Adhesives in Microelectronics and MEMS Applications

Helge Kristiansen



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Helge Kristiansen Conpart AS

Gåsevikvn. 4, Kjeller P.O. Box 144, N-2027 Kjeller NORWAY Phone +47 64 84 43 00 Mobile +47 930 36 073 E-mail: helge@conpart.no www.conpart.no







Monosized polymer particles

Polymer particles with exceptional properties

- Mono sized particles
- Size 1 200 μm
- Polymer composition
- Surface chemistry
- Functional groups
- Porosity
- Magnetic
- Metal plated
- Core & shell









Adhesion

- Adhesion relates to the interface between adherent and adhesive
- The most important mechanism for adhesion is inter-molecular and surface forces
 - Van-der Waal (dispersion forces)
 - Hydrogen bonds
 - Very short range (sub nm)
- Generally no chemical bonds
- Other factors like mechanical "interlocking" have very little importance in typical electronic systems
- Cohesion: Internal "strength" of the adhesive (often chemical bonds)



Adhesive / cohesive







Contact angle





Criteria for wetting

Force balance (along interface)

$$\gamma_{AB} = \gamma_{AC} + \gamma_{CB} \cdot \cos \vartheta$$

- $\gamma_{A(B)}$: Surface energy solid (-air) [N/m], [J/m²]
- $\gamma_{C(B)}$: Surface energy adhesive (-air)
- γ_{AC} : Surface energy solid-adhesive
- For a good wetting

$$\gamma_A > \gamma_B$$



Polymer properties

- Low weight (0.9 1.5 g/cm³)
- High thermal expansion
- Hygroscopic
 - Affects mechanical and electrical properties
- Glass transition
 - Introduces new degrees of freedom in the material
 - Increases thermal expansion
 - Reduced mechanical strength



Polymer

- Long chains of monomers
- Linear or branched
- Thermoset
 - Best chemical and mechanical stability
 - Epoxies, polyurethane, silicone
- Thermoplastic
 - Simplifies rework
 - Teflon, polyesters



Thermoplastics

- Reversible melting ↔ solidifying
 - Heating provides thermal energy for polymer chains to move "freely"
 - Cooling reduces the molecular motion
- Linear molecular chains
 - Entanglement
 - Inter-molecular forces
 - No chemical cross bonding
- Mechanical anisotropy
 - Preferential orientation of molecules
- Polyesters, acrylics



Properties of thermoplastics

Fillers	Тg	Bond Temp	Rework	Die Shear	Thermal	Modulus
	°C	°C	min. °C	MPa	W/m°C	GPa
None	-40	100 - 150	110	11	0.20	0,4
Ag, AIN, None	25	150 - 200	160	14	0.3-3.0	0,4
Ag, AIN, None	45	160 - 220	170	17	0.3-3.0	3,2
Ag, AIN, None	85	160 - 250	170	19	0.3-3.0	2,5
None	145	200 - 230	210	24	0.22	1
Ag, Au, AIN, None	180	325 - 400	350	25	0.3-3.0	2,2
None	280	350 - 450	400	31	0.25	2,3



Thermoset

- Do not melt upon heating
- Forms links or chemical bonds between adjacent chains, during curing (intra-molecular bonds)
- Three dimensional rigid network
- Properties depend on the molecular units, and the length and the density of the cross-links
- Thermosetting resins are usually isotropic
- Epoxies, silicones, urethanes



Glass temperature

- Second order phase transformation
- Discontinuous volume expansion, heat capacity and mechanical properties
- Thermal energy sufficient to allow rotation about chemical bonds
 - Depends on bond (Carbon or silicone)
 - Adjacent molecular groups (dipoles, bulkiness and symmetry)



Different classes of organic adhesives

- Solvent-based adhesives: The adhesive is solved in a suitable solvent or dispersed in water. The adhesive solidifies during drying (not curing)
- Thermoplastic adhesives: Based on thermoplastic materials, that is solid to liquid is a reversible phase change. Typically polyimide- and polyester (easily oxidized)
- Thermosetting adhesives: Improved mechanical properties, high temperature and chemical resistance



Structural adhesive

- Good load-carrying capability
- Long-term durability
- Resistance to heat, solvent, and fatigue
- 6 main types:
 - Urethanes
 - Acrylics
 - Epoxies
 - Silicones
 - Anaerobic adhesives
 - Cyanoacrylates



Structural adhesives

Cyanoacrylate

- Cyanoacrylates adhesive bonds quickly to plastic and rubber but have limited temperature and moisture resistance.
- Cured by humidity present on surfaces
- Acrylics
 - Acrylics, a versatile adhesive family that bonds to oily parts, cures quickly, and has good overall properties.
 - Cure at room temperature when used with activators.
 - The adhesive and activator can be applied separately to the bonding surfaces. Often a low viscosity activator
 - The adhesive and activator premixed in a static mixer prior to application. Anaerobic
- Anaerobics, or surface-activated acrylics
 - Bonding threaded metal parts etc.



Silicones

- Solvent born resins
 - Evaporation of solvent
 - Curing at elevated temperature
- Room Temperature Vulcanisation RTV
 - One part RTV systems generally cured by moisture
 - Give of by-products during cure
 - Two part RTV generally cured by a platinum complex
- UV cured
- Very wide temperature range
 - -50 200 °C



Silicones (II)

- Soft, low modulus material
 - Very low Tg (typically -65 °C)
- Very high CTE (Typically 350 ppm/ ^oC)
- Very low dielectric constant
 - Low dielectric loss
- Easily modified to provide a range of physical and mechanical properties, cure system, and application techniques.
- Very low surface tension (24 mN/m)
- Very mobile, vapor attaches to all surfaces
 - Wire bonding problems



Silicones (III)

- Good water and moisture resistance
 - However, very high water permeability If adhesion is good, a continuous water film is <u>not</u> obtained at the interface
 - NB! Oxygen bridge bonding to die surface prevents Al corrosion)
 - Relatively low equilibrium moisture content
 - Very low levels of mobile ions
- Good sealing properties
 - Very durable for glass sealing
- Weather well out-of-doors
- Low surface tension expels liquid water



(Poly)urethanes

- One or two component systems
- Often solvent based
- Low stress materials
 - Good flexibility and elasticity
 - High thermal shock resistance
 - Good peeling characteristics
- Moisture curing system (~ 50%RH)
- Good adhesion to many organic materials



Epoxies

- Thermoset
- Thermal cure (UV or light cure optional)
- Relatively high E-modulus
 - Brittle
- Generally good adhesion
 - Hydrogen bonding (NB! Except gold, due to lack of oxygen at the surface))
 - Mechanical interlocking
- Typical shrinkage upon curing is in the order of 1 to 2 percent
- Relatively low moisture permeability



Curing

- The selection of a curing agent is as important as the choice of the resin
 - Rate of reactivity
 - Degree of exothermal
 - Gel time
 - Curing time
 - Mechanical properties of the cured adhesive.
- The number of epoxide groups in the molecule determines the "functionality" of the resin
 - Increasing glass transition temperature
 - Decreasing Thermal Coefficient of Expansion (TCE)



Epoxide group





Modification of properties

- Choice of resin system
- Choice of hardener
- "Fillers"
 - Electrical (dielectric) properties
 - Mechanical properties
 - Possible ionic contamination



Fillers

Plasticizers, flexibilizers or elastomers

- Plasticizers (an additive that is physically blended into the resin (do not become part of the polymer). Plasticizers in epoxies are typically rubber or thermoplastic particles. They have to be > 1 micron to be efficient
- Flexibilizers are chemically reacted into the epoxy system (often thermoplastic polymers)

Reduces solvent and moisture resistance and lowers Tg

Elastomers remains as a distinct second phase (two separate cross-linked networks)



Plasticisers

- Absorbed liquids (soft solids), decrease the glass temperature
- Increased "free volume"
 - Reduces the internal viscous friction

$$\frac{1}{T_{g(PF)}} = \frac{w_p}{T_{g(P)}} + \frac{w_L}{T_{g(L)}}$$

■ Ex. Glass temperature of water : approx. –135 °C.



Influence of water



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Silver epoxies

- Low impact strength
 - High loading of silver particles
- Solutions
 - Reducing filler rate by use of porous silver particles (Fraunhofer)
 - Randomise particle orientation, by making conductive composite particles (Georgia Tech)
 - Introduce plastizisers, to increase the ability to absorb mechanical energy (Ablestik)
 - Polymer spheres with silver coating



Mechanical properties



Filler content silver [weight %]

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Criteria for adhesive selection

- Means of "dispensing" of adhesive
 - Screening, film, dispensing, stamping etc...
 - Viscosity / rheology:
 - Unwanted flow (capillary driven), leaching
- Good adhesion to parts:
 - What is the main components to be bonded (surface!!)
 - Surface cleaning
- Demands for mechanical properties
 - Strength flexibility
 - E-module / Elongation before break
 - Sensitivity to mechanical stress
 - Requirements for temperature cycling



Criteria for adhesive selection

- Processing temperature
- Thermal expansion adhesive:
 - High CTE will often increase stress in adhesive joint due to the increased miss-match with the components to be bonded
 - High thermal expansion is likely to increase diffusion of humidity etc..
- Low ionic contamination
- Thermal (and electrical) conductivity
- Void free bond line
 - Local stress concentration (crack initiation)
 - Poor local thermal contact



Requirements from application (I)

- Glass transition temperature relative to operational (and storage) temperature of the device.
 - Radical change of mechanical properties
 - Reduced "E-modulus"
 - Increased thermal expansion
 - Increased diffusivity above Tg.
- Water absorption:
 - Changes mechanical properties (plasticizer)
 - Reduced T_G
 - Changes dielectric properties



Resin bleed

- Resin bleed is the unwanted capillary action of low viscous parts of the adhesive
- Contamination of bond pads
 - Destroy the ability to perform wire bonding
- Relatively low molecular weight thermoset
 - During initial heating
 - Ultra clean surfaces (high surface tension)
 - Rough surfaces (large surface area)



E-modulus of different die attach adhesives

Adhesive		T_g [C]	E-modulus (dynamic) [GPa]			
			@ -65	@ 25	@ 150	@ 250
А	Ероху	53	2,68	2,30	0,21	0,17
В	Ероху	30	1,81	1,63	0,01	
С	Ероху	88	5,78	4,98	0,36	0,27
D	Ероху	40	5,40	2,87	0,12	0,05
E	Ероху	67	6,27	5,30	1,18	0,45
F	Thermoplastic	98		2,40		
G	Cyanate Ester	245		6,90		



Stress in "Die attach"



	Chip	Substrate	Adhesive
E-modulus	190 GPa	20 GPa	-
СТЕ	2,6 ppM/K	18 ppM/K	50 ppM/K
Thickness	0,4 mm	2,0 mm	0,03 mm
Poisson ratio	0,25	0,4	0,45


Shear stress in adhesive





Normal stress in die





Measured stress in silicon die



- Silicon chip onto copper substrate
- Compressive stress along the centre-line
- Measured with Piezo-resistors



Measured stress in silicon die (II)



- Compressive stress normal to the centre-line
- Measured with Piezo-resistors



Measured and calculated stress

Adhesive	Cure temp	Strain calc.	Strain meas.
958-2	150°C	1740.10-6	543·10 ⁻⁶
H20E-175	160°C	1880·10 ⁻⁶	343.10-6
K/5022-81	210°C	2570·10 ⁻⁶	105·10 ⁻⁶
Adhesive	Stress calc.	Stress meas.	
958-2	429 MPa	132 MPa	
H20E-175	457 MPa	84 MPa	
K /5022_81		.	



Comments: Measured stress

- Observed strain (stress) much lower than calculated!
- K/5022-81 (polyimide based): problems with the curing of the adhesive
- What is the effective "Zero-stress" temperature?
- Plastic deformation?



Transient Hot Wire



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Results

- λ increase with increased amount of conductive filler
- For Nano scale particles λ increase more than theory suggest; 0% 0.20W/mK 10% 0.35 W/mK 20% 0.56 W/mK
 Surface treated alumina better: Untreated: 0.26W/mK (10%)

Treated: 0.32W/mK

Nanoscale particles better than micro scale particles:

> Micro: 0.26 W/mK Nano : 0.35 W/mK (10%)





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Silver epoxy



Silver flake distribution in Ablebond 952-8

Elongated particles



Thermal interface resistance



- Ablebond 958-2
- Silicon chip onto molybdenum substrate



Thermal interface resistance (II)



- Epo-Tek H20E-175
- Silicon chip onto copper substrate!



Temperature cycling of die attach





Adhesive as underfill

- Bump lifetime under thermal cycling decreases with induced strain
- Bumps without underfill:
 - CTE mismatch => cyclic shear strain
 - Crack growth
- Bumps with underfill
 - Strain reduction
 - Lifetime increase 10X



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FR4 (CTE= 18 ppm /K)
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Effect of Underfill

- Mechanical coupling chip/substrate
 - Reduces bump shear strain
 - Strain highest at chip edge
 - Strain depends on shear modulus of underfill
- Introduces axial strain
 - CTE mismatch solder/underfill
 - Depends on underfill CTE
 - Affects all bumps equally
- Impact on lifetime?



Shear mode





Measurement of bump lifetime - Aims

- Measure number of thermal cycles to failure
- Two underfill materials (different CTE)
- Measurements as function of distance to chip centre
 - No variation: Axial strain dominates
 - Lifetime decreases with distance: Shear strain
- Establish simple analytical model for bump lifetime
- Compare experimental lifetimes with model



Experimental method

Test sample:

- Silicon test chip with eutectic solder bumps
- Reflowed to FR4 substrate
- Underfill applied and cured
- Thermal cycling
 - -55 145 °C
 - 2 cycles per hour





Lifetime measurements

- Daisy chain connections on chip/substrate
 - Grouped in "rings" with similar distance to centre
 - Continuity of each ring monitored
 - In situ
 - For each 50 cycles (at RT)
 - Resistance increase = failure

- Substrate connection
- Chip connection





Underfill characteristics

- Two different types used:
 - Filled: CTE = 28 ppm/K
 - Unfilled: CTE = 58 ppm/K
 - Tg: 120 °C
 - CTE and Tg measured by DMA
- Curing: 150 °C
- Maximum cycling temperature (145 °C) exceeds Tg!



ACA technology



Overview

- Introduction
- Anisotropic conductive adhesive
 - Z-axis conductive film
- Typical products
- Joint quality
- Reliability
- Different FlipChip techniques
- Conclusions



ACF History



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Anisotropic Conductive Adhesive

- The adhesive film is applied uniformly
- Pressure is applied during curing, giving conduction only between pads
- Thermoplastic or thermosetting
- Film (tape) or paste







Particle compressed between bump and pad





Driving force

- Possibly higher reliability
 - Right choice of adhesive and bonding surface
- Fewer process steps
 - No fluxing or cleaning
- Finer pitch
 - Anisotropic Conductive Adhesive
 - Non-conductive Adhesive
- Environmental friendly
 - No lead



Introduction

Lower temperature processing

- Lower thermal stress
- New materials in packaging
 - Polyester based flex circuits
 - Low cost plastics
- Non solderable surfaces
 - ITO conductors (LCD's)



Optimising process conditions

- Large number of particles on pad
- Low particle density between neighbouring pads
- Fast process time
- Reliable and uniform connection resistance



Curing cycle





Curing cycle (II)

- T 1: Start of pressurisation
- T 2: Start of heating
- T 3: The resistance increase depending on electrode material
- T 4: End of heating
- T 5:
- T 6: End of pressure
 - If curing is insufficient, the resistance may start to increase



Bonding force





- The applied bonding force is counter balanced by
 - Squeezing of the adhesive film
 - Compression of particles
- Squeeze film pressure
 - Film thickness
 - Chip dimension
 - Viscosity of adhesive
 - Rate of squeezing

$$F = \int_{A_{Chip}} p dA + \sum_{i} \kappa_{p} \mathcal{E}$$



Squeezing of adhesive film

- Flat silicon surfaces
- 1st stage: squeeze of adhesive only
- 2nd stage: compression of particles





Factors influencing on joint quality

• Coplanarity.

- Bump height and uniformity
- Pressure and pressure distribution.
- Particle distribution
- Cure temperature and cure time
- Temperature ramp rate
- Alignment accuracy



Contact stability (I)

- Stable contact
 - Uniformly deformed particles
 - Adequate pressure
- Unstable contact
 - Too low pressure during connection







Contact stability (II)

- Uneven particle size
 - Not uniformly deformed particles



- Uneven bump-height
 - Not uniformly deformed particles





Degradation mechanisms

- Oxidation and hydration of conductors
- Polymer degradation by moisture or UV-light
- Adhesive failure due to humidity adsorption
- Crack formation
- Thermal and mechanical fatigue



Failure mechanisms I

Adhesive

- Thermal and mechanical fatigue
- Humidity
- UV light
- Cohesive
 - Humidity
 - Thermal and mechanical fatigue



Failure mechanisms II

- Oxidation of metal surfaces
 - Humidity
 - Corrosive gases
- Expansion / swelling
 - Thermal and mechanical fatigue
 - Humidity


Typical reliability tests

- Temperature cycling from -40 to +125 °C
- Constant humidity test: 85 °C, 85%RH
- High temperature ageing at 125 °C
- Temperature cycling from -40 to +125 °C
- NB!: Tests are typically adopted from solder
 - Different failure mechanisms



The use of ACA Technology

- Typical applications:
 - Flat panel displays
 - Smart cards
 - Single or multi-chip modules
 - Piezo electric components (printer heads etc.)
 - Micro mechanical and Micro optical components
- Low temperature bonding
 - Plastic, clothing



Mounting trends





TAB connection





Chip on Glass





Chip on Glass; Sharp DVD player









ACF applications



Chip on FlexFlex on Glass

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ACF Flip Chip on rigid board

- Personal digital assistant (PDA) by Casio Computer
- Six IC ´s (Microcontroller, Gate Array, Memory, decoder
- and amplifier) are mounted with flip-chip.
- Minimum pitch is 124 μm
- Sequential build-up substrate.





Key factors for Chip on Glass

- More than 5 particles per bump
- Ensure insulation
 - Insulated particles for low pitch?
- Development of more elastic binder material
- Higher T_g material
- Less moisture absorption



Sharp; "ELASTIC"



Adhesive IC Glass



Sharp; "ELASTIC "

- ELASTIC: Electrical interconnection using lightsetting adhesive
- Placing particles on tacky adhesive
 - Photo process
 - Gold plated plastic spheres
 - No need for bump plating
- 50 micron pitch demonstrated



Mitsubishi

Photo process with conductive particles
UV transparent substrate
Non transparent pads
Waste of conductive particles?





Matsushita; Stud "wire" bumps "Isotropic Conductive Adhesive"





Casio; "Microconnector"





Mitsubishi





Hitachi: Double layer ACA







Conductive particles

• Volume fraction 5 to 10 %

- Responsible for the electrical contact
- Pure metals such as gold, silver or nickel
- Metal-coated particles with plastic or glass cores.
- Typically 3 to 10 micron in size,
- Treating particles separately from the adhesive.
 - Small volume fractions of particles in the ACA, gives minor changes in mechanical behaviour, at least in the case of metallised polymer particles.



Conductive particle



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Particle development

- 1st generation (Dyno Specialty Polymers), focus on
 - Different polymer compositions
 - Cross-linking densities
- 2nd generation, focus on
 - Adhesion between metal and polymer core
 - Added chemical groups for bonding to the metal





Testing of mechanical properties





Results, mechanical testing (@RT)





2nd generation particle (@ 150°C)



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SEM picture of 2nd generation particle (tested at 150 °C)



- Very good adhesion between polymer and metal
 - Adhesion promoters included in polymerisation process
- Highly reliable contacts due to integrity of particles



Commercial particles (testing at 150 °C)



 Particles fully des-integrated
 Lack of adhesion between polymer and metal



Measurement of contact resistance

- 4-wire measurement
- Ensemble of free particles
- Au-Pt electrodes





Electrical resistance AU-54



- Contact resistance versus "contact force"
- 4-point measurement
- "Free" particles
- Gold electrodes



Contact resistance versus cycling



