Nanoelectronics & Packaging Lab

Portland State University

Isotropic
Electrically Conductive Adhesives

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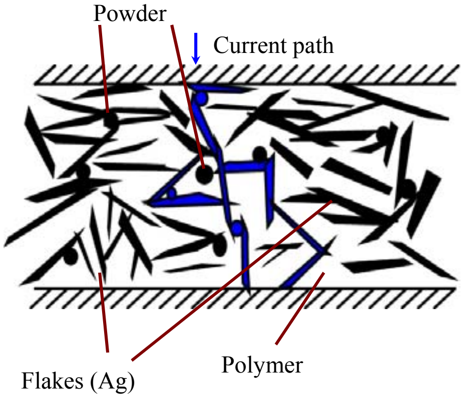
ICA: Isotropic Conductive Adhesives



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- Introduction
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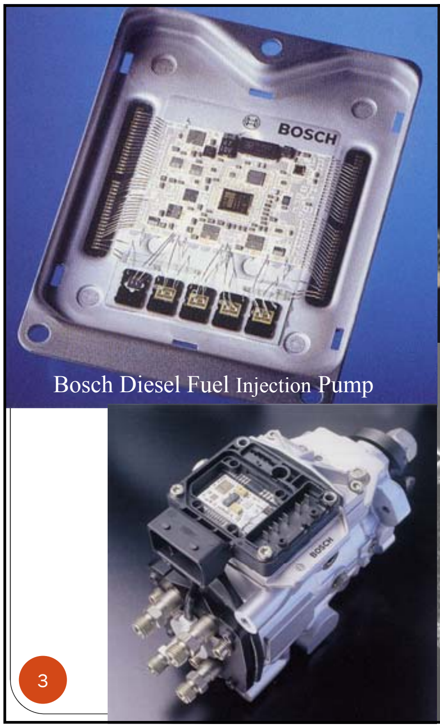
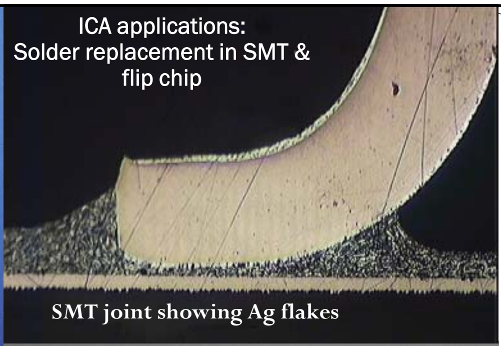
- Galvanic corrosion
- Cure models
- Miscellaneous

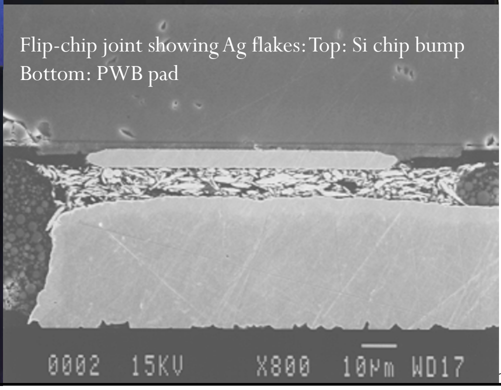


Bosch Diesel Fuel Injection Pump



ICA applications:
Solder replacement in SMT &
flip chip

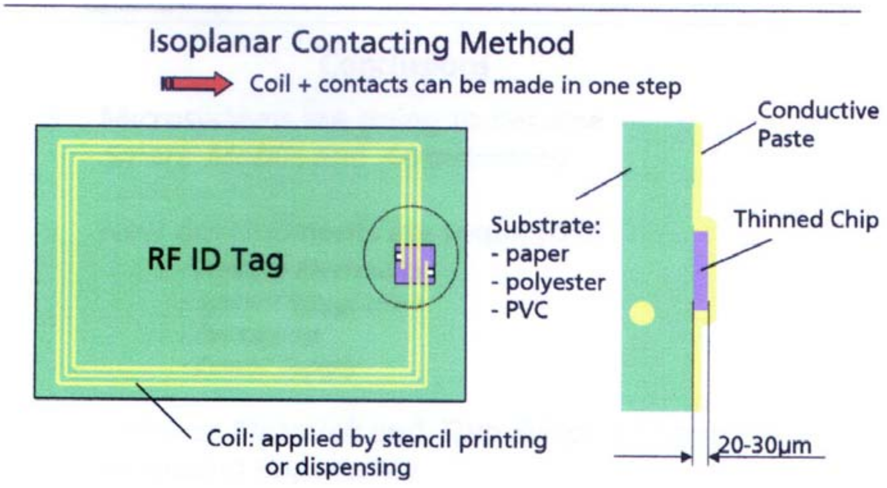
SMT joint showing Ag flakes



Flip-chip joint showing Ag flakes: Top: Si chip bump
Bottom: PWB pad

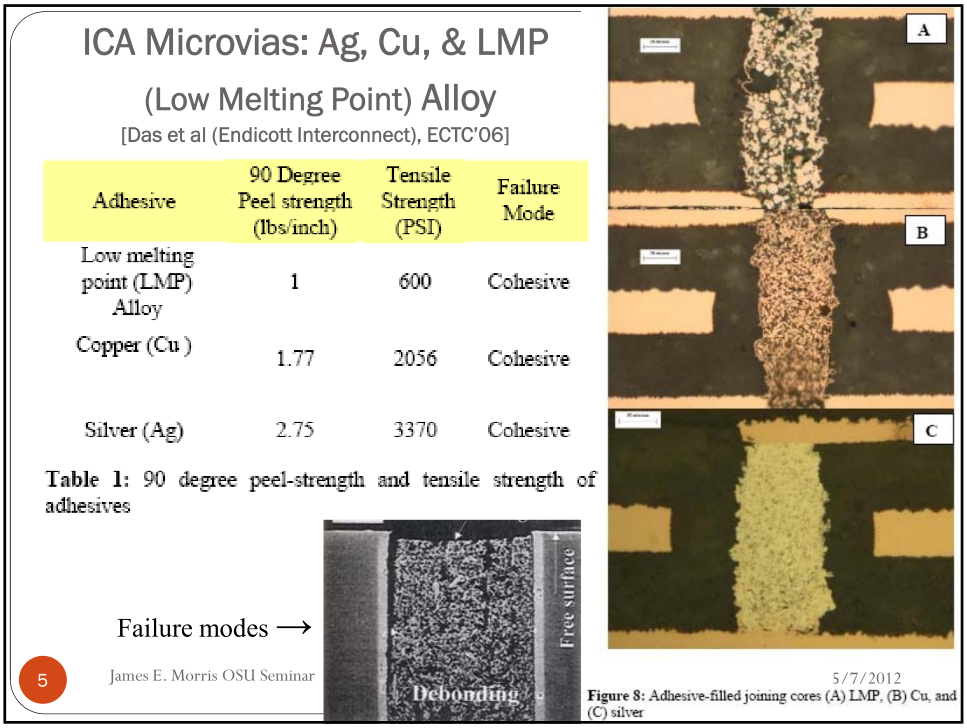
ICA Smart Cards & RF ID

(IZM-Berlin)



Isoplanar Contacting Method

Coil + contacts can be made in one step



ICA Microvias: Ag, Cu, & LMP (Low Melting Point) Alloy

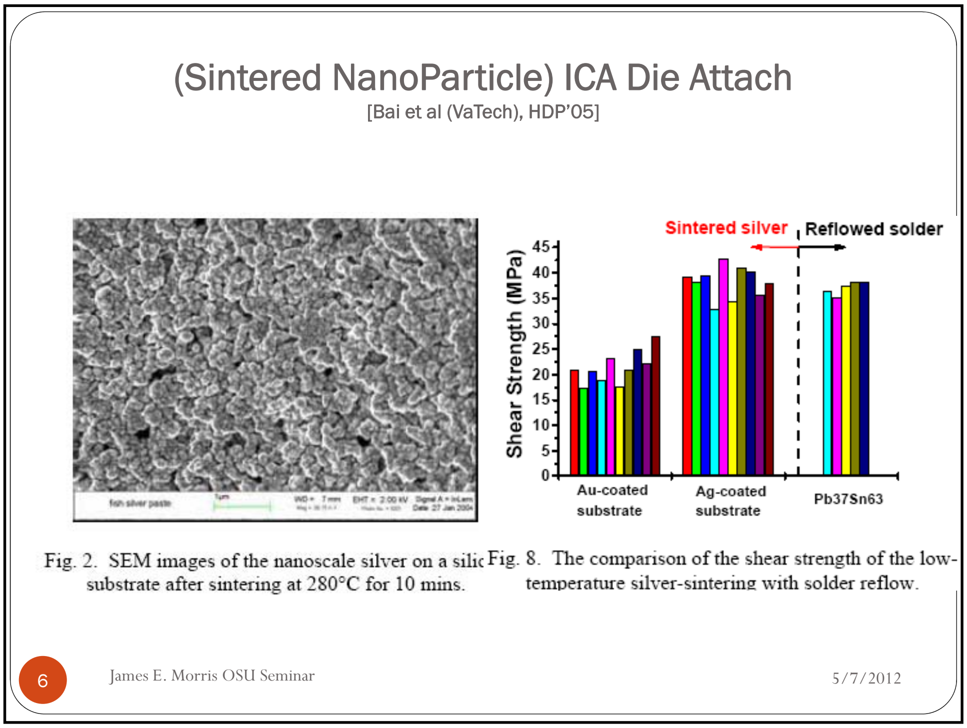
[Das et al (Endicott Interconnect), ECTC'06]

Adhesive	90 Degree Peel strength (lbs/inch)	Tensile Strength (PSI)	Failure Mode
Low melting point (LMP) Alloy	1	600	Cohesive
Copper (Cu)	1.77	2056	Cohesive
Silver (Ag)	2.75	3370	Cohesive

Table 1: 90 degree peel-strength and tensile strength of adhesives

Failure modes ⟶

Figure 8: Adhesive-filled joining cores (A) LMP, (B) Cu, and (C) silver



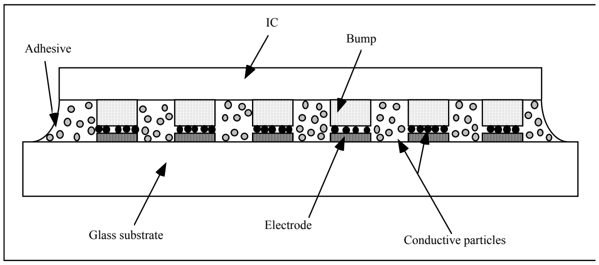
(Sintered NanoParticle) ICA Die Attach

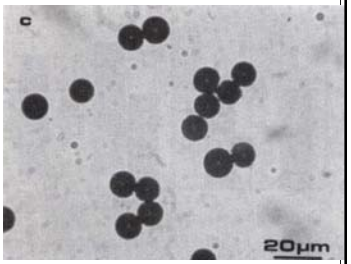
[Bai et al (VaTech), HDP'05]

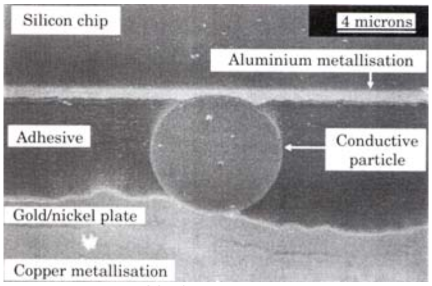
Fig. 2. SEM images of the nanoscale silver on a silic substrate after sintering at 280°C for 10 mins.

Fig. 8. The comparison of the shear strength of the low-temperature silver-sintering with solder reflow.

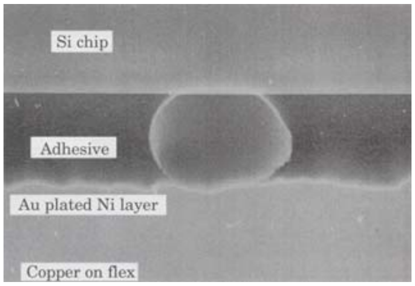
ACA: Anisotropic Conductive Adhesive (& ACF)







Ni particle

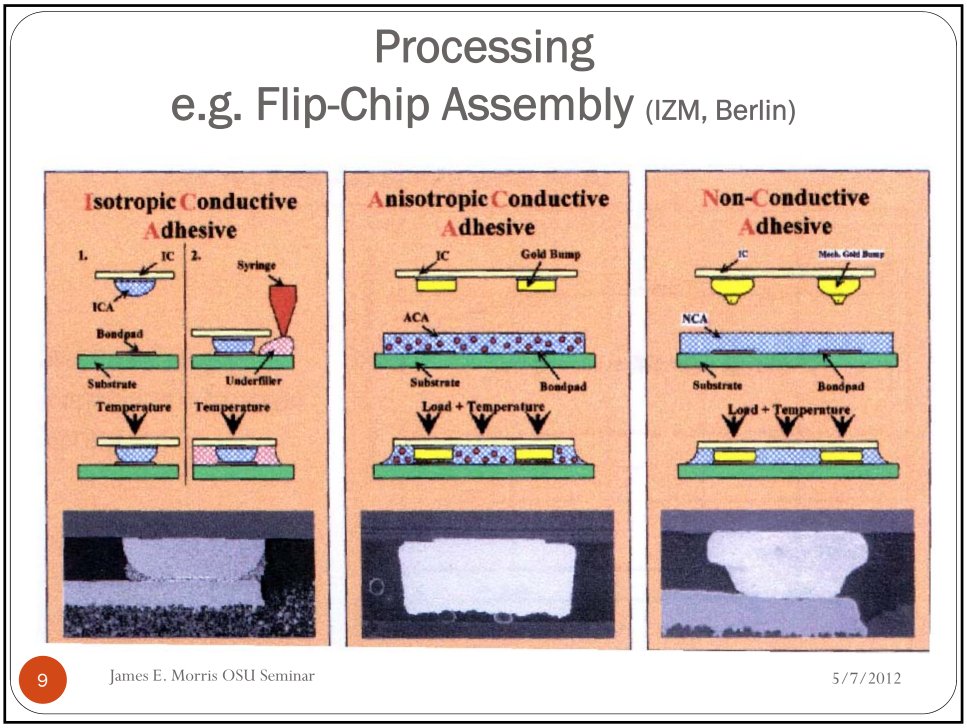


Coated polymer particle

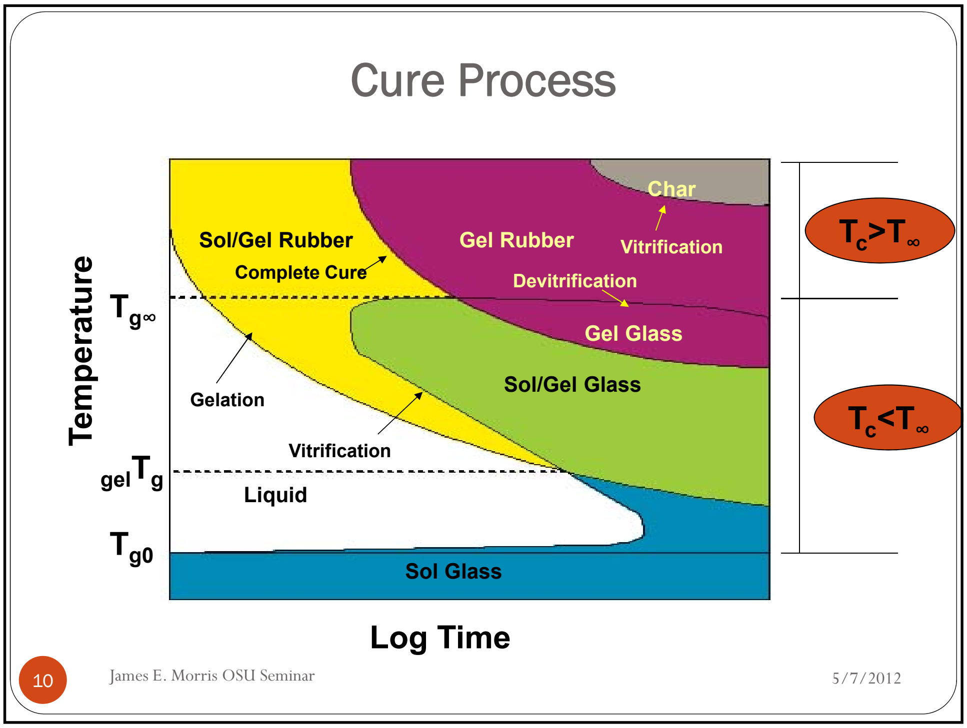
Technology Drivers

- Environment
  - Environmental:
    - - No-flux, no-Pb
  - No-Pb solders
    - -Melting temperatures
    - -Thermomechanical stress
  - Silver effects
- Economics
  - Manufacturing
    - Fewer process steps
    - Available technologies (stencil/screen/dispense)

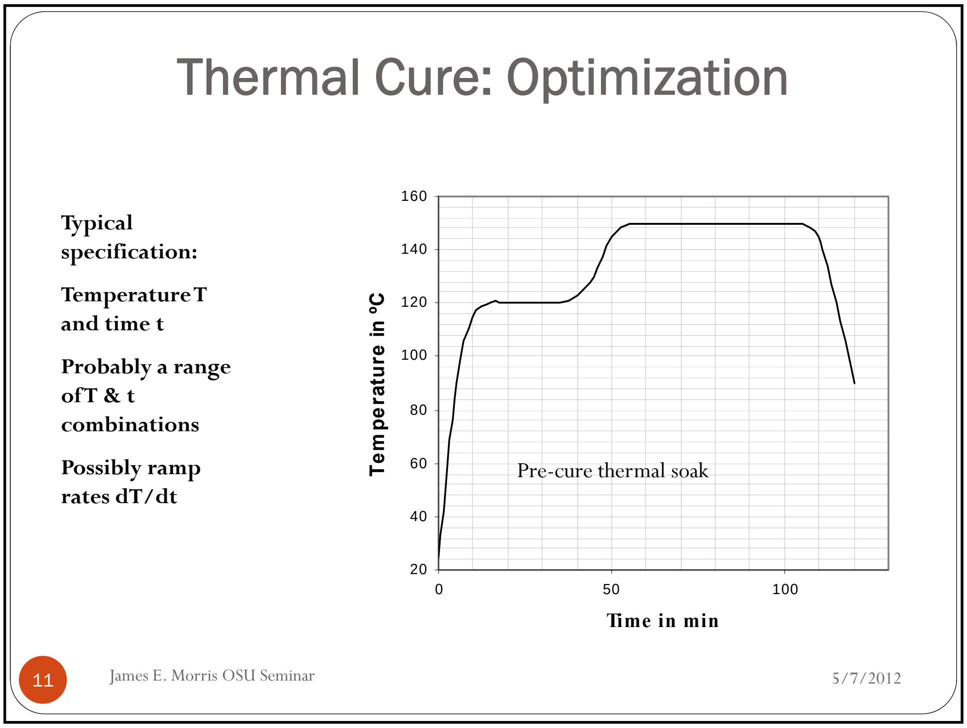
- Technology drivers (c.f. solder)
  - Thermomechanical stress
    - Low process temperature
    - High compliance
  - Fine-pitch (area array) interconnect
    - Smaller particles than solder
    - No slumping
    - Inter-metallic diffusion in solders
    - Electromigration



Processing
e.g. Flip-Chip Assembly (IZM, Berlin)



Cure Process



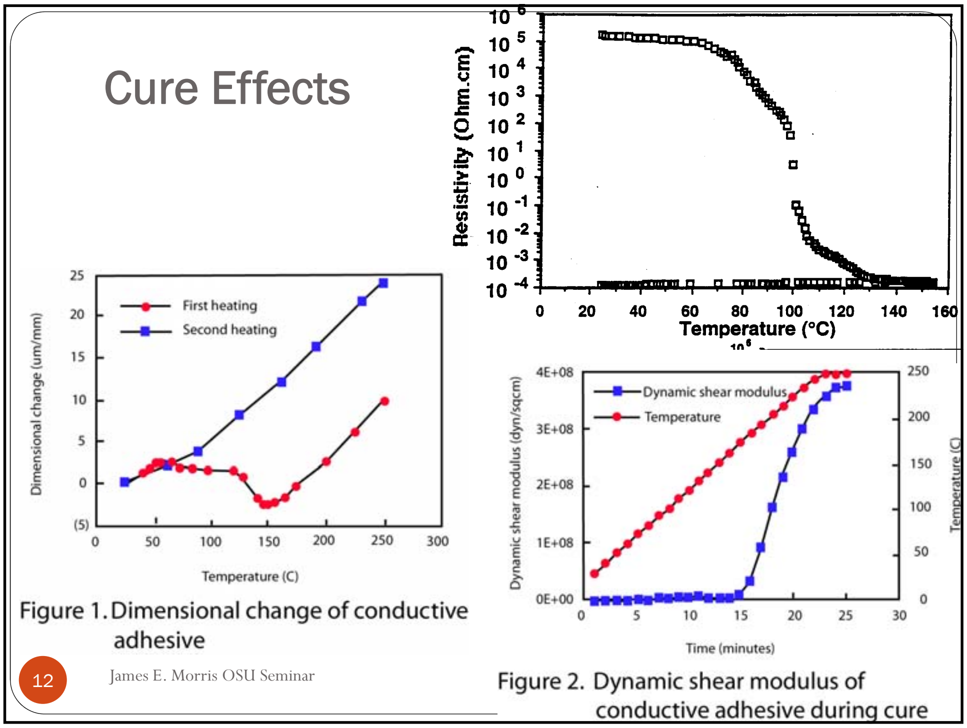
Thermal Cure: Optimization

Typical specification:

Temperature T and time t

Probably a range of T & t combinations

Possibly ramp rates dT/dt



Cure Effects

Figure 1. Dimensional change of conductive adhesive

Figure 2. Dynamic shear modulus of conductive adhesive during cure

Properties

Commonly used isotropic conductive adhesives

(Jagt, Chapter 11, Conductive adhesives for Electronics Packaging)

Adhesive & Type	Viscosity (Pa.s)	Potlife	Glass transition	Volume Resistivity Ωcm	Shear strength (MPa)	Curing time (min.)	Curing Temp. (°C)
ICA 1 (1 comp.)	65	3 days	80	2.10^{-4}	11	10-15	130-150
ICA 2 (2 comp.)	25-35	3-4 days	85	$1\text{-}4.10^{-4}$	10	30	130-140
ICA 3 (2 comp.)	50	2 days	50	$2\text{-}4.10^{-5}$	8	90	130-140
ICA 4 (1 comp.)	160-200	4 days	80	5.10^{-3}	5	20-30	120-130
ICA 5 (1 comp.)	310-350	4 days	80	1.10^{-3}	4	20-30	120-130
ICA 6 (2 comp.)	150-200	8-12 hr	75	$2\text{-}5.10^{-4}$	14	10-15	170-180

Compare intrinsically conducting polymers,

e.g. Polyaniline: $\rho = 10^{5}$ (intrinsic) to 10^{-2} Ω.cm (doped)

Compare Ag: $\rho_{Ag} = 1.6 \times 10^{-6}$ Ω.cm; $\rho_{ICA} = 12.5$ to $312.5 \times \rho_{Ag}$

Glass Transition Temperature

Table 4.3. TMA experimental results for cured block samples.

Materials	T_g (°C)	CTE ($<T_g$) (μm/m°C)	CTE ($>T_g$) (μm/m°C)
Adhesive A	90	56	155
Adhesive B	90	61	168
Adhesive C	90	78	218

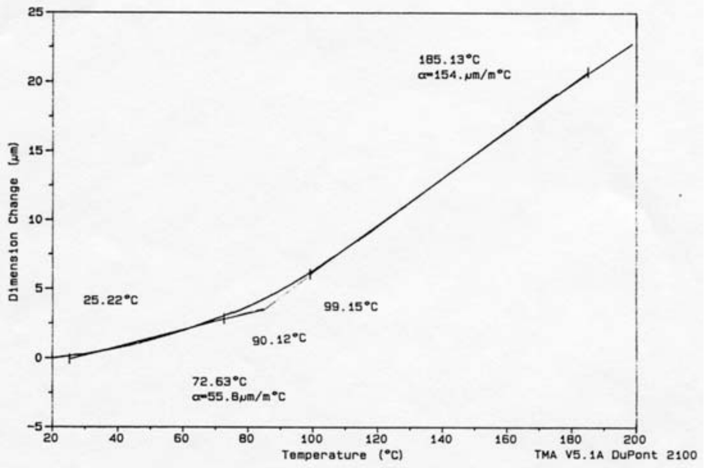
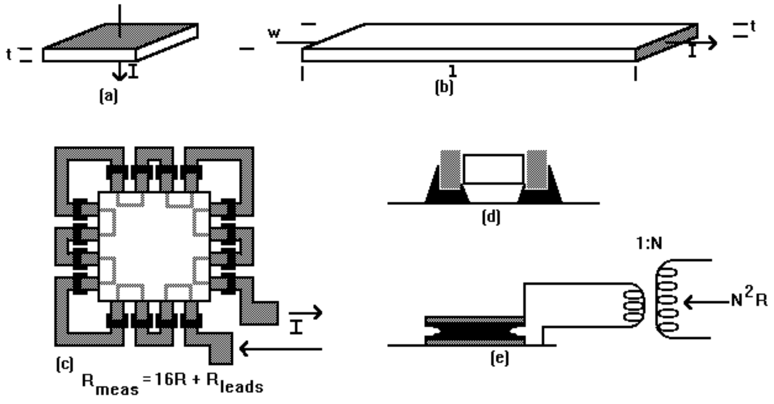


Figure 4.4: Typical TMA graphs for Adhesive A showing CTE above and below T_g.

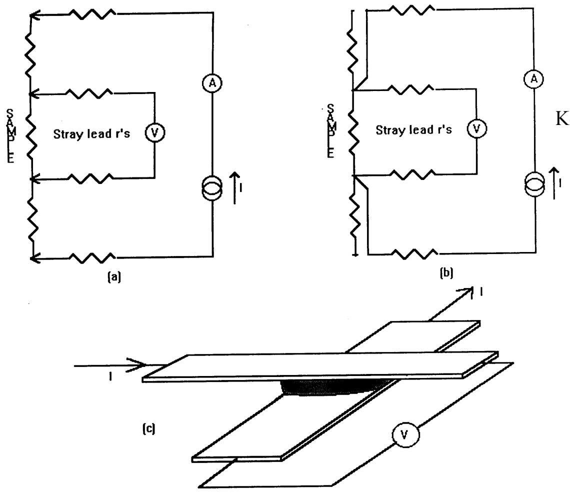
Compare CTEs:
Si = 4-5 ppm/°C
Ag = 20 ppm/°C
Epoxy = 54 ppm/°C
FR4 = 36 ppm/°C

Low Resistance Measurement

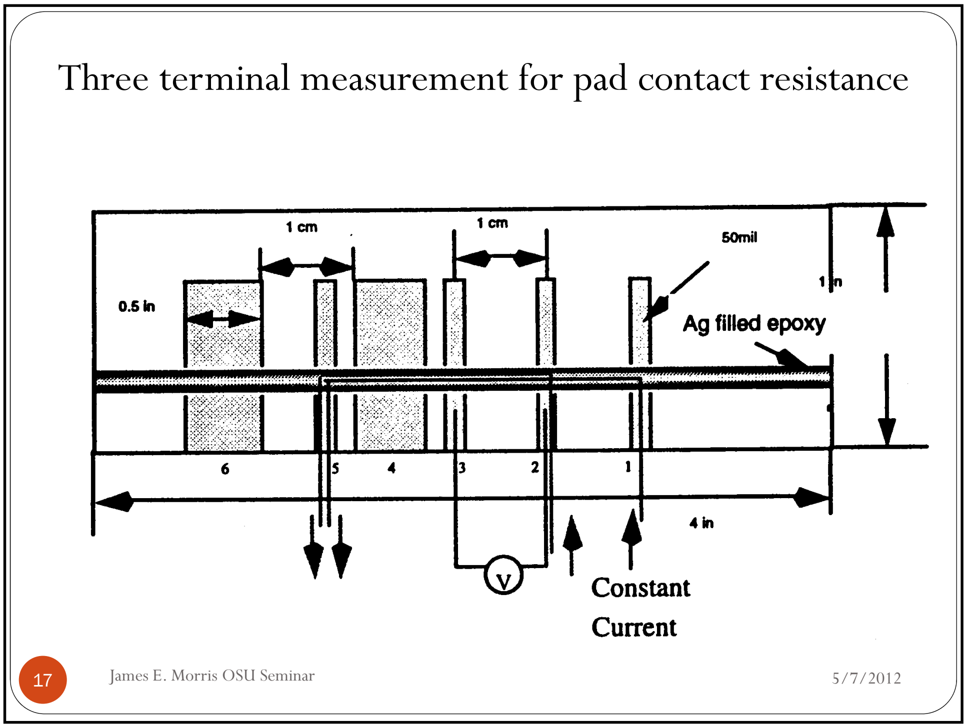


Wheatstone bridge

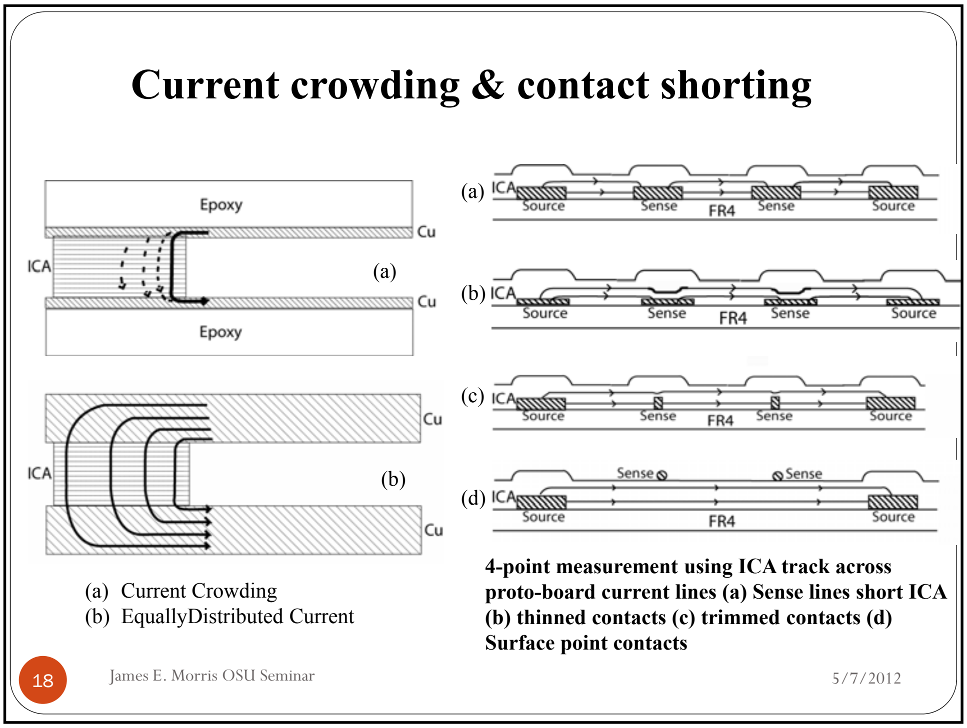
Electrical Test: Four-terminal measurement



Kelvin probe



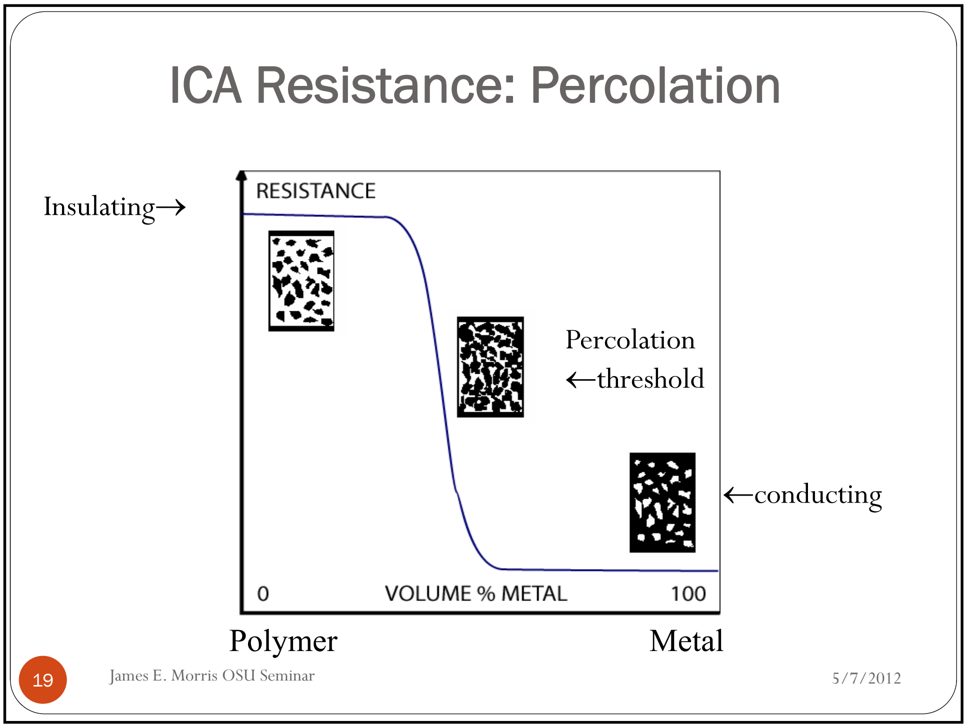
Three terminal measurement for pad contact resistance



Current crowding & contact shorting

(a) Current Crowding
(b) EquallyDistributed Current

4-point measurement using ICA track across proto-board current lines (a) Sense lines short ICA (b) thinned contacts (c) trimmed contacts (d) Surface point contacts



ICA Resistance: Percolation

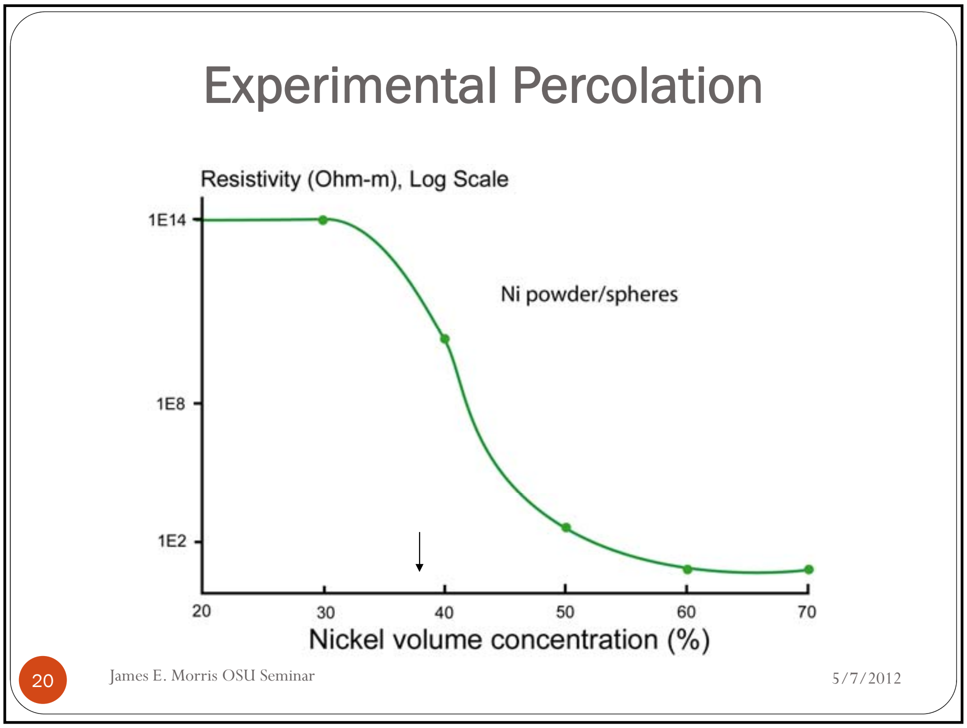
Insulating→

Percolation
←threshold

←conducting

Polymer

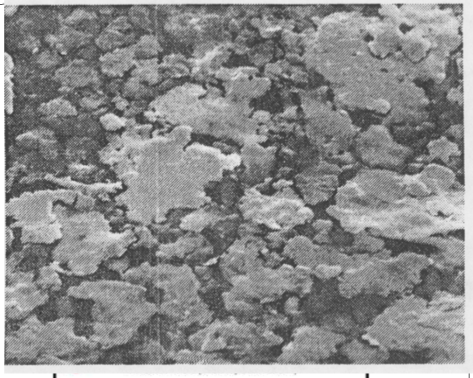
Metal



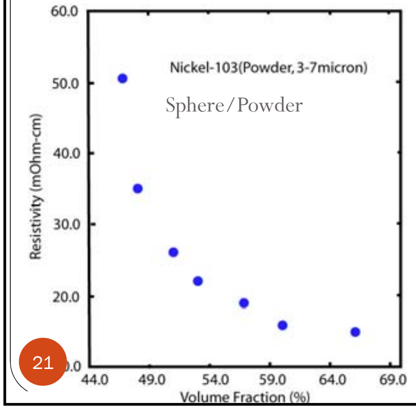
Experimental Percolation

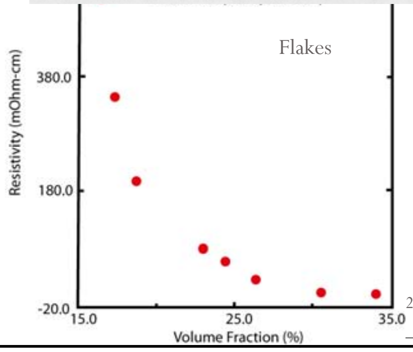
Ni powder/spheres

Flakes: surface/vol ratio

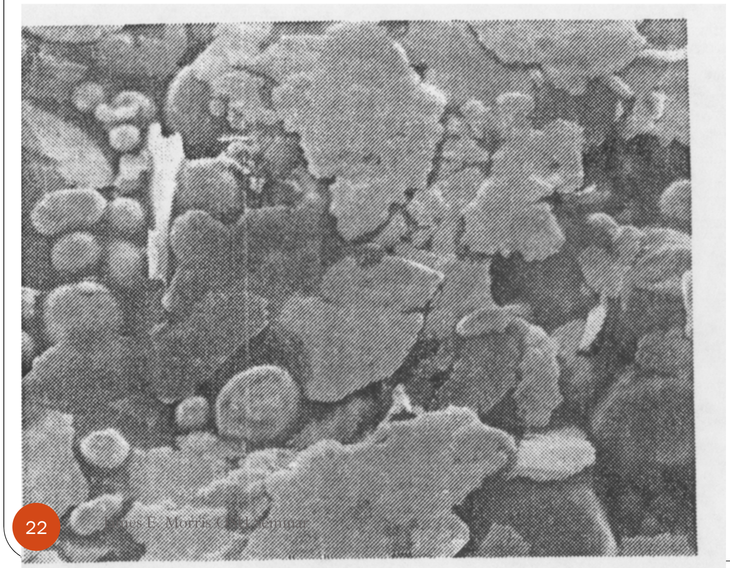


Percolation Threshold Comparison (Sancaktar)





Bi-modal: Flakes + powder



e.g.

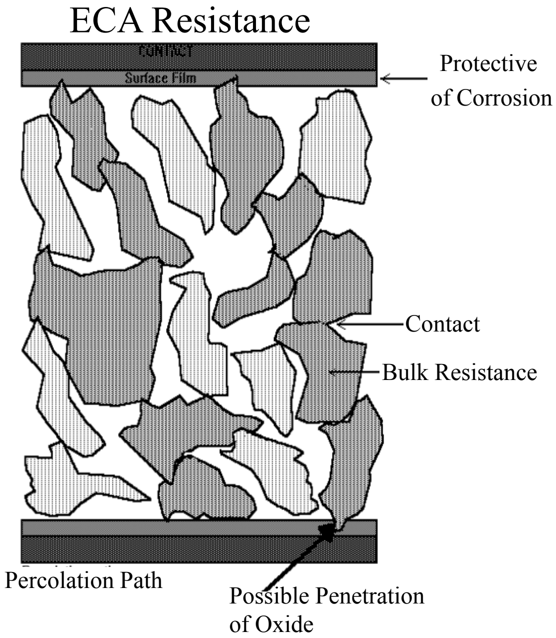
10μm diameter flakes

(<1μm thick)

plus

1-3μm diameter powder

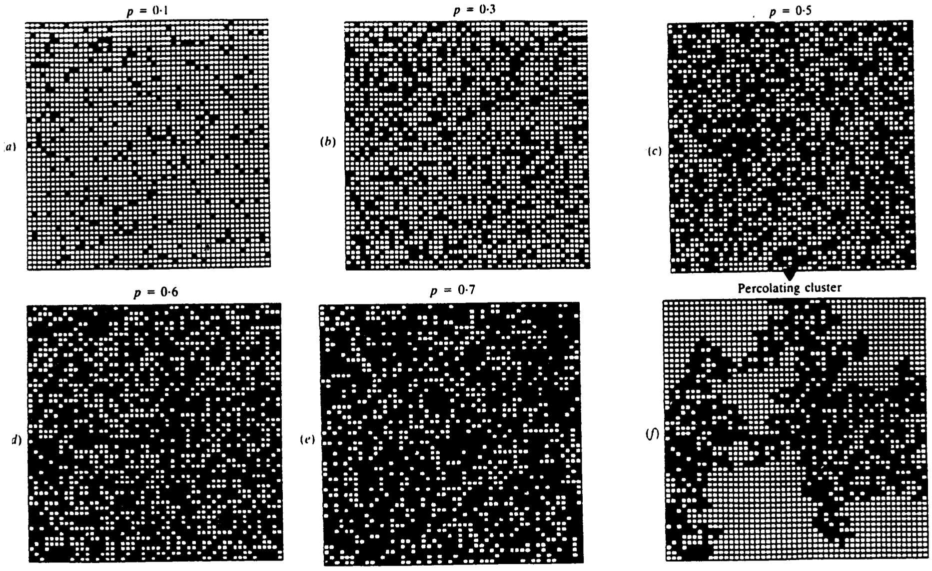
(spheres)



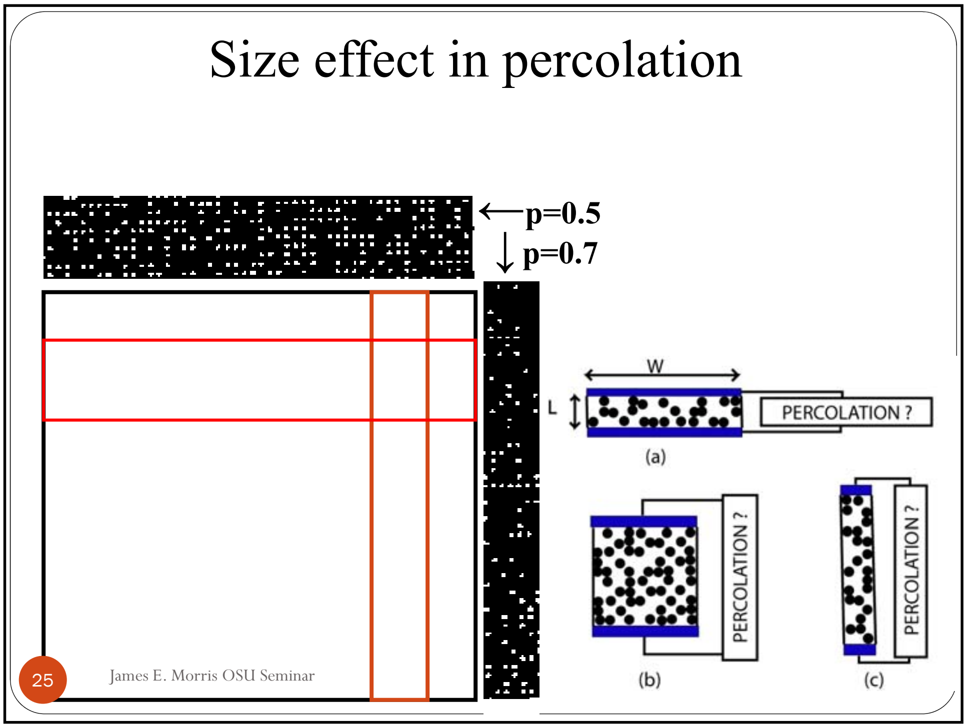
ICA Resistance

- Percolation
- Particle
  - µm particles
  - 10’s nm e^- mfp
  - Negligible size effects
- Inter-particle
  - And pad contact
- Experimental
- (Modeling)

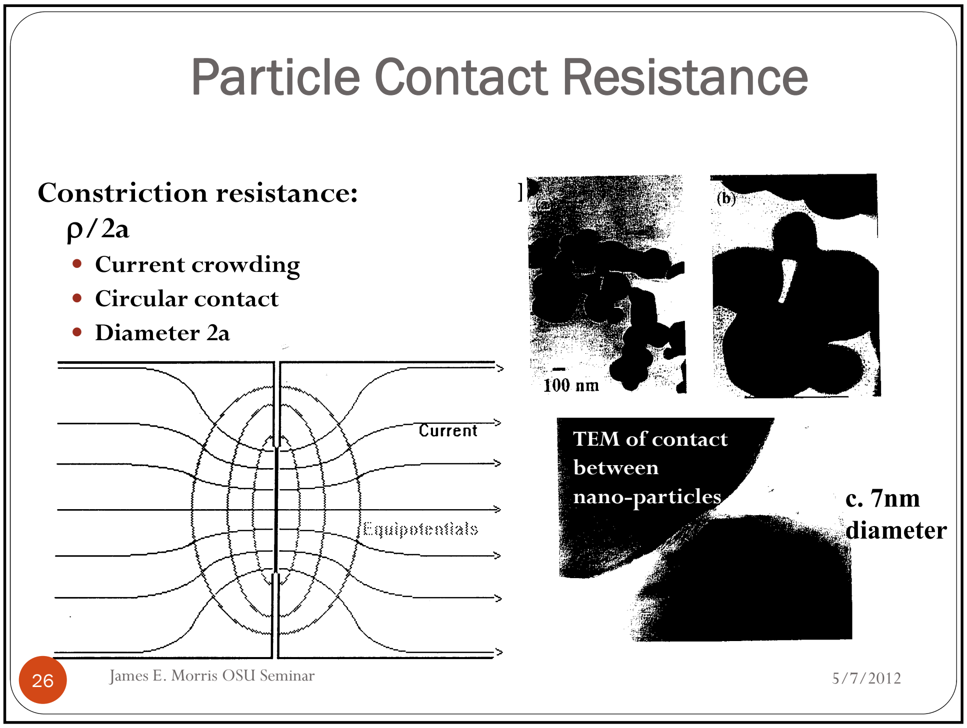
Monte Carlo Percolation Models



- (Smilauer)



Size effect in percolation



Particle Contact Resistance

Constriction resistance:

$\rho/2a$

- **Current crowding**
- **Circular contact**
- **Diameter 2a**

TEM of contact between nano-particles

c. 7nm diameter

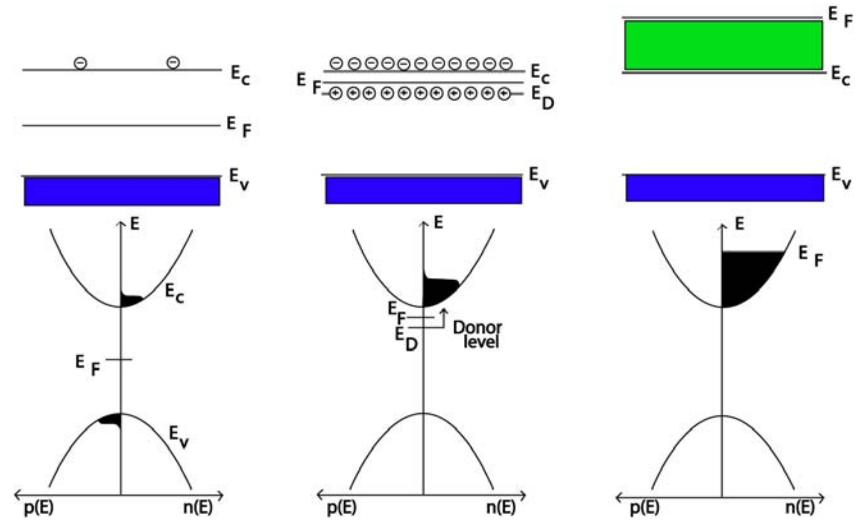
Polymer/Insulating Oxide

- **Thermionic emission (with Schottky effect)**
- **Electron tunneling (with image effect)**
- **Poole-Frenkel emission**
- **Fowler-Nordheim tunneling**

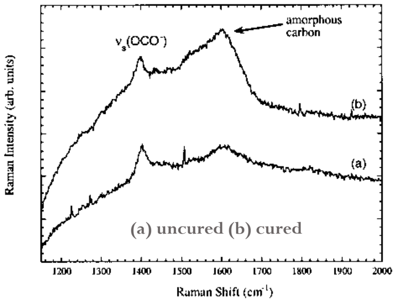
- **TCR ≤ 0 & field effects for various mechanisms**
- **None of these observed**

AgO/Ag$_2$O Degenerate Semiconductor

Intrinsic **Extrinsic** **Degenerate**



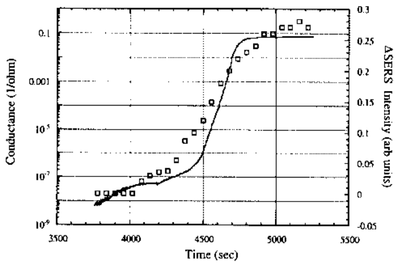
Silver oxide (degenerate semiconductor) Also $\propto 1/a^2$



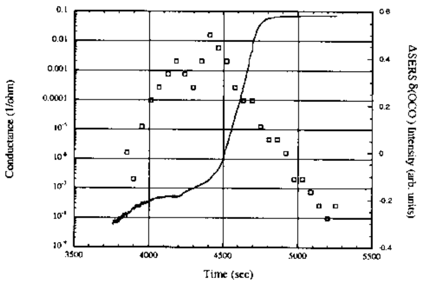
(a) uncured (b) cured

Carbon on flake surface appears after cure: Changes in peak intensities with temperature during cure

Miragliotta, Benson, Phillips, & Emerson: MRS '01, 2002 Materials



LHS: 1600cm-1 C peak

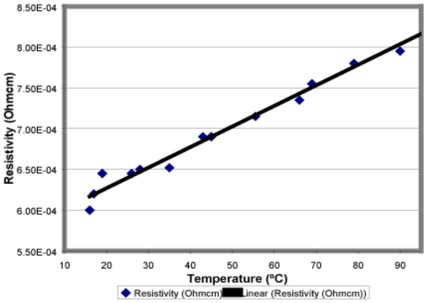


RHS: 744 cm-1 carboxylate peak

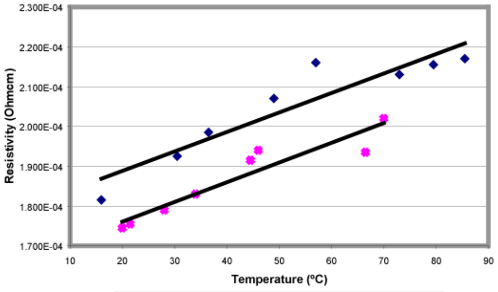
Figure 6. Change in the peak intensity of the carbon ode at 1600 cm^{-1} in the Raman spectrum from the g-filled epoxy. The corresponding sample

Figure 6. Change in the peak intensity of the carboxylate bending mode at 744 cm^{-1} in the Raman spectrum from the Ag-filled epoxy. The

TCR Results



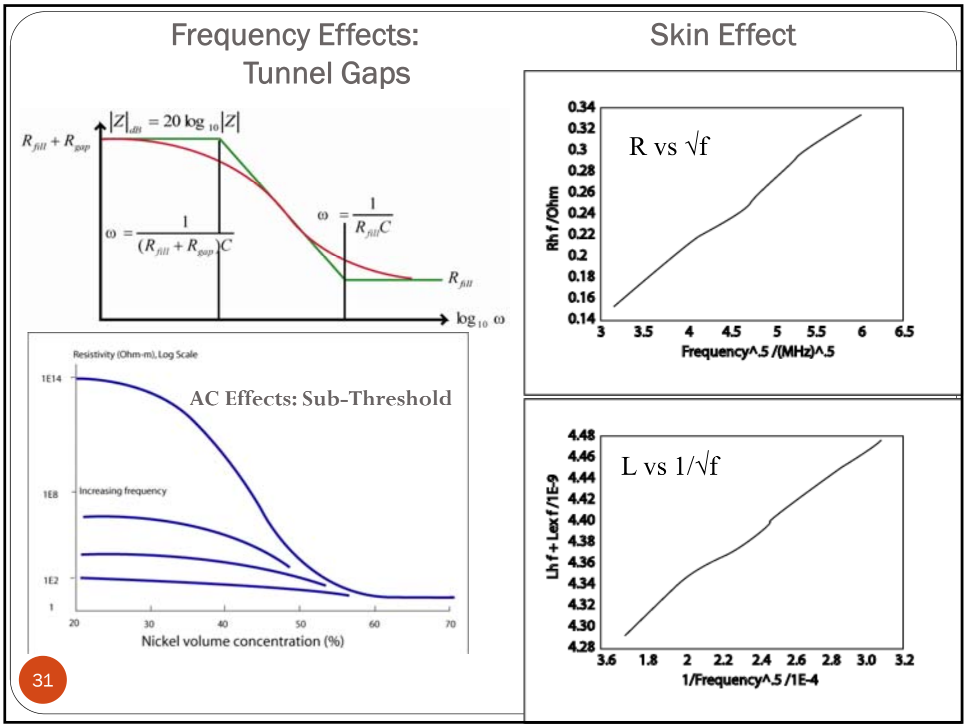
- $TCR_{ICA} \approx TCR_{Ag}$
- $\therefore R_{ICA} \approx R_{Ag}$
- Contact R negligible



Resistivities for various temperatures.

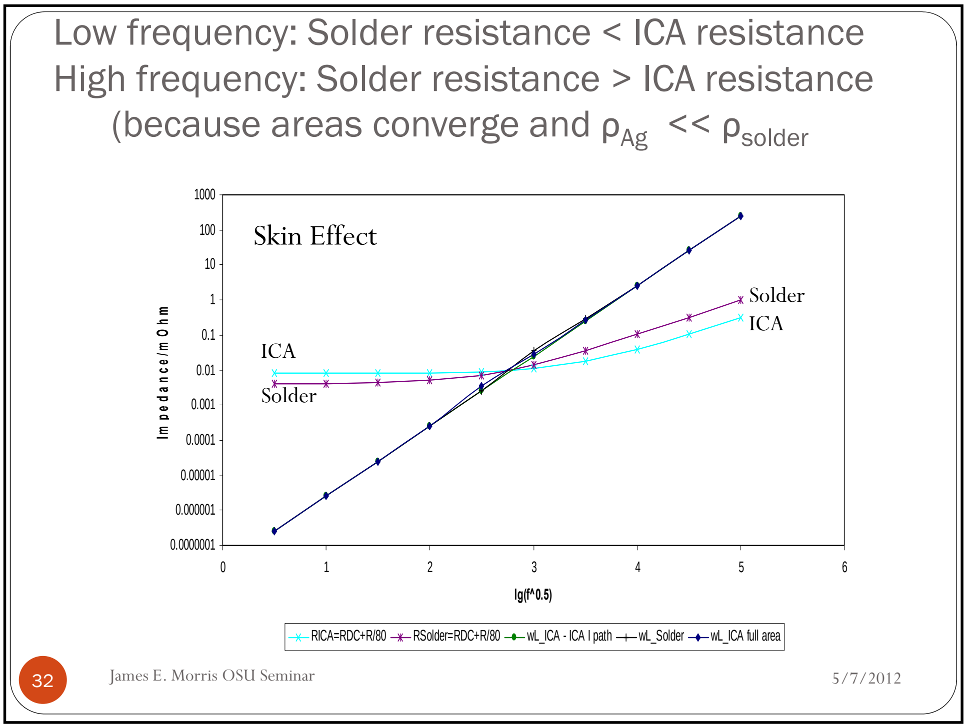
(a) Brass stenciled CT-5047-02 thermoset sample (TCR-0.0039/ºC).

(b) (b) CSM-933-65-1 screen printed thermoplastic sample {TCR=0.0038/ºC}

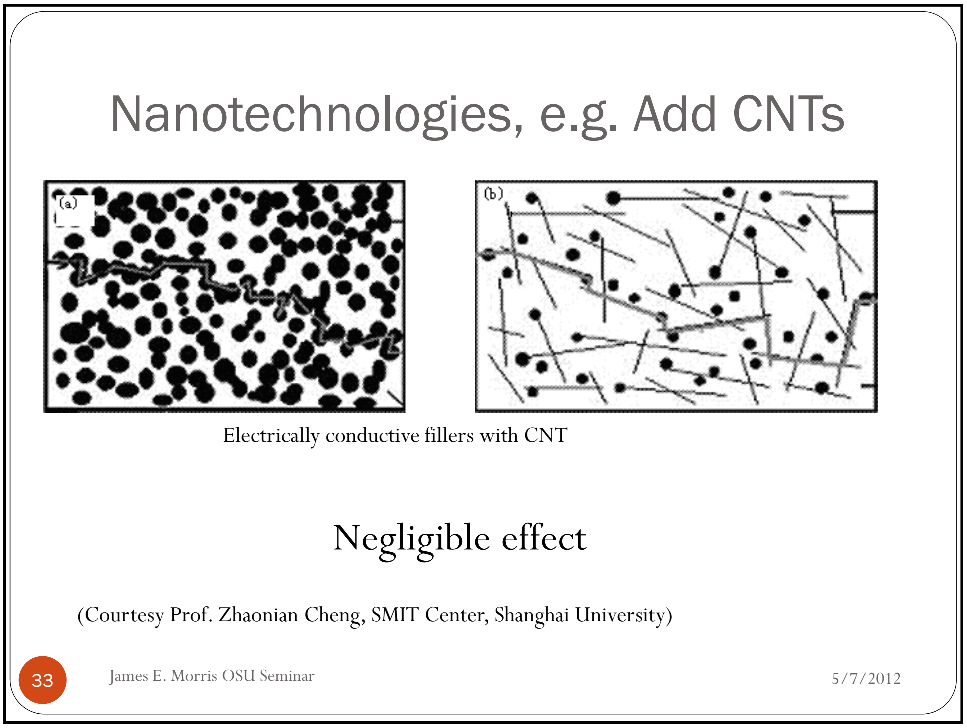


Frequency Effects: Tunnel Gaps

Skin Effect



Low frequency: Solder resistance < ICA resistance High frequency: Solder resistance > ICA resistance (because areas converge and ρ_{Ag} << ρ_{solder}

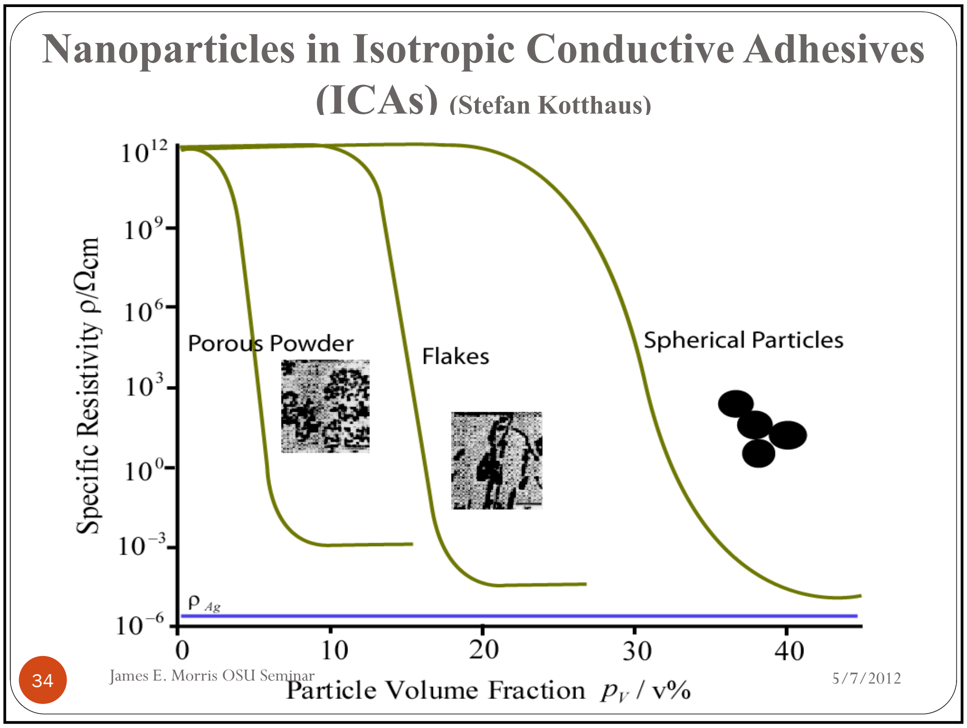


Nanotechnologies, e.g. Add CNTs

Electrically conductive fillers with CNT

Negligible effect

(Courtesy Prof. Zhaonian Cheng, SMIT Center, Shanghai University)



Nanoparticles in Isotropic Conductive Adhesives (ICAs) (Stefan Kotthaus)

Nanoparticle Sintering

[Wong et al, ECTC'06]

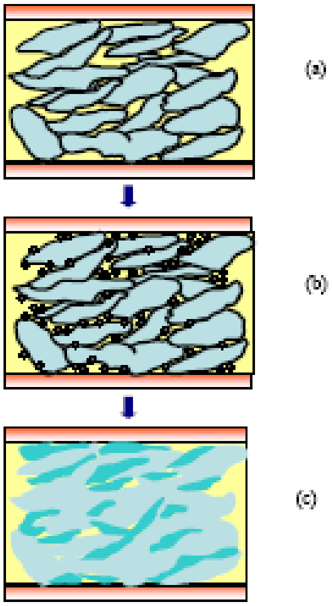


Figure 1. Schematic of particles and flakes between the metal and pads. (a) is conductive adhesives with silver flakes as fillers; (b) is conductive adhesives with both flakes and nanoparticles as fillers; (c) is conductive adhesives with sintered particles among flakes as fillers.

Figure 10. Side view of neck formation for particles of sizes 1014 and 2439 atoms.

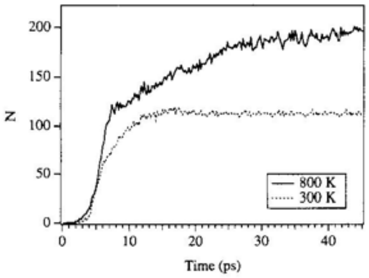
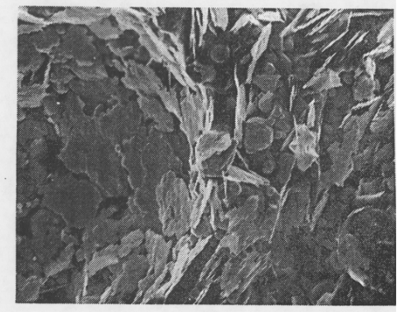


Figure 12. Increase in number of atoms N in the neck region during sintering at 300 K and 800 K.

Raut, Bhagat, Fichthorn, Nanostruct. Mater. 10(5) 1998, 837-851

Layering Effect



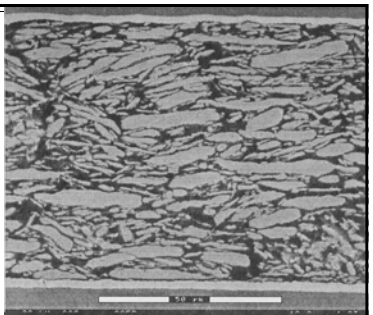
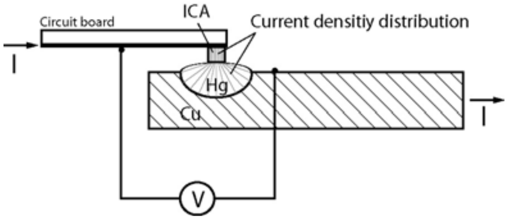
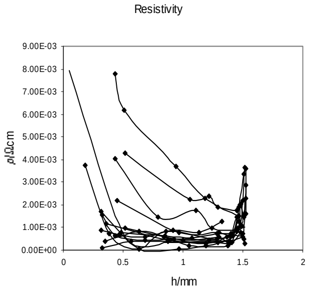


Fig. 3a Adhesive A. 900x magnification.

Constable et al (Adhesives'98)

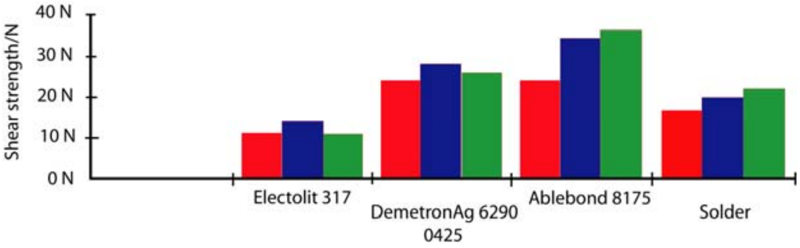
Z-axis Size Effect Expt





Resistivity as a function of the thickness.

Adhesion



Danfoss

(Detert, Herzog, Wolter, Zerna (TU-Dresden))

🟥 Solder 🟦 AgPd 🟩 Au

Adhesion

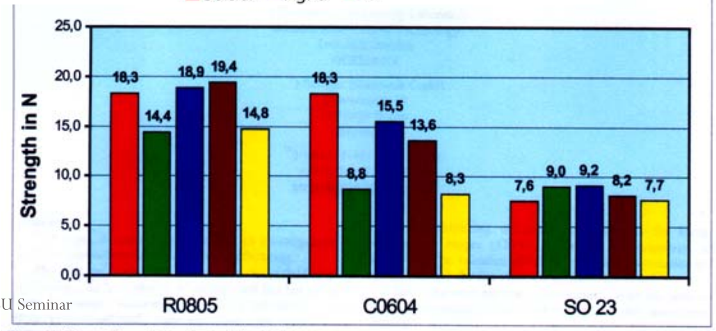


Figure 5: Shear test results for best printing ICA A

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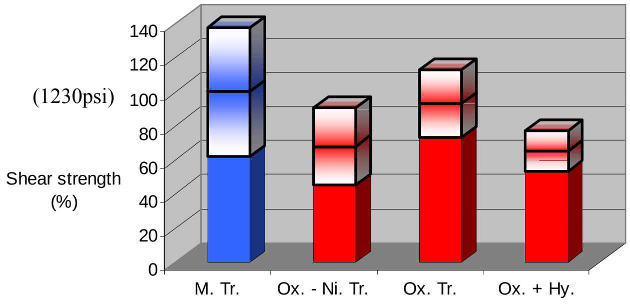
James E. Morris OSU Seminar

Shear test result with plasma treatment



Upper two columns show the standard deviation

M. Tr. - Mechanical treatment

Ox. - Ni. Tr. - Oxygen Nitrogen treatment

Ox. Tr. - Oxygen treatment

Ox. + Hy. Tr. - First oxygen treatment then hydrogen treatment

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5/7/2012

Adhesion: Surface Roughness

(Chow, Li, Yuen: 2002 Adv Pkg Materials Sympos)

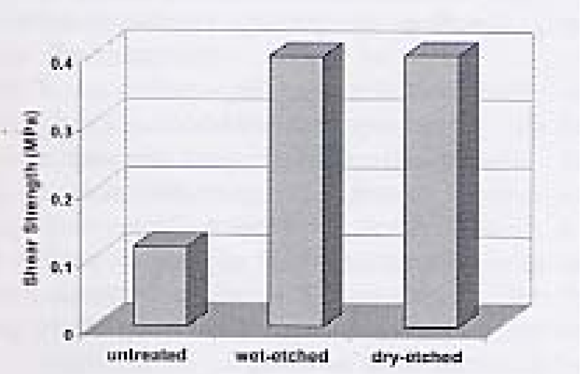


Fig. 3 Die shear test results show adhesion enhancement of PANI on etched Au substrate compared to untreated.

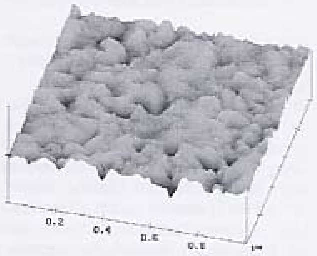


Fig. 4 Typical surface topographic image of untreated gold substrates

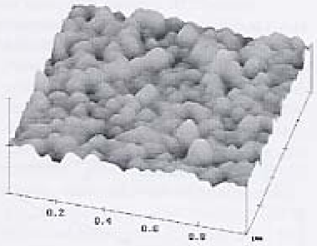
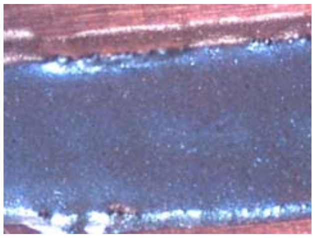


Fig. 5 Typical surface topographic image of etched gold substrates.

Adhesive before and after vacuum process

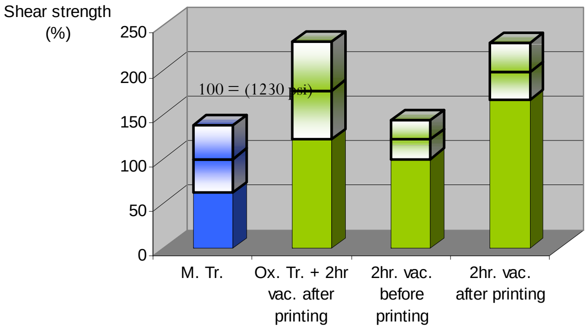
ICA before vacuum process



ICA after vacuum process

Change of surface by:

- **removal of air and water**
- **contraction of adhesive**



	No Vacuum	Vacuum
Average Resistivity	$4.22 \cdot 10^{-3}\,\Omega\text{cm}$	$2.92 \cdot 10^{-3}\,\Omega\text{cm}$
Standard Deviation	$3.29 \cdot 10^{-3}\,\Omega\text{cm}$	$1.53 \cdot 10^{-3}\,\Omega\text{cm}$

	No Vacuum	Vacuum
Average Pull Test strength	160 N	235 N
Standard Deviation	108 N	56 N

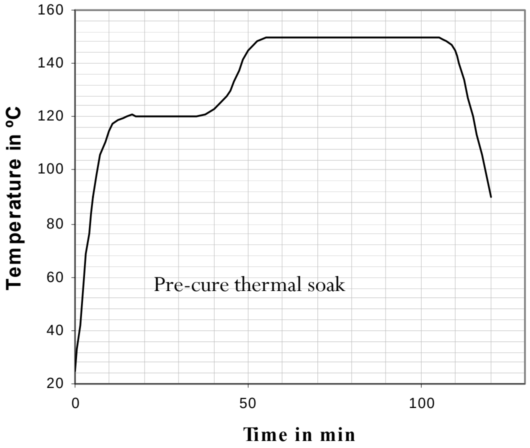
Thermal Cure: Optimization

Typical specification:

Temperature T and time t

Probably a range of T & t combinations

Possibly ramp rates dT/dt



Impact Strength/Drop Test (Tong)

- Adhesion tests passed
- Devices fall off PWB if dropped
  - Large devices fail; small OK
- No correlation between drop test results and adhesion strength testing
- Complex shear modulus
  - Storage and loss moduli

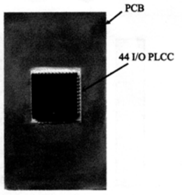
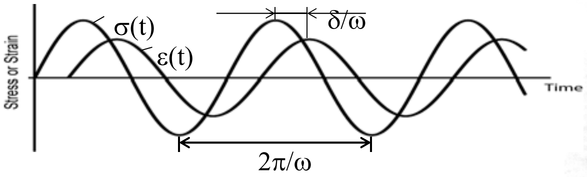


Figure 2. A Photograph of a Drop Test Sample



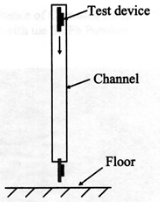
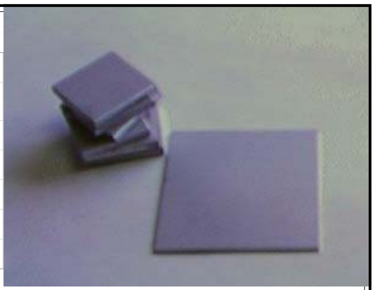
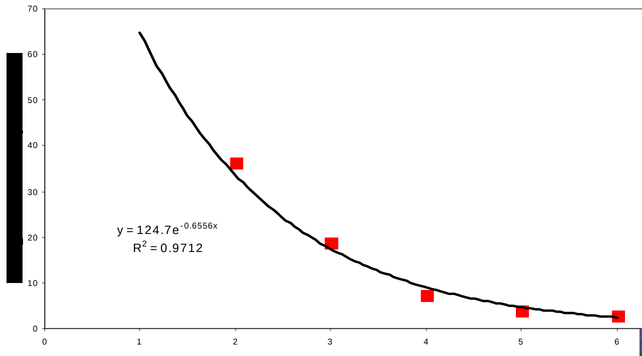


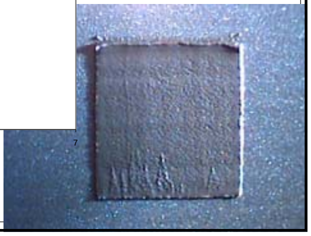
Figure 3. A Schematic of Drop Test Set-up

Variation with inertial mass

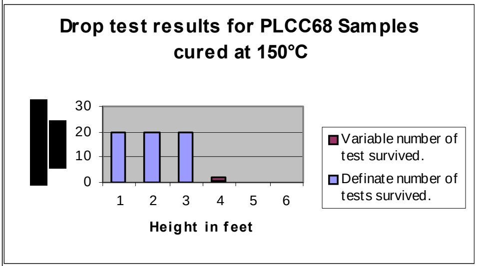
Blocks	Drops till failure
1	More than 120 (no failure)
2	30, 43
3	17, 21
4	7, 4,11
5	4, 4
6	3

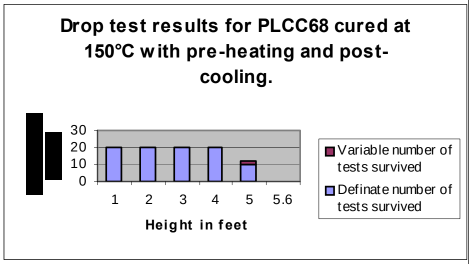


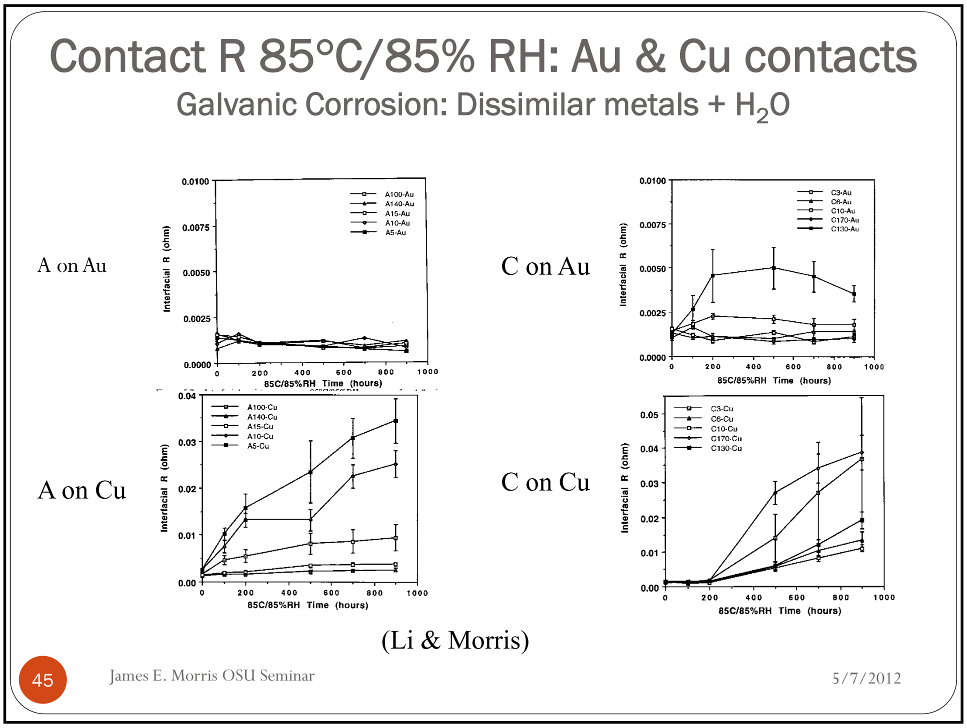




Multiple Drop Testing:
1. Cumulative damage
2. Pre-heat effects



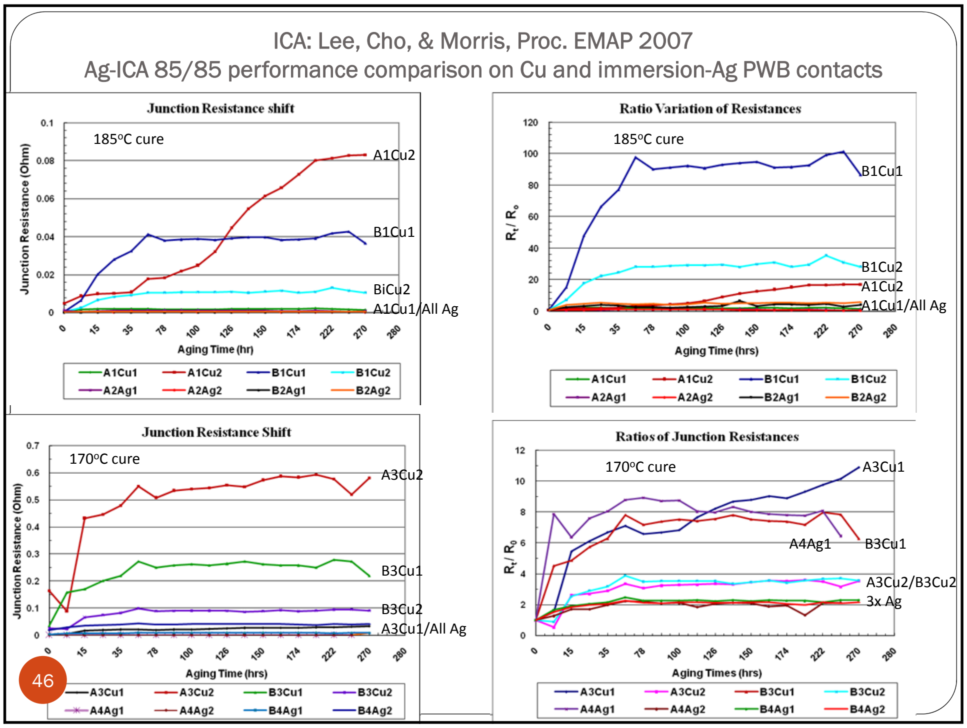




Contact R 85°C/85% RH: Au & Cu contacts

Galvanic Corrosion: Dissimilar metals + H_2O

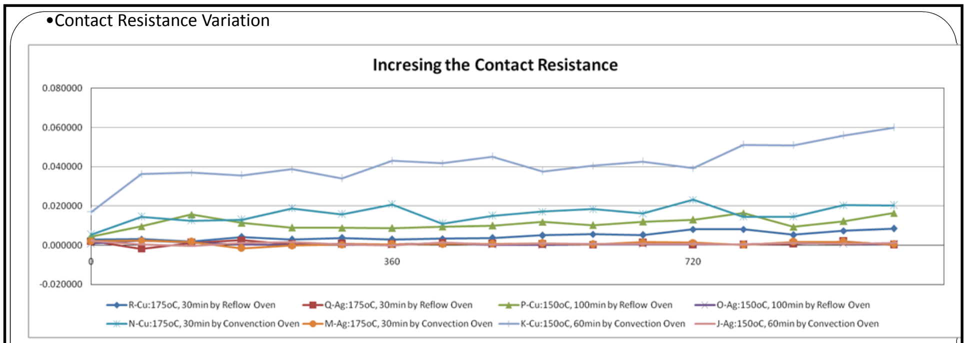
(Li & Morris)



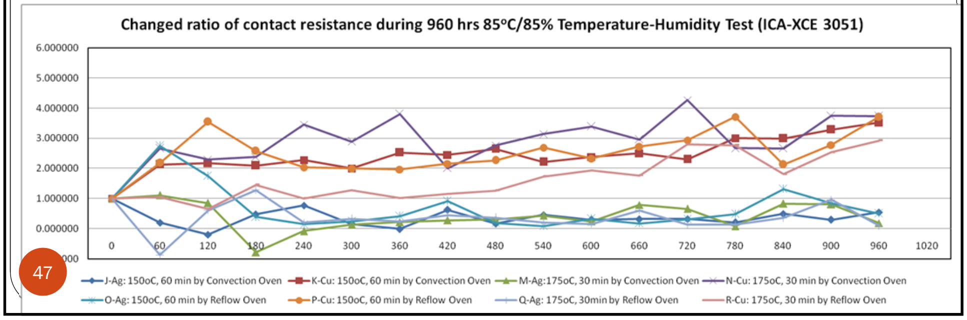
ICA: Lee, Cho, & Morris, Proc. EMAP 2007

Ag-ICA 85/85 performance comparison on Cu and immersion-Ag PWB contacts

•Contact Resistance Variation



• Ratio Variation of Resistances



Creep & Coffin-Manson Lifetimes: Comparisons with Solder (Rusanen)

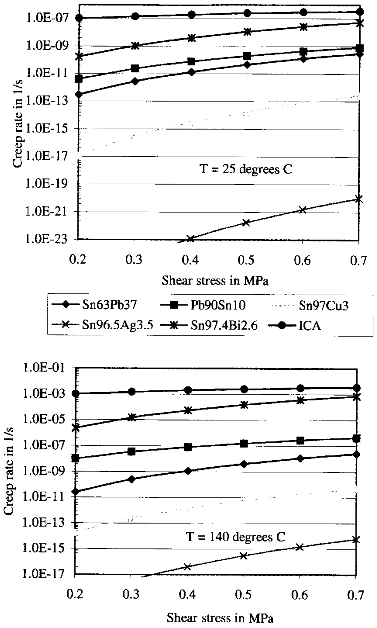
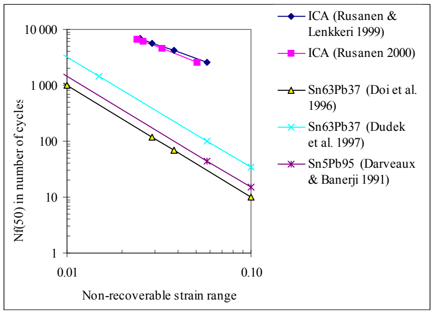
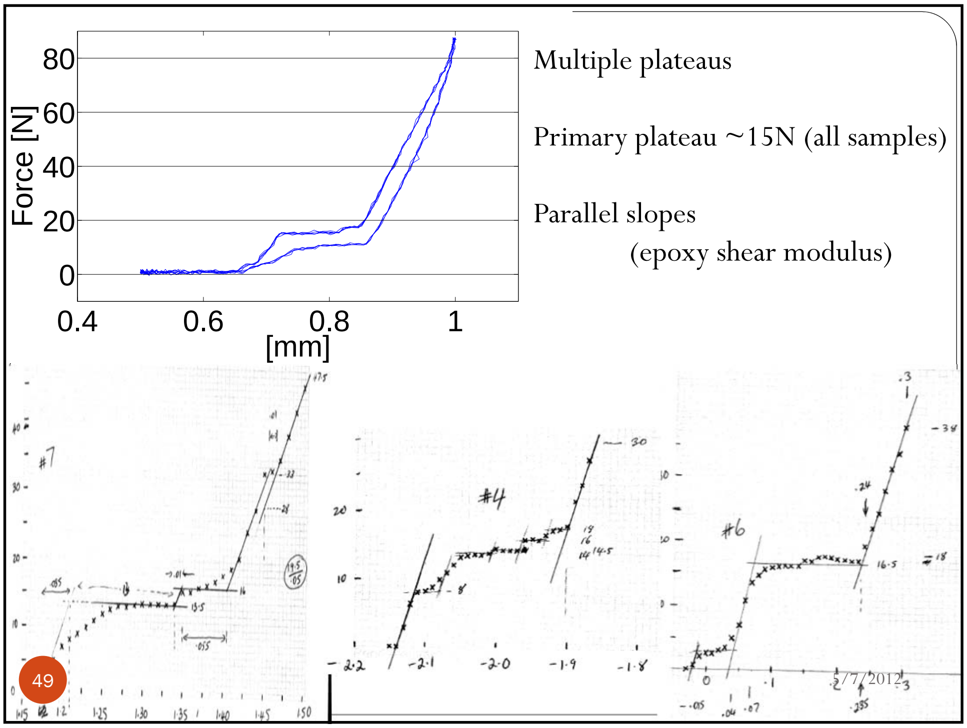


Figure 8. Creep rates of joining materials at temperatures of 25°C and 140°C.



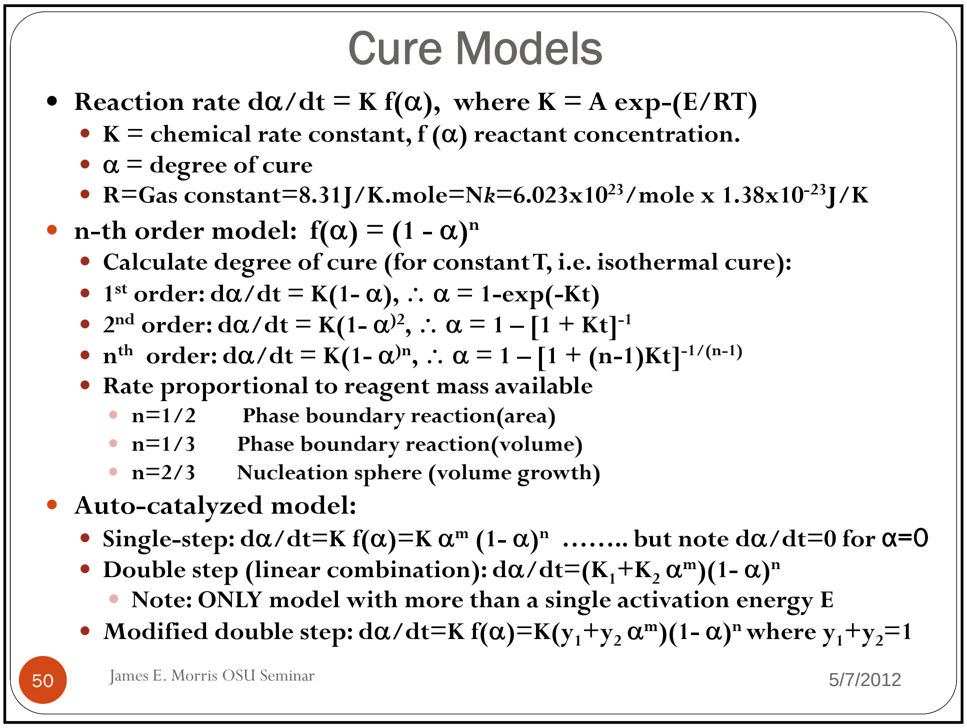


Multiple plateaus

Primary plateau ~15N (all samples)

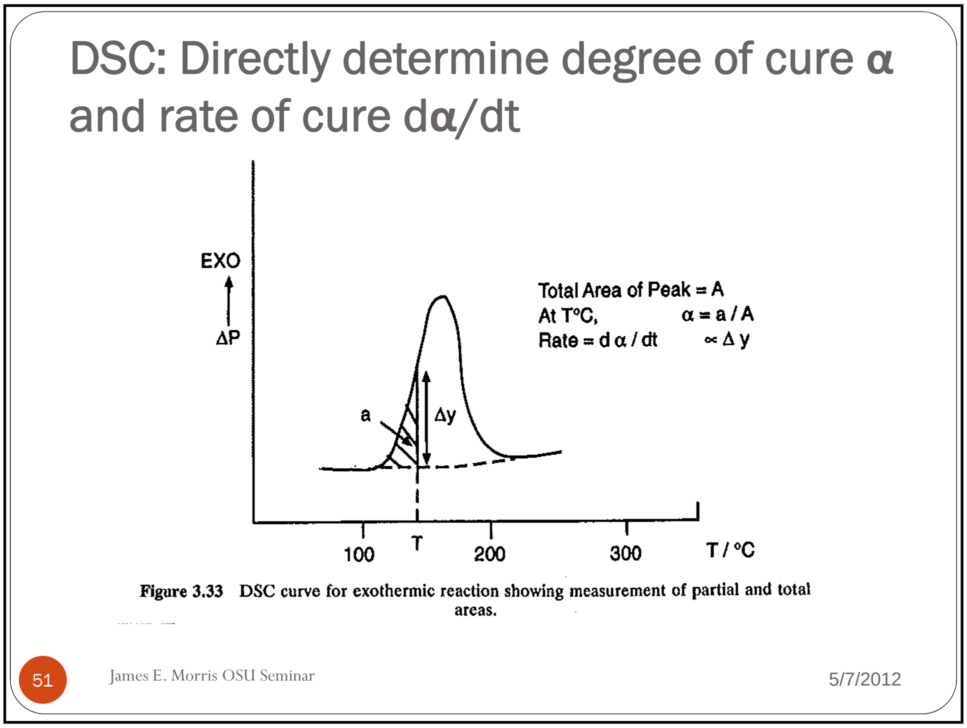
Parallel slopes

(epoxy shear modulus)



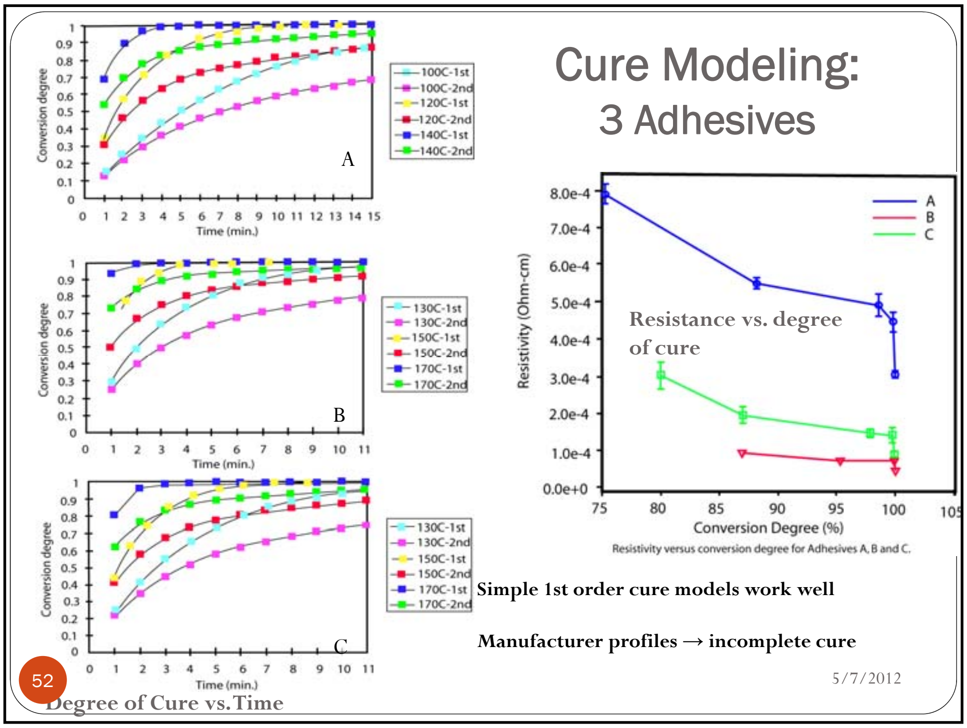
Cure Models

- Reaction rate $d\alpha/dt = K\ f(\alpha)$, where $K = A\ \exp\text{-}(E/RT)$
  - K = chemical rate constant, $f(\alpha)$ reactant concentration.
  - α = degree of cure
  - R=Gas constant=8.31J/K.mole=Nk=6.023×10^{23}/mole x 1.38×10^{-23}J/K
- n-th order model: $f(\alpha) = (1 - \alpha)^n$
  - Calculate degree of cure (for constant T, i.e. isothermal cure):
  - 1st order: $d\alpha/dt = K(1-\alpha)$, $\therefore\ \alpha = 1-\exp(-Kt)$
  - 2nd order: $d\alpha/dt = K(1-\alpha)^2$, $\therefore\ \alpha = 1 - [1 + Kt]^{-1}$
  - nth order: $d\alpha/dt = K(1-\alpha)^n$, $\therefore\ \alpha = 1 - [1 + (n-1)Kt]^{-1/(n-1)}$
  - Rate proportional to reagent mass available
    - n=1/2 Phase boundary reaction(area)
    - n=1/3 Phase boundary reaction(volume)
    - n=2/3 Nucleation sphere (volume growth)
- Auto-catalyzed model:
  - Single-step: $d\alpha/dt=K\ f(\alpha)=K\ \alpha^m\ (1-\alpha)^n$ …….. but note $d\alpha/dt=0$ for $\alpha=0$
  - Double step (linear combination): $d\alpha/dt=(K_1+K_2\ \alpha^m)(1-\alpha)^n$
    - Note: ONLY model with more than a single activation energy E
  - Modified double step: $d\alpha/dt=K\ f(\alpha)=K(y_1+y_2\ \alpha^m)(1-\alpha)^n$ where $y_1+y_2=1$



DSC: Directly determine degree of cure α and rate of cure dα/dt

Figure 3.33 DSC curve for exothermic reaction showing measurement of partial and total areas.



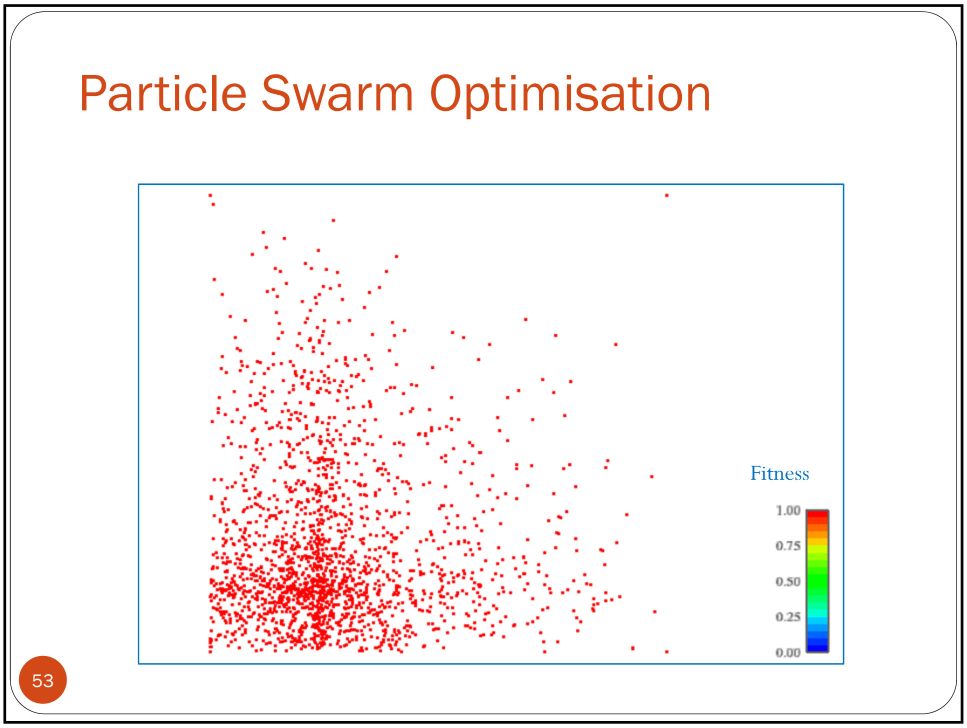
Cure Modeling: 3 Adhesives

Resistivity versus conversion degree for Adhesives A, B and C.

Degree of Cure vs. Time

Simple 1st order cure models work well

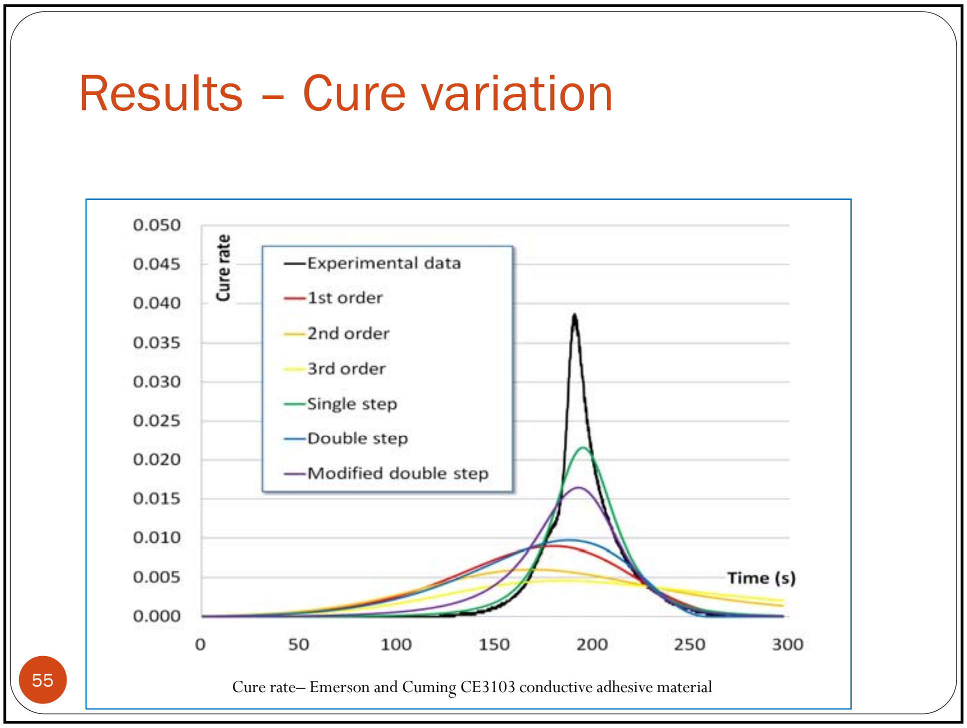
Manufacturer profiles → incomplete cure



Particle Swarm Optimisation

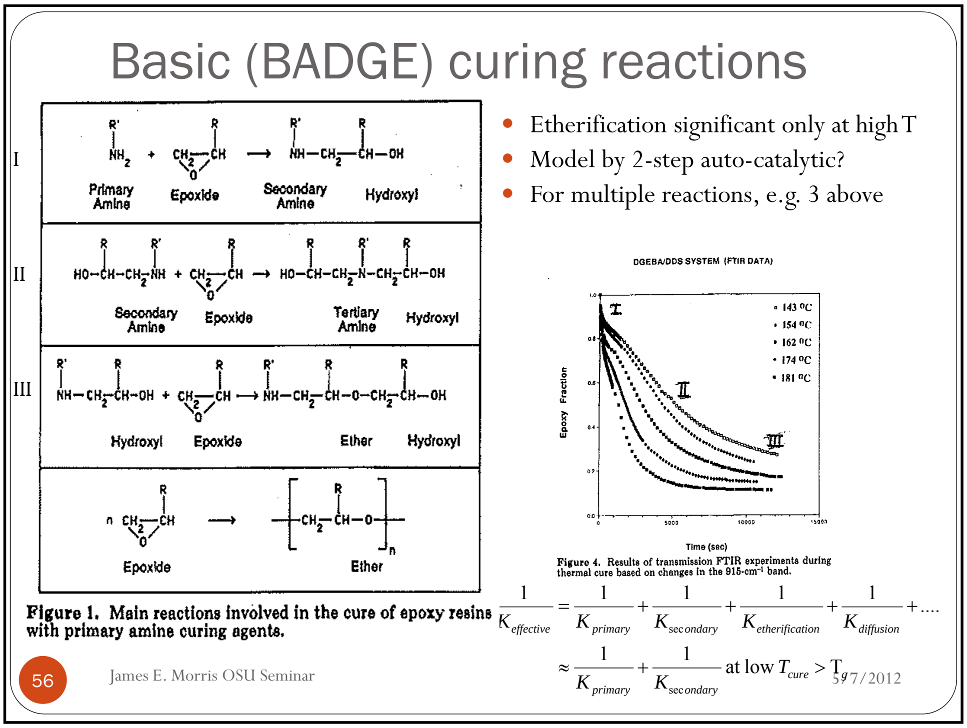
Results – Optimal Coefficient Sets

Model	E_1	A_1	n	m	E_2	A_2	y_1
1st order	37882	1021.64	1	-	-	-	-
2nd order	35917	630.83	2	-	-	-	-
3rd order	38364	841.82	3	-	-	-	-
Single step auto	31017	711.40	1.536	1.118	-	-	-
Double step auto	37039	666.04	0.767	3.958	309930	854.81	-
Modified double	33983	1074.40	1.326	1.115	-	-	0.0393



Results – Cure variation

Cure rate– Emerson and Cuming CE3103 conductive adhesive material



Basic (BADGE) curing reactions

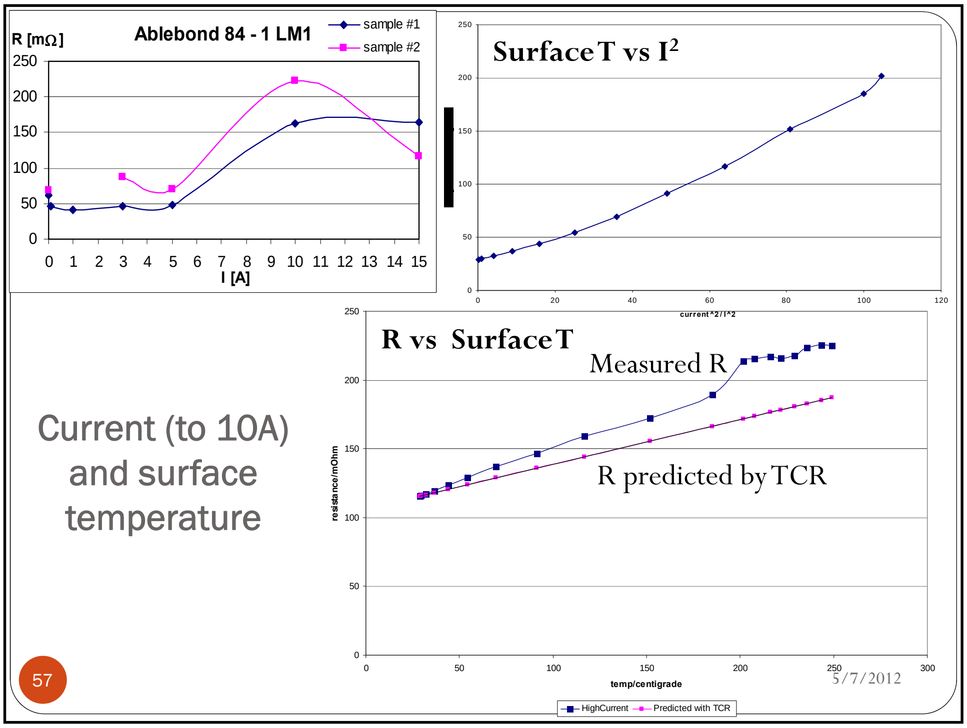
Figure 1. Main reactions involved in the cure of epoxy resins with primary amine curing agents.

- Etherification significant only at high T
- Model by 2-step auto-catalytic?
- For multiple reactions, e.g. 3 above

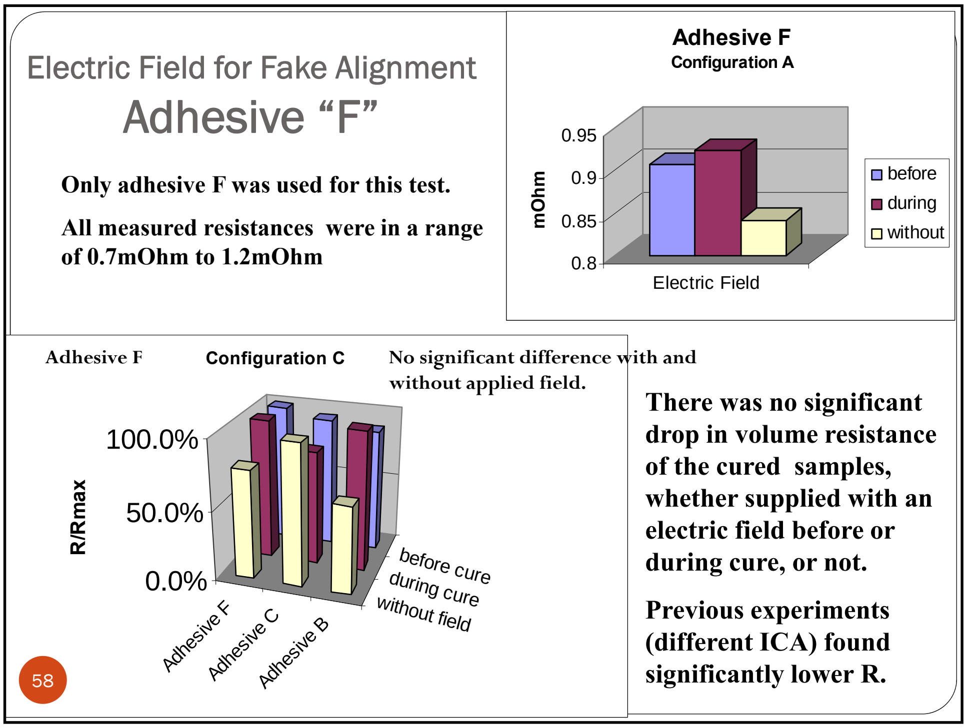
Figure 4. Results of transmission FTIR experiments during thermal cure based on changes in the 915-cm^{-1} band.

$$\frac{1}{K_{effective}} = \frac{1}{K_{primary}} + \frac{1}{K_{secondary}} + \frac{1}{K_{etherification}} + \frac{1}{K_{diffusion}} + \ldots.$$

$$\approx \frac{1}{K_{primary}} + \frac{1}{K_{secondary}} \text{ at low } T_{cure} > T_g$$



Current (to 10A) and surface temperature



Electric Field for Fake Alignment

Adhesive "F"

Only adhesive F was used for this test.

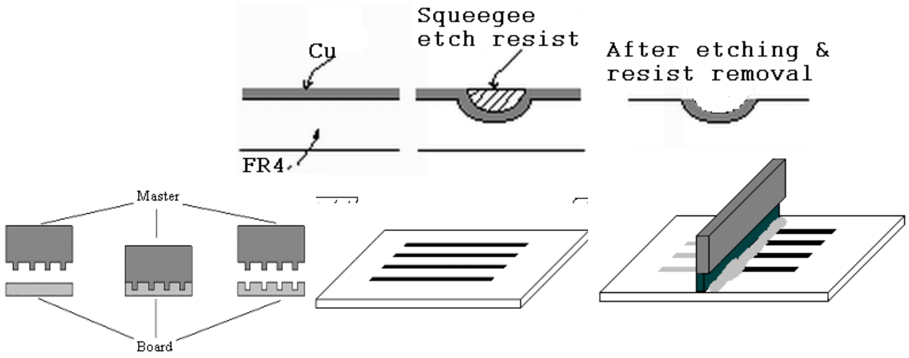
All measured resistances were in a range of 0.7mOhm to 1.2mOhm

No significant difference with and without applied field.

There was no significant drop in volume resistance of the cured samples, whether supplied with an electric field before or during cure, or not.

Previous experiments (different ICA) found significantly lower R.

Imprint Boards



Summary: ICA

- Applications; processing
  - Cure modeling
- Electrical conduction
  - Sources of resistance; measurement; layering effects
  - TCR/frequency data
  - (Conduction modeling)
  - Nanoparticles (sintering) & CNTs
- Reliability issues
  - Impact resistance
  - Adhesion
- Continuing research
  - Cure modeling
  - Mechanical cycling
  - Drop test & crack propagation modeling

Nanoelectronics & Packaging Lab

Portland State UNIVERSITY