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Synthesis of oxygen-free aluminium nitride ceramics

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The aluminium nitride raw material in the form of powder was synthesized using the Self propagating High temperature Synthesis (SHS) method which provides no oxygen impurities. Then AlN powder was sintered to the full density without sintering additives and under a high pressure in a belt apparatus. For the AlN ceramics obtained the temperature dependences of the thermal diffusivity were measured with the laser-flash method. Finally we produced oxygen-free aluminium nitride ceramics with parameters comparable with theoretical data. © *1998 Kluwer Academic Publishers*

1. Introduction

Aluminum nitride (AlN) has a superior combination of physical properties which render it especially useful for hybrid and power circuits, for multichip modules and as packaging material for high-speed integrated circuits. Another potential market for AlN is high-heat-conductivity plastic package applications. In such applications AlN would serve as a filler to increase the thermal conductivity of epoxy moulding compounds.

These properties include a high thermal conductivity, a high electrical resistivity and a thermal expansion coefficient close to that of silicon which is connected with the strong covalent bonding between the light atoms constituting the AlN lattice. As a consequence of the nature of the AlN crystal lattice the low anharmonicity is also apparent.

Despite Slack's [1] prediction which says that at room temperature the thermal conductivity of the single crystal of AlN should be $320\,W\,m^{-1}\,K^{-1}$ the typical thermal conductivity of commercially available ceramics is about $150\,W\,m^{-1}\,K^{-1}$. The discrepancy between thermal conductivities of single crystal and ceramics does not occur for other materials. For example [2] the thermal conductivity of chemically vapour-deposited diamond films easily achieve value of 85% of the single-crystal thermal conductivity; thus the special mechanism of phonon scattering responsible for the reduction in the mean free path of phonons should be identified.

The fact that commercial materials do not achieve the predicted theoretical limit, despite being sintered to full density, is generally attributed to the presence of substitutional oxygen impurities in the nitrogen sublattice which generate one third as many aluminium vacancies [3]. It is significant to note that the vacancies are very effective defects in phonon scattering.

According to Klemens [4], the single aluminium vacancy scatters phonons 100 times more effectively than any other mass defect with the mass deficiency equal to two atomic units, e.g., the oxygen substitutional defect. On the other hand commonly used sintering additives especially those which contain heavy elements e.g., Y_2O_3) are perfect sources of atomic impurities which potentially scatter phonons even more effectively than vacancies. On the basis of the above argument, one can expect that any improvements in the thermal propeties (thermal diffusivity and conductivity) of the AlN ceramics could be achieved by elimination of the oxygen impurities.

The development of a method to produce and characterize AlN oxygen-free substrates for eventual electronic packaging applications in terms of thermal conductivity, resistivity and dielectric constant is the subject of this work.

2. Oxygen-free AlN synthesis process

AlN powder has been industrially prepared by direct nitridation of metallic aluminium or by the carbothermic reaction of alumina, carbon and nitrogen. The major drawback of these methods is the high oxygen content. During direct nitridation of aluminium the starting metal powder with the main particle size within the range 2–13 μm is typically used. Since such powder has a surface area of about $3\,m^2\,g^{-1}$, unless passivated or processed in an inert environment, it absorbs moisture and oxygen which results in an oxygen content in the final AlN powder. The oxygen trapped during synthesis on the surface of the particles of AlN powder is introduced into microcrystallites of the ceramic after sintering which results in decreasing thermal properties of the AlN heat sinks.

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To avoid oxygen impurities we developed the combustion synthesis of AlN from bulk Al, under a high-pressure nitrogen–argon mixture [5]. Combustion synthesis was carried out at a high pressure at 2 kbar. The gas chamber was capable of withstanding applied pressure of because of up to 10 kbars.

A high-purity (99.999%) aluminium rod was used as the starting material. Bulk aluminium was placed into a BN crucible and heated in a graphite furnace until combustion of aluminium in the pressurized atmosphere had started. Boćkowski *et al.* [5] showed that the structure of the combustion products strongly depends on the argon partial pressure. Burning Al in pure nitrogen leads to inhomogeneously sintered AlN samples. The addition of Ar to the nitrogen improves the homogeneity and for a mixture with an argon content of 75% we obtained AlN powder. The grain size of this powder is a few micrometres which is essential from the standpoint of the future sintering processes.

It is also worth mentioning that for the aforementioned gas content and pressure the bulk Al is fully converted into AlN powder and no traces of the oxygen have been detected by energy-dispersive spectroscopy measurements.

The additional annealing of the powder obtained in nitrogen at 1 kbar and 1600 °C makes the synthesized powder ready for sintering process.

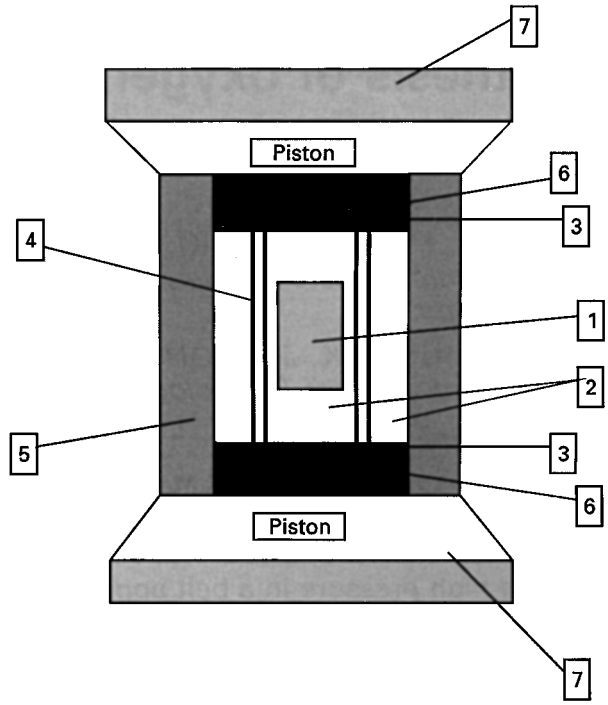

Figure 1 High-pressure high-temperature sintering cell assembly. 1. sample; 2. CaF_2 outer sleeve and inner spacer; 3. tantalum discs; 4. graphite heater; 5. pyrophyllite sleeve; 6. iron insert; 7. tungsten carbide pistons.

3. High-pressure high-temperature AlN sintering

Commercially available AlN substrates are sintered using the sintering additives such as YF_3, Y_2O_3, CaO and CaF_2. The addition of these impurities enhances the sintering and densities to as high as 99.5% of the theoretical value (3.28 g cm^{-3}) [6]. However, the sintering mechanism in doped powders appears to involve a liquid phase so that true self-bonding is only partly achieved. Second phases, some of them in the grain boundaries, are probably unavoidable by this method.

On the other hand, the sintering additives are sources of the oxygen and metal impurities which in the form of the lattice substitutional defects can, as was explained in the introduction strongly affect the thermal properties and structure of AlN. In other words there is no sense in introducing impurities which were avoided in the synthesis process of our AlN powder.

This reason has driven us to implement the high-pressure high-temperature method for sintering our oxygen-free AlN powder. A belt apparatus [7] capable of applying pressures up to 85 kbar has been built by the ASEA Company. Our belt with an inner bore diameter equal to 40 mm was primarily applied for producing industrial diamonds. Electrical contact to the cell heater was made through the rams and a temperature as high as 2600 °C was attainable. The high-temperature calibration versus applied power has been made on the basis of the well-known melting points of steel and molybdenum.

The temperature uncertainty over 2000 °C was estimated at $\pm$ 100 °C. The specimen cell is shown in Fig. 1. The cell assembly consists of two pyrophyllite gaskets to support the pistons, two soft iron cups (with inserted pyrophyllite discs) which deform themselves during the experiments to close off the high-pressure volume, two tantalum discs to transfer the graphite heater, a calcium fluoride sleeve around graphite heater and a pyrophillite sleeve around the CaF_2 sleeve.

The sleeve around the graphite heater was CaF_2 powder doped with 5% black carbon and pressed in the die to the required form. The black carbon was used to prevent radiative heat transport from the graphite heater to the tungsten carbide belt. The sintered AlN sample was placed inside the heater and insulated from the heater wall by pressed calcium fluoride spacers.

The oxygen-free AlN powder was pressed in a 10 mm die into pellet form and immediately placed in the sintering cell assembly. The sintering process was performed under a pressure of 65 kbar at a temperature of 2000 °C for 30 min. After completing the sintering process the sample was removed from the belt apparatus and polished to the form of a cylindrical plate with a thickness from 1.5 to 2.5 mm.

The density of such prepared samples was measured using an AccuPyc 1330 helium pycnometer and was typically within experimental error equal to the theoretical density of 3.27 g cm^{-3}.

The microstructure of the sintered AlN samples were examined via direct scanning electron microscopy observation of the broken ceramics. The microstructure of

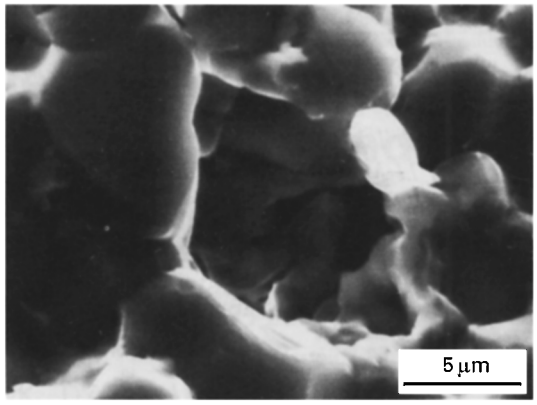

Figure 2 The microstructure of the AlN ceramic sintered in the belt apparatus. The grain dimension $d = 5\,\mu m$ is reflected in the microporosity.

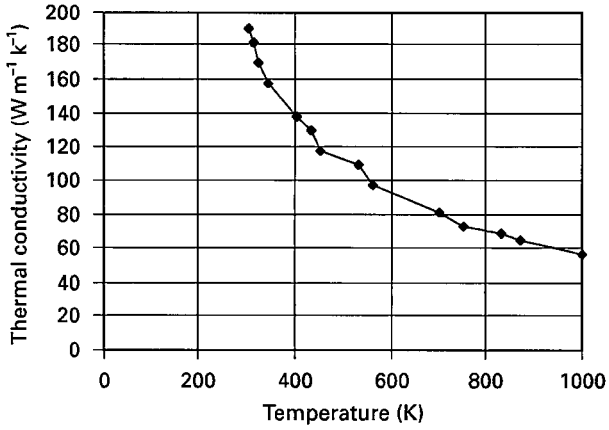

Figure 3 The temperature dependence of the thermal conductivity k, of the AlN oxygen free ceramic sample.

such cleavage is shown in Fig. 2. Despite the fact that our samples demonstrate almost theoretical density, residual microporosity can be observed in the form of niches with high aspect ratio. These niches are believed to be created as a result of the relaxation of the stresses during pressure removal.

It is worth noting that for hexagonal symmetry single crystals the compressibility is not equal along the c and a axis [8]; so after the high-pressure high-temperature treatment, sintering reduction of the pressure creates residual stresses due to aforementioned mismatch. Fortunately, as can be shown on the basis of recently reported elastic constants of AlN [9] the compressibility anisotropy is not very significant for the AlN single crystal.

4. Thermal conductivity measurements

The temperature dependence of the thermal conductivity of samples has been measured by the laser-flash method. This method provides an extremely rapid technique for the determination of thermal diffusivity α, permitting calculation of the thermal conductivity k of the samples.

Attaining the required accuracy presented the most difficult challenge because of the combined effects of the thickness of the sample and high thermal diffusivity. For the laser-flash technique, it is well known that for a given pulse duration, as the sample thickness decreases and as the diffusivity increases, departures occur from the ideal behaviour on which the theory is based.

When this work started, no commercial instruments were known to be available which could meet the requirements stated above. Finally for our AlN ceramics thermal conductivity–diffusivity investigation one of us (A. Witek) developed a new Q-switched laser-flash experimental set-up and it has been described in detail elsewhere [10]. The duration of the pulse in our system could be switched from 10 up to 250 μs.

A typical temperature dependence of the thermal conductivity of our belt sintered AlN samples is shown in Fig. 3.

5. Resistivity and dielectric constant measurements

All measurements of the resistivity and dielectric constant were made with Schlumberger SI 1258 HF frequency response analyser. In turned out that the measured resistivity was close to the theoretical value. In our experiments we produced samples with a resistivity of 10^{11}–$10^{12}\,\Omega\,m$ and a dielectric constant of 8.5 at 1 mHz and of 8.0 at 10 MHz.

6. Conclusions

We have proved that the high-pressure SHS synthesis of AlN powder could provide almost oxygen-free powder which can be sintered without sintering additives to form highly conducting ceramic samples ($K(300) = 190\,W\,m^{-1}\,k^{-1}$).

On the other hand the absence of additives required high-pressure high-temperature sintering technology which could produce microporosity as a result of pressure removal. The resistivity and dielectric constant have been found to be close to the theoretical value.

In our belief this ceramic fulfils electronic and industrial requirements.

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