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All Wet Stripping of Implanted Photoresist

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Introduction

Photoresist stripping in IC manufacturing has become more challenging. The number of photoresist levels has increased while the allowable material loss and allowable surface damage has decreased. Heavily implanted photoresist is especially challenging due to the dehydrogenated, amorphous carbon layer that forms on the surface [1]. The carbonized layer can be removed by plasma etching, or can be broken up by physical processes such as ion bombardment or the swelling of the underlying photoresist material. Physical processes, however, tend to leave residues where the carbonized resist contacts the wafer at the edges of features and particularly at the inner boundary of the wafer edge bead removal area. In addition, new plasma-doped (PLAD) implant processes provide very high implant doses and require complicated, multi-step ashing sequences for complete resist stripping. Plasma ashing processes used to strip implanted photoresist tend to oxidize the wafer surface and cause an unacceptable increase in Si material loss in subsequent processing steps. Interest in ash-free, all-wet stripping processes is driven primarily by the desire to reduce surface damage and material loss, but is also by a desire for a simplified stripping process for PLAD implants, and the elimination of a process step for all implants (wet strip/clean vs dry ash followed by a wet clean).

A liquid mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), also known as "piranha" or "SPM", can be used to remove photoresist that is unimplanted or only lightly implanted, up to about $1x10^{14}$ ions/cm^2. When H_2SO_4 is mixed with H_2O_2, monopersulfuric acid (H_2SO_5 or "Caro's acid") is formed. Caro's acid, and to some degree H_2SO_4 itself, breaks down the undamaged carbon polymer chain, eventually forming H_2O and CO_2 reaction products [2]. Caro's acid, however, does not effectively remove heavily carbonized resist.

Fortunately, H_2O_2 and Caro's acid break down to form radicals of $OH^\bullet$ and $HSO_4^\bullet$. These radicals rapidly react with the carbonized layer, but are very short-lived (lifetime ~10^{-6}s,) and so are present at a very low concentrations. Current piranha processes are heated as high as 150°C in order to accelerate radical formation and achieve sufficient reactivity and stripping rates on partially carbonized resists. If we assume Arrhenius behavior, and a radical formation activation energy of 200 kJ/mol, then the radical formation rate (and therefore concentration) will increase by over 400 times with a temperature increase from 150°C to 200°C. The rate of attack by Caro's acid will be similarly increased. While beneficial for stripping, this rapid decay makes 200° C immersion processing impractical. In this work, achievement of freshly mixed chemistries with 200°C on-wafer temperature has enabled the wet stripping of implanted photoresist exposed to doses of over $1x10^{15}$ ions/cm^2.

Achieving Elevated SPM Temperature

Elevated SPM temperatures can be achieved with point-of-use (POU) mixing since the mixing of H_2SO_4 and H_2O_2 is exothermic. Figure 1 shows that a maximum solution temperature of 118°C can be achieved with a 4:3 volume ratio of 98% H_2SO_4 and 30% H_2O_2 SPM mixture, with both chemicals starting at room temperature (98°C rise). If the H_2SO_4 is first heated to 95°C before mixing with H_2O_2, a POU mixture temperature of 150°C can be achieved with the 4:3 volume ratio blend. By preheating the H_2SO_4 to 150°C, a POU mixture temperature near 180°C can be achieved. The actual on-wafer temperatures, however, are limited to well below 150° C due to the thermal mass of the wafers and chamber components, and other heat losses from the chamber. Further, the chemical activity of H_2SO_4 drops rapidly with water dilution. (30% H_2O_2 is 70% H_2O, and the H_2O_2 is converted to H_2O in the decay process.) Increasing the on-wafer temperature at the expense of dilution can cause a net decrease in etch rate. A minimally-diluting heating mechanism is needed.

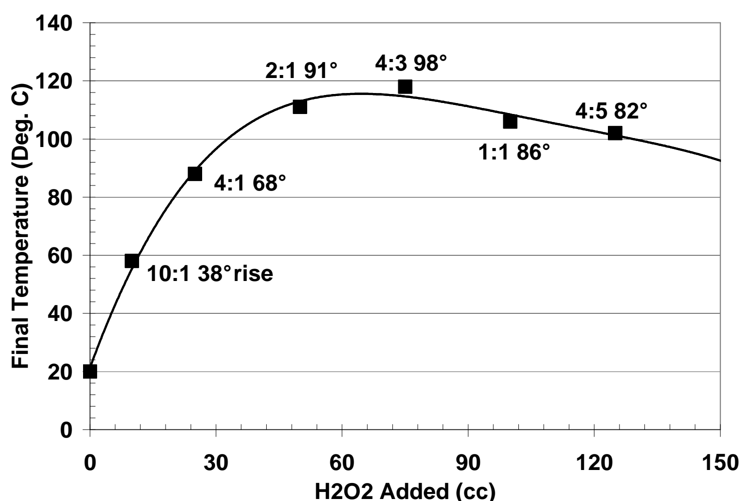

Figure 1: Resulting temperature when 20° C H_2O_2 is mixed with 100 cc of 20° C H_2SO_4.

In this work a high SPM ratio is used to avoid over dilution of the H_2SO_4. The high SPM mixture is mixed at POU using H_2SO_4 pre-heated to 150°C. An additional, a proprietary, in-chamber heating method is used to raise the actual on-wafer temperature to 200° C. Rapid radical production occurs while the fresh solution is in contact with the carbonized layer, so the radicals can react with the carbonized layer before they themselves decompose. The additional heating process also maximizes the on-wafer concentration of Caro's acid, which has a life time of a few seconds at these elevated temperatures.

Experimental Procedure

The equipment used in this work is a commercially available, 300 mm, FSI batch spray system (Figure 2) Twenty-five, 300 mm wafers are held horizontally in each of two PFA process cassettes. The cassettes are placed on a PFA turntable which can be rotated at speeds up to 300 rpm in a nitrogen purged chamber with a sealed lid. Chemicals, rinse water, and nitrogen are dispensed from a central spray post which extends from the

chamber lid, or from a side spray post mounted in the wall of the chamber. Fresh, stock chemicals are mixed and diluted using a mixing manifold or can be mixed in-situ within the chamber. In-line heaters can be used to heat the chemicals before dispensing them into the chamber. In order to prevent premature breakdown of H_2O_2, and to achieve the maximum on-wafer temperature, H_2O_2 can be mixed with H_2SO_4 after the H_2SO_4 is heated. In this work, H_2SO_4 was pre-heated up to 150°C. The maximum wafer surface temperature is measured using temperature indicator strips attached to the wafer and protected by a thin glass plate (TL series from Omega Engineering). The variation of on-wafer temperature with time was inferred from real-time measurements by a probe fixed to the side wall of the chamber. The new process was tested by treating a variety of patterned and unpatterned photoresist layers which had received different levels and types of ion implantation.

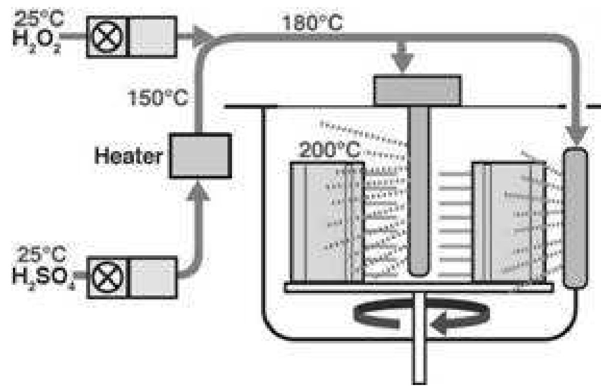

Figure 2: Batch spray process system for new process able to achieve on-wafer temperature of 200°C.

Results and Discussion

Using the on-wafer temperature indicator strips is was found that POU mixing with 95°C preheated sulfuric could produce on-wafer temperatures on 90-100°C. Using 150°C preheated sulfuric and the proprietary in-chamber heating method, on-wafer temperatures of 200°C can be achieved. This much higher on-wafer surface temperature during exposure to the fresh SPM mixture enables removal of highly implanted photoresist.

Table I is a sample of the types of implanted photoresist which could be removed with the new process. Table 1 shows that strip capability is not a simple function of dose. Rather the strip capability is determined by the thickness and degree of carbonization of the layer of carbonized resist. Heavy ions such as arsenic tend to cause more carbonization than do light ions such as boron. High energy implants tend to create thicker carbonized layers. So while a $1x10^{17}$ ions/cm^2, 7 keV boron implant can be stripped (plasma doping or PLAD), a $1x10^{16}$ ions/cm^2, 50 keV phosphorous implant cannot currently be stripped. The effects of implant angle, wafer cooling and implant rate have yet to be explored. There may still be 1 or 2 high-dose/high-energy implant masks that will require at least partial ashing, but over 80% of the implanted photoresist masks can be stripped with this new high-temperature piranha process.

Table 1: Example of types of implanted photoresist that can be removed with the new all-wet process.

Resist type	Resist thickness (Å)	Implant Dose (ions/cm^2)	Implant energy (keV)	Strip time (min)
DUV	7000	$6x10^{15}$	5	3
DUV	7000	$6x10^{13}$	40	3
DUV	12000	$2x10^{13}$	400	5
DUV	12000	$2x10^{13}$	1200	5
DUV	12000	$1x10^{16}$	7	5
DUV	12000	$1x10^{17}$	7	5
DUV	7000	$2.5x10^{14}$	40	5.5
DUV	5000	$1.6x10^{15}$	2	10
DUV	3200	$3x10^{15}$	5	10
DUV	7000	$6x10^{14}$	55	13.5
DUV	7000	$1x10^{15}$	55	13.5

As mentioned previously, a key driver for the implementation of ash-free, all-wet photoresist stripping is the desire for reduced material loss. While piranha mixtures at standard temperatures of ~150°C cause negligible surface etching, we have found that at temperatures of 200°C or higher, piranha mixtures can etch thermal silicon oxide at a rate of 0.1 to 0.2 Å/minute. As with the Si/H_3PO_4 system, water content has some effect. Iler explains the occurence of etching with H_2SO_4 by noting the reaction of silicon with phosphoric acid to create silicon phosphates and "suggests that the sulfate might also exist," since SO_4^{-2} and PO_4^{-3} are similarly shaped [3]. Piranha processes that can strip $1x10^{14}$ ions/cm^2, 40 keV As implanted photoresist result in a negligible SiO_2 loss of less than 0.1 Å. Stripping $1x10^{15}$ ions/cm^2, 40 keV As implanted photoresist the new piranha results in about 0.5-1Å of thermal SiO_2 loss. Integration work indicates that material and dopant loss with the ash-free, all-wet processes is significantly less than that with traditional ash+wet clean processing.

Summary

A new all-wet piranha-based process capable of reaching 200°C on-wafer temperatures has been demonstrated for stripping implanted photoresist. Results indicate that this process should be able to strip over 80% of the implanted photomask levels currently used to produce logic devices, but with material and dopant loss levels superior to traditional ash+wet processes.

References

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