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Towards an atomistic understanding of the activation of plating additives at the copper/electrolyte interface

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Additives are crucial ingredients of electroplating formulations used for the on-chip metallization of vias and trenches.
Polymeric and monomeric additives dissolved into these solutions are often only the precursors of the accelerating or suppressing ensembles being active at the interface. Activation of these additives is often required in terms of a secondary process that is superimposed on the primary copper deposition reaction.
A common way to gain deeper insights into the atomic-scale mechanism of these activation processes is to make use of single crystalline model substrates. These allow the use of scanning probe techniques that provide high spatial resolution. In particular those activation steps that involve surface reactions are worth to be studied with in-situ STM.
One of the key steps in the course of the superfill of vias and trenches is the activation of the so-called accelerator. SPS (bis-(3-sulfopropyl)disulfide) typically serves as specific antagonist for the PEG based suppressor ensembles. Dimeric SPS needs to be activated on the metallic copper surface by dissociation thus producing monomeric MPS (mercaptopropane sulfonic acid) units that are considered as the active anti-suppressing or accelerating species. Due to the high concentration of sulfate anions and trace amounts of chloride anions in the plating formulations the SPS needs to compete with these strongly adsorbing species for surface sites on the copper. Various STM studies [1-5] reported in particular on the barrier properties of those anionic chemisorption layers that are capable to significantly slow down the SPS activation. In contrast to that we will demonstrate that SPS dissociation on the bare copper surface occurs almost barrierless.
In this contribution we will review the current status of this SPS activation mechanism.
We will demonstrate that the rate of SPS dissociation and the lateral ordering of the formed MPS strongly depends on the nature of the co-adsorbed anion and the crystallographic orientation of the underlying substrate.
On Cu(111) modified by a sulfate/water co-adsorption layer we observe a slow SPS dissociation preferentially taking place at defect sites such as step edges while the (111) terraces remains largely resistant towards SPS dissociation. An intermixing of the pre-adsorbed sulfate anions and the formed MPS does not take place. Instead we observe a clear phase separation and the co-existence of the sulfate/water phase and a laterally disordered MPS phase.
This situation completely changes when chloride is pre-adsorbed on the copper. Here the SPS dissociation takes place preferentially on terraces and more specifically at defect sites in the 2D chloride matrix while the step edges appear less reactive. In contrast to the sulfate modified Cu(111) the MPS forms characteristic co-adsorption phases in the presence of chloride. Their lateral ordering can be best studied when using Cu(100) as model substrate since most of these mixed MPS/chloride co-adsorption layers are laterally well ordered. In particular the pre-adsorbed $c(2 \times 2)$-layer on Cu(100) with chloride residing in the fourfold hollows has to be considered as an effective barrier with respect to the SPS dissociation. Chloride can be much faster displaced by the formed MPS on Cu(111) where the chloride forms uniaxially incommensurate phases with individual chloride anions residing not only in the threefold hollows but also in energetically less favorable bridge and interstitial surface sites.
In general the SPS dissociation can be accelerated by creating defect sites in the 2D chloride matrices. One way of creating point defects is to initiate copper deposition or dissolution processes that involve anion desorption/re-adsorption dynamics. An alternative approach would be to reduce the chloride surface concentration by lowering the potential.
Not only is the SPS/MPS capable to partially displace the pre-adsorbed halide from the copper surface. Also the chloride is capable to partially displace the pre-adsorbed MPS from the surface thus proving a certain (quasi)reversibility in the MPS/chloride surface interaction. Our findings clearly demonstrate that the MPS is not irreversibly adsorbed on copper. The MPS/Cl ratio at the surface can be controlled and fine-tuned by the particular SPS/Cl concentration in the bulk electrolyte.
In this contribution we will pay attention to certain contaminants that appear in particular in the SPS containing electrolytes.
Sulfide-like surface phases appear on both Cu(100) and Cu(111) surfaces after extended exposure to the SPS containing electrolytes. Surface corrosion in conjunction with Cu(I)sulfide surface precipitation might even occur under certain experimental conditions. We will discuss the origin of these undesired parasitic reactions.

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