Thick Film Systems for Challenging Applications

Michail Moroz

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# Advanced Approach to the Development of Thick Film Inks

- 1. Resistors: proprietary unique composite conductive phases
- 2. Set of proprietary special glasses as effective control tool for performance of fired elements
- 3. Concept of controlled paste rheology
- 4. Observing resistance formation directly during firing
- 5. Controlled crystallization approach for ultra-high value resistors and dielectrics

# Advanced Approach to the Development of Thick Film Inks **Resistors: Composite Conductive Phases**

- Composite conductive phases:
  - ✓ have unusual parabolic dependence of resistivity vs. glass content
  - ✓ solve one of the thick film resistor technology key problems such as anomalous conduction loss
  - ✓ provide new technique of TCR precise control
  - ✓ have unique sintering ability
  - ✓ provide flexibility with firing temperatures of resistive inks from 550°C to 1,300°C (not limited, may be raised to 1,600°C)

### High Resistivity Compositions: Stability Predicting Based on Shape of Dilution Curves

Pierce, Kuty, Larry, "The Chemistry and Stability of Ruthenium-Based Resistors", Third European Hybrid Microelectronics Conference 1981, Avignon, pp.283-301 8 Log Sheet Resistance 6 5 RuO Pyrochlore Series 17 Volume Fraction Conductive (VF)

 contrary to any commercially available high ohmic resistive ink, proprietary high-ohmic resistive inks have ~zero slope at the usable area

- How the shape of the dilution curve appears used to be a prime factor in predicting resistor stability
- dilution curve stands for a chart of resistivity or conductivity vs. glass or conductive phase content
- the smaller **rate of change in slope** of the dilution curve, the lower sensitivity to firing temperature variation, the better long-term, post trim, and under-electrical-load stability
- the lower the slope of dilution curve, the better resistor stability is expected
- ultimate case is zero slope of dilution curve
- **slope** of dilution curves **of commercially available** resistive inks:
  - $\checkmark\,$  has never approached to very low values
  - ✓ the only difference is how steep is the slope while it always stays quite high
- a unacceptably steep slope indicates **the anomalous conduction loss problem**

# Anomalous Conduction Loss in High Resistivity Compositions

- The properties of resistors having a low content of conductor phase relative to glass are extremely sensitive to the content of components and processing parameters
- very small changes in content of functional phase of resistive composition alter resistor parameters to a great extent
- resistor parameters affected: sheet resistivity, TCR, sensitivity to firing conditions, and all kinds of stability
- ruthenium-based resistors exhibit critical threshold of concentration and a critical conduction behavior
- the anomalous loss of conductivity in low-RuO<sub>2</sub>-content thick film resistors (striking increase in resistivity) is derived from the critical loss of ruthenium ions/clusters in the glass (Adachi, Kuno, "Effect of Glass Composition on the Electrical Properties of Thick Film Resistors", Journal of American Ceramic Society, 83 [10], 2000, pp. 2441-48

# **Publications Regarding Anomalous Conduction Loss Problem**

- R.Cote, "Progress in Thick Film Materials and Processes". Electronic Engineering, Sept. 1984, pp.173-175
- P.F. Carcia and A.Suna, "A Comparison of the Conduction Properties of RuO<sub>2</sub> and Pyrochlore Thick Film Resistors". Proceedings 33rd Electronic Components Conference, 1983, pp.280-283
- J. R. Rellick and A.P. Ritter, "Non-Trimmed Buried Resistors in Green Tape™ Circuits", Proceedings of International Conference on High Density Packages & MCMs, Apr 6 – 9, 1999, Denver, CO
- K. Adachi & H. Kuno, "Effect of Glass Composition on the Electrical Properties of Thick Film Resistors", Journal of American Ceramic Society, 2000, Vol. 83, No 10, pp.2441-2448
- M. Moroz, "High Ohmic Value Resistive Inks", Proceedings of the 45th IEEE Electronic Components and Technology Conference; May 21-24, 1995; Las Vegas, Nevada, USA, pp. 964 – 969
- M. Moroz, "A New Generation of Ruthenium-based Thick Film Resistors", Annual Can-Am ISHM Symposium on Advances in Microelectronics & Packaging; Sept. 23-24, 1996; Granby, Quebec, Canada
- F. Zandman, P. Simon, and J. Szwarc, "Resistor Theory and Technology", 2001 by Vishay Intertechnology, Inc., Malvern, PA

# Anomalous Conduction Loss in High Resistivity Compositions



M. Moroz, "High Ohmic Value Resistive Inks", Proceedings of the 45th IEEE Electronic Components and Technology Conference; May 21-24, 1995; Las Vegas, Nevada, USA, pp. 964 – 969



Fig. 6 The curve above represents the variation in conductivity of the mixture as a function of the ratio p, where p = number of conducting balls/total number of balls.

F. Zandman, P. Simon, and J. Szwarc, "Resistor Theory and Technology", 2001 by Vishay Intertechnology, Inc., Malvern, PA

# Resistivity and TCR Change vs. Glass Content for Composite Conductive Phase Based Inks



- Each parabolic curve corresponds to single desired resistivity
- All compositions are blendable and provide uninterrupted series of resistive inks
- As calculated, RuO<sub>2</sub> content in composite conductive phases (CCP) is from 2% to 10%
- CCP/glass ratio in composite conductive phases is ~ 50/50
- Total content of  $RuO_2$  in any resistive ink is  $\sim (1-5)\%$
- Ruthenium-based conductive phases are distributed in powder compositions on colloidal level
- New technique for precise TCR control has been contrived

# Resistivity and TCR Change vs. Glass Content for Composite Conductive Phase Based Inks

 In contrast to an exponential dependence of resistivity versus glass/conductive phase ratio typical for traditional high ohmic resistive compositions, resistivity of developed materials has a parabolic dependence with a minimum value at specific range of ingredients content, i.e. relatively wide range of practically constant minimum resistivity

 In the range of glass content in composition from ~50% to 60% resistivity remains practically constant but TCR smoothly alters from - 100 ppm/°C to +100 ppm/°C. As part of this work, a new method of TCR precision control was contrived

Glass Content, %	Resistivity, KΩ/⊡	TCR, ppm/°C
22	7950	-420
32	800	-350
40	270	-290
45	150	-190
50	95	-60
55	85	30
60	95	100
70	315	150
75	1190	140
78	3980	130

# Resistivity vs. Peak Firing Temperature



# Advanced Thick Film Inks Development Approach: Set of Special Glasses as Control Tool

- > 160 glass compositions starting from basic three-components to complicated multicomponent glasses were made and tested during 10 years
- at least 6 resistive inks were made with each glass and tested
- correlation between glass compositions and resistors / conductor properties has been used as effective control tool for inks development
- own glass compositions allow effective control of resistor characteristics such as:
  - $\checkmark\,$  resistivity vs. resistor size and number of squares
  - TCR values and dependence from testing temperature (TCR curve slope) vs. resistor size and number of squares
  - $\checkmark\,$  re-firing and overglaze firing shift





# Advanced Thick Film Inks Development Approach: **The Concept of Controlled Paste Rheology**



# Concept of Controlled Paste Rheology: Viscosity and Slope Up/Down Curves



- judicious choice of organic vehicle compositions allows forming of required shapes of viscosity/slope up/down curves for fine line and thick print applications
- actual optimal for specific applications viscosity/slope up/down curves differ greatly from the typical ones

# Advanced Thick Film Inks Development Approach: Direct Observing of Resistance During Firing/Re-firing

Taking resistance measurements during firing and re-firings helps to:

- ✓ control resistor formation process
- ✓ develop glass compositions for specific resistor applications
- ✓ define and improve resistor stability and sensitivity to firing conditions
- ✓ predict resistance shift after re-firing and overglazing
- ✓ monitor resistive ink reproducibility and identify different resistive ink lots
- ✓ clarify and split resistor/substrate/overglaze ink interaction problems
- ✓ save time required for resistive ink development

## Observing Resistance Formation During Firing: Low Ohmic vs. High Ohmic



Low ohmic resistors are much more stable than high ohmic resistors and have specific resistance formation curve shape during firing

Regular high ohmic resistors just drop resistance during firing that makes them very sensitive to firing conditions

### Observing Resistance Formation During Firing: Composite Conductive Phase-based 100 KΩ/□ Ink



Resistance formation shape of represented high ohmic resistive inks is similar to the shape of low ohmic resistors providing much better resistors sensitivity to firing conditions and stability

## Direct Observing of Resistance During Firing/Re-firing: **Predicting Re-firing Shift**



- Resistance shift versus refiring temperature may be chosen deliberately for the given resistor system
- re-firing at 850°C:
  - ✓ three critical areas were observed: 1,2,3
- area 1: <670°C
  - ✓ resistance decreased
- area 2: (670-800)°C
  - ✓ resistance started increasing at 680°C
- area 3: 800°C
  - ✓ resistance grows reached maximum at 800°C
- results of separate firings at 650°C, 750°C, and 800°C confirmed data obtained during re-firing at 850°C:
  - ✓ 1: initial R decreased
  - ✓ 2: initial R increased
  - ✓ 3: initial R increased at maximum value

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# Advanced Ink Development Approach: Controlled Crystallization

- Controlled crystallization approach for ultra-high value resistors and dielectrics:
  - ✓ vitrification / de-vitrification balance must be controlled for:
    - ⇒ ultra-high ohm value resistive inks containing composite ruthenium-based conductive phases and glasses
    - $\Rightarrow$  dielectric inks containing ceramic fillers and glasses
- Crystallization intensity must be kept in narrow range:
  - ✓ high enough to initiate sufficient rate of crystallization and CTE change dynamics
  - ✓ slow enough to provide specific ratio of glass phase for adhesion and filling voids inside film being fired

# Ultra High Ohm Value Thick Film Resistors The Approaches Being Used in the Industry

- Although there are no commercially available high ohmic resistive inks above at least 1 GΩ/□ with satisfactory performance, circuit manufacturers supply resistor networks with resistance up to Tera-Ohms total resistance
- it becomes possible through the use of alternating techniques of increase of actual number of squares for achieving of the highest actual resistance while conventional thick film techniques presume only paste resistivity increase along with moderate number of squares
- **first approach**: using of middle-range resistivity inks with out of the ordinary number of laser cuts:
  - $\checkmark$  some thousands of squares
  - $\checkmark$  the cuts cover substantial part of resistor surface
- **second approach**: direct writing of resistive lines in fine-line patterns:
  - ✓ ultra-fine resolution (4 8 mil line/gap)
  - the key features are: special equipment and carefully developed specific process that cannot be easily established and employed by any circuits/resistor networks manufacturer
- **common feature** for two approaches:
  - very high total resistance values can be produced from a given thick film compositions with a lower sheet resistivity providing better performance comparing to commercially available higher resistivity inks
  - ✓ estimated employed inks resistivity range: (1 10) KΩ/□

# Ultra High Ohm Value Thick Film Resistors **A Multitude of Laser Cuts Approach**



Experimental precise resistor inks were laser trimmed with number of cuts 10, 20, 40, and 80. The effect of number of laser cuts on resistivity and TCR was examined.

The biggest difference was observed between non-trimmed resistors and laser trimmed resistors groups. Initial TCR  $\sim +25 \text{ ppm}/^{\circ}\text{C}$  of non trimmed resistors after first 10 cuts dropped down to  $\sim < \pm 10 \text{ ppm}/^{\circ}\text{C}$ .

Then within laser trimmed resistor group the dependence of TCR versus number of cuts was minimal. Such predicted shift provides additional process control of resistors production.

# Ultra High Ohm Value Thick Film Resistors **A Multitude of Laser Cuts Approach**



5 K $\Omega/\Box$  experimental resistive ink with controlled TCR curve close to zero slope was used

 $80\ cuts$  provided total resistance  $16\ M\Omega$ 

Although significant increasing number of squares through multitude laser cuts is feasible, practical use of this technique is limited due to required expenditure of labor and expensive equipment units cost required for high volume circuits production

As an alternative for the given circuit, 2,500-squares resistor may be printed at 6-mil line/gap resolution by conventional screen printing technique using a very precise 40 K $\Omega/\Box$ experimental fine line resistive ink on the major resistor area providing 10 M $\Omega$  total resistance

# Ultra High Ohm Value Thick Film Resistors

Development Concept:

- ✓ ultra high ohm value resistor range is achieved by combining of two factors:
  - ⇒ resistor compositions with resistivity much greater than  $10 \text{ M}\Omega/\Box$  having enhanced stability up to  $1 \text{ G}\Omega/\Box$
  - $\Rightarrow$  resistive inks capable to form fine line resistor networks with fired film thickness inherent to regular print resolution
- ✓ resistors must have microstructure of sintered ceramics formed during firing of resistive inks
- ✓ resistive inks should be capable to form serpentine fine print resistor networks by conventional screen printing technique with resolution / number of squares comparable to those achievable by using of unique OhmCraft Micropen technology
- ✓ minimized and controllable dependence of resistivity versus number of squares is a matter of great importance

# Ultra High Ohm Value Thick Film Resistors Silver Migration from 100% Ag Termination



- The silver diffusion zone may extend up to ~15 mils distance from each side of resistor conductor boundary after initial firing
- Each additional post-firing may enlarge the diffusion zone
- Resistor square size 30 to 40 mils is considered as critical
- Ag migration into resistor becomes a matter of vital importance for small size chip resistors
- Proper resistor ink development must always include minimizing of R and TCR dependence on resistor size in the specified resistor size range

# Ultra High Ohm Value Thick Film Resistors **Resistor Test Patterns**



- Resistor test pattern for manual data readout
- Resistor sizes, millimeters:

✓ 0.3 x 0.3	✓ 0.4 x 1
✓ 0.4 x 0.4	✓ 0.5 x 1
$\checkmark 0.5 \times 0.5$	✓ 1 x 1
$\sqrt{1 \times 1}$	✓ 2 x 1
$\sqrt{2}$	✓ 3 x 1
• 2 x 2	✓ 5 x 1
• 3 X 3	✓ 10 x 1
• 4 X 4	✓ 25 x 1



- Resistor test pattern for automatic computerized data readout
- Resistor sizes, mils:

✓ 15 x 15	✓ 40 x 40
✓ 20 x 20	✓ 80 x 40
✓ 30 x 30	✓ 120 x 40
✓ 40 x 40	✓ 200 x 40
✓ 80 x 80	✓ 400 x 40
	✓ 2,340 x 20

# Ultra High Ohm Value Thick Film Resistors **Resistivity Versus Resistor Size**

1, 2, 3, 5, 10 - Squares @ 40-mil Width and 117 squares @ 20-mil Width Resistors

	Resistivity, Ω						tor	
Juk	40x40 80x40	80=40 120=40	120-40	200x40	400x40	117 Sq		onpu
		00240	120140			Total	<u>Ω</u> /□	Ŭ
99-64 വ	8.6E+07	1.5E+08	2.8E+08	4.5E+08	6.8E+08	6.1E+09	5.2E+07	CSP-10

8-mil Line/Gap Serpentine and 1-Square @ 40-mil Width Resistors

Ink	Line /	Resistance Total, Ω Number of		Resistivity, Ω/□		
IIIK	mil	Serpentine	Squares	1 🗖	Serpentine	
99-64	8	6.00E+11	5,848	1.15E+08	1.03E+08	



15-mil square resistor printed above pre-fired conductor Conductor printed above pre-fired 15-mil square resistor

Small-size resistors (≤15-20 mil square) may be printed/fired before conductor for better print definition provided that resistor and TCR shift after re-firing is predicted and minimized.



8-mil Line/Gap Serpentine Resistors

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6-mil Line/Gap Serpentine Resistors

Michail Moroz



M28456@outlook.com



6-mil Line/Gap Serpentine Resistors



5-mil Line/Gap Serpentine Resistors

For conventional screen printing technique achieving of high resolution with no shortcuts is a challenging target number one.

Second challenging task is keeping acceptable thickness at fine line patterns ≤ 10 mil line/gap resolution

Height decrease of printed thick film lines is a common phenomenon

Developed materials have desired fired film thickness up to 5 mil line/gap resolution

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4-mil Line/Gap Serpentine Resistors

3-mil Line/Gap Serpentine Resistors

4-mil and 3-mil line/gap resolution with no shortcuts was achieved

Fired print thickness at 4-mil resolution was still reasonable but not uniform

Fired print thickness at 3-mil resolution dropped to unacceptable ~ 3  $\mu$ m fired thickness

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# Ultra High Ohm Value Thick Film Resistors Surface Quality



325-mesh screen, 20-mil Line/Gap Serpentine Ultra-High Ohm Value Resistor Thickness of Resistor at 145 Mesh Screen 80x80 mil Ultra-High Ohm Value Resistor

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# Ultra High Ohm Value Thick Film Resistors Surface Quality



80x80 mil Ultra-High Ohm Value Resistor 145 Mesh Screen

Such applications as trimmers and potentiometers require very smooth and thicker resistive layers

When using 325-mesh screen, fired thickness is ~ 12  $\mu$ m

Coarse 145-mesh screen allows fired thickness ~ 25  $\mu$ m while surface quality does not suffer

# Thick Film Resistors for Harsh Environment Applications High Temperature



#### **Resistance Change vs. Storage Temperature**

# Thick Film Resistors for Harsh Environment Applications High Temperature



**Resistance Change vs. Storage Temperature** 

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## Thick Film Resistors for Harsh Environment Applications High Temperature



## Thick Film Resistors for Harsh Environment Applications High Temperature



Storage Time at 450°C, Hours

#### Thick Film Resistors for Harsh Environment Applications **Extreme Cold**



#### Thick Film Resistors for Harsh Environment Applications Extreme Cold, TCR vs. Temperature from 25°C to -155°C



Regular hybrid resistors with TCR ~-100 ppm/°C at -55°C have TCR ~-250 ppm/°C at -150°C due to excessive slope of TCR curves vs. testing temperature



Specified and minimized controlled TCR curve shape and slope in wide resistor size range is mandatory requirement for thick film resistor designed for working at extreme temperature environments

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#### Thick Film Resistors for Harsh Environment Applications Extreme Cold, R<sub>1</sub>/R<sub>2</sub> Ratio Change from 25°C to -155°C



The issues inherent to standard resistors:

- ✓ acceptable at -55°C -1%, R<sub>1</sub>/R<sub>2</sub> ratio for 10 to 1 square resistor pair rises to -2.5% at -150°C
- $\checkmark$  due to Ag migration from conductor,  $R_1/R_2$  ratio strongly depends on resistor size

High precision thick film resistor system:

- ✓ R<sub>1</sub>/R<sub>2</sub> ratio has minimal change from 25°C to -150°C
- ✓ even with 100% Ag conductor, dependence on resistor size is minimal

#### Co-fired Buried LTCC Resistors for Harsh Environment Applications -**150°C to +300°C**



Co-fired buried resistors in A6S tape:

- TCR within ±-100 ppm/°C at -150°C to +300°C after first firing and third re-firing at 850°C
- Resistor size from 15x15 mil to 80x80 mil

#### "Thrifted" Ag/Pd Surge Resistors

- "Thrifted" Ag/Pd surge resistor term means:
  - ✓ low ohmic value resistor pastes containing a minimized quantity of palladium in comparison to the industry standard 44/56 Ag/Pd resistors
  - ✓ this reduction in palladium content results in a significant reduction in cost, while performance of the materials remains similar to standard ones
- challenges dealing with Pd content reduction:
  - ✓ very high positive TCR
  - ✓ undesirable ink rheology change (viscosity/slope balance) and resultant poor resistor print shape deteriorating surge performance
  - ✓ lower voltage performance:
    - $\Rightarrow$  noticeable negative resistance drop after surge test
    - $\Rightarrow$  much less voltage to failure
  - ✓ much higher long-term resistance drift

#### "Thrifted" Ag/Pd Surge Resistors **Performance of Developed Materials vs. Standard**

- Standard Ag/Pd surge resistors characteristics:
  - ✓ Pd/Ag ratio: 56/44
  - ✓ resistivity:  $0.1 \Omega/\Box 1.0 \Omega/\Box$
  - $\checkmark$  TCR: < ± 100 ppm/°C
  - ✓  $R_1/R_2$  ratio relative change vs. temperature: < ± 0.2%
  - ✓ R<sub>1</sub>/R<sub>2</sub> ratio change after surge test: < 0.1%</li>
  - ✓ long-term drift after lighting surge: < 0.1%</li>
- both standard and "thrifted" Ag/Pd systems are:
  - ✓ Pb-free
  - ✓ compatible with AlN substrates

- "Thrifted" Ag/Pd surge resistors development results:
  - $\checkmark\,$  reduced palladium content by 30% 50%
  - ✓ resistivity: 0.1  $\Omega$ /□ 1.0  $\Omega$ /□
  - ✓ TCR: < 400 ppm/°C
  - ✓ TCR deviation from -55°C to +125°C:
     < 30 ppm/°C</li>
  - ✓  $R_1/R_2$  ratio relative change vs. temperature: < ± 0.2%
  - ✓  $R_1/R_2$  ratio change after surge test: < 0.1%
  - ✓ long-term drift after lighting surge: < 0.1%
  - ✓ optimized:
    - $\Rightarrow$  inks rheology and printability
    - $\Rightarrow$  resistivity vs. peak firing temperature
    - $\Rightarrow$  hot/cold TCR curve slope
    - $\Rightarrow$  long-term stability
    - $\Rightarrow~$  resistance shift after lighting surges
    - $\Rightarrow$  voltage to failure

#### "Thrifted" Ag/Pd Surge Resistors **R & TCR vs. Ag/Pd Ratio**

Pd Content, %wt 55 45 40 30 2520 15 10 0.8 900 TCR of Ag-Pd Alloys 4000 800 0.7 Resistivity,  $\Omega/\Box$ 2000 yg 1000 3000 700 0.6 1000 600 0.5 ppm 20 30 KO 60 60 60 10 80 90 00 500 Pd Content 0.4 400 300 L 0.3 0.2 200 ←Resistivity ←TCR 0.1 100 0 0 45 55 60 70 75 80 85 90 Ag Content, %wt

- TCR of pure Ag and Pd: several thousands of ppm/°C
- Ag/Pd mixtures ~ 44/56 exhibit TCR ≤ 100 ppm/°C
- In Ag-rich area TCR is very high and very sensitive to Ag/Pd ratio small changes
- TCR in the area
   ~Ag(55-75) / Pd(45-25)
   is relatively stable
   acquiring values ~ ≤ +400
   ppm/°C

#### "Thrifted" Ag/Pd Surge Resistors



- ✓ TCR of standard Ag/Pd resistors is:
   < ± 100 ppm/°C</li>
- ✓ TCR of "Thrifted" Ag/Pd resistors is:
   < + 400 ppm/°C with controlled TCR slope: TCR deviation from -55°C to + 125°C: < 30 ppm/°C</li>
- ✓  $R_1/R_2$  ratio relative change of resistor pair vs. temperature is within ± 0.2 % in both cases
- ✓ for surge resistor applications using pair of matched resistors on a common single-inline (SIL) substrate, R<sub>1</sub>/R<sub>2</sub> of resistor pair vs. temperature is even more important than TCR absolute value of single resistor

#### "Thrifted" Ag/Pd Surge Resistors **Rheology Optimization and Printability**



Viscosity/slope balance of organic vehicles must be taken in consideration as it determines print quality and thus determines surge performance

Print imperfection: dry line due to improper viscosity/slope ratio

200kV FERRO

#0000

#### "Thrifted" Ag/Pd Surge Resistors **R<sub>1</sub>/R<sub>2</sub> Relative Ratio Change After Surge Test per Bellcore Spec**



#### "Thrifted" Ag/Pd Surge Resistors Long-Term Resistance Drift After Surge Test



- More positive resistance shift (+2% - +5%) was initially observed for "thrifted" surge resistors with much lower Pd content
- RE88 resistive compositions were optimized in order to minimize the observed positive shift
- long-term resistance shift may differ depending on the overglaze ink composition and overglaze firing profile but may be easily minimized for the specific overglaze conditions

- Ag/Pd "thrifted" resistive compositions may be employed as shunt resistors with pre-selected resistivity/TCR balance
- distinctive feature of the developed materials:
  - thick print capability based on judicious choice of Ag and Pd powders morphology and organic vehicles compositions that provide required ink rheology:
    - $\Rightarrow$  30  $\mu m$  thickness, <7 mΩ/□, TCR <550 ppm/°C at 200M 35ET screen, one layer
    - $\Rightarrow$  45-50  $\mu m$  thickness, <4 mΩ/□, TCR < 550 ppm/°C at 145M 20ET screen, one layer
    - $\Rightarrow$  65 µm thickness, <3 mΩ/□, TCR 550 ppm/°C at 105M 40ET screen, one layer
    - $\Rightarrow$  95-100 µm thickness, <2 m $\Omega/\Box$ , TCR < 550 ppm/°C at 145M 20ET screen, two layers
    - $\Rightarrow$  ~170 µm thickness at 105M 40ET screen, three layers may be obtained, if applicable
  - ✓ adhesion > 7.5 Lbs. on 2mm x 2mm pads
  - ✓ Pd/Ag ratio < 20/80



Ag/Pd shunt resistive compositions represent a typical trade-off between resistivity and TCR defined by palladium/silver ratio



Thick print capability for low-resistance shunt application plays a key role as it allows achieving of the lowest resistivity at the required TCR value

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100.

80.

60.

40

20.



145-mesh 20-micron emulsion 2 layers 95-100  $\mu m$  thickness

 $<2 \text{ m}\Omega/\Box$ , TCR <550 ppm/°C Pd/Ag < 20/80

#### Cu/Ni/Cr System as an Alternative to Ag/Pd Surge Resistors

Cu/Ni/Cr resistors/conductor system:

- ~ 10 times lower cost comparing to Ag44/Pd56 surge resistors
- compatible with AlN substrates
- Pb-free
- extended resistivity range: from 50 m $\Omega/\Box$  to 5  $\Omega/\Box$  with TCR < ± 100 ppm/°C, and down to 20 m $\Omega/\Box$  with TCR < + 200 ppm/°C
- small size under 15-mil square and fine print serpentine resistors starting from 6 mil line/gap already suitable for reliable production and may be extended
- fine print ability (~150 squares on 1206 size (@ 6 mil line/gap) can provide new technical solutions for applications like hybrid resistors and integrated resistors for LEDs
- compatible pure copper conductors with fine line and thick print abilities provide additional advanced design opportunities
- compatible copper/nickel conductor is suitable for high temperature applications when pure copper is susceptible to oxidation

#### Cu/Ni/Cr System as an Alternative to Ag/Pd Surge Resistors



 $50 \text{ m}\Omega/\Box$  20-mil Line/Gap 200 mesh,  $950^{\circ}\text{C}$ 

 $75 \text{ m}\Omega/\Box$  6-mil Line/Gap 325 mesh, 950°C

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#### Cu/Ni/Cr System as an Alternative to Ag/Pd Surge Resistors



 $5 \Omega/\Box$  6-mil Line/Gap 325 mesh 950°C

## Thick Film Resistors for AlN Substrates

- Problems with commercially available resistors on AlN substrates:
  - ✓ glasses, especially with high PbO and Bi<sub>2</sub>O<sub>3</sub> content, react with AlN substrate during firing process forming bubbles and non-functional layers
  - ✓ chemical reactions between RuO<sub>2</sub> and AlN are another reason for the bubbles and for the sensitivity to firing conditions
  - ✓ referring to the literature, the most intensive AlN oxidation and chemical reactions between AlN, RuO<sub>2</sub> and glass start at the temperatures greater that 750°C
- the most difficult problem so far:
  - ✓ development of resistor pastes with sheet resistivity from > 1 KΩ/□ to 1 MΩ/□ and greater

#### Thick Film Resistors for AlN Substrates

Commercially available materials at the present time:

- ✓ Ag/Pd series:
  - $\Rightarrow$  DuPont AN590 series: 200 m $\Omega/\Box$  1 $\Omega/\Box$
  - $\Rightarrow$  Fraunhofer IKTS FK9900 series: 100 m $\Omega/\Box$   $1\Omega/\Box$
  - $\Rightarrow$  Tanaka AN9000 series: 30 m $\Omega/\Box$  500 m $\Omega/\Box$
- ✓ Ruthenium-based series:
  - $\Rightarrow$  DuPont AN600 series: 10  $\Omega/\Box$  1 K $\Omega/\Box$
  - ⇒ Fraunhofer IKTS FK9600 series: 10  $\Omega/\Box$  1K $\Omega/\Box$
  - $\Rightarrow$  Tanaka RAN series: 10  $\Omega/\Box$  1 K $\Omega/\Box$

# Thick Film Resistors for AlN Substrates **Development Results**

- Three groups of materials were developed for AlN substrates:
  - 1) low temperature firing Ru/Ag/Pd series:
    - ✓ some sub-series for firing @ temperature range 620°C 725°C in air:
      - $\Rightarrow$  from 1  $\Omega/\Box$  to 10 M $\Omega/\Box$
      - $\Rightarrow$  Ag/Pd is used for low-end resistivity range only
  - 2) directly fired in nitrogen Ni/Cr/Ru series:
    - ✓ for firing @ temperature range 950°C 1,000°C:
      - $\Rightarrow$  from 20 m $\Omega/\Box$  to 20 M $\Omega/\Box$
  - 3) high ohm value Ru-based series fired in air:
    - ✓ for firing @ temperature range  $900^{\circ}$ C 1,100°C:
      - $\Rightarrow$  from 1 K $\Omega$ / $\Box$  to 100 M $\Omega$ / $\Box$
- **common features** of all three series for AlN substrates:
  - ✓ are based on unique ruthenium based composite conductive phases allowing sintering of resistor microstructure during firing prior to the temperature range when AlN affects resistors
  - $\checkmark\,$  fine line printing ability, at least 6-mil line/gap

#### Thick Film Resistors for AlN Substrates Low Temperature Firing Ru/Ag/Pd series



1 M $\Omega$ / $\Box$  ruthenium-based resistors on AlN 620°C

10 K $\Omega$ / $\Box$  ruthenium-based resistors on AlN 620°C

#### Thick Film Resistors for AlN Substrates Directly fired in Nitrogen Ni/Cr/Ru series



8 M $\Omega$ / $\square$  Ni/Cr/Ru resistors on AlN 900°C N<sub>2</sub> on Cu conductor

8 M $\Omega$ / $\square$  Ni/Cr/Ru resistors on AlN 900°C N<sub>2</sub> on Cu/Ni conductor

Compatible Cu/Ni conductor is suitable for high temperature applications when pure copper is susceptible to oxidation

## Thick Film Resistors for AlN Substrates Directly fired in Nitrogen Ni/Cr/Ru series



650 m $\Omega$ / $\square$  Ni/Cr resistor on AlN 950°C N<sub>2</sub> 6-mil line/ 4-mil gap  $3 \Omega/\Box$  Ni/Cr/Ru resistor on AlN 950°C N<sub>2</sub> 10-mil line/gap

## Thick Film Resistors for AlN Substrates Directly fired in Nitrogen Ni/Cr/Ru series



30 K $\Omega$ / $\Box$  Ni/Cr/Ru resistor 80x40 mil on alumina fired in N<sub>2</sub> 950°C

35 K $\Omega$ / $\square$  Ni/Cr/Ru resistor 80x40 mil on AlN fired in N<sub>2</sub> 950°C

The same ink printed on alumina and AlN. Surface quality and resistivity are the same.

AlN substrate does not affect the resistor.



## Thick Film Resistors for AlN Substrates Suppliers'1 (Japan) 1 KΩ/□ Ink Fired in Air



- supplier's 1 (Japan) 1 KΩ/□ rutheniumbased resistor ink for firing on alumina, applied **on alumina** substrate at 850°C
- supplier's 1 (Japan) 1 KΩ/□ ruthenium-based resistor ink for firing on alumina, applied on AlN at 850°C, resulted in open circuit
- the temperature ~750°C when resistor started reacting with AlN substrate, was recorded during firing

## Thick Film Resistors for AlN Substrates High Ohm Value Ru-based Series Fired in Air



 own 10 KΩ/□ Ruthenium-based resistor ink printed on alumina fired in air at 950°C

- own 10 KΩ/□ Ruthenium-based resistor ink printed on AlN fired in air at 950°C
- same resistivity on alumina and AlN
- no reaction of resistor with AlN substrate

#### Thick Film Resistors for AlN Substrates Samples on AlN for High Temperature Storage



- 500 K $\Omega$ / $\Box$  resistors on AlN
- made of ruthenium-based composite conductive phase
- fired at 975°C in BTU belt furnace, 10 min at peak, 60 min total
- prepared for prolonged high temperature storage at 450°C

## Thick Film Resistors for AlN Substrates **High Temperature Storage on AlN and Al<sub>2</sub>O<sub>3</sub>**



Storage Time at 450°C, Hours

Results of high-temperature storage 550 hr. at 450°C:

- 500 K $\Omega$ / $\Box$  # 1 on AlN:
  - $\Rightarrow \ negative \ direction \ of \\ resistance \ shift \ <5\%$
- 500 K $\Omega$ / $\Box$  # 2 on AlN:
  - $\Rightarrow$  positive direction of resistance shift <8%
- $3 \text{ M}\Omega/\Box$  on  $\text{Al}_2\text{O}_3$ :
  - $\Rightarrow$  very small resistance shift < 1%

As it can be seen from the results for own 500 K $\Omega/\Box$  inks # 1 and #2 on AlN:

• resistance drift is controllable, may be adjusted for specific application and minimized

While the highest resistivity of commercially available inks on AlN is  $1K\Omega/\Box$ , own 500  $K\Omega/\Box$  on AlN has superior stability at 450°C high temperature storage test

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#### LTCC Resistors

LTCC resistors integration challenges:

- shrinkage mismatch and complications due to chemical reactions and iterative re-firings strongly affect resistor performance
- unusual effects of common modifiers on TCR
- unpredictable resistor performance shift
- buried resistor values commonly cannot be adjusted by laser trimming
- required resistor performance stability after multiple re-firings at 850°C
- electrical properties of co-fired buried resistors after subsequent re-firings must be accurately predictable

### Co-fired Buried 100 KΩ/ □ LTCC Resistors: Resistivity & TCR vs. Size & Re-firings



• 100% Ag conductor was used for terminations

Temperature, °C

- 100 K $\Omega$ / $\Box$  co-fired buried Pb-free LTCC resistors after first firing and three re-firings exhibited:
  - $\checkmark$  relative resistance change within  $\pm 10\%$  for resistor size range from 15x15 mil to 80x80 mil
  - ✓ TCR within  $\pm$  100 ppm/°C for resistor size range from 15x15 mil to 80x80 mil

#### Co-fired Buried 100 KΩ/ □ LTCC Resistors: **Resistivity vs. Number of Firings & Resistor Size**



#### Co-fired Buried 100 KΩ/ LTCC Resistors: **TCR vs. Number of Firings & Resistor Size**



## Silver-based Fine Line/Thick Print Conductors

Ag-based conductor inks system:

- ✓ completely Pb-free
- $\checkmark\,$  intended for use on both alumina and AlN substrates
- ✓ excluding resolution ≤ 5 mil line/gap, the same ink may be used for both fine line and thick print applications by changing applicable screens
- ✓ fired thickness of fine line samples is within the range18-20 µm at both 10-mil and 5-mil line gap resolution
- $\checkmark\,$  fired thickness of thick print samples is within the range170-180  $\mu m$  at three layers when screen 105 mesh 20  $\mu m$  emulsion was used
- ✓ resistivity of fine line samples at 5-6 mil line/gap resolution: < 2 m $\Omega/\Box$
- ✓ resistivity of thick print samples at 105 mesh 20  $\mu$ m emulsion drops from < 0.5 mΩ/□ at 1 layer to < 0.2 mΩ/□ at three layers
- $\checkmark$  adhesion > 5 N/mm<sup>2</sup>
- paste supplier's 4 (Japan) Ag-based conductor inks were 15 μm thick at 10-mil and 11
   μm at 5-mil line/gap resolution while printed and fired in the same conditions
- ✓ paste supplier's 5 (USA) Ag-based conductor inks were 10 µm thick at 10-mil and 6 µm at 5-mil line/gap resolution while printed and fired in the same conditions
## Silver-based Fine Line Conductors



Paste Supplier's 4 (Japan) Ag-based conductor ink 10-mil line/gap 325 mesh, 850°C Own Ag-based conductor ink 10-mil line/gap 325 mesh, 850°C

## Silver-based Fine Line Conductors



Paste Supplier's 4 (Japan) Ag-based conductor ink on alumina 5-mil line/gap 325 mesh, 850°C Own Ag-based conductor ink on AlN 5-mil line/gap 325 mesh, 850°C

# Silver-based Fine Line Conductors



Paste Supplier's 4 (Japan) Ag-based conductor ink 5-mil line/gap 325 mesh, 850°C

Own Ag-based conductor ink on AlN 5-mil line/gap 325 mesh, 850°C

## Silver-based Thick Print Conductors



Paste Supplier's 4 (Japan) Thick print Ag-based conductor ink 3 layers 40-mil line/gap 105 mesh, 20 µm emulsion, 850°C Own Thick print Ag-based conductor ink 3 layers 40-mil line/gap 105 mesh, 20 µm emulsion, 850°C

## Silver-based Thick Print Conductors



Own Ag-based conductor ink (170-180)  $\mu$ m thick @ 3 layers 40-mil line/gap 105 mesh, 20  $\mu$ m emulsion, 850°C, 0.14 m $\Omega/\Box$ 

## Silver-based Thick Print Conductors



# Silver-based Thick Print Conductors Effect of Unsuitable Morphology of Ag Powders



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# Silver-based Thick Print Conductors for Sharp Definition Prints for Microwave Applications



# Silver-based Thick Print Conductors for Extra Smooth Conductors Surface



# **Copper-based Fine Line/Thick Print Conductors**

Cu-based conductor inks system:

- ✓ completely Pb-free
- $\checkmark\,$  intended for use on both alumina and AlN substrates
- $\checkmark\,$  compatible with Cu/Ni/Cr and Ni/Cr/Ru resistor systems
- ✓ excluding resolution ≤ 5 mil line/gap, the same ink may be used for both fine line and thick print applications by changing applicable screens
- $\checkmark\,$  fired thickness of fine line samples is within the range19-20  $\mu m$  at 10-mil and 16-18  $\mu m$  at 5-mil line gap resolution
- ✓ fired thickness of thick print samples is within the range170-180 µm at three layers when screen 105 mesh 20 µm emulsion was used
- ✓ resistivity of fine line samples at 5-6 mil line/gap resolution: < 3 m $\Omega/\Box$
- ✓ resistivity of thick print samples at 105 mesh 20 µm emulsion drops from < 0.6 mΩ/□ at 1 layer to < 0.25 mΩ/□ at three layers
- $\checkmark$  adhesion:
  - $\Rightarrow$  > 5 N/mm<sup>2</sup> on alumina
  - $\Rightarrow$  > 5 N/mm<sup>2</sup> on AlN with base conductor layer on thick print samples
  - $\Rightarrow$  > 2.5 N/mm<sup>2</sup> on AlN fine print single layer samples

## **Copper-based Fine Line Conductors**



Own Cu-based conductor ink, 10-mil line/gap 325 mesh, 12.5  $\mu$ m emulsion, 950°C, 2.4 m $\Omega/\Box$ 

## **Copper-based Fine Line Conductors**



325 mesh, 12.5  $\mu$ m emulsion, 950°C, 2.6 m $\Omega/\Box$ 

## **Copper-based Fine Line Conductors**



Own Cu-based conductor ink, 5-mil line/gap 325 mesh, 12.5  $\mu$ m emulsion, 950°C on AlN substrate, 2.9 m $\Omega/\Box$ 

## **Copper-based Thick Print Conductors**



Own Cu-based conductor ink, 40-mil line/gap, 105 mesh, 20  $\mu$ m emulsion, 950°C, 0.2 m $\Omega/\Box$  at 3 layers

## **Copper-based Thick Print Conductors**



Own Cu-based conductor ink, 40-mil line/gap 105 mesh, 950°C,  $0.2 \text{ m}\Omega/\Box$  at 3 layers

# Copper-based Thick Print Conductors Effect of Unsuitable Morphology of Cu Powders



# Complete Thick Film System on Aluminum Substrates

Own advanced thick film system on aluminum substrates consists of:

- front side dielectric paste:
  - ✓ provides electrical isolation of electronic circuit on the top of dielectric
  - $\checkmark$  serves as a carrier of an electronic circuit on it
- reverse (back side) dielectric paste (when applicable):
  - ✓ counteracts the bending of the substrate during firing process for larger substrates
  - ✓ minimizes stress-strain state in both metal and glass enamel coating
- Ag conductor paste:
  - $\checkmark$  depending on screen used, the same ink may form:
    - $\Rightarrow$  fine lines 10-mil line/gap, 20 µm thick (280 325 mesh)
    - $\Rightarrow$  thick print lines 150-180 µm thick at 3 layers (105 145 mesh)
- Ruthenium composite conductive phase based resistor series:
  - ✓ hybrid resistors from  $1 \Omega/\Box$  to  $20 M\Omega/\Box$
  - ✓ Ag/Ru heater resistor series from 10 mΩ/ $\square$  to 1 Ω/ $\square$

### Complete Thick Film System on Aluminum Substrates **The Challenges for Dielectric Coating Paste**

- Mutually exclusive and incompatible requirements:
  - ✓ usually achieved by high content of alkali oxides in the glasses:
    - ⇒ unusual for any thick film material very high CTE for matching to the CTE of aluminum substrate (250 x  $10^{-7}$  /°C)
    - $\Rightarrow$  very low firing temperature due to restrictions inherent to aluminum (< 640°C)
    - $\Rightarrow$  continuous, with no pinholes and shortcuts fired dielectric films
  - ✓ impossible for glasses with high content of alkali oxides in the composition:
    - ⇒ mandatory request for stability during 1,000-hr 85°C/85RH/24V biased test i.e.: resistance to glass electrolysis and decomposition under concurrent prolonged exposure of elevated temperature, humidity, and electric voltage
  - request for being a rigid carrier of electronic circuit (requires more crystallized structure) and isolating it from the aluminum substrate (requires less crystallized structure to avoid pinholes and shortcuts)
- dielectric coating must not interact during firing with further layers of thick pastes printed above dielectric coating
- migration of metal from conductor paste through dielectric under the influence of temperature, humidity, and applied voltage is not allowed as it decreases isolation resistance up to short circuit

#### Complete Thick Film System on Aluminum Substrates Commercially Available Dielectric Coating Pastes for Aluminum



- dielectric paste from Supplier 5 (USA) had excellent stability at biased test, when copper conductor was employed
- silver from conductors migrate through dielectrics and cannot be employed with these dielectrics
- due to excessive crystallization, massive pinholes appear after firing
- such pinholes cannot be observed with optical microscope, but can be seen with high resolution scanner
- acceptable dielectric total thickness at 3 layers must be carefully controlled:
  - $\checkmark\,$  when finer screen is used, even copper migrates through thinner dielectrics
  - $\checkmark$  when thickness is higher, dielectrics cracking may be observed after firing of conductor

#### Complete Thick Film System on Aluminum Substrates Commercially Available Dielectric Coating Pastes for Aluminum



- dielectric paste from Supplier 3 (USA) practically has no pinholes
- isolation resistance of dielectrics at standard conditions is excellent
- no migration through dielectrics of metals from conductors at standard conditions was observed
- both silver and copper conductors may be employed
- it may be assumed that above listed features were achieved by using high content of alkali oxides

- disadvantages of this dielectric system:
  - ✓ biased test  $85^{\circ}C/85RH/24V$  failed
  - ✓ as noted by the ink supplier: "not suitable for wet applications"
  - $\checkmark\,$  has very low crystallization ability
  - ✓ could be more rigid to serve as a circuit carrier: fired elements "sink" in dielectric to some extent

#### Complete Thick Film System on Aluminum Substrates Chemical and Biased Test Stabilities





1-hr 10% HCl chemical stability test

Dielectric coating practically disappeared

Both chemical and biased test stabilities are very low for dielectric compositions with high alkali oxides content and CTE ~  $200 \times 10^{-7}$  /°C

After 100 hr. of 85°C/85RH/24V biased test

Dielectric coating practically disappeared



5-hr 10% HCl chemical stability test

Dielectric coating not affected

Dielectric compositions with lower alkali oxides content and CTE  $\sim$  150x10<sup>-7</sup> /°C:

- ✓ chemical stability satisfactory
- ✓ biased test stability not satisfactory

After 500 hr. of 85°C/85RH/24V biased test

Despite of improved chemical stability, dielectric coating is still affected

#### Complete Thick Film System on Aluminum Substrates 85°C/85RH/24V Biased Test



a substrate with improved chemical stability but insufficient biased test stability after 250 hours of  $85^{\circ}C/85RH/24V$  biased test:

- dielectric system residues in the vicinity of fired dielectric are observed
- the major element found in the residues was potassium
- it may be assumed that glass electrolysis occurs for such dielectric systems even if chemical stability in acid and boiling water was excellent

#### the fixture used for $85^{\circ}C/85RH/24V$ biased test



#### Complete Thick Film System on Aluminum Substrates An Approach to Development of Dielectric Coating Pastes

- 1. Well-known systems employing substantial content of alkali oxides for CTE increase and firing temperature decrease to the desired values, are not suitable for microelectronic applications due to insufficient stability during 85°C/85RH/24V biased test
- 2. content of alkali oxides in glass compositions used in pastes for dielectric coatings should never exceed critical threshold
- 3. another technique for achieving of high enough CTE is a must
- 4. dielectric coating total performance represents a trade-off between:
  - ✓ vitrification/de-vitrification balance
  - ✓ glass flowability
  - ✓ CTE
  - ✓ alkali oxides content
  - ✓ firing conditions
- 5. actual fired dielectric layer on aluminum is always a compromise of pinholes presence and CTE value
- 6. pinholes appearance must be carefully controlled

## Complete Thick Film System on Aluminum Substrates An Approach to Development of Dielectric Coating Pastes

- 7. achieving of higher CTE with lower alkali oxide content glasses:
  - ✓ initial glass(es) may have relatively low alkali oxides content and CTE
  - ✓ new crystalline phase with higher CTE is formed during firing
  - ✓ the approach has been based on the controlled crystallization concept successfully used for development of ultra high ohmic ceramic-type resistors
  - ✓ crystallization intensity must be kept in a narrow range:
    - $\Rightarrow$  intensive enough to initiate sufficient rate of crystallization and CTE increase
    - ⇒ moderate enough to allow proper formation of glassy phase that provides adhesion of dielectric to substrate and fills in voids inside dielectric film eliminating pinholes appearance after firing
  - crystallization is a dynamic process affected concurrently by many factors such as:
    - $\Rightarrow$  glass composition
    - $\Rightarrow$  ceramic fillers
    - $\Rightarrow$  organic vehicle composition
    - $\Rightarrow$  firing profile

### Complete Thick Film System on Aluminum Substrates Dielectric Coating Pastes



- Glass(es) with relatively low CTE values are used for own dielectric system
- CTE increased during firing process of the actual dielectric composition while new crystalline phased were formed

Glass	CTE x-10-7 1/°C			T °C
	20°C-200°C	20°C-300°C	20-t <sub>g</sub>	Ig, C
1	150	158	168	395
2	184	200	210	390
3	177	189	208	400
4	133	140	159	450

Typical CTE and Tg values for glasses with high alkali oxides content



temperature is well-known for sintered glass-ceramic structures

#### Complete Thick Film System on Aluminum Substrates 85°C/85RH/24V Biased Test Stability



Substrates with copper conductor after 1,400 hours  $85^{\circ}C/85RH/24V$  biased test, no shortcuts and/or dielectric decomposition



Substrates with thick print silver conductor after 1,400 hours 85°C/85RH/24V biased test, no shortcuts and/or dielectric decomposition

## Complete Thick Film System on Aluminum Substrates **Thermal Conductivity**



- Commercially available dielectric ink from paste supplier #5 (USA) was used for making samples
- the supplier recommends total fired thickness of dielectric layers on aluminum up to 100-125 μm
- for own dielectric inks, controlled crystallization approach eliminating pinholes, has allowed decreasing of total fired thickness down to 45-50 µm
- commercially available dielectric could not provide proper insulation properties at the same 45-50 µm total thickness even with copper conductor
- therefore actual samples made of commercially available dielectric ink had total thickness 80-90 µm
- as the dielectric ink from the paste supplier provides more crystallized structures, measured thermal diffusivity (**material-specific** property) was better for dielectric samples made of ink from the supplier
- effective thermal conductivity at the given total dielectric layers thickness was better for own ink

#### Complete Thick Film System on Aluminum Substrates Dielectric Reverse Layer Paste

- There are at least two reasons for development of reverse layer dielectric paste:
  - ✓ stress-strain state (SSS)
  - ✓ possible warpage of bigger size aluminum substrates
- SSS in both metal and glass enamel coating may arise in a while with unpredicted consequences being a time bomb for dielectric coated aluminum
- it would be much safer to minimize possible problems dealing with SSS
- even for stainless steel/dielectric system with twice lesser CTE mismatch, reverse layer is recommended by dielectric paste supplier #5 (USA)
- smaller size ~1"x1" substrates are nearly flat, depending on total dielectric layers thickness and coverage, but bigger size ~2"x2" ones with >50% dielectric coverage may be warped unacceptably
- compositions of developed reverse layer pastes are quite different than compositions of the front side pastes due to their different functions
- CTE mismatch has always existed in dielectrics/aluminum substrate systems, but should be adjusted and taken into consideration

### Complete Thick Film System on Aluminum Substrates Front Dielectric and Reverse Layers



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## Complete Thick Film System on Aluminum Substrates Warpage Control of Big Size Aluminum Substrates

- the features of dielectric reverse layer pastes:
  - ✓ crystalline phase prevails on glassy phase
  - continuous layer with no pinholes is not the target
  - thermal conductivity is higher due to onpurpose highly crystallized dielectric layer
  - printed area should not cover whole back side area
  - CTE and printed area can be adjusted providing minimal warpage and maximum flatness of bigger size substrates
  - ✓ both front and reverse layer dielectric inks are fired concurrently



back to back 2" x 2 aluminum substrate with reverse layer





Insufficient warpage compensation, 4" x 6" substrate





No warpage, completely flat 4" x 6" substrate

Michail Moroz

101

M28456@outlook.com

#### Complete Thick Film System on Aluminum Substrates Warpage Control of Big Size Aluminum Substrates



commercially available dielectric ink, pinholes in fired dielectric layer, 2x2" dielectric coated aluminum substrate with no back side layer, Ag thick print conductor 40-mil line/gap Ag thick print conductor 145-mesh 40-mil line/gap on 2x2" dielectric coated aluminum substrate with back side layer, own system

#### Complete Thick Film System on Aluminum Substrates Warpage Control of Big Size Aluminum Substrates



Insufficiently compensated warpage: Ag thick print conductor 40-mil line/gap on 2x2" dielectric coated aluminum substrate with back side layer, own system Excessively compensated "negative warpage": concave downward shape instead of usual convex one. Ag thick print conductor 40-mil line/gap on 2x2" dielectric coated aluminum substrate with back side layer, own system

#### Complete Thick Film System on Aluminum Substrates 10-mil Line/Gap Fine Line Ag Conductor



- 100% Ag and Ag/Pd fine line conductor inks were formulated:
  - ✓ firing temperature: 600°C
  - ✓ resistivity of 100% Ag conductor at 10-mil line/gap: < 2.5 m $\Omega/\Box$  at 325-mesh 0.5-mil emulsion screen, 20 µm fired thickness
  - ✓ adhesion > 7.5 Lbs. on 2mm x 2mm pads
- A combination of selected morphology of powders and organic vehicles ensures required print quality



### Complete Thick Film System on Aluminum Substrates Thick Print Ag Conductor



Ag-based thick print conductor 105-mesh 20-µm emulsion, 40-mil line/gap, 3 layers firing profile: 600°C, 12 min at peak, 60 min total

- 2 layers: 0.28 m $\Omega/\Box$ , 110  $\mu$ m thick
- 3 layers: 0.20 m $\Omega/\Box$ , 160  $\mu$ m thick
- adhesion > 7.5 Lbs. on 2mm x 2mm pads

### Complete Thick Film System on Aluminum Substrates Thick Print Ag Conductor



Ag-based thick print conductor 105-mesh 20-µm emulsion, 40-mil line/gap, 1 layer firing profile: 600°C, 12 min at peak, 60 min total Ag Thick Print Conductor 4x4 mm Pad 105-mesh 20-µm emulsion on Dielectric Coated Aluminum Substrate firing profile: 600°C, 12 min at peak, 60 min total

Michail Moroz



M28456@outlook.com

### Complete Thick Film System on Aluminum Substrates Thick Print Ag Conductor



3 layers of dielectrics: 280-mesh, 0.5-mil emulsion, ~ 60 μm total dielectric thickness dielectric firing profile: 620°C, 12 min at peak, 60 min total 3 layers of Ag-based thick print conductor: 105-mesh 20-μm emulsion, 40-mil line/gap, conductor firing profile: 600°C, 12 min at peak, 60 min total


#### Complete Thick Film System on Aluminum Substrates **Full-Range Ruthenium-based Resistive Inks Series**

**The challenges** of low temperature firing Ru-based full-range thick film resistors on dielectric coated aluminum development:

- ✓ ultra-low temperature firing at the temperatures ≤ 620°C does not allow proper sintering of cermet resistors based on ruthenium oxide conductive phases even if high-Pb low melting glasses are employed
- ✓ no such resistor systems are commercially available
- interaction of dielectric coating with resistors may have place because softening points of resistor glasses and of dielectric coating are very close due to low firing temperature profile
- special organic vehicle system is required: it must burn out at the temperature range below low-melting glasses softening temperature that is not possible for regular ethyl cellulose-based organic vehicles

#### Complete Thick Film System on Aluminum Substrates **Full-Range Ruthenium-based Resistive Inks Series**

- **An approach** to low temperature firing Ru-based full-range thick film resistors on dielectric coated aluminum development:
  - original ruthenium-based composite conductive phase technology with unique sintering ability and set of own glasses allow proper sintering and complete resistor microstructure development in the designated temperature range
  - during firing resistance monitoring technique allows observing resistors formation process and possible resistor/dielectric interactions
  - ✓ original in-house conductive phase technology possesses enough productivity for resistor inks high-volume manufacturing
- ruthenium composite conductive phase based resistor series fired at 620°C:
  - ✓ hybrid resistors from 1  $\Omega/\Box$  to 20 M $\Omega/\Box$ :
    - $\Rightarrow$  controlled and minimized dependence of resistivity and TCR on resistor size
  - ✓ Ag/Ru heater resistor series from 10 mΩ/□ to 1 Ω/□



#### Complete Thick Film System on Aluminum Substrates Direct Monitoring of Resistors Formation During Firing



Referring to this kind of data, it is possible to judge if resistor would be stable enough at the particular peak firing temperature or to choose proper peak firing temperature for the given composition

Three expected areas can be seen on the chart:

- sintering of ruthenium-based composite conductive phase before glass melting
- 2. resistance increase with glass melting
- sintering with participation of liquid phase, resistance decrease and stabilization

Resistance readings during firing for resistive ink were collected every 6 seconds (550°C peak, 60 min total)

#### Complete Thick Film System on Aluminum Substrates **Resistivity vs. Peak Firing Temperature**



Peak Firing Temparature, °C

Resistance readings were collected after every firing at the given peak firing temperature, 60 min total each firing cycle

Similarly to data collected during firing of resistors, three areas can be seen on the chart:

- sintering of rutheniumbased composite conductive phase before glass melting
- 2. resistance increase with glass melting
- sintering with participation of liquid phase, resistance decrease and stabilization

Further temperature rise increases resistivity due to excessive melting of glass phase

Dependence of resistivity on resistor size on 100% Ag conductor has been minimized

#### Complete Thick Film System on Aluminum Substrates Low-temperature Fired Ag-based Heater Resistors Issues



Similarly to high-ohmic resistors fired at 850°C, anomalous conduction loss is observed for low resistivity silver-based resistors fired at 620°C when glass content in resistive composition exceeds critical threshold

For the given pure silver-glass heater resistor system, only resistors  $\leq 20 \text{ m}\Omega/\Box$  are really stable

An attempt to increase resistivity just by increase of glass content noticeably deteriorates resistor stability and spreads resistor values to unusable levels

The problem solving is dealing with technical solution allowing resistivity increase keeping glass content under critical threshold

Complete Thick Film System on Aluminum Substrates Low-temperature Fired Ag/Ru-based Heater Resistors



 Ag/Ru heater resistor series from 10 mΩ/□ to 1 Ω/□ (not limited) has been developed and verified

- Employing of Pb-free composite conductive phases and set of proprietary glasses formulated for low temperature firing has been found as a very effective tool of resistivity control of Ag-based heater resistors on aluminum and stainless steel substrates
- composite conductive phase ensures proper sintering at low temperature and a very homogenous distribution of small amounts of ruthenium-based compound in the resistor body
- calculated amount of  $\mathrm{RuO}_2$  in resistive compositions is from 0.5% to 2%
- proprietary organic vehicle system ensures low burn out temperature similar to nitrogen-fired system and, along with proper powders morphology, provides thick print ability of the heater resistors

#### Complete Thick Film System on Aluminum Substrates Ag/Ru Heater Resistors



- At 200-mesh 20 micron emulsion screen fired thickness is ~ 30  $\mu m$  at one layer
- 105-mesh 20-40 micron emulsion more typical for thick print applications, allows fired thickness ~ 50  $\mu m$  at one layer

# Low-Ohmic NTC Thermistor Inks



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- If ln(RT) is plotted versus 1/T, the slope of the resulting curve is equal to Beta
- Beta can be used to calculate resistance values of a thermistor at a particular temperature when the resistance at another temperature is known

$$BETA = \ln \frac{RHigher}{RLower} : (\frac{1}{TLower} - \frac{1}{THigher})$$
  
For the temperature ranges (-40 ÷ +35)°C and (+35 ÷ +105)°C:  
$$Hot BETA = \ln \frac{R105}{R35} : (\frac{1}{308} - \frac{1}{378})$$
$$Cold BETA = \ln \frac{R35}{R(-40)} : (\frac{1}{233} - \frac{1}{308})$$

- the Beta value of NTC thermistors is calculated using only two temperatures over a given range and is not the most accurate way to calculate the R vs. temperature. A more accurate method is to use the Steinhart and hart method, it uses three temperatures over a given range
- in order to obtain the most reliable data, resistance vs. temperature readings were taken in 10°C increments from -55°C to +125°C
- Beta vs. temperature was calculated more precisely providing more accurate tool to ink customers for calculating resistance

## Low-Ohmic NTC Thermistor Inks



TCR curve shape must be carefully controlled. For low ohmic value resistors there is a tendency to a more positive values of cold TCR. It must be detected and fixed. Otherwise hot and cold Beta values will unacceptably strongly differ.



Beta vs. Temperature

An example of excessive difference between Beta 105 and Beta -45 associated with inappropriate shape of TCR curve in cold area

## Low-Ohmic NTC Thermistor Inks A Correlation Between TCR and Beta



When a customer represents a spec with controlled Beta, acceptable TCR value range must be defined. The most critical is an issue how negative should be cold TCR to assure minimal difference between hot and cold beta values.

Two charts above represent thermistor ink with not enough negative cold TCR and ensuing excessive Delta Beta at hot and cold temperature ranges.

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Required TCR values may be calculated and TCR targets for the specific Beta requirements may be set up.

An effective tool for precise control of TCR curves shape of low-ohmic thermistor ink compositions has been elaborated. The lower thermistor ink resistivity, the more challenging is the task as cold TCR has to reach very high negative values not inherent to low-ohmic resistors.

## In-house Paste Manufacturing Advantages

- Provided that necessary resources are available, in-house manufacturing of own pastes has the following advantages:
  - ✓ performance control of fired thick film elements starts at ink ingredients manufacturing stage:
    - $\Rightarrow$  own glass compositions and glass powders with predetermined characteristics
    - ⇒ unique technology of resistors possessing zero-slope dilution curve that solves such fundamental resistor technology problem as anomalous conduction loss for higher resistivity (850°C) and low temperature-fired resistors (<700°C)</p>
    - ⇒ on-purpose development of paste up/down viscosity/slope curves balance for controlling and predicting printability of inks with specific requirements such as fine print, thick print, low temperature burning out, etc.
  - ✓ development of fully compatible complete thick film materials systems
    - $\Rightarrow$  employing same basic material system for materials to be compatible
    - $\Rightarrow$  live monitoring during firing of possible interactions for materials to be compatible

## In-house Paste Manufacturing Advantages

- ✓ the lowest cost of own inks as raw materials cost is 5-15% only, excluding Ag/Pd systems
- ✓ paste supplier is a part of circuit manufacturer's process:
  - $\Rightarrow$  the highest yield of circuits all inks are custom-tailored
  - $\Rightarrow$  ink supplier is involved in circuit production process at circuit design step
  - $\Rightarrow$  circuit manufacturer's needs are not neglected
  - $\Rightarrow$  continuous monitoring of production results
  - $\Rightarrow\,$  increase of circuit's yield based on real manufacturing process results is primary goal of ink supplier
  - $\Rightarrow$  fastest ink delivery
  - ⇒ pro-active actions instead of re-active ones: ink performance should forestall circuit manufacturer's current needs
- an ability to respond market new challenges faster than competitors by taking the lead with advanced thick film materials over today's industry level

# **Commercially Available Inks**

- Any ink performance variation from batch to batch within the range defined by the ink spec may be expected
- no correlation with final hybrid circuit yield and performance of used ink given batch
- hybrid circuit manufacturer has to choose among available inkls only while sometimes custom-tailored materiaks are a must for success
- full cooperation between paste supplier and circuits manufacturer in terms of further ink improvement toward specific circuit yield enhancing based on circuits manufacturing records is not usually possible
- some weeks ink delivery
- tech support from ink supplier is not immediate and pursues only proof of compliance with own ink spec

#### In House Made Inks vs. Commercially Available



# **Resistive Inks Manufacturing Features**

- Making low-performance resistive inks has no benefits and is not the way to make the inks cheaper
- supplying of precise resistive inks requires systematic purposeful R & D efforts on permanent basis including continuous improvement based on feedback from the circuit production
- resistor performance is a result of dynamic equilibrium of the constantly changing:
  - ✓ resistor ingredient properties
    - $\Rightarrow\,$  particle morphology and size distribution
    - $\Rightarrow$  surface area
    - $\Rightarrow\,$  actual compositions of the given glass batches
    - $\Rightarrow$  actual properties of the given conductive phase batches
  - $\checkmark$  processing
    - $\Rightarrow$  screen printing conditions
    - $\Rightarrow$  peak firing temperature, ramp, and dwell time
  - ✓ silver diffusion rate from the terminations into resistors
- own inks production is justified when own technology of proprietary unique materials surpassing similar materials of leading paste suppliers is available

## **Resistor Ink Quality Criteria**

#### Treatment Conditions:

- screen printing: mesh and emulsion
- firing / re-firing: temperature and time
- overglaze firing : paste, temperature and time
- laser trimming: power and number of pulses

#### Majority of commercially available inks:

- ✓ R, TCR for single resistor size only
- ✓ hot/cold TCR ratio is out of control
- ✓ treatment conditions effects are not clearly specified

#### Advanced proprietary inks:

- ✓ specified R & TCR, vs. resistor geometry
- ✓ hot/cold TCR ratio controlled
- ✓ minimized and specified sensitivity to treatment conditions
- ✓ final performance is defined on the step of making powder components



Michail Moroz

## **Targeting Resistor Performance**



## Summary

- Non-standard concepts, approaches, and techniques used for the described materials:
  - $\checkmark\,$  unique sintering ability of composite conductive phases for resistors
  - ✓ parabolic dependence of resistivity vs. glass content with minimum values area
  - ✓ new technique for precise control of Temperature Coefficient of Resistance
  - ✓ forming of ceramic-type microstructure of high-ohmic resistors during ink firing process
  - ✓ controlled crystallization of ceramic-type high-ohmic resistors and dielectric coatings
  - ✓ predictable screen printing process based on controlled paste rheology
  - ✓ monitoring of resistance formation during firing
- Development results :
  - ✓ set of advanced conductor, resistor, overglaze, and dielectric cermet thick film inks:
    - $\Rightarrow$  fired in the temperature range from 550°C to 1,300°C
    - $\Rightarrow\,$  on various substrates such as alumina, AlN, stainless steel, aluminum, crystallized glass, and copper
    - ⇒ majority of the described materials are Pb-free, some resistors have some Pb in glass compositions and may be converted into 100% Pb-free
    - ⇒ the major sintering agent for resistors is composite conductive phase while conventional materials use Pb in glasses as the major sintering agent preventing its replacement

## Selected Publications List

- Moroz, M; "Performance of LTCC Resistors in Extreme Cold Environment", IMAPS Advanced Technology Workshop on Reliability of Advanced Electronic Packages and Devices in Extreme Cold Environments, Pasadena, CA, February 21- 23, 2005 <u>https://www.researchgate.net/publication/272092904\_Performance\_of\_LTCC\_Resistors\_in\_Extreme\_Cold\_Environment\_-Presentation</u>
- Moroz, M; "Development of LTCC Post Fired Resistors for A6M/Gold Material System", 37th International Symposium on Microelectronics, November 14-18, 2004, Long Beach, CA <u>https://www.researchgate.net/publication/272093371\_Development\_of\_LTCC\_Post\_Fired\_Resistors\_f</u> <u>or\_A6MGold\_Material\_System</u>
- Sridharan, S., Moroz, M; "Electronic Device Having Lead and Cadmium Free Electronic Overglaze Applied Thereto", US Pat # 7,740,899, filed 05/07/2003 <u>https://www.researchgate.net/publication/272747557\_Electronic\_device\_having\_lead\_and\_cadmium\_free\_electronic\_overglaze\_applied\_thereto</u>
- Moroz, M; "Investigation of Surface LTCC Resistors During Firing and Subsequent Re-Firings", Proceedings of the 2004 Conference on Ceramic Interconnect Technology - The Next Generation, Apr 26-28, 2004, Denver, CO, pp. 183-188 <u>https://www.researchgate.net/publication/272092958\_Investigation\_of\_Surface\_LTCC\_Resistors\_Dur</u> ing\_Firing\_and\_Subsequent\_Re-firings
- Moroz, M; "Performance of Co-Fired Buried Resistors in A6S Tape", Proceedings of 36th International Symposium on Microelectronics - IMAPS 2003, Nov 16-20, 2003, Boston, MA, pp. 161-166 <u>https://www.researchgate.net/publication/272171481\_Performance\_of\_Co-Fired\_Buried\_Resistors\_in\_A6S\_Tape</u>

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- 6. Moroz, M; "Performance of Low-Ohmic Co-Fired Buried Resistors in A6S Tape", Proceedings of the 2003 Conference on Ceramic Interconnect Technology: The Next Generation, Apr 7-9, 2003, Denver, CO, pp. 200-204 <u>https://www.researchgate.net/publication/272171284\_Performance\_of\_Low-Ohmic\_Co-Fired\_Buried\_Resistors\_in\_A6S\_Tape</u>
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- 8. Moroz, M; Shaikh, A; "New Low Cost Surge Resistive Inks", Proceedings of 35th International Symposium on Microelectronics IMAPS 2002, Sep 4-6, 2002, Denver, CO, pp. 421 426 https://www.researchgate.net/publication/272093064\_New\_Low\_Cost\_Surge\_Resistive\_Inks
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- 10.Moroz, M; Shaikh, A. "A New Generation of Low-Cost Surge Resistor Materials". Passive Component Industry; Sep-Oct 2000, pp. 34 – 35 <u>https://www.researchgate.net/publication/272093414\_A\_New\_generation\_of\_Low-Cost\_Surge\_Resistor\_Materials</u>

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- 14.Moroz, M.; Achmatowich, S. "The Influence of RuO2 Powders Preparation Method on the Parameters of Fired Resistors". Proceedings of 17th Conference of the International Society for Hybrid Microelectronics - Poland Chapter; Sept. 15-18, 1993, pp. 127 - 130, Rzeszow - Solina, Poland

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