Using megasonic agitation to extend chemical cleaning for nano technology device production

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Solvents and semi aqueous solutions show better selectivity with advanced material stacks over aqueous solution. Aqueous fluids appear to promote much more damage for the same applied megasonic power than do most solvents. We will show the latter is partly related to the fact that the relation between applied power and the resulting pressure field is liquid dependent. A second reason is the higher cavitation threshold, which is observed for some solvents when compared to de-ionized water. To further understand the process window of cleaning we are investigating the impact of liquid properties in sound fields. These investigations will yield the cavitation threshold and the relation between applied power and pressure in the liquid. This information will be used to apply acoustic power to advanced device wafers above and below the cavitation threshold. By doing this we can find a safe area to clean wafers.

1   Introduction

Megasonic agitation in solvents and aqueous solutions has been shown to enhance polymer and photo-resist removal (see fig. 1). Because materials get more complicated as technology advances several investigations have shown exposure to aqueous based chemicals can promote corrosion [3,4,5,6]. Specifically an all wet approach to photo-resist removal using solvents to prevent damage to low k [1] has been demonstrated. More understanding about solvent megasonic agitation is needed to expand on the work shown in figure 1 [1].
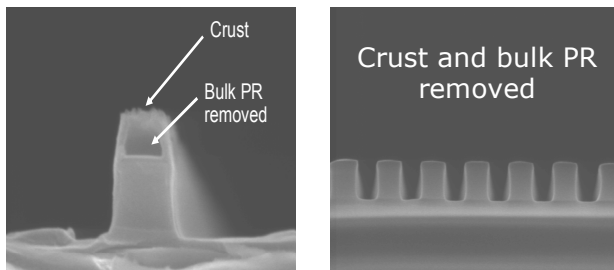

Fig.1 Solvent PR removal on BEOL trench

In general the impact of megasonic energy across a wide range of chemicals is needed. This information should help to guide experiments and build more knowledge for commodity chemicals and off the shelf liquid formulations when applying megasonic agitation. We need to be able to explain why some cleaning applications result in a clear benefit when using megasonic cleaning for sensitive nano structures, while other cleaning approaches result in damage to nano structures.

In studying cavitation impacts to cleaning and damage we found that we could control the amount of damage by controlling the temperature of the solution, gas type, filtration of large cavitation nuclei, and appropriate applied megasonic power for aqueous chemicals [2]. With this combination we have improved process control. But at times this damage control can limit the process window. To get another level of control we need to take a step back and improve our tool set for implementing megasonic agitation on these sensitive nano structures. The element of control we are looking for are the physical properties of the liquid medium in a sound field.

2   Results

The relationship between electrical power I (W) and the resulting amplitude P_A (Pa) of the pressure field in the cleaning chemicals can be estimated by

$$I = \frac{1}{\eta} \cdot \frac{P_A{}^2}{2Z_m} \qquad (1)$$

The relationship between the measured pressure and the applied power depends on coupling transducer-liquid efficiency (e.g.: quartz wall): η where $1/\eta$ in less than and on the acoustic impedance for the liquid is $Z_m = \rho c$.

Liquid	Z_m (10^6 kg.m^{-2}.s^{-1})	ρ (kg.m^{-3})	c (m.s^{-1})
Ethanol	0.903	789	1144
IPA	0.968	790	1225
water	1.48	1000	1480
NMP	1.6	1033	1546
Acetic acid	1.66	1049	1584

Table 1

The acoustic impedance Z_m, calculated from the density and sound speed, is listed for different liquids in table 1. Simplifying equation (1) by assuming a perfect coupling transducer-liquid (η =1). A simulated (s) curve between input power density for a transducer and the resulting pressure in the liquid is seen in Fig 2.
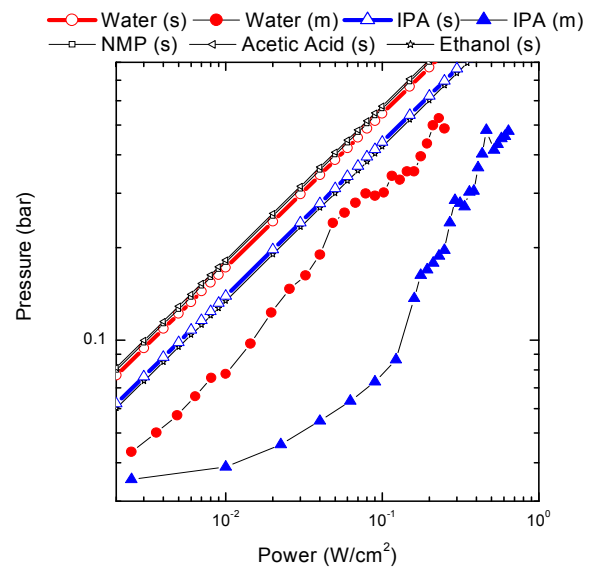

Fig.2 Applied transducer power and liquid pressure

In figure 2 we can also compare the measured (m) relationship between the transducer and pressure field in the liquid by a small experimental cell (Fig. 3), where a

hydrophone is positioned in a liquid in a glass cell on top of a transducer.

Besides water a mild solvent was used to benchmark the setup. Isopropyl alcohol (IPA) is used widely in the semiconductor industry as a wetting agent in many semi aqueous formulations. Also, IPA has a low surface tension and there is some history of formulations using IPA that resist cavitation damage. In figure 2 we measured a higher pressure for the onset of cavitation for de-ionised water compared to IPA, but IPA required twice the applied power than de-ionised water did. This may help explain why we have experienced better control of megasonic cavitation damage while using IPA containing formulations.
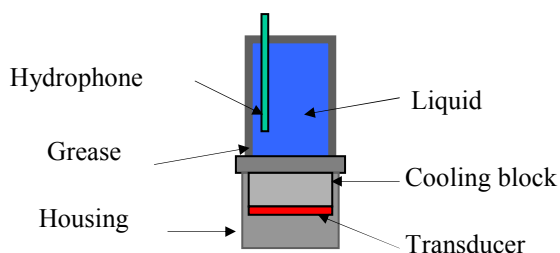

Fig.3 schematic of liquid cell

In the testing we position the hydrophone at one wavelength above the transducer as a starting point. We then dither around that point until we find the highest energy reading to be sure we are at the anti-node of the sound wave. This helps to maintain good repeatability in the readings. The hydrophone signal is sent to an oscilloscope for data gathering and signal manipulation. With the hydrophone pressure amplitudes are recorded for particular chemicals as a function of input power.

Parameters of interest are not only the pressure field in the liquid but mainly the onset of cavitation (cavitation threshold) and the violence of the bubble action in this pressure field for determining the cleaning/damaging effect of ultrasound. Therefore we need to get a better insight on the impact of liquid properties on bubble dynamics.

A second application of this experimental cell is the determination of the cavitation threshold by analysing the signal from a hydrophone in detail. From the distortion of the hydrophone signal by cavitation we will get clues how aggressively a liquid responds to an applied sound field.

It is important to know what is happening in real time (Fig. 4). Note that the time scale (ms) is larger compared to the driving frequency (MHz), thereby preventing a clear image of a single period. For a hydrophone reading of about 50kPa we have a relatively quiet signal in figure 4. When we increase the applied power to 100kPa a clear deformation in the signal is observed [12]. It is clear that at 100 kPa some threshold is exceeded. The idea is to record these values for different liquid setups.
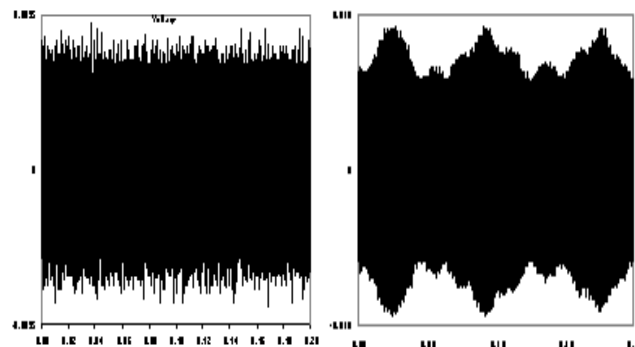

Fig.4 On the left water at 50kPa, on the right at 100kPa

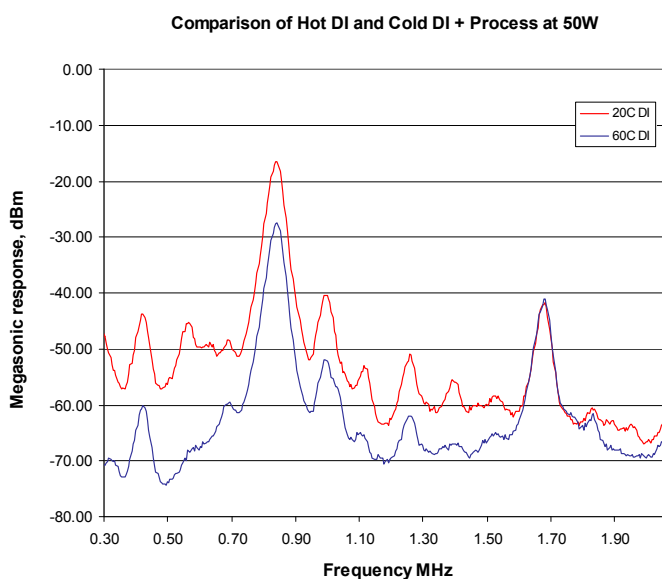From this distorted signal [8] we can obtain a frequency spectrum as in figure 5.

Fig.5 frequency spectrum of hot and cold water

From the frequency spectrum we can determine how much cavitation activity we have from one condition to another. The difference in acoustic impedance between hot and cold water is marginal, so we can overlay the frequency response to applied power. It is believed that the lower spectrum from hot water is due to the reduction in cavitation threshold [8] producing larger bubbles that absorb the sound. Numerical simulation of bubble dynamics, using the Gilmore equation [12], shows increased radial growth of the bubble for the same applied pressure in hot water (60˚) and ambient water (20˚) (Fig. 6).

For liquids like hot water we can take measures to control megasonic agitation on nano structures [2]. In this case it helps provide a path for the sound energy to dissipate away from the wafer. For solvents we have found a much wider process window [2] with good cleaning ability without taking much care to gasify the liquids. Some solvents show much lower gas solubility than water. So we understand we may have very little gas in the solvent during our cleaning tests. This is an area where we still need to look into the cavitation nucleation mechanism.
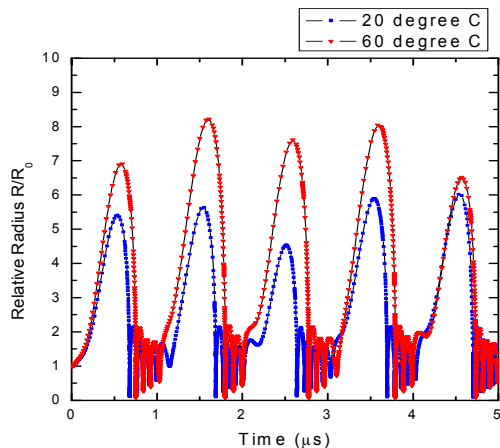
Fig.6 bubble growth of hot and cold water

From historical [13] data we know we get better cleaning for gasified liquids and that we are working at higher pressure for degasified liquids. This is mostly true for water, diluted ammonia and other dilute aqueous based cleaning fluids. For gasified aqueous fluids the gas level in the liquid can change the acoustic properties of the liquid. This is of particular interest because literature typically refers to the applied electrical power in W/cm2 during cleaning and damage tests. The data can get confusing because there are changes to the acoustic pressure a particle or device receives that is unaccounted for.
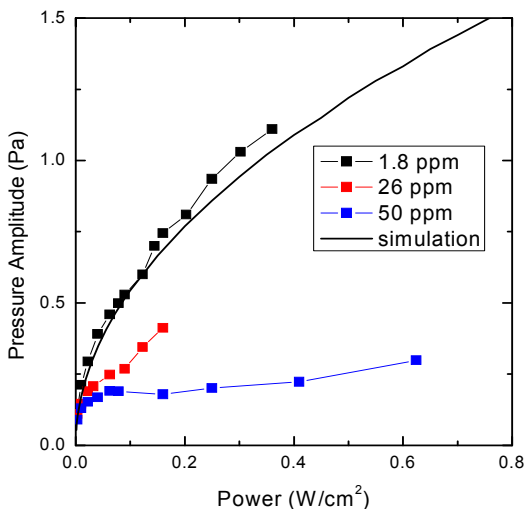

Fig.7 sound transmission in gasified water

In our liquid cell we see the changes in the gas level changes the impedance of the water (fig 7). Lower gas levels than saturation indicates sound speeds higher than what is reported in the literature for water. Above the saturation point for dissolved oxygen there is a reduction in sound speed. It is understood that some of the sound level reduction is due to large bubble coalescence. In general, the impact of gas on the liquid solution in figure 7 is mostly related to the impact of reduced sound speed caused by the amount oxygen molecules present in the system.

The industry is in need of more selective chemical to process the advanced materials. We found in our own testing and in the literature that surface tension and vapor

pressure can reduce cavitation damage [1,7,9,10]. So we want to expand our investigation to organic solvents and semi-aqueous formulations in order to stay in step with the device makers. Building on the data from the setup we need to run selective removal tests on full wafers.

Comparing various chemical setups and overlaying the FFT's is not possible unless we normalize the data because of acoustic impedance. In figures 2 and 7 we see there is a large difference between some liquid mixtures. For comparing chemicals we identify a preferred energy spectrum for nano-structures. This can provide the basis for applying acoustic power to various liquids to stay in the damage free zone.
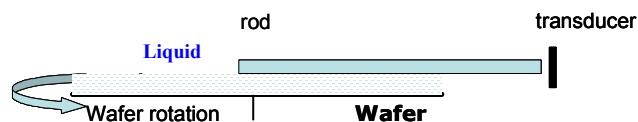

Fig.8 schematic of the Goldfinger

Verification studies were performed on the Akrion 300mm single wafer-cleaning tool using the Goldfinger megasonic system (fig 8). This system uses a megasonic rod that is positioned over the wafer surface and is contacted through a liquid meniscus. The frequency is near 1MHz and the applied power travels through an optimized but self-forming liquid meniscus before coming in contact with the structures on the wafer surface.

The information from the hydrophone measurements on the test cell was combined with historical data from hydrophone measurements for the rod type megasonic. To form a reference point for the two systems we used de-ionized water. Full wafer tests were performed on 300mm wafers for several applications using solvents and semi aqueous blends.
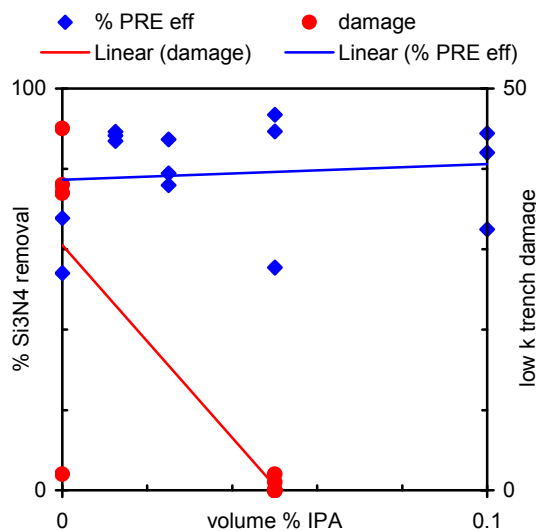

Fig.9 100nm cleaning vs 80nm trench damage

We ran tests using a dilute semi-aqueous organic commodity blend for copper low k trench cleaning. IPA was added to the chemical and cleaning and damage tests were performed (see figure 9). These tests were performed above the cavitation threshold. In figure 9 we can see a

slight increase in cleaning efficiency while damage to the low k trench is going down. So for particle removal we were able to improve the cleaning without increasing the damage by using IPA as an additive.

In the front end of the manufacturing line there is a need for an all wet photo resist removal solution because of the potential for galvanic reactions in water-based solutions. There are also concerns about etch rates because of dopant loss with better scalability in solvents. In figure 10 we were able to show enhanced photo resist removal using a commodity solvent combined with megasonic agitation.
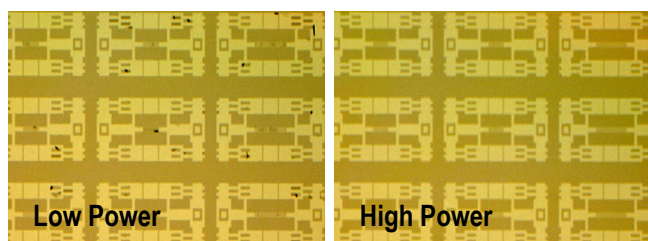

Fig.10 As doped 5keV, 45° tilt E15/cm2 implant

Tests were also run using off the shelf semi-aqueous organic formulated blend on BEOL 50nm ultra low K trenches. We applied the megasonic energy above and below the cavitation threshold to obtain a damage free result. The goal of this test is to improve etch profile of the trench. This could be achieved by reducing the process time from 120s with no megasonic to 60s using megasonic agitation. This should allow us to reduce the dielectric etch amount by about half.
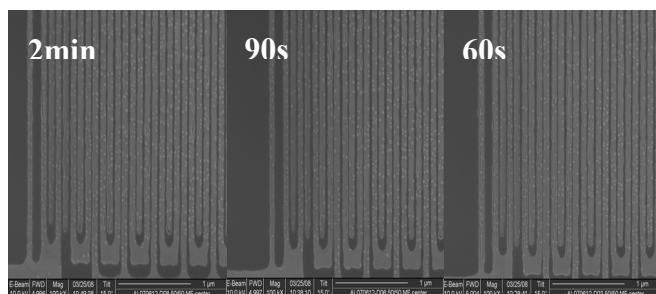

Fig.11 megasonic agitation to reduce process time

In figure 11 we were able to apply 60s using megasonic agitation on the post etch trench without any damage. The above result is after clean and after copper deposition the copper is polished back by chemical mechanical polishing and if the wafer is not cleaned enough typically we see an increase in void formation. If the dielectric structures were damaged by the megasonics there would be shorts. So the results did not show shorts related to the megasonic cleaning. For power levels under the cavitation threshold we could reduce the process time to 90s but saw void formation at 60s. For testing just above the cavitation threshold we did not see any voids appear even at 60s process time.

By applying megasonic agitation above and below the cavitation threshold for different liquids we have not found any damage. This is because we are tightly controlling the applied electrical power to stay out of the damage region.

The main cleaning outputs are faster processing with megasonic agitation than with chemical alone. We see a good trend on 50nm low k trenches for damage free megasonic agitation for wet photo resist strip and post etch residue removal.

4   Conclusion

We showed that the relationship between applied power and the resulting pressure field is liquid dependent. For IPA we saw a higher cavitation threshold for the applied power from the transducer but cavitation occurs at a lower pressure than water when referring to the measured output. This helps explain why we have more process window for semi aqueous liquids that contain a solvent such as IPA. From these results we should pay attention to the liquid properties that are designed into cleaning fluids. Managing liquid properties for megasonics will help to design in megasonic agitation for sensitive structure cleans.

Acknowledgments

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