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Microwave assisted processing of silver thick films for microelectronic applications

Sunit Rane*, Rushna Bhatkar[b], Uttam Mulik[a] and Dinesh Amalnerkar[a]

Microelectronics and Thick Film Materials Group, Centre for Materials for Electronics Technology,
Panchawati,Off. Dr. Bhabha Road, Pune-411008, India

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Abstract. This paper aims to focus on the microwave processing of thick films which is a fast, cheap technique and could be the alternative to the currently used conventional high temperature processing technique. Microwave processing has gained worldwide acceptance as a novel method for heating and sintering a variety of materials, as it offers specific advantages in terms of speed, energy efficiency, process simplicity, finer microstructures and lower environmental hazards. Silver conducting thick films were prepared and processed in the household microwave oven. The films sintered at different time period by keeping the other parameter such as microwave power, film thickness etc constant. The microstructure analysis revealed that the surface morphology of the microwave processed films become compact with respect to the processing time. The sheet resistance for microwave sintered silver films is in the range of 0.003 to 1.207 Ω / □where as the films fired at 750 and 850^{o}C showed the resistance of 0.009 and 0.003 Ω/□ which can be comparable. The results revealed that the microstructure of the microwave sintered films has more uniform and compact surface than that of the conventionally fired films. The paper reports upon the preparation of silver thick film by screen printing technique and processing the same by microwave which also compared with the conventionally processed thick films.

Keywords: microwave; silver; thick films; conductor; sheet resistance

1. Introduction

The technology for realizing conductive thick films is of considerable importance in the manufacture of various electronic devices, such as hybrid integrated circuits, multilayer ceramic capacitors and displays. Various electrode materials have been developed for many applications in the electronic industry and silver has been used as the main conductive component in a conductive thick film material due to its extremely low resistivity and the lowest cost among the noble metals. However, the silver conductive thick film is a well matured technology which has been mainly studied in silver with the sintering behaviours being examined at around the conventional temperature of 850℃ (Lin and Wang 1996, Rane *et al.* 2000, Rane *et al.* 2003a, Rane *et al.* 2003b, Rane *et al.* 2004a, Rane *et al.* 2004b, Deshpande *et al.* 2005, Kshirsagar *et al.* 2007, Bangali *et al.*

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*Corresponding Author, Ph.D., E-mail: sunitrane@yahoo.com
[a] Ph.D.
[b] M.Sc. Student

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2008, 2009, Bai *et al.*2006, Park *et al.* 2008a, 2008b, Seo *et al.* 2009, Hwang *et al.* 2009). However, such a high processing temperature is not suitable for many electronic circuitries in particular to plasma display panels in which silver electrode can be a potential use for bus and address electrode where the sintering temperature must be lower than 600^{o}C. Microwave heating can overcome this problem since now a day the use of microwaves to materials processing have been applied to a wide variety of materials. Microwave processing is a unique, more and more popular technique alternative to the conventional thermal process for material synthesis, sintering, and processing reported by many researchers. The application of microwave energy to the processing of various materials such as ceramics, metals and composites offers several advantages over conventional heating methods. These advantages include unique microstructure and properties, improved product yield, energy savings, reduction in manufacturing cost and synthesis of new materials (Leonelli *et al.* 2008, Fang *et al.* 2009, Das *et al.* 2009, Sreeram *et al.* 2008).

Microwave heating is fundamentally different from the conventional one in which thermal energy is delivered to the surface of the material by radiant and/or convection heating that is transferred to the bulk of the material via conduction. On the contrary, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. Microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion rather than heat transfer. Since microwaves can penetrate the material and supply energy, heat can be generated throughout the volume of the material resulting in volumetric heating. Hence, it is possible to achieve rapid and uniform heating of thick materials (Das *et al.*2009).

The aim of this work is to use microwave oven instead of conventionally thick film firing furnace as an alternative, efficient way to process silver conductive thick film so that this technique can be useful for the low temperature processing electronic circuitry in particular to the PDP (plasma display panels) industry. The other aim is to compare the microwave processed silver conductor films with the conventionally sintered films.

2.Experimental techniques

Thick film paste (SP06B) was indigenously formulated using the well-established procedure with the composition of silver as a conducting phase, glass frit as an inorganic binder and organic vehicle. The specific paste formulation process is reported earlier (Bangali *et* 2009). Square thick film conductor pattern of 1 cm × 1 cm size of the prepared silver pastes were screen-printed on to the 1” × 1” × 0.635” alumina substrate (96%) through nylon screen of 250-mesh. Fig. 1 depicts the screen printing process whereas schematic of the silver thick film pattern is shown in Fig. 2. After screen printing, the printed silver thick films were allowed to settle for 10 min. at room temperature and then fired in a household microwave oven (Electrolux, 2.45 GHz, 900 Watt, Model- EM26EC90SL) for 5-30 min using 100% of microwave power. On the other hand, for the comparative study, two samples from the same screen printed batch were fired at 750 and 850^{o}C respectively for a dwell of 10 min in a conventional four zone thick film firing furnace (BTU make) with the typical 60 min thick film firing profile. The thickness of the fired film was measured using Digimatic Calliper (Mitutoyao, Model CD6”CS). The thickness of the fired films was in the range of 10 ± 1 μm in both the cases viz. Microwave processed and conventionally processed. The sheet resistance of the films were measured by four probe technique. The surface microstructure of the fired films was characterised by scanning electron microscope (Philips, Model XL-30).

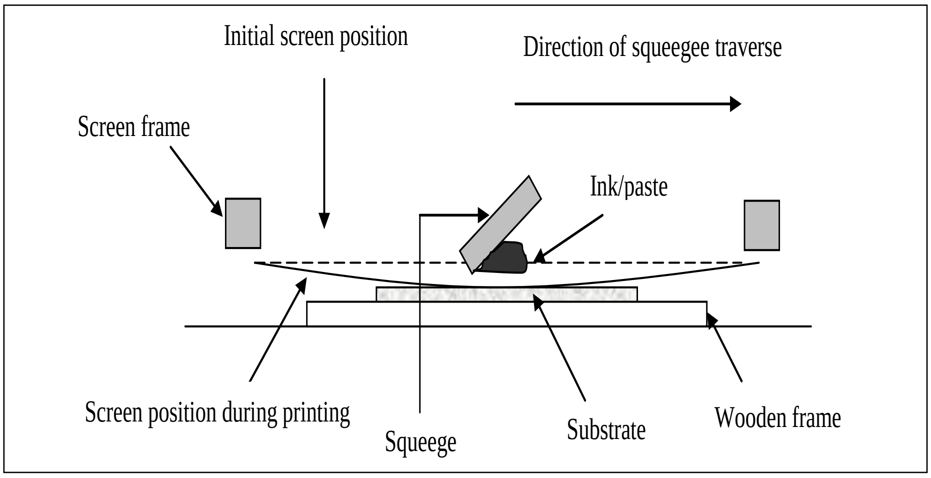

Fig. 1 Schematic of the screen printing process

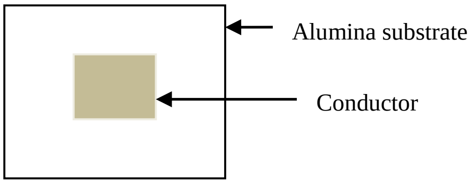

Fig. 2 Schematic of the silver thick film conductor pattern on alumina substrate

3. Results and discussion

3.1 Silver thick films processed in microwave oven

Fig. 3 show the surface microstructure of the films fired in the microwave oven at 100% microwave power for different time durations. It is seen that the change of surface texture in films processed at different time exhibited different sintering behaviour for silver thick films. Sintering of the silver particles proceed uniformly with the increase in the processing time. More uniform, smooth surface texture and remarkable grain development observed in case of film processed for 30 min. as compared to the lower processing times. It has been reported (Anklekar *et al.* 2001, Gupta and Wang 2006, Minay *et al.* 2004) that microwaves interacts directly with the material, also in the case of conductive powder compacts, and thus avoiding heating others part that are not directly involved in the process, like air or the oven’s walls. A remarkable energy and time saving can be observed and the resulting products revealed enhanced surface properties with respect to conventional treated ones due to the penetrating feature of microwaves in microwave absorbing materials; microwave heating seems to be more uniform and volumetric within the conductor. The microwave energy deposits directly within the material which possibly create a uniform temperature distribution among the materials. Consequently, microwave sintering can proceed at greater speed than conventional heating in virtue of the presence of more efficient mechanism of mass transport, in presence of liquid or vapour phase. Moreover, the microwave assisted sintering

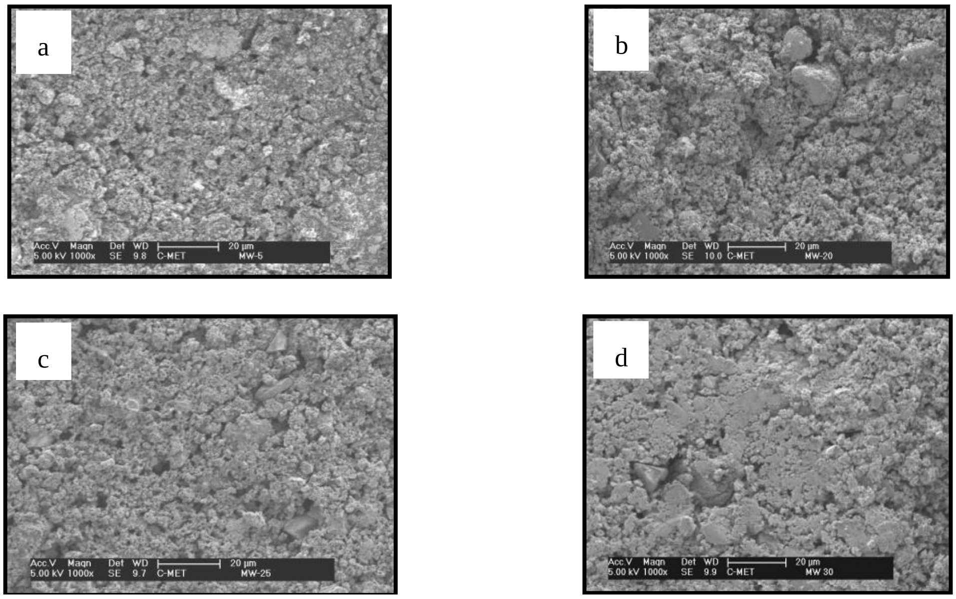

Fig. 3 Micrograph of surface microstructure of films fired at 100% power for different time in the microwave oven: (a) 5 min (b) 20 min (d) 25 min and (e) 30 min

process can be self-regulating, because the necks formation progressively generates longer and longer conductive paths, thus reducing the areas of electromagnetic field concentration in comparison with the initial particles dispersion. Materials with high conductivity (σ) and permeability (μ_a) present a lower penetration depth, for a given frequency, but there is also implicit temperature dependence due to the changes of σ and μ_a. Most metals generally have a skin depth of the micrometer order, so the direct heating tends to remain superficial, but using powders with particle size of the skin depth order, it is possible to heat them directly and use microwave in the sintering process (Leonelli *et al.* 2008). However, some researchers (Minay *et al.* 2004, Whittakar 2005) have reported the complex phenomena intervene during microwave assisted sintering of metallic powders, in particular local concentrations of electric field can occur, in excess of the dielectric strength of the medium (air, polymer or glass), leading to arcing, localized melting or very rapid phenomenon of evaporation.

It was reported that the thermal gradient in the microwave processed material is the reverse of that in the material processed by conventional heating where slow heating rates are selected to reduce steep thermal gradient leading to process-induced stresses. Thus, there is a balance between processing time and product quality. During microwave processing, the potential exists to reduce processing time and enhance product quality as microwaves can transfer energy throughout the whole volume of the material. In this case, energy transfer occurs at a molecular level that leads some additional advantages. When microwave energy is in contact with materials having different dielectric properties, it will selectively couple with the higher loss tangent material. Therefore, microwaves can be used for the selective heating of the materials (Thostenson and Chou1999).

Fang *et al.* (2009) has reported the effective sintering of ferrite, multilayer chip inductors and Ag-Pd electrode multilayer ceramic capacitors by microwave processing.They observed significantly accelerating kinetics and enhancement in the sintering properties leading to very good densification, linear shrinkage, and effective activation energy of diffusion of ferrite at a constant

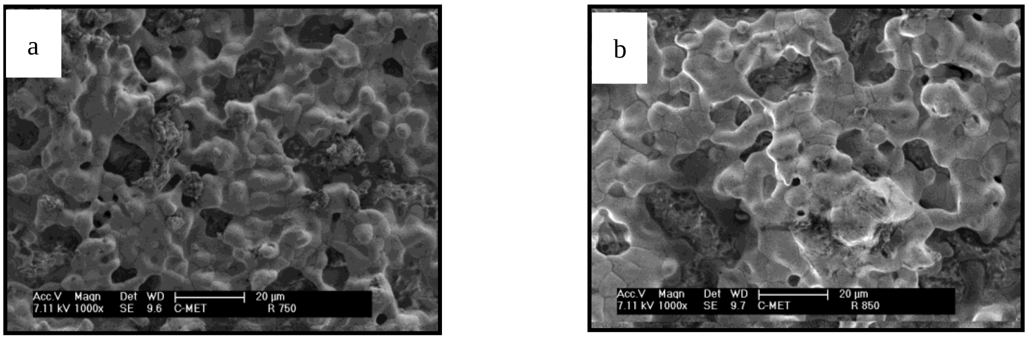

Fig. 4 Micrographs of surface microstructure of films fired at different temperatures for a dwell of 10 min with the 60 min firing profile in the conventional thick film firing furnace: (a) 750^{o}C (b) 850^{o}C

heating rate. They also observed the fast sintering process in case of MLCC with the normal distributionof capacitance for microwave processed MLCC resulting significantly better properties that the conventional sintered sample.

3.2Silver thick films processed conventionally in thick film firing furnace

Fig. 4 show the surface microstructure of the films fired conventionally in the thick film firing furnace for different temperatures. Grain growth, together with neck formation, is very pronounced in the SEM images. However, as expected there are blisters seen on the surface which are caused by the release of gas from within the film after metal on the surface has sintered to a high density. The main source of gas is oxidation of the residual carbonaceous materials from the organic screening agent and chemical/vitreous reactions between the bonding agent in the thick film material and the substrate. Homogeneous dispersion of particle provides a large interfacial area for softening of glass which in turn enhances the granular transformation. Surface irregularities and large particle size distribution promote uneven sintering during the firing stage which ultimately leads to poorly defined conducting layers.

When a dried film is fired at higher temperature, the organic vehicle is removed and the inorganic binder is softened. The capillary force resulting from the softened binder is responsible for the mass transport at higher temperatures which activates granular transformation. The more dispersed the inorganic part, the more substantial is the capillary effect. This in turn, lowers the temperature required for obtaining a dense fired film. When the firing temperature is increased, mass transport became more significant which leads to grain growth (Rane *et al.* 2000). Densification of silver paste printed film is an important requirement to improve the conductivity of silver particles. Silver nanopaticles can be a good candidate to achieve densification due to their high sinterability. Park *et al.* (2008a, b) reported that silver paste using nano particles (of the size 50-100 nm) could be sintered/fired at 450^{o}C leading to good densification of the films. It is also reported that amount of glass frit plays the important role in the densification of the silver film and the densification is enhanced due to the increase of glass frit content (Bangali *et al.* 2008, Seo *et al.* 2009). In the present study, the glass frit content was only 6% by weight. Therefore, further increase in glass content may lead to better densification as well as good sinterability of the film. An increase in glass frit content would also accelerate active repacking of thick film by the larger amount of liquid glassy phase which assists fast rearrangement process and interconnection of

Table 1 Data of sheet resistance for the films processed at different firing conditions

Processing technique	Firing time (min)	Sheet resistance (Ω/□)
Microwave oven	5	1.207
	10	0.308
	15	0.180
	20	0.090
	25	0.025
	30	0.003
	Firing Temperature (^{o}C)/ time(min)	
Conventionally BTU furnace	750/15	0.009
	850/15	0.003

metal particles resulting enlargement in their contact area and make a short current path corresponding to the lower resistivity. The final film density and hence electrical conductivity are intrinsically related to the density of metal compact, which exists even after removal of organic constituents.

The sheet resistance of the fired films was measured by four probe technique and calculated using the Eq. (1).

$$R_s = 4.532 \times V/I \tag{1}$$

The data of the sheet resistance is given in Table 1. The microwave fired films shows the sheet resistance spans of 0.003 to 1.207 Ω/□ whereas the conventional fired films shows resistance span of 0.003 and 0.009 Ω/□ for firing temperature of 750 and 850^{o}C respectively. From the above results it can be stated that the sheet resistance decrease with an increase of the firing for the case of microwave processed films and increases when the there is decrease in the firing time in case of conventional fired films. The sheet resistance of the microwave fired (30 min.) film is similar to that of the films fired conventionally at 850^{o}C. Therefore, based on the above results, it can be stated that the microwave heating (with the appropriate power/temperature settings) can be a powerful alternative technique to the conventional thick film firing process for processing of silver thick film conductors. However, more detailed research is required particularly in the processing/firing of thick film circuits which contents resistors, dielectrics that are highly sensitive to firing conditions since the above results are only related to the processing of silver thick film conductor by microwave. Also, more detailed study is required explicitly to the temperature setting and the appropriate profile of the firing cycle since the above experiments were carried out in the house hold microwave oven where setting of these parameters have limitations. Also, it may be noted here that till today no reports are available on the processing of thick film circuits by microwave and hence this will open the new area of research.

4. Conclusions

Silver conducting thick films were prepared using indigenously formulated paste and processed in the household microwave oven as well as in the conventional thick film firing furnace. The films were sintered at different dwell times; keeping all the other parameter constant, such as microwave power, film thickness etc. Microstructure analysis revealed the surface morphology to become more compact with increased processing time. The microstructure of the microwave sintered films have more uniform, compact surface as compared to that of conventionally fired films. The sheet resistance for microwave sintered silver films is in the range of 0.003 to 1.207 Ω /□. On the other hand, the films processed in the conventionally thick film firing furnace at the firing temperature of 750 and 850^{o}C showed the resistance of 0.009 and 0.003 Ω/□. Therefore, the sheet resistance values are comparable. A remarkable energy and time saving can be obtained and the resulting products present often enhanced surface properties with respect to conventional treated ones because the heating is more uniform and volumetric. However, more detailed investigations are needed towards the optimization process, adhesion, stability of the films and other specialized analysis so that microwave firing can be used as a cost effective solution for the production of thick film components.

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