Fluorocarbon Film and Residue Removal Using Super-critical CO_2 Mixtures

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Integrated circuit (IC) manufacture involves numerous resist removal and surface cleaning steps. The efficiency of these processes ultimately affects the yield and reliability of the ICs. Some of these critical cleaning steps involve removal of fluorocarbon films such as fluorinated resist layers, and etch residues from fluorine-containing etch processes. Fluorine-containing gases, such as C_2F_6 and CHF_3 are used to etch inter-metal dielectric layers such as SiO_2. During these processes, the photoresist materials that serve as etch masks are bombarded by energetic ions, neutrals, and photons, thus forming a highly cross-linked surface layer with C-C and CF_x linkages. During pattern etching, the feature bottom and the feature sidewalls are coated with fluorocarbon films. These films must be removed completely to reduce contact resistance and eliminate metal corrosion.

Traditionally, photoresist films are ‘ashed’ in oxygen-containing plasmas. However, the ash step is generally followed by a liquid cleaning step to ensure complete residue removal; etch residues are removed using liquid solvents such as hydroxylamine. However, these solvents may corrode metals and may pose disposal problems. Furthermore, a de-ionized (DI) water rinse is normally used after liquid cleaning steps, and the rinse is subsequently followed by a drying step. An improved alternative to this multi-step process is a single step, dry process compatible with cluster tooling.

We are investigating the use of super-critical CO_2 ($SCCO_2$) as an alternative approach to remove these fluorocarbon/photoresist films and etch residues. $SCCO_2$ has good transport properties (high diffusivity, low surface tension) similar to gases, and solvent properties (high density) similar to liquids. $SCCO_2$ is also a good solvent for fluorine-containing materials. The films investigated in this study were 0.6μm thick photoresist films that served as etch masks during a fluorocarbon-based plasma etch process. The highly cross-linked crust on the resist surface must be attacked chemically in order to ensure adequate removal. Therefore, we have added co-solvents and other additives to enhance the polarity of $SCCO_2$, improve the solvent strength, and facilitate chemical attack in addition to promoting physical dissolution of films and residues. By tailoring the temperature, pressure, and mass fractions of the additives, we were able to obtain effective removal of these layers. Film samples were analyzed by x-ray photoelectron spectroscopy (XPS). A good correlation was obtained between the atomic composition as measured by XPS and the extent of removal as observed in scanning electron micrographs (SEM) of the film surfaces and cross-sections. In this paper, we report the effect of temperature, pressure, and mixture composition on the removal efficiency of post-etch photoresist and fluorocarbon films/residues.