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Broadband dielectric response of AlN ceramic composites☆

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Abstract

Aluminium nitride (AlN) is considered as a substrate material for microelectronic applications. AlN ceramic composites with different amount of TiO_2 (up to 4 vol.%) were obtained using hot pressing at different sintering temperature from 1700 to 1900 °C. It was shown that milling of the raw AlN powder has strongly influence on sintering and improves densification. Broadband dielectric spectroscopy was used as a nondestructive method for monitoring of the ceramic microstructures. TiO_2 additive affects the key properties of AlN ceramics. Thus, porosity of 0.1 %, dielectric permeability of σ = 9.7 and dielectric loss tangent of $\tan\delta = 1.3\cdot10^{-3}$ can be achieved if up to 2 vol.% TiO_2 is added.

Keywords: *ceramic substrates, aluminum nitride, hot pressing, dielectric response, polarization*

I. Introduction

In recent years, development of substrate materials for Multi Chip Modules (MCM-C) or Multilayer Ceramics Technology (especially HTCC) are more advanced since electronic packages have become more complex, high-efficiency and they tend to be smaller. It was shown [1] that high-resistance, thermal conductive monolithic ceramic bodies with conductive and dielectric layers made by appropriate tapes and sintered then together in one step could be obtained.

In this work aluminium nitride is considered as substrate material for MCM applications because of its high thermal conductivity (200–320 W/(m·K)), low dielectric constant (9), and the similarity of its thermal expansion coefficient (2.6–5.5·10^{-6} 1/K) with that of silicon (2.6–4.3·10^{-6} 1/K). However, it has low flexural strength (300–400 MPa) and is prone to fracture (fracture toughness ≈ 2.7 MPa·$m^{1/2}$). Nowadays investigations on creation of cost-effective technologies of AlN ceramics mass production are provided. As properties of aluminium nitride are very susceptible to producing technology and pollutions, obtaining of high quality AlN ceramics with desirable performance characteristics is very difficult and costly. To produce a dense material without activators, high pressures of up to 30 MPa or more are required. The research of AlN sintering process with different modifiers or activators is carrying out as well.

Previous experiments [2] revealed a beneficial effect of addition of large cations to AlN ceramics. Thus, titanium cations can possess a strong positive influence on the mechanical and electrical properties of dielectric substrates. It was shown that addition of small amount of TiO_2 (< 1.5 vol.%) increases relative density, decreases dielectric permittivity and losses [3]. In addition, O^{2-} cations in this case can increase toughness due to the elongated grains allocation and plate-like morphology formation (i.e. the formation of polytypes in AlN) [4], but limits of such phenomenon are still not clear. Some other additives can also be attractive, such as TiH_2, which dissociates at 600–800 °C [5] and in this case Ti^{2+} cations may be deposited on the grain surface as thin films and increase thermal conductivity of composites [6]. The influence of hydrogen atmosphere on technically pure AlN powders was investigated [7] as well. It was shown that the toughness of composites was improved due to the structure refinement and formation of solid solution of hydrogen in aluminium nitride. Improvement of materials toughness, thermal conductivity

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and self-reinforcement due to adding of TiC and TiN were investigated too [4,8]. It was shown that dielectric permittivity of AlN composites with these refractory additives is equal to 9.8–23.7 (at 3.0 GHz) and the highest value of ε = 23.7 was observed in AlN composites with 25 mas of TiN (dielectric particles were smaller than conductor, percolation threshold for this type of materials was 16.4–16.6 vol.%). The experiments showed that dielectric properties of AlN composites weakly depend on frequency of applied electric field in the frequency range of 3.0–37.0 GHz.

As far as direct methods of structural analysis hardly distinguish the influence of light doping, non-destructive method of microstructure's investigation were chosen, namely dielectric response and DC conductivity. Dielectric response of materials has been studied almost for a half of last century. Investigations cover already extremely broadband range of frequencies (10^{-6}–10^{16} Hz). Methods of impedance spectroscopy [9] allow to model the microstructure of composites using equivalent electrical circuits. However, relaxation dispersion of ε' described by the Debye's equation or another equation [10] for more indistinct range of dispersion compared to the Debye's response should be present. On this reason such equations are more appropriate for dipole systems: liquid dielectrics or polymers, i.e. the systems consisting of dipoles (in model approximation), available for free rotation but do not interact with each other and have the same relaxation time. In amorphous materials hopping polarization prevails and AC conductivity is the sum of leakage and bias conductivity: $\sigma(\omega) \propto \sigma_0 + 2\pi f \varepsilon\varepsilon_0 \tan\delta$. This dependence is an exponential function of frequency $\sigma(\omega) \propto \omega^n$. In previous works [11,12] a number of n values were given and it was stated that $n \leq 1$. Dielectric losses do not only determine power dissipated in the material which can cause a strong overheating and destroying but also they are a sensitive indicator of structure defects which act as scattering centers. That is why the analysis of their dependence on the structure defects and external influence (temperature, electric field strength and frequency etc.) is of great interest for physics and technology of dielectrics.

In polycrystalline materials, particularly in ceramics, the phases with different physical properties (concentration of charge carriers) can be present. In this case, charge accumulation on the inclusion's boundaries or on the layer surface can cause polarization. Many researchers consider such system in terms of Maxwell-Wagner polarization, according to which a conductive layer in electric field is characterized by a constant value of electric conductivity σ. It is considered that such layer will be characterized by even electric field and all the charges will be located only on the interfaces. Trukhan [13] suggested such system as homogeneous dielectric with no leakage currents. It was shown that as for the flat conductive layer surrounded by dielectric layers and for conductive spherical particles surrounded by dielectric medium, ε' decreases monotonically with frequency, ε'' has its maximum at the dispersion region. Frequency of dispersion increases with the decrease of charge carriers' concentration at large Debye's screening radius, i.e. at low charge carriers' concentration or at increasing of dielectric contribution (geometrical enlargement or ε' decrease). At high enough charge carriers concentration frequency of dispersion approaches to Maxwell-Wagner's dispersion asymptotically. It means that the discrepancy of these two theories results increases at decrease of dielectric contribution. Thus as the variation of phase distribution in heterogeneous medium always takes place, dispersion region will be less clearly shown than it follows from the Maxwell-Wagner theory.

Thus the aim of our work was the complex study of AlN ceramics with various amount of TiO_2 additive. The influence of processing conditions (powder milling, sintering temperature) on electrical and dielectric properties was investigated.

II. Experimental

AlN ceramics with 0, 0.5, 2, 3 and 4 vol.% TiO_2 were prepared from technically pure (95 vol.% pure) AlN powder (the raw powder) grounded 3 h in a planetary mill (the milled powder). The ceramic samples were prepared in the form of pellets (diameter 18 mm; thickness 1 mm). Hot pressing was done by applied pressure of 30 MPa, for 20 min at temperature between 1700 °C and 1900 °C with the step of 50 °C.

Bulk density was determined from hydrostatic weighing. Theoretical density (TD) was estimated using the rule of mixtures, while the relative density was calculated from the ratio of the bulk density and the theoretical density. For electrical measurements the sintered ceramic samples were mounted between two electrodes inside a metallic sample holder (diameter of the presser graphite contact 5 mm). DC resistance of the samples was measured with teraohmmeter. Dielectric characteristics within the range of 10^2–10^7 Hz were also analysed. The bridge method was used in low-frequency range (10^2–10^5 Hz), thus, capacitance and loss tangent values were directly measured. Real and imaginary parts of dielectric permittivity as well as real part of AC conductivity were calculated. The resonance method was used in radio-frequency region (10^4–10^7 Hz). In both cases parallel scheme was selected. Moreover dielectric properties of AlN ceramics at heated from 20 °C up to 350 °C with the speed of 4 ± 1 °C, by immersing the measurement cell into a furnace, were also measured.

III. Results and discussion

3.1. Sintering behaviour

The influence of milling on the particle size distribution is shown in Fig. 1. It can be seen that milling caused considerably decrease of particle sizes. This is the rea-

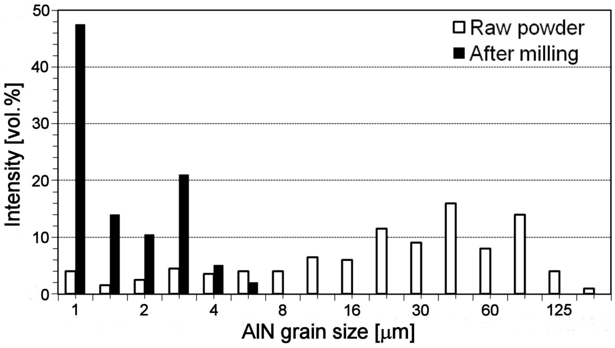


Figure 1. Grain size distribution in AlN powder

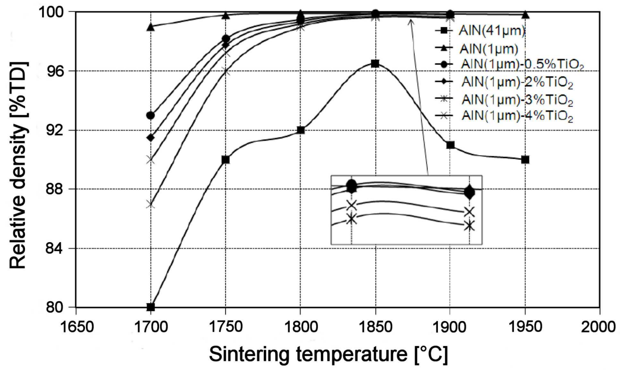


Figure 2. Effect of grinding, TiO_2 addition and sintering temperature on relative density of AlN ceramics

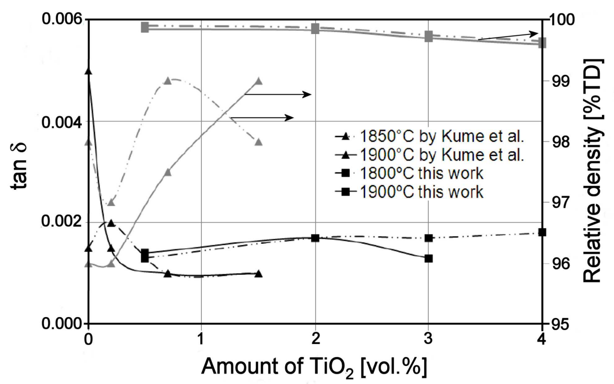


Figure 3. Effect of TiO_2 addition on relative density and loss tangent of AlN ceramics

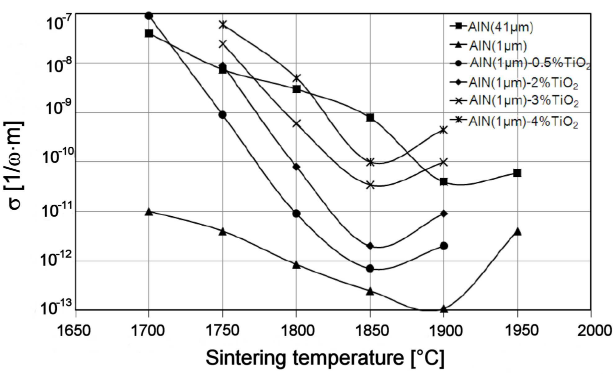


Figure 4. Effect of grinding, TiO_2 addition and sintering temperature on conductivity (at 20 °C) of AlN ceramics

son for the obvious difference in sintering behaviour between the raw and milled AlN powders (Fig. 2). The milling of the raw AlN powder improved sinterability, i.e. increase relative density and reduce sintering temperature. Shrinkage of AlN samples, prepared from the milled powder, was activated due to increasing of bulk and grain-boundary diffusion caused by increase number of structure defects, mainly dislocations, formed after pre-shock-abrasive processing [14]. Relative density of the pure AlN (Fig. 2), prepared from the milled powder and sintered at 1850–1900 °C was 99.9 %TD. Kume *et al.* [3] investigated the influence of TiO_2 addition on densification of the AlN ceramics. It was shown (Fig. 3) that TiO_2 enhanced densification of AlN ceramics, however, they obtained density less than 98 %TD for the pure AlN ceramics sintered at 1900 °C. Our results confirmed that densities higher than 99 %TD can already be obtained at 1800 °C, but the increase of TiO_2 content slightly decreases the density of AlN/TiO_2 composites sintered at 1800 °C and 1900 °C (Figs. 2 and 3).

3.2. DC conductivity

Although DC conductivity of the samples obtained from the raw AlN powder at optimal sintering temperature was rather low, i.e. $\sigma = 4 \cdot 10^{-11}$ 1/Ω·m, milling of the powder reduced electrical conductivity in more than two orders (Fig. 4). Kobka *et al.* [15] studied DC conductivity of polycrystalline semiconductors according to grain size and additive content. It was shown that if the bulk conductivity is given by equation:

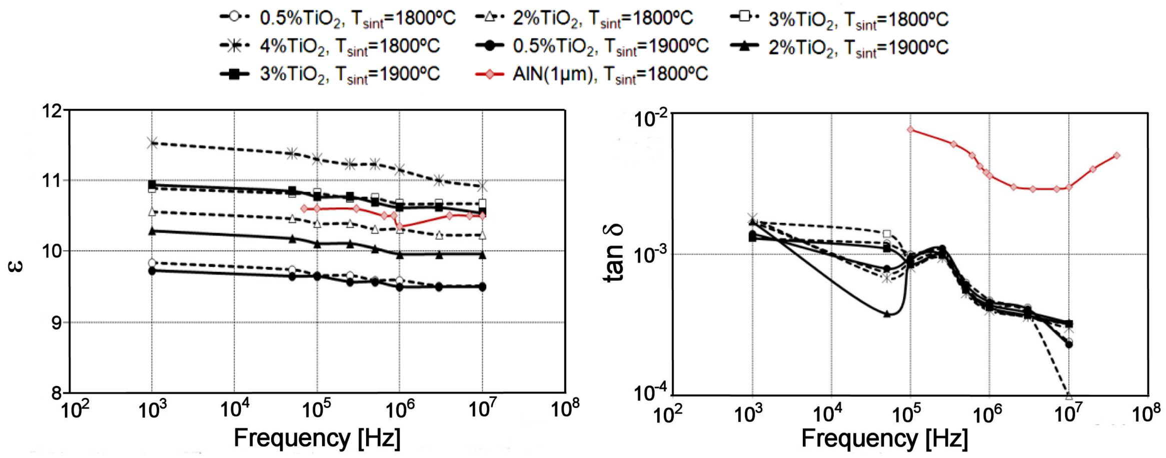
$$\sigma = \sigma_g + \sigma_b(h/r_0) \tag{1}$$

where σ_g - barrier conductivity of polycrystalline sample; σ_b - the same for materials with electrons localized on the grain boundaries; h - full thickness of the border; r_0 - grain radius, there is some critical value of grain size r_c:

$$r_c = \left(\frac{3\varepsilon\varepsilon_0}{2\pi e^2 n_0}\right)^{1/2} \tag{2}$$

Note that σ_g is proportional to an average concentration of charge carriers remaining in the grain $n_0 - (3hn_b/2r)$. Thus if $r_0 \rightarrow r_c$, $\sigma_g \rightarrow 0$ and in the case of $r_0 \leq r_c$, Eq. 1 has only the second term, which corresponds to the current flow only along the grain boundaries. If $r_0 > r_c$ the second term in Eq. 1 can be neglected. In this case the charge paths through the grains. In previous works [16] it was shown that at small enough grain size almost all the charge carriers move from the grain to the boundaries and grain conductivity becomes very low which is most probably happens in our case.

Increase of TiO_2 amount from 1 to 4 vol.% increased conductivity from $7 \cdot 10^{-13}$ up to $1 \cdot 10^{-10}$ 1/Ω·m (Fig. 4) due to TiN formation in AlN ceramics as a result of reaction between TiO_2 and AlN at temperatures > 1600 °C.



(a) (b)

Figure 5. Frequency dependences of dielectric permittivity (a) and loss tangent (b) of AlN ceramics with different TiO_2 content

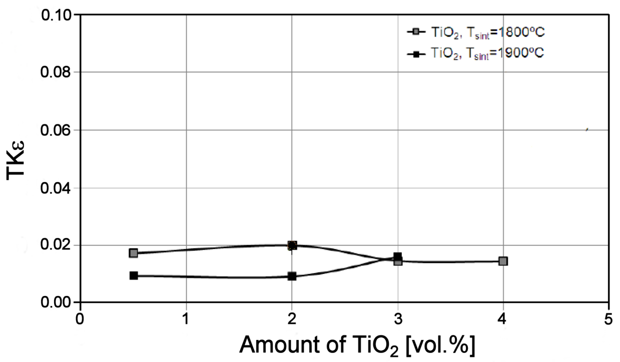


Figure 6. Temperature coefficient of dielectric permittivity of AlN ceramics obtained at different sintering temperatures in dependence of TiO_2 amount

3.3. AC conductivity

Dielectric permittivity of the AlN/TiO_2 composites with a constant amount of additive mainly decreases in approximation to the optimal sintering temperature; and increases at increasing of TiO_2 content at constant sintering temperature (Fig. 5). Our results are consistent with already published data of Kume *et al.* [3] as the similar values for $\tan\delta$ were obtained (Fig. 3) for the AlN/TiO_2 composites with TiO_2 amount higher than 0.5 vol.%. This effect should be caused by TiN *in-situ* complexes. All AlN/TiO_2 composites showed decrease of ε' and $\tan\delta$ with a threshold decline of permittivity and maximum of loss tangent at 10^5–10^6 Hz (Fig. 5). Frequency dispersion of ε' and $\tan\delta$ revealed the contribution of two polarization mechanisms with different relaxation time: spacecharge polarization at low frequencies and hopping polarization at radio frequencies.

Dielectric permittivity and loss tangent did not respond to increasing temperature below 200 °Cand increased with temperature above 200 °C. Thus, all the samples had a positive temperature coefficient of dielectric constant (Fig. 6) which showed that energy dissipation was caused by conduction losses. Moreover, dielectric losses highly increased with the deviation from the optimal sintering temperature which indicated the formation of a large number of structure defects.

IV. Conclusions

It was shown that fine technically pure AlN powder can be used for producing of ceramic substrates with good dielectric properties. Milling of the raw AlN powder before sintering strongly reduces porosity of the samples, sintering temperature and dielectric loss. Sintering temperature defines dielectric losses due to the formation of defect structures in a greater degree than phase composition. TiO_2 additives affect the key properties of AlN ceramics in a parabolic way: the lowest porosity (0.1 %), dielectric permeability ($\sigma = 9.7$) and dielectric loss tangent ($\tan\delta = 1.3 \cdot 10^{-3}$).

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