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Characterization and Process Development of CVD/ALD-based Cu(Mn)/Co(W) Interconnect System

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Abstract

A new materials system of a single layered Co(W) barrier/liner coupled with a Cu(Mn) alloy seed was investigated. Atom probe tomography visualized the sub-nanoscale structure of Cu(Mn)/Co(W) system, and thereby revealed Cu diffusion behavior of Co(W). Grain boundaries of Co were found to be the diffusion path, and successfully stuffed by W. Mn in Cu(Mn) also segregated to stuff the grain boundaries of Co. Combination of these two additives enabled high barrier property against Cu diffusion of Cu(Mn)/Co(W). Foreseeing tiny and high-aspect-ratio Cu interconnect features, Cu(Mn)/Co(W) was fabricated by ALD/CVD processes. To maximize the performance, minor impurities of the film incorporated from the ligand of the precursors were controlled by precursor selection. Thin, conformal, and smooth films were finally demonstrated onto a trench substrate.

1. Introduction

We have previously proposed a Co(W) single-layered barrier/liner layer in place of Co/TaN [1-3], Ru/TaN [4-6], and Ta/TaN [7-9] double-layered ones. Co(W) has high barrier property and high work of adhesion with Cu. [10] Our current targets are to examine the performance of ultra-thin Co(W) barrier/liner and to develop their fabrication processes. To stuff pinholes of ultra-thin Co(W), Cu(Mn) alloy seed was employed as Mn is expected to scab the pinholes of ultra-thin barrier layer. (Fig.1) [11-13] To form Co(W) and Cu(Mn) layers onto tiny and high AR features, CVD and ALD techniques are necessary. In this study, the sub-nanoscale structure and barrier performance of Cu(Mn)/Co(W) was investigated using atom probe tomography (APT), which enables 3D observations of each atom with sub-nanometer resolution. [14,15] The process of CVD-Cu(Mn) onto ALD-Co(W) was developed in terms of enhancing the initial Cu nucleation, and thus forming ultra-thin and smooth Cu(Mn) seed layers onto trench substrates.

2. Experimental

Showerhead type ALD and CVD cluster chamber system was used. O- and F-free amidinato precursors were used for both ALD-Co(W) and CVD-Cu(Mn) growth. (Fig.2) First, a Cu(Mn)/Co(W) stack was grown, and the sub-nanoscale structure and the barrier performance were studied by APT. As a comparison, three control samples of Cu/Co(W), Cu(Mn)/Co, and Cu/Co were also examined. Next, to form thin and smooth CVD-Cu(Mn) on ALD-Co(W) underlayer, the initial Cu nucleate density was studied. Finally, conformal and smooth Cu(Mn)/Co(W) films were formed onto a trench substrate using an optimized growth condition.

3. Results and discussion

3.1 Sub-nanoscale structure and barrier performance

Figure 3 shows the elemental mappings of W and Mn near the interface of Cu(Mn) and Co(W) by APT. The 1D elemental concentration profiles through grains and grain boundaries (GBs) of Co(W) are compared. The result indicates a selective Mn segregation into Co(W) GBs, which means Mn effectively suppresses Cu diffusion through Co(W) GBs while minimizing the negative effects on the adhesion of Cu/Co(W).

Figure 4 shows vertical elemental mappings of Cu after 400°C-1h annealing at H_2 atmosphere proved by APT. The Cu(Mn)/Co(W) sample minimized the Cu penetration compared to the other samples, and thus the Mn addition was revealed to be effective to enhance barrier property of Co(W).

Here, Mn should completely diffuse out from Cu in order not to increase the line resistance much. Figure 5 shows the overall pictures of Mn diffusion profile, which comes from Cu(Mn) seed layers after annealing. These measurements were by secondary ion mass spectrometry (SIMS) or APT measurements. Elemental concentration profiles shows amidinato-based CVD-Cu(Mn) seed layer promoted Mn diffusion and successfully eliminated residual Mn in Cu due to the absence of O and F in the film contrary to β-diketonato-based one.

3.2 Process development for 1X-nm-node Cu interconnects

In order to form ultra-thin and smooth Cu(Mn) films by CVD, high-density nucleation of Cu is required. In this study, Cu and Mn precursors were simultaneously supplied onto the wafer to form Cu(Mn) [Mn: 7 at.%] alloy seed layers. The ratio of partial pressures of Cu and Mn precursors were controlled to 9:1 by needle valves. Figure 6 indicates Cu nucleate density is not affected by a Mn precursor addition into Cu-CVD. Thus, Cu(Mn)-CVD is compatible with a traditional Cu-CVD method.

To form a thin and smooth CVD-Cu(Mn) film on an ALD-Co(W) underlayer, temperature modulated Cu-CVD was introduced. At the nucleation stage, where the film is discontinuous and Cu grain growth proceeds, the wafer was set as low temperature (150°C) to enhance the nucleate density of Cu. [16] After the film became continuous, the temperature was elevated to 200°C to increase the growth rate. This growth sequence improved both the smoothness of Cu(Mn) films and the throughput. Finally, a thin, smooth, and highly conformal Cu(Mn) seed layer was grown by CVD onto an AR10 trench substrate covered by a 2.0-nm-thick ALD-Co(W) barrier/liner.

4. Summary

Cu(Mn)/Co(W) system was studied using atom probe tomography in terms of the barrier property and the sub-nanoscale structure. Mn selectively segregated into Co(W) grain boundaries and enhanced the barrier property of Co(W). CVD/ALD processes for Cu(Mn)/Co(W) using O- and F-free precursors were also developed. The optimized growth condition enabled high Cu nucleation, and thus a thin, conformal, and smooth Cu(Mn) seed layer onto a trench substrate covered by an ultra-thin Co(W) barrier/liner with AR of 10:1.

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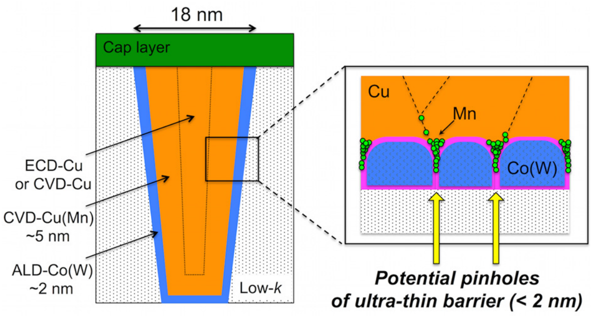

Fig. 1. Ultra-thin and pinhole-free single layered Co(W) barrier/liner layer coupled with Cu(Mn) seed layer for reliable 1X-nm-node Cu interconnects.

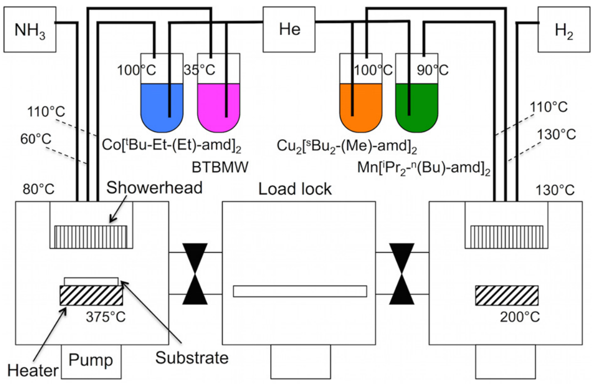

Fig. 2. Configuration of cluster chamber system for Co(W)-ALD and Cu(Mn)-CVD.

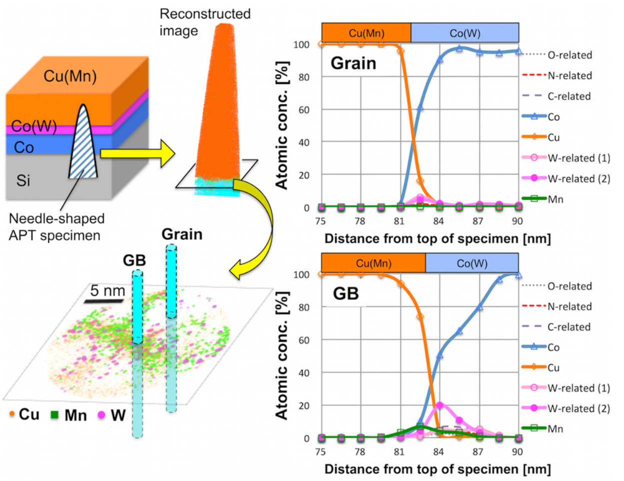

Fig. 3. Selective Mn segregation into the grain boundaries (GBs) of 7.9-nm-thick Co(W) barrier/liner after 400°C-1h annealing proved by APT.

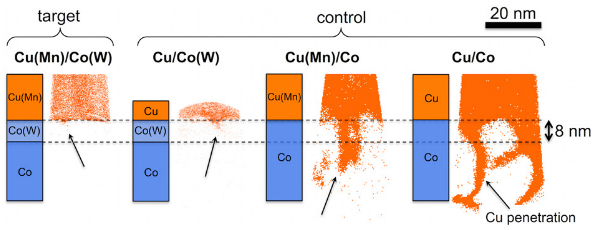

Fig. 4. APT elemental maps of Cu with 2-nm-thick vertical slices after 400°C-1h annealing for Cu(Mn)/Co(W), Cu/Co(W), Cu(Mn)/Co, and Cu/Co samples. The thickness of Co(W) was 7.9 nm.

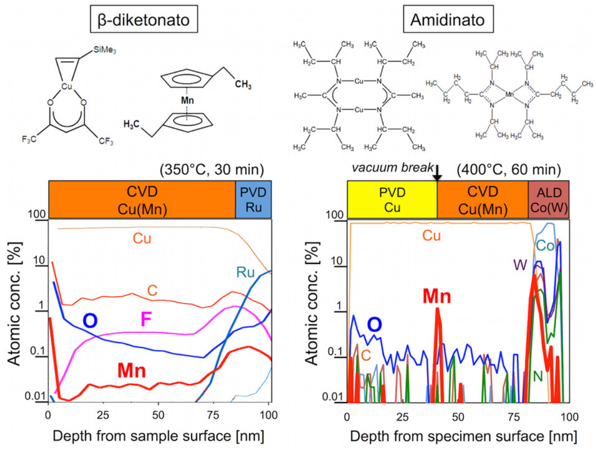

Fig. 5. Elemental concentration profiles of CVD-Cu(Mn) seed layers grown using β-diketonato and amidinato after annealing at H_2 atmosphere. SIMS and APT measurements were applied, respectively.

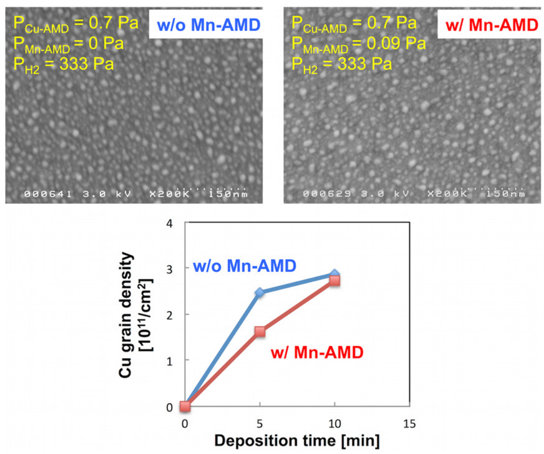

Fig. 6. Effect of Mn-amidinato (Mn-AMD) addition on the nucleation of CVD-Cu. (PVD-Ru underlayer, 150°C, 10 min)