Investigation of the oxidation and reduction behavior of thin copper surfaces in semiconductor technology

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During the processing of semiconductors, defects may occur and may cause yield or reliability issues. Filling voids in copper lines and/or vias are known and are a prominent defect type [1]. Figure 1 shows a transmission electron microscopy (TEM) image of such a void. Extensive investigation on the phenomena over the past years and decades using production-optimizing methods, revealed many influencing parameters and knobs to reduce the occurrence of the defects. But a proper solution to this issue has not been found. It is known that the transportation of wafers and its duration between the copper seed layer deposition and copper electroplating steps have a crucial influence on defect formation. Defects can be reliably introduced by storing or transporting wafers in open 200mm cassettes in the cleanroom for extended periods. The proposed defect mechanism behind this is thought to occur as follows: local oxidation of the copper seed layer prevents the plating process from initiating correctly, leading to overplating on adjacent surfaces.

This work aims to characterize the physiochemical processes occurring at the Cu surface. The experiments were conducted on 200mm blanket wafers using either a Ta or TaN/Ta barrier and a 30nm thin Cu seed layer. To this end, an ellipsometric model is developed, which can measure the thin copper oxide layer on top of the copper seed layer. The model was optimized using external measurements by time-of-flight spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) on freshly prepared samples. Various storage conditions for the copper seed layer in a cleanroom environment were tested and compared. Also, a potential influence of different barrier systems is investigated.

The ellipsometric model confirms expectations from the literature showing a logarithmic growth rate of the oxide layer [2]. Moreover, the model verifies the reported order of magnitude of a few nanometres of oxide formation after several days of storage [3,4]. It was found that the thickness of the oxide layer depends strongly on the storage and transport conditions. Older storage conditions like open cassette storage, or storing in boxes, which provide protection from laminar cleanroom airflow, were compared to more modern methods like storage in front-opening unified pods (FOUPs), either unpurged or nitrogen purged. The lowest oxide formation was found for the storage in nitrogen purged FOUPs, leading to nearly no oxide formation. Figure 2 compares the growth rates found for different storage modes.

Additionally, the effectivity and stability of a diluted sulfuric acid step removing the copper oxide layer was investigated. However, a rapid re-oxidation of the surface is observed after successful reduction, occurring at a significantly faster rate than the initial oxidation (Fig. 3).

References

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Figure 1. TEM image of the fill defect in a copper via. Image taken after anneal and CMP.

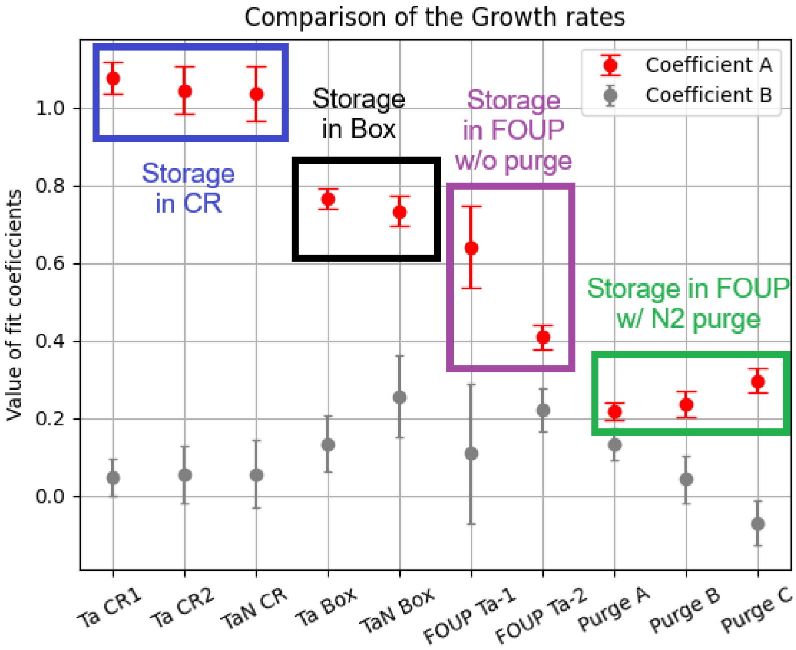

Figure 2. Comparison of growth rates for different modes of storage. The description codes Ta, TaN refer to a Ta or a Ta/TaN barrier underneath the seed layer. The abbreviation CR refers to cleanroom conditions, box means a 200mm transport box. A FOUP is a modern 300mm transport container. The fit function is *f(x)*=Aln(x+1)*+B.**

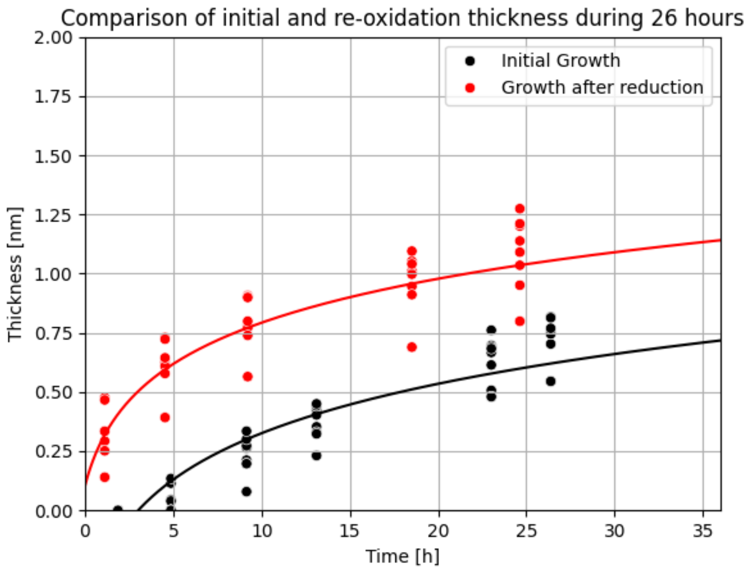

Figure 3. Comparison of re-oxidation after sulfuric acid treatment and initial oxidation during the first 26 hours. The wafers were stored in the clean room.