Conformal Copper Seed Layers for Through-Silicon Vias Using Chemical Vapor Deposition

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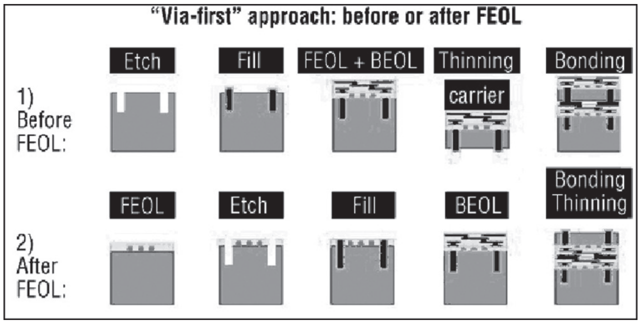

Figure 1: A typical technique for semiconductor integration of TSV features.

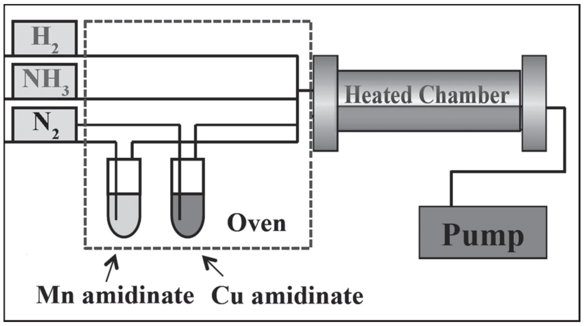

Figure 2: A basic schematic of our custom CVD system.

Abstract and Introduction:

In recent years, leading semiconductor manufacturers have acknowledged that the time-tested technique for increasing processor performance—shrinking transistor size—cannot be sustained much longer [1]. Soon, performance will be enhanced by expanding today's two dimensional integrated circuits to the third dimension [1]. One significant issue that arises from this radical rethinking of design is interconnectivity between the circuit's stacked device layers. Recent advancements in through-silicon via (TSV) technology solve this problem by allowing for cheap internal interconnects with high-current capabilities that can be easily incorporated into modern circuit processing techniques (Figure 1) [2]. Because these vias must be filled with copper before functioning, we have explored an efficient two step filling procedure. We use chemical vapor deposition to deposit a thin conformal copper seed layer on the TSV structures, which can subsequently be filled completely with electroplated copper. In this paper we highlight our procedure's successes on current TSV technology and discuss its ability to satisfy the needs of future TSV developments.

Experimental Procedure:

After receiving blank TSV substrates from one of our industrial collaborators, we first exposed the substrates to five minutes of UV ozone treatment to remove surface contamination and increase the surface density of reactive sites. The wafer coupons were then placed in a custom-built chemical vapor deposition (CVD) reactor that employed a bubbler system to transport both copper and manganese precursor molecules to the growth chamber (Figure 2). Both the manganese precursor, bis(N,N'-diisopropylpentylamidinato) manganese (II), and the copper precursor, copper (N, N0-di-sec-butylacetamidinate) dimer, were synthesized by previously-described methods [3, 4].

Growth of the seed layer began with a five minute deposition of manganese nitride. Manganese (Mg) was evaporated from the precursor liquid at 90°C into a 60 standard cubic centimeters per minute (sccm) flow of highly purified nitrogen (N) and then mixed with 60 sccm of N and 60 sccm of purified ammonia before entering the growth chamber, which we maintained at 130°C and 5 Torr.

The reactor was then cooled to approximately 30°C under a flow of 60 sccm purified N before exposure to an ethyl iodide (CH_3CH_2I) source for 30 seconds. This exposure occurred without a carrier gas and was controlled by a needle valve to a pressure of 0.05 Torr. We completed growth of the copper seed layer by simultaneous deposition of both copper and Mg. Manganese vapor was evaporated at 90°C with 100 sccm N carrier gas. Copper was evaporated from liquid at 130°C with 100 sccm N carrier gas.

An additional flow of 100 sccm hydrogen gas mixed with the precursor gases upstream from the growth chamber, which was maintained at 180°C and 10 Torr. Deposition duration varied from 60 to 120 minutes. In some trials the substrates were then annealed at 350°C for one hour in a purified nitrogen atmosphere.

Results and Conclusions:

Under the conditions described above, we conformally coated up to 20:1 TSV features. SEM and x-ray fluorescence revealed the seed layer to be approximately 90 nm thick with 1% manganese content (Figure 3). Upon inspection, we found that the narrowing sidewalls of our TSV structures significantly increased the features' effective length to diameter aspect ratios. As such, we hypothesize that our procedure could conformally coat uniform features with aspect ratios of 25:1 or even 30:1 (Figure 4).

Most substrates passed the Scotch® tape adhesion test without annealing, indicating sufficient adhesion for subsequent via fill by electroplating. We believe that this enhanced adhesion stemmed from the manganese atoms in our copper film, which diffused, even at deposition temperatures, to the silicon-manganese nitride interface. At this substrate interface, the manganese formed manganese silicate compounds and improved film adhesion as indicated by previous research [5]. An additional post-deposition anneal has been shown to further increase copper film adhesion [5]. Such strong bonding energies, combined with the diffusion barrier properties provided by the film's manganese nitride underlayer, ensure that our CVD films can survive both semiconductor processing and operation.

Without our procedure's brief ethyl iodide exposure, we would not be able to achieve such high aspect ratio conformal coatings in a reasonable timescale, if at all. Previous research has indicated that the iodine atoms form a weakly-adsorbed monolayer and catalyze copper nucleation before detaching from the MnN_x underlayer [5]. Iodine then pools at the bottom of each via and augments the local catalytic effect, resulting in a bottom-up superfill that maintains a similar film thickness along the entire structure.

Although we were able to conformally coat most 20:1 vias, we discovered that 20:1 TSV features patterned in very high densities could not be adequately coated. We hypothesize that the large effective surface area created by the high feature density resulted in a local depletion of reactive gases before all vias were coated. Fortunately, this loading effect only became problematic for feature densities that were much too high for practical uses.

Future Work:

Although recent semiconductor outlooks call for 50:1 TSV features by 2015, we currently cannot test our procedure on such structures because are not yet mass producible. As such, we are currently refining our process for 20:1 features in order to optimize both growth efficiency and film characteristics.

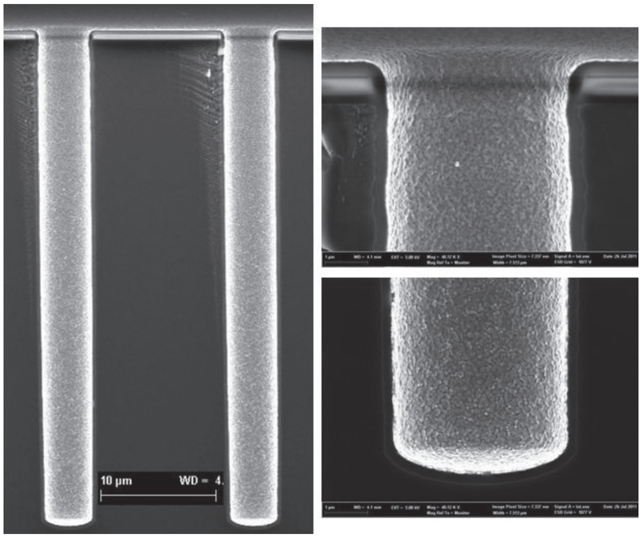

Figure 3: Conformally coated 10:1 aspect ratio TSV features.

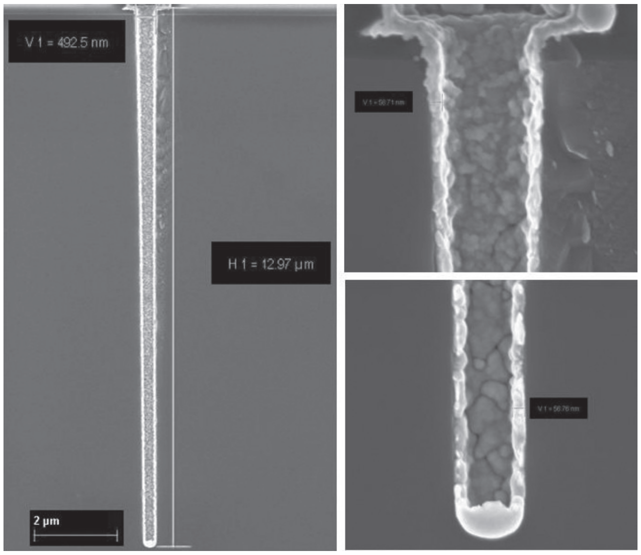

Figure 4: Conformally coated 25:1 aspect ratio TSV features.

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