Jetting of Isotropic Conductive Adhesives with Silver Coated Polymer Particles

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Abstract
The development of novel interconnection materials for production of electronics is of considerable interest to fulfill increasing demands on interconnect reliability in increasingly demanding environments with respect to temperature extremes, mechanical stresses and/or production limitations. Adhesives are playing an increasingly significant role in the continuously evolving electronics industry.

Electrically conductive adhesives have developed to the stage that they offer a viable alternative to traditional solders for applications that demand high reliability in structurally challenging environments. Conductive adhesives are often divided into groups based on conductive directions; Isotropic Conductive Adhesives (ICA) normally provide almost equal electrical properties in all spatial directions, and Anisotropic Conductive Adhesives (ACA) which are insulating in an unstressed state, but provide directional electrical conduction through connections between filler particles and the local connection points.

Both ICA and ACA have traditionally demanded a high filler content to ensure adequate electrical connectivity. Epoxy based adhesives are often selected due to the vast selection of combinations availability, and traditionally silver fillers are used for obtaining electrical conductivity in ICA. Silver is advantageous since even its oxide maintains high conductivity. Unfortunately, the high cost of silver prevents many applications from using it. An ICA was developed at a much lower cost where solid silver is replaced with metal coated polymer spheres. The polymer spheres are essentially mono disperse in size and can be specifically chosen for different applications. The silver coating of the spheres is approximately 100 nm thick.

Specific applications will be presented that highlight the feasibility of the technology with respect to conductivity, structural reliability and lifetime standards. The deposition of the novel ICA has been performed using a jet printing technology to ensure both precise and accurate positioning, size and volume delivery.

Key words - jetting, conductive adhesive, polymer sphere

Introduction
Surface mounting technology has come to dominate the production of commercial electronics over the last thirty years. The connection of components to metallic pads using a metallic alloy delivered onto the printed circuit board (PCB) as a suspension and a reflow step is the dominant methodology for electronics production. This connection strategy has a number of drawbacks for a growing number of applications due to its high reflow temperature and environmental deficiencies. In these applications, specific substrates can crack due to the high processing temperature. Other applications introduce flexible substrates that are insensitive to the rigid solder joints that are the result of traditional reflow with solder paste.

An alternative to traditional reflow with solder paste is conductive adhesives, which allow significantly lower bonding temperature. Most commercially available conductive adhesives are based on silver flakes, and these conductive adhesives contain roughly 70 – 80 wt% or 25 – 30 vol% of silver, causing this alternative to be less cost efficient than traditional solder pastes.

The high volume fraction of silver flakes makes the cost of this method prohibitive. In this study, the replacement of silver flakes by silver-covered polymer spheres is evaluated. In Figure 1, a comparison of a traditional flake-based silver conductive adhesive is shown together with a cross-section of the proposed silver-coated polymer sphere adhesive. With silver-coated polymer spheres, the silver content of a suitable adhesive is typically in the range of 1 – 3 vol%.

At the same time, the electrical conductivity is of the same order as conventional flake-based conductive adhesives [1].

In this work, the non-contact deposition of novel conductive adhesives have been tested using a jetting technology to ensure precise and repeatable deposition volume and positioning. The affect of fluid rheology is studied with respect to jetting quality. In addition, the effect of particle properties, such as particle size, silver thickness and particle concentration electrical conductivity, on electrical conductivity are studied.

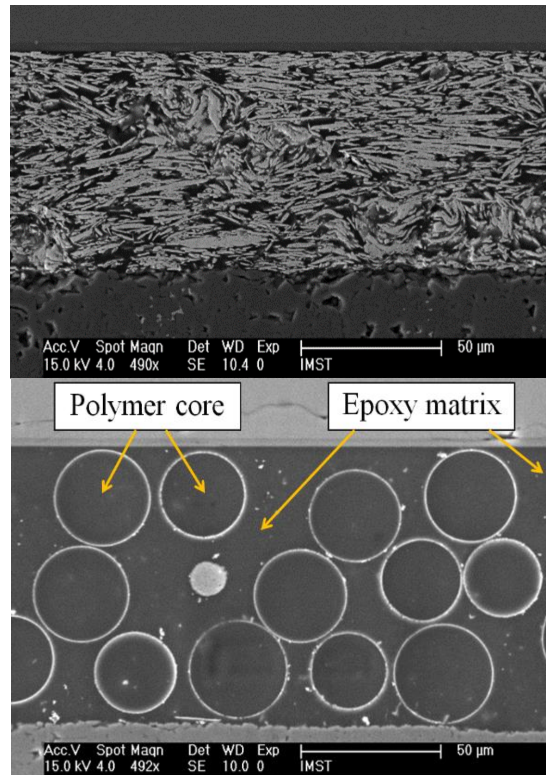

Figure 1: SEM images of cross-section of silver-flake based conductive adhesive (upper) and conductive adhesive based on silver-coated polymer particles (lower) [2].

While traditional conductive adhesives utilise silver flakes, the adhesives used in this study are filled with silver-coated polymer particles that provide conduction through the thin silver shell of the spherical particles. There are a number of advantages to this technological solution. Pro primo, the reduced volume of silver required decreases the cost burden of the product. The use of spherical particles enables a more precise control of rheological properties of the adhesive when compared to silver flakes, which allows more reliable deposition through dispensing or jetting [4]. The spherical polymer core of the particles are flexible which will aid in efforts to minimise thermal mismatch issues, which are a natural concern with silver connections due to the brittle nature of the material. Sedimentation effects are also alleviated due to the small density difference between the polymer spheres and the epoxy.

The polymer spheres are produced with a very narrow size distribution and very homogeneous properties [3]. Particles have been manufactured in the range of 5 – 30 µm, while the silver coating has been produced with thicknesses of 50 - 250 nm.

Experimental details

Materials

The particles used in this study were manufactured in house. A number of different particle types were manufactured by varying particle diameter, silver coating thickness and coating morphology and these are described in Table 1. The coefficient of size variation of the particles is > 3 %. The thickness of the silver coating of the spherical polymer particles is estimated form the amount of silver used during chemical plating. Slightly different plating procedures were used for the different particles, processes A and B denotes the present state-of-the art process for 10 and 30 µm particles, respectively, whereas process C is an older process.

Table I: Overview of particles used in this work

Ref. name	Core size	Silver thickness	Plating process	Test
10A035	10 µm	35 nm	A	Bulk & contact resistivity
10A050	10 µm	50 nm	A	Bulk & contact resistivity
10A070	10 µm	70 nm	A	Bulk & contact resistivity
10A100	10 µm	100 nm	A	Bulk & contact resistivity
10A140	10 µm	140 nm	A	Bulk & contact resistivity
10A200	10 µm	200 nm	A	Bulk & contact resistivity
30B100	30 µm	100 nm	B	Bulk resistivity
30C230	30 µm	230 nm	C	Bulk resistivity & Test modules

Two types of adhesive matrix were used, both commercially available two component epoxy systems. They are denoted as Adhesive A and Adhesive B in this study, and the main difference between them were the degree of cross-linking. A production high speed mixer was used to mix all of the adhesives. A balance with a resolution of 1 mg was used to weigh out the different components of the adhesives. Adhesive A had a glass transition temperature (T_g) of ~90℃ and Adhesive B ~65℃, measured by DSC. Samples for resistivity measurements were cured at 150°C for 30 minutes.

Resistivity measurements

The samples used in this study were prepared by mixing particles into Adhesive B and stencil printing the adhesive onto specially designed test circuits. These test circuits were PCBs manufactured using FR4 laminate material with a standard Ni/Au surface finish on standard copper foil conductors. Bulk resistivity was obtained by printing adhesive lines with a cross section of 2 mm x 0.2 mm. The resistance was measured using a four wire method, and the resistivity of the material calculated based on the geometry. The sample preparation method and bulk resistivity measurement procedure is described in more detail in [5]. Contact resistance between the conductive adhesive and gold pads was measured separately using dedicated PCB substrates and corresponding PCB components, where defined adhesive contacts were made between orthogonal conductors on the substrate and components, respectively. The contact resistance was measured by a kind of the transmission line method [6].

Material application

The jetting for this study was performed with a production jet printer. The jetting mechanism is based on the increase of pressure in a jetting chamber due to the movement of a piston induced by the expansion of a piezo-lamellae stack. A schematic of the jetting mechanism used in this study, as well as a photograph of a droplet being ejected from the nozzle, can be found in Figure 2.

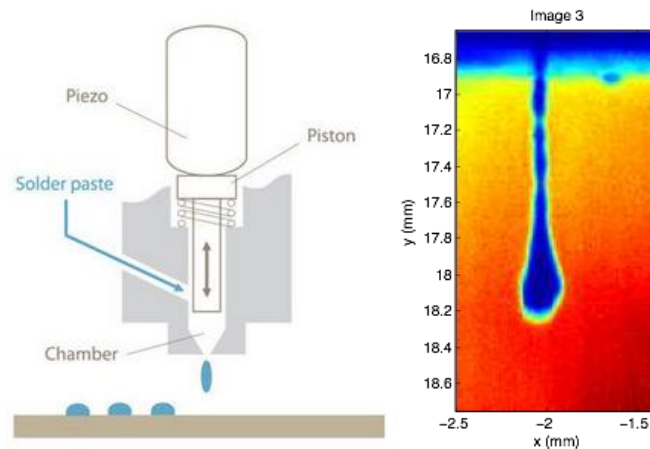

Figure 2: a) Schematic of jetting and b) photograph of droplet.

The piezo actuation device is activated by an applied time-dependent voltage. This signal was originally controlled only by a rise time, t_r, and plateau time, t_p, see Figure 3. The implementation of a new electronics control system enables an elaborate control of the signal with a choice of control points along the voltage signal. In the described study, a three-step signal with a given rise time, t_r, plateau time, t_p, and fall time, t_f, is used to study the quality of jetting, see Figure 3.

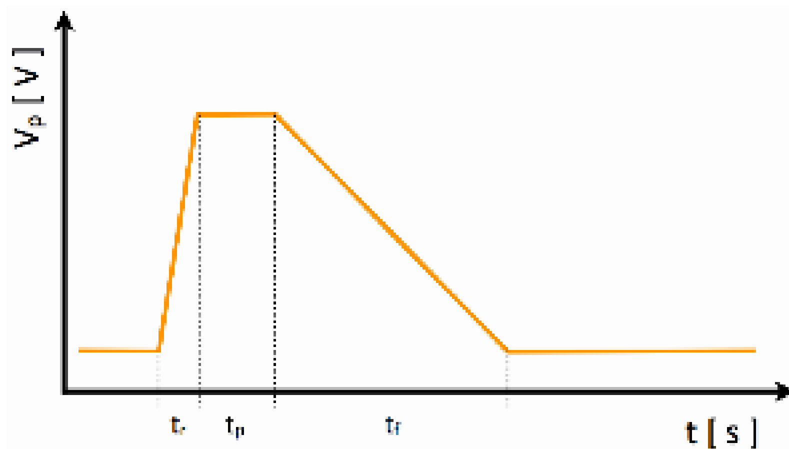

Figure 3: The time-dependent voltage applied to the piezo via a three-step signal with a given rise time, t_r, plateau time, t_p, and fall time, t_f, is used in the study.

Rheology measurements

While the rheological properties of any electronic material used for deposition is important for the quality of the final deposit irrespective of the method of material application, in the case of jetting, they are of primary importance. While traditional rheological characterizations have consisted of a single shear rate specific measurement using for example a production viscometer, to obtain further rheological information on the jetting medium, a series of rheological tests were performed. All rheological tests were performed with a production rotational rheometer.

The first measurement paradigm that was used concerned a basic shear sweep, such that the viscosity is measured during a sweep of increasing shear rates. From Figure 4, it can be seen that the conductive adhesive is strongly shear thinning. The behavior at different shear rates is important since the fluid will encounter different shear situations at different stages in the ejector, such as pump and the ejection nozzle.

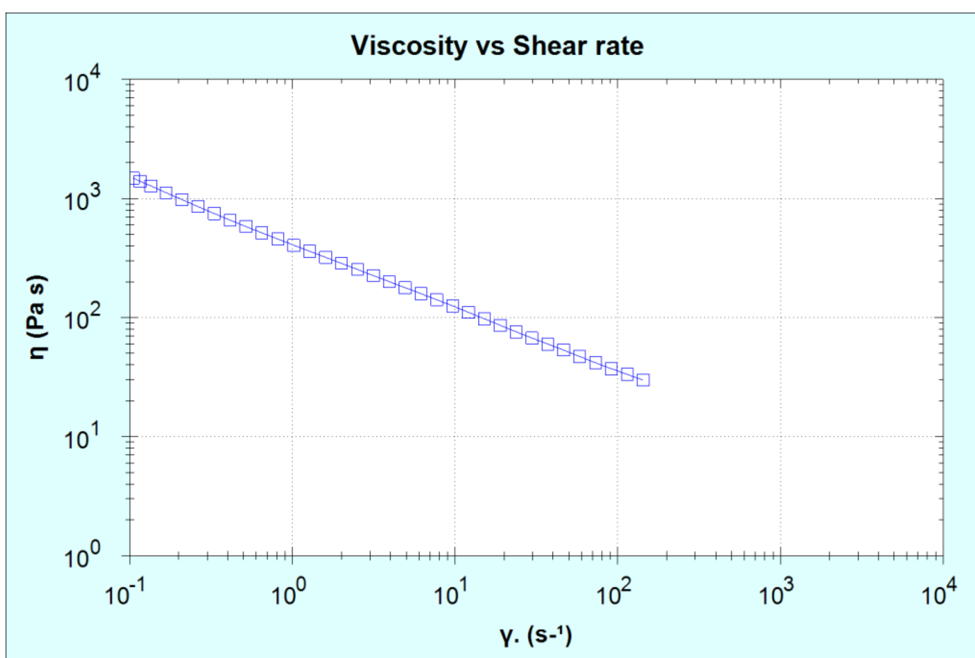

Figure 4: Rheological plot of viscosity as a function of shear rate.

The second rheological study looks at the temporal behavior of the fluid viscosity during a rapid change in shear, specifically where a high-shear stress is induced on a fluid followed by a period of low shear, where after a high-shear stress is induced and the rate of recovery is measured.

A third rheometric technique studies the linear viscoelastic response to dynamic oscillations of shear. In the dynamic oscillation approach, increasing cyclic levels of stress and strain are applied at a constant frequency. It is of interest to study the extent of the linear viscoelastic region which extends to the point at which a dynamic viscoelastic function, either modulus or viscosity, deviates by more than 10% from the plateau value. The linear viscoelastic response to a set of oscillatory shear profiles of the conductive adhesive studied in this paper is shown in Figure 5. The linear region extends to approximately 0.1%, which is somewhat lower than for comparable jetting fluids. This text exposes the relationship between the elastic and viscous components of the fluid which naturally will effect the break-off of the fluid filament when jet dispensing. A dominant elastic component will utilize more energy of the moving fluid for the break-off process.

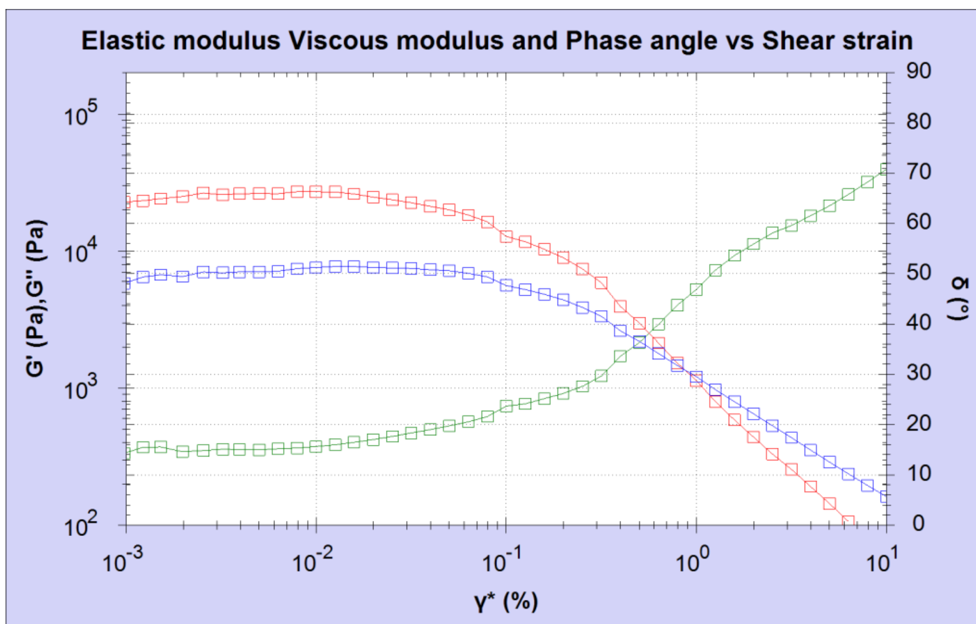

Figure 5: Rheological plot of the elastic modulus and phase angle of the fluid as a function of strain (G' - red, G" - blue, delta - green).

In addition to these rheological properties, the material and morphological properties of the particles themselves are studied. A scanning electron microscopy (SEM) image of 10 µm polymer particles with a 140 nm silver surface covering is shown in Figure 6. The particles are very spherical and the surface is quite smooth.

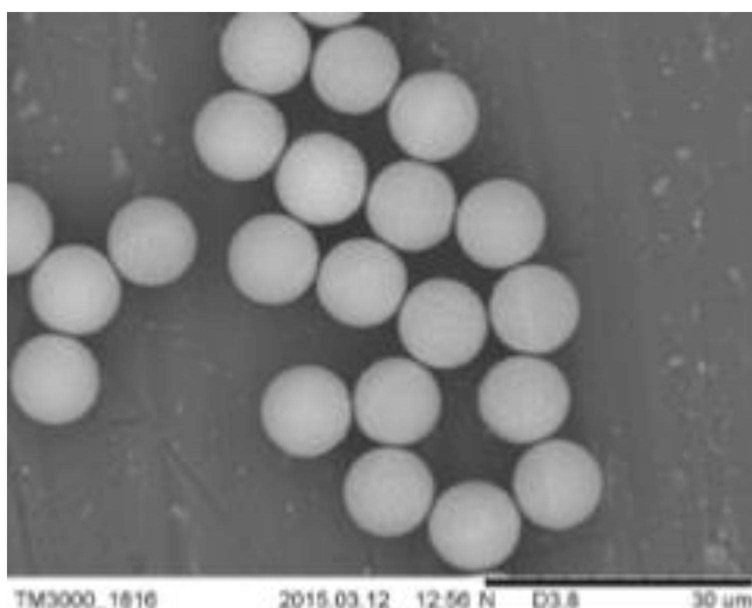

Figure 6: SEM image of 10 µm polymer particles with a 140 nm silver surface coating.

A final test that is of fundamental importance for the industrial utilisation of the electronic material is the material interaction of the jetting material and the materials that are utilised within the jetting head. These tests have not yet been performed on these preliminary materials.

Results and discussion

Electrical properties of conductive adhesive

The electrical properties of the conductive adhesive based on silver-coated polymer particles were investigated, including the bulk resistivity and contact resistance. The effect of particle size and particle concentration on bulk resistivity was measured by comparing conductive adhesives based on particles 10A140, 30B100 and 30C230, with varying volume fraction of particles. The results are shown in Figure 7. Experiments showed that for the 10 µm particle 10A140, contact was established at 35 Vol%, indicating a percolation threshold of < 35 Vol%. For the 30 µm particle 30B100, an infinite resistance was measured at 35 Vol%, indicating a percolation threshold in the interval 35 – 40 Vol%. Additionally, it was found that a higher volume fraction could be obtained for the 30 µm particles compared to the 10 µm particle, before the adhesive mixture became too dry for jet printing .. As expected, resistivity decreases with increasing particle concentration for both particle sizes. Higher resistivity was measured for the conductive adhesive based on 30 µm particles with smallest silver thickness, and this can be explained by a lower total silver content. The conductive adhesives based on 30B100 contain around 1 Vol%, the 30C230 around 2 Vol%, and the 10A140 roughly 3 Vol% silver. For comparison, the resistivity of reflowed SAC305 is approximately 13 µΩ·cm, while a traditional conductive adhesive may have a resistivity of the order of 100-1000 µΩ·cm [7].

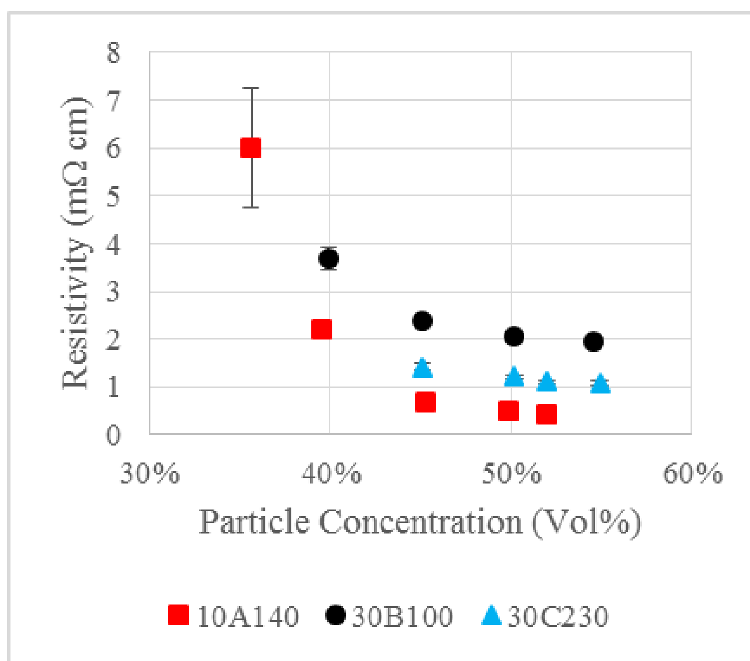

Figure 7: Effect of particle size and particle concentration on bulk resistivity of the conductive adhesive.

Jetting trials were performed by performing a series of parameter combinations of rise time, t_r, plateau time, t_p, and fall time, t_f, and analysing the resulting deposit quality. The optimization was based on deposit shape, positioning error, and variation in diameter and volume. An example of the jetting results can be seen in Figure 8. Imaging of the droplets occurred within minutes after jetting. While the deposits in Figure 8 are approximately 300 µm, the possible diameter range for the tested conductive adhesives was ca 270 - 470 µm. The rheological properties are of primary importance for the shape of the final deposit, which is related to or dependent on the formulation rheology.

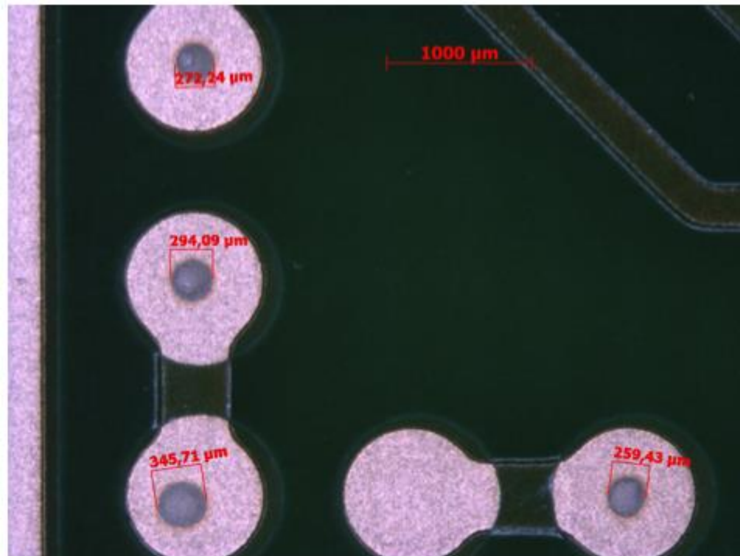

Figure 8: EL images of test module made with Adhesive A.

Conclusions

From the tests that were performed in this study, it has been demonstrated that a conductive adhesive utilising spherical, polymer silver particles can be used for no-contact jet printing. The electrical properties of such an adhesive can be controlled by changing the particle size, suspension concentration and/or silver thickness. The electrical resistivity measured in this study is low enough to ensure no measurable resistive losses on the test PCBs. Further work is needed for optimising the properties of the adhesive matrix to improve reliability and deposition quality and reliability.

Acknowledgements

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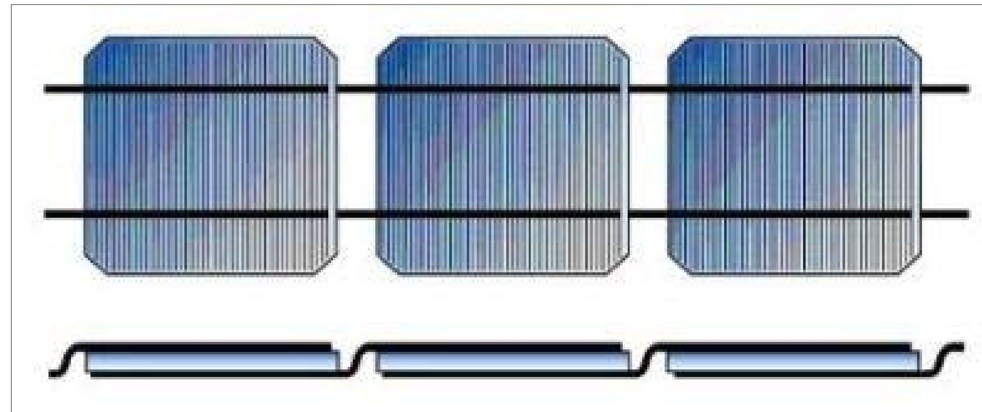
Interconnect technology



- Low contact resistance
- Reliable contact
- Minimize stress on cell
- Manufacturability
- Low cost
- Environmental friendly

Conductive Adhesive with Company Product

- Thinner wafers
- Applicable for different cell types
- Low process temperature
- No toxic lead

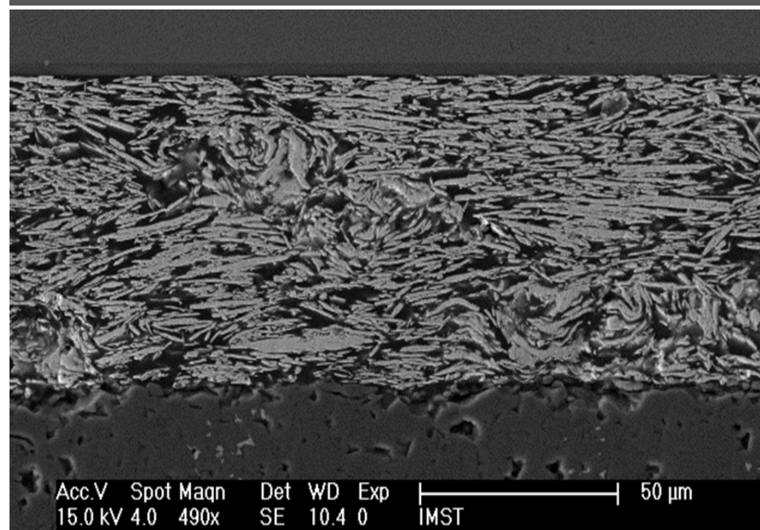
Silver-Coated Polymer Particles

Interconnect material	Process temperature	Mechanical stress	Cost	Contains toxic lead
Lead-Based Solders	*~ 210℃*	*Medium*	*Low*	*YES*
Lead-Free Solders	*~ 250℃*	*High*	*Low*	*NO*
Conductive Adhesive	*<< 180℃*	*Low*	*Medium -> Low*	*NO*

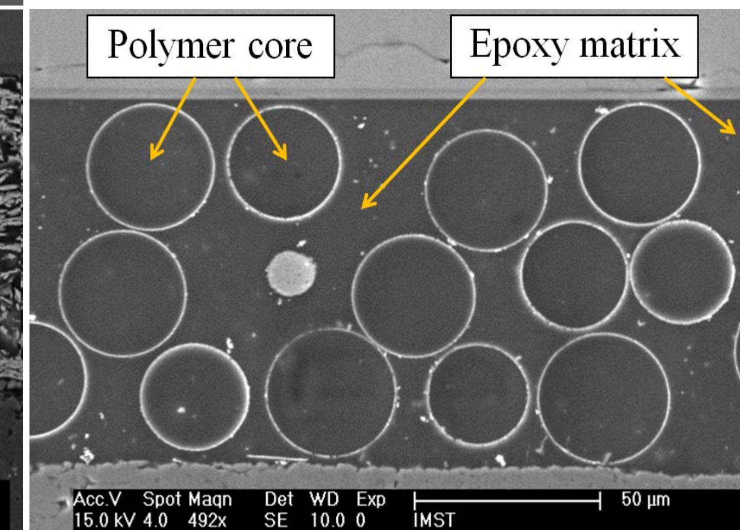
Electrically conductive adhesive…

- Reduced silver consumption
  - Lower cost!
- Spherical shape
  - Easy dispensing and printing!
- Lower density
  - Less sedimentation!
- Reduced anisotropy
  - More efficient use of silver!
- Lower metal content
  - Improved thermomechanical properties!

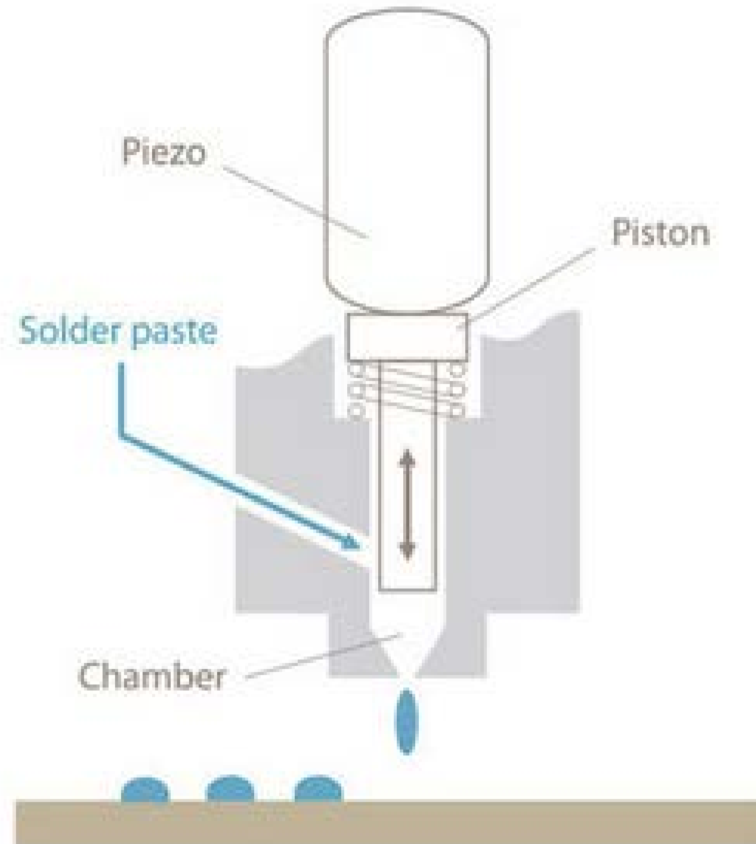
… with silver flakes

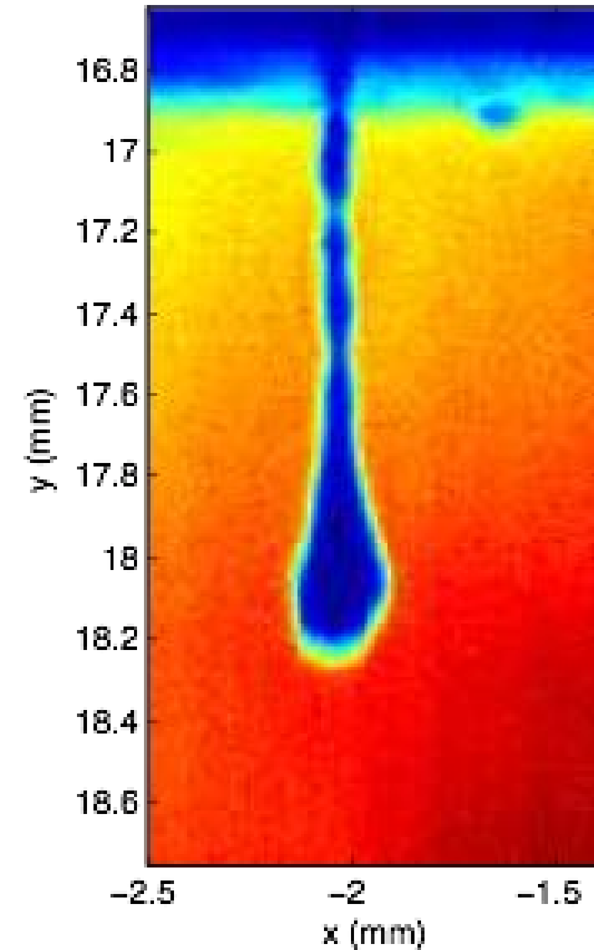


… with silver-coated polymer particles



Jetting technology

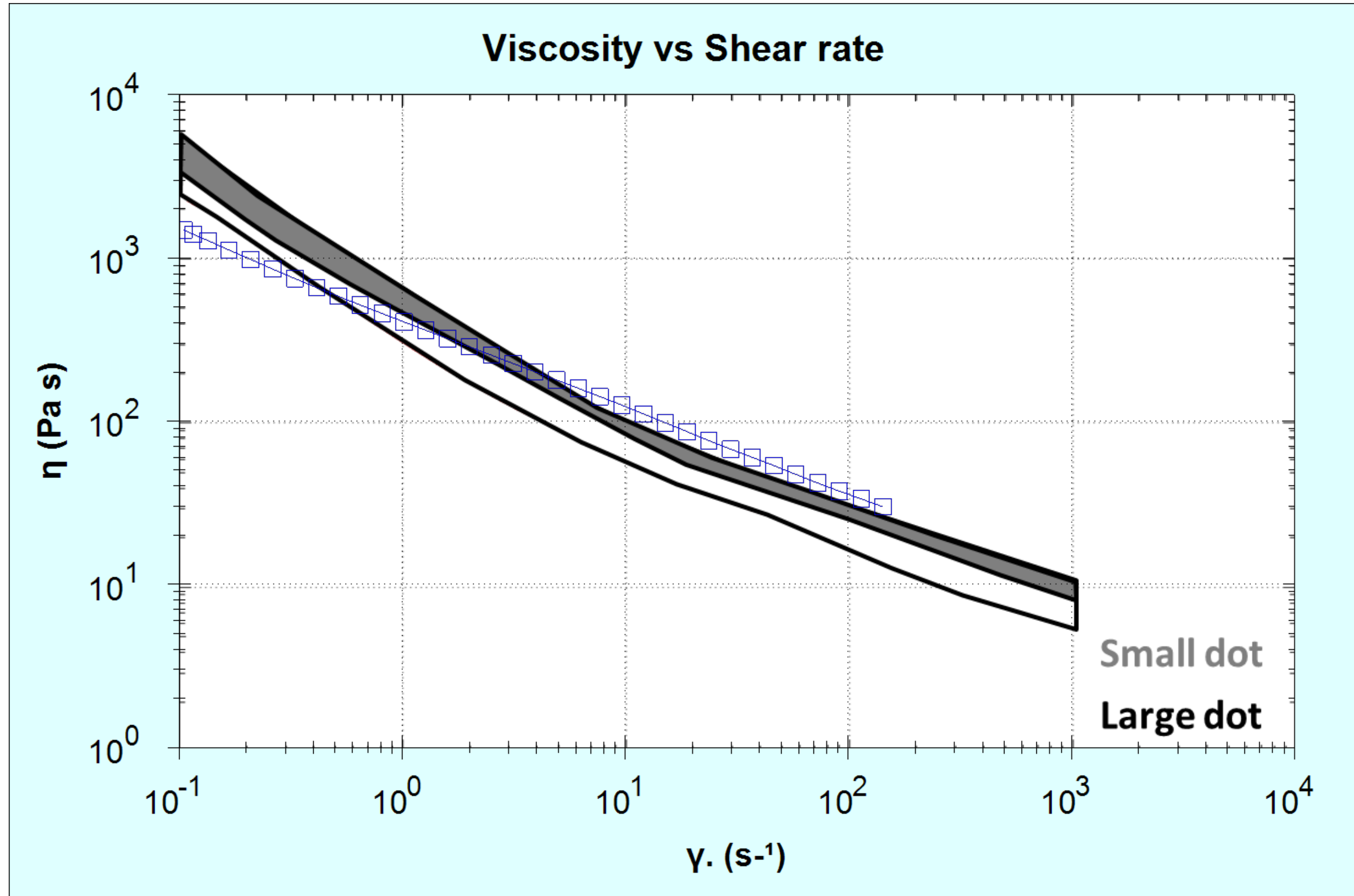




Shear viscosity

Sample	η @ ~0.1 s⁻¹ (Pas)	η @ ~1.0 s–1 (Pa s)	η @ ~100 s–1 (Pa s)
Company ICA4	1482	410	35.5

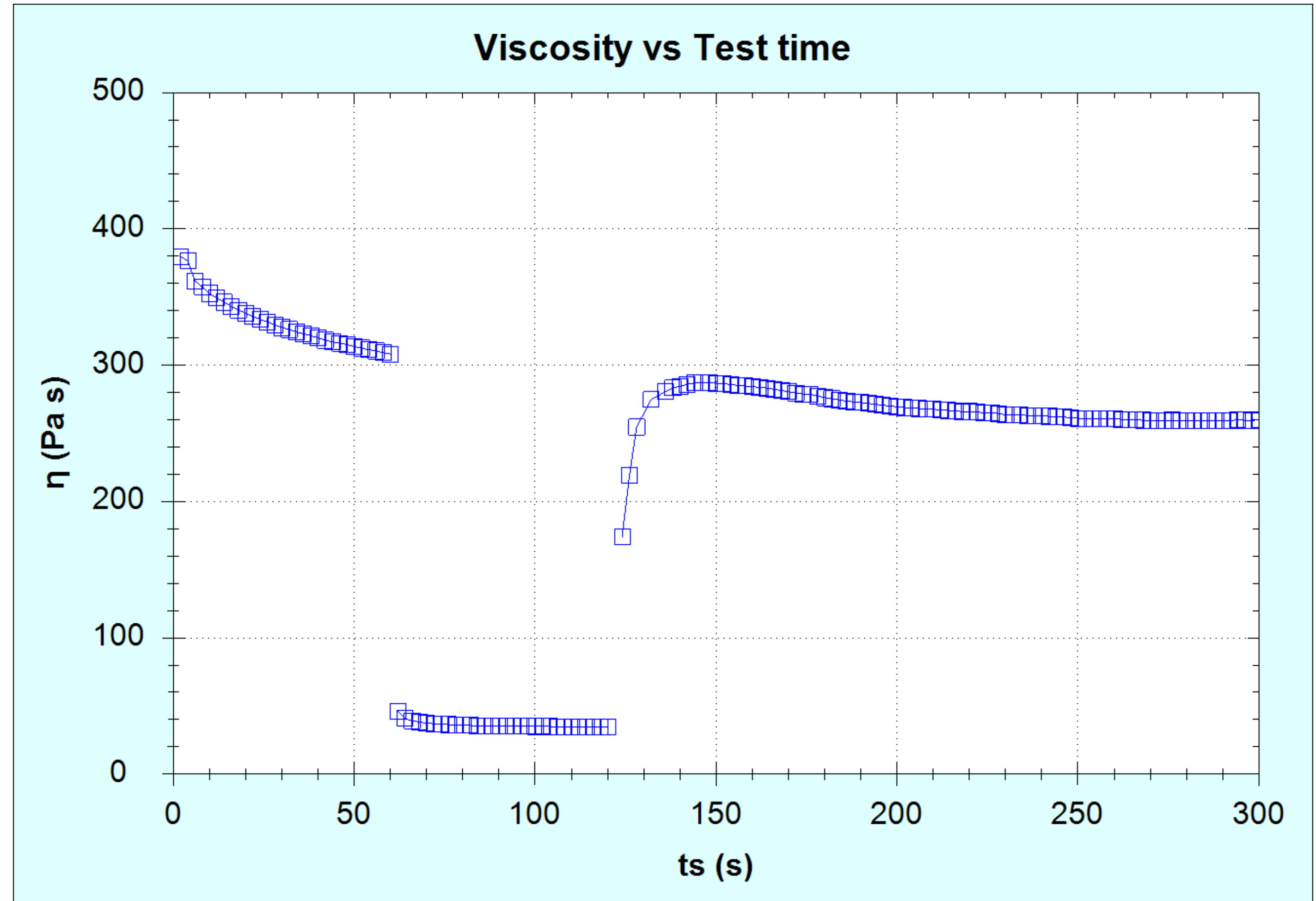
Low viscosity at low shear rate, high viscosity at high shear rate. Less shear-thinning than typical solder pastes



Recovery

Sample	Viscosity ratio			Recovery ratio rate
	6 s	10 s	150 s	
Company ICA4	0.71	0.90	0.84	0.76

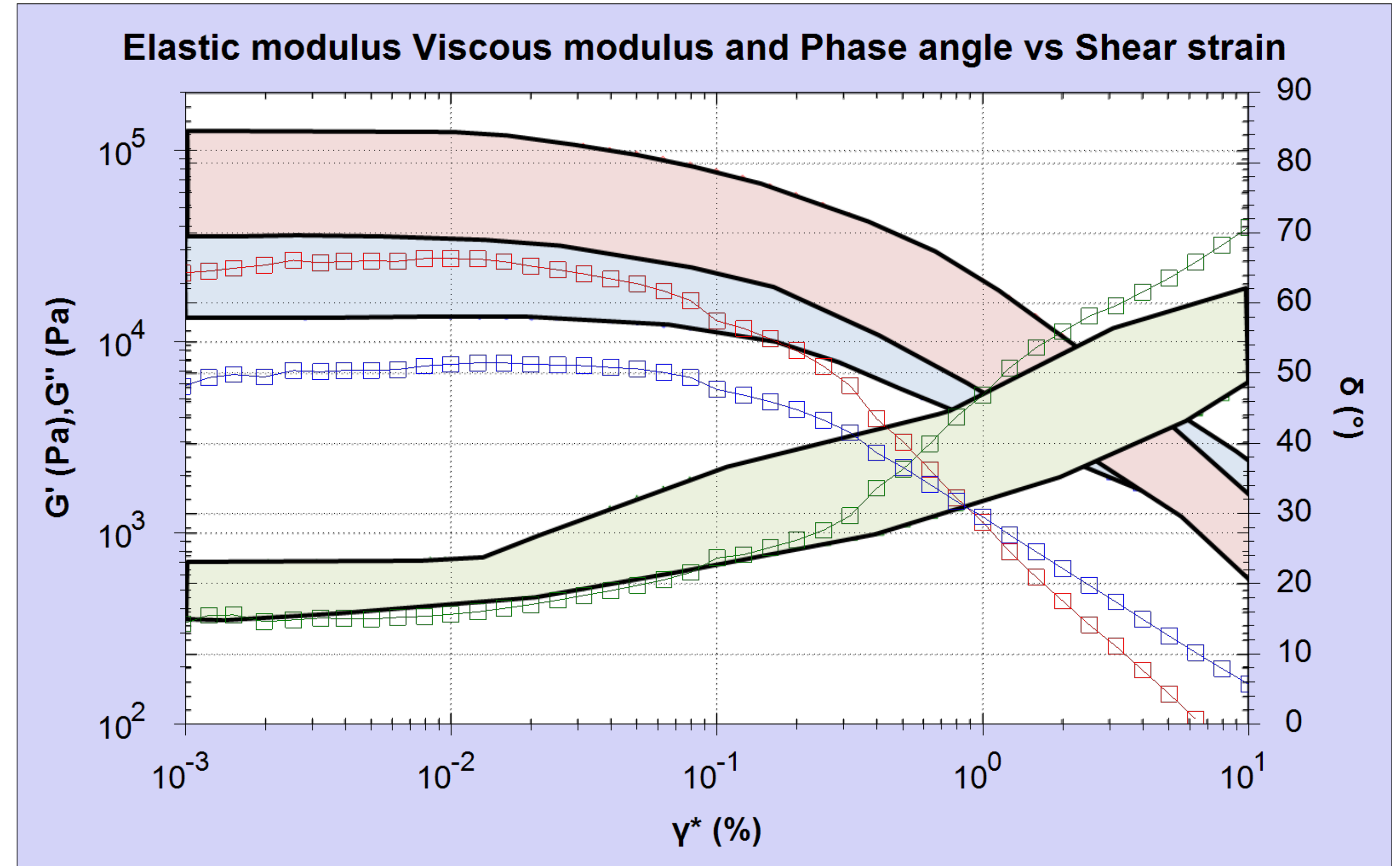
Recovery should actually be faster, but correct shear rate not achieved during step 3 until > 8 sec.



Amplitude sweep

Sample	Company ICA4
G' (Pa)	27120
G'' (Pa)	7440
G'/G'' crossover (Pa)	17
δ (deg)	14.6–70.8
Damping Factor (Tanδ)	0.27

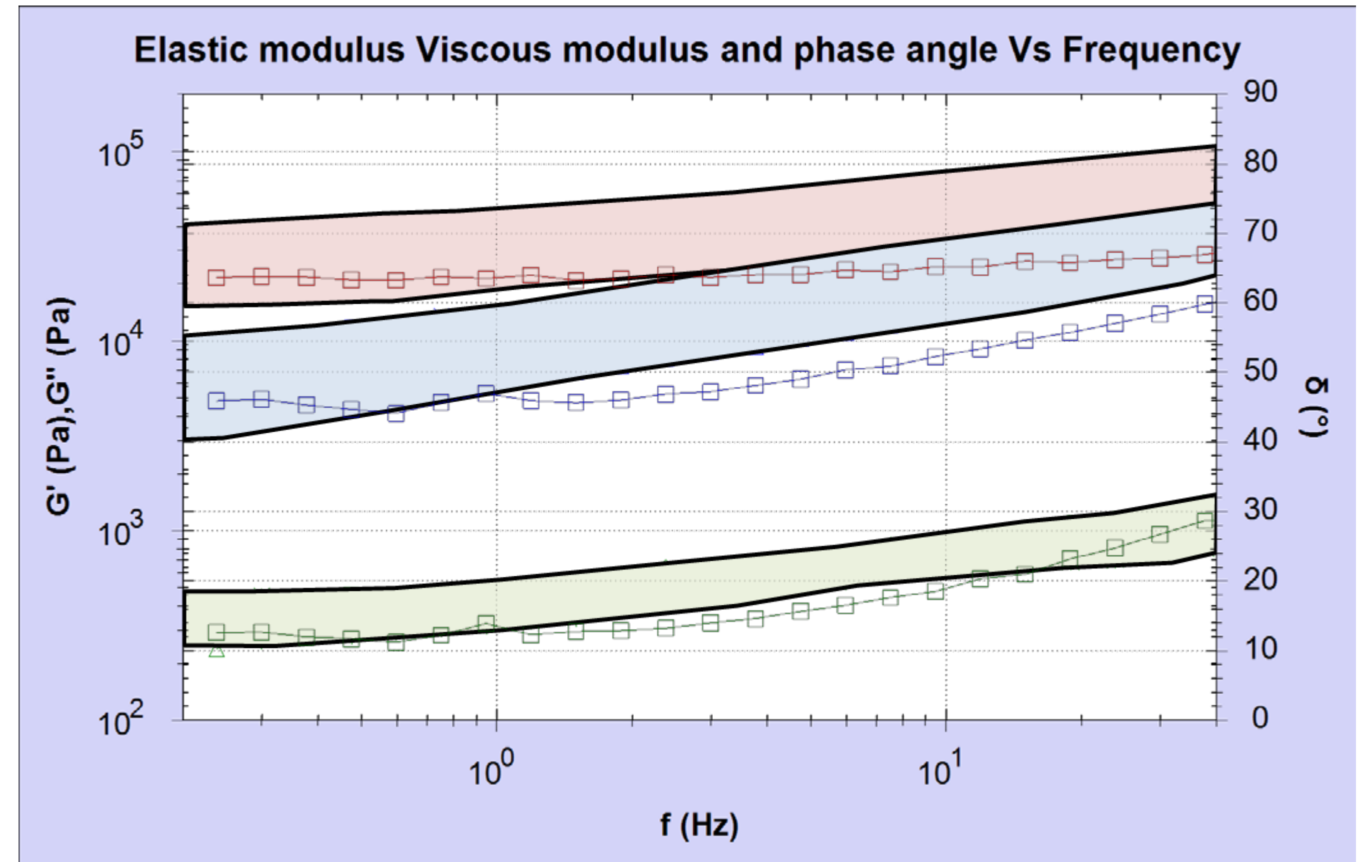
- Ideal ratio of elastic/viscous properties in linear region
- Relatively low G' and G'' compared to standard jettable pastes
- Fast breakdown of paste and low yield stress



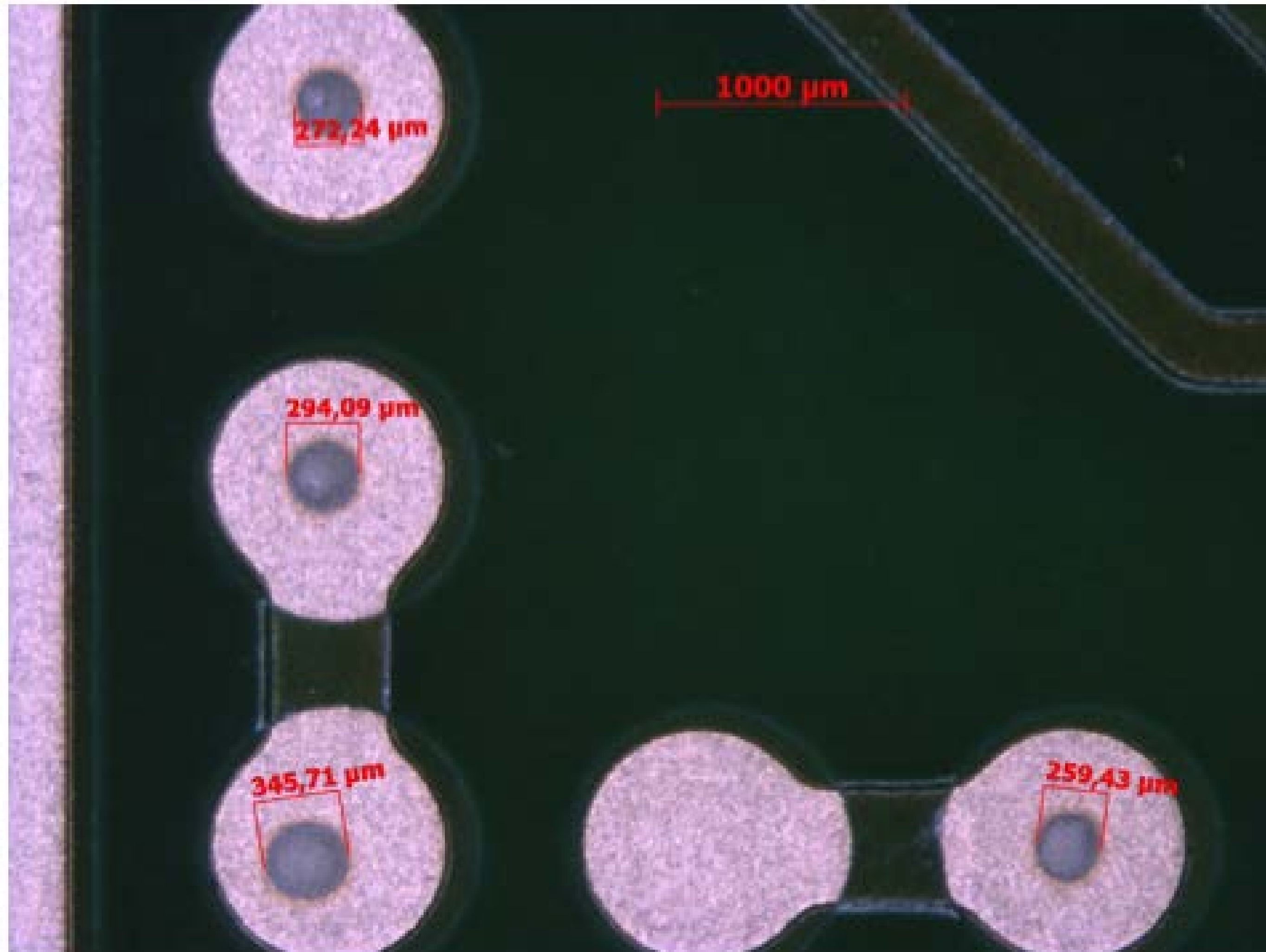
Frequency Sweep

Sample	Company ICA4
G' (Pa) at 1 Hz	21500
G'' (Pa) at 1 Hz	5200
Damping Factor (G''/G')	0.24
η* at 1 Hz (Pa s)	3540

- Relatively low G' and G'' compared to standard jettable pastes



Jetting

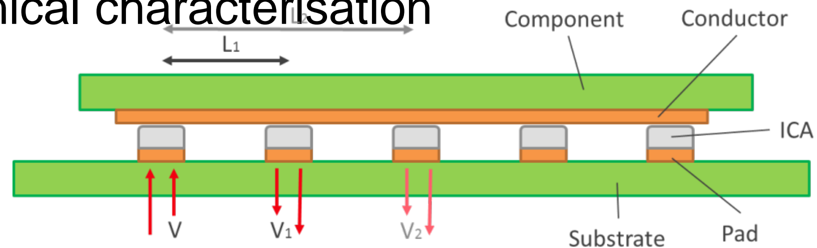


Adhesive characterisation

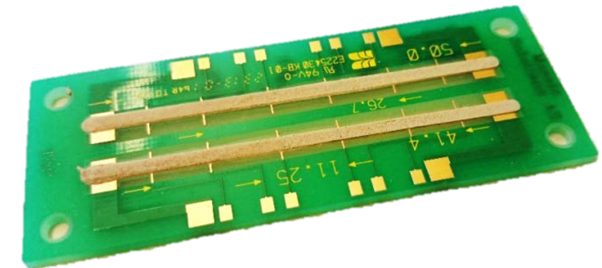
Electrical characterisation

- Bulk resistivity measurements
- Contact resistance measurements
  - Dedicated PCBs with Ni/Au surface finish
  - 4 wire measurements

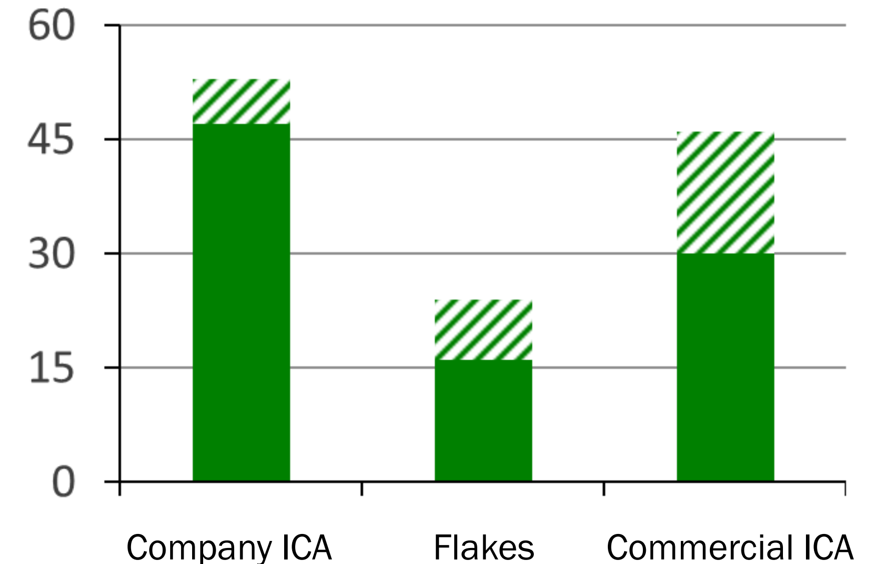
Mechanical characterisation



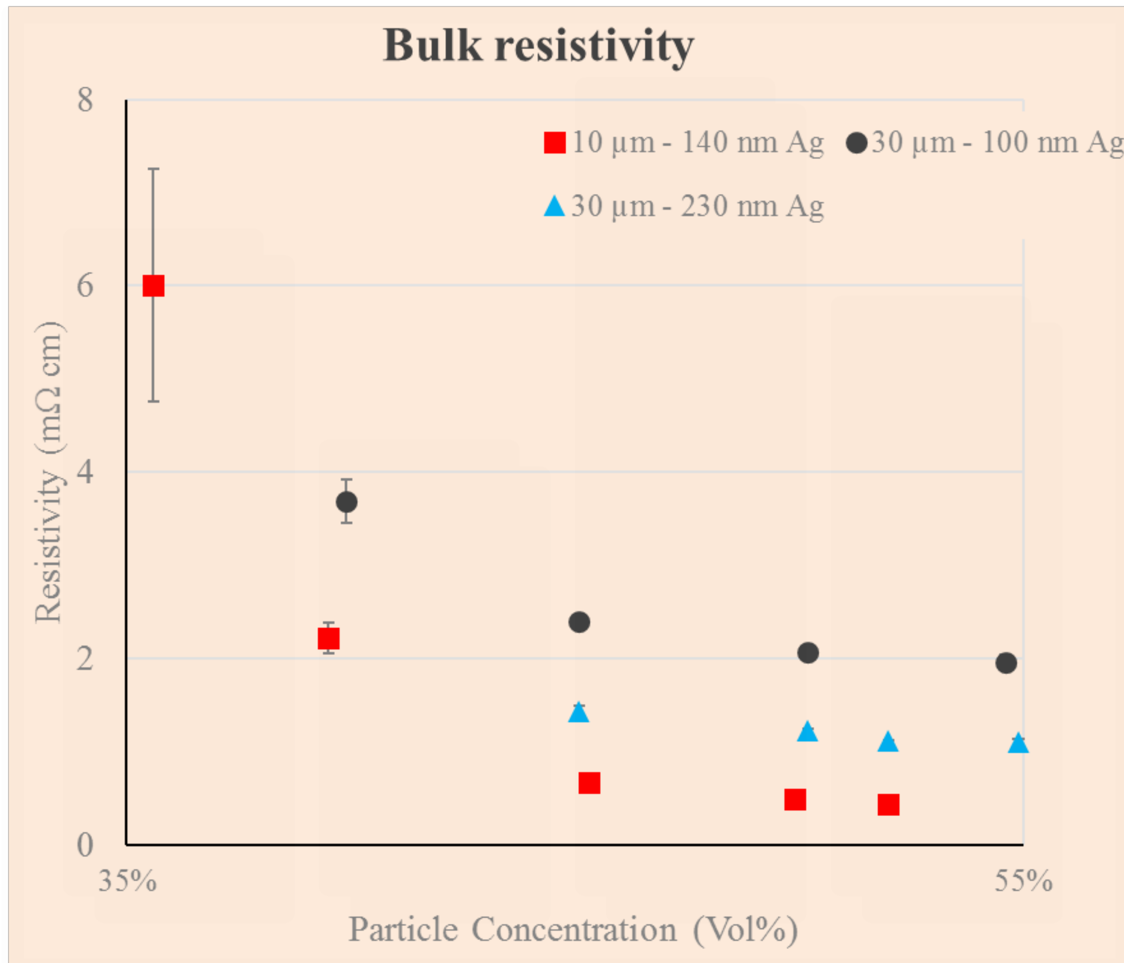
Modified Transmission Line Method (TLM) for contact resistance measurement

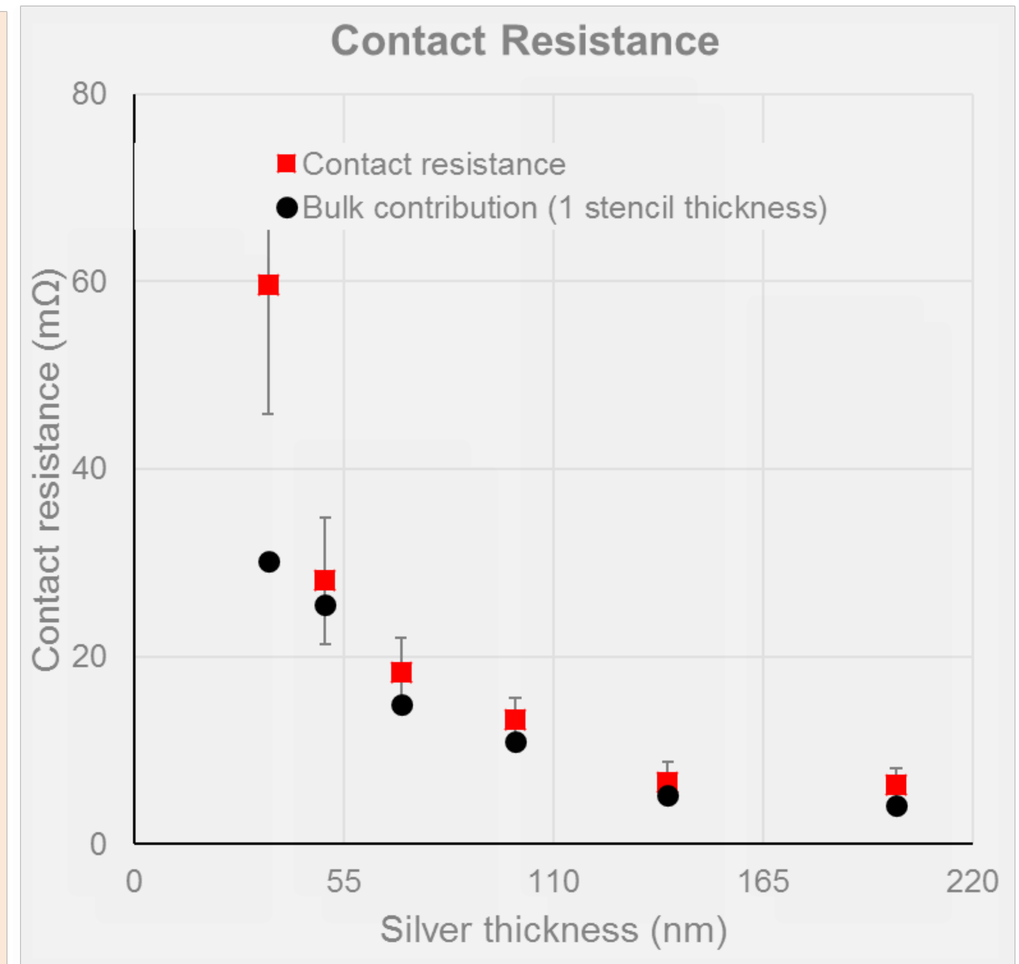


Test PCB with printed adhesive strip for bulk resistivity measurements



Effect of particle concentration on bulk resistivity





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SweModul AB for the use of their lab and their manufacturing facility

The End

Any Questions?