Steam-Injected SPM Process for All-Wet Stripping of Implanted Photoresist

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Introduction

Photoresist stripping in IC manufacturing has become more challenging as the number of photoresist levels has increased while at the same time allowable material loss and surface damage has decreased. Heavily implanted photoresist is especially challenging due to the dehydrogenated, amorphous carbon layer that forms on the surface [1]. To facilitate implanted photoresist removal, this layer can be attacked by physical processes such as ion bombardment as part of the common dry ashing approach. However, these physical approaches can lead to surface damage and increased material loss. Another approach is to increase the reactivity of the sulfuric acid – hydrogen peroxide mixture (SPM), so that it can penetrate and dissolve the amorphous carbon layer and achieve complete photoresist removal.

Temperature is a key process variable for achieving a fast and aggressive all-wet photoresist strip process. Batch immersion tools typically operate at ~110-150 °C to limit the breakdown rate of the H_2O_2. Single pass (or "fresh dispense") systems are not limited by the breakdown of H_2O_2, but are limited instead by the temperature limits of the fluoropolymer components of construction, typically 150-180 °C. Single pass systems are further able to increase SPM temperature by using point-of-use (POU) mixing. In POU mixing systems, the heat of mixing (ΔH_{solv}) of H_2SO_4 with H_2O_2/H_2O can be used to increase SPM temperature near the wafer surface, thereby limiting the temperature experienced by the process hardware. This enables on-wafer temperatures of up to approximately 200 °C. Unfortunately, the chemical activity of the SPM solution decreases as the H_2SO_4 is diluted by the water contained in the H_2O_2 solution.

In order to overcome the limitations of standard POU SPM mixing techniques to achieve higher on-wafer temperature, a new approach has been developed. By injecting steam into the process environment, on-wafer temperature is greatly enhanced without excess dilution, thereby achieving maximum implanted photoresist stripping capability [2].

Experimental Procedure

The equipment used in this work includes batch spray and single-wafer spray systems capable of processing 300mm wafers. Chemicals are heated and mixed before dispensing them into the chamber. In order to prevent degradation of H_2O_2, and to achieve maximum mixing temperature, H_2O_2 is mixed with H_2SO_4 after the H_2SO_4 is heated. In this work, the H_2SO_4 is heated to 150 °C. Either saturated or dry steam can be added to the process chamber. Wafer surface temperature is measured using temperature indicator strips attached to the wafer and protected by a thin glass plate. The new process was tested by treating a variety of patterned and unpatterned photoresist wafers with different levels and types of ion implantation.

Results

The batch spray steam-injected SPM process has been implemented on the FSI ZETA® batch spray system in DRAM manufacturing for removal of photoresist exposed to very high dose, ~$1x10^{17}$ ions/cm^2, BF_3 plasma immersion ion implantation (also known as plasma doping or "PLAD") [3,4]. This high-dose boron implantation process is used in the formation of dual-doped polysilicon gates (DPG) to counter-dope the phosphorous in-situ-doped polysilicon. The use of counter-doping is driven by the need to deposit n-doped polysilicon for the DRAM recessed channel array NMOS transistor [5]. However, the PMOS transistors in the I/O circuitry work much better with a p-doped polysilicon gate. Therefore, boron counterdoping is required to change the polysilicon over the PMOS transistors to a p-doped state.

If standard ashing is used after the PLAD process, a three step, wet-ash-wet process is required for complete removal of the photoresist mask. However, the steam-injected SPM process is able to completely remove the photoresist and residues in a single process [4], including the most difficult residue located at the border of the edge bead removal region. As previously reported, this "edge bead" residue can require up to two times longer for removal than the central, patterned areas of the wafer [6]. Use of the steam-injected SPM process has shown a 50% reduction in polysilicon loss and a 30% reduction in dopant loss compared to the wet-ash-wet process. Recent improvements of the steam-injected batch spray process have resulted in very low, very uniform material loss as shown in Table 1. These results show that $1x10^{15}$ ions/cm^2 40 keV As implanted patterned photoresist can be stripped with less than 0.9 Å of thermal oxide loss while patterned photoresist exposed to $5x10^{14}$ ions/cm^2 40 keV As implantation can be stripped with less than 0.2 Å of thermal oxide loss. In addition, patterned resist exposed to $3x10^{16}$ ions/cm^2 BF_3 plasma doping (PLAD) is also stripped with less than 0.2 Å of thermal oxide loss

Table 1. Photoresist strip time and average thermal oxide loss using batch-spray steam-injected system.

Dose (ion/cm^2)	Energy & species	SPM time (min)	oxide loss (Å)
$5x10^{14}$	40keV As	4	<0.2
$3x10^{16}$	7keV BF_3 (PLAD)	4	<0.2
$1x10^{15}$	40keV As	15	<0.7

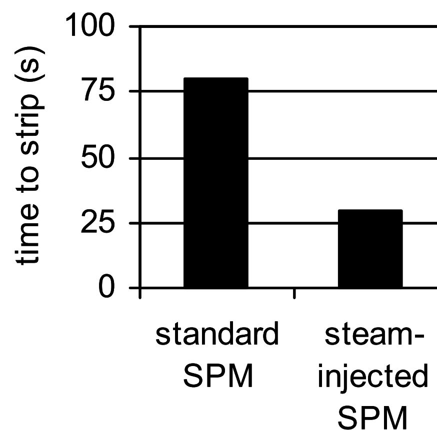

Figure 1. Time to strip patterned photoresist exposed to $5x10^{14}$ ions/cm^2 40keV As implant using single-wafer steam-injected system.

The single-wafer steam-injected SPM process [7] has been demonstrated on the FSI ORION® Single Wafer Cleaning Platform. Figure 1 shows a comparison of the stripping time for a $5x10^{14}$ ions/cm^2 40 keV As implanted patterned photoresist. The single-wafer steam-injected SPM process clears this resist in 30 seconds, including the edge bead residue. The improved process performance achieved with steam injection reduces the single-wafer SPM process time by more than 60%.

Discussion

As H_2O is mixed with H_2SO_4, energy is released as the water molecules form hydration shells around the SO_4^{--} and H^+ ions. The energy released during mixing causes the temperature of the mixture to increase. A temperature rise of as much as 100 °C is possible when mixing 20 °C water and sulfuric acid in the right proportions [3].

The temperature increase generated through water addition from 30%H_2O_2/70%H_2O is key to a fresh-dispense SPM strip process; however it does result in some undesired consequences. The first and most obvious downside is the dilution of the chemistry. The reactivity of an SPM solution drops rapidly with increasing water content. The most desirable SPM process has both a high temperature and concentrated chemistry. In practice, however, optimizing the SPM blend ratio in a conventional process requires a compromise between higher H_2SO_4 concentration and higher POU mixing temperature.

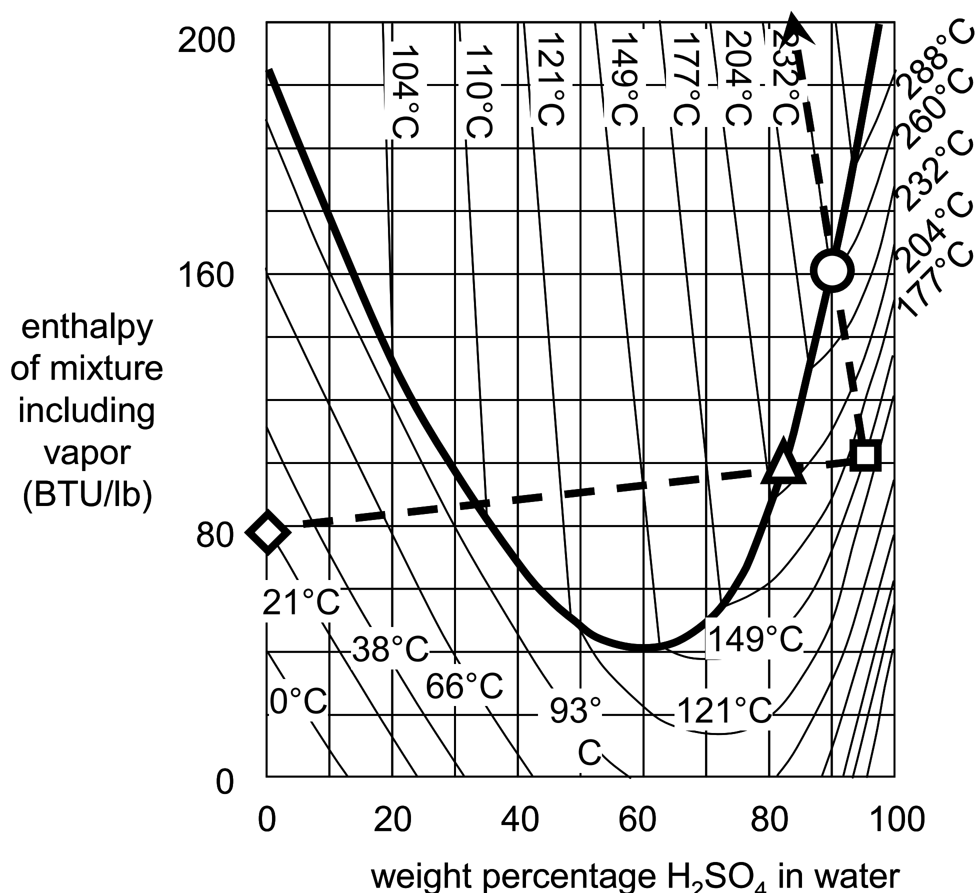

Figure 2. Enthalpy-concentration diagram for aqueous sulfuric acid showing the difference between mixing liquid water (◊-△-□) and steam (○-□) with suluric acid [8].

The novel steam injection process largely eliminates this compromise. The SPM blend ratio can be adjusted to optimize the concentration, while the desired temperature rise is accomplished through steam injection with very little dilution effect. The key to this process is the fact that steam carries a tremendous amount of energy: the heat of vaporization of steam is 2.26 kJ/g, five times greater than the 0.42 kJ/g needed to heat water from 0 °C to 100 °C. This energy is released when the

steam dissolves into the SPM mixture on the wafer surface. Because the steam carries so much energy, relatively little is needed to produce a substantial temperature increase in the SPM, and very little dilution occurs. The enthalpy-concentration diagram for aqueous sulfuric acid, shown in Figure 2, is a convenient way to see the differences between mixing water or steam with sulfuric acid. The square symbol (□) shows the pre-heated, 150 °C state of concentrated sulfuric acid. Adding liquid water at 21 °C will move the mixture along the dashed line towards the point on the left axis representing 0% sulfuric acid at 21 °C (◊). This dashed line intersects the liquid-vapor equilibrium line (dark solid line) at about 210 °C and 82% (△), representing the maximum temperature that can be achieved on the wafer surface. Adding steam to the pre-heated sulfuric acid on the wafer surface will move the mixture along the other dashed line pointing towards the top of the diagram, which ultimately ties to a point on the y-axis at 0% sulfuric acid and 100 °C vapor. This second dashed line intersects the liquid-vapor equilibrium line at about 260 °C and 90% sulfuric acid (○) showing how steam addition provides a higher maximum on-wafer temperature at a higher sulfuric acid concentration.

Summary

A steam-injected SPM process capable of reaching >200 °C on-wafer temperatures has been demonstrated for stripping implanted photoresist. This process has been implemented on both batch spray and single wafer spray platforms. Removal of highly implanted photoresist is demonstrated with less than 1 Å of thermal oxide loss.

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[8] Adapted from *Perry's Chemical Engineer's Handbook*, Figure 2-30, p. 2-303, (1997, McGraw-Hill).