# Metallization of high density TSVs using super inkjet technology

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**Abstract**

Filling or metallization of the through silicon vias (TSVs) with the conductive materials to act as vertical electrical interconnections through the wafers, is one of the key steps in the microelectromechanical systems (MEMS) wafer level packaging. Previously, metallization of the vias with inkjet printing technology is demonstrated. However, little attention has been paid to the possibility of metallization of high density TSVs; because drop diameters of conventional inkjet printers are larger than the top diameter of thin vias. Therefore, in this work we investigate the potential of super inkjet (SIJ) technology with 0.1 femtoliter droplets to metallize the vias with top diameter of 23 µm using three different silver nanoparticle inks. The filling processes are monitored by the observation camera and after the sintering, cross-sections of the vias are studied by the optical and scanning electron microscope (SEM).

**Introduction**

Using inkjet printing, as a digital fabrication method, has seen a considerable increase in electronic application lately. Inkjet printing offers the ability to apply a controlled amount of functional materials (i.e. conductive, dielectric, and semiconductive) with very high precision on many different substrates ranging from ceramics to low-cost plastics and even paper. Thus, the direct deposition of functional materials adds flexibility to the production process. Inkjet printing technology can be used, for instance, in RFIDs [1], intelligent packages [2] and microelectronic packages [3]. Generally, the focus of printed electronics research has been focused more on organic devices (e.g. OLEDs) rather than on fabrication steps of semiconductor technologies.

One of the interesting application areas of the inkjet technologies could be in fabrication process of the microelectromechanical systems (MEMS), integrating both miniaturized electrical and mechanical components, such as different kinds of sensors (e.g. accelerometers, gyroscopes, etc.). There are selected steps in MEMS packaging (introduced in the PROMINENT consortium [4]) that inkjet printing could be used instead of conventional techniques to simplify the process as described in Figure 1. However, the focus of this work is on fabrication of metal through silicon vias (TSVs) being used for 3D integration. The vias act as an electrical interconnection through the stacked wafers and devices in case they are partially or completely filled (most cases) with conductive material [5].

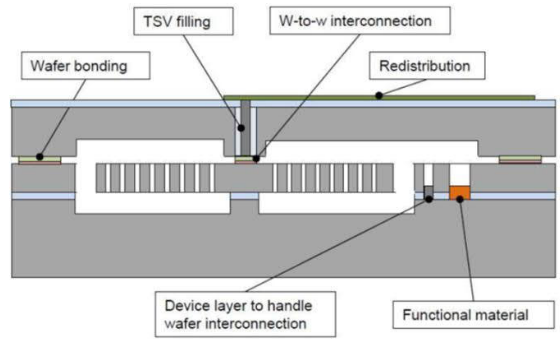


**Figure 1.** Selected steps in MEMS wafer level packaging with the potential to be fabricated by additive method

Currently, chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating or electroless deposition are used to deposit the material into the vias [5]. Since these subtractive methods are time-consuming, inkjet technology as an additive digital fabrication technique can be implemented to make the filling process much faster, reduce production cost and of course reduce environmental impact since there is less amount of materials and chemicals. Previously, we [6] and other research groups have studied the feasibility of using inkjet printing for complete filling or plating of the vias with inks based on metal nanoparticles. Andreas Ratline et al. studied the homogeneity of silver fillings and also compared partial filling with complete filling [7]. Gerard Cummins et al. [8] used copper nanoparticle ink and studied the effect of substrate temperature and evaporation rate on uniformity and crack formation. Vias with diameter of 50-100 µm are also filled without any void in [9]. Same group also did 3D bumping on top of completely filled vias with flat surfaces using very high substrate temperature and delay between the droplets [10].

For increasing the density of the 3D interconnections, very small vias are needed with the lowest possible pitch to have higher inputs and outputs per package. Conventional inkjet printers cannot be a suitable candidate to metallize high density TSVs because the diameters of the droplets are usually larger than the diameters of very small via holes. For instance, 1 pl cartridges are available for Dimatix inkjet printer with drop diameter of 12.4 µm, but the jetting cannot be stable long enough as with 10 pl cartridges jetting behavior. It is also hard to quickly check the filling process from the top view because of the low magnification of Dimatix fiducial camera. Because of all these limitations, another printing setup with super fine nozzles and very small droplets is needed.

Super inkjet technology (SIJ) has several advantages that make it a good candidate to be used for metallization of high density TSVs. First: this technology enables us to produce super-fine droplets (0.1 femtoliter) with diameter of less than 1 µm. Second: since the size of droplets is so small, the evaporation of the solvent is much faster during the printing enabling almost dry deposition of material on substrate. Third: very small droplets could also decrease the chance of having the air pockets during the printing process or after the sintering.

**Materials and equipment**

*Inks*: in this work, silver nanoparticle inks form Advanced Nano Products, Harima Chemicals and ULVAC Technologies are used for the printing trials. Table 1 shows the specifications of the inks reported by the manufacturers.

**Table 1.** Properties of the silver nanoparticle inks reported by the manufacturers

| | |
|---|---|
| **DGP 40LT-15C (ANP)** [11] | |
| Solid content | 30~35 wt% |
| Viscosity | 10~17 mPa.s |
| Surface Tension | 35~38 dyn/cm |
| Solvent | TGME (Triethylene glycol monoethyl ether) |
| Curing Temp. | 120~150 ºC |
| Specific Resistivity | 11~12 µΩ.cm |
| **NPS-J silver nanopaste (Harima)** [12] | |
| Particle size | 8~15 nm (Mean dia.12 nm) |
| Metal contents | 62~67 wt% |
| Viscosity | 7~11 mPa.s |
| Specific gravity | 1.8~2.2 |
| Solvent | Tetradecane |
| Curing conditions | 220 ºC (60 min) |
| Specific Resistance | 3 µΩ.cm |
| Shrinkage | 80~85% |
| **CAg-2000 (ULVAC)** [13] | |
| Particle size | 3~7 nm |
| Metal contents | 55~60 wt% |
| Viscosity | 5~15 mPa.s |
| Solvent | Tetradecane |
| Curing conditions | 220 ºC (30 min) |
| Specific resistance | About 3 µΩ.cm |

*TSV structure*: tapered vias with bottom diameter of 10 µm, top diameter of 23 µm and depth of 36 µm, provided by Okmetic, are selected for the printing trials. TSVs are fabricated by photoresist masking and plasma etching. After mask removal, roughness of the TSV sidewalls is reduced by thermal oxidation and then oxide removal. Finally, a second thermal oxide is applied for electrical insulation.

*Printing setup*: commercial sub-femtoliter inkjet printer, developed by SIJ Technology Inc., located in the cleanroom is used for the printing trials as shown in Figure 2. Standard glass nozzle (provided by SIJ Technology) is installed on print head above the stage which is controlled by computer. Three-axis pulse motor stage is also controlled by computer.

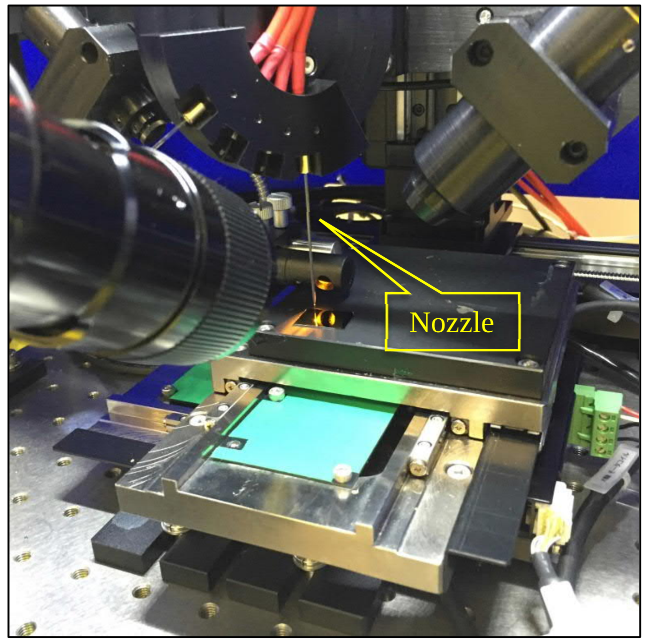


**Figure 2.** SIJ printing setup

**Experiments and results**

SIJ machine includes two dispensing modes that could be utilized in TSV filling: 1) bumping mode and 2) spiral mode. In bumping with short holding time, very little amount of ink and fast evaporation make it possible to grow 3D features. In spiral mode the nozzle jets the ink while it rotates in spiral way clockwise and counterclockwise from the center to circumference and vice versa, so that after some time we observe the growing. Figure 3 shows the 3D features printed by the spiral mode on plane silicon wafer using CAg-2000 silver ink. These printing modes could be implemented for printing into the vias. However, regarding the spiral mode, precise alignment of the nozzle on top of very small vias is not that straightforward. Therefore this work concentrates on just bumping mode. Of course, we should also consider that, printing inside the vias is different from printing on the surface since we have a limited etched volume, which affect the evaporation rate.

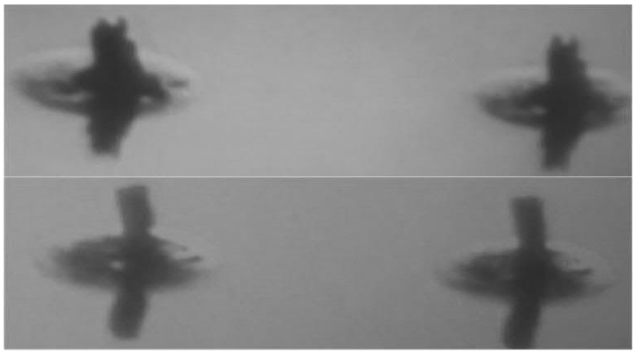

**Figure 3.** 3D structures fabricated by the spiral mode

The experiments were divided into three trials using three different silver nanoparticle inks described in Table 1. The differences between the printing trials are listed in Table 2.

**Table 2.** Trials used in this work

| Trial | Mode | Material/ink |
|---|---|---|
| 1st | Bumping with long and short holding time | DGP40LT-15C |
| 2nd | Bumping with long and short holding time | CAg-2000 |
| 3rd | Bumping with long holding time | NPS-J |

For the *1st trial*, first four samples were diced from the wafer including via structures using Dynatex and diamond scribe. Next, ten vias in a row in sample #1, #2 and #3 were selected and filled by four, seven and ten times of printing DGP 40LT-15C ink into the vias so that each time vias were fully filled with the ink (Figure 4 left) and the nozzle moves to the next via. Because of the fast evaporation and also delay time (~120 s) until we again print into a via for the next shot, we were able to repeat the printing without the substrate heating. In this approach the aim was to understand how much the number of printings affects the filling coverage.

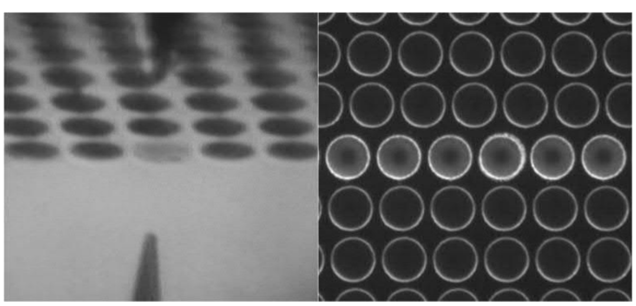

**Figure 4.** Via structure, left) filled via and nozzle dimension and right) filled vias from top view

Nozzle holding time, i.e. filling time, on top of the vias depends on different printing parameters like amplitude voltage, bias voltage, frequency and waveform. Since 30 seconds is the maximum holding time for each printing shot, we adjusted the parameters so that it was suitable for the filling of the vias with the volume of 32.4 pl in 30 seconds. The parameters are shown in Table 3. Another sample (sample #4) was also metallized by much shorter holding time (0.5 s) and different waveform as listed in Table 4. In order to have conductive fillings, all samples were sintered in 150 °C for 1 hour to remove the remained solvent, organic dispersant material and also welding of the nanoparticles to each other.

**Table 3.** Printing parameters for the 1st approach

| | |
|---|---|
| Waveform | Sine wave |
| Amplitude [V] | 175 |
| Bias (DC) [V] | 175 |
| ON speed [mm/s] | 1 |
| Frequency [Hz] | 10 |
| Holding time [s] | 30 |

**Table 4.** Printing parameters for the bumping with short holding time

| | |
|---|---|
| Waveform | Square 75% |
| Amplitude [V] | 150 |
| Bias (DC) [V] | 150 |
| ON speed [mm/s] | 1 |
| Frequency [Hz] | 1000 |
| Holding time [s] | 0.5 |

Sintered samples were cold mounted in the epoxy for the preparation of via cross-sections. Samples were grinded first with 1200 SiC paper (150 rpm, 10N) to reach the vias and then 2400 and 4000 papers to reveal the vias properly with the minimum damage to the vias; but after the grinding we noticed that adhesion of the DGP 40LT-15C ink to the vias was not enough to survive because of the heavy smearing and detachment of the filling that was observed. In the beginning of the cross-section preparation (grinding) we observed a very good level of filling for the sample #1 with four times of printing into the via, but it did not survive until the end of the sample preparation process. However, no specific filling was detected for the sample #2 and #3 with even more printed ink or sample #4 metallized by bumping with short holding time. Therefore, another series of samples were prepared with the same approach in order to be cut through with dicing saw and check if the sample preparation method was the problem or adhesion of the ink. Nonetheless, the result was not much different from mechanically prepared cross-sections and again no specific filling was observed for the vias with more amount of printed ink.

As shown in Figure 5, presenting the SEM images of the via cross-sections prepared by the dicing saw, we see an empty space in the bottom of some of the vias so that the filling material has shifted a bit upwards. This could be attributed to the residual trapped solvent during the sintering. Besides, it can be seen that the fillings are quite uniform except the smearing of the material resulted by the sample preparation method and also poor adhesion of the ink.

Since the adhesion of the ANP ink (DGP 40LT-15C) was not good enough during the cross-section preparation, other silver nanoparticle dispersions (ULVAC and NPS-J) were also tested for printing into the vias (see Table 1).

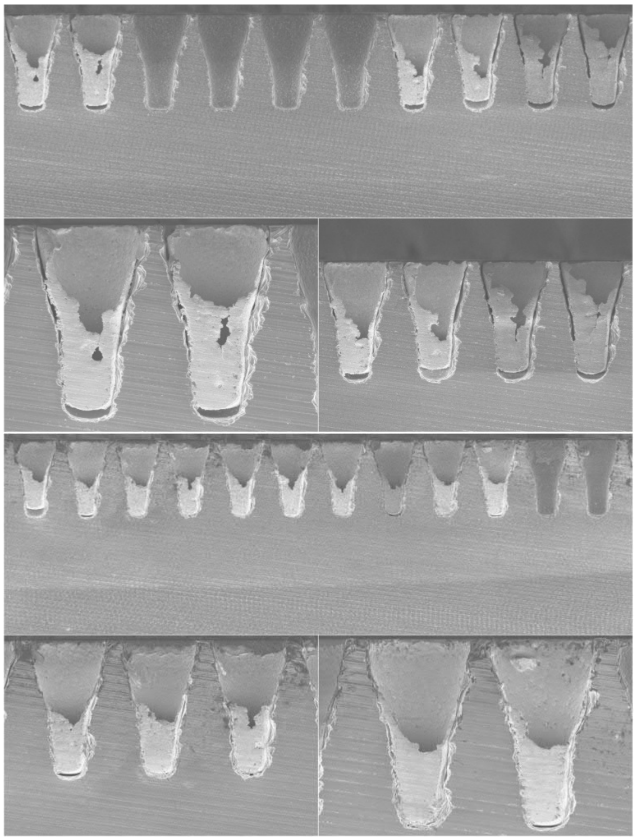

**Figure 5.** SEM image of the via cross-sections after four times of printing with sine and square wave

For the *2nd trial*, CAg-2000 silver nanoparticle ink from ULVAC Technologies was chosen for the metallization. First, bumping option with short holding time (0.5 s) was used. This type of ink and surface energy of the substrate was so that columnar pillars could grow quickly as shown in Figure 6. Growth mechanism of the pillars involving three stages (wetting, tapering and growth) can be found in [14] with more details, except in this work no heating was applied during the printing. Nonetheless, first, the size and also shape of the pillars were not compatible with the tapered vias used for this work, but could be suitable for the vertical vias. Second, although the pillars seemed to be exactly inside the vias, SEM analysis showed that the pillars were actually grown on the edge of the vias. Third, even in case of aligning the pillars inside the vias, still there will be no support for the pillars. Thus, bumping mode with longer holding time and bias ~200 V was used in order to print into the vias in several shots. Since the metal content of the ink was much higher (55~60 wt%), four shots of printing was the maximum, while using the inks with lower metal content, it is still possible to continue printing after 10 shots of printing.

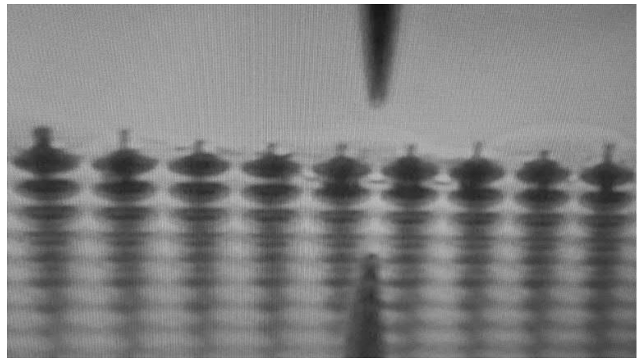

**Figure 6.** Difference between the size of the pillars and vias

Figure 7 shows the optical micrographs of mechanically prepared cross-sections through the middle of the vias metallized by CAg-2000 ink. After the sintering at 230 °C for 60 min, samples were mounted in Specifix-20 epoxy and then Struers RotoPol-21 and Rotoforce-1 were used for grinding and polishing processes. First, grinding was done to reach the vias. In next step, 3 µm and 1 µm diamond suspensions were used for the polishing and after that colloidal silica suspension (0.04 µm) for the final polishing. Again, in spite of careful sample preparation we noticed smearing of the TSV fillings. Regarding the big voids, it seems that because of the ink specifications, drying of the solvent during the printing has not been enough so that resulted in the voids during the sintering, or alternatively the filling could have been detached because of the sample preparation and poor adhesion. The solvent of the ink in 1st trial had lower boiling point compared to solvent of ink in 2nd trial. However, wall coverage (~2 µm) and bottom filling for the first three vias from the right seems to be acceptable and also no voids can be seen at the bottom of the vias.

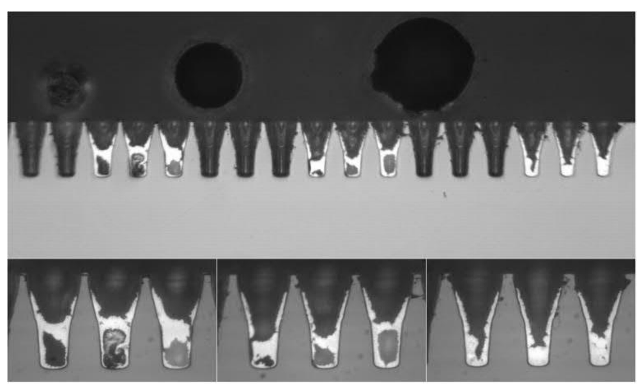

**Figure 7.** OM images of mechanically prepared cross-sections of the vias metallized by 2nd trial

For the *3rd trial*, NPS-J silver nano paste from Harima Chemicals was used to fill ten vias. Again, similar to the 2nd trial, after four shots of printing into the vias, no more ink could be jet into the vias and the vias were completely filled. After the filling, the sample was sintered in 220 °C for 1 hour. For the next step, the dicing saw was used to cut through the middle of three selected vias in a row to prepare the via cross-sections as shown in Figure 8. Finally, cross-sections were analyzed by SEM microscopy to see the filling ratio and also quality of the metallization. Although the specification of this ink is quite similar to the ULVAC ink used for the 2nd trial, the vias could be completely filled by just four times printing and of course no heating during the printing. As shown in the SEM micrograph, except the level of the filling, uniformity and also quality of the metallization was promising with an adhesion good enough to be survived after the preparation of the cross-section. Therefore, we could conclude that NPS-J silver nano paste was the best among the inks we tested for this work. However, printing with NPS-J was not straightforward like printing with lower metal content inks because of the high chance for the clogging of the nozzle during the printing. To overcome this problem though, filtration of the ink just before loading the nozzle could be helpful to keep the nozzle open for a longer time.

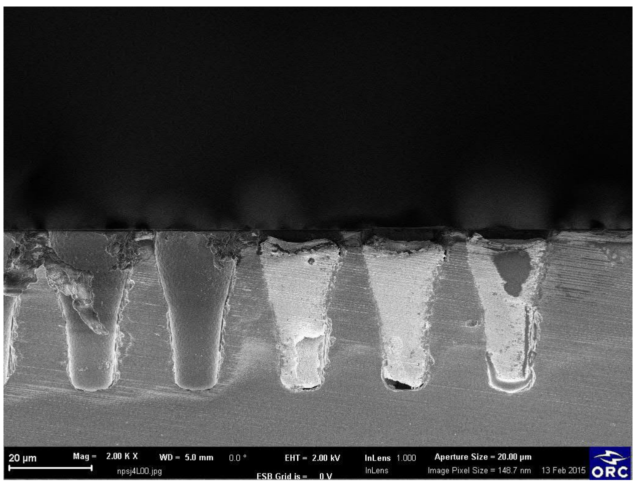


**Figure 8.** SEM picture from the vias completely filled by 3rd trial

## Summary

For this work three different trials were investigated to metallize thin vias by SIJ printing, using three types of silver nanoparticle inks.

Regarding the convenience for the printing, the inks with lower metal content and TGMA as the solvent were found to be better options for the SIJ printing. However, although these inks could be successfully used for the via filling, but they could not survive after at least the sample preparation because of the poor adhesion and showed not enough reliability. On the other side, inks with higher metal content and Tetradecane as the solvent showed better adhesion after the sintering and cross-section preparation processes. Among the inks used in this work, NPS-J nano paste from Harima Chemicals was the most reliable material with much better adhesion to the walls. Moreover, just four times of printing was enough to completely fill the vias without any heating during the process. Also, quality and uniformity of the filling material was promising.

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