon at weight gains below about 40%.

1. Introduction

Increasing interest has been shown in silicon nitride (Si_3N_4) since its technological potential has been identified. Thin film silicon nitride has been extensively described in the literature and a recent review by Morosanu [1] indicates the scope of research in this area which includes its widespread use in semiconductor and integrated circuit technology. In bulk form silicon nitride has been identified as a useful refractory ceramic with a combination of properties found in very few others [2]. It possesses a high specific modulus, a high decomposition temperature, high-temperature strength, low coefficient of friction, good oxidation resistance and is highly resistant to corrosive environments. The use of silicon nitride as a dielectric is important in several of these applications and early measurements, e.g. [3], suggested that the values of both the permittivity (ϵ') and dielectric loss (ϵ'') were significantly dependent on the method of preparation and purity of the silicon nitride. Two main ways of manufacturing bulk silicon nitride are now used, hot-pressing and reaction bonding, giving the identifications HPSN and RBSN for hot-pressed and reaction-bonded Si_3N_4, respectively. Hot-pressed silicon nitride (HPSN) is manufactured from commercial silicon powder which is nitrided directly to give α-Si_3N_4 powder. This is then hot-pressed at 1700° C in air at a pressure between 150 and 300 $MN\,m^{-2}$ to give a maximum density pore-free β-Si_3N_4 [4]. The availability of high-density material is the main attraction of the technique but there is, however, a severe disadvantage in that it is not possible to hot-press complex shapes. A different situation arises with reaction-bonded silicon nitride. Here a silicon powder compact is initially produced, either as a billet or in the shape of the component being fabricated, by isostatic pressing of silicon powder at up to 200 $MN\,m^{-2}$ in an argon atmosphere. After shaping, the component is heated in nitrogen to between 1250 and 1450° C when reaction-bonding occurs. An attractive feature of this fabrication route is that very little size change is observed during densification and close tolerances (approximately 1%) on the dimensions of a finished component can be readily achieved. However, high density cannot be achieved, owing to the presence of pores, typical porosities being about 20 to 25% with roughly four-fifths of the pores less than 0.1 μm in size [5]. In some previous work on the dielectric behaviour of nitrogen ceramics [6], Thorp and Sharif examined bulk hot-pressed silicon nitride. In the present work attention has been given to reaction-bonded silicon nitride in order to enable a comparison of their respective electrical properties to be made and to examine the effects of partial nitridation.

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TABLE I Characterization of silicon nitride samples

Firing run	Mean weight gain (%)	Nitrided density (g cm^{-3})	Phase composition			Green ceramic density (g cm^{-3})	Peak firing temp. (° C)
			C_{sn}	C_{Si}	C_p		
1	20.0	1.95	0.277	0.461	0.262	1.60	1250
2	33.5	2.15	0.435	0.333	0.232	1.60	1240
3	38.0	2.24	0.506	0.275	0.219	1.60	1150
4	41.5	2.25	0.514	0.268	0.217	1.60	1340
5	46.5	2.35	0.593	0.204	0.203	1.60	1370
6	55.0	2.40	0.683	0.172	0.195	1.60	1440
7	57.0	2.54	0.744	0.082	0.174	1.60	1440
8	63.2	2.52	0.783	0.020	0.197	1.53	1440

2. Experimental procedure

2.1. Sample characteristics

The silicon nitride ceramics studied in the present work were supplied by Advanced Engineering Materials Ltd (Ruabon) and details of their fabrication have been described by Bushell [7]. These materials were in various degrees of nitridation; this degree of nitridation was assessed by the "weight gain" of the ceramic, the percentage by which the weight has increased in the nitriding reaction. If all available silicon is converted to silicon nitride the maximum weight gain would theoretically be 66.5%. However, in practice the maximum weight gain that could be achieved was slightly less (63.2%) indicating that there is a small amount of unreacted free silicon, owing to the inability of nitrogen to reach the remaining silicon as the reaction progresses.

The materials studied were manufactured using different firing schedules and nitrogen partial pressure profiles [7] and Table I lists the compositions of the silicon nitrides giving also the peak firing temperatures and nitrided densities. In Table I the phase compositions were calculated from the equations [2]

$$C_p = 1 - 0.218\rho_g - 0.148\rho_n \quad (1)$$

$$C_{Si} = 1.072\rho_g - 0.643\rho_n \quad (2)$$

$$C_{sn} = 0.791(\rho_n - \rho_g) \quad (3)$$

in which C_p, C_{Si} and C_{sn} are, respectively, the volume fractions of porosity, silicon and Si_3N_4 in a nitrided compact, ρ_g is the density of the prenitrided (green) ceramic, while ρ_n refers to that of the nitrided material. Analysis of the silicon powder used revealed that the major impurities were iron, aluminium and calcium present at respective levels of 0.45, 0.25 and 0.05 wt%.

2.2. Measurement techniques

In order to obtain measurements over as wide a frequency range as possible coaxial line methods were adopted. These techniques have been described in detail by Kulesza *et al.* [8]. In brief, a coaxial holder, which accommodates a thin disc-shaped sample, is terminated by either a short-circuit, a matched termination or a resonant circuit and the features of the voltage standing wave pattern are determined with and without the sample. Here the real part of the complex permittivity (ϵ') was measured from 500 MHz up to 5 GHz with both the matched and short-circuit termination coaxial line methods. Additional measurements were also made at 9.34 GHz using a resonant cavity technique [6] in which the resonant frequencies and Q-factors of the cavity with and without the sample (for known volumes of the sample and empty cavity) are directly related to the dielectric constants. Another advantage of the coaxial line methods was that only small sample shapes were required; discs of about 6.8 mm diameter and thicknesses from 0.43 up to 0.68 mm were cut from the bulk material which is very hard, using diamond cutting wheels. It was important to ensure that the surfaces were parallel and smooth; this was done using a Logitech mechanical polishing machine which gave a surface flatness to within 0.25 m. Much care was necessary in the sample preparation process since the thin discs were brittle. The frequency variation of the loss factor (ϵ'') for the range of samples was determined using the coaxial line matched termination method up to 1.5 GHz and the coaxial line resonance method from about 1.5 to 8 GHz. Values of (ϵ') required for the determination of ϵ'' from about 6 GHz to 8 GHz were obtained by interpolation between the measured values up to 5 GHz and that of the resonant cavity method at 9.34 GHz. The same disc-shaped samples were used in

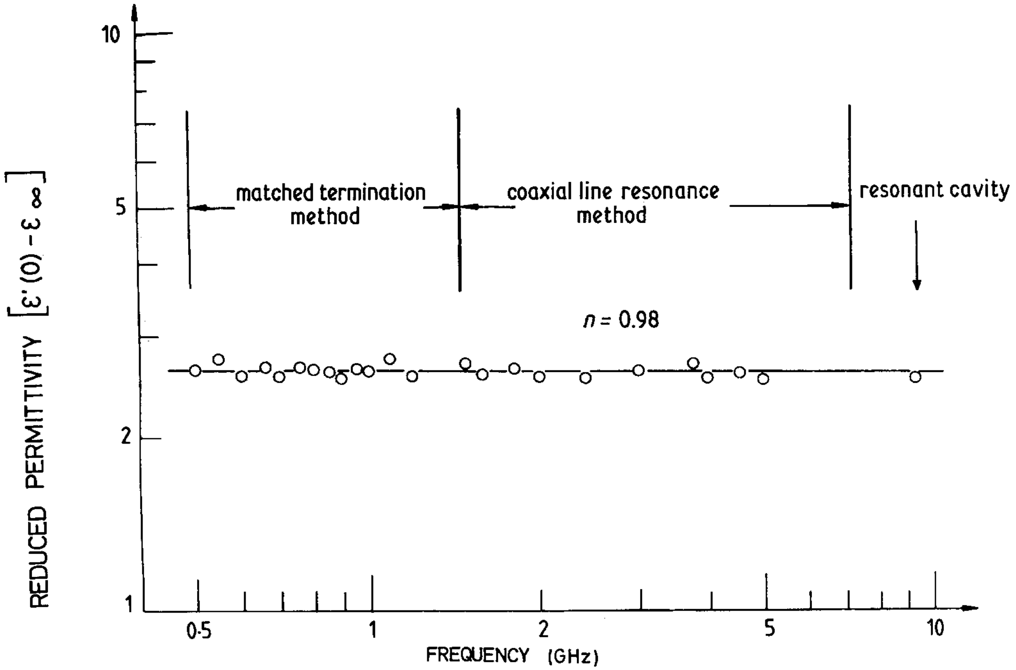

Figure 1 Variation of reduced permittivity with frequency for full nitrided (63.2% weight gain) specimen.

both the coaxial line and cavity methods of measurement. All the data were obtained at room temperature.

3. Results

3.1. Fully nitrided samples

The initial experimental data showed that, for the fully nitrided (63.2% weight gain) RBSN specimens the measured permittivity was bout 4.6 and was virtually independent of frequency over the whole range examined. In order to make meaningful comparisons with hot-pressed silicon nitride, however, account must be taken of the porosity of the reaction-bonded materials. The permittivity measured experimentally here corresponds to $\epsilon'(p)$ and for these specimens the percentage volume fraction of pores (p) was 19.7%. Walton [3] has given an expression relating the permittivities for porous and fully dense ($p = 0$) material as

$$\epsilon'(p) = \epsilon'(0)^{(1-p)} \qquad (4)$$

and using this the values of $\epsilon'(0)$ were determined. The reduced permittivity $[\epsilon'(0) - \epsilon_\infty]$ was then estimated by inserting the value of ϵ_∞ obtained from optical data on thin film silicon nitride [8]. A log–log plot of $[\epsilon'(0) - \epsilon_\infty]$ against frequency is given in Fig. 1 which also shows which techniques were found to be most appropriate for precise measurements in the various frequency ranges. Fitting this data to the relation,

$$[\epsilon'(0) - \epsilon_\infty] \propto \omega^{(n-1)} \qquad (5)$$

where ω is the angular frequency, predicted by the Universal Law of dielectric response [9–11] gave a value of the exponent n of $n = 0.98 \pm 0.02$.

The dielectric loss for the fully nitrided RBSN measurements showed that ϵ'' was virtually constant throughout the frequency range, having a value $\sim 7 \times 10^{-3}$. Fitting with the Universal dielectric response law for the loss component, $[\epsilon'' \propto \omega^{(n-1)}]$, gave the value of the exponent as $n = 0.97 \pm 0.02$, in close agreement with the value deduced from the variation of the permittivity with frequency.

3.2. Partially nitrided samples

The partially nitrided samples had weight gains from 38% up to 57% compared to the weight gain of 63.2% for the fully nitrided samples. For this range of composition the matched termination method was found to be suitable only up to about 1.5 GHz; above which up to 5 GHz, the short-circuit termination method was preferable. Measurements became increasingly more difficult and less accurate as the weight gain decreased. It was impossible to obtain data for weight gains less than 38% as the samples became very lossy and the equivalent circuit assumed for the short-circuit

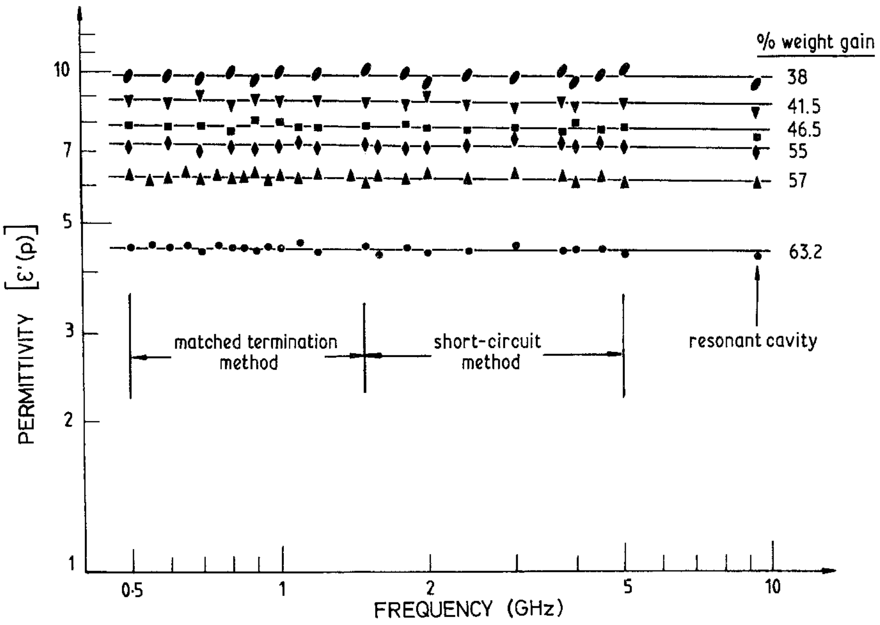

Figure 2 Frequency dependence of permittivity for various weight gains.

method is no longer valid. The variations of $\epsilon'(p)$ with frequency for the measurable samples are given in Fig. 2. An almost frequency-independent behaviour is evident for all the various weight gains. The measurement of the loss (ϵ'') presented more difficulties especially for low weight gain samples. Below 1.5 GHz the coaxial line with matched termination proved quite satisfactory. In the range 1.5 to 8 GHz both the coaxial line with short circuit termination technique and the coaxial line resonant method were tried, measurements with the former being relatively easier to perform since, as the losses were high, the VSWR values were low. It was found that these two methods gave good agreement for the higher loss samples. On the whole the loss factors obtained by the resonant cavity method at 9.34 GHz appeared slightly lower for all weight gains. Fig. 3 shows the variations of the dielectric loss (ϵ'') with frequency for the range of percentage weight gains measured.

4. Discussion

4.1. Fully nitrided samples

The measured permittivity (ϵ') of the fully-nitrided samples, having a 19.7% volume fraction of pores, was virtually independent of frequency throughout the measurement range. The values obtained over the frequency range 0.5 to 9.3 GHz lay between 4.50 and 4.65, giving corresponding values of $\epsilon'(0)$ between 6.51 and 6.67. A summary of other reported results for both RBSN and HPSN is given in Table II and comparison shows that the values of $\epsilon'(0)$ derived from the present measure-

TABLE II Literature values of the permittivity of various silicon nitrides

Frequency (Hz)	Dielectric constant	Fabrication method	Comments	Reference
$(8-10) \times 10^9$	4.5–5.6	reaction-bonded	–	Walton [3]
1×10^5 9.34×10^9	9.58 5.65	hot-pressed	5 wt% MgO added	Thorp and Sharif [6]
1×10^{10}	5.52–9.3 6.65 7.37	reaction-bonded hot-pressed	up to 5 wt% MgO added	Messier and Wong [12]
9.37×10^9	4.85 6.8 8.3 5.5–5.9	slip-cast flame-sprayed hot-pressed isostatically pressed		Perry and Moules [13]

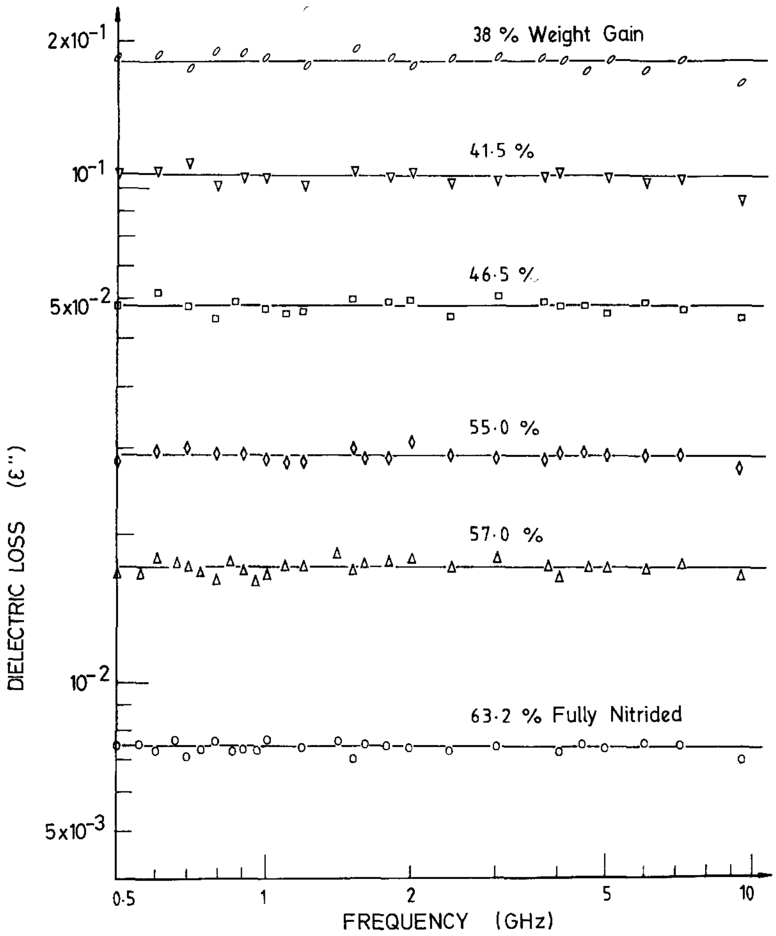

Figure 3 Frequency dependence of dielectric loss for various weight gains.

ments are approaching the values (7.3 to 9.5) found previously for HPSN. It may be noted, in particular, that the dielectric constants obtained here for RBSN are in good agreement with the low loss silicon nitrides measured by Walton [3]. As can be seen from Table II, the reported values, taken as a whole, vary greatly, from 4.5 to 9.5; this may be due to the diverse fabrication techniques employed but it is evident that the values for the more dense HPSN are higher, as would be expected.

The loss tangents for the fully nitrided samples are compared in Table III with values previously reported for various silicon nitrides prepared by various fabrication routes. The present values appear considerably lower than those for the earlier silicon nitrides investigated by Messier and Wong [12] and Perry and Moules [13] for radome applications and are also about two times less than those given more recently by Thorp and Sharif [6] for HPSN.

TABLE III Loss tangents of various silicon nitrides

Frequency (Hz)	tan	Fabrication method	Reference
1.0×10^9 9.34×10^9	1.67×10^{-3} 1.58×10^{-3}	Reaction-bonded	Present study
9.37×10^9	7.0×10^{-3}–1.7×10^{-2}	Hot-pressed	Perry and Moules [13]
1.05×10^5 9.34×10^9	5.0×10^{-3} 4.02×10^{-3}	Hot-pressed	Thorp and Sharif [6]
1.0×10^{10}	1.0×10^{-2}–1.49×10^{-1}	Reaction-bonded	Messier and Wong [12]

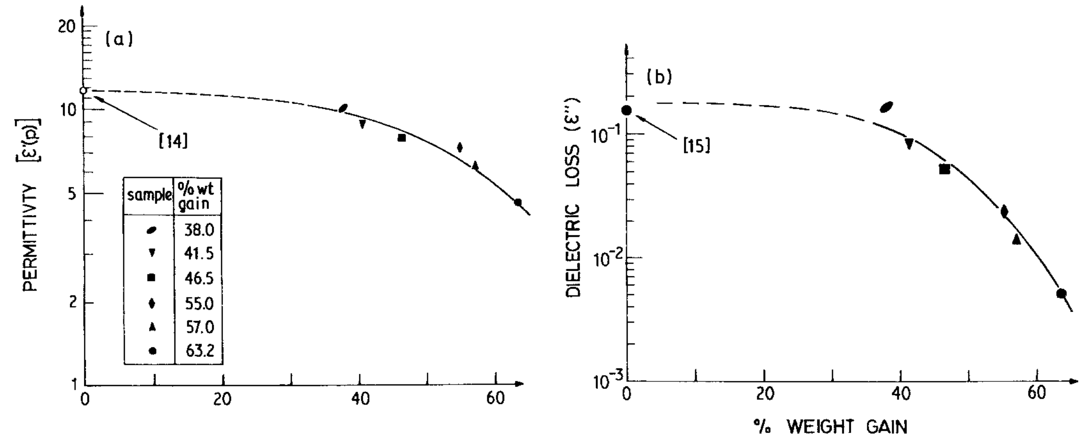

Figure 4 The dependence of (a) permittivity (ϵ') and (b) loss (ϵ'') on percentage weight gain; (1 GHz data).

4.2. Partially nitrided samples

The variation of reduced permittivity $(\epsilon' - \epsilon_\infty)$, with frequency could not be obtained since no values of ϵ_∞ were available for any of the partially nitrided samples. Nevertheless, since ϵ_∞ is a constant quantity for each material, subtracting this from the measured dielectric constant would not alter the gradient of each of the plots in Fig. 2. It can thus be inferred that the data for the partially nitrided samples are consistent with the unversal dielectric response law in that $(\epsilon' - \epsilon_\infty) \propto \omega^{(n-1)}$ with all n values close to unity.

The variation of ϵ' with weight gain at an particular frequency is illustrated by the plot in Fig. 4a where the value for pure silicon [14] ($\epsilon' = 11.7$) has also been included. The variation suggested by the curve indicates that the incremental change in ϵ' with increasing weight gain is much more pronounced at higher weight gains. Fig. 3 shows that the loss factors ϵ'' of samples ranging from the highest to the lowest weight gains spanned about one and a half decades from about 4.5×10^{-3} to 1.8×10^{-1}. The variation of loss factor with weight gain is illustrated more conveniently by the plot in Fig. 4b which applies for any particular frequency in the measurement range. In this plot the value of the loss factor for pure silicon (of resistivity 16 000 Ωcm [15]) is included in order to show the most likely shape of the curve. The point for the lowest weight gain sample measurable (38%) deviates from the curve but this is probably due to experimental error, since measurements are much more difficult when the samples are very lossy. If it is assumed that a decrease in weight gain represents an increase in free silicon content the present data would support (though do not directly prove) the widely held supposition that both the dielectric constant and loss factor are noticeably dependent on the free silicon content. It is interesting to note here that this effect is not restricted only to bulk material in so far as an increase in dielectric constant of thin film silicon nitride has been reported [16] as the films become rich in silicon. Measurements of the permittivity could thus provide a basis for the estimation of the degree of nitridation or of free silicon content.

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