Vapor Deposition of Highly Conformal Copper Seed Layers for Plating Through-Silicon Vias (TSVs)

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Metal interconnections in microelectronics have been typically fabricated in a planar, 2-dimensional (2-D) fashion. 3-dimensional (3-D) integration has gained a lot of interest as a way to enhance the performance of microelectronic systems. 3-D integration has been shown to reduce the number and the average lengths of 2-D global conductors (ITRS) calls for copper TSVs with aspect ratios of 10:1 by 2012 and 20:1 by 2015.4 One critical step in the production of TSVs is to increase. The 2010 International Technology Roadmap for Semiconductors (ITRS) calls for copper TSVs with aspect ratios of 10:1 by 2012 and 20:1 by 2015.5 One critical step in the production of TSVs is the preparation of a continuous barrier that will keep metals from diffusing out from the vias. A smooth and conductive copper seed layer is also necessary to initiate copper electroplating. Strong adhesion must also be provided between the copper seed layer, the diffusion barrier and the underlying insulator. Due to their poor step coverage, conventional physical vapor deposition (PVD) methods will no longer be able to cover the sidewalls of these high aspect ratio features with the necessary layers.5

In this report, we introduce a new method to make conformal, smooth and strongly adherent barriers and copper seed layers inside holes with aspect ratios greater than 25:1 by vapor deposition. A rapid ALD process is first applied to form a conformal insulating layer of silicon dioxide (SiO$_2$) inside the vias.6 Next manganese nitride (Mn$_4$N), an effective copper diffusion barrier and adhesion layer, is deposited conformally on the silica surface by chemical vapor deposition (CVD). Mn$_4$N forms an effective copper diffusion barrier and provides strong adhesion between the silica and the subsequently-deposited copper. Conformal copper or copper-manganese alloy films are then deposited by an iodine-catalyzed direct-liquid-injection (DLI) CVD process. Diffusion of manganese during post-deposition annealing further enhances the barrier and adhesion properties at the copper/dielectric interface.

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make a solution with a concentration of 0.72 molal or 0.43 molar and a density of 0.79 g/mL, measured at 21°C. The saturated solubility of the copper precursor in dodecane was determined to be ~1.3 molar. The precursor solution was kept at room temperature in a stainless steel syringe sealed by 2 O-rings. The flow of the precursor solution was controlled by a syringe pump (KD Scientific model 210) at flow rates from 0.05 cm³/min. The precursor solution was mixed with 0.8 ohms per square) was formed in the vias, which typically took around 10 minutes. The Mn/Cu ratio was quantified by X-ray fluorescence (XRF). A post-deposition annealing step at 350°C for one hour in nitrogen ambient was carried out after the iodine-catalyzed CVD process to diffuse the manganese from the copper-manganese alloy to the copper/insulator interface. The conformality of the Mn₄N and the copper seed layers were evaluated by scanning electron microscopy (SEM). A thicker Mn₄N layer was deposited for 100 minutes so that its conformality could be observed more clearly by SEM. The surface morphology of the copper seed layer was studied by atomic force spectroscopy (AFM). The sheet resistance of the films was measured by a four-point probe.

Results and Discussion

A conformal layer manganese nitride film can be prepared by CVD at 130°C in holes with aspect ratios of 26:1. A thick (95–100 nm) Mn₄N layer is shown in Figure 3 to demonstrate conformal deposition. The effective aspect ratio of the holes is much greater than 26:1 as the diameter of the holes is narrowed during the course of deposition. The defect in the bottom of the via is caused by damage during the hand-cleaning of the sample. The polycrystalline manganese nitride film is conductive, with a resistivity value of 198 mΩ-cm. Annealing the manganese nitride film at 200°C for one hour promotes the formation of larger grains and results in a lower resistivity value of 2.01 mΩ-cm. It is possible to prepare conformal manganese nitride films at higher substrate temperatures, but the flow rate of NH₃ must then be decreased to prevent fast surface reactions, which lead to poor conformality. For example, vias with aspect ratios up to 50:1 can be coated with conformal Mn₄N using NH₃ and H₂ flow rates of 5 and 55 sccm, respectively, at a substrate temperature of 180°C. Surface reactivity may also be lowered by choosing a manganese amidinate precursor with bulkier ligands, such as tert-butyl groups, attached to the nitrogens in place of the smaller iso-propyl groups. Manganese nitride films as thin as 2.5 nm form barriers against copper diffusion. A four-point bend method was used to evaluate the adhesion between silica and the later-deposited CVD of copper, and the debonding energies were found to be greater than 6.5 J m⁻², which is high enough to survive further fabrication by chemical-mechanical polishing. When vapors of ethyl iodide are exposed to manganese nitride films, iodine atoms are chemisorbed onto the surface. During subsequent CVD of copper, the iodine desorbs from the Mn₄N surface and floats on the surface of the growing copper film. The presence of iodine atoms may weaken the bond between copper and its ligands and facilitate the dissociative chemisorption of the precursor on the copper surface, resulting in the enhancement of the growth rate and surface smoothness of the copper films.
Smooth and continuous copper seed layers can be deposited by vaporizing the copper precursor from a conventional bubbler. TSV via features with aspect ratios up to 4.6:1 can be conformally coated with a copper seed layer. Vias with aspect ratio up to 10:1 can be conformally coated by increasing the copper precursor carrier gas to 100 sccm and the working pressure to 10 Torr, both of which changes increase the partial pressure of the copper precursor inside the deposition region. This conventional bubbler delivery of precursor vapor, however, fails to form a continuous copper layer in the bottoms of vias with aspect ratios beyond 10:1 due to insufficient concentration of precursor vapor, especially for substrates with extremely high via density (9 × 10^6 holes cm^-2). The direct-liquid-injection (DLI) method delivers a much higher partial pressure of the precursor vapor than vaporization from conventional bubblers. By supplying a high concentration of copper precursor vapor, the deposition is operating in the surface reaction-controlled regime. At deposition temperatures around 180°C, slow surface reactions permit a uniformly high concentration of precursor vapor to be delivered to the entire length of the vias. As a result, continuous and highly conformal copper-manganese films are deposited on manganese nitride underlayers inside via holes with aspect ratio over 26:1 due to insufficient concentration of precursor vapor, especially for substrates with extremely high via density (9 × 10^6 holes cm^-2). The direct-liquid-injection (DLI) method delivers a much higher partial pressure of the precursor vapor than vaporization from conventional bubblers. By supplying a high concentration of copper precursor vapor, the deposition is operating in the surface reaction-controlled regime. At deposition temperatures around 180°C, slow surface reactions permit a uniformly high concentration of precursor vapor to be delivered to the entire length of the vias. As a result, continuous and highly conformal copper-manganese films are deposited on manganese nitride underlayers inside via holes with aspect ratio over 26:1 (Figure 4). The vapor delivery rate from the DLI system is stable, reproducible and accurately known because the concentration of the solution and the liquid and carrier gas injection rates are known and steady. In contrast, the vapor delivery rate from a conventional bubbler is subject to uncertainty in vapor pressure, temperature variation, thermal decomposition, and effects of fill level.

Cross-section SEM and AFM images of a thicker copper film on a planar substrate show that the copper seed layer deposited on an iodine-exposed manganese nitride underlayer is fairly smooth, with a root-mean-square roughness equal to 6.2% of its thickness (Figure 5). Manganese content in the copper-manganese alloy was analyzed by XRF to have approximately 0.5 atomic% of manganese in copper. Adjusting the temperature of the manganese precursor bubbler or the flow rate of the nitrogen carrier gas through the bubbler can vary the concentration of manganese in the alloy film.

A post-deposition annealing step at 350°C is incorporated to diffuse the manganese from the copper-manganese alloy to the copper/insulator interface and to return the resistance of the copper seed layer to a lower value. Our earlier report^1^ showed that manganese diffuses through the grain boundaries of the polycrystalline copper, and this diffusion process enhances the interfacial adhesion between copper and insulators such as silicon oxide, silicon nitride and low-k dielectric. While manganese nitride provides sufficient adhesion energy to survive chemical-mechanical polishing, the presence of additional manganese in the seed layer can further strengthen the copper/insulator interface and potentially achieve longer electromigration lifetime. The debonding energy increases approximately linearly with the manganese content at the interface, up to values beyond 14 J m^-2.1^ The resulting self-aligned interfacial layer, manganese silicate (MnSiO_x), forms within a few nm of the surface of the insulator, and is an excellent barrier to diffusion of copper, oxygen and water. By diffusing the manganese out from the copper-manganese alloy...
film, the sheet resistance is determined to be 0.46 ohms per square for the copper seed layer shown in Figure 4, which is sufficiently conductive for the later electroplating step (<0.8 ohms per square). The resistivity of this seed layer is about 2.69 $\mu \Omega \cdot \text{cm}$, which is about the resistivity expected for a pure copper layer 58 nm thick. It is also possible to carry out the annealing step after the electroplating of copper to diffuse manganese in the seed layer to the Cu seed/electroplated Cu interface, thereby preventing delamination of the plated Cu film from the seed layer.

**Conclusions**

Conformal and conductive copper seed layers for metallization of TSVs were successfully prepared in high aspect ratio holes by DLI-CVD. A conformal insulator layer was first deposited by ALD to separate the metal from the substrate silicon, and a manganese nitride liner layer was then deposited on the insulator. The CVD process was catalyzed by iodine as a catalytic surfactant to achieve higher growth rate and smoother morphology. The DLI-CVD method enhanced the delivery of precursor vapors even to the bottoms of dense arrays of vias and resulted in nearly perfect conformality. The presence of manganese at the copper/insulator interface further improves the adhesion and barrier properties at the interface. This process forms a highly robust and conductive seed layer for metallizing future generations of copper vias in advanced 3-D integration. It satisfies the ITRS requirements beyond the end of the roadmap.

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**References**