Adhesive and Conductive – Inkjettable nano-filled inks for use in microelectronics and microsystems technology

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ABSTRACT

Current technology, Inkjet is an accepted technology for dispensing small volumes of material (50 – 500 picolitres). Currently traditional metal-filled conductive adhesives cannot be processed by inkjetting (owing to their relatively high viscosity and the size of filler material particles). Smallest droplet size achievable by traditional dispensing techniques is in the range of 150 µm, yielding proportionally larger adhesive dots on the substrate. Electrically conductive inks are available on the market with metal particles (gold or silver) <20 nm suspended in a solvent at 30-50%. After deposition, the solvent is eliminated and electrical conductivity is enabled by a high metal ratio in the residue. Some applications include a sintering step. These nano-filled inks do not offer an adhesive function. Work reported here presents materials with both functions, adhesive and conductive. This newly developed silver filled adhesive has been applied successfully by piezo-inkjet and opens a new dimension in electrically conductive adhesives technology.

The present work demonstrates feasibility of an inkjettable, isotropically conductive adhesive (ICA) in the form of a silver loaded resin with a 2-step curing mechanism: In the first step, the adhesive is dispensed (jetted) and pre-cured leaving a "dry" surface. The second step consists of assembly (wetting of the 2nd part) and final curing.

Keywords: conductive, nano-filled, silver, inkjet, microelectronics

1 DESCRIPTION

Generally speaking, jetting of liquids by piezo-actuators can generate droplets of as low as 30 pl whereas dispensing with the most recent valve equipped instruments produces droplet sizes of 10 nl typically. Inkjet nozzles have diameters ranging from 100 µm to 30 µm and smaller. It is widely accepted that the maximum silver filler particle size should not exceed 4 µm (with spherical morphology) for inkjetting. Also, viscosity of the loaded adhesive should be low, typically <100 mPas in order to be ink-jettable. Thus the unloaded resin material needs to have a very low base viscosity. The results reported here have been obtained with a 75 µm nozzle. Further work with a 50 µm inkjet nozzle is in progress. Preliminary results show that adhesive droplet sizes can be further reduced.

2 SILVER POWDER PROPERTIES AND REQUIREMENTS

Under these conditions, special care has to be taken to prevent agglomeration and sedimentation of the filler particles in the resin matrix: agglomeration results in large particles blocking the nozzle, sedimentation modifies the loading ratio of silver locally and may also obstruct the ink-jet nozzle. High purity silver particles of small size possess a chemically and metallurgically very active surface. Unprotected it may cold-weld and sinter already at room temperature under high shear stress conditions, as they occur during jetting inside the nozzle. These factors require an effective protection coating on the silver surface which at the same time needs to enhance dispersion properties of the powder particles in the resin matrix. However, a balance has to be found between these "positive" properties and the detrimental electrical insulation typically provided by an effective surface coating. Also, the coating chemicals have to be neutral in terms of curing reactions and viscosity stability. An additional feature of the filler particles is reflectivity. Especially in the case of photo-initiated curing mechanisms, this property is key to obtain curing in depth of the adhesive layer. The success of the powder is determined by the final properties of the material, i.e. electrical conductivity and mechanical bond strength. The silver powder that fulfils all the above mentioned requirements is of >99.997% purity and has been developed specifically for this project.

3 2-STEP CURING MECHANISM – A COMBINATION OF UV AND THERMAL CURE

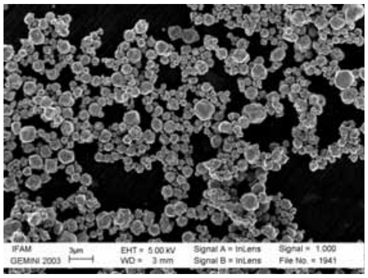

Figure 1: SEM of Silver powder. Main characteristics of the silver powder. Specific surface area: 0.55 m^2/g (single point BET); Tap density: 7.0 g/cm^3 (Tap pack); PSD D50: 2.4 µm (light scattering); Ag purity: >99.997%.

The technical approach retained to match the specificities of ink-jetting is based on a 2-step curing system: Dispensing into a final form, pre-cure to a material that can be easily handled (the jettable material would not allow easy processing outside of the inkjet itself), followed by the component assembly step and final curing of the conductive adhesive.

The resin system was designed with a first UV-cure with radical mechanism. After inkjet deposition on the substrate, the adhesive is partially cured by UV (Prepreg) and can be processed immediately or stored at <4°C for processing at a later stage. Because of its radical nature, the pre-cure step has to be performed under inert atmosphere, e.g., nitrogen, as oxygen could interfere in the curing reaction. At this stage the adhesive surface is "dry", similar to a thermoplastic material containing unreacted epoxy functional groups.

The second (and final curing) step involves heating of the adhesive (i.e., melting), followed by wetting of the 2nd part (component assembly) and cross-linking of the epoxy groups. Bonding of the 2nd part (component) has to be performed under pressure as thermoplastic materials exhibit very high viscosities. Final curing is achieved in a classical furnace/oven. The cross-linking ratio determines the mechanical properties and can be fine tuned through the number of epoxy groups in the initial resin material. At the end of the process a 3-dimensional network of cross-linked polymer chains is formed.

The 2-step cure is based on a specifically developed Acrylate-Epoxy-Resin matrix with Newtonian properties. It has a very low base viscosity, typically in the range of 3 mPas. To ensure high electrical conductivity in the final product the silver filler particle concentration must overcome the percolation threshold. Therefore, a loading of 70% by weight was chosen as a minimum silver filling rate of the adhesive (approx 20% by volume).

A further constraint is the fact that the metallic silver particles are not transparent to UV. Therefore UV light cannot penetrate deeply into the formulation to initiate the first radical curing reaction. Again, not every silver powder can be used. Surface morphology plays an important role and some degree of UV reflectivity could be achieved with the selected Ag material. Special attention had to be paid to include various UV initiators. They are essential for propagation of the reaction into the resin matrix shadowed by the filler particles. With the present adhesive, curing of layers up to 30 µm thick was achieved successfully. (This fact is noteworthy, as to the best of our knowledge, there are no commercially available conductive adhesives based on radical UV curing.)

The second, thermal curing step is accelerated by imidazoles. A specific electrical resistance of 10^{-4} Ωcm and bond strength of 10-15 N were achieved with SMD-resistors (case size 1206) on copper.

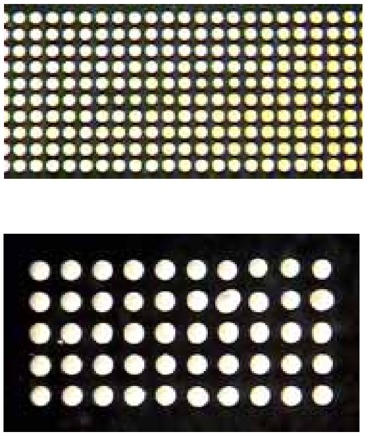

Figure 2 & 3: Array of ICA dots deposited by inkjet, pitch size 200 µm.

4 JETTING OF THE CONDUCTIVE ADHESIVE

Inkjet dispensing was performed using an innovative design based on a glass capillary nozzle, surrounded by a piezo-actuator.

5 POSITIONING SYSTEM

The experiments were conducted with the AutoDrop positioning system MD-P-801. This positioning system is designed for high accuracy with 1 µm repetition accuracy. The necessary stiffness is achieved by using granite components for the base plate as well as for the bridge which carries the z-axis. The substrate is fixed on

Figure 4 : AutoDrop positioning system

the x-y-table and is moved relative to the dispenser heads, while the z-axis which moves the dispenser heads up and down is fixed. This design minimizes the moved mass and improves positioning accuracy considerably. It is possible to move and control up to 8 dispenser heads or pipettes in parallel. Dosing can be done in “start-stop“-mode or in-flight, i.e. while the head is moving.

6 WORKING PRINCIPLE OF THE MICRODROP SYSTEM

The microdrop technology (Dispenser Patent n° DE 10153708) uses the same principle as that of the ink jet printing. However, the dispensing system developed by microdrop GmbH differs fundamentally. The core of the microdrop dispensing head consists of a glass capillary which is surrounded by a tubular piezo actuator. At one end, the capillary is formed to a nozzle (diameter 30 to 100 µm). Applying a rectangular voltage pulse, the piezo actuator contracts and creates a pressure wave which propagates through the glass into the liquid. At the nozzle the pressure wave is transformed into a motion of the liquid which is accelerated with up to 100 000 g. A small liquid column leaves the nozzle, breaks off and forms a droplet which flies freely through the air. Droplet size is mainly determined by the nozzle diameter. Volumes of 30 up to 500 picoliters can be dispensed. Ejection frequency can be varied between 0 and 2 kHz. Volume variation is approx. 1 %. Nozzle diameter can be produced with high accuracy (±1 µm) depending on the desired drop volume.

A stroboscopic video camera monitors the process of droplet formation. Varying the time delay between the signals to the piezo actuator and the strobe allow the operator to monitor the entire process of droplet formation.

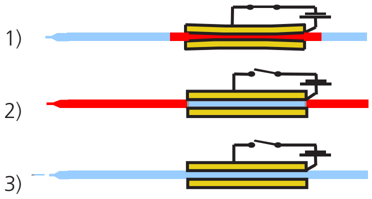

Figure 5 : 1) Voltage is applied to the piezo actuator; contraction of the actuator induces a pressure wave.

2) Voltage is switched off and the piezo actuator relaxes to normal state, the pressure wave propagates through the capillary to the nozzle.

3) The accelerated fluid jet at the nozzle outlet forms a drop which freely flies away from the nozzle.

7 INKJETTING TEST RESULTS

The samples of the dot array (ref. Fig. 2 and 3) were produced on the positioning system. It is the platform for dispensing the ICA on different microelectronic devices.

A special nozzle with a reduced flow resistance for fluids with a viscosity up to 200 mPas at room temperature was used. This innovative design prevents cavitation and agglomeration of particles which occurred with standard nozzles. Cavitation and agglomeration of particles destroy the jet and create a multidirectional spray.

Figure 6: Jetting of a transparent fluid (ethylene glycol)

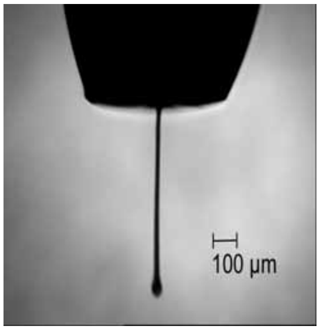

Figure 7: Jetting of ICA with a 75 µm nozzle

Successful dispensing of ICA is shown in Fig. 7. Droplet size is nearly 500 pl with the 75 µm diameter nozzle creating 130 µm dots on a glass substrate. The volume results from the size of the jet, which is dependent on the viscosity of the ICA.

The viscosities of the presented adhesives vary from (up to) 1 Pas at very low shear rate to 20 – 40 mPas at high shear rate. The shear rate occurring in the nozzle during jetting is estimated to reach 2500 s-1. Under these drastic conditions, silver particles tend to agglomerate. As mentioned above - silver being a ductile metal with high tendency of cold welding - its surface has to be coated for mechanical protection. However this protection does not remain functional in the cured material, otherwise it would prevent electrical conductivity. In the jetting conditions, care has to be taken to avoid separation (sedimentation) of the silver particles from the resin matrix. This is not an easy task as specific densities of the ink components are quite different: just above 1 g/cm^3 for the organic matrix and >10 g/ cm^3 for silver!

8 OUTLOOK

Future work will be done with a 50 µm nozzle. This will reduce the dot diameter. The current objective is to generate 80 µm dots.

Additionally a new dispenser system (Dispenser Patent n° DE 10153708) is under development. It is characterized by a reduced dead volume and integrates a fluid circulation device. With this system the sedimentation of particles in the fluid can be prevented. First tests with ethylene glycol and fluids with low particle content have been performed already. They show a similar performance as the system described above. The optimization is still ongoing.

Figure 8: Single ICA dot deposited by inkjet

9 CONCLUSIONS

Arrays of ICA dots of 130 µm diameter with a pitch of 200 µm have been produced reproducibly. Specific electrical resistance of 10^{-4} Ωcm and bond strengths of 10-15 N were achieved with SMD-resistors (case size 1206) on copper substrate.

This joint development of resin system, silver particles and inkjet device has opened the door to apply the technology for electrically conductive joining in the microsystem and microelectronic fields.

10 ACKNOWLEDGEMENT

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