Slurry Dependent Variation of Zeta Potential and Open Circuit Potential of Different Metal Surfaces During Chemical Mechanical Planarization

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Chemical Mechanical Planarization(CMP) has become an acceptable enabling technology in the manufacturing of integrated circuits. Due to the increasing use of copper as the interconnect material of choice and tantalum (and in some cases tungsten) as the barrier metals of choice, almost all the commercially available (or under development) slurries for CMP are tailored for the removal of these metals.

Any conducting metal in an electrolyte solution always forms an electrochemical interface between the metal surface and solution surface facing the metal. This interface is associated with an electrochemical potential difference called Open Circuit Potential(OCP) or Free Corrosion Potential which is always in a state of dynamic equilibrium. In colloidal solutions containing particles, there is another kind of electrochemical potential which is developed at the slip plane or the outer Helmholtz plane facing the bulk of the electrolyte and responsible for the stability of the colloids. This is called Zeta Potential(ZP)

Usually, the Copper CMP process is performed in two steps. In the first step, a slurry or reactive liquid is used to planarize and remove excess copper from the wafer surface. When the excess copper from the wafer surface is removed, another slurry is used to remove the barrier metal layer. Due to the different chemical and mechanical nature of different metal surfaces, it is necessary to have different chemical formulations for these 2 slurries and their pH also varies from acidic to alkaline region. It is therefore necessary to understand the effect of different slurries on the ZP as well as the OCP of these metals. At the transition time between first and second steps, situations occur when copper and the barrier metal form galvanic couple in the CMP slurries. Further, zeta potential measurements without the presence of the metals of interest in the slurry differ from the zeta potentials in the presence of the metal surface of interest in the slurry.

In this paper, the experimental results are presented of the simultaneous measurements of ZP and OCP of Cu, Ta and W in three different CMP slurries with pH varied from 3 to 10. The slurries are either commercially available or are under development. All the data were recorded at room temperature with the working electrode rotating at 50 rpm. A rotating disc electrode assembly from Radiometer Analytical was used along with Voltalab 10 potentiostat for all the electrochemical measurements. For zeta potential measurements, ESA-9800 from MATEC Applied Sciences was used. This instrument is based on the Electrokinetic Sonic Analysis, allowing the measurement of ZP without sample dilution.

Figures 1 & 2, show the effects of different metals and pH on the ZP and OCP. It is important to note that thermodynamically speaking, the slurries used here show favorable conditions for the purposes they are formulated. As shown in **Table 1**, at pH 3 (corresponding to the first step slurry), Cu is thermodynamically active to Ta and W. This means that when the galvanic couple forms, Ta or W as barrier metal will not be etched electrochemically. On the other hand, in the slurries with pH 8 and 10 (both correspond to different second step slurries), Cu is noble to Ta and W. Therefore, during the second step polishing, Cu will not be etched away electrochemically. The variation of ZP from positive to negative values are in agreement with the pH values changing from acidic to alkaline domain. Further thermodynamic implications will be presented during the symposium. The electrochemical corrosion rates of all the working electrodes will be presented at the symposium. This will show the extremely low and insignificant corrosion current densities of the metals when they would act as active metals in their respective situations.

Figure 1. Metal and pH Dependence of Zeta Potential

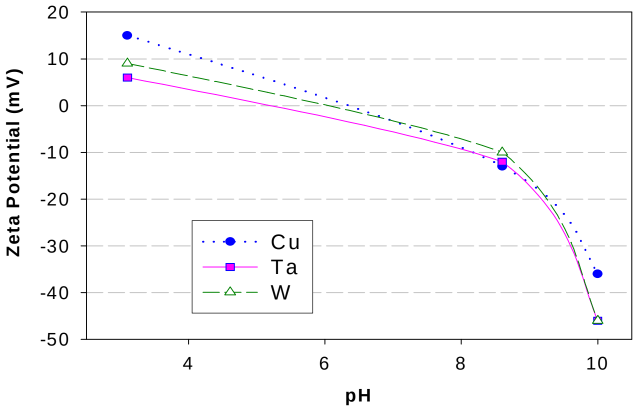

Figure 2. Metal and pH Dependance of Open Circuit Potential

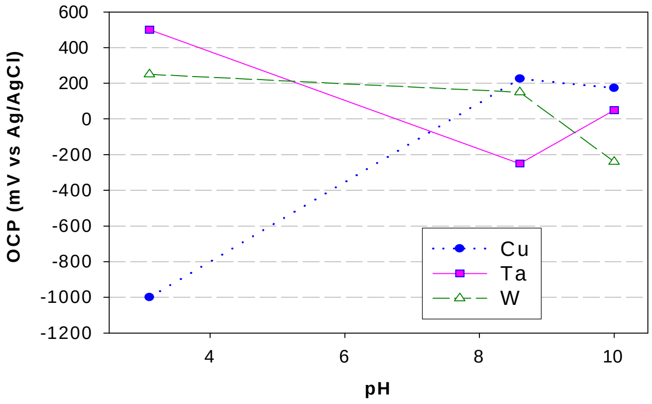

Table 1: Variation of OCP and ZP for Different Metals in Various Slurries

Slurry pH	ZP (mV)	OCP (mV vs Ag/AgCl)	Metal
3.1	15	-1000	Cu
	6	500	Ta
	9	250	W
8.6	-13	225	Cu
	-12	-250	Ta
	-10	150	W
10	-36	173	Cu
	-46	50	Ta
	-46	-240	W