IMPACT
International Microsystems, Packaging, Assembly and Circuits Technology conference

VitroCoat GI - Ultra-thin adhesive layer for metallization of glass interposer

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ABSTRACT

In this paper a glass-copper interface adhesion promoting thin film is described that forms chemical bonds with glass, and mechanically and possibly chemically anchors to copper to create strong, reliable adhesion between the glass substrate and the deposited metal. Wet chemical deposition of a low volatile organic content (VOC), emissions free, cost-effective, water based coating solution was used to create a thin, transparent metal oxide film that then enables electroless, and electrolytic copper plating directly onto glass. With this approach, a copper film thickness of 30µm can be applied without delamination from the smooth glass. Adhesion at 15µm Cu thickness as measured by 90^{o} peel strength tests can achieve values of ≥4 N/cm. Thermal and stress tests using lead free reflow conditions and Highly Accelerated Stress Testing (HAST) were carried out with manageable to minimal adhesion loss. Through hole plating of aspect ratios up to 5:1 are also demonstrated. Photolithography of fine-lines as small as 5/5 µm was feasible, with very small undercut observed.

INTRODUCTION

Rapidly changing consumer preference is driving the demand for devices that perform faster, have longer lasting batteries, all whilst being contained in smaller packages. This sets the pace for advances impacting the space and performance requirements in electronics packaging. The resulting shift toward higher I/O densities and finer line/space highlights a need for smooth substrates with excellent dimensional stability. Organic substrates exhibit relatively poor dimensional stability and co-planarity, which limits them in terms of Input / Output (I/O) pitch [1]. Inorganic interposers made of silicon or glass have exceptional dimensional stability as they allow a straightforward matching of the Coefficient of Thermal Expansion of the interposer to the Silicon Chip. Silicon has a lead in manufacturing but suffers from disadvantages when compared to glass. In particular glass has inherently superior electrical properties and offers the possibility to use larger area panel sizes, which results in significant cost savings versus a wafer based platform. As a low cost, smooth, low CTE material, glass is a good candidate for interposer applications.

Unlike organic substrates metallizing a smooth substrate such as glass or silicon is a challenge, since the smooth surface affords little possibility for mechanical anchoring of copper for good adhesion. Roughening the glass substrate would lead to minimal mechanical anchoring [2], and would greatly compromise the ability to pattern fine lines and spaces. Physical seed layer deposition methods such as sputtering have been attempted [3], but may suffer from lower through put and lower adhesion. In this paper a wet-chemistry method of directly plating copper on to glass is described, where the metal oxide adhesive layer VitroCoat GI W is deposited on to the clean substrate, enabling subsequent plating of electroless and electrolytic copper with high adhesion.

Chemical deposition of metal oxide films have been used in the semi-conductor industry for various applications [4]. The metal oxide film described in this study enables plating of copper of a desired thickness on glass. It makes use of chemical and mechanical anchoring to function as an intermediate layer between glass and copper. The film forms a strong interaction at the glass interface that is robust enough to anchor the plated film, and acts as a mechanical anchoring station for copper to be plated with high adhesion. The proper release of internal stress in the plated layers also plays a significant part in ensuring good adhesion.

In addition to its metallization advantages, the VitroCoat GI W process described in this paper is unique in its low volatile organic content (VOC) composition. Waterborne formulations are significantly more cost effective than their solvent borne counterparts, have low environmental emissions, are nonflammable and much safer to operate. Waterborne formulations are more challenging to apply on fine structures and require thorough fine-tuning of components and processing parameters for success. The final product is a lean process that produces an ultra-thin layer (5-40nm) capable of adhesion of upwards of 4 N/cm as tested on 15µm of electrolytic copper. Through via structures of up to 5:1 aspect ratio were successfully metallized. Current focus on the project involves improving via structure throw-power capabilities with this low VOC formulation.

METHODS AND RESULTS

A. Methods

A water based, minimal VOC (volatile organic compound) coating method was used to build a controllable, ultra-thin metal oxide film of thickness ranging from 4 to 40 nm on glass substrates provided by Corning. The following general procedure was used:

(1) Glass substrate cleaning and activation
(2) Aqueous thin-film coating and baking

This controllable, transparent film was then catalyzed in a Palladium system to plate electroless copper followed by electrolytic copper onto glass, according to the general procedure below:

(3) Electroless Copper (Atotech) with thickness of 0.3-0.5µm and annealing
(4) Electrolytic Copper (Atotech) with variable thickness and annealing

The annealing process after copper plating releases the stress in the plated deposition by recrystallizing the copper structure.
Thermal stress testing using lead free reflow conditions at 260^{0}C and Highly Accelerated Stress Testing (HAST) at 90% humidity

and 130^{0}C for 96 hours were carried out on water-based thin-film metallized glass.
Photolithography for RDL patterning is feasible on glass metalized with this process and seed layer removal from the glass is very efficient.

B. Results

1. Thin film deposition

1. 1. Glass cleaning and activation

Water based coatings generally have higher surface tensions and lower evaporation rates than their high VOC counterparts, and can lead to coating non-uniformities. The challenge with applying a water based coating is obtaining good wetting on a flat substrate, and especially around edges and sharp corners. Dewetting, coffee rings and crystallization are some of the signs of a formulation that is not properly optimized or an improperly cleaned substrate. The glass substrate must be very clean and free of any organic contaminants, as well as ideally hydroxylated for good reactivity with the coating material. Several improvements in the substrate cleaning and coating formulation were made to produce a uniform, ultra-thin film with good coverage from a water based solution. Good wetting of the coating solution was confirmed with contact angle measurements.

Figure1: Glass panel with film deposited from water based coating formulation VitroCoat GI W.

1.2. Film deposition

Various methods exist for the chemical deposition of thin-film on semi-conductors. Spray pyrolysis, spin-drying and dip-coating can be used for the deposition of thin metal oxide layers, with dip-coating offering the most opportunity for control in the coating of double sided glass substrates with through-hole structures. In this study the ultra-thin water based film VitroCoat GI W was deposited using dip-coating as an easily controllable, cost-effective metallization interface on glass. Opportunities for film thickness control exist in (i) the solution formulation (concentration, viscosity, etc.) and (ii) the dip-coating step (withdrawal speed). Ultra-thin films of as low as 4-40 nm can be generated in short cycle times and with reduced material usage (Figure 2).

Uniformity of coated layer can be a concern especially when working with a relatively high surface tension (72 dynes/cm without surfactants), low evaporation rate (water = 0.3, where butyl acetate = 1) solvent such as water.

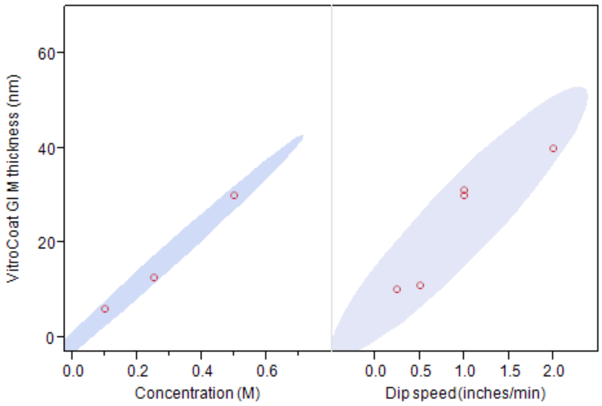

Figure 2: Control of water based ultra-thin film deposition thickness by dip-coating.

The coating solution has been optimized to give good wetting and film uniformity on a flat surface with good reproducibility. XRF measurements were conducted on as deposited film to assess any non-uniformity on a plain glass surface. The coating profile for a 10nm film on glass is shown in Figure 3 below. SEM images show a mesoporous layer with uniform grain morphology.

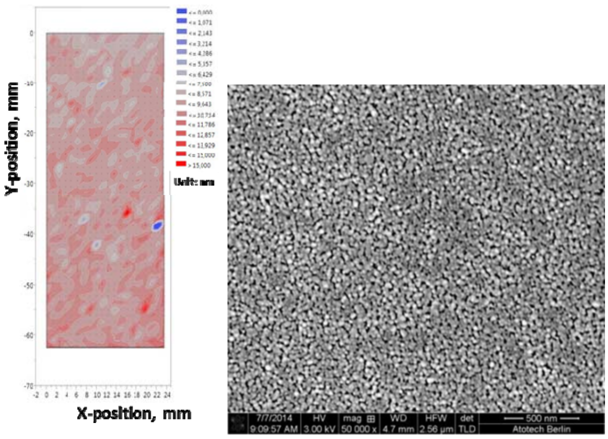

Figure 3: (Left) thickness distribution of VitroCoat GI W on glass surface. (Right) Grain strucutre of deposited and sintered VitroCoat GI W

2. Adhesion on glass

2.1. Initial adhesion of thin film metallized glass

The VitroCoat adhesive film acts as a metallization layer for the deposition of electroless and electrolytic copper on to glass with good adhesion. After the electroless copper plating step the adhesion is so strong that it can be challenging to measure without breaking the glass. The adhesion of thick electrolytic copper is usually lower due to internal stress in the copper layer, but can be optimized to achieve high adhesion of around 5-6 N/cm, as measured with 90° peel test of 15µm thick copper. Considerable dependence of adhesion on film thickness is observed in this low film-thickness region (Figure4). Nevertheless ultra-thin films can achieve above 4 N/cm of adhesion strength, which has been found to be sufficient for good performance in downstream steps such as through-via filling and fine-line patterning. Current optimizations are focused on improved performance using ultra-thin VitroCoat GI W layers (5 – 20nm).

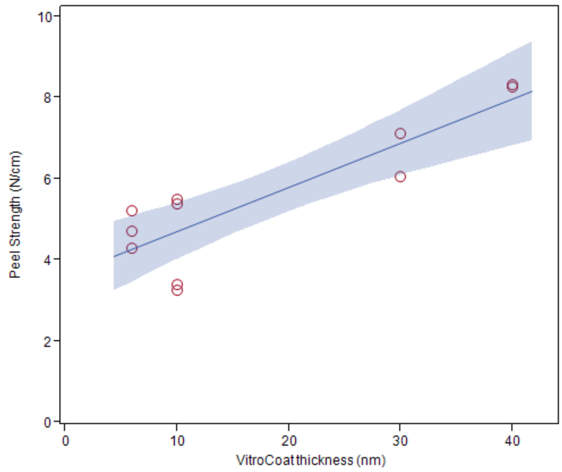

Figure 4: Peel strength vs. VitroCoat GI W film thickness

2.2. Adhesion performance after stress tests

To ensure reliability of adhesion throughout downstream processes in packaging, multiple passes of lead free reflow and HAST test was conducted on 15 µm of copper plated on VitroCoat GI W metallized glass. Reliability of the copper plating on glass is also dependent on VitroCoat thickness, with minimal deterioration of adhesion during high temperature excursions in the 30nm film thickness region, but more severe deterioration in the lower thickness regime (Figure 5).

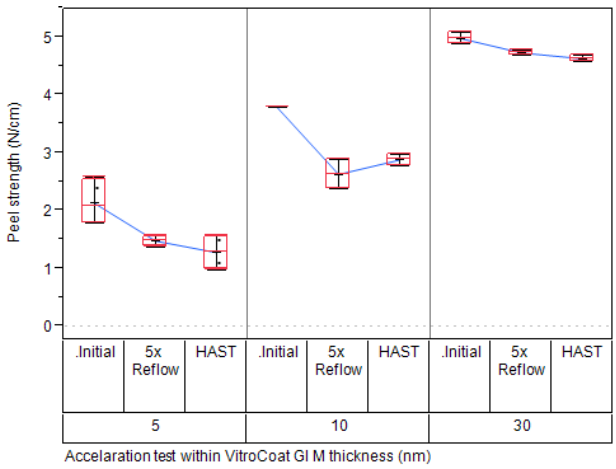

Figure 5: Initial, 5x Reflow, HAST adhesion on thin film deposited using water based ultra-thin film

3. Through hole plating

The modified dip-coating technology has been previously optimized by this group with a volatile coating solution to give good throwing power inside via walls with minimal differences in deposited thickness along the length of the wall and on the surface of the sample. However with a non-volatile coating solution the uniformity in vias is more challenging due to a slow drying rate that leads to a possible pooling of fluid inside the vias. Careful optimization of formulation and dip-coating conditions is necessary to achieve uniform coverage. Through-via plating of VitrCoat GI W was tested on samples with various via diameters, aspect ratios and thicknesses.

3.1 Surface and through-hole coverage

Various dimensions of TGVs and BMVs were coated with VitroCoat GI W resulting with good surface and through via coverage (Figure 6, 7). The assessment of coverage uniformity inside vias by cross-section is currently on-going. A general process limitation of around 5:1 aspect ratio, 90 micron pitch was reached before further optimization efforts were employed.

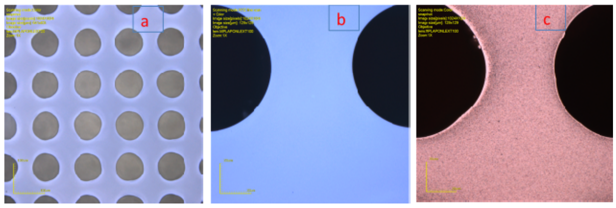

Figure 6: 90micron diameter, 300micron thick TGVs after (Left, center) VitroCoat GI W coating followed by (Right) electroless copper plating.

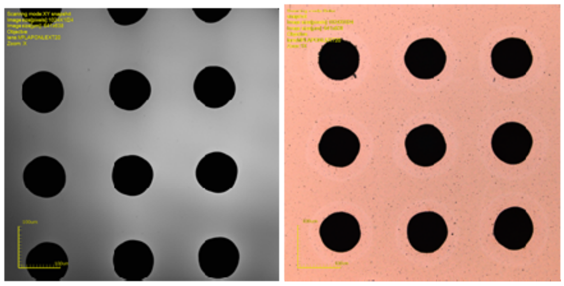

Figure 7: 90micron diameter, 300micron deep BMVs after (Left) VitroCoat GI W coating followed by (Right) electroless copper plating.

3.2. Through-hole coating yield/reliability

The large scale production of devices that employ VitroCoat GI W depends on feasibility of very high yield for blockage free through holes. This low volatility version can coat TGVs up to aspect ratios of 5:1 with no blockage. However several challenges persist for the low volatility coating for application on more difficult via arrays.

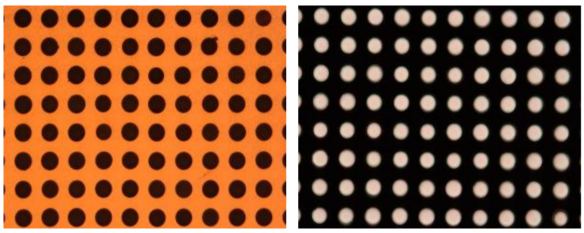

Figure 8: Backlight view: TGV coating of 100micron diameter vias with no blockage (Aspect ratio 3:1).

Due to the slower drying rate of the solvent used, excess material can accumulate in very small through-vias during withdrawal from solution, later developing into a blockage. Mainly two types of via arrays were observed to have higher tendency for blockage: (i) high aspect ratio via arrays (ii) high pitch via arrays. Both conditions inhibit good flow out of dipping solution resulting in pooling and solidification. This is demonstrated in Figure 9 below.

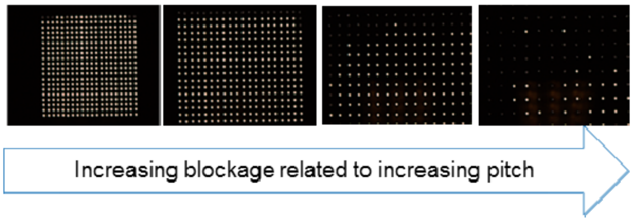

Figure 9: Backlight view of blockage due to increasing pitch: Increasing blockage of vias as pitch increases (left to right) at fixed 25µm diameter and fixed aspect ratio of 5:1.

Several measures were taken to improve the blockage-free yield of various diameter, pitch and aspect ratio of TGVs. Substrate cleaning optimization, coating solution concentration and coating speed/solution drying rate are some of the parameters found to have a significant impact on blockage percentage. Optimizing the cleaning method of substrate can reduce the blockage in high aspect ratio vias by more than 50% (Figure 10), where as a very slow coating rate can potentially eliminate blockage (Figure 11). However further tests are necessary in order to eliminate blockage while maintaining the thickness necessary for good adhesion.

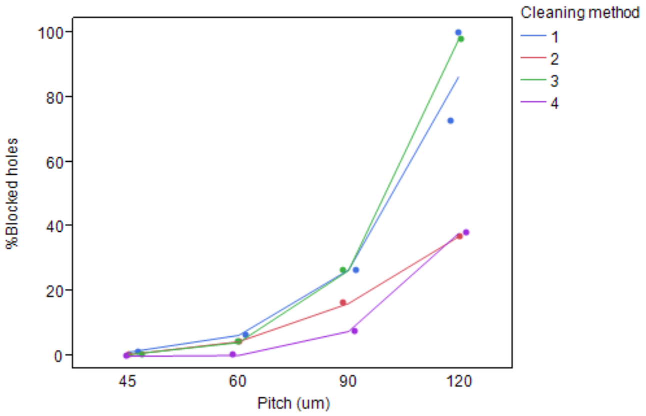

Figure 10: Reduction of blockage in water-based coated through holes by improving substrate cleaning method

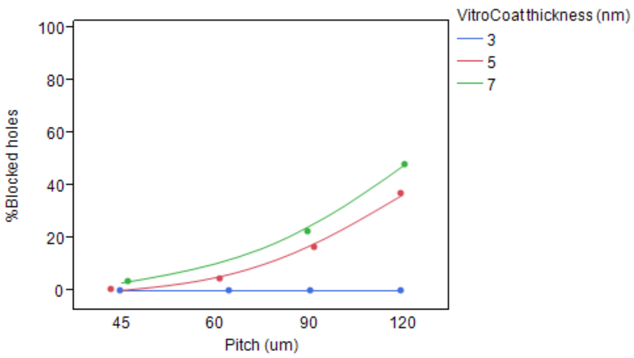

Figure 11: Reduction of blockage in water-based coated through holes by adjusting coating parameters

4. Fine-line patterning

Photolithography was done on VitroCoat GI W metallized glass to test the feasibility of RDL patterning without significant line damage by the process. Various line lengths and shapes were attempted with moderate to good yield. Line/space of down to 5/5µm was achieved with cross-section investigations revealing undercut of around 0.5 µm (Figure 12). The seed layer removal process is under further optimization to minimize or eliminate undercut. Further tests on improvement of photolithography film adhesion to electroless copper should improve the yield for even finer line and spacing.

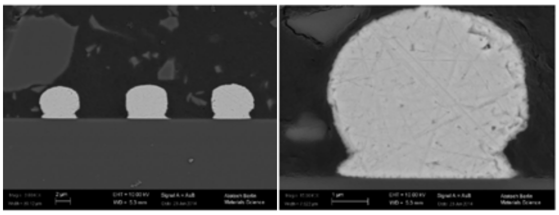

Figure 12: Cross-section of VitroCoat mediated fine-lines (L/S: 5/5µm) on glass after seed layer removal.

CONCLUSION

The VitroCoat GI W thin film technology described in this paper is a robust and cost-effective method of directly metallizing glass substrates. The application potential is emphasized with a demonstration of adhesion reliability, TGV plating, and fine-line patterning capabilities. The use of a low flammability, "green" process is doubly impactful in addressing the design requirements of the future.

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