AN EVALUATION OF AN EXPERIMENTAL GLASS FRIT FREE THICK FILM METALLIZATION FOR AIN-CERAMICS

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Abstract: A glass frit free thick film paste has been especially developed for metallization of AIN ceramic. The metallized ceramic has been characterized theoretically as well as by experiment. A numerical analysis of temperature distribution induced by a continuous and pulsed mode operating heat source has been conducted by means of a finite element program. With regard to evaluate the adhesion properties of the metal film the tensile strength of the metallization has been determined.

Vrednotenje eksperimentalne prevodne debeloplastne paste brez steklene faze za metalizacijo AIN keramike

Ključne besede: polprevodniki, naprave polprevodniške, elektronika močnostna, AIN keramika nitridi aluminijevi, metalizacija debeloplastna, metalizacija AIN keramike, paste prevodne, paste metalizacijske, paste debeloplastne, paste metalizacijske brez zmesi kalcinirane za steklo, Ti-Cu-Ag metalizacija debeloplastna, SEM analize, analiza površine, vrednotenje preskusov

Povzetek: Razvili smo prevodno debeloplastno pasto brez steklene faze, namenjeno posebej za metalizacijo AIN keramike. Metalizirano keramiko smo ovrednotili teoretično in eksperimentalno. Numerična analiza porazdelitve temperature substrata za stalni in pulzni izvor toplote smo opravili s pomočjo programa, ki uporablja tehniko končnih elementov. Oprijemljivost metalnega filma pa smo določili z meritvijo natezne trdnosti metalizacije.

I. INTRODUCTION

Aluminium nitride shows an excellent thermal conductivity and a thermal expansion coefficient which is well matched to that of silicon. The lack of toxicity in comparison to beryllia makes AIN-ceramic a very competitive substrate material for power electronics application. A range of standard thick film pastes are available for the metallization of ceramics. Glass frits or different oxides which are added to thick film conductor pastes are responsible for the adhesion of the metal film on conventional alumina substrates. During the firing cycle the glass frits form a glass phase which interlocks the metallic conductive phase and the substrate. The thermal expansion coefficient of the glass phase must be matched to that of alumina. In contrast to the so called glass bonded systems the oxides of chemical bonding systems interact during the firing cycle with the alumina and form spinels which are responsible for adhesion of metallization. Mixed bonding conductive pastes comprise both kinds of bonding systems. The selection of a conductor paste with a specific bonding system depends on the requirement of application. Conductor pastes based on a chemical bonding system are very well suited for circuits built up in chip and wire technique. On the other hands the glass phase of glass bonding systems penetrates frequently the surface of metallization which consequently impedes the development of reliable bonding sites. Metallized substrates carrying power devices are acting as heat sinks and are

responsible for heat removal. For an efficient heat management it must be provided that the thermal resistance between the power dissipating device and the substrate is as small as possible. The thermal resistance formed by the glass phase of a glass bonding conductor system becomes critical if a substrate with a high thermal conductivity is applied while it is ignorable for a standard alumina substrate.

Although thick film technique enables to realize conductor lines with a sufficient thickness which is necessary for circuits carrying high current some problems arise with regard to its application to AlN-ceramic substrates. There exists often paste incompatibilities between standard thick film pastes utilized for conventional Al_3O_2-substrates and AlN-substrates which result in poor adhesion and blistering of metallization. Unfortunately only glass frit containing pastes are suitable for applications onto AlN ceramic substrates. The advantage of the high thermal conductivity of the AlN-ceramic will be affected by the *glass* phase acting as interlocking layer. Till today not any chemical bonding thick film conductor system for AlN is available which would provide an interface of low thermal resistance between AlN and the metallization.

2. TiCuAg-METALLIZATION SYSTEM

In our project we have developed a glass free conductor thick film system which would be accommodated to the requirements of AlN. Actually a TiCuAg thick film composition has been prepared where the amount of added Ti varied between 1 at% and 20 at%. The Ti should act as bonding agent between the metallic AgCu-solution and the AlN ceramic. The considered thick film paste must be fired under an inert atmosphere to avoid oxidation. It was expected that at the interface between the aluminium nitride ceramic and the thick film metallization a continuous titanium nitride layer and a compound of $(TiCuAl)_6N$ a so called η-phase should be formed (Figure 1).

The latter compound and other related nitrides play a significant role with regard to the adhesion and the development of stresses at the interface. Aluminium nitride and TiN grains comprise arrays of dislocations which are presumably arising from thermal expansion mismatch between the involved materials. Above the TiN layer a continuous layer of equiaxed and nearly defect free η-phase grains is formed. Beyond this η-phase layer the metallic solution of Cu and Ag is built up. These structures and the morphology of the interface between metallization and AlN-ceramic have been detected by studying the reactive bonding mechanism of Ti doped metal foils and aluminium nitride. By analogy with the metal foil-AlN ceramic compound the same phases should develop at the interface between AlN ceramic substrate and corresponding thick film metallization.

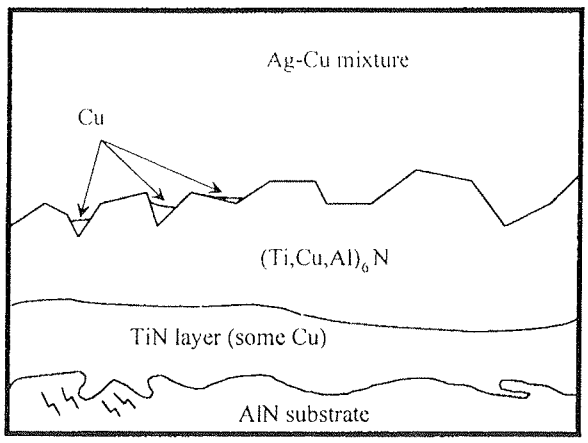

Figure 1: Structure of interface between glass frit free metallization and AlN /1/

2.1 Paste formulation

By application of the so called polyol process Ag and Cu frits with a grain diameter <3 µm have been produced. Ti frits have been prepared by cracking and milling the intermetallic compound Cu_3Ti_2. A binder system on the base of polyacrylic acid (PAS) has been selected. This binder organic provides a paste rheology suitable for the screen printing process and enables a firing process under a non oxidizing atmosphere, as well. The binder should decompose and evaporate completely during the firing cycle. A typical paste composition is listed in Table 1 /2/.

Table 1: Typical paste composition

Component	Weight%
PAS	13,1
α-terpineol	12,9
metal powder	60,7
dibutylphtalate	5,4
tertbutanol	7,9

2.2 Preparation of metallization

The experimental paste was printed on AlN-substrates by a conventional screen printing process utilizing a 200 mesh screen as well as a metal stencil of 100 µm thickness. The printed layer was leveled at room temperature for few minutes and dried at 75°C for 10 minutes in a drying furnace.

Firing of the samples has been carried out in a conventional thick film furnace under a nitrogen as well as an argon atmosphere with a maximum oxygen content of 15 volppm at a standard heat profile with a peak temperature of 850°C or 950°C, respectively, a dwell time of 10 minutes and a total heat cycle time of 60 minutes.

3. CHARACTERISTICS OF METALLIZATION

Different types of effects have been observed on the fired metal films. The paste fired at 850°C shows cracks extending to the bottom of metallization (Figure 2). The metallization exposed to firing temperature of 950°C shows ball shaped structures dispersed on its surface as well as cracks (Figure 3).

By means of microprobe analysis the ball shaped structures have been identified as grains especially containing Ti and Cu. Sometimes the irregularities of the surface finish of the metallization may be related to the marks of wire mesh caused by the screen printing process. In this case an improvement should be achieved by stencil printing. Neither by screen printing nor by stencil printing an uniform crack free metallization surface has been obtained.

To study the influence of film thickness on crack formation paste has been applied with increasing thickness by a single free hand stroke utilizing a rubber blade. The sample has been exposed to the above mentioned standard drying and firing process. This experiment reveals that with increasing layer thickness the cracks develop already during the drying process while during the firing cycle the growth of cracks only proceeds. Regions of the thin layer exhibit a crack free surface (Figure 4) while areas with high layer thickness are perforated by cracks extending to the surface of the substrate (Figure 5). To provide a voidfree uniform paste coverage of AIN-substrate the paste with the considered formulation has to be applied by screen printing of three layers. Each layer was dried and tired separately. The fired metallization thickness varied between 80 and 100 μm.

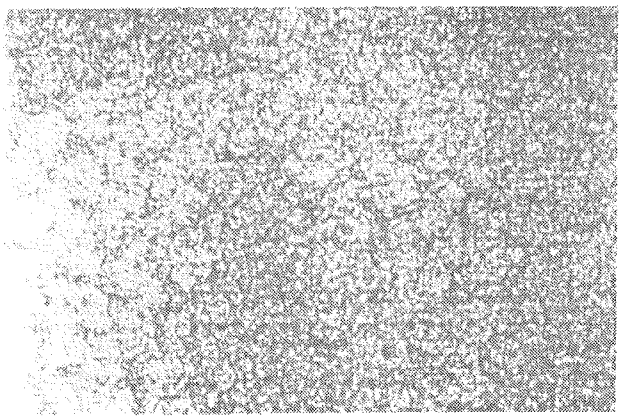

Figure 2: Metallization with cracks (paste containing 1 at% Ti, firing temperature: 850°C).

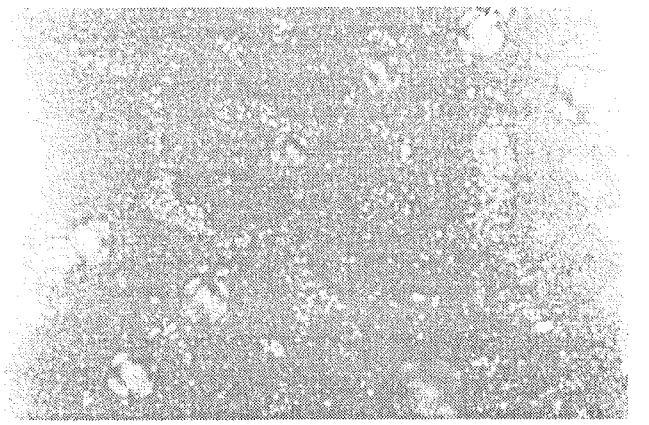

Figure 3: Metallization surface with dispersed ball shaped structures (paste containing 1 at% Ti, firing temperature: 950°C).

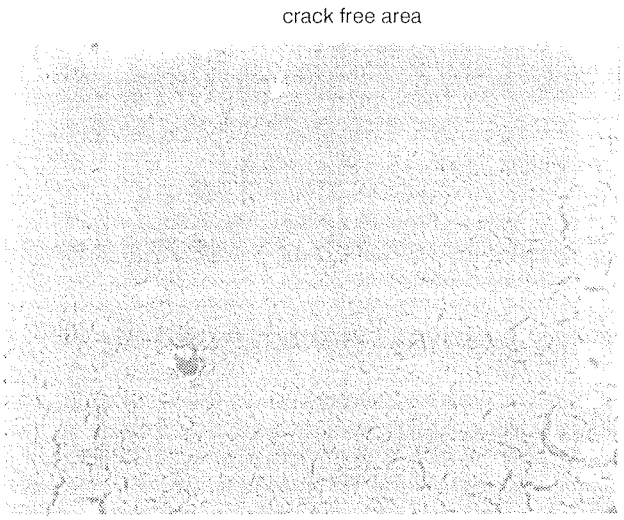

Figure 4: Crack free metallization (paste containing 2,5 at% Ti, firing temperature: 850 °C, dwell time: 30 minutes, firing atmosphere: argon, film thickness: <10 μm).

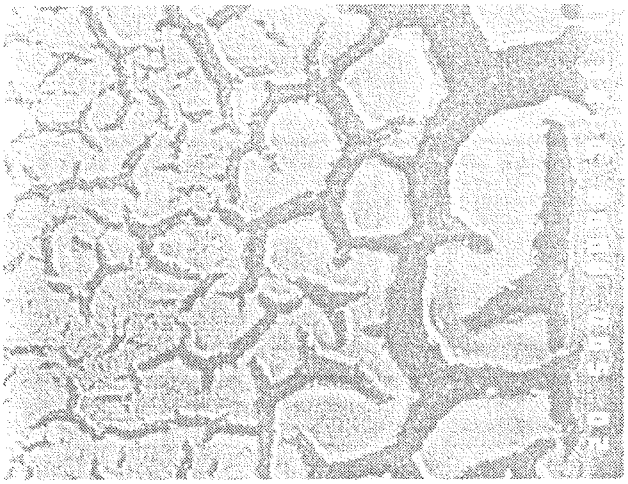

Figure 5: Metallization perforated by cracks (paste containing 2,5 at% Ti, firing temperature: 850 °C, dwell time: 30 minutes, firing atmosphere: argon, flm thickness: 25-30 μm).

3.1 Formation of TiN-interface and adhesion strength

A cross sectional view of a metallographically prepared metallized aluminium nitride fired under nitrogen is shown in Figure 6. The titanium distribution analysis carried out by means of an energy dispersive spectroscopy shows not any agglomeration of titanium at the interface between metallization and the ceramic (Figure 7). The adhesion strength of metallization is a significant measure if a TiN layer has been already developed.

The pull test has been conducted with the metallizations realized by our glass frit free conductor system as well as by commercially available glass frit containing copper pastes for comparison purpose. Epoxy precoated aluminium nail head pins were bonded to the surface of the metallization pads. The test samples were inserted in a pull tester. A pulling force was applied on the pins and continuously increased until failure occurred. Because of the significant poor adhesion strength and the lack of any Ti agglomeration at the substrate/metallization interface the time of firing at peak temperature has been increased from 10 minutes to 120 minutes. An increase of exposure time should promote the Ti-diffusion to the interface and subsequently the formation of TiN which would improve adhesion strength.

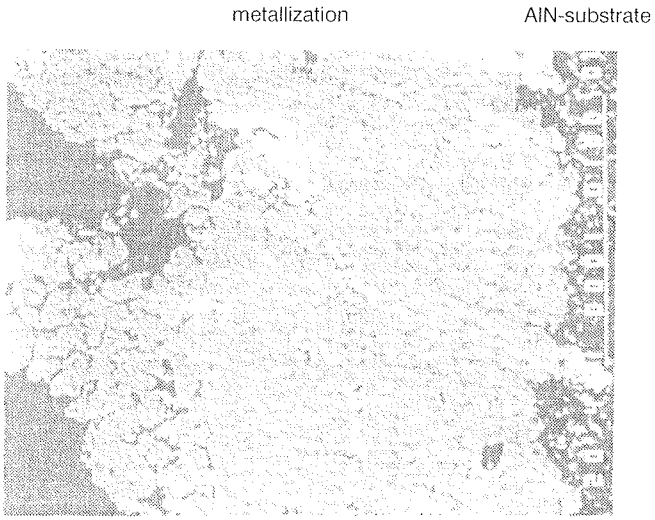

Figure 6: SEM image of the metallization cross section (paste containing 2,5 at% Ti, firing temperature: 850 °C).

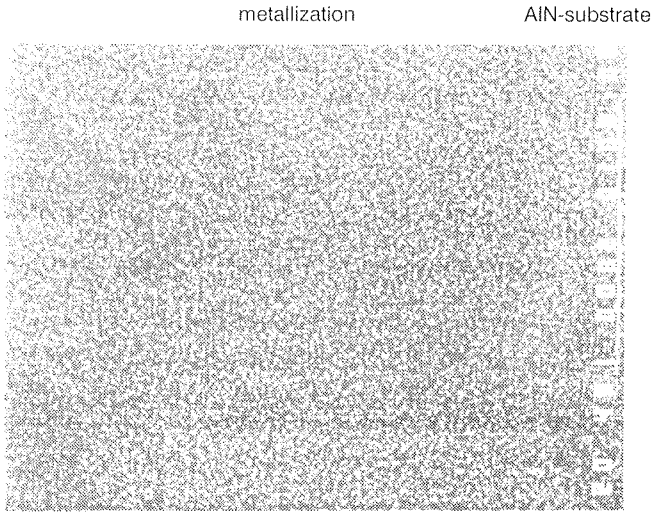

Figure 7: Ti-distribution along the cross section of metallization (paste containing 2,5 at% Ti, firing temperature: 850 °C).

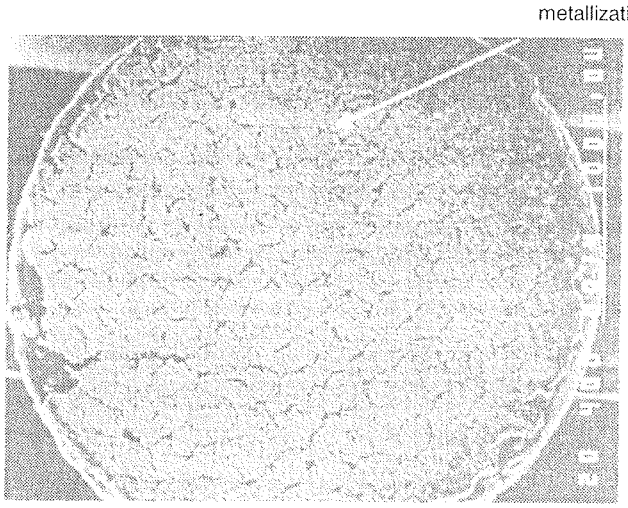

Figure 8a: SEM micrograph of the nail head after exposure to pull test (paste containing 2,5 at% Ti, firing temperature: 850 °C. dwell time: 30minutes. firing atmosphere: nitrogen).

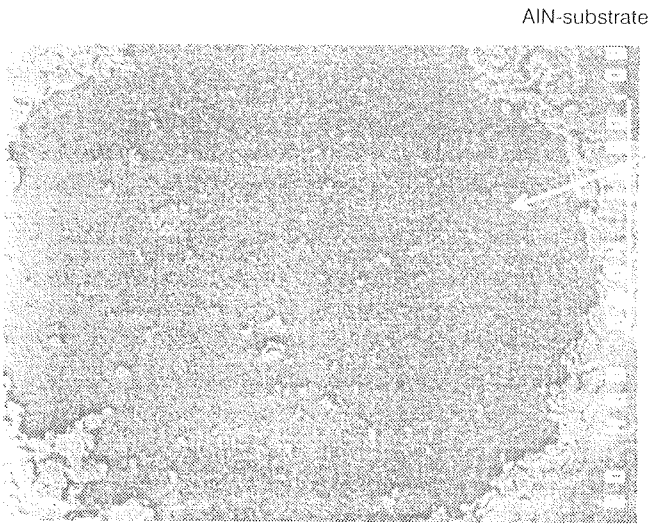

Figure 8b: SEM micrograph of the AlN-substrate after exposure to pull test (paste containing 2,5 at% Ti, firing temperature: 850 °C, dwell time: 30 minutes, firing atmosphere: nitrogen).

Actually, an increase of firing time contributes to an improvement of adhesion strength but nevertheless the results are quite unsatisfactory. The recorded adhesion strength of our experimental metal films amounts only 20 to 50 percent of the values achieved with glass containing metallizations. Figure 8 shows SEM-photographs of the nailhead and the corresponding area of aluminium nitride ceramic after the pull test has been carried out. Nearly all the metallization film has been lifted off from the ceramic and adheres consequently on the nail head.

A change of processing conditions has resulted in a drastical increase of adhesion strength. Instead of nitrogen the samples were purged with an argon-atmosphere during firing cycle. Evidently under the nitrogen atmosphere the dispersed Ti-particles react already with the surrounding atmosphere and TiN is formed. Consequently, the driving force for the Ti diffusion to form TiN at the interface between metallization and the ceramic is missing. In contrary the argon atmosphere does not react with titanium. This fact evidently provides the ability of titanium to react with the nitrogen sites of AlN and is the driving force for the Ti-diffusion.

Although the titanium element distribution analysis carried out on argon fired metallizations shows also not any agglomeration of Ti (similar to that of Figure 7) the TiN-layer must have been already formed. The adhesion strength of the metallization is already comparable to that of the different glass bonded copper pastes. Therefore it must be supposed that the amount of added Ti to the paste is still so small that an agglomeration of Ti in a very thin layer is not detectable by means of microprobe analysis. The excellent adhesion of metallization is also documented by the REM-photographs (Figure 9) of the lifted off nail heads and the corresponding area of the metallized AlN-substrate where the studs have been attached. The metallization could not be removed from the substrate by the applied force.

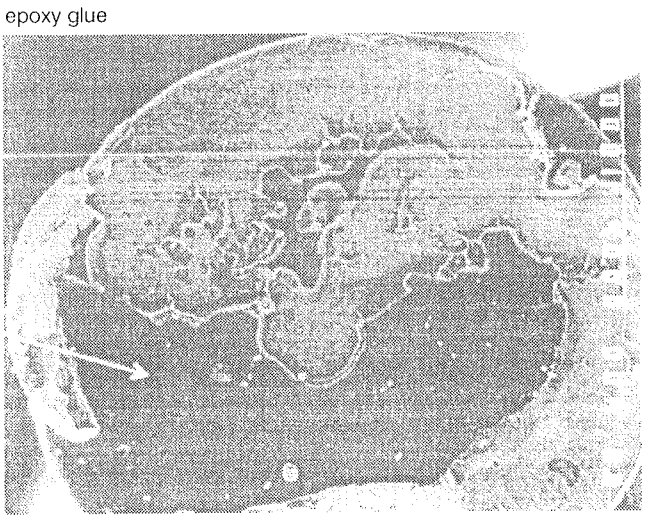

Figure 9a: SEM micrograph of the nail head after exposure to pull test (paste containing 2,5 at% Ti, firing temperature: 850 °C. dwell time: 30 minutes, firing atmosphere: argon).

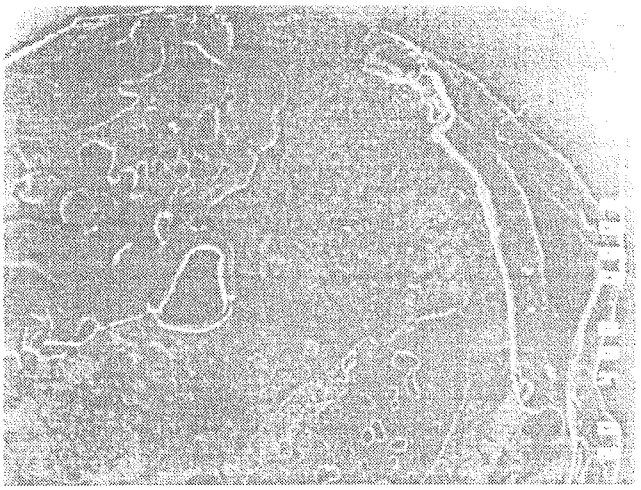

Figure 9b: SEM micrograph of the corresponding AlN-substrate area after exposure to pull test (paste containing 2,5 at% Ti, firing temperature: 850 °C, dwell time: 30 minutes, firing atmosphere: argon).

Actually, the adhesion strength of the metallization must be higher as recorded in the graph of Figure 10. Actually the tensile strength was limited by the bonding strength of the epoxy glue.

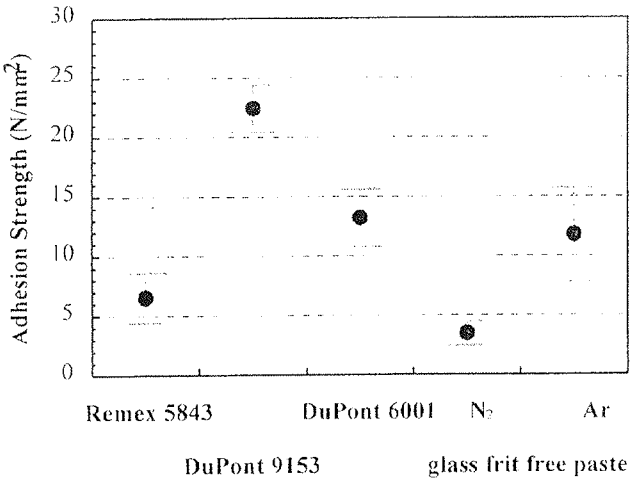

Figure 10: Adhesion strength distribution of commercially available glass frit containing copper pastes and experimental glass frit free Ag-CuTi-paste containing 2,5 at% Ti, firing temperature: 850°C, dwell time:30 minutes) fired under nitrogen as well as under argon.

4. NUMERICAL SIMULATION

Beside the practical investigations numerical analyses of metallized ceramic substrates have been carried out by means of a finite element program. The aim of the numerical simulation was to quantify the influence of the interlocking phase between ceramic and metallization. The object of simulation concerns a ceramic substrate

Table 2: Materials property data

Material	Density ρ [kg/m^3]	Thermal Expansion α [$10^{-6}K^{-1}$]	Thermal Conductivity k [W/mK]	Specific Heat c_p [J/kgK]
AlN	3 260	4,9	170	72
Al_2O_3	3 780	6,8	24	800
Lead-Boron-Silicate-glass	4 650	6,96	1,5	669
Copper	8 960	17	394	386
TiN	5 220	6	20	650
Ti_3Cu_2AlN (η-phase)	5 622	-	45,2	536

where a metallized pad was positioned in the center of the substrate surface. Aluminium nitride as well as conventional alumina for comparison purpose have been considered as substrate material. The metallization thickness was committed to be 15 µm a thickness which is usually achieved by thick film technique. Table 2 shows the data of materials properties utilized for computer simulation.

The models considered in this simulation are based on the assumption that the pads consists of a layered structure with different performances (Figure 11).

Because of the symmetrical structure of the metallized substrate it is sufficient to restrict the simulation model to one quadrant of the substrate. Actually, the results of simulation will be identical for all remaining three quadrants. The computations were carried out for different power applied on the surface of the copper film. The absorbed power flows vertically through the metal film into the substrate where it dissipates.

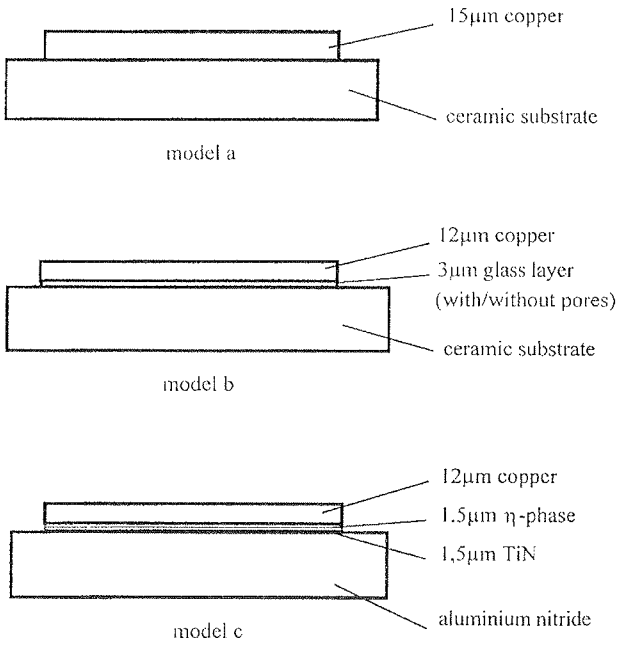

Figure 11: Models of layered metallization pads.

An applied power of 1 W induces a temperature distribution in the compound after a settling time of 100 s as shown in Figure 12. The temperature distribution analysis yields nearly identical results for all considered metallization models.

A summary of the resulting peak temperatures for the different metallization models are shown in Table 3. T_1 and T_{100} denote the temperature (peak temperature) in the center of the surface of the substrate after a settling time of 1 s and 100 s, respectively. T_{100} is characterizing already the steady state condition. Evidently there exists not any significant differences for a bulk layer (model a) or a copper pad comprising a glass phase which may also contain pore inclusions (model b). Significant temperature differences with regard to the steady state condition may be contributed to the thermal properties of the different substrate materials. While the performance of the interface layer between metallization and ceramic is of negligible interest for a power device operated in a continuous mode the thermal resistance of the interface governs the thermal management of devices working in a pulsed mode.

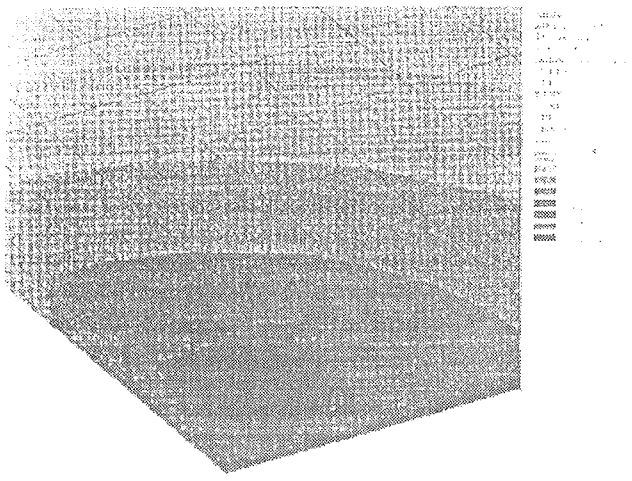

Figure 12: Temperature distribution after a settling time of 100 s of a metallized aluminium nitride substrate induced by a power of 1 W.

Table 3: Peak temperature of metallization pads.

		1 Watt (10^5 W/m^2)		10 Watt (10^6 W/m^2)	
		Al_2O_3	AlN	Al_2O_3	AlN
model a	T_1/°C	28,79	22,72	107,94	47,16
	T_{100}/°C	58,31	38,14	403,05	201,44
model b: without pores	T_1/°C	29,15	22,92	111,51	49,23
	T_{100}/°C	58,47	38,35	404,68	203,52
model b: 50 vol% pores	T_1/°C	29,17	23,25	111,65	52,51
	T_{100}/°C	58,77	38,61	407,74	206,14
model c	T_1/°C	-	22,73	-	47,68
	T_{100}/°C	-	38,31	-	202,75

Figure 13 shows the temperature swing of a metallization with a glassy interface and an interface built up by an TiN-layer induced by a device operating in a pulsed mode. The temperature difference within a metallization containing pores amounts approximately 7°C while the temperature drop in a glass frit free layer is negligible. The advantage of a glass frit free metallization becomes especially evident for high power circuits operating in a pulsed mode.

5. SUMMARY

The development of a glass frit free thick film metallization for AlN-ceramic substrates shows already promising results. It shows an excellent adhesion to the AlN-ceramic. Nevertheless the morphology of the metallization layer has to be improved. Surface topography and morphology of metallization are governed by paste formulation. The reason for a rough surface as well as the development of cracks may be caused by a low solid content of the paste or by a small surface area of added metal frits. An increase of solid content of the paste seems therefore to be advisable. Unfortunately an increase of solid content would impair the printability of paste. Another binder and organic system must be selected and evaluated.

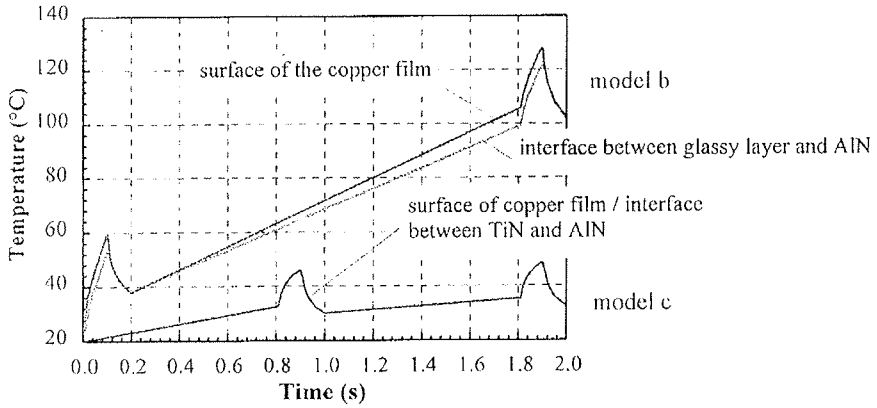

Figure 13: Temperature characteristic of metallization pads (model b comprising 50 vol% pores in glass layer and model c) operated in a pulsed mode (1 W, 5 Hz).

The electrical characteristic as well as solderability of the metallization are further topics of investigation.

6. REFERENCES

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