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Additive-Driven Sinterability Improvement of Mullite Ceramics for Co-firing with Cu-Mo†

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The needs for electrodes and materials to realize a low resistance are increasing as the line widths of a circuit are reduced for an increase in the number of layers due to increasingly higher integration of semiconductor wafers as well as impedance matching of transmission lines. Consequently, Cu-Mo electrodes have been considered for application to realize a lower resistance than that of the existing Mo electrodes used with mullite materials. When mullite ceramics and Cu-Mo electrode were simultaneously fired, resistivity was not reduced because of interaction between the electrode and the ceramic at 1400 ºC, while resistivity decreased below 1370 ºC. It was verified that sintering should be conducted at a temperature as low as 1350 ºC to realize a low resistance by applying Cu-Mo electrodes to the mullite ceramics. When sintering was conducted at 1350 ºC with addition of 1 wt % of SiO_2, 1 wt % of MgO, 1.5 wt % of Y_2O_3 and 7 wt % of $SrCO_3$ to mullite, an excellent sinterability was exhibited at a density of 3.22 g/cm^3.

Key Words: Mullite, Cu-Mo, Additives, SiO_2, MgO, Y_2O_3.

INTRODUCTION

With development of semiconductor industry, the size of Si wafers has been increased to a large diameter through 6", 8", 12" and the size of ceramic substrates for a measuring device to measure these with also tends to increase so as to measure chips on the wafer. Therefore, the need has been increased for studies on substrate materials having as a major composition the mullite characterized by a thermal expansion coefficient approaching that of Si wafer and a low dielectric constant.

Since resistance of signal transmission lines is increased as the length of transmission lines is elongated and the width of circuit lines reduced for impedance matching resulting from an increase in the number of layers due to high integration and large scaling of the wafer areas, reduction in resistivity of the electrode material is in demand for realization of a low resistance. Thus, replacement of the existing Mo electrode with a Cu-Mo electrode mixed with Cu of an excellent electrical conductivity is considered to realize the low resistance and a new ceramic composition in the mullite system with a low sintering temperature is required for application of these Cu-Mo electrodes[1,2]. A representative approach involves promotion of densification by inducing liquid-phase sintering through use of various additives that can form a liquid phase in sintering processes to lower the sintering temperature of mullite ceramics.

In this study, SiO_2[3], MgO[4,5], Y_2O_3[6,7], $SrCO_3$[8] were selected as sintering additives to secure a mullite composition applicable to the Cu-Mo electrode and subsequently sintered in a reducing atmosphere with the amount of additive contents varied, after which observation was made on the sintering densities. Green sheets were prepared with a compositions producing an excellent sinterability, simultaneously fired with Cu-Mo electrodes followed by resistivity measurements to find the optimal firing conditions for Cu-Mo electrode and mullite ceramics to realize a low resistance.

EXPERIMENTAL

Average particle diameter of commercial mullite powders was 1.69 μm and the composition corresponded to coexistence of Al_2O_3 and mullite phases as a result of excessive addition of Al_2O_3 to a weight ratio of 82.5:17.5 for Al_2O_3 *vs.* SiO_2. For the purpose of forming a liquid phase that will lower sintering temperatures of mullite, SiO_2, MgO, Y_2O_3, $SrCO_3$ were employed. After weighing the starting raw materials according to the composition ratio, mullite additives and ZrO_2 balls were mixed and pulverized in a mixed state for 24 h with ethyl alcohol as a dispersion medium. Mixed powders were dried for 24 h in an oven at 100 ºC and mixed with PVA binder, followed by preparation of 12 Φ pellet-type specimens as per composition and subsequent sintering for 2 h in a reducing atmosphere at a temperature range of 1350-1400 ºC. Sintering

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densities were measured for the sintered specimens using Archimedes method.

Cu-Mo electrodes were printed on the sintered Al_2O_3 substrate and sintered in a reducing atmosphere at 1400 ºC, after which resistivity characteristics dependent on the amounts of Cu addition were measured. And to prepare test coupons for measurement of electrical characteristics, a composition having an excellent sinterability was selected and 100 µm-thick mullite green sheets were prepared. Patterns were formed by printing Cu-Mo electrodes on these green sheets which were then laminated and simultaneously sintered in a reducing atmosphere at 1300-1400 ºC. To make observations on electrical characteristics of sintered test coupons, resistivity was measured using CMT-SR1000 N. For cross sections of sintered specimens, an analysis of microstructures and composition was made using SEM (JSM-6700F, Jeol, USA) and EDS (Genesis 2000 XMS, EDAX Inc., USA).

RESULTS AND DISCUSSION

Fig. 1 shows changes in the sintered density of specimens sintered for 2 h at 1400 ºC after addition of SiO_2, MgO, Y_2O_3 to mullite in varying amounts for the content of 0.5-2.0 wt % and after addition of 0.5-1.5 wt % of Y_2O_3 followed by addition of 1 wt % of SiO_2 + 1 wt % of MgO. In the case of adding SiO_2 to mullite, sinterability was low and density changes dependent on the change in additive amounts were not great. Since the tendency was shown where the density slightly increased and then decreased upon addition of 1 wt %, a small amount of SiO_2 addition was expected to be able to exert a significant influence on sintering. Since an increase of sintered density may be confirmed with a greater amount of MgO addition to mullite and MgO is often used as an additive to improve sinterability, its addition is considered to contribute to partial formation of a liquid phase. In the case of adding 0.5-2.0 wt % of Y_2O_3, it could be verified that the highest increase in sintering density was obtained at 1400 ºC as compared with SiO_2 and MgO. When 1.5 wt % of Y_2O_3 was added, a density of 2.52 g/cm^3 was indicated, which, however, was much lower than the mullite density of 3.2 g/cm^3. Hence it may be seen that addition of a single additive to mullite has a limitation in obtaining a sufficient sintering density at 1400 ºC. Therefore, when SiO_2, MgO were added respectively to mullite, sinterability was greatly improved in the case of adding Y_2O_3 to 1 wt % of SiO_2, 1 wt % of MgO that produced the highest density. When 1.5 wt % of Y_2O_3 was added, the density value at 1400 ºC was 3.12 g/cm^3 representing an excellent sinterability.

Fig. 2 shows resistivity values of the Cu-Mo electrode that was sintered for 2 h at 1400 ºC after being printed on a Al_2O_3 substrate. With an increase in Cu contents of the Cu-Mo electrode as 10, 30, 40 wt %, resistivity could be verified to decrease as 2.68, 3.07, 1.78 10^{-6} Ωcm. With Cu-Mo electrodes, Cu phase is melted with an exponential increase in the internal vapour pressure on a Cu vapour curve as a function of sintering temperatures above 1400 ºC. Since Cu component melt in the Cu-Mo electrode becomes volatilized from the surfaces, application of Cu above 1400 ºC is considered to be difficult.

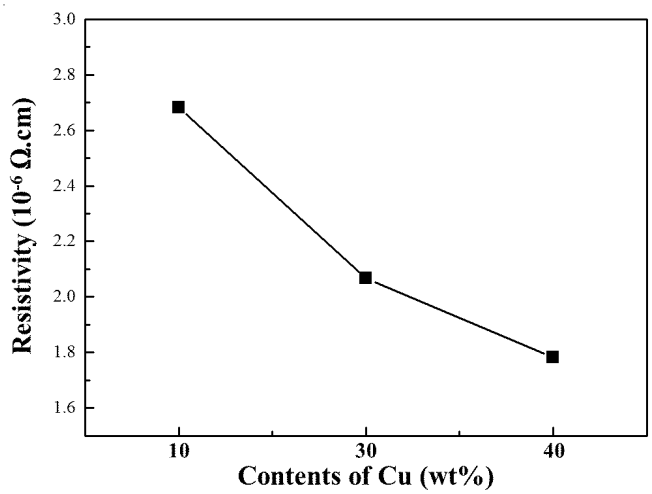


Fig. 2. Resistivity with various amounts of Cu co-fired at 1400 ºC for 2 h

Fig. 3 represents measurement values of resistivity for the electodes obtained after printing Cu-Mo electrodes on a green sheet with a composition of mullite + 1 wt % of SiO_2 + 1 wt % of MgO + 1.5 wt % of Y_2O_3 that showed an excellent sinterability at 1400 ºC, followed by simultaneous firing in a

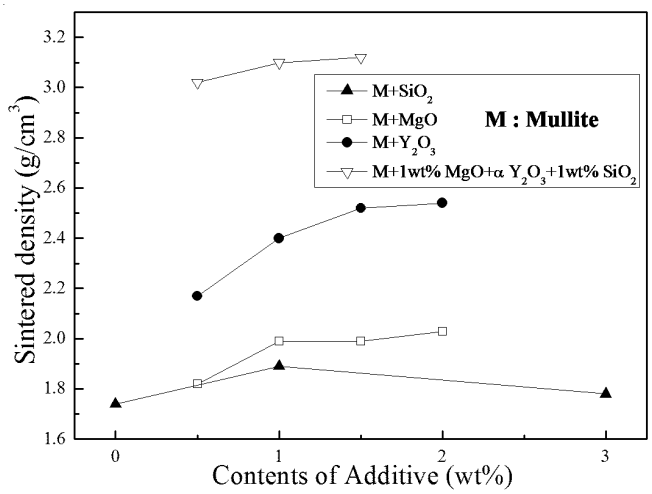


Fig. 1. Sintered density of mullite with contents of additives at 1400 for 2 h

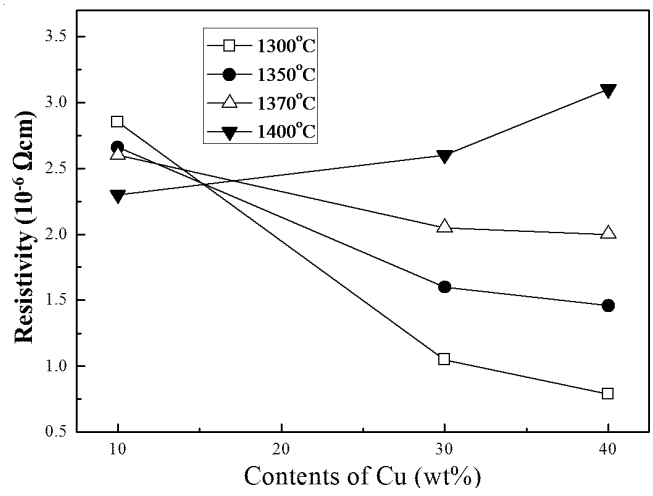
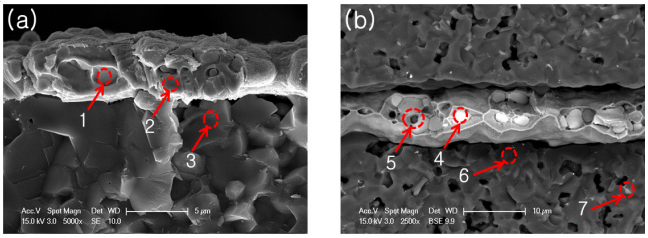


Fig. 3. Resistivity with amount variations of copper applied on mullite green sheet and co-fired at 1300-1400 ºC for 2 h

reducing atmosphere for 2 h at 1300-1400 ºC. Unlike Fig. 2, resistivity of Cu-Mo electrodes simultaneously sintered at 1400 ºC showed an increasing tendency, while the resistivity exhibited a decreasing tendency from the simultaneous firing temperature of 1370 ºC. Thus, to realize a low resistance by applying mullite ceramic to Cu-Mo electrodes, it may be seen that a ceramic composition with an excellent sinterability at least at 1350 ºC is required.

Fig. 4 shows a microstructure along with EDS for specimens where Cu-Mo electrodes were simultaneously fired with Al_2O_3 substrate and mullite at 1400 ºC. Fig. 4(a) showed that no ceramic compositions were detected other than Mo and Cu elements in the Cu-Mo electrode area on the sintered Al_2O_3 substrate. And Mo element may be seen to be surrounded by Cu. Such phenomenon is considered attributable to the fact that the low-melting Cu is melted, remained in a molten state between Mo and then solidified when temperature was cooled down. In view that only Al and Si components were detected in the ceramic area of Al_2O_3 substrate, no reaction is considered to have occurred between the electrode and the Al_2O_3 substrate. In a Cu-Mo electrode layer of Fig. 4(b), the phenomenon of Mo element surrounded by Cu was also observed and Al element not detected in Fig. 4(a) was observed (EDS data-1,2). In the ceramic area, Mo and Cu elements other than ceramic elements were detected (EDS data-6) and reactions between mullite and electrode could be confirmed to have occurred based on the fact that Cu element was detected at several places in the ceramic area (EDS data-7). This is considered to have resulted from infiltration of molten Cu component in the Cu-Mo electrode during simultaneous firing. Resistivity characteristics the Cu-Mo electrode are considered to have increased as a result of interactions during co-firing of mullite ceramic and electrode at 1400 ºC, unlike with the Al_2O_3 substrate.

Since sintering should be conducted below 1350 ºC to realize a low resistance by applying Cu-Mo electrodes to mullite



element [atom%]	1	2	3	4	5	6	7
Mo	100			100	21.31	2.80	
Cu		100			60.51	3.99	74.50
O			17.92		14.94	57.28	15.94
Al			77.96		3.24	23.78	7.41
Si			4.11			9.61	2.15
Mg						1.91	
Ca						0.63	

Fig. 4. EDS result of (a) the case of mixed paste applied on the sintered Al_2O_3 substrate then fired and (b) the case of mixed paste applied on mullite green sheet and co-fired at 1400 ºC for 2 h

ceramic in Fig. 3, $SrCO_3$ was added to the composition of mullite + 1wt % of SiO_2 + 1 wt % of MgO + 1.5 wt % of Y_2O_3 that exhibited an excellent sinterability at 1400 ºC and fired at 1350 ºC as well as 1400 ºC, with densities of such specimens shown in Fig. 5. With increased amounts of $SrCO_3$ addition, sintering density was improved. Excellent sinterability was exhibited by the density of 3.22 g/cm^3 at 1350 ºC when 7 wt % of was added, while additions greater than 7 wt % did not have a great influence on the sintering density.

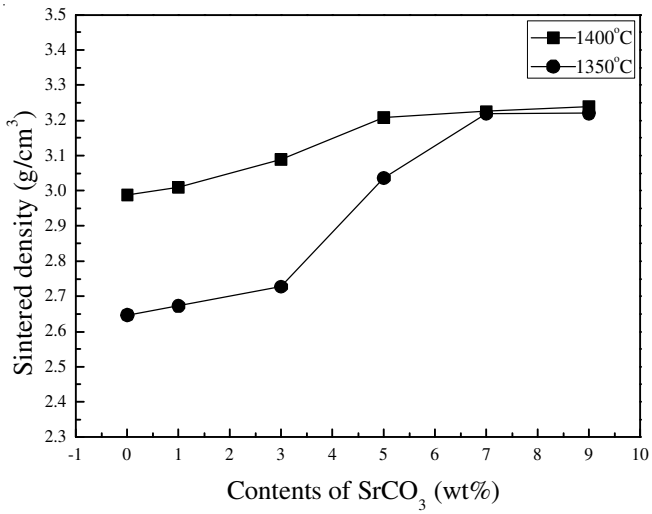


Fig. 5. Sintered density of mullite with $SrCO_3$ at 1350 ºC and 1400 ºC

Conclusion

From the experiments with sintering additives to develop mullite ceramic compositions applicable to Cu-Mo electrodes for realization of a low resistance, the following conclusions could be drawn. (1) While resistivity decreased when Cu-Mo electrodes were printed on a fired Al_2O_3 substrate and co-fired in a reducing atmosphere at 1400 ºC, resistivity increased due to interactions between mullite ceramics and Cu-Mo electrodes. To realize a low resistance with Cu-Mo electrodes, it could be seen that sintering should be conducted at 1350 ºC at least. (2) When 1 wt % of SiO_2, 1 wt % of MgO, 1.5 wt % of Y_2O_3 and 7 wt % of $SrCO_3$ were added to mullite, sufficient densification was observed at 1350 ºC with a sintering density value of 3.22 g/cm^3 indicated.

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