Electrochemically Deposited Ruthenium Seed Layer Followed by Copper Electrochemical Plating.

Introduction

Copper has nearly replaced aluminum in ultralarge scale integrated (ULSI) logic-based devices due to its lower electrical resistivity and superior resistance to electromigration compared to Aluminium. ln contrast, due to the poor properties of copper oxides. it diffuses rapidly into low k dielectrics. However. it does not fornt carbides or silicates readily, which ntakes integration with low k dielectrics challenging} Refractory metal barriers. such as TaN, and TiN are currently used for Cu/low-k and Al/low-k integration.

ln the ULSI devices, films with excellent step coverage for high aspect ratio features are needed for copper baniers and seed layers.

Sputtered copper has limitations for step coverage and cost of ownership for depositing the TaNx/Ta/seed stacks. Electrochemical deposition (EC D) of copper can be employed to deposit films with shrinking via dimensions. Electrochemical plating for interconnections in high-performance integrated circuits requires a seed layer to provide a conductive path for the electric current that is required to electroplate the copper-fill material. As such, an underlying conductive seed layer is generally applied to the wafer before it is subjected to an electrochemical deposition process. Hence, a continuous seed layer must be deposited on diffusion barriers. In addition the seed layer needs to be an air-stable metal for ULSl devices, Cltyan et al. have proposed ruthenium, a conductive noble metal, as a good choice for a seed layer since it has the advantage to be plated in standard plating solution}; They also investigated the ultrathin layer of ruthenium as a replacement adhesive diffusion barrier layer.

Therefore a two-step barrier metal process, for example TaNx/Ta, may be reduced to a single ruthenium layer with adhesive and barrier properties.

Chemical vapor deposition (CVD), electroless deposition (ELD), and atomic layer deposition (ALD) have been used for the deposition of Ru films. Electrochemical deposition has not been looked at yet for depositing a Ru seed layer conformally. This technology would have to address the conformal deposition on high aspect ratio (A/R) features with a size of 22

and 45 nm nodes. And three-dimensional deviccs. Ru is a conductive and air-stable transition noble metal with a high melting point (2.3l0°C). One of the electronic applications of ruthenium is as a capacitor electrode in gigabit memory. Kwon et al. investigated the electrochemical deposition of the Ru film on a Pd catalyst deposited by an acid solution, including $PdCl_2$. HF. and HCI for a high density dynamic random access memory (DRAM) capacitor. in addition, ruthenium is a potential metal gate electrode for complementary metal-oxide semi-conductor (CMOS) device, Cho et al, also investigated that Cu conductor/Ru CVD barrier/SiO_3 dielectric structure was tested as an interconnection of deep submicrometet device application. They reported that Ru CVD was very effective in the formation of smooth, conformal, and pure Ru thin films with well-developed texture. Combined with Pd activations this also provided all appropriate substrate to Cu electrodeposition resulting in continuous and super conformal Cu film by the two-step elcctrodeposition.

Reid and Blake reported the simple ruthenium salts were used as nitrosyl derivatives such as ruthenium nitrosyl-sulfate. Ruthenium sulfate, ruthenium phosphate for ruthenium ECD. These solutions have been proposed for electrodeposition of ruthenium but these were either unstable in operation or plated at extremely low cathode current efficiencies. A number of aqueous eleclrolytes for ruthenium electrode are also based on ruthenium chloride. Recently, Bamba et al. studied the oxidation of d-glucose on $RuCl_2(azpy)_2$ (azpy = 2-phenylazopyridine), as electrochemical mediator for oxidizing dglucose in carbonate buffered medium. Reddy and Taimsalu proposed an electrolyte based on the N-bridged complex of ruthenium (lV) nitrosyl chloride (RuNC) for Ru ECD. Figure l shows RuNC. They had described the preparation and charrlcteristics of stable electrolytes based on the ruthenium complex of RuNC formed with sulfamic acid at a cathode current efficiency up to 100%. The reaction for the RuNC shown in Fig. 1 is the following

$$2Rucl_3.3H_2O + 2HCL + 4NH_2SO_3H \rightarrow (NH_4)_3[(RuCl_4)N(RuCl_4] + 4SO_4^{2-} + 8H^+ + H2\uparrow \quad [1]$$

ln this paper, we deposited ruthenium by ECD onto blanket Ti and patterned TiNx films followed by Cu ECD. We investigated Ru ECD on barrier layers

without Pd activation using the high efficiency electrolyte RuNC. Moreover, we have also tried Ru deposition for smooth morphology with Ru ECD and gap filling by Cu ECD for ULSI.