Development of mechanically compliant flip chip interconnect using single metal coated polymer spheres

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Abstract

Most available fine pitch interconnects, like micro bumps and copper pillars, are not particularly compliant whereas available compliant interconnects, like plastic core solder balls, are not fine pitch. Using Ag-plated polymer spheres (MPS) in conjunction with a nano-Ag conductive ink has the potential to achieve mechanically compliant flip chip interconnects since the structural integrity is maintained by the flexible polymer core while the electrical conductivity is maintained by the Ag plated shell. Additionally, the low processing temperature means that it is relevant for systems that require low temperatures or that are very sensitive to thermo-mechanical stress, like MEMS sensors.

Previous work has shown that a major challenge in the proposed process was the confinement of the conductive ink onto the Au pad. This work focuses on finding an oleophobic coating that can be patterned to confine the ink on the contact pads. Two materials were tested, a fluoroacrylate additive for photoresists and a fluoropolymer that needed to be patterned separately. The latter showed superior oleophobicity and was therefore chosen. Patterning by positive and negative photoresist was tested. Using positive photoresist as a masking layer for reactive ion etching proved incompatible with the desired output. The use of negative photoresist with a lift-off technique showed potential, but needs to be optimized. Using reactive ion etching through a stencil mask showed the best results.

Key words: Metal coated polymer spheres, MPS, flip chip, low temperature

Introduction

Most available fine pitch interconnects, like micro bumps and copper pillars, are not particularly compliant whereas available compliant interconnects, like plastic core solder balls, are not fine pitch. Using Ag-plated polymer spheres (MPS) in conjunction with a nano-Ag conductive ink has the potential to achieve mechanically compliant flip chip interconnects since the structural integrity is maintained by the flexible polymer core while the electrical conductivity is maintained by the Ag plated shell, as illustrated in Figure 1. Additionally, the low processing temperature means that it is relevant for systems that require low temperatures or that are very sensitive to thermo-mechanical stress, like MEMS sensors.

Previous work on establishing such an interconnect focused on using ink jet printing to deposit nano-Ag ink onto the surface. The main issue with this approach was to confine the ink on the electrical pad, as the surface energy of the surrounding passivation layer was usually lower than the gold surface of the pad and hence the ink would run out [1].

This work takes a new approach by applying and patterning an oleophobic coating to the passivation layer. The work concentrates on finding the appropriate coating, measuring contact angles and patterning the oleophobic coating

Experimental

Material selection

Two oleophobic materials were identified for testing our approach:
- Cytonix FluorAcryl 7298
- CYTOP

Cytonix FluorAcryl 7298 is a perfluoropolyether (PFPE) acrylate used as an additive in other UV curable coatings to reduce surface tension and improve water, oil and stain resistance. For this work it was mixed into both a positive (AZ 4533, Merck Materials) and negative photoresist (Ma-N 1440, Microresist Technology) at different mix ratios. An approximate amount of Cytonix was added into a UV-opaque bottle on a scale and then the appr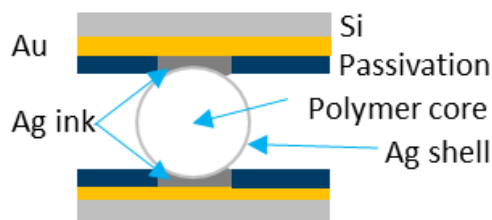opriate amount of photoresist was added to reach the desired concentration. The mixture was stirred on a magnetic stirrer for at least 5 minutes.

CYTOP in an amourphous fluoropolymer designed for water and oil repellency for transparent surfaces. For this work, CYTOP type M was diluted in the appropriate solvent at 1% and 5% concentration for initial testing. Subsequent development of patterning processing used 1% concentration.

To ensure adhesion to the passivation layer, a silane coupler (aminopropyltrimetoksysilane) was mixed in pure ethanol at 0.05%. Since the silane coupler degrades quickly, a new batch was made within 3 hours of each experiment.

The nano-Ag ink used was Silverjet DGP 40LT-15C from ANP. This ink is designed for ink jet printing and is based on triethylene glycol momoethyl ether (TGME) which has a low vapour pressure and thus dries very slowly at room temperature, which is a vital characteristic for this process, as is relies attaching MPS to the ink while the ink is wet.

Sample preparation

The photoresist with Cytonix additive mixtures were spun on quartered Cz-Si (100) wafer at 3000 rpm for 30 s followed by a 30 s bake at 100 °C on a hot plate.

To ensure a representative process for the samples with negative photoresist, areas of these samples were exposed to UV using a Heidelberg UV writer with a dwell time of 60 μs. The samples were then developed in Microposit MF319 developer for 60 s.

The samples with positive photoresist were developed in Microposit MF19 for 60 s after which they received a post bake at 100 °C for 60 s on a hot plate.

For Cytop, the Cz-Si wafers first received the silane coupler spun at 1500 rpm for 30 s, followed by drying at 80°C for 1 minute. Thereafter, the Cytop mixtures were spun at 1000 rpm for 30 s, targeting thicknesses of 0.5 μm and 1.0 μm for 1% and 5% concentrations, respectively. After spinning, the samples were heat treated on a hot plate with the following profile; 30 min at 50°C, 45 min at 80°C and 30 min at 180 – 240 °C.

Contact angle measurements

Contact angle measurements were carried out using a manual contact angle setup. The Si wafer was placed on the holder and drops of Ag-ink were applied using a micro-pipette set at 2 μl. The actual volume varied slightly between the measurements due to the pipette tip being plastic. After application of the drop, the reference line was adjusted to intersect with both edges of the drop. The measuring line was then aligned at both edges of the drop. Each material was tested with at least 8-10 drops.
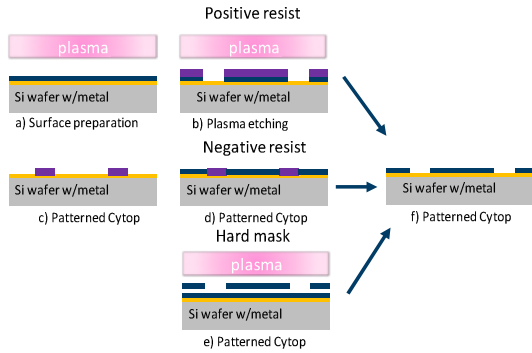

Figure 1: Illustration of the MPS interconnect. Nano-Ag ink supplies electrical and mechanical contact between Au electrical pad and MPS.

Figure 2: The three different approaches to patterning the Cytop coating.

Patterning Cytop

Three approaches to patterning the Cytop coated samples are illustrated in Figure 2. The first approach used positive photoresist to define an etching mask. Since the Cytop is oleophobic a surface treatment in an O_2 plasma (a) was needed to lower the surface energy in order for the photoresist to adhere to the Cytop. The photoresist was then patterned, developed and used as a mask for plasma etching (b). The second approach was to apply negative photoresist prior to Cytop application and do a lift-off process (c, d). The last approach was using a hard mask for patterned plasma etching of the Cytop (e). The specific parameters used for each approach is covered in the next section.

Results and discussion

Contact angles

The results of the contact angle measurements can be seen in Figure 3. For Cytonix in positive photoresist, the contact angle did not increase much outside the margin of error. For the negative photoresist, the addition of Cytonix increased the contact angle from $22° \pm 1°$ to $43° \pm 10°$. The high uncertainty on the latter measurement was due to some unevenness in the photoresist. Although the Cytnoix did improve the contact angle, it did not render the photoresist sufficiently oleophobic to repel the Ag ink when the sample was tilted to let the ink run off. Additionally, it was found that the TGME in the
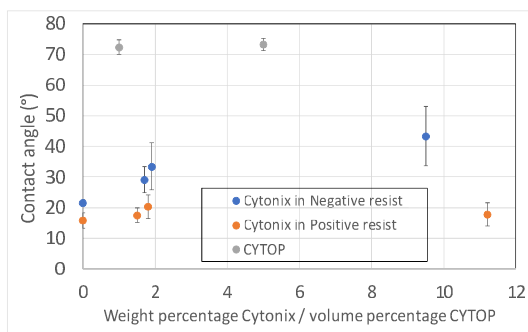

Figure 3: Contact angle results for Cytop and Cytonix in positive and negative photoresist.
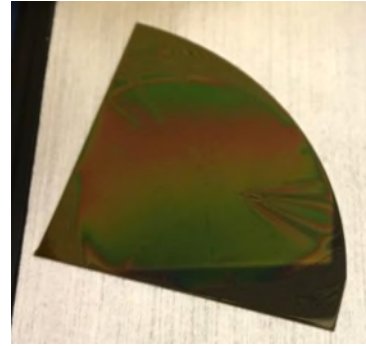

Figure 4: Positive photoresist adhering to the Cytop coating after surface treatment of the Cytop.

Ag-ink dissolved both the positive and negative photoresists. These issues are both vitally important to the process and thus further testing of the Cytonix was abandoned.

The contact angle of the Cytop was basically identical for both 1% and 5% concentrations, at $72° \pm 2°$. More important, however, is the fact that when tilted, the ink ran off the sample with minimal residue left on the surface, making it very compliant to the intended process.

Patterning Cytop with positive photoresist

For patterning the Cytop with positive photoresist, the photoresist had to be applied onto the Cytop. Depositing any coating on a surface that is designed to be oleophobic is counterintuitive. Contact measurements revealed that the photoresist had a contact angle towards the Cytop of $69° \pm 3°$. The photoresist also failed to adhere to the Cytop when spun. To increase the surface energy of the Cytop it was plasma treated (O_2, 50 sccm, 500 W, 0.65 Torr, 1 minute). The contact angle was measured to $67° \pm 3°$, which is a minimal change within the margin of error, but it resulted in the photoresist adhering to the surface when spun, as seen in Figure 4. However, after the photoresist was stripped, the contact angle towards the Ag ink was only $6° \pm 1°$ and thus not compatible with the intended process. The supplier of Cytop recommended a heat treatment (80 °C for 1 hr
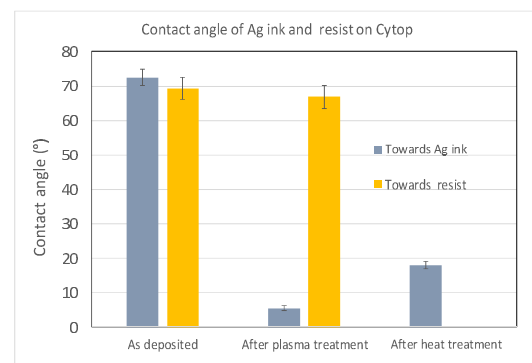

Figure 5: Contact angle results for Ag ink and photoresist on Cytop after different treatments.

followed by 180 °C for 1 hr) to revitalize the oleophobic properties. However, this only increased the contact angle to $18° ± 1°$,while also leaving Ag ink residue when the sample was tilted. These results are summarized in Figure 5 Hence, it was concluded that using positive photoresist to pattern the Cytop was not compatible with the intended process.

Patterning with negative photoresist

An obvious advantage of using a lift-off approach with a negative photoresist is that the photoresist is applied before the Cytop, hence the adhesion of the photoresist to the surface is not a problem. However, one challenge is that the coupling agent needed for Cytop's adhesion to any passivation layer is diluted in ethanol, which is an organic solvent that can dissolve the photoresist. A short test confirmed this.

A design of experiment was set up to find parameters that would render the photoresist capable of withstanding the brief exposure to ethanol while still being able to strip the photoresist after use. Six samples of Au coated Si dies were first spun with photoresist at 3000 rpm for 30 s, targeting a photoresist thickness of about 2 μm. The photoresist was then soft baked at 100 °C for 2 min and subsequently exposed in a UV writer in a pattern containing 40 μm diameter contact holes. The photoresist was then developed for 60 s, rinsed and dried in N_2, after which the samples received a post bake for 1 minute at different temperatures.

In the first round of tests, the UV dose in the writer was varied together with the post bake temperature. After treatment, the samples were placed in the spin coater, ethanol was applied and then the sample was spun at 1500 rpm for 30 s. Exposure at the higher ranges tested were chosen for further work on optimising the post bake temperature. Samples were thereafter spun with Cytop followed by a heat treatment for 1 hour at 50 °C and then 80 °C. The photoresist dots did not seem affected by the Cytop. Subsequently the photoresist was attempted removed in acetone.

Table 1 shows micrographs summarising the findings of the above process. After the post bake the 40 μm dots are fairly similar, but the samples baked at 200 °C have a slightly more defined edge. After ethanol spin, the samples baked at 180 °C and 190 °C both showed some photoresist residue close to the dot, while the sample baked at 200 °C did not.

On samples that were post baked at 180 °C the photoresist was largely removed after 1 minute in acetone. There were a few dots where there seemed to be residual photoresist.

On samples post baked at 190 °C the photoresist seemed removed but the hue suggested a slight residue residing on the dots. This was confirmed by scraping the surface of the pad using a probe needle.

Samples post baked at 200 °C had most of the photoresist intact after exposure to acetone. Several trials with long acetone exposures, and in combination with ultra sound, failed to remove the photoresist completely.

Similar tests were done using dimethyl sulfoxide (DMSO) to strip the photoresist. DMSO completely removed photoresist that had been post baked at 190 °C and 200 °C, which was a promising result. After application of Cytop, however, the photoresist appeared impossible to remove completely. On closer inspection by SEM, seen in Figure 6, the residues observed in the optical microscope was largely remains of the Cytop coating. This suggests that the Cytop coating had created protective cap over the photoresist dots. In some cases the Cytop remained almost fully intact in a punctured state. In other cases the Cytop was ripped but largely intact. Hence, the integrity of the Cytop coating is undermining the ability to

Table 1: Micrographs of 40 μm photoresist dots after development, baking, a brief exposure to ethanol and photoresist removal in acetone.

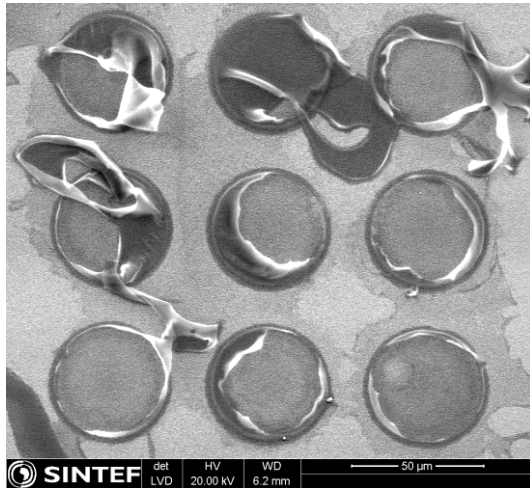| T (°C)	Before bake	After bake	After ethanol spin	After Cytop application and photoresist removal in acetone
180				
190				
200				

Figure 6: Remains of Cytop coating after attempted liftoff using DMSO to remove photoresist.

Figure 7: Si sample with stencil mask attached face down for plasma opening of Cytop coating.

remove it using a lift-off process. One possible solution, not studied in this work, is to apply thinner coatings of Cytop that will enable full removal.

Patterning with stencil mask

For these tests Si samples were prepared with Cytop as described in the experimental section. A Si stencil mask from the HyperConnect project [ref] was laid face down onto the sample and attached with tape, as seen in Figure 7. The stencil mask was fabricated from 400 µm thick Si wafer with 300 µm recesses in areas with 40 µm diameter through holes. The samples were thereafter exposed to a 5 minute O_2 plasma etch at 300 W. Nano-Ag ink was thereafter spun onto the sample at 400 rpm.

By comparing the left and centre image in Figure 8, one can clearly see that the pattern transfer from the stencil mask onto the Cytop coating was largely successful. The size of the etched holes, however, are highly dependent on the hole's proximity to the recess wall and hence the stencil mask design will have to be design optimised for the transfer pattern. Within the large recess openings most holes were within 2 µm of the
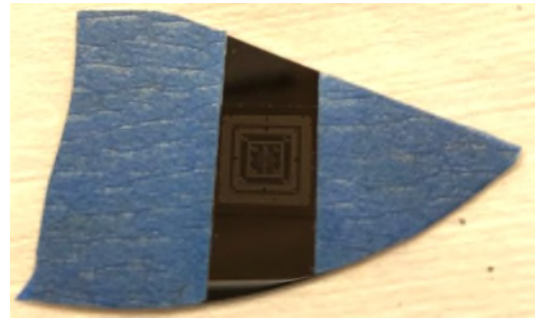
targeted diameter, as can be seen in the right most image in Figure 8. White light interferometry (WLI) was used to analyse the ink volume of eight nano-Ag ink droplets in one of the arrays in Figure 8. The results can be seen in Table 2. The large variation in droplet volume was mainly due to the variations in droplet height, not diameter. The cause of this large variation is not clear, but there are probably many factors that can influence the result and that have to be understood and optimised for a more even droplet calumet to be achieved.

Table 2: results of droplet analysis using WLI

Parameter	Value
Droplet volume (µm3)	307 ± 179
Height (µm)	0.6 ± 0.3
Diameter (µm)	34 ± 2

MPS application and analysis

After a successful pattern transfer using plasma etching and a stencil mask, MPS was applied onto the samples by drizzling from a meshed canister, resulting in very random scattering of MPS. The sample was the dried at at 80 °C for 5 minutes and sintered at 150 °C for 30 minutes. Some results are shown in Figure 9. The image on the left shows at least four individual MPS fairly well centered in the nano-Ag ink droplet. However, as the MPS have been applied in
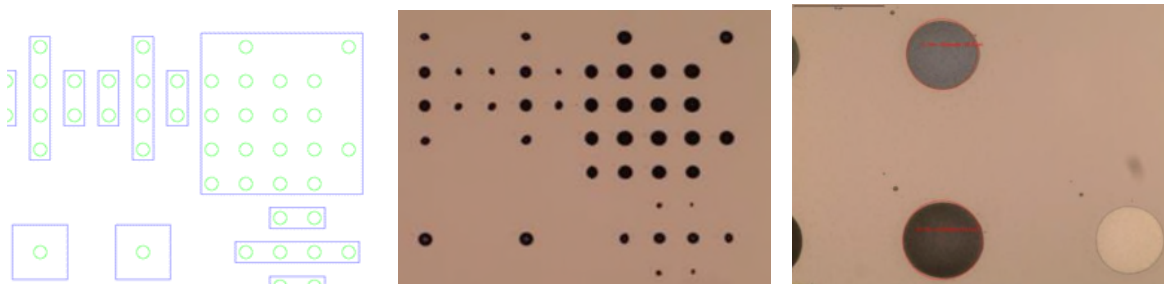

Figure 8: Left: stencil mask pattern. Purple lines indicate the recess lines while green circles are the through holes. Middle: Nano-Ag droplets on sample surface. The pattern transfer is good, but the size of the etched hole openings depends largely on the proximity to the recess walls. Right: Three hole openings in the Cytop. The color difference in the holes on the left probably indicate difference in Nano-Ag ink drop volume. The right most hole has not managed to attract nano-Ag ink.
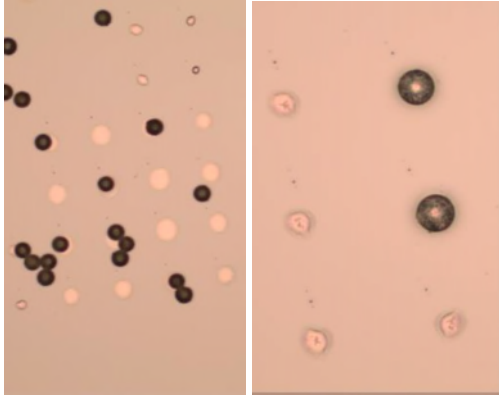
Figure 10: MPS attached to Si sample by patterned nano-Ag ink. Left: at least four MPS that are individually centered on an ink droplet. Right: Two MPS more or less perfectly positioned on the ink droplets.

a random fashion, there are also agglomerations of MPS on pads. One surprising result, especially considering the hydrophobic nature of the Cytop coating, is the residing MPS outside the of the opened holes in the coating. One would expect that the adhesion to the Cytop was sufficiently weak to allow these MPS to be removed in the air flow. Hence, for further development of the process the air flow would need to be optimised in order to remove superfluous MPS wile retaining the intended attached MPS.

The image to the right shows two MPS perfectly located according to the droplet pattern, showing that this process has potential for accurately placing MPS as individual contacts.

Figure 10 shows an SEM of the neck formed by sintered nano-Ag ink. It clearly shows that the ink has been drawn up onto the MPS surface. As both the ink and MPS surface are Ag, elemental analysis could not be used to distinguish between the ink and the metal layer. It is fair to assume that the rough surface of the MPS is pivotal for generating the capillary forces needed to draw the ink onto the MPS.

One potential challenge of this interconnect as depicted in Figure 10 its mechanical strength. A wider neck would be desirable and that would demand a larger volume of ink residing on the contact openings before MPS application. However, one can envisage a process where a die that has received MPS on each contact pad is flipped and dipped into a thin reservoir of nano-Ag ink for attachment to a substrate die. In the process of dipping the rough surface of the MPS will most likely drawn the nano-Ag ink up onto the already formed neck. This will of course depend on the depth of the dipping reservoir. In this process the oleophobic properties of the Cytop coating is advantageous once again as it would limit the nano-Ag ink from protruding farther than the contact opening edge.
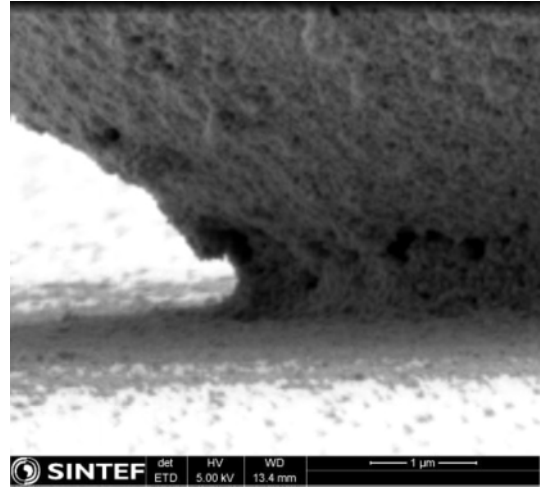

Figure 9: SEM image of the neck between the substrate and the MPS formed by sintered nano-Ag ink.

The fabrication process was repeated for a sample with an Au coating on Si for measurement of electrical resistance. A probing needle was carefully positioned on the top of three MPS and the resistance measured between this and the Au surface was 6-7 Ω per MPS. If using a dipping and flip chip process as mentioned above, the increase in nano-Ag ink would most certainly decrease this resistance.

Conclusion

This paper describes the development of a fine pitch and mechanically compliant interconnect comprising a single metal coated polymer sphere (MPS). The work has focused on finding a process for confining nano-Ag ink on contact pads, as previous work showed that the area surrounding the contact pads often has lower surface energy than the Au pad. A flouroacrylate additive for photoresists was found to have insufficient oleophobic properties for the process. However, a fluoro-polymer coating was found to have excellent oleophobic properties. Methods for patterning the fluoro-polymer were tested. Using a negative photoresist for a lift off technique showed promising results, but needs to be optimised to allow full removal of the Cytop coating. The most reliable method was reactive ion etching through a stencil mask. Single MPS on contact pads were measured to have a resistance of 6-7 Ω.

References

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