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Dielectric properties of aluminium nitride–γ-alon materials

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Abstract

The self-propagating high-temperature synthesis (SHS) method and hot-pressing were used to prepare materials composed of aluminium nitride and aluminium oxynitride with spinel structure – γ-alon. The chemical composition of the hot-pressed powders decided on phase composition of the sintered samples and structural properties of both phases. Dielectric loss and dielectric constant were measured as a function of frequency. For all samples frequency changes of tan δ fulfilled an inverse power-law. Such behaviour and the vales of tan δ were independent of the phase composition of the samples. For the low frequencies the ε values decreased continuously with increase of frequency and then they were independent of it. Increase of the γ-alon content in the samples caused increase of their dielectric constants.

Keywords: Dielectric properties; Nitrides; Insulators

1. Introduction

Aluminium nitride is characterized by the specific combination of the properties important in the field of electronic materials. AlN presents relatively high dielectric constant (8.6–9.0)[1], large bandgap energy (6.5 eV)[2], good thermal conductivity (even 320 W m^{-1} K^{-1})[3] and good chemical and temperature resistance. This is the reason why aluminium nitride is often used as sputtered layers, in the heterostructure field-effect transistors (HFET) or as a substrate material for high packing density integrated circuits (ICs) or large-scale integrated circuits (LSI).[4] Aluminium nitride is being considered as a potential material alternative to alumina and berillia in the field of power electronics and high frequency devices, especially RF windows.[5] The same features take full advantage in the plasma equipments using microwaves above 1 GHz, e.g., plasma etching attachment or plasma CVD devices.[6] Aluminium nitride was also successfully used as a material for the barriers in magnetic tunnel junctions (MTJ).[7]

Densification of aluminium nitride is usually performed at high temperatures, exceeding 1800 °C, due to covalent character of the chemical bonds and low diffusion coefficient of AlN components. To obtain dense aluminium nitride materials some additional substances are necessary as the sintering aids forming a transient liquid phase which promotes sintering during the early sintering stage.[8] Generally, it was stated that the presence of impurities or lattice defects decreased thermal properties of aluminium nitride, while increasing the electric conductivity.[9] On the other hand, the dielectric loss is also associated with imperfections in the crystal structure such as lattice defects, dislocations, grain boundary and residual stresses. The influence of sintering conditions, microstructure and additives on electrical properties of aluminium nitride was studied by different authors.[10–15]

Kume et al.[10] investigated the effect of cooling schedule on tan δ of AlN ceramics pressureless sintered at 1900 °C for 2 h with addition of 1 mol% of yttria. It was shown that slow-cooling of the sintered materials and/or additional annealing of them are useful in lowering of the tan δ. González and Ibarra[11] stated that the addition of Y_2O_3 and/or Er_2O_3 as sintering aid compounds does not influence the temperature and frequency dependence of either permittivity or loss tangent. It is also concluded that oxygen diffuses into the AlN lattice, changing the dielectric properties at low frequency. Khor et al.[12] prepared dense aluminium nitride from commercial powder by the spark plasma sintering method at different temperatures (1500–1800 °C), and CaF_2 (1 and 3 wt.%) was used as the sintering additive. The dielectric constant was found to be proportional to the relative density of the sintered AlN materials. Reaction bonding material was prepared using Al and AlN powders as starting materials and the effect of the CaO additive on dielectric properties was investigated.[13] The significant role of CaO addition in

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the sintering process was stated while its detrimental influence on dielectric properties was not observed. Similar results were reported in connection to the influence of small amounts of MgO on the dielectric properties of aluminium nitride sintered in the presence of Y_2O_3.[14] Mg_3N_2 was chosen as another substance for lowering tan δ of AlN materials sintered with yttria. It was observed that the resulting AlN ceramics became denser due to the addition of magnesium nitride and tan δ was improved with increasing Mg_3N_2 amount.[15]

Aluminium oxynitride with spinel structure, γ-alon, is also an interesting material in the field of electroceramics,[16,17] but the dielectric behaviour of the materials in the AlN–Al_2O_3 system is still poor investigated. The aim of the present paper is to prepare materials in this system and to study their dielectric properties.

2. Experimental

Self-propagating high-temperature synthesis (SHS) was used as a method for powder preparation. Metallic aluminium (pure grade, 99.5%) and α-aluminium oxide (MA 250/5 Alcan Chemicals Europe) powders were used as the substrates. The powders were mixed for 2 h in propanol using a ball mill and zirconia grinding media. Weight proportions between the substrates were established from pure aluminium to (20% Al/80% Al_2O_3) with 10% interval. The mixtures were placed into a steel reactor which was filled with pure (99.8%) nitrogen of 0.5 MPa pressure and the combustion synthesis was initialized by electric current flow for several seconds. The synthesized powders were crushed and then ground in dry isopropyl alcohol for 8 h using a rotary-vibratory mill and silicon nitride grinding media. Dried and granulated powders were hot-pressed at 1950 °C for 2 h under 25 MPa in nitrogen flow.[18]

Phase composition of the sintered samples and lattice parameters of the relative phases were determined by X-ray diffraction analysis (X'Pert Pro, Philips) using the Rietveld refinement method.[19] For electrical measurements the hot-pressed materials were cut into rectangular samples (~5 mm × 5 mm × 3 mm) and two parallel plates were coated by silver electrodes. Dielectric loss was measured within the 20 Hz to 1 MHz range at room temperature using a QuadTech 1920 Precision LCR Meter. Complex impedance spectroscopy measurements were performed at room temperature with Solartron equipment (FRA 1260 + dielectric interface 1294) over the frequency range of 1 Hz to 1 MHz.

3. Results

X-ray diffraction analysis shows that the hot-pressed materials are composed of aluminium nitride and γ-alon phases. Phase composition of the sintered samples, presented in Fig. 1, substantially depends on chemical composition of the powders used in SHS synthesis. The content of γ-alon increases with the aluminium oxide content in the starting mixture.

The chemical differences in the starting powders influence also structural properties of both phases. Fig. 2 shows the compositional changes of lattice parameter of γ-alon and of AlN unit cell volume. In both cases increase of the aluminium oxide content in the mixture for SHS, and consequently increase of γ-alon in the hot-pressed sample, lead to the decrease of the respective cell volume. Linear relations between chemical composition and unit cell sizes suggest that aluminium oxynitride and γ-alon behave as solid solutions. It may be supposed that the decrease of the AlN cell volume is mainly caused by formation of nitrogen vacancies but in the case of γ-alon the explanation may be not so unequivocal due to divergences in its structure description.[20] The decrease of the γ-alon lattice parameter can be attributed to the absolute decrease of nitrogen and/or oxygen content (constant cation model) as well as to the decrease of aluminium content (constant anion model). Partial substitution of nitrogen for oxygen in the aluminium oxynitride structure can also be taken into consideration.

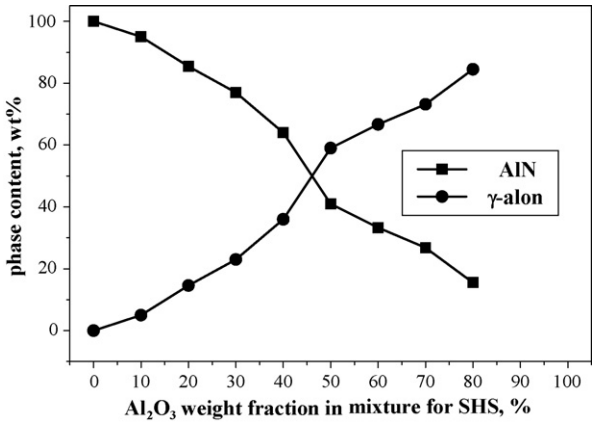

Fig. 1. Phase composition of the sintered samples.

Measurements of the dielectric properties reveal that in each case dielectric loss, tan δ, rapidly decreases with the increase of frequency up to about 10 kHz and then further changes are very small. Fig. 3 shows typical changes of the tan δ as a function of frequency for three samples. The same measured values drawn in $\log(\tan\delta) - \log f$ coordinates can be estimated by straight lines that means an inverse power-law dependence of the dielectric loss tangent on frequency. This relationship is in good agreement with the model proposed by B.J. West based on the equilibrium

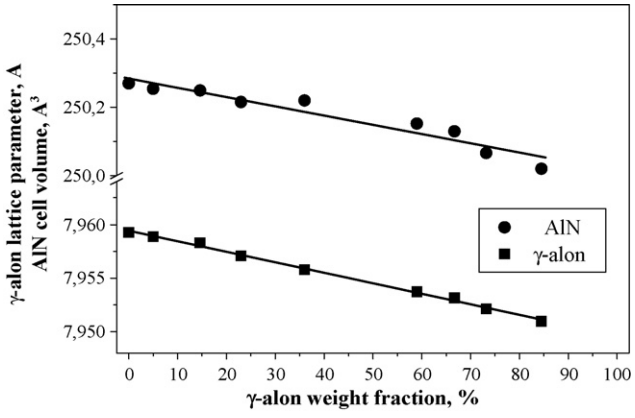

Fig. 2. Compositional changes of lattice parameter of γ-alon and of AlN unit cell volume.

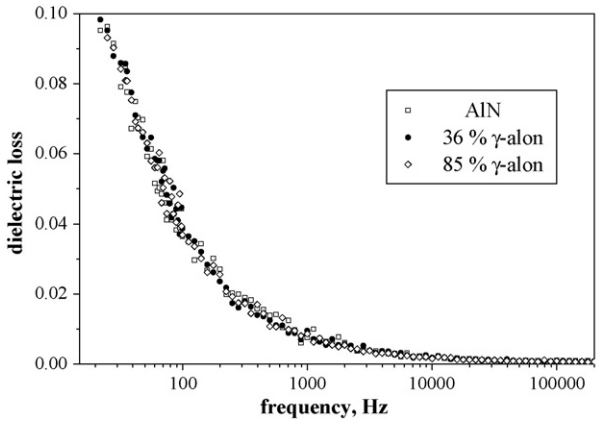

Fig. 3. Frequency dependence of the dielectric losses of some selected samples.

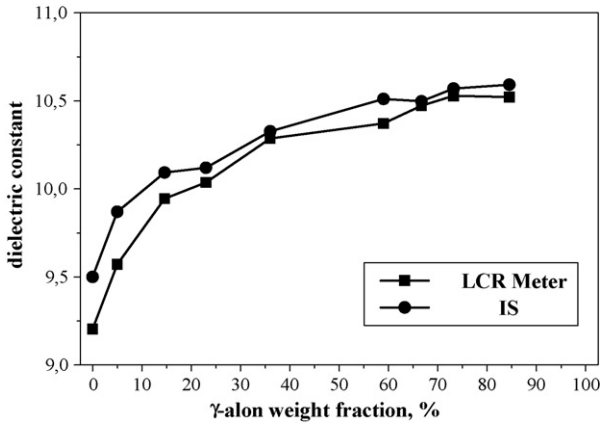

Fig. 5. Compositional dependence of the dielectric constant measured by LCR meter at 1 kHz and by impedance spectroscopy (IS).

thermal fluctuations of the molecular dipole frequencies in pure γ-alon.[17] It is worth to notice that at frequencies higher than 10 kHz dielectric loss is as low as 0.001.

The frequency behaviour of the dielectric constants, ε, are similar to the changes of $\tan\delta$, however, contrary to that, differences between the samples are visible (Fig. 4). For low frequencies the ε values decreased continuously with increase of frequency and then they are independent of it. Such effect is usually attributed to the space charge polarization and relative long relaxation time of this polarization.[21] Fig. 4 presents example of the frequency relation of the dielectric constants. Increase of γ-alon fraction in the hot-pressed materials causes increase of their dielectric constants in the whole frequency range. Compositional dependence of the dielectric constant measured at 1 kHz is shown in Fig. 5.

All impedance spectroscopy patterns, taken at room temperature, were approximated as a part of a semicircle. In such a case the overall impedance could be modelled by an equivalent circuit composed of resistance and constant phase angle element (CPE). The values of exponent in CPE vary from 1 for pure AlN to 0.96 for the sample with the highest γ-alon content, which may be related to phase and microstructural diversity of the samples.[22] The values of capacitance and shape factors

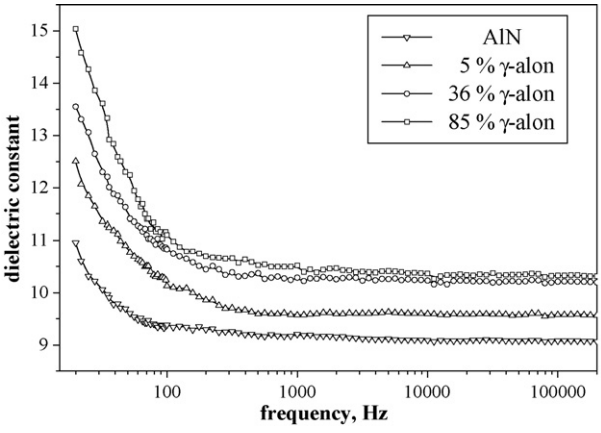

Fig. 4. Frequency dependence of the dielectric constant of some selected samples.

of the samples were used for calculating the respective dielectric constants presented in Fig. 5. Introduction of γ-alon to the aluminium nitride hot-pressed samples causes increase of their dielectric constants regardless of the measure method. The reason of such behaviour is related to the changes of the structures of both phases; kind and amount of lattice defects should be mainly taken into consideration. The microstructure of the investigated materials may be the other cause of the observed changes. The important factors would be grain sizes, their mutual orientation and especially nature of interfacial boundaries. Oxygen-rich layers formed at the interfacial boundaries can influence dielectric properties of the materials by inducing a space charge polarization.[11] Decrease of resistance observed in the γ-alon-rich samples can be the other aspect of the mentioned changes and probably be at the origin of the increase of the dielectric constant.

4. Conclusions

The SHS method combined with hot-pressing was successfully applied to prepare dense materials in the AlN–Al_2O_3 system. The chemical differences in the starting powders influence phase composition of the sintered samples and structural properties of both phases. It was stated that changes of the dielectric loss as a function of frequency fulfil inverse power-law dependence. Such behaviour and the vales of $\tan\delta$ are very similar for all samples. For low frequencies the ε values decreased continuously with increase of frequency and then they are independent of it. No differences among the samples in the frequency dependence of the dielectric constants are observed. Increase of the γ-alon content in the samples causes increase of their dielectric constants. The observed effects could be attributed to the structural changes of both phases and to the microstructure of the investigated materials.

Acknowledgements

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