Electrochemical deposition of copper and ruthenium on titanium

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Abstract

Copper electrochemical deposition on titanium with a ruthenium seed layer was investigated. The chemicals for the acid-bath ruthenium electrochemical deposition were ruthenium(III) chloride hydrate (RuCl3·3H2O), hydrochloric acid (HCl), sulfuric acid (H2SO4), and polyethylene glycol. The chemicals for the acid-bath copper electrochemical depositions were copper(I) sulfate hydrate (CuSO4·5H2O), sulfuric acid (H2SO4), and polyethylene glycol. Results were analyzed by field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectrometry (RBS). Ruthenium thin film of ~30 nm thickness, with equiaxial grains <10 nm, was deposited, on a blanket Ti with a root mean square roughness of 8.3 nm, at 2 V for 90 s. XPS and RBS analyses showed the presence of metallic Ru. The Ti substrate was found stable with respect to ECD of Ru but the Ru/Ti bilayer was not found stable in the Cu acid bath, resulting in the diffusion of Ti into Ru film. The depth profiling studies indicates that Ru film thickness ca. 1.4 nm and deposition time of 10s can act as a good seed layer.

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1. Introduction

In the semiconductor industry, aluminum has been the conductor of choice, even though superseded by copper due to its lower resistivity and better resistance to electromigration in case of ultra-large scale integrated (ULSI) devices. In case of Cu metallization, the Cu diffuses rapidly into the interlevel dielectrics (ILDs). Therefore, refractory metal or metal nitrides such as Ti, TaN, TiN, and TaN are used as a diffusion barrier. Sputtered copper has limitations for step coverage and cost of ownership for depositing a seed on the barrier stacks.

On the other hand, electrochemical deposition (ECD) provides a continuous buildup of metal coating on a substrate in a suitable aqueous solution. Electrochemically deposited copper (ECD Cu) has emerged as the most efficient way to fill nano features that are based on the dual-damascene technology [1, 2]. Because of its high filling capability and low process cost we can expect ECD Cu a suitable candidate for the interconnect metallization in future technology nodes. ECD Cu requires a seed layer as a conducting path for the electrons that are needed for the redox surface reactions [3]. Josell et al. and Chyian et al. have reported the application of ruthenium for Cu interconnects as well as a good candidate for the seed layer [4, 5]. In addition, ruthenium could potentially replace the Cu/Ti/TaN stack; however, Ru diffuses into Cu during subsequent annealing, which increases the Cu line resistivity [6, 8]. Instead, a thin layer of Ru can act as a seed layer to minimally impact Cu line resistivity.

Electrochemical deposition of ruthenium is an attractive technique to deposit a conformal thin seed layer because of its good step coverage, low cost of ownership, and its amenability to ECD Cu. In our previous studies, we reported growth study of conformal seed layer using ECD Ru on patterned TiN 130 nm trenches [9]. This technology would have to address the Cu conformal deposition on high aspect ratio (A/R) features with a size of 22 nm and 33 nm nodes, and three-dimensional devices.

Reid and Blake undertook ECD Ru with a number of aqueous electrolytes based on simple ruthenium salts and nitrosyl derivatives [10]. Nitrosyl sulfamate emerged as the acid-bath reagent.

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