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Effect of Microstructure of Substrate on the Metallization Characteristics of the Electroless Copper Deposition for ULSI Interconnection Effect of Plasma

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Copper has attracted much attention in the deep submicron ULSI metallization process as a replacement for aluminum due to its lower resistivity and higher electromigration resistance. Electroless copper deposition method is appealing because it yields conformal, high quality copper at relatively low cost and a low processing temperature.

In this work, it was investigated that effect of the microstructure of the substrate on the electroless deposition. The mechanism of the nucleation and growth of the palladium nuclei during palladium activation was proposed. Electroless copper deposition on TiN barriers using glyoxylic acid as a reducing agent was also investigated to replace toxic formaldehyde. Furthermore, electroless copper deposition on TaN_x barriers was examined at various nitrogen flow rate during TaN_x deposition. Finally, it was investigated that the effect of plasma treatment of as-deposited TaN_x barriers on the electroless copper deposition.

As a result of electroless copper deposition on TiN barriers using glyoxylic acid as a reducing agent to replace toxic formaldehyde, glyoxylic acid can be an alternative to formaldehyde for electroless copper deposition.

It was investigated the nucleation and growth of electrochemically deposited palladium on polycrystalline TiN thin films. The formation of the palladium nuclei during the palladium activation is determined in the early stage of electroless deposition of palladium on TiN films and the growth of the palladium nuclei on TiN films is shown to be three dimensional island growth. TEM images of electrochemically nucleated palladium on TiN films for 5 s showed that the palladium nuclei were mainly formed on the grain boundaries, especially on the grain boundary edges, of polycrystalline TiN thin films . HR-TEM results showed that the palladium nuclei on the TiN barriers were crystallized within 5 s of palladium activation with no preferred orientation. These results indicate that the microstructure of the substrate plays an important role in the electroless deposition of palladium, and the grain refinement of the substrate is considered to be an attractive method of acquiring high quality films in electroless deposition.

As a result of electroless copper deposition on TaN_x ($x=0\sim1$) barrier films prepared with various nitrogen flow rate, the quality of electrolessly deposited copper was enhanced with increasing the nitrogen flow rate. However, the electrical resistivities was also increased upto 70000 $\mu\Omega\cdot cm$, which is caused by the transformation and decrease in grain size of TaN_x films with respect to increase in nitrogen flow rate and is not an acceptable value as a diffusion barrier. The palladium nuclei mainly formed on grain boundaries of TaN_x barrier films. This result also shows the importance of the grain refinement.

The effect of NH_3 plasma treatment of the TaN_x barrier films on electroless copper deposition on TaN_x films to enhance the quality of electroless Cu was incvstigated. Electrical resistivity of the plasma treated TaN_x barrier films was increased by less than 10 % compared to that of the films without plasma treatment, which is an acceptable value for the application to interconnection as a diffusion barrier. FE-SEM micrographs of the palladium activated TaN_x films showed that the density of palladium nuclei on the TaN_x barriers was remarkably increased by NH_3 plasma treatment. The quality of the electroless copper on the TaN_x films was enhanced by NH_3 plasma treatment without a large increase in electrical resistivity. TEM results showed that the outermost surface of the TaN_x films were amorphized by plasma treatment caused by ion bombardment with kinetic energy during NH_3 plasma treatment. The improvement in the palladium activation process after NH_3 plasma treatment is caused by an increase in the surface energy of TaN_x films during plasma treatment, which is thought to provide more palladium nucleation sites.