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### **Development of Supercritical Processing in BEOL Cleans**

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Supercritical CO<sub>2</sub>-based (SC-CO<sub>2</sub>) processing permits rapid mass transport, high penetration capability into pores and narrow features, low reagent concentrations, and an environmentally benign alternative to current back end cleans—key issues in future semiconductor technology nodes. Because of these assets, supercritical processing is a candidate for a number of semiconductor cleans applications such as plasma damage repair, pore sealing, photoresist/BARC removal and metal deposition. Plasma processing of porous low-k films often remove surface layers and hydrophobic functional groups (creating silanol (Si-OH) species), densify near-surface layers, and increase dielectric constants. Further, this damaged region is vulnerable to additional thickness losses during wet etch. Supercritical silylation reactions (e.g., SC-CO<sub>2</sub> + hexamethyldisilazane (HMDS)) have been shown to react with post-plasma silanols replacing some fraction of the lost hydrophobic groups, thus, repairing the dielectric constant. We have examined the depth of reactant penetration into the low-k and the fraction of silylated silanols as functions of temperature, pressure, pore size, and silylating agent (e.g., HMDS and alkylchlorosilanes). In addition, we have detailed the effect of heat treatments on pre- and post-silylated silanols, and the impact of these heat treatments on film dielectric constants. Recent efforts have shown that supercritical silylation reactions protect plasma-damaged regions from wet etch losses and prevent intrusion of metal species into low-k pores. We have examined damage protection as functions of ashing conditions, silylating agents, and wet etch conditions. Pore sealing has been studied as functions of silylating agent, heat treatment, and penetrant species.