SUPERCRITICAL CARBON DIOXIDE: THE NEXT GENERATION SOLVENT FOR SEMICONDUCTOR WAFER CLEANING TECHNOLOGY

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Abstract: In this paper, we report on the removal of photoresist, post-etch process residues and particles for various patterned semiconductor wafers using supercritical carbon dioxide (SCCO2)/chemical modifier formulations. Optimization of the chemical formulations was determined using data obtained from statistical analysis and designed experiments. Characterization of the processed samples via scanning electron microscopy (SEM), optical microscopy and fourier transform infrared spectroscopy (FTIR) revealed that process conditions and chemical derivatization are important to cleaning patterned wafers. The results of our investigations illustrate the potential of SCCO2 as a viable cleaning technology for next-generation integrated circuits.

INTRODUCTION

The importance of clean surfaces throughout the various stages of semiconductor wafer processing, from front-end transistors to back-end interconnects, has driven substantial research efforts in the microelectronic device industry since the 1950s. However, the semiconductor "boom" of the 1990s, along with the increased complexity of multi-layered thin film devices, has increased the demands for the methods used during the fabrication process. Modern integrated electronics would not be possible without robust technologies for cleaning and contamination control, further reducing contamination of the semiconductor device. Wafer cleaning is the most frequently repeated step in IC manufacturing and is one of the most important segments in the semiconductor-equipment business. It has been stated that for 0.18-micron design rules, 80 out of ~ 400 total steps are related to cleaning. As a result, the semiconductor industry has developed a process formulation for photoresist and residue removal on next-generation semiconductor devices, specifically for copper interconnect schemes. However, as critical dimensions become small, it is difficult to remove residues from the patterned wafers containing high aspect ratio trenches and vias. Thus, conventional wet-cleaning methods begin to suffer limitations, as critical dimensions decrease below 100 nm due to the high surface tension of water in the cleaning solution. Moreover, aqueous cleans can strongly influence porous low-k dielectric properties, such as the dielectric constant, mechanical strength, moisture uptake, coefficient of thermal expansion, and adhesion to different substrates.

Supercritical carbon dioxide provides an alternative method for cleaning integrated circuits. SCCO2 has the characteristics of both a liquid and a gas. Like a gas, it diffuses rapidly, has low viscosity, near zero surface tension, and thus, penetrates easily into deep trenches and vias allowing more effective cleaning. Like a liquid, it dissolves other chemicals, such as alcohols, forming a homogenous supercritical fluid solution. However, SCCO2 is non-polar and thus will not solubilize many species, including inorganic salts and polar organic compounds that are usually necessary for efficient cleaning, therefore co-solvents such as alcohols were added to the SCCO2 to increase the solubility of these species. Thus, SCCO2 technology has been recognized as a viable cleaning alternative satisfying the environmental and safety requirements of next-generation manufacturing technologies [1, 2]. In addition, it presents a cost-effective cleaning technology since it requires only supercritical CO2 and a small amount of chemical additives (< 10 wt % total in SCCO2) to effectively clean high aspect ratio vias/trenches and low-K dielectric films [3].

In close collaboration with SC Fluids, one of the leading developers of commercial equipment that employs Supercritical Fluid technology for IC fabrication, we have successfully demonstrated the utility of this technology and scalability to 300 mm wafer processing. Herein, we present data supporting: (1) the removal of Si_3N_4 particles from Si/SiO_2 patterned surfaces; (2) the removal of aluminum post-etch residues, and (3) the removal of non-implant and ion-implant photoresist on aluminum and silicon layers, respectively. Fourier transform infrared spectroscopy (FTIR), optical emission spectroscopy (OES), and scanning electron microscopy (SEM) data provides insight towards the optimization of SCCO2/chemical additive cleaning formulations for aluminum post-etch residue removal, photoresist removal, and particle removal.

I - MATERIALS AND METHODS

Figure 1 shows a schematic diagram of the high-pressure system designed to study the feasibility of supercritical CO_2 cleaning the surfaces of patterned aluminum wafers. The system is composed mainly of: (1) two high-pressure 316 stainless steel vessels, one serving as a dynamic mixer/mass exchanger (MIX) while the second is the wafer cleaning chamber (WCC). (2) A high-pressure gas booster (GB) to maintain a constant flow and/or pressure of the supercritical fluid, and (3) an HPLC sample pump (SP) to deliver the co-solvent/chemical modifier solutions to the mass exchanger.

In a typical cleaning experiment, an uncleaned sample wafer (20 × 20 mm) was loaded into a 1.5 in. ID stainless steel wafer cleaning chamber (total volume 25 mL). High purity carbon dioxide (99.999%; Tech Air) from a gas cylinder is fed through a gas booster and subsequently chilled through a cooling cylinder (CC) to insure that the CO_2 is undercooled and can be easily compressed by the high-pressure CO_2 pump (CP) before introduction into the CO_2 heater.

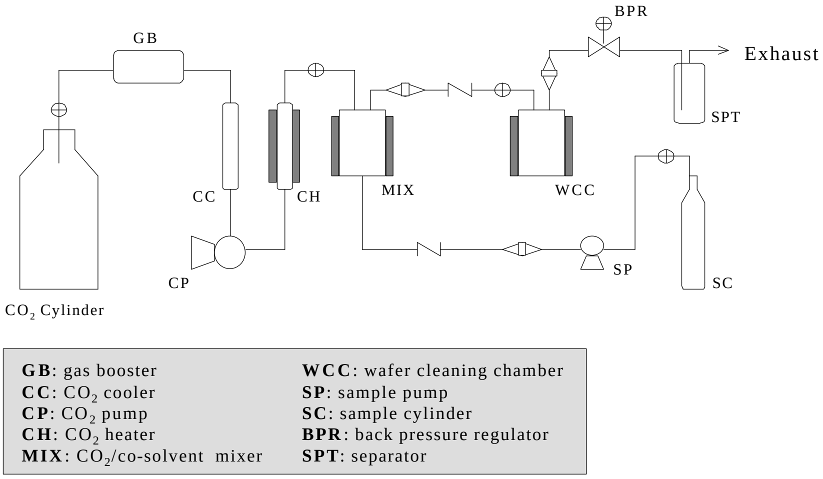


Figure 1. Schematic diagram of the continuous flow SCCO2 cleaning apparatus used in these studies.

The heated CO_2 and co-solvent are then delivered to the mixing chamber (MIX) via separate delivery lines and dynamically mixed before being transferred to the wafer-cleaning chamber (WCC). In the cleaning chamber, the pressure is adjusted by a back-pressure regulator (BPR) to the desired level and controlled to within 20 psi. The CO_2 heater, mixer and cleaning chamber are heated by heating tapes, which are controlled by a multi-loop temperature controller and provide a stable temperature to within ± 1 °C. In addition, each pressurized vessel is equipped with a pressure transducer to monitor the pressure inside the vessel. After cleaning was complete, the $SCCO_2$/chemical solution was purged from each individual chamber separately, as to not contaminate the processed wafer from chemical remaining in the mass exchanger, and vented into a high pressure trap to collect any residual chemicals and/or wafer residue during the phase separation induced by the venting process.

II - RESULTS AND DISCUSSIONS

IIA - Silicon Nitride Particle Removal from Patterned Silicon/Silicon Dioxide Surfaces

The effectiveness of SCCO2 for the removal of surface particles, specifically silicon nitride particles deposited on a patterned silicon dioxide/silicon wafer, was investigated. Novel cleaning formulations were explored and resulted in 100% removal of these particles from the wafer surface. The samples were first processed using pure SCCO2 at 50 °C and 4400 psi, and although the velocity of the flow rate (50 mL/min) removed some of the particles, it was ineffective at completely removing the contaminate particles. After screening several different chemical additives and surfactants, and combinations thereof, we determined that a multi-component cleaning formulation was necessary to clean both the oxidized and non-oxidized areas of the wafer surface (left), with little etching of the underlying layers. Figure 1 shows the SiN contaminated control wafer along with the SCCO2 processed wafer (right), and clearly illustrates that the cleaning solution resulted in nearly 100% removal of the SiN particles. The multi-component cleaning solution consisted of a SiN etchant and surface passivation additives for both the silicon and silicon dioxide layers. Each additive (surfactant) indirectly aided in particle removal by competing with the van der Waals forces responsible for the adhesion of these particles to the wafer surfaces. Thickness measurements were taken before and after processing; silicon and silicon dioxide etch rates as low as 2 Å/min were obtained.

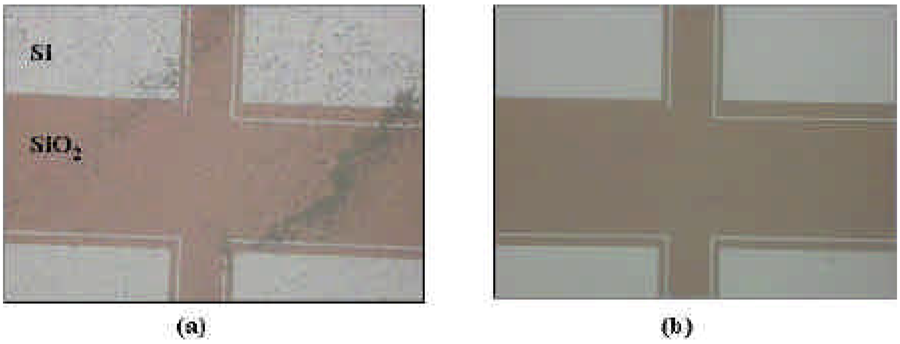
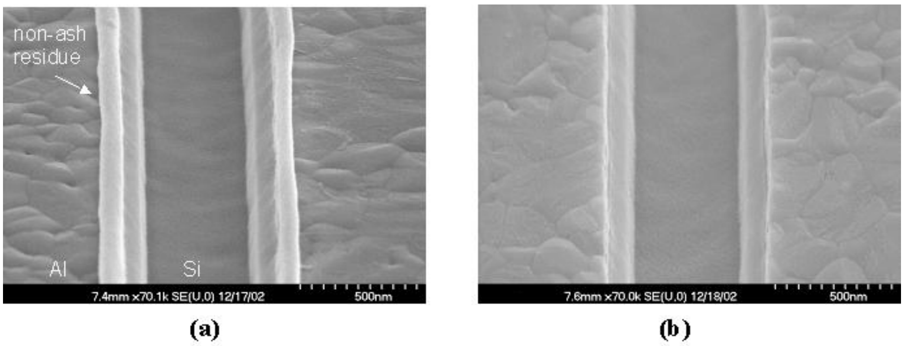


Figure 2. Optical microscope photos of (a) SiN particle control wafer, and wafer processed using (b) a $SCCO_2$ cleaning solution containing a fluorinated surfactant, SiN etchant and silicon dioxide passivator.

IIB - Ashed and Non-Ashed Aluminum Post-Etch Residue Removal

Photolithography is widely used for defining patterns in multi-layered thin films on a silicon wafer. A light sensitive polymer is UV exposed through a mask to induce regions of varying solubility. After aqueous development of the mask image, reactive ion etching (RIE) is used to transfer the pattern to under-lying layers. The etching process usually results in the formation of a tough, carbonized crust that protects the underlying bulk photoresist. Currently, removal is achieved by employing wet processes that result in polluting waste streams. Therefore, conventional methods of cleaning typically employ an oxygen-plasma ash, often in combination with halogen gases, to penetrate the crust and remove the photoresist. Unfortunately, plasma ashing oxidizes the metal interconnect and dielectric layers, leaving an inorganic residue that may contain stable oxides and halides of the underlying layer constituents. Plasma ashing usually requires a follow-up wet-clean to remove the residues and non-volatile contaminants that remain. We have demonstrated, however, that SCCO2 cleaning has the capability to remove the post-etch residue in a single step, while incorporating short process times and consuming only small amounts of chemical additives.

A SCCO2 cleaning formulation for the removal of aluminum post-etch residues is a multi-component system that quickly and efficiently removes post-etch residue. The SCCO2 formulation consists of a SCCO2 soluble co-solvent, fluoride and hydroxyl-containing additives for etch residue removal and a corrosion inhibitor for aluminum. Figure 2a shows the SEM image of the sample with post-etch residues before cleaning while Figure 2b shows the same wafer after SCCO2 cleaning. The sidewall residue is completely removed with minimal impact on critical dimensions of metal lines and trenches, and without corrosion of the Al conductors.



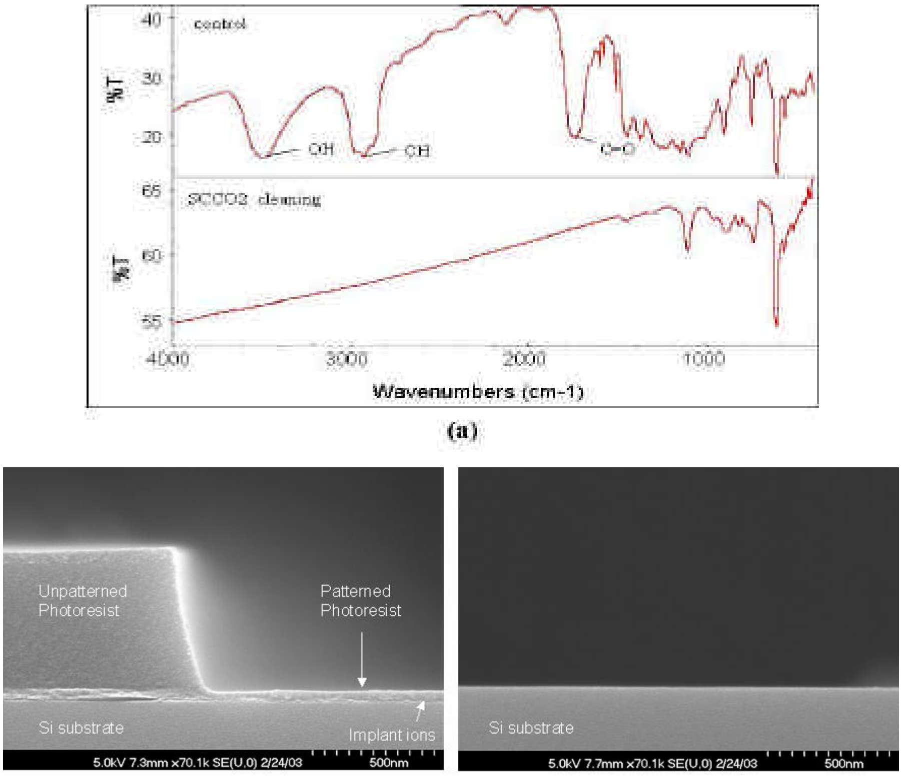
(a) (b)

Figure 3. SEM images of the samples with post-etch residues (a) before cleaning and (b) after SCCO2 cleaning. Formulation included SCCO2, co-solvent and additives processed at 50 ºC, 4000 psi for 120 seconds.

IIC - Photoresist and Ion-Implanted Photoresist Removal

The complete removal of polymeric photoresist, that was exposed to deep UV light and/or to high-dose ion implant, is usually a problem for conventional stripping and cleaning methods. High-dose ion implantation treatment results in the formation of a tough, carbonized crust that inhibits removal of the underlying bulk photoresist from the wafer. SCCO2 cleaning solutions can effectively penetrate, swell, dissolve and subsequently remove the photoresist without damaging the underlying structure. For non-implanted photoresist removal, co-solvents were experimentally determined to be the most efficient additives for processing. Figure 4a shows the FTIR spectra taken before and after SCCO2 processing at 35 °C and 4000 psi for 2 minutes for the non-implant photoresist. The FTIR illustrates the disappearance of the characteristic bands associated with organic polymers (i.e. -CH, -OH, C=O, etc.), indicating that the photoresist was completely removed under these process conditions.

Co-solvents alone proved to be ineffective for removing the ion-implanted photoresist. However, we have demonstrated that the addition of small amounts of soluble additives can remove ion-implant hardened photoresist from patterned aluminum films. A fluoride-containing additive was added to the co-solvent to extract the ion-implanted constituents via reaction with the implanted cations, thereby forming SCCO2-soluble species that aid in the dissolution of the photoresist. Figure 4b shows the SEM image of the control wafer, while Figure 4c shows the same wafer after processing for 2 minutes in an SCCO2/co-solvent formulation at 55 °C and 4000 psi. The SEM image clearly shows that the ion-implanted photoresist is efficiently removed with no etching of the silicon substrate.



(a)

(b) (c)

Figure 4. FTIR spectrum of (a) control and post-SCCO2 processed sample at 35°C, showing complete photoresist removal and (b) SEM photo of a 650 nm thick ion-implanted photoresist control wafer and (c) the same wafer after SCCO2 processing for 2 minutes at 55°C.

CONCLUSIONS

Optimized chemical formulations were determined for photoresist stripping, post-etch residue and Si_3N_4 particle removal while completely maintaining the structural integrity of the wafer structure. Our investigations reveal that reactant concentration, molar ratio of chemical additives, process time and pressure are critical for optimal cleaning efficiency. In some cases, it was proven beneficial to incorporate additives to the formulation to prevent etching of the aluminum and silicon surfaces. In addition, we were successful in performing these experiments on both R&D bench-top reactors as well as a 200 mm tool for large scale semiconductor processing. Lastly, several different methods to control various response factors such as etch rate and cleaning efficiency during cleaning can be monitored and optimized.

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