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In-situ Analysis of PEG Surface Adhesion on Cu

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The copper damascene electroplating mechanism is found to be about accelerator accumulating[1] at trench(via) bottom and mass transfer limiting[2] of suppressor so these additives' behavior bring superfilling on submicron patterns. And most well known PEG adheres with chlorine ion[3] on electrode surface and suppresses. In this study, we introduce *in-situ* analysis method AFM(LFM) and FT-IR while it's electroplating.

The suppression effect was investigated as a function of the PEG with chlorine ion on Ra<2nm smooth sputtered blanket copper wafer. Comparing the only SPS bath, inclusion of chlorine ion and PEG and also applied constant current(constant potential when necessary).

Controlling few tens of milliseconds applying current can show initial stage of nucleation and growth phenomena with and without suppression by AFM(Atomic Force Microscopy) in Fig. 1(a-c) and (d-f) respectively. When suppressor exists(Fig. 1(b)) only the number of mono size distributed copper clusters increased besides without suppression not only nucleated but also grain grew(Fig. 1(e)) was observed. With and without PEG deposits can clearly compared at similar coulomb of 400uC(30ms) and 200uC(100ms).

To investigate adhered PEG directly, *in-situ* AFM method was carried out and for this analysis only additives bath was used due to surface morphological noise of copper deposits and analytical noise of diffuse reflection of corroded cantilever. The roughness of sputtered wafer substrate was increased from 2nm to over 10nm with the PEG and inclusion of chlorine ion made cantilever oscillates a lot at certain area which oscillation were matched exactly on forward and backward scanning which shown in Fig. 2. This oscillation is so called damping effect at AFM contact mode. From the oscillation of *in-situ* AFM results the covering area can be assumed. Although knowing adhesion strength in absolute value, from the *in-situ* LFM(Lateral Force Microscopy) analysis adhesion strength can usefully rank in order such as in this system with chlorine ion over several hundred times larger adhesion strength in Table 1. Depending on adhesion strength value bath design can be optimized.

Furthermore *in-situ* three deflection FT-IR electrode is attached to micrometer to adjust few tens of microns gap so that this surface will be mass transfer limiting. In this case 10.5mA/㎠ was applied and after 100s later suppression decreased which shown in Fig. 3(c). This cell voltage drop corresponds to the FT-IR result in Fig. 3(b). PEG's characteristic peak of rocking vibration mode at $1018cm^{-1}$ is increased to maximum while applying current and peak of PEG binding chlorine ion vibration mode on surface at 1160 and $1241cm^{-1}$ appeared. When PEG is diffused out then this disappear right away. With this method diffusion furthermore *in-situ* FT-IR analyses supports to understand mass transfer limiting part.

Reference

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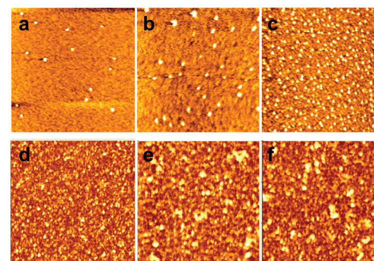

Figure 1. AFM topographic images of specimens electroplated; 30, 50, 100ms respectively to a, b, c and d, e, f with and without PEG inclusion. ($3um^2$)

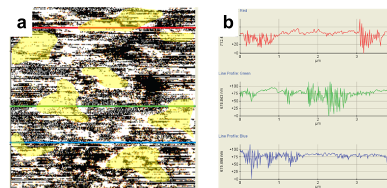

Figure 2. *in-situ* AFM damping oscillation image and line profile.

Table 1. Calculated LFM offset difference

	PEG	PEG + Cl-	Applied Current
forward – backward scan offset difference (V)	0.011	1.761	2.475

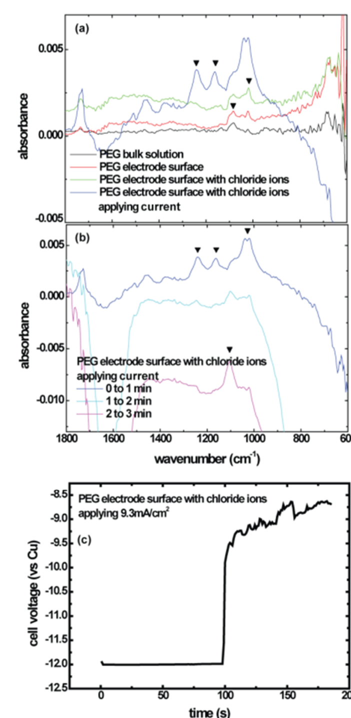

Figure 3. *in-situ* FT-IR spectra measured at various conditions (a), while applying current (b), and Potential transient at 100s in galvanostatic method (c)