

Properties of nano-porous mullite thin films for direct material writing

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In this study, nano-porous mullite nano-powders were prepared to deposit the low-K thin films on the LTCC by the direct material writing. For the first step, prepared nano-porous mullite nano-powders were spin-coated on a Si wafer with Pt electrode to investigate the electrical properties of the resulting nano-porous low K thin films. As a result, nano-porous thin films of mullite with enough high resistivity were successfully deposited by the spin-coating using the highly nano-porous mullite nano-powder. The electrical properties of the resulting nano-porous thin films depended on the hybrid structure of the films, showing the possibility for the material direct writing by using the nano-porous mullite nano-powders for the low K thin films on a LTCC.

Key words: Materials Direct Writing, Mullite, Nanoporous Powders, Thin Film

1. INTRODUCTION

Stoichiometric mullite consisted of relatively high covalent Al_2O_3 and SiO_2 is very promising for a high-temperature structural material because of its superior mechanical properties compared with a silicon nitride or a silicon carbide ceramics even under the oxidizing atmosphere [1, 2]. The excellent high-temperature mechanical properties such as high creep resistance and high mechanical strength could be applied for high-temperature porous filters and catalyst worked at high temperatures, if very porous ceramics with high purity, homogeneity and high crystallinity were prepared below eutectic temperature of mullite (1585 °C). So far, many preparation methods have been reported [3, 4, 5]. However, it is very difficult to prepare a stoichiometric mullite powder with high purity and homogeneity. The authors successfully prepared a stoichiometric mullite powder with high purity and homogeneity as well as the high specific surface areas from molecular-designed Al,Si-double alkoxide [6]. The surface areas of the mullite powders are affected by the compositions and a stoichiometric mullite precursor powder showed a very high surface area after calcination at elevated temperatures below 1400 °C [7]. The primary particles precipitated by the hydrolysis of the precursor solution could form agglomerates during aging and drying steps to increase the surface areas of the resultant calcined powders. Therefore, ultrafine xerogel powders would change their agglomerate structures depending upon the aging and drying conditions, leading to the control of the specific surface areas of the resultant nanoporous mullite powders.

This paper describes the relation between agglomeration behavior and the specific surface areas of the resultant nanoporous mullite powders and the nanostructure of the thin films deposited from the slurry of the nanoporous mullite precursor powder for the Materials Direct Writing (MDW) on the substrate. Mullite also exhibits the low dielectric constant and the relatively low thermal expansion coefficient, and

therefore, is useful as a substrate for high-speed computer and then the candidate material of thin film insulator with very low dielectric constant. This paper also focuses on the basic research for deposition of the nanoporous thin films on a LTCC substrates by MDW. In this study, nanoporous thin films with different stacking structures of silica and mullite precursor were deposited on a silicon substrate and evaluate the electrical properties of the resultant hybrid films.

2. EXPERIMENTAL

2.1 Preparation of nanoporous ultrafine mullite powder.

The preparation method of precursor sols was described elsewhere [8]. After the hydrolysis of the precursor solution for 5 minutes by the 40 times water to TEOS, the resultant precursor powders were dried at 110 °C for 48 hours in an electric furnace to obtain xerogel precursor powders. These xerogel powders were pulverized for 3 minutes using alumina mortar and pestle, followed by the calcination at different temperatures for two hours up to 1400 °C.

2.2 Characterization

The specific surface areas of calcined powders were measured by BET method and shown in figure 1. N_2 gas and liquid nitrogen were used as an adsorbing gas and coolant, respectively. The morphology of the calcined powders were observed by scanning electron microscope (SEM) and the size distribution of pores were measured by mercury pore sizer. The size distribution of the nanoporous ultrafine powders were measured by using dynamic light scattering method. Planetary mill and zirconia beads of 2 mm were used to pulverize the nanoporous precursor powders calcined at 800 °C for 2 h. Surface morphology of the thin film was observed by Atomic Force Microscope (AFM). After the pulverizing, the calcined powders were dispersed again into the solvent of *i*-butanol. As a result, porous nanoparticles with very high surface area of 376 (m^2/g) and average particle size below 200 nm were successfully prepared

from the molecular- designed mullite precursor solution. The prepared slurries with different calcined powder concentrations and silica sol were spin-coated on a Si substrate to form hybrid films with different stacking structures and the electrical properties of the resultant hybrid films were measured by the ferroelectric thin film test system (Toyo corporation, FCE-PZ).

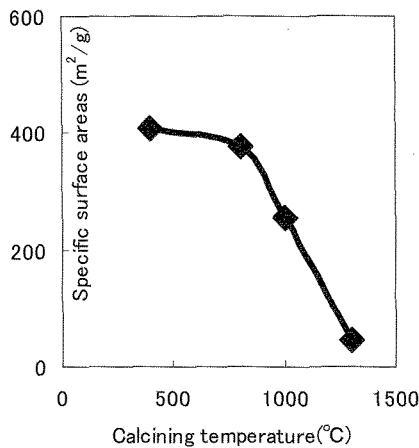


Fig.1. Change in SSA for nanoporous mullite precursor powders with calcining temperature.

3. RESULTS AND DISCUSSION

The prepared amorphous porous nanoparticles in mullite system were distributed in the solvent to deposit the hybrid films with different stacking structures of silica and/or porous mullite precursor nanoparticles by spin-coating. After the film deposition, electrical conductivity or resistivity was measured.

We prepared the 5 types of hybrid films as shown in the Fig. 2, because the objective of this paper is to deposit porous thin film with dense surface layer, showing the lower dielectric constant. Figure 3 shows the AFM images of the resultant films from silica sol and porous mullite precursor, respectively. The surface of the film derived from silica sol was very smooth and the Ra = 1.2 nm, whereas the surface of the film derived from nanoporous mullite sol exhibited crinkling structure made by typical interlaced structure of relatively linear oligomer with Ra = 1.4 nm, leading to the nanoporous film with low dielectric constant.

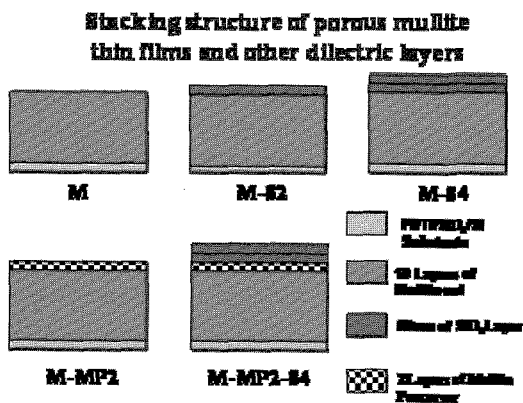


Fig. 2 Stacking structure of the hybrid films.

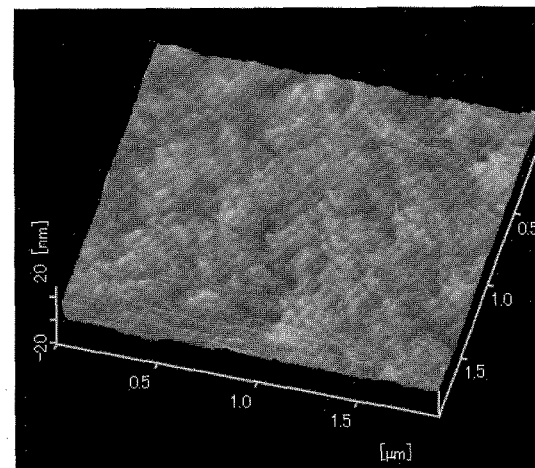
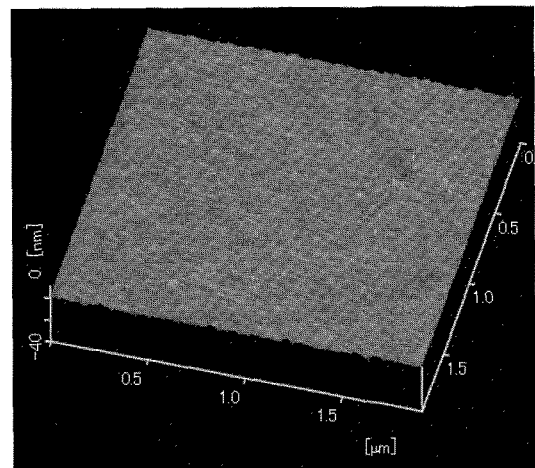


Fig. 3 AFM images of the surface of (a) film derived from silica sol, and (b) film derived from amorphous mullite precursor sols.

Then we measured the I-V characteristics of the resulting hybrid films and shown in figure 4. After evaluating the I-V characteristic of these dielectric layers with different stacking structures, it was clarified that some deposited dielectric layers (MS-2) exhibited relatively high resistivity more than 10¹²Ω · cm, which was the goal of this study by changing the stacking structures. (for example, M-MP2-S4)

These results indicated the possibility for the nanoporous film with very low dielectric constant by materials direct writing using these precursor sols with nanoporous mullite precursor powders.

4. CONCLUSIONS

In this study, nano-porous mullite precursor powders were successfully prepared by the sol-gel method and then hybrid films with nanoporous structures were deposited by the spin coating from sols of nanoporous mullite precursor. As a result, it is concluded that the development of the raw material source for the Low K dielectric layer with the dielectric constant less than 5 and the electrical resistivity above $10^{12} \Omega \cdot \text{cm}$ could be successfully prepared. The deposited layers by the spin coating technique exhibited a smooth surface and enough electrical properties for source of the low K dielectric layer by the materials direct writing using the developed precursor sols. Further investigation is essential to develop the direct writing technique using these precursor sols.

5. REFERENCES

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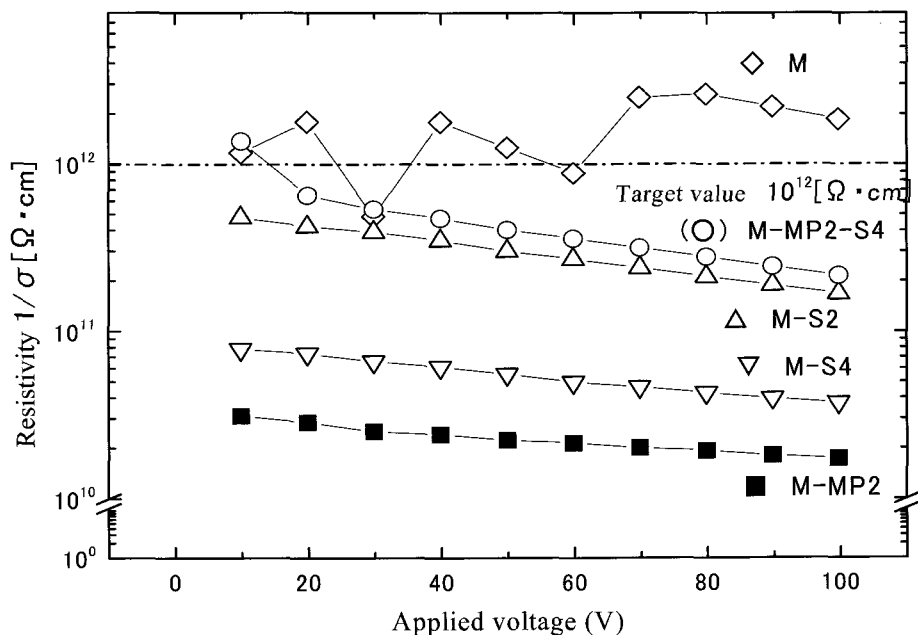


Fig. 4 Resistivity of the nanoporous hybrid films with different structures as a function of applied voltage.