Megasonic Enhanced Photo Resist Removal Using Unique Solvent Free Phase-Fluids on an Advanced Single Wafer Resist Processing System

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In this work the application of a new generation of phase-fluid stripping solutions (intelligent fluid®) to a variety of semiconductor photoresists was studied. The unique water based intelligent fluid formulas used in these experiments were all VLSI grade, copper compatible and non-toxic. The first phase of experiments was to establish if there was a reaction with the photoresist type and intelligent fluid® formula within a reasonable time period, with the most promising combinations carried forward to phase two for in depth study. The follow-on experimental results demonstrate the optimal process parameters through variation of process temperature settings and the additions of megasonic acoustic energy. Photoresist stripping results were quantified though visual inspection and contact angle measurement.

Introduction

Removal of photoresist materials (resist stripping) is very straightforward in theory, but can be difficult and complicated in practice. Classical methods have included SPM (sulfuric peroxide module) /piranha, ozone and UV ozone. Solvent based fluids such as n-methylpyrollidone (NMP), Acetone, Dimethylsulfoxide (DMSO) and Tetramethalammonium (TMAH) have all been applied to this process in various forms and combinations. Typically solvents have been combined with temperature or gases (1) to enhance throughput and reduce the damage caused by swelling in thick PR scenarios. Dynamic dispense systems have also been applied to the standard solvent combinations including aerosol sprays (2) and physical activation of the solvents through acoustic energy (3) to help reduce process times and damage induces through PR film swelling. Many dry and wet dry combinations have been implemented using various Plasma and CO_2 combinations. All of the legacy methods include hazardous and toxic materials and/or high equipment expense as well as multi-step process control complexity. The stripping process becomes even more challenging by factors such as thick resist, cross-linked resist or sensitive metals or materials under the resist. This study was carried out In order to determine feasibility of the use of a unique phase-fluid based photoresist-stripper in commercial semiconductor resist removal process steps. Due to their highly dynamic inner structure, phase-fluids penetrate into the polymer network of photoresists and lift the material from the surface as opposed to the surface or boundary reaction of a solvent solution. (4) As these water-based stripping fluids are non-aggressive, non-toxic, and require no special handling, the ability to apply them to industry standard resists will result in a reduction of toxic and dangerous chemistries and the environmental impact of their disposal.

Theory

This work reflects the combination of two distinct mechanisms applied to the photo resist stripping process, Phase-fluid (intelligent fluid®) and Single Wafer Megasonics.

Phase-Fluid (intelligent fluid®) (4) intelligent fluids® consist of a heterogeneous mixture of two immiscible liquids that form a stable micro-emulsion. There is a balance established between the separation forces that keeps the components of the emulsion in constant motion or shape changing on a nano basis. When this very physically dynamic fluid is exposed to a film such as photo resist, the low surface energy allows for the penetration of very small gaps in the polymer surface, and the eventual forcing of the resist layer from the substrate. The film removal from the substrate is in the form of an actual physical lift-off separation and not a dissolution or etching of the film. Dilution of the Phase-Fluid is not proscribed as the equilibrium of the micro emulsion will become unbalanced and the forces will be neutralized immediately stopping any reaction. The intelligent fluid® formulas have proven to be very robust and stable in both storage time, temperature and shipment.

Single Wafer Megasonic The addition of megasonic range acoustic energy to wet semiconductor processes has been an industry standard for many years. The addition of megasonic acoustic energy at a certain amplitude induces cavitation in the process fluid. The imploding cavitations and subsequent micro shockwave extend the fluid exchange below the conventional surface flow boundary layer. This enables a rapid and uniform exchange of fluid directly at the wafer surface. The initial application of megasonic enhanced processing was targeted to particulate removal as the ability of the cavitation to move micro and nano particles to the macro stream and away from the substrate surface was critical to cleaning performance. Later applications of proximity Megasonics to photo resist and high aspect ratio processes in single wafer configurations added both uniformity and accelerated process times (increased throughput) (5). The rapid exchange of fluid below the conventional boundary layer accelerated the conventional etch/solvent/develop processes by eliminated the diffusion layer leading to much shorter process times and process fluid usage. As the intelligent fluids® act to physically penetrate access to the substrate film interface the additional forces of the cavitation implosions would assist in the exchange of fluid as well as enhancing the the lift-off of the resist layer below the standard boundary layer.

Experimental

Experimental materials Five different photoresist materials were applied to 200mm Semi standard silicon wafers. Table I lists the resists and bake conditions tested in the initial screening process. After the initial screening process two of the photoresist types were eliminated from the test plan due to lack of reaction within 600 seconds, the time limit established as the outside parameter for commercial application.

TABLE I. Initial Photoresist Selection, Thickness and Bake Conditions

Photoresist Type	Film Thickness	Bake Profile
AZ15NXT	9um	No Bake
AZ15NXT	9um	100c/90s
AZ9260	10um	No Bake
SU-8	20um	No Bake
SU-8	20um	180c/60s
JSR THB 151N	50um	No Bake
JSR THB 151N	50um	100c/90s
BCB 4024-40	10um	180c/60s
BCB 4024-40	10um	100c/90s

Table 2 lists the photoresists employed in the balance of this study. They are identified as PR-1 through PR-5. Five different formulations of intelligent fluids® were tested on all photoresist samples and under all process conditions. For the purpose of this study, the intelligent fluids® formulations are identified as if-A through if-E.

TABLE II. Photoresists Selected After Initial Screening

Photoresist Designation	Photoresist Type	Film Thickness
PR-1	AZ15NXT	9um
PR-2	AZ15NXT (with bake)	9um
PR-3	AZ9260	10um
PR-4	JSR THB 151N	50um
PR-5	JSR THB 151N	50um

Experimental setup All testing was carried out in a Bowl Meg process chamber shown in Figure 1. This system incorporates a sapphire megasonic transducer integrated into the bottom of the process chamber providing the option of introducing 925kHz megasonic acoustic energy directly into the process fluid with watt densities of up to $2W/cm^2$. Process fluid temperatures were maintained at 20c, 40c, and 60c for the various tests. Figure 2 illustrates the basic process flow for all experiments. The fluid was used in a single pass, so that fresh process fluid was used for each individual test at a specific temperature. Megasonic energy was introduced at $1.5W/cm^2$ at both 20c and best temperature for each intelligent fluid® / photoresist combination.

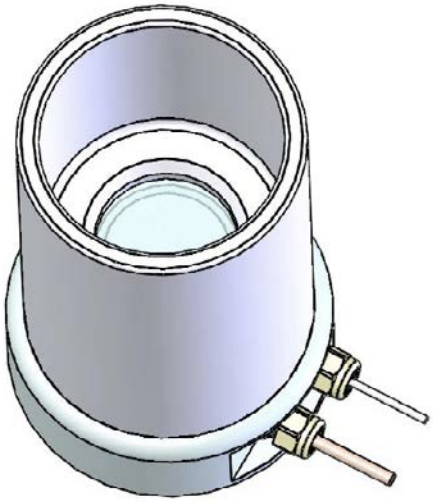

Figure 1. Bowl Meg megasonic process chamber incorporating single crystal sapphire direct megasonic transducer in chamber bottom.

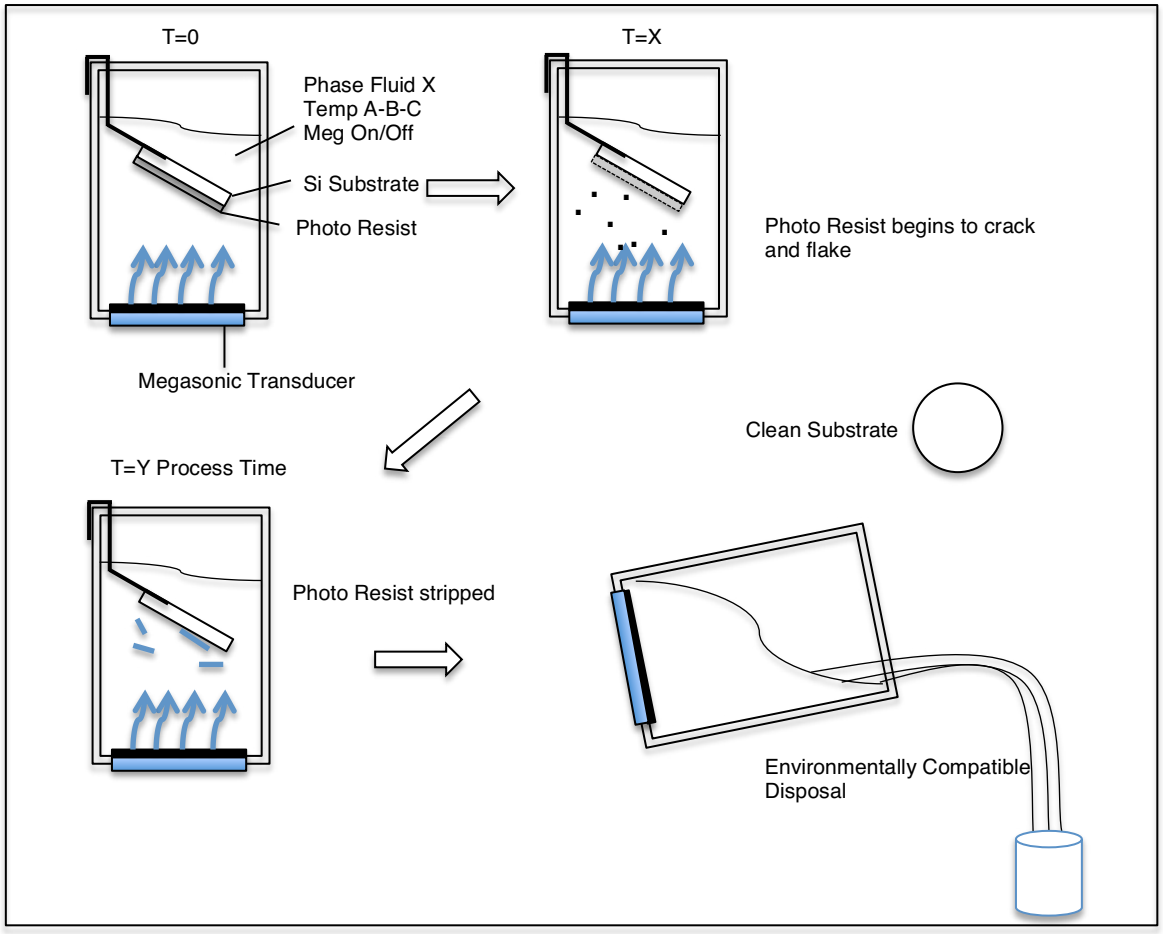

Figure 2. Diagram of the single pass process flow used in all testing, megasonic energy was applied in selecting testing at two different process fluid temperatures.

Experimental Results

The two main performance criteria for each process and material combination are: Time to initial reaction, defined as the first observed physical reaction between the fluid and photoresist film. Time to complete removal defined as the point of complete photoresist strip. Following the strip and a rudimentary rinse, contact angle was measured and compared to the silicon wafer reference. The contact angle measurements and comparisons were not conclusive due to variations in rinsing conditions. Refined residual detection methods will be implemented in further testing when an active rinse and automated drying sequence can be integrated into the total process flow. While all of the phase two tests resulted in complete photoresist strip the results for the two best performing intelligent fluids® for each photoresist are presented in Tables III through VII.

TABLE III. PR-1 AZ15NXT (no bake)

intelligent fluid®	Temperature	Megasonic	Change Observed	Cleared
if - E	20c	off	60s	190s
if - E	40c	off	80s	80s
if - E	60c	off	30s	30s
if - E	20c	1.5W/cm^2	60s	170s
if - E	60c	1.5W/cm^2	20s	20s
if - D	20c	off	20s	190s
if - D	40c	off	80s	80s
if - D	60c	off	30s	30s
if - D	20c	1.5W/cm^2	20s	170s
If - D	60c	1.5W/cm^2	20s	20s

TABLE IV. PR-2 AZ15NXT (100c/90s bake)

intelligent fluid®	Temperature	Megasonic	Change Observed	Cleared
if - E	20c	off	210s	420s
if - E	40c	off	30s	100s
if - E	60c	off	30s	30s
if - E	20c	1.5W/cm^2	120s	280s
if - E	60c	1.5W/cm^2	30s	30s
if - D	20c	off	60s	290s
if - D	40c	off	40s	120s
if - D	60c	off	50s	50s
if - D	20c	1.5W/cm^2	150s	220s
If - D	60c	1.5W/cm^2	30s	30s

TABLE V. PR-3 AZ9260 (no bake)

intelligent fluid®	Temperature	Megasonic	Change Observed	Cleared
if - A	20c	off	20s	30s
if - A	40c	off	20s	30s
if - A	60c	off	10s	10s
if - A	20c	1.5W/cm^2	10s	20s
if - A	60c	1.5W/cm^2	10s	10s
if - E	20c	off	20s	20s
if - E	40c	off	30s	30s
if - E	60c	off	20s	20s
if - E	20c	1.5W/cm^2	10s	10s
If - E	60c	1.5W/cm^2	10s	10s

TABLE VI. PR-4 JSR THB 151N (no bake)

intelligent fluid®	Temperature	Megasonic	Change Observed	Cleared
if - E	20c	off	70s	170s
if - E	40c	off	50s	90s
if - E	60c	off	10s	50s
if - E	20c	1.5W/cm^2	50s	130s
if - E	60c	1.5W/cm^2	50s	50s
if - D	20c	off	50s	90s
if - D	40c	off	20s	80s
if - D	60c	off	30s	50s
if - D	20c	1.5W/cm^2	50s	90s
If - D	60c	1.5W/cm^2	50s	50s

TABLE VII. PR-4 JSR THB 151N (100c/90s bake)

intelligent fluid®	Temperature	Megasonic	Change Observed	Cleared
if - D	20c	off	140s	140s
if - D	40c	off	40s	80s
if - D	60c	off	10s	50s
if - D	20c	1.5W/cm^2	10s	120s
if - D	60c	1.5W/cm^2	50s	50s
if - E	20c	off	280s	280s
if - E	40c	off	10s	150s
if - E	60c	off	50s	50s
if - E	20c	1.5W/cm^2	30s	140s
If - E	60c	1.5W/cm^2	50s	50 s

Conclusions

Standard photoresist films can be successfully removed with intelligent fluid® phase-fluid solutions with process times that are compliant with mass volume production throughput requirements. It was further demonstrated that process fluid temperatures in the 40c-60c range provided for a significant reduction in total strip process times. The addition of megasonic range acoustic energy to the fluid further enhances the efficiency of the photoresist stripping process. Based on this data set, further study into variations of the megasonic energy and waveform is indicated as well as applying the best process parameters and fluids found in this work to an automated production tool. The automation of this simple process will help to reduce variations in acoustic energy delivery and provide for a uniform, active de-ionized water rinse and drying sequence.

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