JOURNAL OF MATERIALS SCIENCE 22 (1987) 2641–2644

# The temperature and frequency dependencies of permittivity and dielectric loss in reaction bonded silicon nitride

J. S. THORP*, T. G. BUSHELL*, D. EVANS‡
*Departments of *Applied Physics and Electronics, and ‡Physics, University of Durham, South Road, Durham DH1 3LE, UK*

N. E. RAD
*Department of Electrical Engineering, University of Tabriz, Iran.*

The temperature dependencies of the permittivity and dielectric loss of reaction bonded silicon nitride (RBSN) have been measured between 20 and 900° C at frequencies covering the range from 3 Hz to 300 kHz. Above about 300° C both parameters have a large effect. Analysis of the permittivity data in terms of the theory discussed by Jonscher and by Dissado and Hill predicts loss peaks at 48 Hz and 8 Hz at temperatures of 900 and 800° C, respectively. These values are in close agreement with those found independently from direct observation of the temperature and frequency variations of dielectric loss. On the assumption that a thermal activation process is responsible for the temperature dependence of the loss peak frequency, the associate activation energy is found to be about 1.94 eV.

## 1. Introduction

In a recent study of the permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of reaction bonded silicon nitride (RBSN) (Thorp *et al.* [1]) attention was primarily given to determining the respective frequency dependencies of $\varepsilon'$ and $\varepsilon''$ at room temperature. Using coaxial line methods (Kulesza *et al.* [2]) $\varepsilon'$ and $\varepsilon''$ were found over the frequency range 0.5 to 7 GHz for a series of specimens in which the degree of nitridation had been varied. For fully nitrided material (having a weight gain of 62% and a volume porosity of 19%) the room temperature permittivity was 4.60 and was almost frequency independent; fitting the data to the "universal" law of dielectric response (Jonscher [3–5]) confirmed that the limiting condition of lattice loss applied with $n = 0.98 \pm 0.02$. We have now made measurements of the temperature and frequency dependencies of $\varepsilon'$ and $\varepsilon''$ in fully nitrided RBSN and the results of this study are reported here.

Since the earlier observations of "universal" behaviour of dielectrics referred to above, a general description has been proposed which has as its natural consequence a variation with frequency of dielectric loss which may show maxima called "loss peaks", and away from such peaks has a power law dependence (Dissado and Hill [6]). This is the result of supposing that the relaxation of the polarization in a material may have two time scales; initially a correlation exists between the polarization centres giving a long relaxation time, this state merging after a characteristic period with a condition for which a much shorter relaxation time pertains. Such a time variation of polarization translates into the frequency domain to give loss peaks corresponding to the characteristic initial relaxation period for the material, and power law behaviour well away from such peaks. The loss peak frequencies are temperature dependent and in the simplest case exhibit an exponential form involving an excitation energy that is a property of the material. Near a loss peak the complex permittivity has a form that allows the determination of the characteristic frequency from the real part alone as will be demonstrated with the present data in Section 3.1 of this paper. A comprehensive review of the theoretical background together with a compilation of data has been published by Jonscher [7].

While the prediction of loss peaks shows up most naturally in a measurement of dielectric loss, the possible presence of free charge carriers in an insulator produces practical difficulties. We shall use the data for the real part of the permittivity to deduce the loss peak frequencies and make a comparison with the dielectric loss data. It will be seen in Section 3.2 that for our sample of fully nitrided RBSN at the two highest temperatures measured the predicted loss peak frequencies are in good agreement with the dielectric loss data. Below 700° C the characteristic frequencies are smaller than the start of the measurement interval, and both the real and imaginary parts of the permittivity show the "universal" power law behaviour.

## 2. Experimental

The specimens studied here were made, (Advanced Materials Engineering Ltd, Ruabon, Clwyd), by a modification of the standard commercial method. The starting material was micronized silicon powder, (whose major impurities were iron, aluminium and calcium at respective levels of 0.45, 0.25 and

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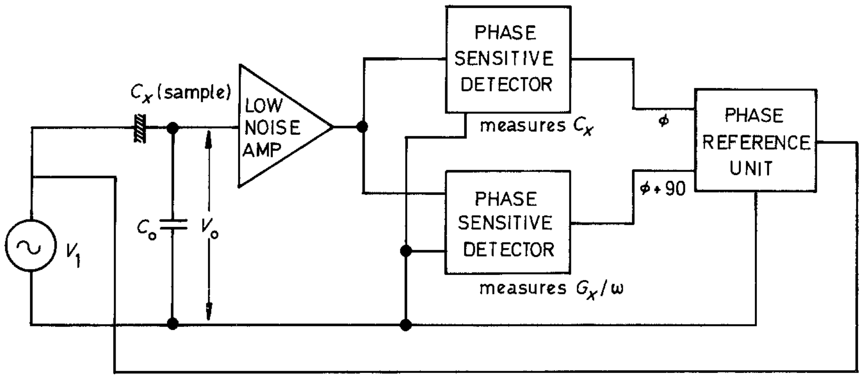

*Figure 1* Phase sensitive detection circuit for capacitance and conductance measurements in the frequency range 3 Hz to 300 kHz.

0.05 wt %) in which 90% of the particles had sizes of less than 30 $\mu$m. The green ceramics were produced by sintering billets isostatically pressed at 185 MNm and temperatures of 1200° C in an argon atmosphere. Nitriding was undertaken in an electrically heated furnace which used silicon carbide electrodes and was operated under a small positive pressure of dry nitrogen. At the level of iron present, iron-promoted growth of silicon nitride took place [8, 9], giving an $\alpha/\beta$ phase ratio of about 1.5. The degree of nitridation is conventionally called the "weight gain" of the ceramic. It expresses the percentage by which the weight of the green ceramic has increased in the reaction. Thus the maximum possible weight gain, assuming that all the available silicon has been converted to silicon nitride, is 66.5%. In practice, as in this instance, the maximum weight gain which is achieved is about 64.5%, which implies that there is a small amount of residual free silicon. The phase composition of this type of reaction bonded silicon nitride ceramic can be calculated from the relations [10]

$$C_P = 1 - 0.281\varrho_g - 0.148\varrho_p \qquad (1)$$

$$C_{Si} = 1.072\varrho_g - 0.643\varrho_n \qquad (2)$$

$$C_{Sn} = 0.791(\varrho_n - \varrho_g) \qquad (3)$$

where $C_P$, $C_{Si}$ and $C_{Sn}$ are respectively, the volume fractions of porosity, silicon and silicon nitride in a nitrided compact; here $\varrho_g$ is the density of the green ceramic and $\varrho_n$ the density of the nitrided material. For the specimens examined a peak firing temperature of 1440° C was used giving a nitrided density of $2.52\,\mathrm{kg\,m^{-3}}$, $C_p = 0.196$, $C_{Si} = 0.021$ and $C_{Sn} = 0.783$.

In order to enable data to be obtained at frequencies including those approaching d.c. conditions a phase-sensitive measurement method was used instead of the coaxial system previously employed for the room temperature studies. Details of the circuit, which measures the two quadrature components of the signal from the specimen, are shown in Fig. 1. With this it was possible for a.c. measurements to be made over the frequency range from 3 Hz to 300 kHz. For high temperature measurements specimen and furnace arrangements similar to those previously adopted in studies on magnesium oxide (Thorp *et al.* [11]) were used; platinum paste electrodes were pre-baked on to the opposite faces of a thin sheet of RBSN, contact to the electrodes being made with platinum wires. The measurements were made in an argon atmosphere and were restricted to an upper temperature limit of 900° C, in order to avoid possible reaction between the platinum and the residual free silicon in the RBSN. Referring to Fig. 1, an a.c. voltage $V_1$ is applied to the sample (of capacitance $C_x$) connected in series with a standard capacitor $C_0$. The voltage $V_0$ measured across $C_0$ is

$$V_0 = V_1 C_x/(C_0 + C_x) \qquad (4)$$

and if $C_0 \gg C_x$ this reduces to

$$V_0 = V_1(C_x/C_0) \qquad (5)$$

Consideration of the conductance in parallel with $C_x$ shows that (Bushell [12])

$$V_0 = V_1 \frac{C_x - jG_x/\omega}{C_0} \qquad (6)$$

when $G_x \ll \omega C_0$. Equation 6 represents two voltages one in phase with $V_1$ and the other in quadrature with $V_1$ given by $V_1 C_x/C_0$ and $V_1 G_x/\omega C_0$, respectively. It follows that the permittivity is given by $\varepsilon' = C_x/C_A$ where $C_A$ is the capacity of the equivalent air cored condenser.

## 3. Results

### 3.1. Permittivity results and analysis

The frequency dependence of the permittivity ($\varepsilon'$) at a series of temperatures up to 900° C, is shown in Fig. 2. It is seen that at room temperature there is practically no variation. As the temperature is increased up to 600° C $\varepsilon'$ decreases with frequency, the rate of fall being greater the higher the temperature. At 900 and 800° C the functional dependence on frequency of $\varepsilon'$ is more complex, there being a region over which the rate of change is a maximum. The data at these two temperatures will now be analysed in terms of the possible presence of loss peaks.

Near a frequency ($\omega_p$) at which there is a loss peak the complex susceptibility has the approximate form (Jonscher [7])

$$X(\omega) = A/(1 + i\omega/\omega_p) \qquad (7)$$

where $A$ is independent of frequency. The real part thus has the form.

$$X'(\omega) = A/(1 + \omega^2/\omega_p^2) \qquad (8)$$

The gradient, $g$, of the function connecting log ($X'$) and log ($\omega$) then depends on $\omega$ as,

$$g = -2(\omega^2/\omega_p^2)/(1 + \omega^2/\omega_p^2) \qquad (9)$$

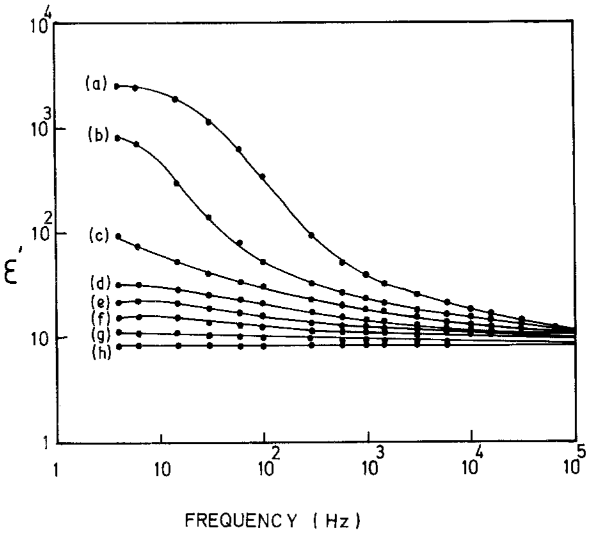

*Figure 2* Variation of permittivity with frequency and temperature; 64.5% weight gain RBSN (a) 900° C, (b) 800° C, (c) 700° C, (d) 600° C, (e) 500° C, (f) 400° C, (g) 300° C, (h) room temperature.

At a loss peak when $\omega = \omega_p$, $g$ has the value $-1$. The values of $\varepsilon'$ should have a frequency-independent constant subtracted, corresponding to the limiting value at large frequencies, but since at the highest temperatures and lower frequencies the measured values are some three orders of magnitude larger than a sensible high frequency limit this will not be important. The slopes of the curves shown in Fig. 2 would therefore be expected to approximate to the functional dependence of $g$ in the vicinity of a loss peak, and such a point would be marked by a slope having a value of $-1$, the corresponding frequency giving $\omega_p$.

Fig. 3 shows the variation of the slopes of the curves in Fig. 2 as a function of frequency for the 900 and 800° C data. In order to demonstrate the effect of subtracting a constant contribution Fig. 3 also shows the effect of subtracting the values of $\varepsilon'$ at room temperature from the higher temperature data before determining the slopes. It is seen that in the frequency region discussed in the following there is no significant

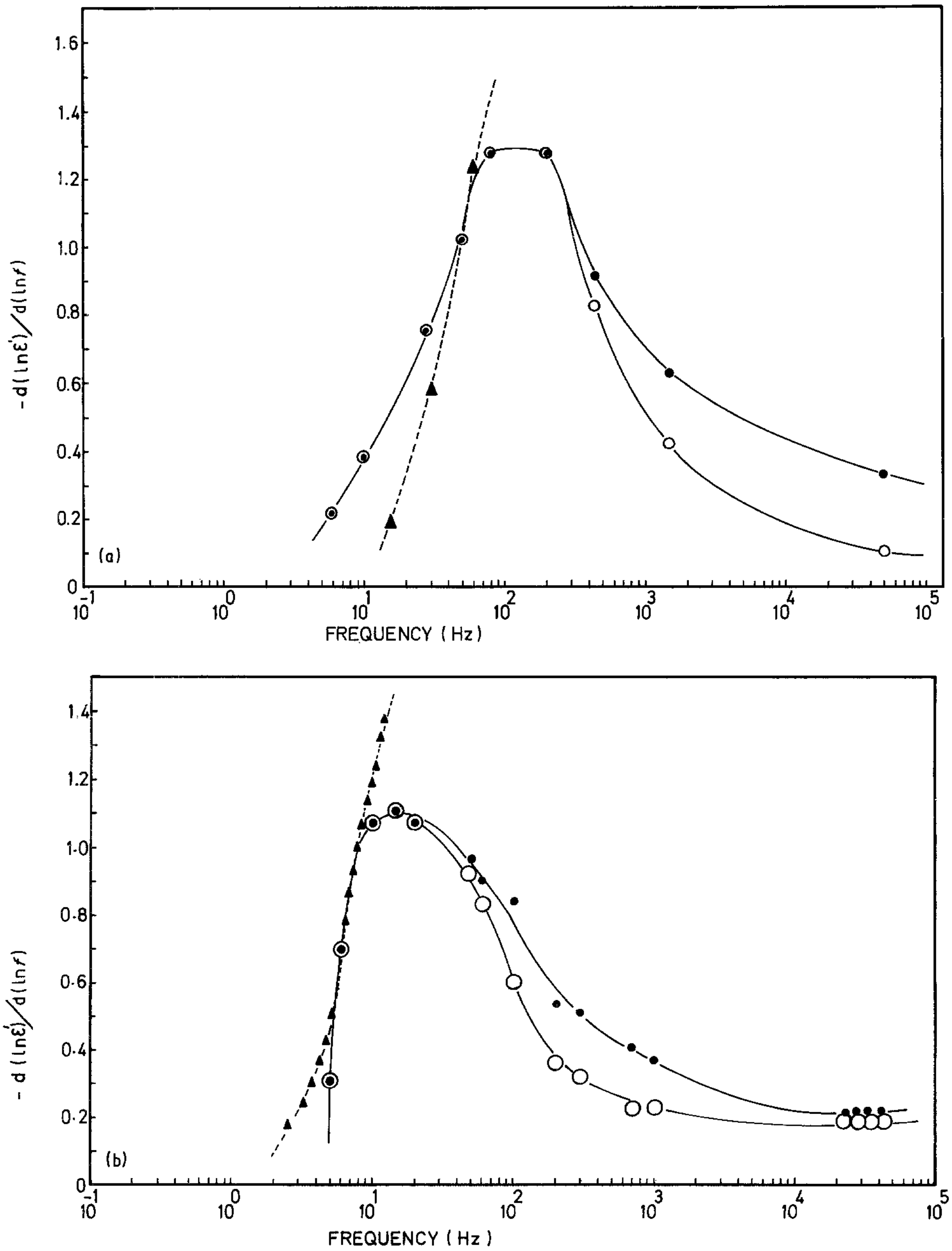

*Figure 3* (●) Variation of $-d(\ln \varepsilon')/d(\ln f)$ with frequency, (○) effect of subtracting room temperature data, (▲) predictions for region of loss peaks. (a) 900° C, (b) 800° C.

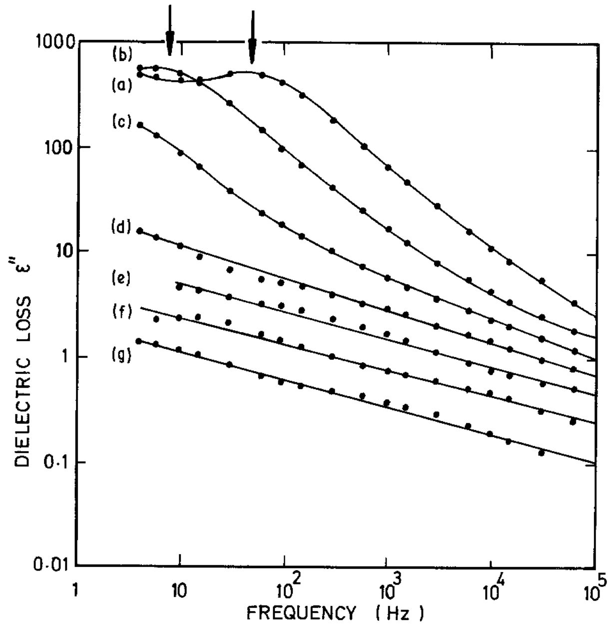

*Figure 4* Variation of $\varepsilon''$ with frequency and temperature; 64.5% weight gain RBSN; arrows show positions of loss peaks predicted by analysing the $\varepsilon'$ data. The prediction of 0.85 Hz for 700° C data is below the range of measurements but coincident with their trend (a) 900° C, (b) 800° C, (c) 700° C, (d) 600° C, (e) 500° C, (f) 400° C (g) 300° C.

difference produced by the subtraction. At the higher frequencies the curves diverge, but as the values of $\varepsilon'$ and the slopes of the curves in Fig. 2 become smaller the errors resulting from subtraction become larger and no attempt is made here to deduce definitive limiting values of slope, and hence the limiting power law at high frequency. The overall variation can be understood in terms of loss peaks at 48 and 8 Hz at 900 and 800° C, respectively, and assuming these values the expected function for $g$ is also shown in Fig. 3. It is seen that near where the curves from the experimental data pass through unity, their shapes do coincide with the theoretical expectation for a loss peak. At frequencies above, the universal power law behaviour takes over and prevents the data in Fig. 3 following the functional shape of $g$, bringing the values of the slopes below unity again.

Assuming that $\omega_p$ depends on temperature through a thermal activation energy ($D$) the expected variation (Jonscher [7]) will be $\exp(-D/kT)$, where $T$ is the absolute temperature and $k$ the Boltzmann constant. Using the values of 48 and 8 Hz at 900 and 800° C deduced above, the value of $D$ is found to be 1.94 eV. At 700° C a loss peak would be expected at about 0.9 Hz and for lower temperatures any effects would be well below the lowest frequency measured. It is interesting to note that the slope of the 700° C curve in Fig. 2 could well extrapolate to $-1$ in the vicinity of 1 Hz and it is clear that at all lower temperatures the data are entirely consistent with coming from a region well above any loss peaks.

### 3.2. Comparison with dielectric loss measurements

As explained in Section 1 the interpretation of measurement of dielectric loss ($\varepsilon''$) in an insulator can be complicated by the presence of a small amount of free charge carriers. In the case of materials with small band gaps at the higher temperatures the conductivity might in fact be dominated at low frequency by thermally activated carriers. The analysis of the last section has been done in terms of $\varepsilon'$ since even fully nitrided silicon might be expected to have sufficient amounts of the free element for thermally released carriers to be of importance.

The measured values of $\varepsilon''$ are shown in Fig. 4 as a function of frequency. The loss peak frequencies deduced from the analysis of the $\varepsilon'$ data in the last section, are marked in this figure. Whatever may be the role of free charge carriers the predicted frequencies do indeed correspond to maxima in the measured values of $\varepsilon''$ at 900 and 800° C and the 700° C data look as if there may be another maximum loss as predicted near 1 Hz. All the other measurements are consistent with being well above any loss peaks and exhibit the limiting power law behaviour.

## 4. Discussion

The data presented here can be well understood in terms of the theories of time dependent correlations being important in the relaxation of polarization in solids. As has been pointed out by the earlier authors (Dissado and Hill [6], Jonscher [7]), the theory should be applicable to a wide variety of physical situations though they used a model involving the presence of intrinsic dipoles. In the case of fully nitrided silicon there is no reason to suppose the presence of such dipoles but the general description does seem to hold. The thermal excitation energy at near 2 eV is quite large compared with, for example, the value of 0.56 eV quoted in [6] for a doped ceramic, and presumably is indicative of the different nature of the microscopic dipoles in silicon nitride. It is finally interesting that a loss peak analysis can be done on permittivity data thus bypassing the possible complicating effects of free carrier current which would give a negligible contribution to $\varepsilon'$ but have a major effect on $\varepsilon''$.

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*Received 8 September*
*and accepted 12 November 1986*