SLURRY SYSTEM ESTABLISHMENT AND OPTIMIZATION FOR ADVANCED COBALT INTERCONNECT METALLIZATION

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ABSTRACT

Performing a chemical mechanical polishing (CMP) process for copper (Cu) interconnect metallization with cobalt (Co) diffusion barrier layer is well developed. However, the research on CMP process and associated polishing slurry system for Co as a novel interconnect wiring metal for sub-7 nm semiconductor device nodes, is still in its infancy. In this study, the establishment and optimization process of polishing slurry system for advanced Co interconnects have been presented on the foundation of a variety of mechanism analysis, including electrochemical survey, X-ray photoelectron spectroscopy measurement, surface wettability characterization, and adsorption isotherm calculation. As application verification, the final proposed CMP slurries for Co interconnects demonstrate the satisfactory material removal rates (MRR), excellent polished surface qualities, minimized particle residues, and flawless microstructures without galvanic corrosion.

INTRODUCTION

Metallization scheme of interconnects in middle of the line (MOL) and back end of the line (BEOL) has become one of the primary limiting factors of performance and yield for the advanced semiconductor manufacturing where technology nodes are lower than 7 nm. With narrower feature sizes, the major challenges for tungsten (W) with a titanium/titanium nitride (Ti/TiN) bilayer in MOL include the growing impact of parasitic contact resistance and the increasing difficulty for conformal deposition of bulk W gap-fill. Furthermore, the resistance of Cu in BEOL is rapidly approaching its limit due to the growing diffusive surface and grain boundary scattering of conduction electrons at such critical dimensions [1]. As a result, multiple material systems are being considered by the industry as promising candidates to replace the conventional W/Ti/TiN stack and Cu wiring metal, where Co presents the most important advantages on scaling contact resistance, thinner barrier layer, and higher electro-migration reliability [2].

Generally, the CMP process for Co interconnects can be mainly divided into two steps, consisting of rapid removal of bulk Co at a MRR of greater than 2000 Å/min and smooth polishing of heterogeneous materials (Co/Ti/TiN/dielectric) at a low Co MRR with a high removal selectivity between barrier/dielectric and Co. Furthermore, several aspects during Co CMP process demand to be paid attention, involving galvanic corrosion, number of particle residues, and surface qualities. Here, attention is given to studying the CMP process for Co interconnects with Ti/TiN as the barrier layer and plasma-enhanced tetraethylorthosilicate (TEOS) as the oxide dielectric layer. Multiple analytical techniques were used to establish and optimize the polishing slurry system for two-steps CMP of Co interconnects. Furthermore, Co/Ti/TiN/TEOS patterned wafers and 12-inches production-level wafers were employed to validate the performance of our proposed slurries.

EXPERIMENTAL

The CMP experiments were performed on a T11 Polisher (Hwatsing Technology) with a 7-zone polishing head, applying a slurry flow rate of 300 mL/min and platen/head rotational speed of 93/87 rpm. Except for 12-inches blanket wafers, a specific kind of patterned wafers which has different line width and space was used in this study, whose two minimum arrays are presented in Figure 1. Potentiodynamic polarization curves were acquired using an electrochemical station (Metrohm) equipped with a three-electrode cell. The element types on Co surfaces were characterized by X-ray photoelectron spectroscopy (XPS, Ulvac-Phi).

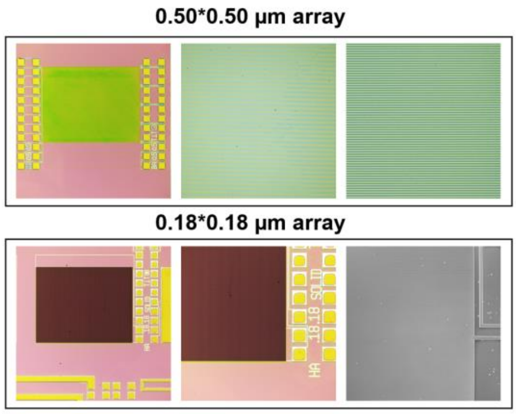

Figure 1: Two minimum arrays on used patterned wafers.

An atomic force microscopy (AFM, Bruker) was applied to map the surface morphology after polishing where a scan rate of 1 Hz was used on a 5×5 μm wafer area to obtain the AFM images. Surfscan SP5 wafer defect detection system (KLA-Tencor) was employed to display the number of particles presented on wafer surfaces, where the whole detected particle size ranges from 90 to 338 nm. The defects of interconnect structures were investigated by focused ion beam (FIB) and transmission electron microscopy (TEM). In particular, the samples for TEM were prepared by FIB. Figure 2 shows the top-view and cross-sectional profiles of the prepared patterned arrays.

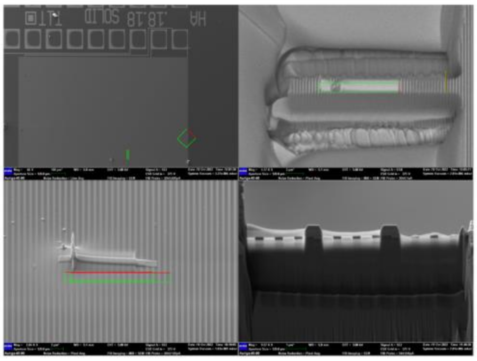

Figure 2: Profiles of the prepared patterned arrays.

RESULTS AND DISCUSSION

Establishment of Slurry System by Complexation and Inhibition Analysis

To design a new slurry system, finding an effective combination of complexing agent and corrosion inhibitor is the only way which must be passed. Considering the particularity and vulnerability of Co, satisfactory MRRs, removal selectivity, and galvanic corrosion potential were treated as the prior decisive factors. Glycine (GLY), dipotassium ethylenediaminetetraacetic acid (EDTA-2K), ammonium sulphate (AMS), nitrilotriacetic acid (NTA), citric acid (CA), and nitrilotriacetic acid trisodium salt (NTA-Na) were employed in this initial polishing tests and electrochemical characterization.

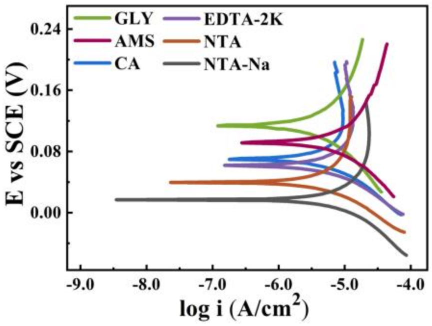

Figure 3: Potentiodynamic polarization curves of Co with different complexing agents.

Figure 3 shows a set of potentiodynamic polarization curves of Co with different complexing agents, where the calculated corrosion current densities present the complexation ability of each agent. Combined with the polarization curves of barrier layer, the minimal corrosion potential gap between Co and Ti could be obtained, indicting the lowest risk of galvanic corrosion. The determination of inhibitor could be realized by the same approach, accompanied by the satisfaction of MRRs and selectivity. Through a lot of experimentation and research, a mixture of hydrogen peroxide, EDTA-2K, and potassium oleate (PO) in alkaline condition was suggested to conduct as the preselected scheme for Co slurries.

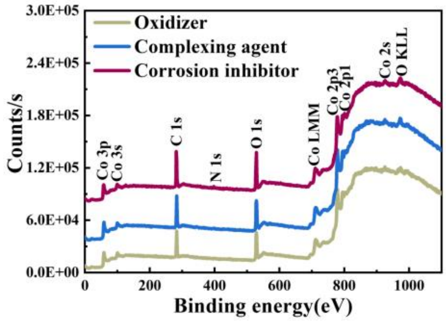

Figure 4: XPS spectra of Co films with different solutions.

The interaction mechanisms between Co surfaces and each component were explored by XPS survey and adsorption isotherm. Figure 4 displays the XPS spectra of Co surfaces after treated by different solutions, where the elements of Co, C, N, and O are recorded and marked. Typically, EDTA-2K could easily form soluble complexes with the ratio of 1:1 between metal ions and its ligand. Because of the soluble production, there is no reflection on the formation of Co surfaces. However, since PO possesses a hydrophobic chain of 18 carbon and a hydrophilic carboxylic acid end group, the carbon and oxygen signal become stronger than that in other conditions, probably originating from the adsorption of PO and the production of Co oxides.

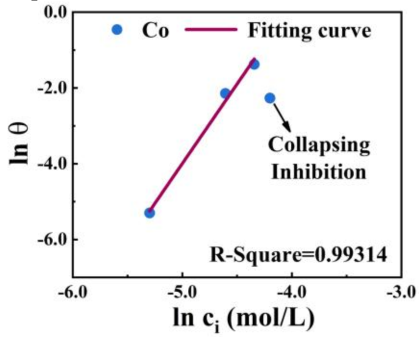

Figure 5: The Freundlich adsorption isotherm for Co.

Figure 5 presents the relationship between the logarithm of Co surface coverage (θ) and the logarithm of PO concentration (c_i). The intercept of the fitting curve provides the logarithm of adsorption equilibrium constant K, which is usually used to calculate the Gibbs energy of adsorption (ΔG^0_{ads}) to express the adsorption behavior. With the effect of low concentration PO, the calculated value of ΔG^0_{ads} is equal to –52.6 kJ/mol, confirming the spontaneity of the adsorption process for the PO inhibitor via chemisorption. However, with the excessive PO added, the stability of the inhibition effect has collapsed.

Improvement of Slurry System by Adding Surfactants

To improve and optimize our basic slurry system, various surfactants were introduced, aiming to control the number of particle residues and surface qualities after CMP process. The initial criteria for each surfactant selection adding in our basic formula is to check its influence on polishing results, including MRRs and removal selectivity. After investigation, three surfactants meet the material removal requirements, involving primary alcobol ethoxylate (AEO), polyvinyl pyrrolidone (PVP), and Tween-80 (T-80).

Figure 6: Images of measured contact angles.

To assess the effect of added surfactants on the wettability of Co films, the contact angles on fresh Co wafers were investigated, as shown in Figure 6. The maximum contact angle on clean Co wafer is ~40 with the addition of AEO, while the least contact angle of ~36 can be observed when PVP was introduced. Contact angle which presents surface energy of wafers is very vital in post-CMP cleaning process, where higher surface energy represents smaller contact angle, leading to better cleaning performance.

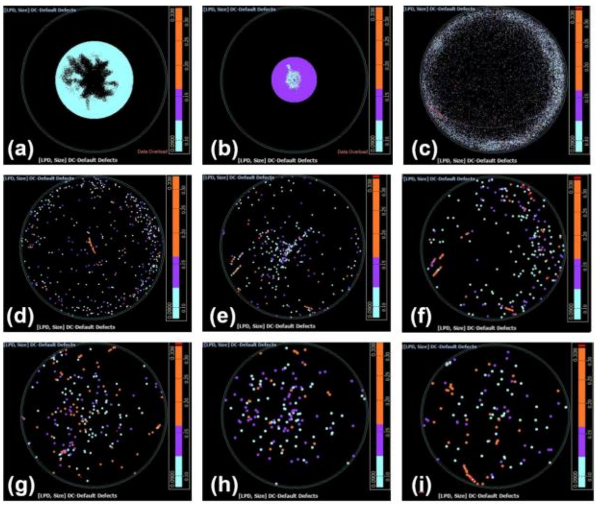

Figure 7: Particle residues on polished wafers.

Figure 7 (a)~(c) depicts the topographic images of 12-inches wafers polished by slurries only containing oxidizer, complexing agent, and inhibitor, where either the particle residues are overloaded or the number of particles are more than 10000. Figure 7 (d)~(e), (f)~(g), (h)~(i) present the particle residues after polishing by the three surfactants in sequence, where the least number of particles is around 160 with the addition of PVP, demonstrating that higher surface energy leads to better surface conditions after polishing. Furthermore, the surface topography and roughness of wafers polished with PVP were presented in Figure 8, showing excellent surface qualities.

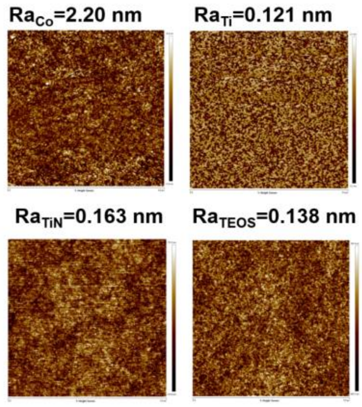

Figure 8: AFM images of polished wafers.

Polishing Performance of Slurry on Co/Ti/TiN/TEOS Stack

Co/Ti/TiN/TEOS patterned wafers were employed to validate the performance of our proposed slurry. Figure 9 presents the TEM images of 0.50*0.50 μm and 0.18*0.18 μm arrays after polishing. Although the erosion defect of ~20 nm both occurred in two arrays, indicating the TEOS MRR is too rapid, there is no Co loss, dishing, fang and galvanic corrosion in the stack, validating the excellent polishing performance of our proposed slurry system.

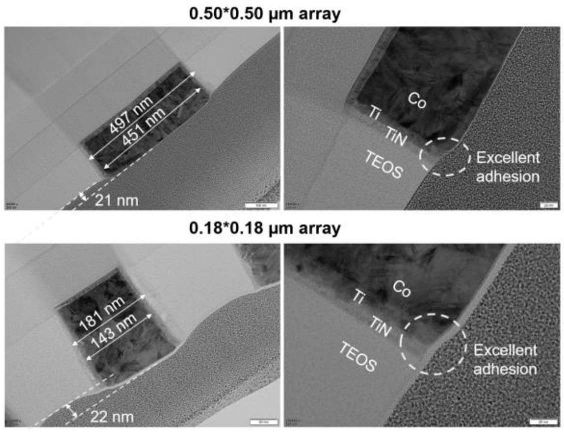

Figure 9: TEM images of patterned arrays.

CONCLUSIONS

In this work, the establishment and optimization of slurry system for Co interconnects have been clearly demonstrated by a variety of mechanism analysis. The proposed slurry system was validated by 12-inches production-level wafers and Co patterned wafers, showing the satisfactory MRRs, excellent polished surface qualities, minimized particle residues, and flawless microstructures.

REFERENCES

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