JOURNAL OF MATERIALS SCIENCE 26 (1991) 1106–1108

High-temperature dielectric behaviour of hexagonal boron nitride measured perpendicular to the cleavage planes

M. A. CHAUDHRY
Department of Physics, Bahauddin Zakariya University, Multan 60800, Pakistan

The dielectric response of hexagonal boron nitride has been measured perpendicular to the cleavage planes at fixed temperatures in the range up to 914 K. The frequency span lies between 10 mHz and 10 kHz range. The dielectric response consists of two loss peaks and a strong low frequency dispersion (LFD). The results are related to the movement of impurity ions.

1. Introduction

Boron nitride (BN) is found to have two structural forms, hexagonal and cubic, the former being the more common. The hexagonal variation resembles graphite in its crystal structure, slippery feel and relative softness; however, it is white in colour [1]. The structural details of hexagonal boron nitride have been reported by Pease [2].

Boron nitride is an excellent insulator and its dielectric parameters were reported by Taylor [3] and Westphal and Sils [4] in the frequency range 100 Hz to 100 GHz and in the temperature range 0 to 1400 °C. The present work is a continuation of our earlier studies [5] and extends the frequency range down to 10 mHz. The highest frequency in our measurements goes up to 10 kHz and the maximum temperature to 914 K.

2. Experimental procedure

To measure the dielectric properties of boron nitride perpendicular to the cleavage planes, samples were cleaved to a thickness of between 0.5 and 1 mm and an area about 10 mm × 5 mm. Platinum paste was used to form electrodes on both sides of the samples. The measuring procedure and method of controlling temperature have already been described elsewhere [6, 7]. The a.c. signal amplitude was 5 V.

The results of measurements are presented as logarithmic plots of real and imaginary components of the complex capacitance against frequency

$$\begin{aligned} C(\omega) &= C'(\omega) - iC''(\omega) \\ &= C'(\omega) - iG(\omega)/\omega \qquad (1) \end{aligned}$$

where $G(\omega)$ is the frequency-dependent a.c. conductivity.

3. Results and discussion

Measurements were carried out over two temperature cycles. In each cycle, data were taken first with increasing temperatures up to a maximum of 914 K and then with decreasing temperatures until room temperature was reached. It was difficult to normalize [8, 9] the data taken for increasing temperatures, therefore the data presented here correspond to decreasing temperatures only.

The results corresponding to the two sets of measurements are collected in Figs 1a and b and 2a and b. These data are subsequently normalized and are shown in Figs 1c and 2c. The shapes of the two normalized plots are similar to each other except for a small discrepancy on the high-frequency side. This can be accounted for by looking at the temperatures at which the measurements were recorded. It can be seen that the lowest temperature indicated in Fig. 1c is 445 K, whereas in Fig. 2c it is 633 K. Dielectric loss could not be measured satisfactorily below 445 K because it approached the measuring limit for the tan δ of our equipment, i.e. 10^{-4}. This explains why the results corresponding to temperatures less than 445 K could not be reported here. An examination of the data below 0.1 Hz shows that both $C'(\omega)$ and $C''(\omega)$ tend towards a logarithmic slope of − 1, and this phenomenon is known as low-frequency dispersion (LFD) [10]. The difference between this and the ordinary direct current (d.c.) conduction lies in the presence of the strong increase of $C'(\omega)$ towards low frequencies in LFD, while d.c. must have a constant $C'(\omega)$ at sufficiently low frequencies [10, 11].

The empirical relationship for LFD is given by the limiting form of the "universal" dielectric relation [9]

$$C'(\omega) = \tan(n\pi/2)\, C''(\omega)\ \omega^{n-1} \qquad (2)$$

in which the exponent n lies close to zero, corresponding to highly lossy systems, while the more conventional dielectric behaviour has n values closer to unity.

The LFD limit corresponds to a slowly frequency-dependent conductivity. Rather than attempting to measure small deviations from the − 1 slope, the value of the exponent n may readily be determined

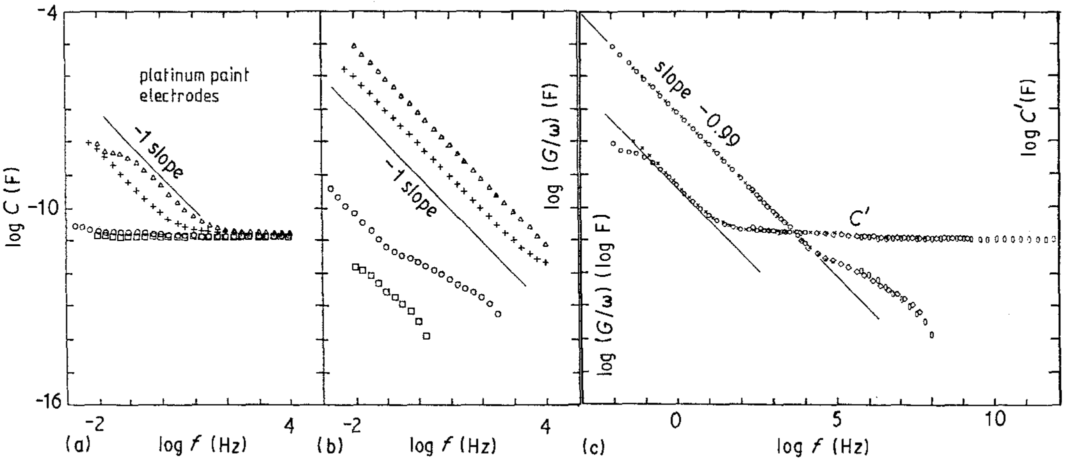

Figure 1 A set of dielectric data for hexagonal boron nitride measured at (a, b) (△) 914 K, (+) 820 K, (○) 633 K, (□) 445 K, (c) (○) 914 K, (×) 820 K, (◇) 633 K, (0) 445 K, for platinum paint electrodes. (a) Capacitance, (b) dielectric loss; (c) the data shown in (a) and (b) normalized with respect to 914 K. Measurements were performed perpendicular to the planes with decreasing temperatures of the first temperature cycle.

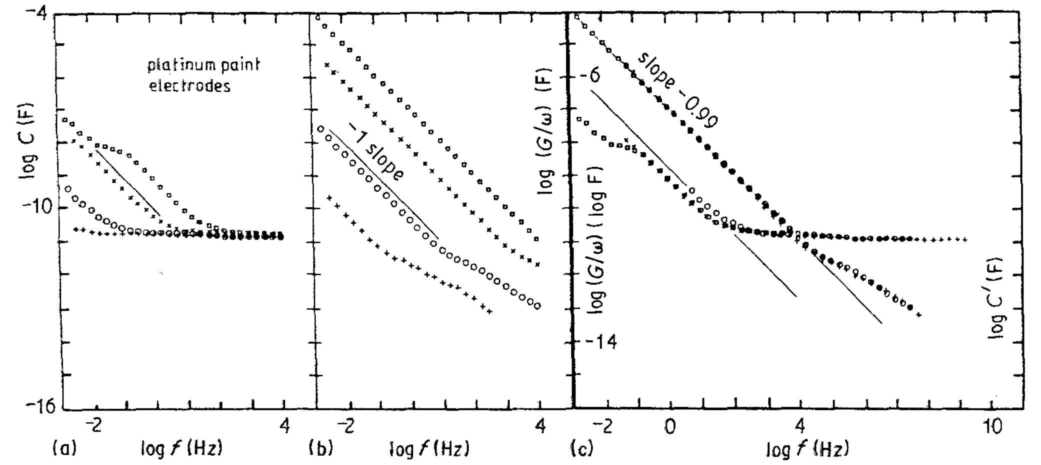

Figure 2 The dielectric response of (a) capacitance, and (b) loss of boron nitride for measurements performed normal to the planes with decreasing temperatures of the second temperature cycle. (c) The normalized plot of the same data. (□) 914 K, (×) 820 K, (○) 727 K, (+) 633 K.

from the ratio

$$C''(\omega)/C'(\omega) = \cot(n\pi/2) \qquad (3)$$

which gives, in our case, $n \sim 0.01$.

The question whether the observed LFD process is due to a volume or an interfacial effect may be answered on the basis of the argument [12] that in the latter case the dominant process, i.e. the interfacial LFD, would have to have a higher impedance than the bulk. Now at high frequencies the capacitance of the sample corresponds well to the geometrical capacitance of the entire volume, and the losses are low. It would be most unlikely that the conductance of the volume should increase with rising temperature so rapidly as to become dominant over that of the presumed much thinner interfacial region. We thus conclude that the process is a volumetric one.

It is too early to be sure of the most likely process for the mechanism responsible for LFD, but two suggestions have been made: one involving extended correlated hopping [12] and the other an electrochemical process [13, 14].

As we move on the normalized plot towards higher frequencies, a dispersion in $C'(\omega)$ is observed at about 0.1 Hz but its corresponding loss peak is not visible due to a strong LFD in this region. However, a shallow loss peak with a very small dispersion in $C'(\omega)$ can be seen at about 1 MHz on these plots. The loss peaks are related either to dipoles or to a double-well hopping of charge carriers which may be electrons or ions. The possibility of ions hopping in a double well, thus giving rise to loss peaks, cannot be ruled out in boron nitride which may contain some impurity ions. Such ions would contribute significantly at high temperatures when they get sufficient energy to surmount the well potential and hence may lead to a strong LFD. In such a case they have an activation energy greater than 1 eV [7]. To check this assertion, LFD activation energy was worked out as usual from the Arrhenius plot shown in Fig. 3 and was found to be 2.1 eV, suggesting that the charge transportation is due to ionic motions.

The data from published results [4] were replotted on a log–log scale. On normalization they gave similar

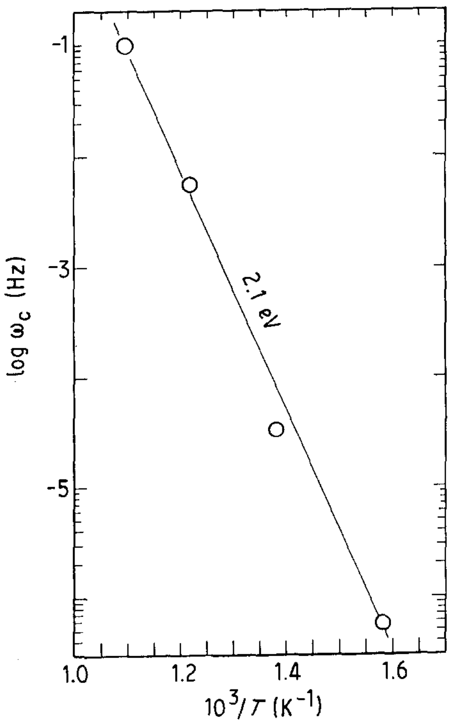

Figure 3 Arrhenius plot for the calculation of activation energy for boron nitride measurements shown in Fig. 2.

plots with some evidence of LFD at low frequencies and high temperatures. The activation energy was found to be 2 eV which is similar to that of the samples investigated in the present study.

From the above discussion it can be concluded that the high-temperature dielectric response of boron nitride consists of two loss peaks and a strong low-frequency dispersion which is probably caused by the movement of impurity ions over limited, but extended, regions.

Acknowledgements

The author thanks Professor Andrew K. Jonscher for his invaluable help and guidance during this work, the Government of Pakistan for a bursary, and Karachi University for study leave. He also thanks the Fulmer Research Institute, UK, for supplying the BN samples. This work was carried out at the former Chelsea Dielectric Group, Chelsea College, University of London, London, UK.

References

1. R. THOMPSON, *Endeavour* **29** (106) (1970) 34.
2. R. S. PEASE, *Acta Crystallogr.* **5** (1952) 356.
3. K. M. TAYLOR, *Ind. Engng. Chem.* **47** (1955) 2506.
4. W. B. WESTPHAL and A. SILS, Massachusetts Institute of Technology Technical Report (1972) AFML-TR-72-39.
5. M. A. CHAUDHRY and A. K. JONSCHER, *J. Mater. Sci.* letters **8** (1989) 1260.
6. *Idem, ibid.* **20** (1985) 3581.
7. *Idem, ibid.* **23** (1988) 208.
8. R. M. HILL, *Thin Solid Films* **7** (1971) R 57.
9. A. K. JONSCHER, "Dielectric Relaxation in Solids" (Chelsea Dielectrics Press, London, 1983).
10. A. K. JONSCHER, *Phil. Mag.* **B38** (1978) 587.
11. A. K. JONSCHER, F. MECA and H. M. MILLANY, *J. Phys. C* **12** (1979) L 293.
12. A. K. JONSCHER, *J. Mater. Sci.*, in press.
13. L. A. DISSADO and R. M. HILL, *J. Chem. Soc. Faraday Trans. 2* **80** (1984) 291.
14. A. K. JONSCHER, *Proc. Electrochem. Soc.* **86-3** (1986) 351.

Received 14 November 1989
and accepted 9 January 1990