the nucleation delay, and increases the density of thin copper films. If the rate-limiting step of the disproportionation reaction is the separation of the VTMS ligand from the precursor, then the role of water can be that of the catalyst that destabilizes the bond between Cu(hfac) and VTMS and helps accelerate their separation leading to increased deposition rates. Alternatively, water may react in the gas phase with the precursor to form an intermediate species which exhibits a higher conversion efficiency to copper metal. In the second regime (high P_{water} levels) the addition of water vapor substantially increases the film resistivity and introduces oxygen to the bulk of the films. This suggests that, in this regime, a chemical reaction is present which operates either on the substrate surface or in the gas phase and leads to oxygen incorporation, possibly in the form of copper oxide. Further work is necessary in order to determine the degree to which the oxidation reaction is present in the first regime.

The selective deposition of copper films from Cu(hfac)VTMS and HMDS is in a preliminary stage, but some general conclusions can be drawn about the viability of a selective deposition process for copper. As demonstrated in the section on Sample Preparation and Deposition, the presence of unpassivated hydroxyls is not the only mechanism by which selectivity can be lost. Previous processing steps can also provide nucleation centers which may lead to selectivity loss. An effective wafer cleaning process which removes process induced nucleation centers is very critical. This work shows that an appropriate cleaning process depends on the type of seed metal used to activate the disproportionation reaction. For example, the cleaning process which we found effective with tungsten, does not work with titanium or aluminum seed metal. For similar reasons (i.e., loss of selectivity due to extraneous introduction of nucleation centers) we suspect that the cleanliness of the deposition chamber will play a significant role in the maintenance of a selective process.

In conclusion, a blanket copper deposition process was developed from mixtures of Cu(hfac)VTMS and water vapor. At low concentrations, water vapor increased the deposition rate and reduced the nucleation delay without degrading the film resistivity, but under excess water conditions there was substantial increase in the film resistivity and increased surface roughness. The impurity levels in the bulk of the films deposited under optimum water vapor conditions were below the Auger sensitivity limit, but oxygen was detected in films deposited under excess water vapor concentrations. In addition, a selective deposition process was demonstrated through the passivation of silicon dioxide nucleation centers by the addition of HMDS. Deposition rates as high as 1,200 Å/min were obtained. Before a selective copper process can become a serious candidate for the deposition of copper films, however, additional progress in the development of effective preclean procedures is required.

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