

TUTORIAL ON THICK FILM METALLIZATION

CMC Laboratories, Inc.



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Outline of Thick Film Tutorial

1. Idealized Microstructure for Thick Film Metallization Systems
2. Bonding Mechanisms in Thick Film Metallization Systems
3. Processing Dynamics in Thick Film Metallization Systems
4. Material and Processing Requirements for Thick Film Fabrication
5. Special Topic: Thick Film Via Fill
6. Alternative Thick Film Technology



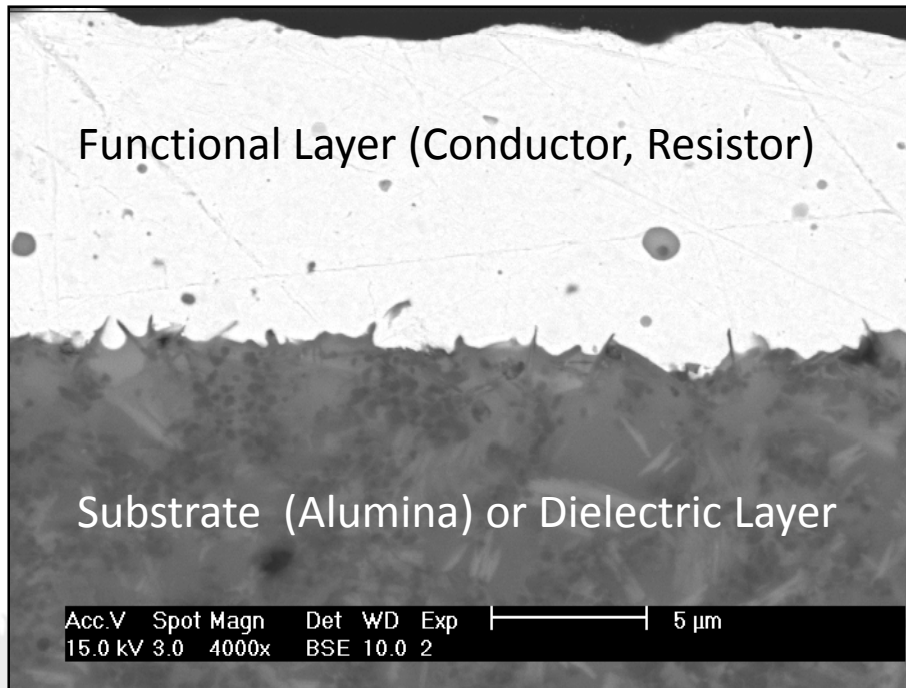
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IDEALIZED MICROSTRUCTURE- THICK FILM METALLIZATION SYSTEMS



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Idealized Microstructure



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Idealized Microstructure: Key Requirements of Microstructural Features

| Layer | Key Functional Requirements |
|------------------------------|--|
| Functional Layer (Conductor) | Electrical conductivity, good line resolution, stability under processing conditions, bondable to next level of interconnect (wirebond, solder, contact), low cost (material cost and processing cost), resistance to migration in humidity/ electric field, corrosion resistant |
| Bonding Layer | Bonds to functional Layer, bonds to dielectric layer or substrate, mediates the TCE mismatch between the functional layer (metal) and substrate, assists in kinetics of film formation, low cost material and low cost processing, stable under processing conditions, thin to minimize tensile fracture failure |
| Substrate Layer | Mechanically rigid, appropriate electric performance for application (low dielectric loss), appropriate thermal performance for application, bondable to bonding layer |



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Summary of Functional Layer Materials

| Layer Function | Typical Materials Used in Thick Film |
|---------------------------|--|
| Conductor | Au, Pt/Au, Ag, Pd/Ag, Cu, Ni |
| Resistor | Pd/Ag, $\text{Bi}_2\text{Ru}_2\text{O}_7$, RuO_2 |
| Dielectric (in capacitor) | BaTiO_3 , Glass, Glass with ceramic additives |



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Properties of Metals used in Thick Film Conductor Layers

| Conductor | T _{melt} (C) | Electrical Resistivity (10 ⁻⁸ Ω cm) | TCE (ppm/K) | TC (W/m-K) | Solderability | Corrosion resistance |
|-----------|-----------------------|--|-------------|------------|---------------|----------------------|
| Au | 1063 | 2.35 | 14.2 | 317 | Poor** | Excellent |
| Ag | 961 | 1.59 | 19.2 | 429 | Good* | Poor |
| Pt | 2045 | 10.6 | 9 | 71 | Good+ | Excellent |
| Pd | 1825 | 10.8 | 11.2 | 71 | Good++ | Excellent |
| Cu | 1083 | 1.7 | 16.5 | 401 | Excellent | Poor |
| Mo | 2610 | 5.2 | 5.43 | 138 | Poor | Good |
| W | 3410 | 5.65 | 4.59 | 174 | Poor | Good |

*Ag reacts with Sn in PbSn or SAC solder to form AgSn intermetallic compounds. This can be a significant reliability issue (low resistance to solder leaching).

+ In combination with Au in an alloy

++ In combination with Au or Ag in an alloy

** Frequently used for solder layer BUT reacts with Sn to form brittle IMC



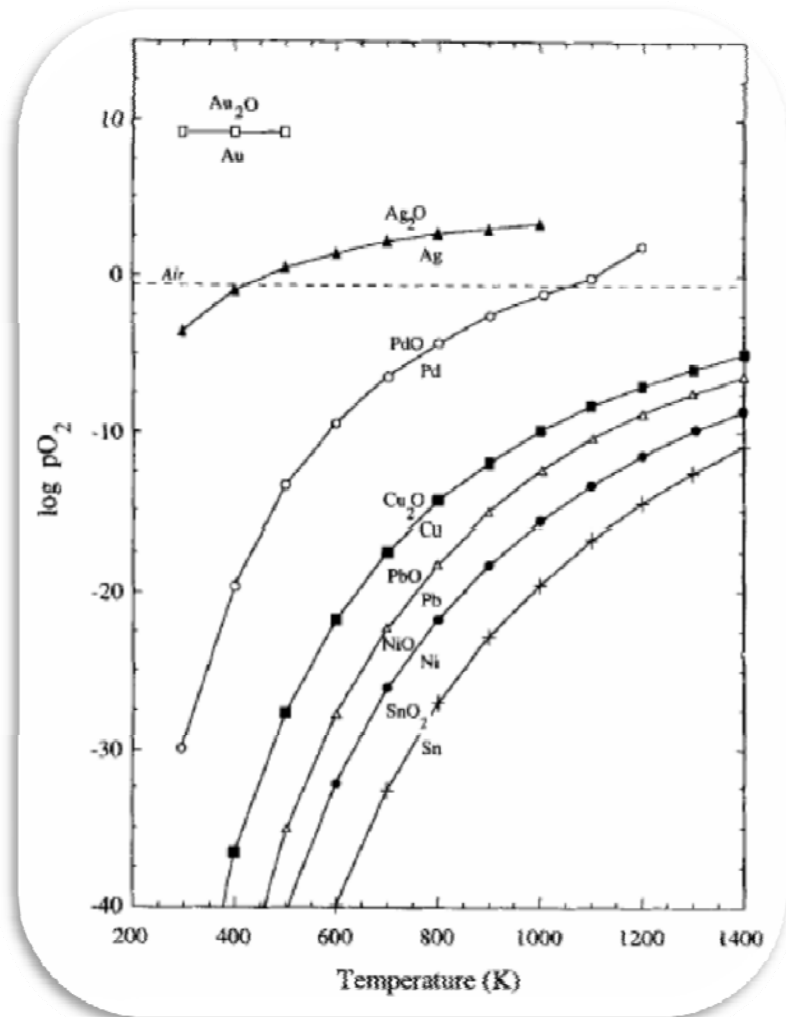
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Oxidation Properties of Metals used as Thick Film Conductors

Oxidation/ reduction chemical potential vs. temperature and oxygen partial pressure for common thick film conductors. Below each curve, the metal is stable. Above the curve, the metal oxide is stable.

NOTE:

- Au oxide never forms at temperatures and pressures associated with thick film processing
- Ag is also always in the metallic state
- PdO is stable up to about 1100K (827C) when it decomposes to the metal and oxygen gas (in air)



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Pd-Ag System

- One of the most widely used thick film systems is Pd-Ag
- Many key properties can be manipulated by modifying the Pd/Ag ratio
 - Electric resistivity
 - Processing temperature
 - Solderability
 - Resistance to Ag migration
 - CTE



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Pd-Ag System

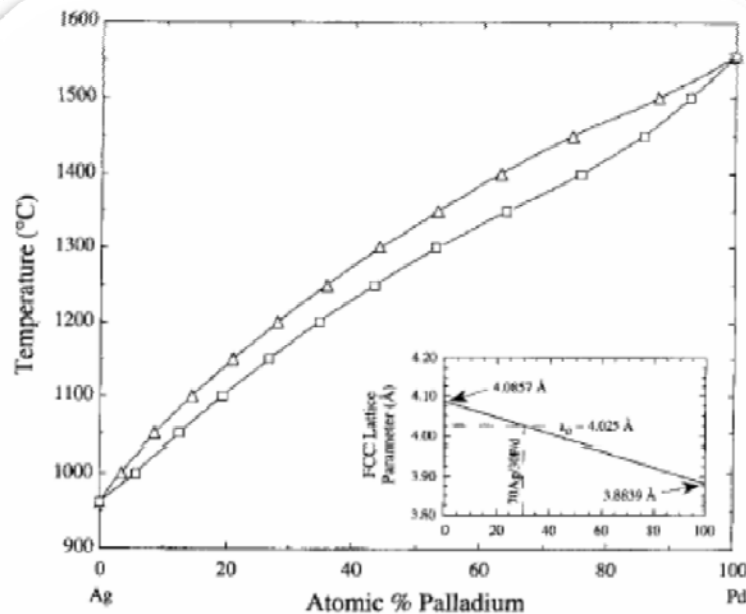


Fig. 7. Phase diagram and room-temperature lattice parameters for the Ag/Pd system.

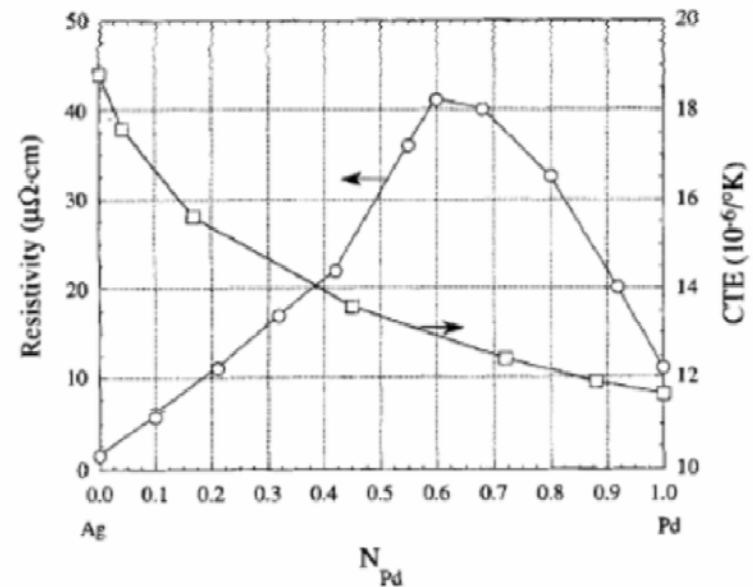


Fig. 17. Bulk electrical conductivity and linear thermal expansion of the Ag/Pd system.

From Wang et al, J. Am. Ceram. Soc. 77(12) 3051 (1994)

Bonding Layer – Typical Chemistry

| Bonding Layer Constituent | Typical Additives | Key Characteristic |
|-------------------------------|---|---|
| Glass forming oxides (65-85%) | B_2O_3 , SiO_2 | Promotes formation of glass phase |
| Glass modifying oxides | CaO , MgO , BaO , ZrO_2 , ZnO , Al_2O_3 , Fe_2O_3 , MnO | Modifies glass properties: forms a liquid phase at firing temperature (600-1000C). Wets metal component. Detailed role will be discussed. |
| Adhesion promoters | Bi_2O_3 , CuO , CoO | Detailed role will be discussed |



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BONDING MECHANISMS IN THICK FILM METALLIZATION SYSTEMS



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Bonding in Thick Film Systems

- Bonding layer composition:
 - Glass forming oxide
 - Glass modifying additive
 - Adhesion promoter (metal oxide)
- Bonding is very difficult and complex in this system!
 - Bonding layer must adhere to a metal layer (above)
 - Bonding layer must adhere to a oxide layer (below)
 - Bonding in metal and oxide systems is COMPLETELY DIFFERENT!
- There are 4 different types of bonding mechanisms that occur in different thick film systems
 - Mechanical Frit bonding
 - Ionic oxide to oxide bonding (for non-precious metals)
 - Reactively bonded systems
 - Systems with a mixture of reactive bonding and mechanical frit bonding



Fundamental Chemistry of Adhesion: Atomic Bonding Types

| Bond Type | Description | Example | Requirements to for this type of Bond |
|-----------|--|-----------------------------------|--|
| Metallic | Atoms at the interface of 2 materials share orbital electrons | Metal-metal bonding | Intimate contact between the 2 materials to allow orbitals to overlap. Both materials must be metals |
| Ionic | Electrons are exchanged between the two materials if one is more anionic and the other more cationic. Strong electrostatic attraction. | Bonding within oxides and glasses | Intimate contact between the two materials. Usually requires heat so that molecules can orient to allow electronic exchange. |



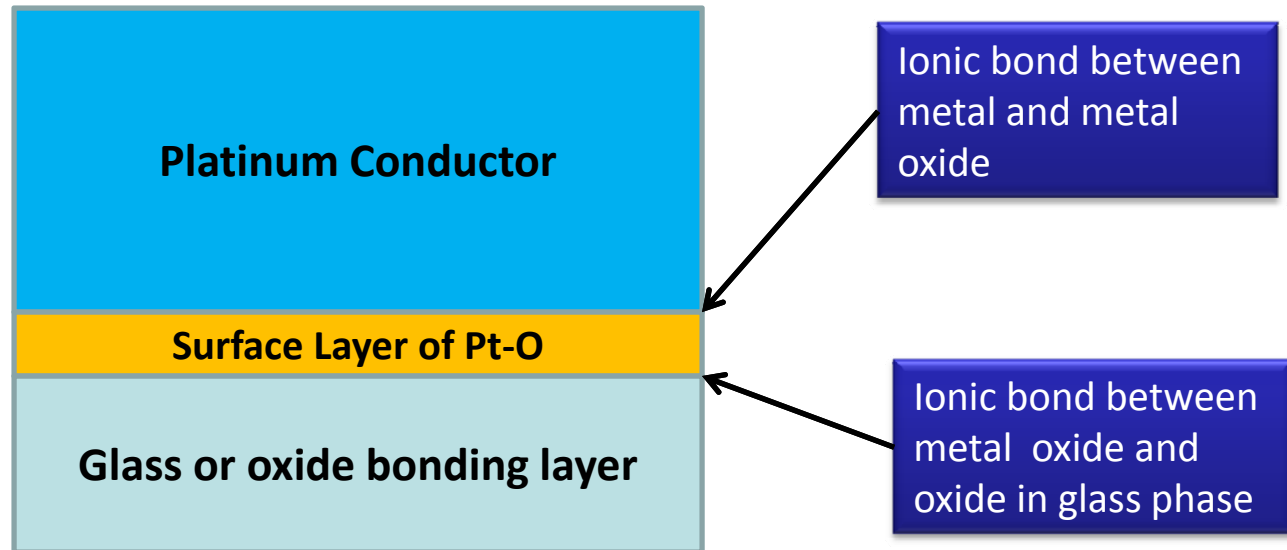
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Bonding Options for Different Metal Systems [Adhesion of Metal Layer to Bonding Layer]

| Metal | Forms surface oxide? | Bonding Options to Oxide or Glass |
|-------|----------------------|---|
| Au | NO | Au will only form metallic bonds. No option for an electrostatic bond with glass. Au will not bond directly to an oxide or glass layer. |
| Pt | YES | Surface oxide on Pt will form electrostatic molecular bonds directly to glass. |
| PdAg | YES | Surface oxide on PdAg will form electrostatic molecular bonds directly to glass |
| Cu | YES | Surface oxide on Cu will form electrostatic molecular bonds directly to glass (for Cu, oxidation is not limited to the surface and will react throughout the film causing poor electrical and mechanical properties if processed in an oxidizing environment) |



Bonding to Metals which form Surface Oxides [Bonding of the Metal Layer to the Bonding Layer]

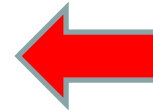


Bonding in Au Thick Films [Bonding of the Au Layer to the Bonding Layer]

Gold Conductor

Glass or oxide bonding layer

?



No electrostatic or metallic bond can form between Au and the glass phase-
How can adhesion be achieved?



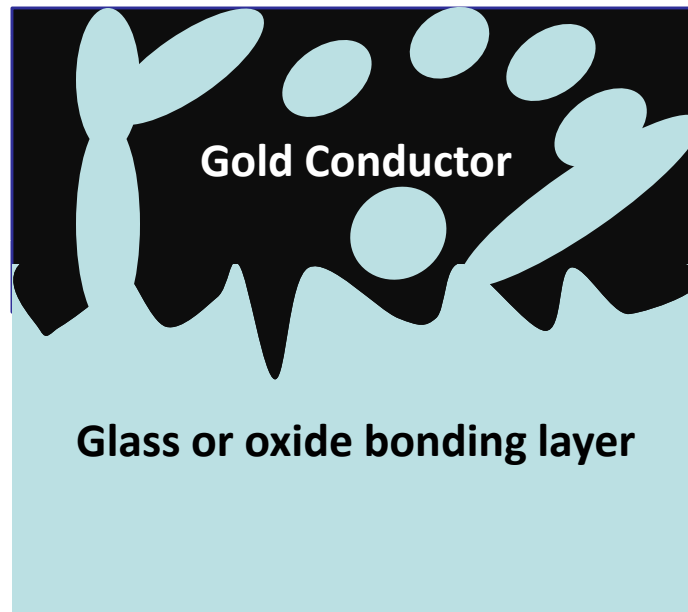
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Strategy for Direct Bonding Au to the Oxide Bonding Layer

- Oxide additives are added to the glass bonding layer material
 - These oxides are chosen because they decompose at the firing temperature
 - $2\text{CuO} \rightarrow 2\text{Cu} + \text{O}_2$ (air, 1026)
 - $2\text{Bi}_2\text{O}_3 \rightarrow 2\text{Bi} + 3\text{O}_2$ (air, 850C)
 - $2\text{CoO} \rightarrow 2\text{Co} + \text{O}_2$ (air, 700-900C)
- The reduced metal component forms a metallic bond with Au
- The new Au containing binary (Au/Cu, Au/Bi, Au/Co) or ternary surface alloy (Au/Cu/Bi, Au/Co/Bi) now has an increased affinity for oxygen and forms a thin oxide layer on its surface
- An ionic bond is formed between the Au/X oxide and the oxide containing glass bonding layer



Bonding in Au Thick Films [Bonding of the Au Layer to the Bonding Layer]



First Generation Au Film Technology: Mechanical Interlocking- No chemical bonding

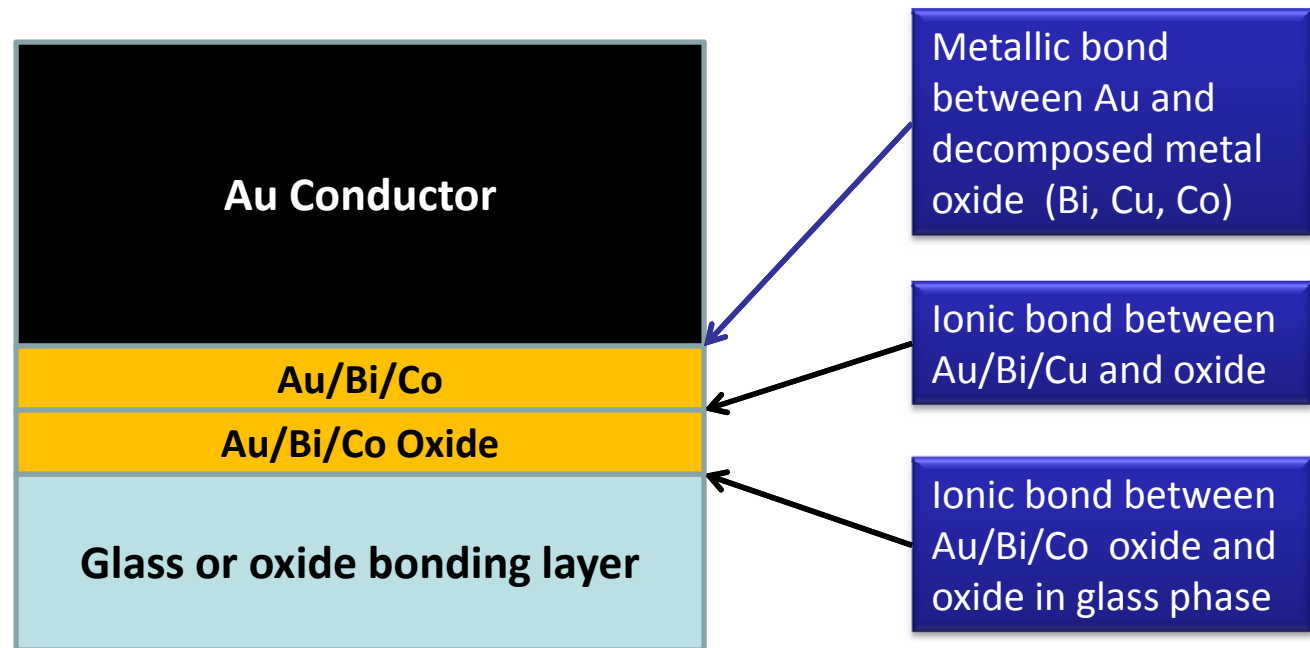
- Requires a high volume of glass (10-40 volume percent)
- Metal density is low
- Electrical conductivity is low
- Adhesion strength is low due to low tensile strength of glass
- Glass usually coats the top surface of the metal requiring an etching step before wirebonding

Glass Frit Bonded System



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Bonding in Au Thick Films [Bonding of the Au Layer to the Bonding Layer]

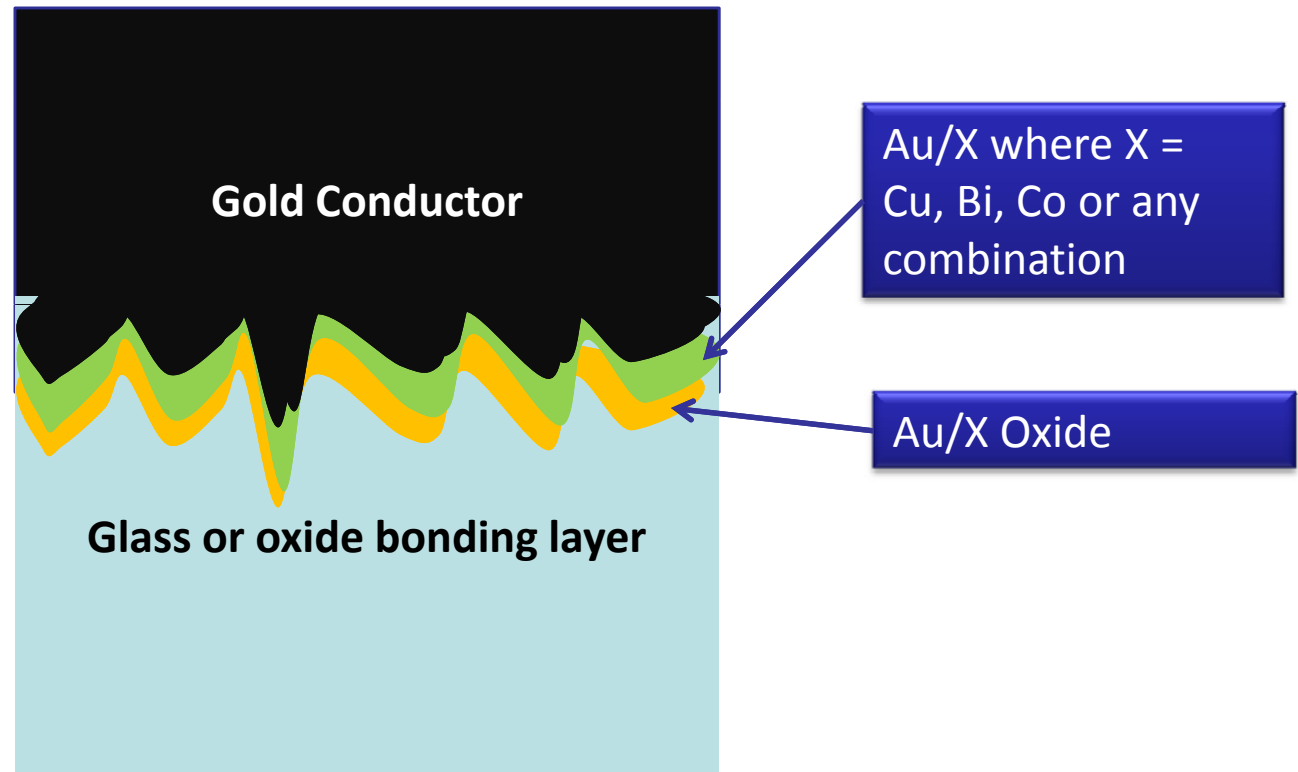


Reactively Bonded System



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Bonding in Au Thick Films [Bonding of the Au Layer to the Bonding Layer]



Mixed Bonded System: A combination of Reactive Bonding and Frit Bonding



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Benefits of the Mixed Bonded Au Thick Film System

- Very clean Au surface (glass phase carries the reactive oxide to the interface with the dielectric/ substrate)
- Small glass concentration is needed (1-3 wt. %)
- Glass phase increases the interfacial area thus increasing the bond strength
- Au metal thickness can be made thin since effective surface bonding occurs



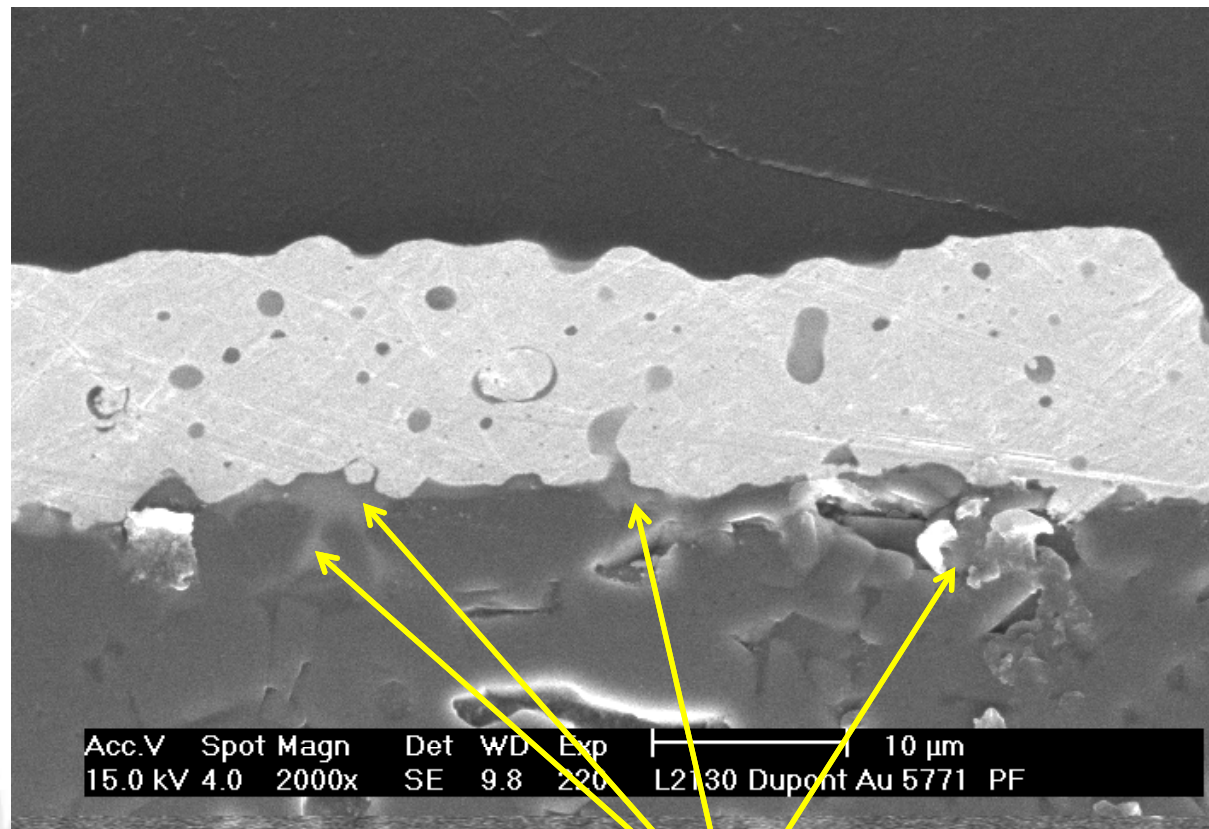
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Bonding of the Bonding Layer to the Dielectric or Substrate

- Typical glass formulations are based on borosilicate or equivalent compositions with additives such as Bi_2O_3 , CuO , CoO , BaO and CaO .
- Borosilicate glass will form an ionic bond directly with alumina, or oxide based dielectric, as long as an intimate interface is formed
- Bi_2O_3 reacts with Al_2O_3 to form a eutectic liquid at 830C.
 - This liquid phase promotes wetting of glass to the ceramic substrate
 - Increases the interfacial area by reacting with the ceramic surface (as well as any glass phase in the ceramic)
- The bonding glass also reacts and bonds directly with the surface silicate layer which is a significant component of 96% alumina



Bonding Layer Adhesion to Alumina

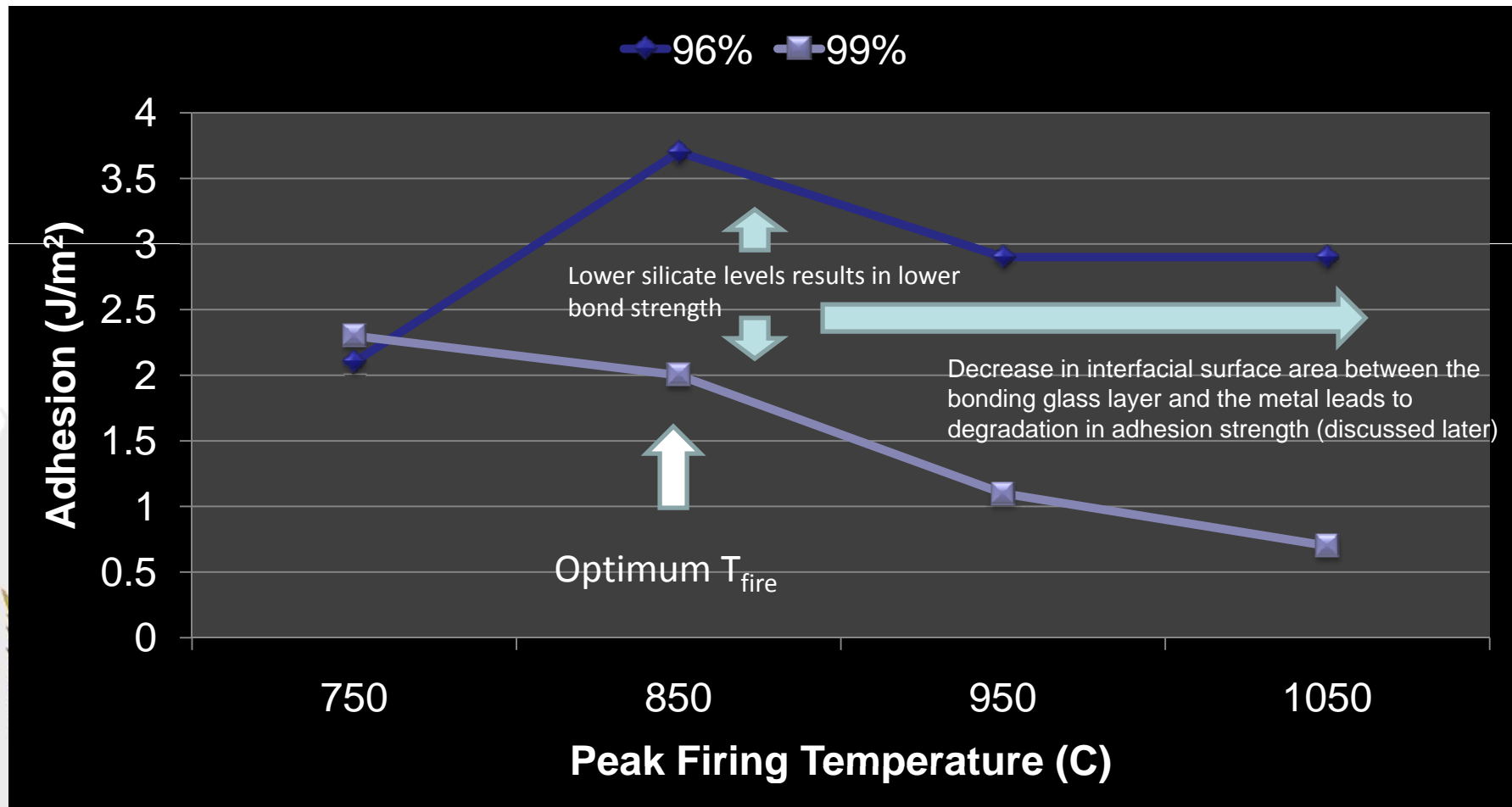


Bi-oxide containing phase that forms eutectic liquid by reaction with Al_2O_3 (and silicate in 96% alumina) and penetrates the ceramic

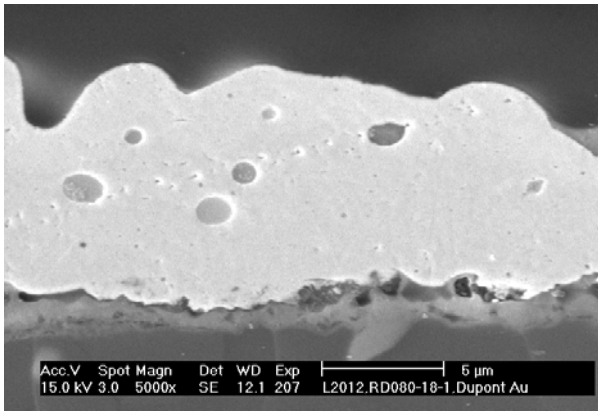


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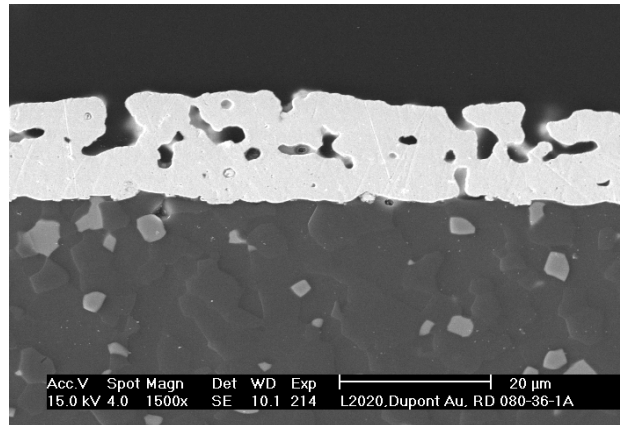
Bonding Layer Adhesion to Alumina



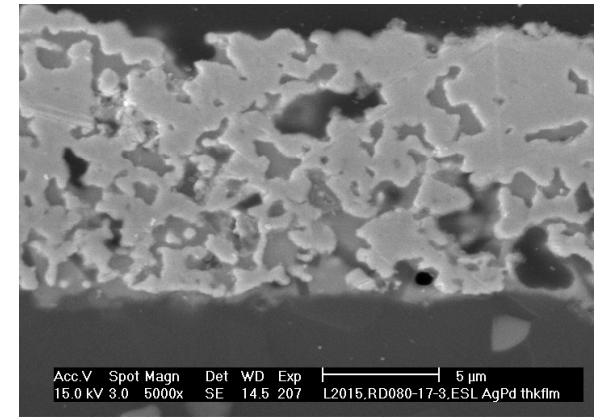
Bonding to Aluminum Nitride



DuPont



DuPont



ESL

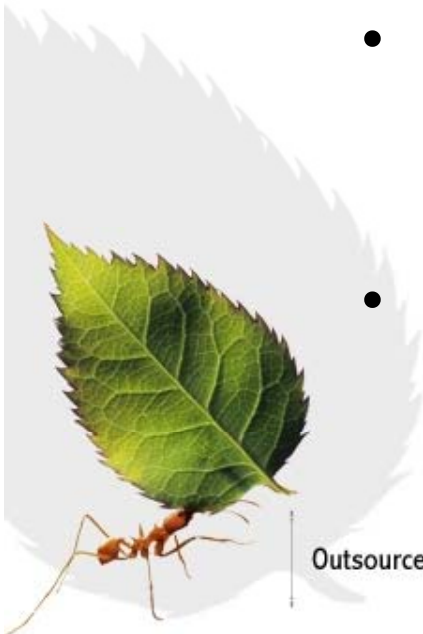


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- Likely AlN reaction sequence during air firing
 - $4\text{AlN} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 2\text{N}_2$ on AlN surface at $T > 600^\circ\text{C}$
 - Surface Al_2O_3 layer reacts with glass phase in thick film metallization paste
 - Similar to 96% alumina surface but with no ceramic glass phase
 - The BiO- Al_2O_3 liquid phase reacts into the AlN grain boundaries
- In general- thick film bond strength is lower to AlN than 96% alumina (no glass phase in the ceramic to react with paste)

Summary of Bonding in Thick Film Metallization

- Atomic bonding is required for high adhesion strength
 - Ionic bonding oxide to oxide
 - Metallic bonding: metal atom to metal atom
 - Intimate contact between each phase is required for bonding to initiate
- For metal conductors which form oxides:
 - Metal surface is oxidized
 - Bonding to glass bonding layer with ionic bonds
- Non- oxide forming metals (Au) have more complex bonding
 - During firing, a metal oxide species is reduced and bonds with Au
 - The Au/X metal oxidizes
 - This oxide bonds with the glass bonding layer
- Glass in pastes bond to Al_2O_3 and silicate in 96% alumina ceramic substrates via ionic bonds



PROCESSING DYNAMICS IN THICK FILM METALLIZATION SYSTEMS



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Processing Dynamics in Thick Film Systems

- Goal of Processing- Create Idealized Microstructure
 - Dense metallization- Metal particles sinter to full density
 - Strong adhesion at all interfaces
 - Glass phase segregates to the metal/ ceramic interface
 - Adhesion additives (Bi-oxide, Cu- oxide) react at metal surface to form Metal/X layer
 - Liquid glass reacts with the Metal/X surface to form bond
 - Bi-oxide react with ceramic to form eutectic liquid
- Key Processing Stages During Firing
 - Dry residual solvents
 - Organic binder burnout
 - Sintering



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Firing Reactions- Air Atmosphere

Solvent
Evaporation

Organic Binder
Combustion

Sintering of
Metal, Bonding at
interfaces

100-
200C

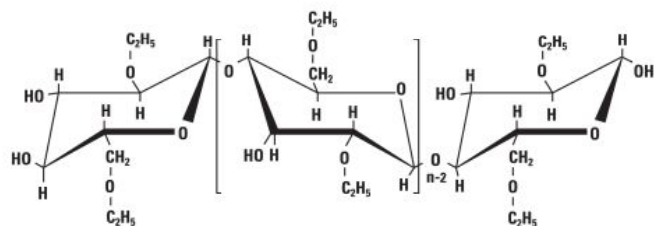
250-
600C

600-
1000C



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Organic Binder Burn-out



Ethyl Cellulose

Chemical driving force: enthalpy and entropy of gas phase => reaction rate and reaction energy increases with temperature

Critical elements for this reaction to proceed to completion:

- (1) O_2 must be able to physically access the binder phase
- (2) Gas reaction products must be completely removed from reaction site

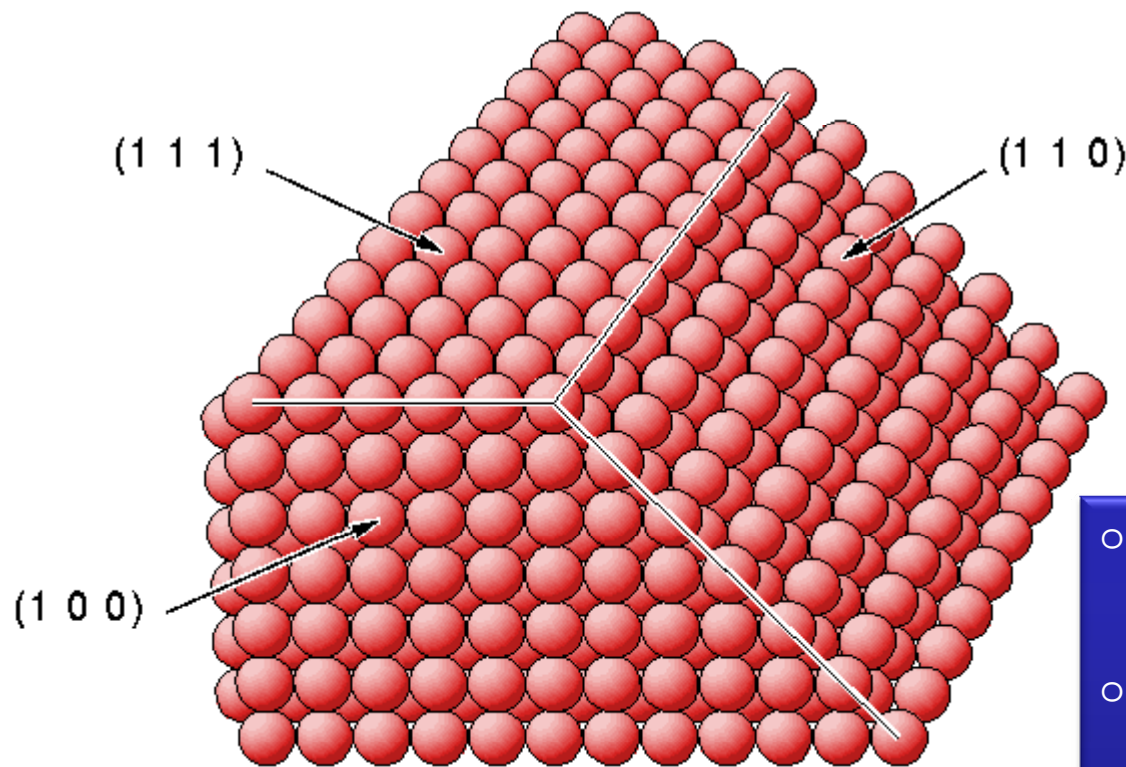
CO is highly reducing. CO must be diluted with air and swept out of the furnace to keep the furnace atmosphere oxidizing.



- Sintering: consolidation of a solid compact at elevated temperature from 60% density (typical) to > 98% density
- Starts to occur at approximately 50% of T_M
- Driving force: Reduction of surface energy (decrease in surface area)
- Atomic diffusion from high energy surface sites to lower energy bulk sites
- Kinetics of sintering can be greatly enhanced by the presence of a liquid phase (“Liquid Phase Sintering”)



Driving Force for Sintering: Reduction in Surface Energy

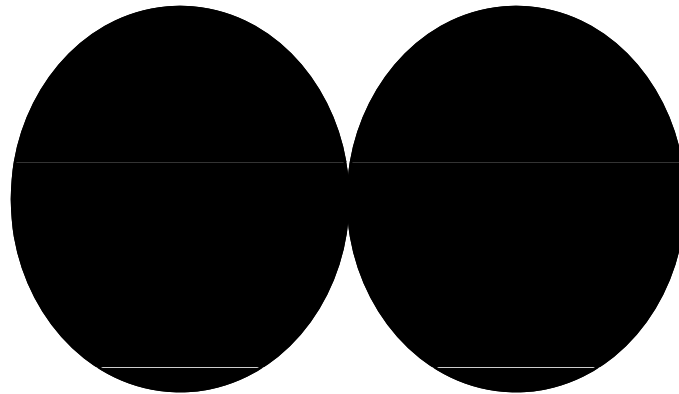


fcc lattice : different net planes

- Bulk atoms
 - 3D bonding is satisfied
 - Low Energy
- Surface atoms
 - Unsatisfied bonding
 - Higher Energy
- Reducing the percentage of surface vs. bulk atoms in a given material system lowers the overall energy



Driving Force for Sintering: Reduction in Surface Energy



Metal Particles- No Sintering



Metal Particles- Sintering has resulted in “neck” formation. Atomic diffusion from surface in bulk neck region.



Liquid Phase Sintering

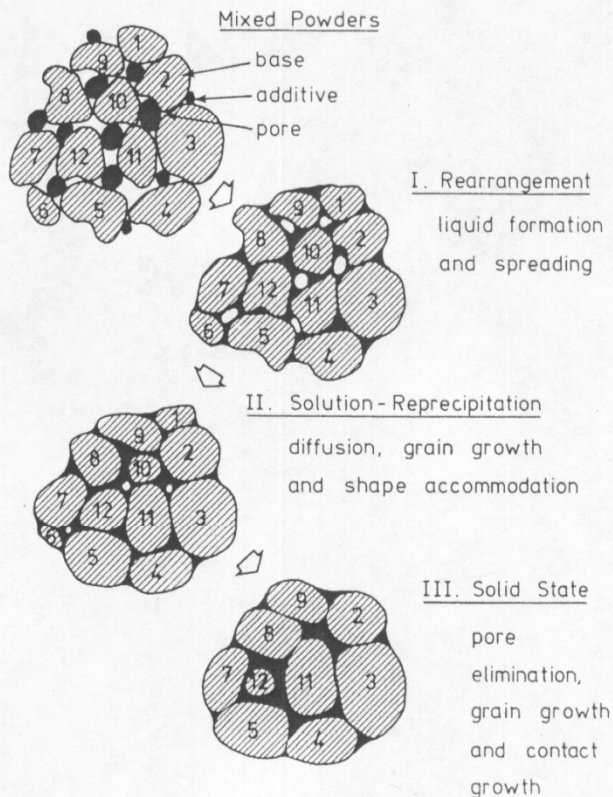


Figure 1.2 The classic stages of liquid phase sintering involving mixed powders which form a liquid on heating.

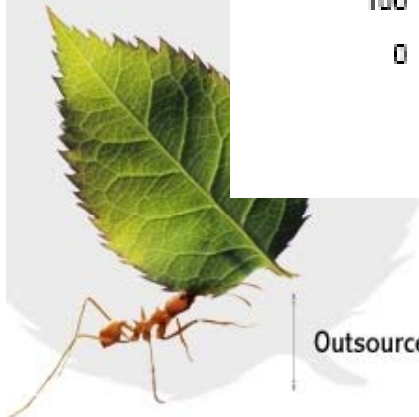
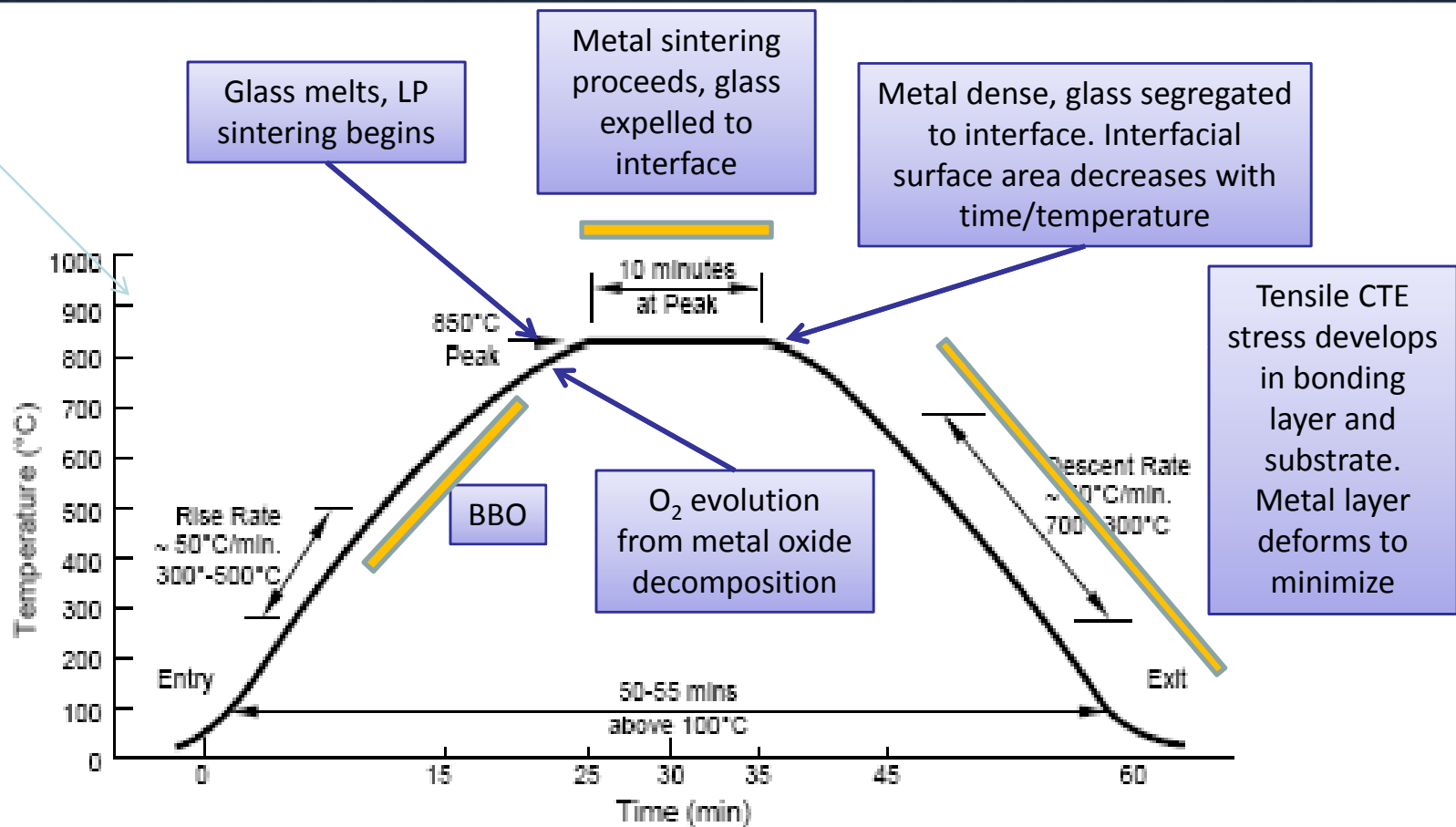
- Metal powder with a additive that forms a liquid at sintering temperature
- Surface diffusion (solid state) is replaced by dissolution of the metal phase followed by re-precipitation out of the liquid
- Kinetics (rate) of densification increases significantly

Liquid Phase Sintering during Thick Film Firing

- The glass additive in the paste (borosilicate) forms a liquid at firing temperature and wets the metal powder
- Metal particle re-arrangement and dissolution/re-precipitation of the metal in the melted glass increases metal densification rates
- As the metal densifies, the glass migrates to the interface with the dielectric/ alumina substrate where a bond is formed. The driving force for this migration is preferred wetting of the glass with the dielectric/ alumina compared to the metal component
- The oxide liquid forms a bond with the (oxidized) metal surface
- The resultant microstructure has only a very small glass content remaining within the metal phase
- This LP Sintering of the thick film layer is constrained by the rigid substrate. This limits XY shrinkage vs. Z shrinkage of the layer.
- For extended sintering times or high temperatures, the interfacial area between the glass bonding phase and conductor decreases.



Firing Profile- Example



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MATERIAL AND PROCESSING REQUIREMENTS FOR THICK FILM INK FABRICATION



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Material Requirements for Successful Processing

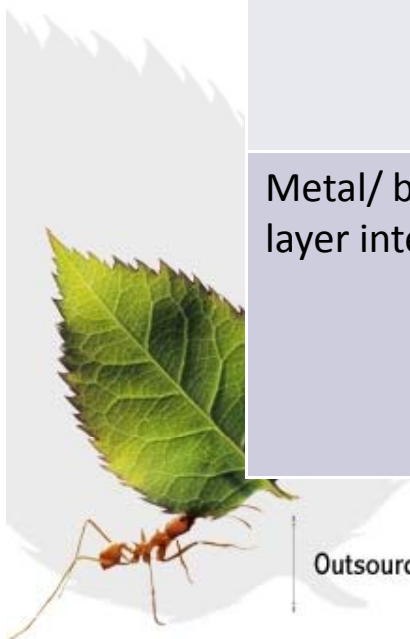
| Component | Material Requirements | Rationale |
|---------------------------------|--|---|
| Glass phase in bonding layer | Must form a low viscosity, low surface tension liquid at T_{fire} | Required for LP Sintering of metal |
| Glass phase in bonding layer | Must not form a liquid at $T_{\text{fire}} - 50\text{C}$ | Formation of a liquid too early leads to early metal sintering without complete BBO |
| Metal phase in functional layer | Must form an oxide alone or after reaction with paste additive (Au only) | Ionic bond to glass can only be formed with an oxide surface on the metal |
| Metal phase in functional layer | Must sinter to full density at a reasonable firing temperature $<1000\text{C}$ | Processing costs are too high for higher temperature firing of thick film. |



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Material Requirements for Successful Processing

| Component | Material Requirements | Rationale |
|---------------------------------|---|--|
| Metal phase in functional layer | Needs to be stable at the firing temperature in an oxidizing (air) atmosphere | BBO is too inefficient in a non-oxidizing atmosphere. Gas cost is also too high for non-air processing. |
| Metal phase in functional layer | Can not react to form intermetallic compounds with glass components ($2\text{Pd} + 2\text{Bi O} \rightarrow 2\text{PdBi} + \text{O}_2$) | Thermal and electrical performance of the metal is degraded. Oxygen is taken from the glass which decreases bond adhesion. |
| Metal/ bonding layer interface | Firing conditions (time and temperature) must be optimized | If temperature is too high, or sintering time is too long, the interfacial area between the metal and bonding glass becomes too low (interface is too smooth). This lowers the bonding adhesion. |



Processing Requirements for Thick Film Fabrication

| Process Stage | Process Requirement | Issues for Non-compliance to Processing Requirements. Trouble Shooting Guide |
|-------------------------------------|--|---|
| Firing- BBO Stage | Furnace atmosphere is oxidizing | Organic binder removal is based on combustion with O_2 . Incomplete BBO will result in poor metal sintering. Air flow must be sufficient to keep furnace atmosphere oxidizing (even with CO produced) |
| Firing- Sintering Stage | Furnace atmosphere is oxidizing | Metal surface must be oxidized to bond with oxide glass. In a reducing atmosphere, the metal-oxide-glass bond will not occur. (Even for Au, the Au/X-surface must oxidize for bonding) |
| Firing- Sintering Stage | Temperature and time must be optimized | For T too low or time too short: low density of metal due to incomplete LP sintering (not enough liquid phase formed or not enough time for the metal to completely densify) |
| Firing of Au paste- Sintering Stage | Temperature must be optimized | For T too low: adhesion promoter oxide additives (CuO, CoO, BiO) may not decompose to the metal phase. Then Au/X alloy does not form, Au/X does not oxidize and no bonding with oxide glass occurs. |

Processing Requirements for Thick Film Fabrication

| Process Stage | Process Requirement | Issues for Non-compliance to Processing Requirements. Trouble Shooting Guide |
|--------------------------|---|--|
| Firing- Sintering Stage | Temperature and time must be optimized | For T too high or fire time too long: Interfacial area between metal phase and glass bonding phase becomes too low (too smooth). Poor overall bond strength. |
| Firing- Sintering Stage | Temperature rise time must be optimized | If rise time is too fast- gas from any gas producing reaction (CuO, CoO, BiO decomposition) will evolve too quickly and will blister or mechanically damage the layer. |
| Firing – Sintering Stage | Temperature rise time must be optimized | If cool time is too fast- CTE stress between metal, glass bonding layer and substrate will be too large. Cracking of glass bonding layer or of the substrate can result. |



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Thick Film Processing- Dynamic “Window” to Achieve Ideal Microstructure and Strong Bonding

Under-Fire: Metal is porous, glass is within metal phase, bonding may not be complete

Optimum Process Window: Dense Metal, Segregated Glass, High SA M/G interface, Strong bonding M/G and G/Substrate

Over fire: Dense Metal, Segregated Glass, low SA M/G interface with low bond strength.

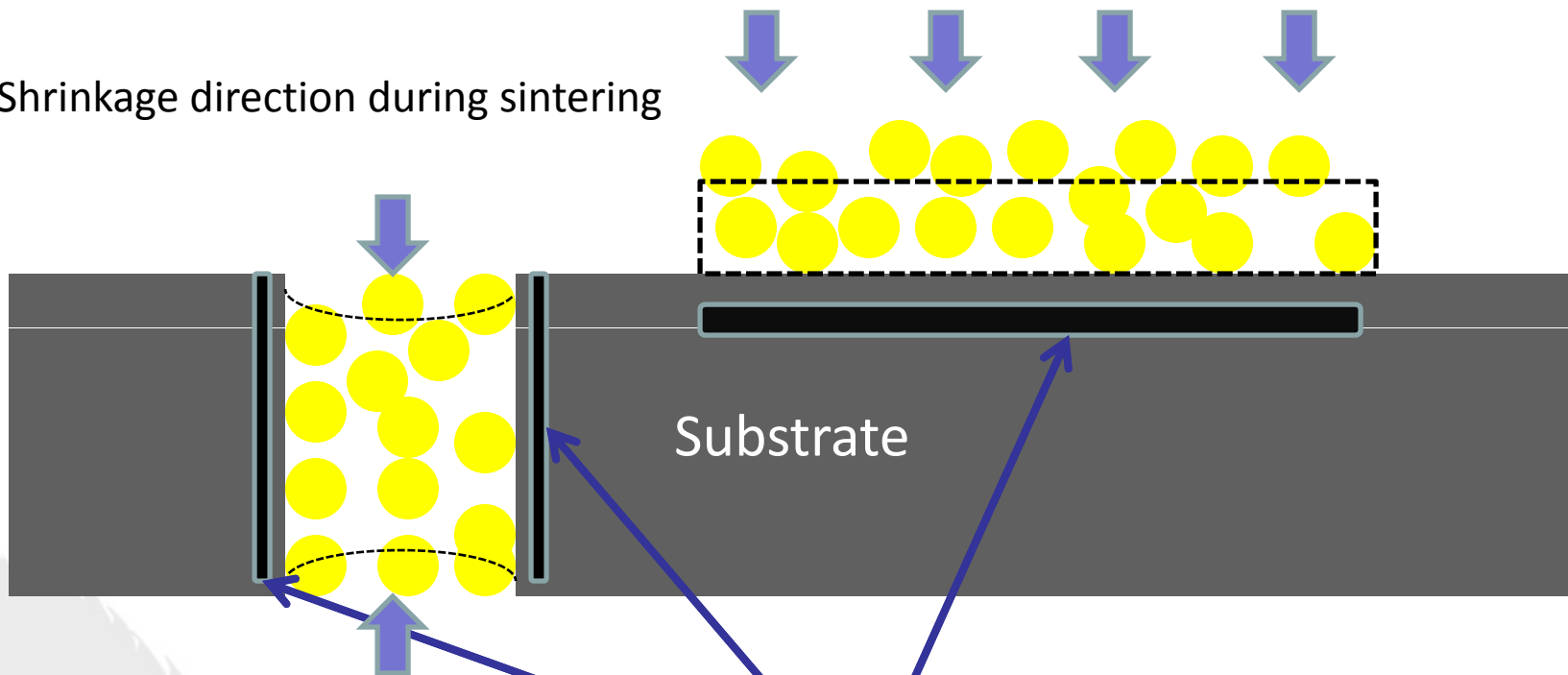
Firing Temperature



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Special Topic- Thick Film Via Fill

Shrinkage direction during sintering

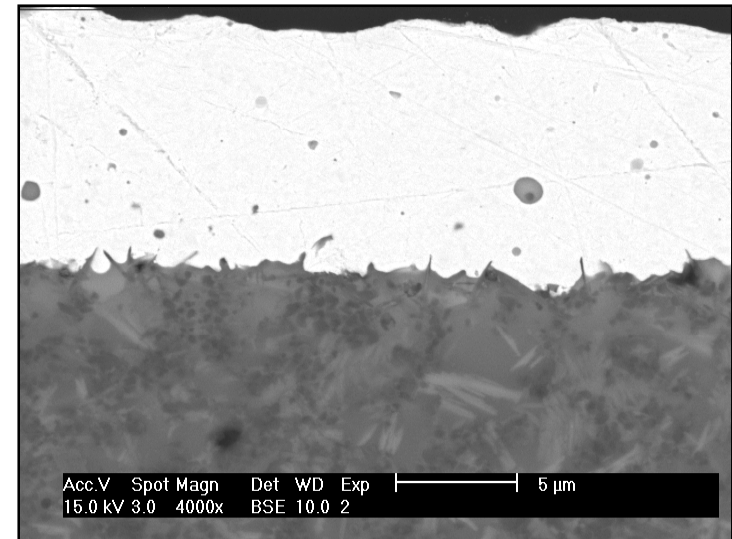
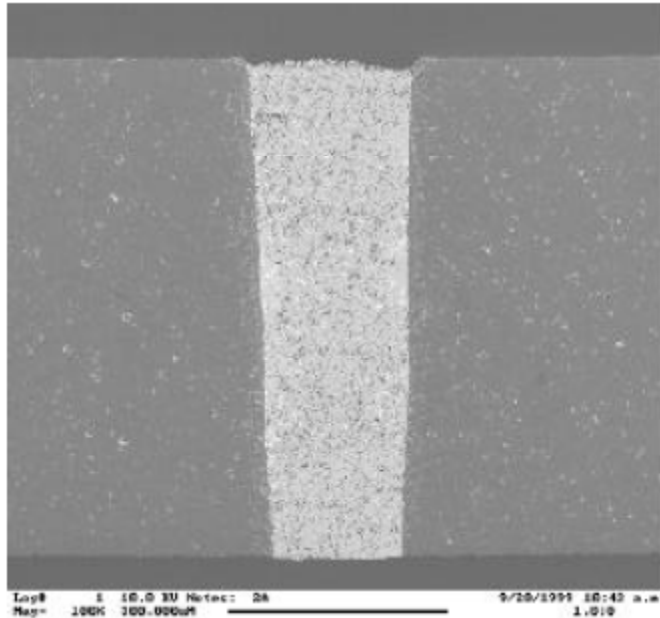


Constrained Surface during thick film sintering
Constraints during sintering control final
microstructure



Thick Film Via Fill

PdAg



Via sintering is highly constrained by adhesion to the via walls. Result is a much lower density metal and non-hermetic vias. Final metal density is largely controlled by non-fired (green) density. Via depressions from z direction sintering can be eliminated by “overfilling” vias.

Free sintering of metal in the z direction allows sintering to full density for printed surface conductors. Final density is not highly sensitive to non-fired (green) density.



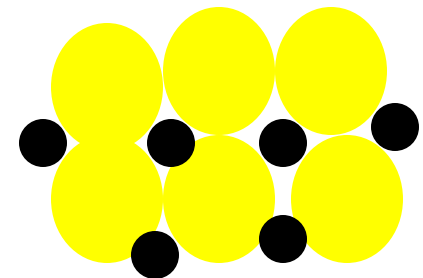
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Via Fill Processing Approaches

- Goal: Highest Green Density
 - Tightest packing of metal particles
 - Achieved by choice of particle sizes in distribution and optimized particle shape
 - Higher green density = lower shrinkage = higher metal density in final film and reduced porosity
 - Very high solids loaded pastes (high viscosity)
- Vacuum assisted screen printing
- Pressure filling of via holes



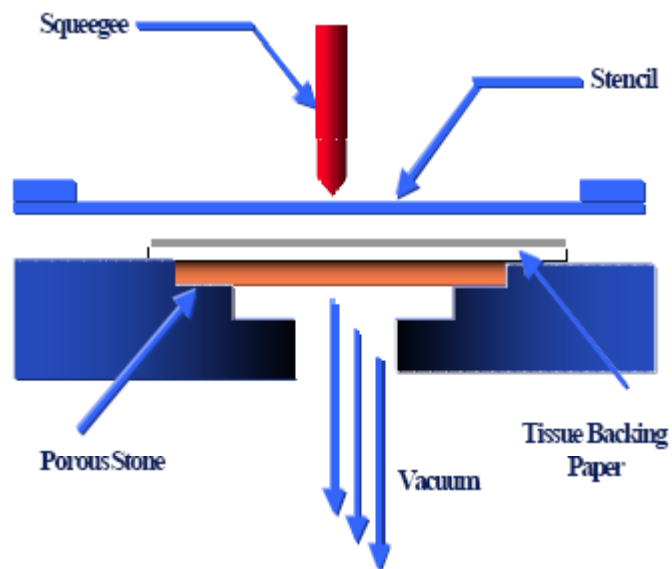
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Bi-modal PSD. Small particles fill interstitial spaces between large particles

Via Filling Techniques- Screen Printer

Screen Printing Method
Off Contact Via Filling



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Via Filling Techniques- Extrusion Pressure Fill



CMC's old unit manufactured by PTC

- Paste resides in a reservoir
- Paste is extruded through a mask using a air pressure activated rubber membrane ("bladder").
- Paste is not exposed to air so that the tape viscosity is constant (no solvent is evaporated)
- Typically achieves a higher green-density than screen printed inks which results in less paste shrinkage during firing (and higher metal loading)
- IBM Microelectronics uses this type of extrusion process for all ceramic metallization (custom unit)



Alternative Thick Film Technology- TiCuAg

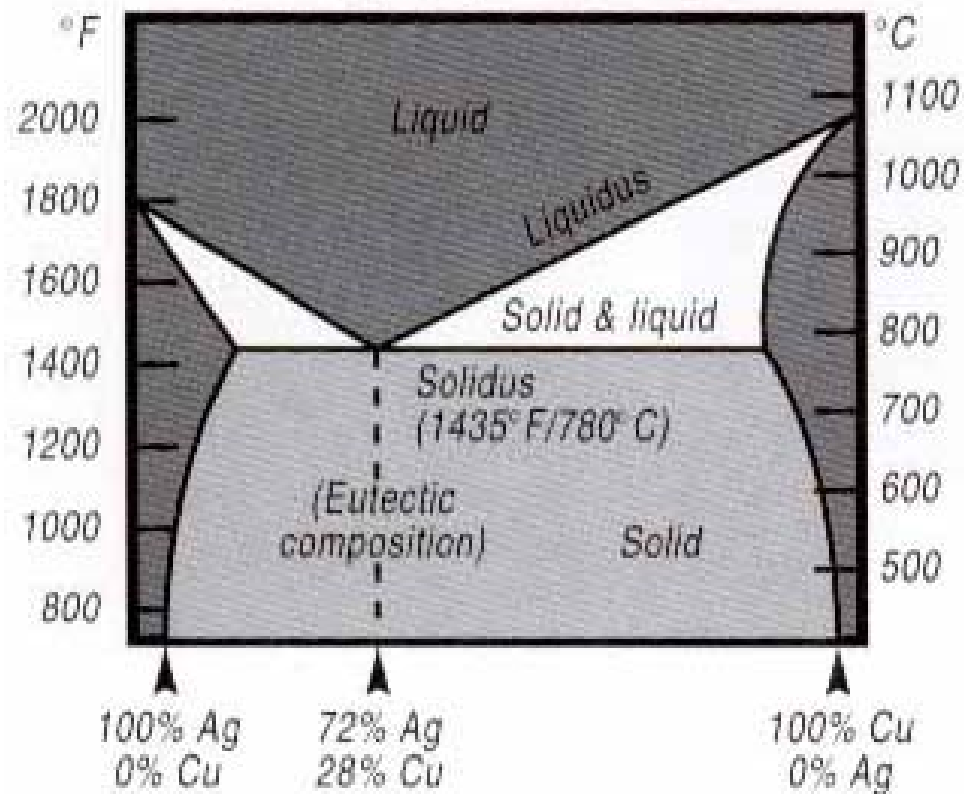
- TiCuAg (0.3 Wt% Ti) metal powder screen printed with an organic binder directly on the ceramic surface
- Firing conditions < 850C in nitrogen or nitrogen/hydrogen
- TiCuAg bonds to both Alumina and AlN- Ti reacts with ceramic to form Ti-oxide or Ti-nitride bonding phase
- Electrical and thermal performance in the metal layer is lower than current Au thick film compositions
- Thermal performance in the vertical direction is enhanced compared to current Au thick film compositions- no glass frit layer at the interface
- Primarily targeted to AlN to optimize heat transfer into the ceramic from devices on the surface
- Performance is a very sensitive function of Ti content and processing conditions



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Alternative Thick Film Technology- TiCuAg

Silver-copper equilibrium diagram



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