Thick film pastes for nitride ceramics for high power applications

Marco Wenzel, Richard Schmidt, Uwe Partsch, Markus Eberstein

Fraunhofer Institute for Ceramic Technologies and Systems

Winterbergstr. 28

01277 Dresden Germany

Phone: +49 351 2553 7233 Fax: +49 3512 554 106

Email: marco.wenzel@ikts.fraunhofer.de

Abstract

Aluminum and silicon nitride ceramics show high potent as substrate materials for thick film- / hybrid applications in the field of power electronics and microwave technology. A main advantage of AlN is its very high thermal conductivity. Si_3N_4 has also a thermal conductivity comparable to AlN but higher thermal shock resistance and fracture toughness. Nevertheless, the use of Si_3N_4 in power electronic packages or heater applications is not achieved due to the lack of suitable connection technology such as thick film pastes. The main challenge for the respective pastes is the adhesion on the substrate. The low thermal expansion (CTE) of about 2.8 ppm/K of Si_3N_4 and material interactions with the thick film components must be considered in the paste development. Therefore, new glasses and glass-ceramic composites are required.

Reason development was performed towards AgPd based thick film heater pastes for Si_3N_4., The pastes consists of AgPd in a 1:1 ratio, an inorganic filler and a glass phase adapted to the CTE of Si_3N_4. By variation of the content of inorganic filler and glass content three pastes with a sheet resistivity of 0.1 ohm/sq, 0.8 ohm/sq, and 7.9 ohm/sq and temperature coefficient of the resistance (TCR) between -100 and 100 ppm/K were developed. The performance of heater films prepared from these pastes under electric pulse load was studied. An electrical power of up to 85 W can be applied without a significant change of the resistivity ($\Delta R/R$) of 0.1%. As reference comparable investigations on AlN were performed with adapted pastes. The film structures were analyzed in FESEM studies.

Key words

AlN, high power, screen printing, Si_3N_4, STOL, thick film heater paste.

I. Introduction

Aluminum nitride (AlN) has been used for several years as high performance substrate material for thick film hybrid technology due to its outstanding properties such as the high thermal conductivity, and the mechanical strength. Thick film pastes, consisting of conductors with high solder adhesion, resistors with sheet resistivities between 0.1 Ω/sq and 1 kΩ/sq and a suitable encapsulating paste are available [1]. However, the flexural strength of AlN is limited (220 MPa) [2], which results in a reduced number of thermal cycles to failure of the manufactured device. Si_3N_4 has a significantly higher flexural strength (610 MPa) [2], a thermal conductivity comparable to AlN of up to 120 W/(m·K) [3] and provides, with its low coefficient of thermal expansion (CTE) of 2.8 ppm/K, a good match for Si dies in power device packaging. Nevertheless, a system of thick film materials specifically for Si_3N_4 has not yet been developed. To the best of our knowledge only Sienna Technolgies, Inc. offers a gold thick film paste [4]. Studies by R. Wayne Johnson and co-workers show that a specific engineered surface layer on the Si_3N_4 substrate is required for the adhesion of the available Au thick film paste [5]. Our own developments result in suitable Ag/Pd conductor paste with high solder adhesion and RuO_2 based resistor pastes suitable for Si_3N_4 as ceramic substrate material [6].

Herein we present the latest results towards developments of Ag/Pd based thick film heaters for Si_3N_4. The performance of the heater films under electrical and thermal load was characterised. As reference comparable experiments were performed with standard IKTS Ag/Pd thick film heaters on AlN. All pastes consist of the conductive material, inert filler and a lead oxide free glass, which has a CTE adapted to Si_3N_4 or AlN, respectively.

II. Experimental procedure

Materials

All heater pastes were manufactured at the IKTS. The pastes contain a Ag/Pd mixture as conductive phase, a glass phase with a CTE adapted to the substrate material (Si_3N_4 and AlN, respectively), an inorganic filler and an inorganic additive dispersed in an organic vehicle. The latter is created out of texanol and ethyl cellulose. The powders were mixed together in a tumbling mixer for one hour. The mixture was ground together in a dissolver with the organic vehicle to prepare a printable paste. Afterwards the pastes were passed through a three roll mill to ensure that there are no large particles or agglomerations. Pastes **I** through **III** are used on Si_3N_4 and pastes **IV** through **VI** on AlN.

As contacts, an IKTS Ag-based thick film conductor paste was used. The pates were printed on one by one inch² aluminum nitride substrates (thickness 625 µm) or one by one inch² silicon nitride substrates (thickness 2.5 mm).

Printing test structure, firing and measurements

A semi-automatic screen printing machine, Microtronic II, from EKRA Automatisierungs-systeme GmbH (Bönnigheim, Germany) was used to print the test structure for the AgPd pastes with a 250 mesh screen. The layout has been previously published [7] and consists of four meander structures, where each meander has a line width of 500 µm and 200 squares.

After each printing step (contacts and resistor structure) the pastes leveled for 10 minutes at room temperature, were dried at 150 °C for 15 minutes to remove volatile organics, and fired separately in a belt furnace at 850 °C for 10 minutes in air atmosphere. Using these structures the resistances were measured by a quasi-4-point probes method. The measured resistances were converted into sheet resistivities and normalized to a 21 µm dried film thickness. The relative resistance (resistance at the measured temperature divided by the resistance at 25 °C – R/R25) is evaluated with respect to the temperature. The temperature behavior of the resistances was measured between -55 °C and 150 °C.

To perform comparable measurements of the resistances under electrical load different layouts were designed, which allows for each substrate the same surface heating (Fig. 1, Table 1). To realize these structures four print, drying and firing steps were carried out subsequently. At first the resistor paste (Fig. 1: red structure; 325 mesh), second the conductor paste (Fig. 1: green structure; 200 mesh) and finally two overglaze layers (200 mesh), if applied. All pastes were dried and fired like described above, with exception of the overglaze layers, which are fired at 650 °C in air atmosphere.

Table 1: Test layout for STOL measurements

Paste	Resistivity [ohm/sq]	Layout	Number of squares
I and **IV**	0.1	Heater 0.1	145.4
II and **V**	1.0	Heater 1.0	16.6
III and **VI**	10	Heater 10	2.11

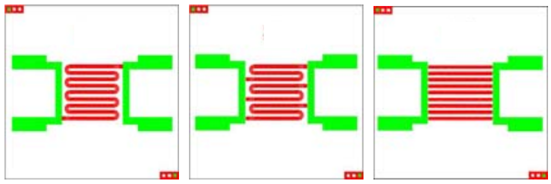

Figure 1: Layouts for STOL measurements: heater 0.1 (left), heater 1.0 (middle), heater 10 (right).

For the investigations of the resistances under electrical load STOL measurements (short term overload) were carried out. For this purpose the substrates were thermally connected to an Al cooling block with a Ag-containing heat-conducting paste. Initial resistance was measured at room temperature. The electric load was applied as 5 second pulses. The power increases stepwise and the resistance were measured 60 seconds after every pulse. This procedure is shown in Fig. 2.

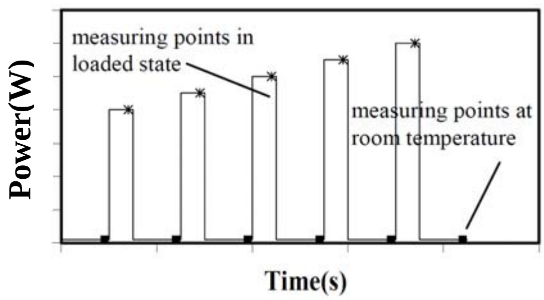

Figure 2: Loading step test with electric pulses

During the measurement the maximum temperature is determined with a pyrometer. The change of the resistance at room temperature for the overload tests is observed. In addition, long term measurements at 200 °C under pulse and constant electrical loads were carried out. The temperature distribution of the resistor and substrate during and after the load was measured with an infra-red camera.

Surface analysis

The surface of the uncovered heater samples on Si_3N_4 was characterized by FESEM, using a dual-beam focused ion beam and scanning electron microscope NVision 40 (company Carl Zeiss AG) at 2 kV.

III. Results and discussion

Resistivity and TCR on Si_3N_4 and AlN

Investigation on AlN demonstrated that heater pastes with a resistivity between 0.1 and 10 ohm/sq can only be manufactured with an Ag/Pd ratio of 1:1 [8]. Further, the use of such an Ag/Pd ratio results in temperature coefficient of the resistivity (TCR) between -100 and 100 ppm/K. Fig. 3 presents the resistivity and the TCR as a function of the glass amount and inert additive concentration for this Ag/Pd ratio.

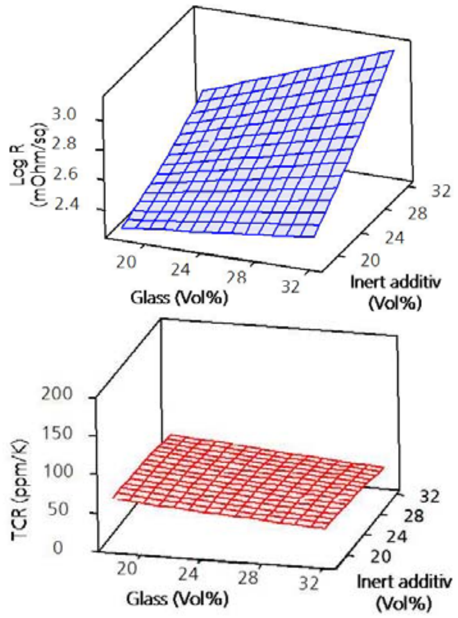

Figure 3: Resistivity (top) and temperature coefficient of resistance (bottom) depending of the solid composition of the IKTS pastes.

Starting from these results, three pastes were formulated with a sheet resistance of about 0.1 ohm/sq (paste **I** and **IV**), 1.0 ohm/sq (paste **II** and **V**) and 10 ohm/sq (paste **III** and **VI**). The sheet resistances obtained on Si_3N_4 are 0.1 ohm/sq for paste **I**, 0.8 ohm/sq for paste **II** and 7.9 ohm/sq for paste **III**. In contrast, the same formulation with the AlN adapted glass gives sheet resistances of 0.1 ohm/sq (paste **IV**), 0.9 ohm/sq (paste **V**) and 8.8 ohm/sq (paste **VI**) on AlN.

Detailed investigations of the temperature influence on the resistivity were performed by in-situ determination of the resistance for paste **I** to **III** on Si_3N_4. The obtained relative resistances are presented in Fig. 4. For paste **I** an almost linear increase of the resistance is observable. The cold-TCR (-55 to 25 °C) was calculated to 83 ppm/K whereas the hot-TCR (25 to 150 °C) is 90 ppm/K. Values of 28 and 9 were obtained for paste **II**, respectively. In contrast, a maximum is observable for paste **III** at about 40 °C with a cold-TCR of 32 ppm/K and the hot-TCR of -45 ppm/K. Thus, the influence of the temperature on the resistivity is decreasing with an increase of the sheet resistance of the paste. Most likely this behavior is due to the reduced content of conductive phase in paste **III** compared to paste **II** and paste **I**.

A summary of the obtained TCR values for the AlN pastes **IV** through **VI** is given in Table **2**. The results show that with increasing sheet resistivity the influence of the temperature is decreasing, again. Overall this effect is less pronounced on AlN, presumable due to the higher thermal expansion of AlN.

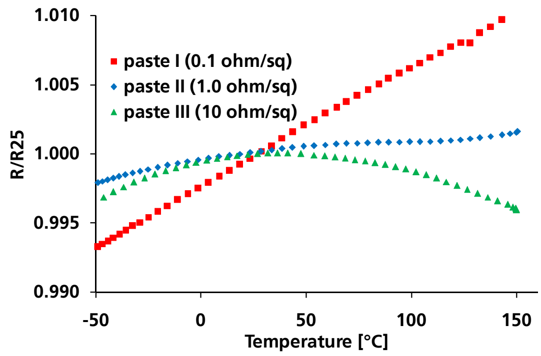

Figure 4: Relative resistance as a function of temperature.

Table 2: Cold-TCR and hot-TCR of paste IV, V and VI on AlN.

Heater film	cold-TCR (-55 to 25 °C) [ppm/K]	hot-TCR (25 to 150 °C) [ppm/K]
paste **IV** (0.1 ohm/sq)	89	52
paste **V** (1 ohm/sq)	57	11
paste **VI** (10 ohm/sq)	37	6

Heater characterization on AlN

For the heater characterization test substrates were prepared with the layout shown in Fig. 1. The layout allows a comparable surface heating in

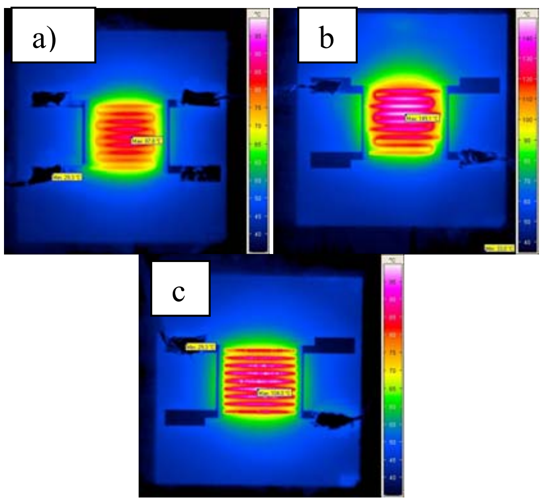

Figure 5: IR-images of three different heater films on AlN: a) heater 0.1, b) heater 1 and c) heater 10.

dependence on the sheet resistance of the investigated pastes, which is demonstrates by the infrared images of the three heaters (Fig. 5).

Electrical pulse load behaviour on Si_3N_4

The change of the resistivity during the electric pulse loading with increasing pulse power of the uncovered heater films prepared by pastes **I** to **III** on Si_3N_4 are shown in Fig. 6. The resistivity was measured at room temperature after each pulse as illustrated in Fig. 2. The graphs show a significant influence of the paste formulation on the behavior of the resulting film during electric power application. With an increase in the content of the glass and the inert additive (paste **I** to paste **III**) an increasing impact of the electrothermic loading is observable. The highest drift in the resistivity is obtained for the heater film manufactured by paste **III** (ΔR/R of 0.1% after a pulse load of 32 W, Table 3). The film based on paste **II** (1 ohm/sq) shows a drift of the resistivity of 0.1% after a pulse load of 61 W. A power of 80 W is required for the same resistivity drift (0.1%) in the film based on paste **I** (Table 3).

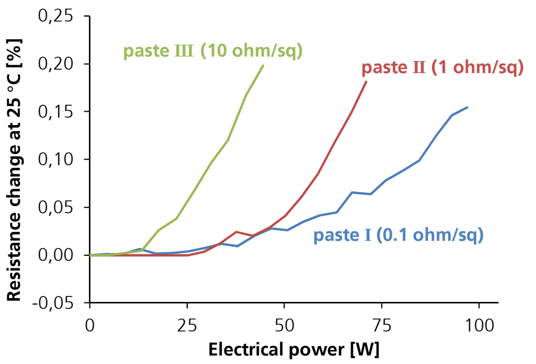

Figure 6: Change of the resistivity at 25 °C in dependence of the electrical power of paste I to III on Si_3N_4.

Comparable experiments were performed with covered heater films. Therefore a suitable overglaze was printed twice on the heater. The required electric pulse loading to initiate resistivity changes of 0.1% are summarized in Table 3. The obtained data show only a slight increase in the power load required to trigger the same resistivity change of 0.1% for the covered heaters. For heater based on paste **I** an increase from 80 to 85 W and for the heater based on paste **II** an increase from 61 to 65 W was observed. The largest enhancement of about 22% is observed for the heater based on paste **III** (32 W for the uncovered and 39 W covered).

In order to probe the long time impact of the electric loading on the manufactured heater films a set of experiments under constant pulses loading were performed. The electric power of each pulse was chosen to generate a heat of approximately 200 °C on the substrate surface,

Table 3: electrical power for a resistivity change of 0.1% at 25 °C for the uncovered and covered heater film on Si_3N_4.

Heater film	Electrical power [W] uncovered	Electrical power [W] covered
paste **I** (0.1 ohm/sq)	80	85
paste **II** (1 ohm/sq)	61	65
paste **III** (10 ohm/sq)	32	39

independent from the layout of the test structure. The experiments were performed for 3000 cycles, which relates to a total load of about 4 hours. The obtained change of the resistivity for each paste is illustrated in Fig. 7. Paste **II** shows a change in the resistivity of about 12% for the timeframe of the experiment. In contradistinction show both, paste **I** and **III** a failure in the conductive paths. The significant increase in the change of the resistivity after 2945 cycles for paste **III** points at a disruption of one (or more) of the 8 parallel heater lines (see Fig. 1, layout heater 10). The total change in the resistivity is approximately 40% (27% after 2945 cycles) which is significant higher than the resistivity change obtained for paste **II**. Paste I failed in this experiment after 93 cycles, only. An image of the test substrate after the experiment is shown in Fig. 8.

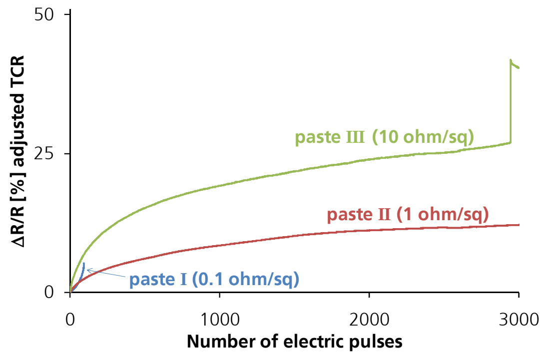

Figure 7: Resistance change for 3000 pulsed electrical load measurements at 200 °C on Si_3N_4.

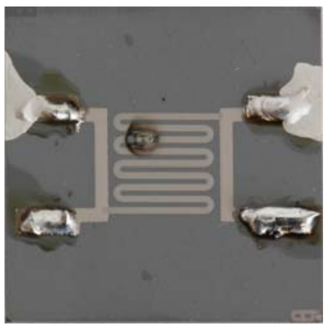

Figure 8: Image of a fused conductive path of paste I (0.1 ohm/sq) on Si_3N_4 after pulsed electrical load experiment.

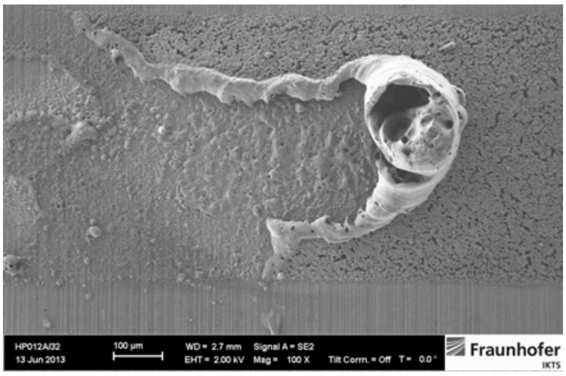

Figure 9: Surface FESEM image of the loaded film manufactured by paste I (0.1 ohm/sq).

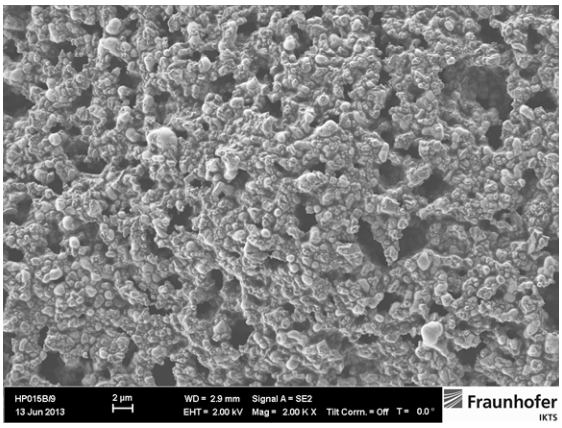

Figure 10: Surface FESEM image of the unloaded film manufactured by paste III (10 ohm/sq).

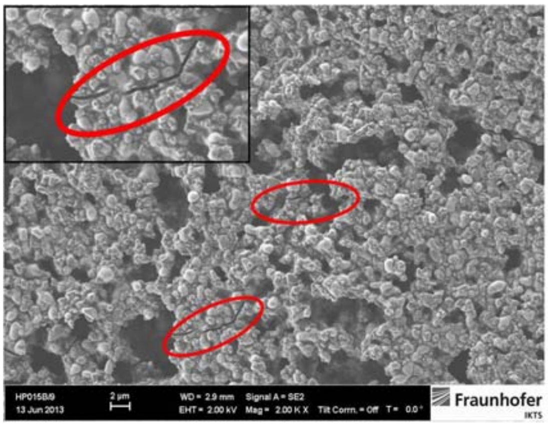

Figure 11: Surface FESEM image of the loaded film manufactured by paste III (10 ohm/sq), cracks indicated by red cycles, insert: enlargement of crack.

Surface analysis of heater films on Si_3N_4

The surface of selected loaded samples was analyzed by FESEM. The obtained image for paste **I** is shown in Fig. 9 and for paste **III** in Fig. 11. An unloaded surface image of paste **III** is shown in Fig. 10. A complete burn away is observed for the film of paste **I** (Fig. 9), whereas significant cracks are noticeable for the loaded sample of paste **III** (Fig. 11). Such cracks are not observed on the unloaded sample. Thus, the failure of the microstructure and subsequent the reduction in the number of available conductive paths in the heater film are responsible for the increase of the resistivity. Presumable a further loading would result in a similar burn away of the heater film for paste **II** and **III**.

Electrical pulse load behavior on AlN

Comparable pulse load experiments were performed with pastes **IV** to **VI** on AlN. The heater films were covered with a new developed overglaze, which is suitable for firing at 800 °C. The obtained change of the resistance with increasing power is shown in Fig. 12. The graphs illustrate a significant higher loading of the AlN heater films (manufactured by paste **IV** to **VI**) in comparison to the Si_3N_4 heaters. An electrical power of 232 W (paste **IV**), 216 W (paste **V**), and 148 W (paste **VI**) is required to result in change of the resistivity of 0.1% (Table 4).

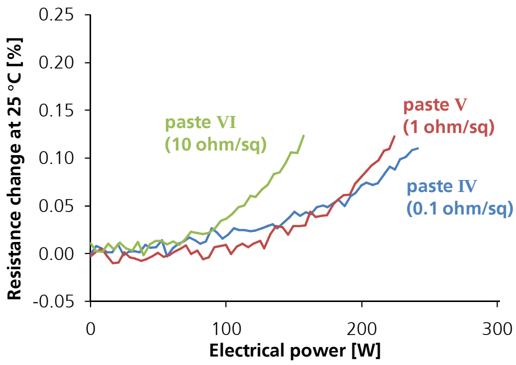

Figure 12: Change of the resistivity of the heater films based on paste I to VI at 25 °C in dependence on the electrical power on AlN.

Table 4: Electrical power for a resistivity change of 0.1% at 25 °C for the covered heater films on AlN.

Heater film	paste **IV** (0.1 ohm/sq)	paste **II** (1 ohm/sq)	paste **III** (10 ohm/sq)
Electrical power [W]	232	216	148

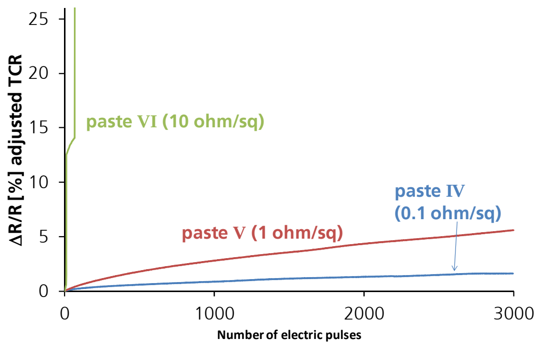

Figure 13: Resistance change for 3000 pulsed electrical load measurements at 200 °C on AlN.

Fig. 13 shows the results of loading experiments with a constant pulse (3000 cycles) for paste **IV**, **V** and **VI** on AlN. Again, the electric power was chosen to generate a surface temperature of 200 °C. The graphs point out that the heater film manufactured by paste **IV** (0.1 ohm/sq) and paste **V** (1 ohm/sq) result in a moderate drift of about 2% and 6%, respectively. Comparable experiments with the heater films based on paste **VI** (10 ohm/sq) show a significant resistivity change within the first part of the experiment.

Apart from the glass composition, the formulation of both sets of pastes (paste **I** to **III** for Si_3N_4 and paste **IV** to **VI** for AlN) is equal. Thus, either the substrate material properties, especially its thermal conductivity or the glass in the pastes is the dominate parameter for the power performance of the heater films. Presumable the latter is of reduced importance as significant changes of the resistivity are observable at temperatures of about 200 °C (Fig. 7 and 13), which is well below the glass transition temperature (Tg) of the used glasses. In contradistinction, the high thermal conductivity of AlN may prevent to a certain extent the formation of hot-spots in the heater films. Thus, the build-up of high peak temperatures on a local scale is reduced and the overall heater can be loaded with a higher electric power.

IV. Conclusions

The development of new Ag/Pd based resistor pastes for Si_3N_4 allows the production of thick film pastes with a sheet resistance of 0.1, 1.0, and 10 ohm/sq. The temperature coefficient of the resistance is between -100 and 100 ppm/K. Electrothermic pulse load investigations show a drift of the room temperature resistivity of 0.1% after a power load of 32 W (10 ohm/sq paste), 61 W (10 ohm/sq paste), and 80 W (0.1 ohm/sq paste), A slight increase in the power load to 39, 65 and 85 W, respectively, was achieved by covering the heater films with an overglaze. Long time cycle tests at a surface temperature of 200 °C reveal a rapid failure of the 0.1 ohm/sq paste. The 1.0 ohm/sq and 10 ohm/sq heater films undergo a resistivity increase by 12 and 40% during the timeframe of the experiment. Surface analysis show the appearance of cracks as main failure mechanism in the film structure after the loading experiments.

Experiments with comparable AgPd pastes for AlN show a significant higher power load. The 0.1% resistivity drift was observed after pulse power loads of 148 W (10 ohm/sq paste), 213 W (1.0 ohm/sq paste), and 232 W (0.1 ohm/sq paste). Cycle experiments (3000 cycles) at 200 °C reveal a drift of 2% for the 0.1 ohm/sq and 6% for the 1.0 ohm/sq paste.

A possible reason for the observed outrange in the power load of the AlN-system over the Si_3N_4-system is seen in the used substrate rather than in the paste glasses. The thermal conductivity of AlN is higher. Thus, the build-up of high peak temperatures on a local scale is reduced and the overall heater can be loaded with a higher electric power.

Acknowledgments

The authors gratefully acknowledge Kathrin Reinhardt and Sebastian Scholz for fruitful discussions.

References

[1] Fraunhofer IKTS; overview available AlN thick film pastes, Available: http://www.ikts.fraunhofer.de/en/research_fields/smartmicrosystems/Thick_Film_TechnologyPhotovoltaics/PastesAlN.html.

[2] M. Watt, “Design considerations for high temperature hydrid manufacturability,” in Proc. *Int. High Temp. Electron. Conf*., Albuquerque, NM, May 12-15, 2008, pp. 279-286.

[3] K. Hirao, K. Watari, M. E. Brito, M. Toriyama, S. Kanzaki, “High thermal conductivity in silicon nitride with anisotropic microstructure”, *J. Am. Cerma. Soc.* 79, 1996, 2485-2488.

[4] Sienna Technologies Inc.; Datasheet Au thick film paste, Available: http://siennatech.com/wp-content/uploads/2011/11/Gold_Silicon_Nitride1.pdf.

[5] P. Hagler, P. Henson, R. W. Johnson, ‘Packaging technology for electronic applications in harsh high-temperature environments’, *IEEE Transaction on Industrial Electronics*, 58, 7, 2011, 2673-2682.

[6] M. Wenzel, R. Schmidt, U. Partsch, M. Eberstein, ‘Thick film pastes for silicon nitride ceramics’, in Proc. *9th CICMT*, Orlando, USA, April 23-25, 2013.

[7] K. Reinhardt, C. Kretzschmar, R. Schmidt, M. Eberstein, ‘Silver/Palladium Pastes for Aluminium Nitride Applications’, in Proc. *18th European Microelectronics & Packaging Conference (EMPC)*, Brighton, UK, September 12-15, 2011, pp. 120-125.

[8] M. Hentsche, C. Kretzschmar, H. Grießmann, P. Marcinkowski, L. Rebenklau, ‘Thick film heater for aluminium nitride ceramics’, in Proc. *41st International Symposium on Microelectronics (IMAPS)*, Providence, Rhode Island, November 2-6, 2008, pp. 1224-1228.