Improvement of wettability of silicon nitride in PECVD environment for copper electrodeposition in HAR vias

M. Saadaoui, W. Wien, H. van Zeijl, A. van den Bogaard and P.M. Sarro

***Abstract*— In this paper we report the improvement of the wettability of low stress silicon nitride used as barrier layer for the fabrication of voids-free high aspect ratio Through Silicon Vias (TSV) filled with electroplated copper. The contact angle of water on hydrophobic surface of the silicon nitride is measured and the flowing test of the copper electrolyte through high aspect ratio vias wafer conformally coated with the nitride is performed using a specially dedicated wafer holder. The poor wettability of the as-deposited silicon nitride is improved by the use of NH_3 plasma enhanced chemical vapor deposition treatment. The enrichment of the surface with N-H bonds tends to reverse the surface from hydrophobicity to hydrophilicity state as proven by the lowering of the contact angle. The effectiveness of the proposed treatment is demonstrated by the observed natural flowing of the electrolyte across the through silicon vias and the successful fabrication of 3D voids free HAR copper vias.**

***Index Terms*—3D integration, through silicon vias, surface tension, contact angle, PECVD,**

I. Introduction

Three-dimensional interconnects and packaging has become relevant for the System-In Package concept (SIP), the new trend in compact package [1]-[2]. The results are the massive integration of devices on both-sides of the wafer with the possible integration of combined IC and RF/MEMS circuits. The key technology behind the success of 3D engineering is the development of High Aspect Ratio (HAR>10) Through Silicon Vias (TSV) in which cylindrical holes are drilled vertically into the silicon wafers and filled with metallic layer to form the interconnects. The metal layer is usually formed by electroplating of copper that exhibits very low resistivity and high electromigration resistance [3]-[4]-[5]. By reducing the length of the highly conductive interconnects path, high speed devices with low power consumption, noise and crosstalk are achieved. The reduction of the device size coupled with high performance and reliability will results in cost effective products.

Two different configurations for TSVs have been proposed previously and are actually still in development. The first one consists of the bottom-up electroplating in which the sidewalls of the TSVs are covered with isolation/barrier layer, and the metallic layer grows from the bottom to the top of the vias [6]-[7]. This isolated layer is commonly formed by high temperature process like LPCVD silicon nitride or thermal oxide. The second approach used coated metallic layer on the sidewalls of the vias and the electroplating starts in the all directions of the vias [8]-[9]. This layer is generally a copper seed layer deposited by sputtering, evaporation or MOCVD technique.

In order to obtain uniform and void-free metallic cylinder for TSV, mass transfer of the ions/additives from the electrolyte has to be guarantied. Several coupled parameters influence the electroplating process: the current density [10], the flow mechanism of the electrolyte within the vias [11], the electrolyte composition [12] and the wetting ability of the vias. This last one is rarely treated in the literature for electroplating in high aspect ratio vias.

In the case where the vias are coated with continuous metallic layer like copper, the wetting ability of the electrolyte within the vias is improved by adding appropriate organics additives in the electrolytic bath, especially the suppressors. These suppressors are strongly absorbed at the surface of the metallic like and tend to enhance both deposition inhibition and wetting ability [13].

On the other hand, if the vias are coated only with an insulator or barrier layer, as in the case of the bottom-up electroplating process, the wetting becomes more challenging. Since most of the dielectrics present an hydrophobic surface, the wettability obstacle has to be overcome. There are several methods to achieve acceptable wettability such as wet chemical cleaning ($NH_4OH/H_2O_2/H_20$ (SC1) [14], HCL/HF [15], RCA [16]) and laser treatment [17].

In this paper, we report a new method for enhancing the surface wettability of the low stress silicon nitride that is used as isolation layer for the TSV. The as-deposited nitride presents an unstable surface state and tends to be more hydrophobic which limits its wetting capability. The method consists of treating the silicon nitride in an ammonia environment in plasma enhanced chemical vapor deposition

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chamber. The wetting of the treated nitride is improved and a continuous flow of the electrolyte across the vias has been obtained by the use a new sealed holder. The proper control of the nitride surface wettability has resulted in successful filling of 20µm diameters, high aspect ratio (AR=15) TSVs.

II. Experiments

A. Sample preparation

For the investigation of the wetting ability of TSV, p-type (100) silicon substrate wafers are used. Then 500nm of low stress silicon nitride is deposited by LPCVD at 850^0C. The contact angle measurement method is used in order to characterize the surface wettability: the lower the contact angle, the more the surface is hydrophilic and consequently the higher the wettability. The contact angle refers to the angle between the solid surface line and the tangent line from the droplet to solid surface (see fig. 1).

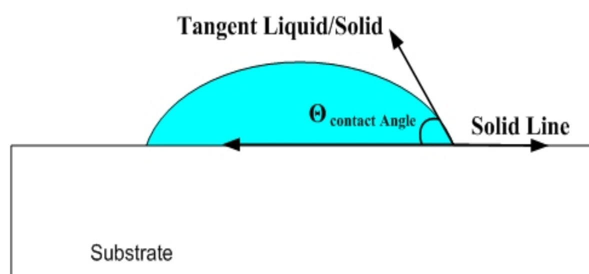

Fig. 1. The contact angle of liquid with solid used to characterize the surface wettability

To evaluate the effect of the surface treatment on the wettability of the silicon nitride, the contact angle of the nitride has been measured before and after treatment using a semi-automatic contact angle meter using sessile drop method [18]. This system uses a video camera to record a live picture of the drop. For the calculation of the contact angles the tangent leaning method [19] was used for all measurements.

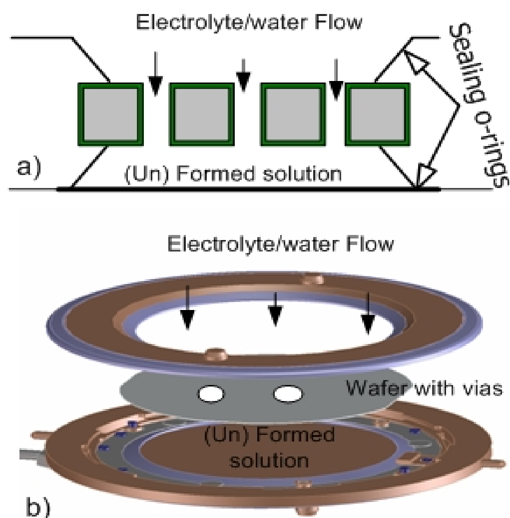

Fig. 2. The dedicated holder for the wetting test of the through silicon vias: a) cross section of the wafer mounted in the holder; schematic 3D view of the holder

In order to verify the wetting of the silicon nitride layer on the sidewalls of the deep vias, a 300µm thick silicon wafer in which 20µm diameter vias are etched through by deep reactive ions etching. The realized aspect ratio is 15. Then, a 500nm conformal silicon nitride is deposited on the vias sidewalls. Finally, the wafer is suspended and fixed in a special clamping holder developed in cooperation with MECO equipments, (MECO, Drunen Holland) (see fig. 2).

The design of the holder is such that the top-side of the wafer sealed at the edge will be in contact with the electrolyte/water, while the bottom-side faces a chamber initially empty. The wetting ability of the vias is considered sufficient if the backside chamber is filled with the electrolyte/water.

B. As-deposited low stress silicon nitride

Prior to the surface treatment, the contact angle of the silicon nitride is measured with DI water as shown in figure 2. The surface of the nitride with contact angle of 40^0 presents a hydrophobic state possibly due the fact that the low stress nitride is silicon rich (see fig. 3).

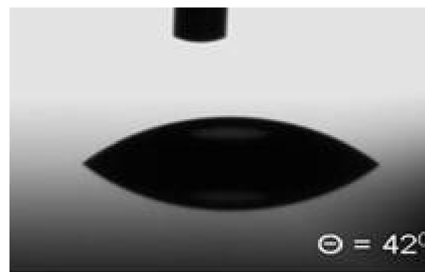

Fig. 3. Contact angle measurement of the as-deposited silicon nitride

The hydrophobic state of the nitride is observed also in the wafer with vias covered with nitride. In fact after mounting the wafer in the sealing holder, no flowing of the electrolyte/ water across the vias is observed, as indicated by the backside chamber of the sealed holder that remains unfilled. This hydrophobic surface of the as-deposited low stress nitride has to be surmounted by the surface treatment in order to make it suitable for the TSV applications.

C. Surface treatment of the as-deposited silicon nitride

In order to improve the wetting characteristic of the nitride, the surface of the film is treated in plasma enhanced chemical vapor environment under ammonia (NH_3) flow. Low frequency plasma (380 KHz) is chosen in order to enhance the dissociation of NH_3 gas molecules and increase the bombardment and incorporation of N-H bonds at the surface. The optimized plasma power is set to 250 W, and the NH_3 flow rate is 125sccm. The temperature of the chuck is fixed at 300°C in order to enhance the absorption of N-H bonds at the surface. After 10min of plasma treatment, significant reduction in the contact angle of the nitride is observed, indicating that the obtained surface has become hydrophilic with a contact angle around 20^0 (see fig. 4).

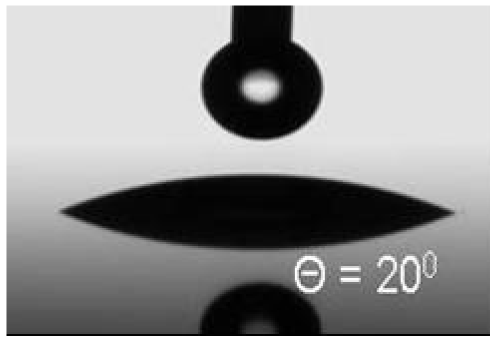

Fig. 4. Contact angle measurement of the silicon nitride after plasma treatment in NH_3

In Ref. [14] the reason behind the reduction of the contact angle is reported. It appears that the enrichment of the surface with hydroxyl and ammonia group (-OH, $-NH_2$,$-NH_3+$) is responsible for the surface modification.

Furthermore, the flowing test with the sealing holder reveals a spontaneous flow of the electrolyte/water across the vias and gives new opportunities for the uniform electroplating and filling of the vias.

The test of the aging effect on the wetting ability of the silicon nitride has been performed as well. The contact angle tends to increase with time and the surface tends to be more hydrophobic again after 3days from the plasma treatment, when the wafer is stored in closed box (see fig. 5).

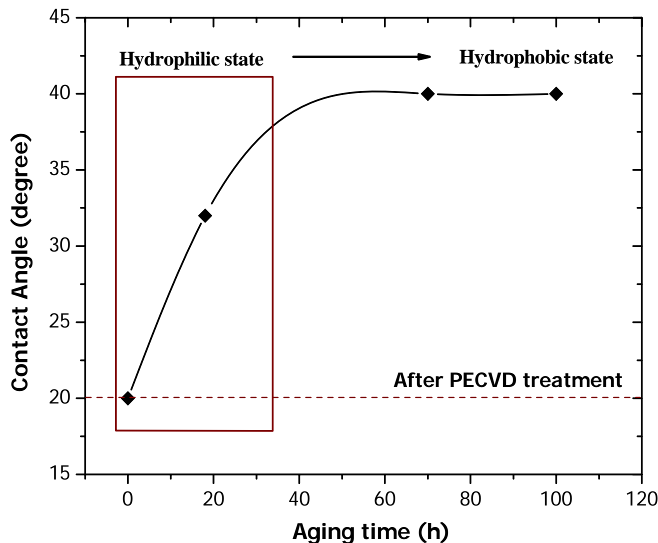

Fig. 5. Influence of the aging time on the surface wettability of the silicon nitride

This effect has been observed previously [20] and it was explained by the fact that the hydroxyl and ammonia group are unstable and tends to deplete from the surface. This aging effect shows that the plasma treatment has to be done immediately before the electroplating in order to keep the surface of the nitride more hydrophilic.

III. Fabrication of High Aspect Ratio TSV

The TSV with an aspect ratio of 15 are fabricated on silicon wafer as shown in figure 6. For the experiment 4 inch (100) silicon substrates thinned down to 300µm are used.

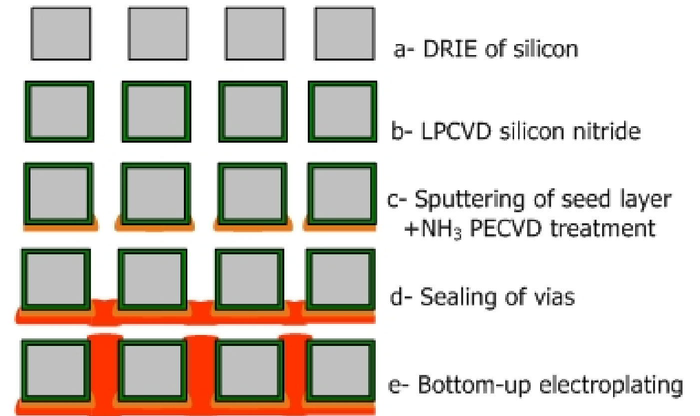

Fig. 6. Process flow for electroplating of through silicon vias with AR=15

After etching the 20µm round vias with deep reactive ion etching, a 500nm thick low stress silicon nitride is deposited conformally by LPCVD. Then 500nm of Ti-TiN-Cu stack seed layer is sputtered on the backside of the wafer. Then, the wafer is treated in ammonia plasma for 10min in order to enhance the wetting ability of the nitride. Finally, the copper is electroplated through the vias with a DC current density of $15mA/cm^2$ and with total time of around 23h.

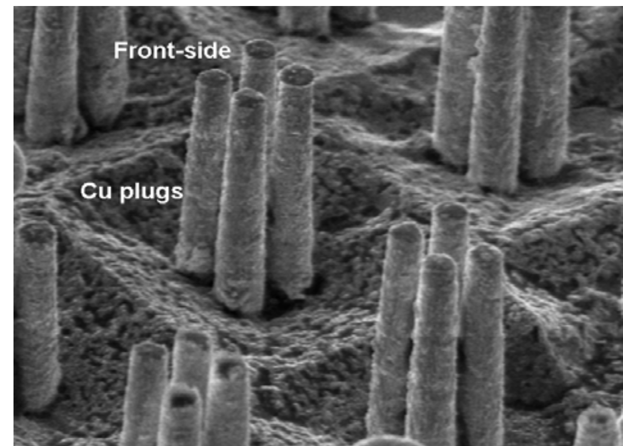

Fig. 7. Copper plugs interconnects after dissolving the first 150µm of silicon in a KOH solution

The electrolyte bath (from Rohm and Haas) is a standard cupric-sulfate aqueous solution that contain cupric ions (CuSO4:5H2O; 75g/l) and sulphuric acid (H2SO4; 190g/l), hydrochloric acid (HCL; 50mg/g) with two organics additives in form of levelers and brighteners (Intervia A and C; 5ml/l). Figure 7 shows an SEM picture of the uniform, void-free vias, observed after dissolving the surrounding silicon in a KOH solution.

IV. Conclusion

In this paper, the wetting ability of the silicon nitride has been investigated through its contact angle and the flowing possibility across high aspect ratio through silicon vias. The study shows that the as-deposited low stress nitride exhibits hydrophobic surface and the possible integration of this nitride on the TSV applications as isolation layer cannot be

performed without enhancing its wettability. A new surface treatment technique is then proposed. It is based on enriching the surface of the nitride with hydroxyl, ammonia group. This is realized by exposing the nitride to an ammonia plasma treatment inside a PECVD chamber at low frequency. Significant improvement of the contact angle is achieved and the hydrophilic state of the nitride is obtained. The instability of the hydroxyl, ammonia bonds on the surface is also demonstrated by measuring the contact angle within the time. The result shows that the treatment of the nitride has to be performed immediately before the electroplating process since the surface tends to be more hydrophobic after 3days. The effectiveness of the proposed treatment is demonstrated by the successful formation of Cu electroplated TSVs with an aspect ratio of 15.

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