

Electrochemical Processing for Adherent Copper Deposition Directly on Air-exposed TaN for ULSI Applications

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Tantalum based materials have emerged as barriers against copper diffusion into dielectric layer and devices as well as adhesion enhancer between copper and dielectric layer in the recent copper wiring for device integration. Ta provides comparably a conductive passage for direct electrochemical deposition (ECD) of copper with the electrical resistivity of $100 \mu\Omega\text{-cm}^{-1}$ while TaN contains nitrogen which is known to contribute to adhesion strength with an affinity to copper, but it has a higher resistivity of about $270 \mu\Omega\text{-cm}$. Seedless copper ECD was developed in order to ensure conformal coverage of copper on barrier layers and reach the flaw-free fill of copper for sub-70 nm dimension with high aspect ratio. Previous works on W_2N^2 and $\text{TiN}^{3,4}$ show that quality copper deposit with high nuclei density, low resistivity, good surface coverage, and good adhesion can be formed by seedless ECD method which employs a plating bath of copper-complexes. There exists a tantalum oxide with exceptional stability on TaN produces exceptionally stable oxide, Ta_2O_5 when exposed in the air. In order to achieve strong adhesion of copper on TaN, total removal of the Ta_2O_5 is necessary.

Experimental

Experiments for seedless copper ECD on TaN have been conducted with the wafer samples having the film structure of 250 \AA TaN / SiO_2 / Si. In order to solve the problem arising from the difficulty of Ta_2O_5 removal, a serial exposure of chemical baths was developed for direct copper deposition on air exposed TaN surfaces. In bath A, a concentrated KOH solution, in conjunction with an applied anodic potential, effectively dissolves the tantalum oxide(s), allows direct deposition of the copper on the nitride, and enhances adhesion of the copper film to the TaN. After exposure to the caustic solution, wafer samples are then transferred into bath B, in a "wet" condition preventing oxide films from reforming. A "wet" transfer in this case simply means that a thin residual film of bath A solution remains on the wafer surface, so that the TaN does not come in direct contact with the ambient atmosphere. Bath B has a composition of 0.08M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.08M $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$, and 0.08M KOH and a pH of 3.39 ± 0.1 . Copper is directly plated on TaN surface in bath B with cathodic potential application.

Results and Discussion

Bath A, the saturated KOH solution, plays a critical role as the etchant of the stable air formed tantalum oxide layer. When an anodic potential of 2.2 V, is applied to the sample, the current density rapidly decreases with time. The initial rapid reduction in current is associated with dissolution of the underlying TaN. Thinning of the TaN layers, by etching after removing tantalum oxide layer, is clearly an undesirable phenomenon considering that the current flow requires the largest cross sectional area of TaN to reduce the effects of resistance controlled voltage drops on the subsequent uniformity of the copper films. Accordingly, experiments to determine the optimum time for etching the wafer surfaces, removing the oxide, but leaving the TaN virtually intact, were performed. Thicker and faster deposit of copper is possible on TaN layer with larger cross section, which results from the shorter etching time, when a constant potential of -1.66 V is applied for 20 s. Copper deposits formed on TaN from this strategy show considerable uniformity of film thickness over the entire sample surfaces. Even when the plating potential is applied to samples for very short times, e.g. 0.1 seconds, very thin and conformal copper films, with smooth surfaces, are created on the TaN. This consequence apparently arises from a minimization of the surface energy of the growing copper islands by reducing their effective surface area. Hemispherical copper nuclei form initially, but undergo lateral growth

at a much faster rate than growth which is normal to the wafer surfaces. Thus, copper growth on TaN surfaces occurs by early saturation copper nuclei and then lateral merger of the nuclei. While smooth planar and conformal films were readily deposited utilizing this technique, practical film thicknesses greater than approximately 100-150 nm showed delamination, presumably due to internal stresses. Results will be presented that will show the process parameters required to obtain conformal films with good adhesion.

References

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