

Megasonic Agitation Allows Removal of Chemically Amplified Photo-resists

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Solvent chemicals are widely used in the removal of chemically amplified photo-resist in advanced packaging and being researched in the front end metal gate step. Internal data shows megasonic agitation can enhance polymer removal without complete dissolution for various solvent chemicals. Data has shown solvents and solvent mixtures show better selectivity with advanced material stacks over aqueous solution. It has been established that megasonic energy can enhance particle removal from semiconductor devices after a solvent strip is performed. However, applied megasonic energy can also damage sensitive semiconductor devices during cleaning, especially in aqueous solutions. Aqueous fluids appear to promote much more damage for the same applied megasonic power than do some solvents. We show that some solvents have a higher threshold for cavitation than de-ionized water mixes. Since device manufacturers are working to extend their current cleaning and stripping chemicals in photo resist stripping, we studied several ways to accomplish this goal for various solvent chemicals. To promote a better understanding in this paper we investigate chemical properties in sound fields and the removal capacity. These investigations will yield the cavitation threshold and the slope of applied power verses pressure applied to the structure. This information will be used to apply acoustic power to a customer strip process above and below the cavitation threshold. By doing this we can find a safe area to process the customer wafers. Further work may be able to quantify the amount of cavitation we apply to a new chemical. For now we can identify the cavitation spectrum that we like and safely transpose that from one chemical process to another.

1 Introduction

It has been established that megasonic energy can enhance particle removal from semiconductor devices during cleaning processes [2]. However, applied megasonic energy can also damage sensitive semiconductor devices [5]. It was shown [1] that a mechanically modified system could be used to apply the necessary energy to clean enough particles and not damage by designing in a wave dispersion tank to control cavitation in aqueous fluids. Because materials get more complicated as technology advances several investigations have shown exposure to aqueous based chemicals can promote corrosion [3,4,5,6]. So as materials become more advanced solvents become more preferred.

To understand the impacts of megasonic energy across a wide range of chemicals, studies were performed with a small sonic agitator to find out more about chemical responses to sound and to determine the cavitation threshold for various liquid types. 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.

2 Discussion

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 [1]. With this combination we have improved process control, however to

get another level of improvement we need to take a step back and improve our tool set for implementing megasonic agitation on these sensitive nano structures because at times the positive results to control the damage can limit what the customer can do in terms of process window. The element of control we are looking for in extending chemicals for nano structures is the properties of the liquid medium in a sound field.

The relationship between electrical power and the resulting pressure field in the cleaning chemicals can be estimated by this formula

$$I = \frac{1}{Q} \cdot \frac{P_A^2}{2Z_m}$$

This formula calculates the electrical power I (W/cm²) induced by a MHz pressure field in a liquid with pressure amplitude P (Pa). The measured pressure and the applied power depends on coupling transducer-liquid (e.g.: quartz wall): Q and on the acoustic impedance liquid Z_m=pc.

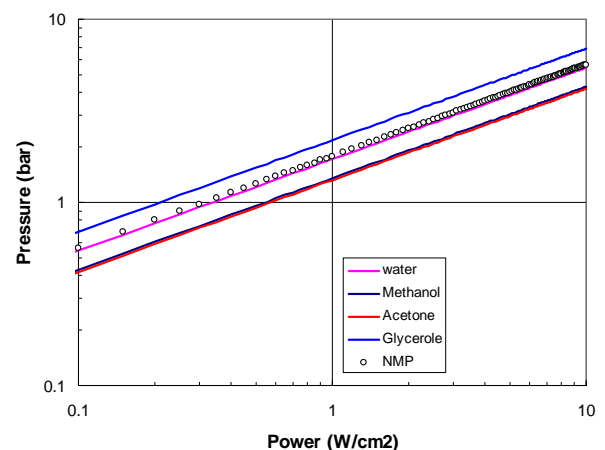


Fig.1 From transducer to pressure in liquid

From equation (1) we have a simulation of the impact of various chemicals (see figure 1) on the resulting sound pressure. To understand this simulation better and to understand where our component fits in with simulations we designed a liquid agitation cell (see fig.2). With this cell we want to determine the cavitation threshold by analysing the signal from a hydrophone. With this signal we will get clues into the aggressive nature of the chemical from the distorted signal.

| Liquid | $Z_m (10^6 \text{ kg.m}^{-2}.\text{s}^{-1})$ | $\rho (\text{kg.m}^{-3})$ | $c (\text{m.s}^{-1})$ |
|----------|--|---------------------------|-----------------------|
| Methanol | 0.876 | 794 | 1103 |
| Acetone | 0.92 | 784 | 1174 |
| water | 1.48 | 1000 | 1480 |
| Glycerol | 2.4 | 1260 | 1940 |
| NMP | 1.6 | 1033 | 1546 |
| IPA | 0.96 | 790 | 1255 |

Table 1 Paragraph formats

The impedance change from liquids in table 1 is shown to have relationships above and below water. So from figure 1 and table 1 we understand how applied power transfers through a chemical to the surface of the wafer. Now we want to take that understanding to a component to check if we can verify the simulation and to manage how to run the product testing. However we want to test chemicals that will remove residues and particles that are known for their good selectivity for advanced materials.

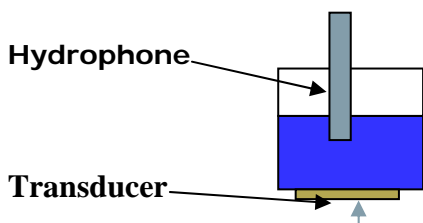


Fig.2 schematic of liquid cell

The set up we used to investigate liquids is shown in figure 2. The signal from the hydrophone is sent to an oscilloscope and pressures are recorded for particular chemicals. From here we can tell if the liquid is above or below the cavitation threshold and what the response is to a particular applied pressure or frequency. We look for when the signal becomes distorted to verify the cavitation signal using fast Fourier transforms.

3 Results

We took the setup from figure 2 and positioned 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. Before we run a frequency spectrum or FFT on the signal it is important to know what is happening in real time. For an applied power setting and a hydrophone reading of about 50kPa in figure 3 we have a relatively quiet signal. 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.

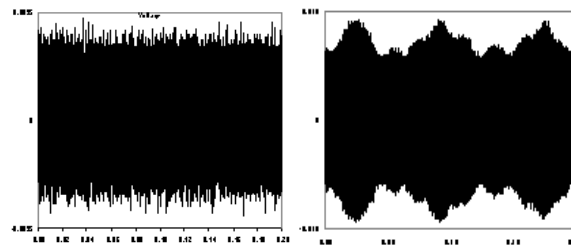


Fig.3 On the left we have an undistorted signal with water at 50kPa and on the right water at 100kPa

From this distorted signal [8] we can obtain a frequency spectrum as in figure 4.

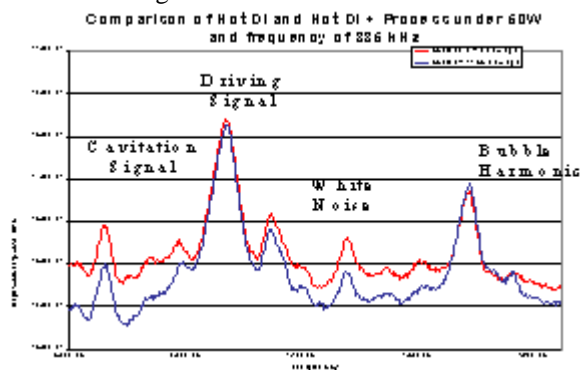


Fig.4 frequency spectrum of hot and cold water

From the frequency spectrum we can determine how much cavitation activity we have from one condition to another. The liquid property difference between hot and cold water is marginal so we can overlay the frequency response to applied power. It is believed that the higher white noise from hot water is due to the reduction in cavitation threshold [8]. Numerical simulation [12] of the cavitation threshold shows increased bubble growth from the same applied pressure for hot water than for ambient water (figure5).

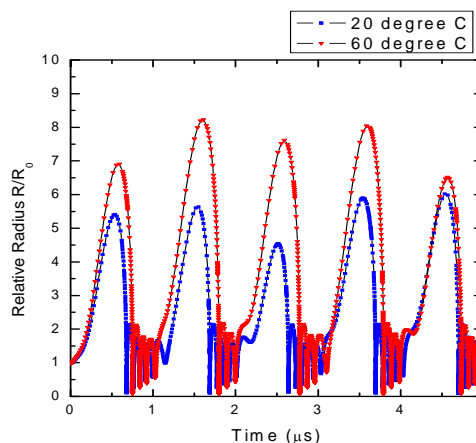


Fig.5 bubble growth of hot and cold water

For aggressive liquids like hot water we can take measures to control megasonic agitation on nano structures [1]. In this case it helps provide a path for the sound energy to dissipate away from the wafer.

From historical 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 power during cleaning and damage tests where the data can get confusing because there are changes to the applied pressure a particle or device receives that is unaccounted for. In our liquid cell we see the increasing gas level changes the impedance of the water where the impact of reduced sound speed decreases the sound pressure within the liquid (fig 6).

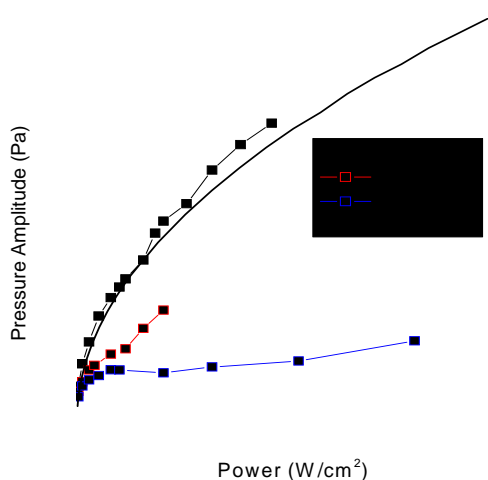


Fig.6 sound transmission in gasified water

However the industry is in need of a more selective chemical to process the advanced materials. So we want to expand our investigation to organic solvents because we have found in our own testing and in the literature that surface tension and vapor pressure can reduce cavitation damage [1,7,9,10].

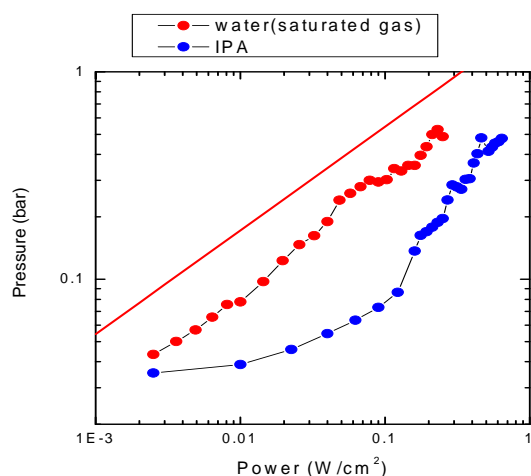


Fig.7 acoustic response and attenuation

Comparing various chemical setups and overlaying the FFT's is not possible unless we normalize the data because

of acoustic impedance. In figures 6 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 chemicals to stay in the damage free zone. Variations of the signal distortion can be seen when we compare one chemical to another. It is then a matter of trade secret to apply our preferred energy spectrum for damage free cleaning

Verification studies were performed on the Akרון Systems 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.

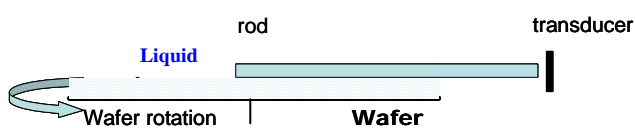
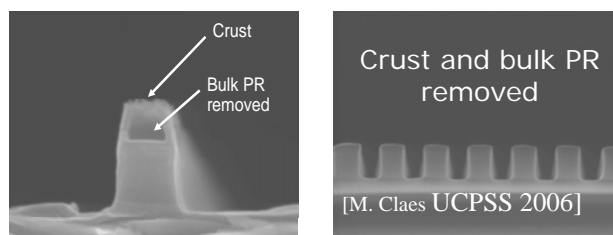


Fig.8 schematic of the Goldfinger

Full wafer tests were performed on 300mm wafers for several applications and process flows in order to obtain results that can shed light into the benefit of Megasonic agitation to extend chemical processes for nano technology.

We have evaluated the ability of megasonic agitation to help remove photo-resist from device wafers in several process flows. For interconnects, the dielectric becomes more porous and can be damaged by dry plasma ash. All wet processing with physical agitation is preferred if we can limit the amount of etching for residue removal. We were able to show, in figure 9, megasonic agitation can assist solvent photo resist stripping by enhancing the chemical process to get the desired result.

Fig.9 Solvent PR removal on BEOL trench



In the front end of the manufacturing line there is a similar requirement to remove the photo resist because the advanced materials tend to produce galvanic reactions. Again in figure 10 (following) we were able to show enhanced removal using megasonic agitation.

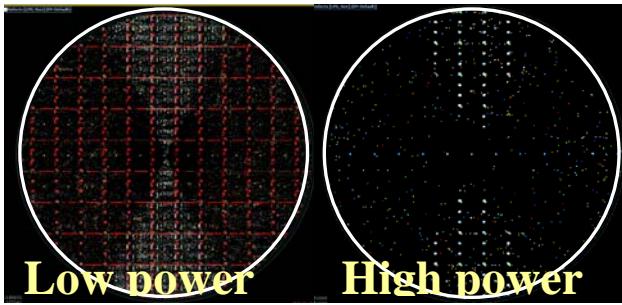


Fig.10 Solvent PR removal of As doped resist at 5keV at 45° tilt E15/cm2 implant

In figure 11 we applied the megasonic energy just above the cavitation threshold for a DMSO mixture to obtain a damage free result to improve the process time from 120°C and 15 minutes with no visible removal with no megasonic to 5min using megasonic agitation at 45°C. Visual inspection on a Leica INS3300 the tests showed removal of the hardened photo resist on high density patterns.

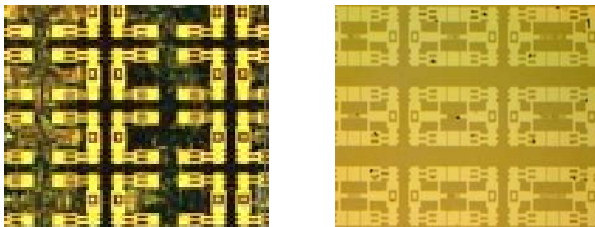


Fig.11 Megasonic agitation to reduce process time

In figure 12 we were not able to completely remove thick chemically amplified photo resist in 120s without megasonic agitation; the photo on the right shows we were able to completely remove the thick resist in 120 seconds at low meg power levels.

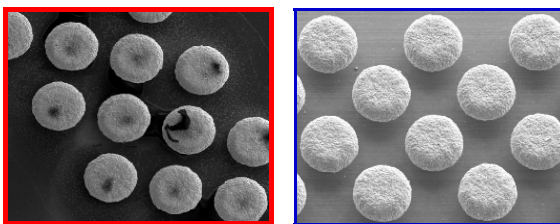


Fig.12 Megasonic agitation improves removal time

For figure 12 we applied megasonic power to a solvent chemical mix at 65°C and optimized it to get full removal of the 50µm thick negative photo-resist on a 300mm wafer. This result is compatible with single wafer processing for advanced packaging.

4 Conclusion

We are still building up our data set for vertical integration of chemical agitation and applications. Measurement of the applied sound field and cavitation threshold gives us important information about the liquid properties. This helps us to perform cleaning optimization tests with less

negative impact to the customer's technology. This will allow us to apply megasonics to photo resist removal steps on single wafer tools in semiconductor manufacturing of advanced packaging, BUMP's, TSV and others.

Acknowledgments

Rita Vos, Martine Claes, Sandip Halder, Guy Vereecke, Twan Bearda, Paul Mertens, Quoc Toan Le, HS Song

References

- [1] Cole Franklin, "Using Megasonics to Extend Chemical Cleans for 45nm Technology", ECS Cleaning Symposium 2007
- [2] Glen Gale, A. A. Busnaina, "Removal of Particulate Contaminants Using Ultrasonics and Megasonics: A Review," Particulate Science and Technology, 13 (1995) 197.
- [3] Susan Cohen, "Studies of the Relationship Between Megasonics, Surface Etching, and Particle Removal in SC1 Solutions," Mat. Res. Soc. Symp. Proc., 13 (1995) 386.
- [4] Jeff Butterbaugh and D. Riley "Update from the Surface Prep Working Group of the 2003 ITRS," ISMT: Wafer Cleaning and Surface Preparation Workshop 2003.
- [5] Paul Mertens, "Damage-free removal of nano-sized particles, heading towards a red brick wall," ISMT: Wafer Cleaning and Surface Preparation Workshop 2003.
- [6] International technology roadmap for semiconductors (ITRS), 2006. Update
- [7] Milton S. Plesset, "Cavitation Erosion in Non-Aqueous Liquids" Office of Naval Research, February 1970, Report No. 85-48
- [8] Ernest A. Neppiras, "Measurement of Acoustic Cavitation" IEEE Transactions on Sonics and Ultrasonics, Vol. Su. -15, No.2, April 1968
- [9] Bogdan Niemezewski, "Estimation of the suitability of selected organic solvents for ultrasonic cleaning", Ultrasonics Sonochemistry 6 (1999) 149-156
- [10] P.I. Golubnichii, V.D. Goncharov, and Kh.V. Protopopov "Sonoluminescence in Various Liquids" Soviet Physics – Acoustics, Vol. 16, No. 3, Jan. – March, 1971
- [11] Klaus-V. Jenderka, Christian Koch "Measurement of Spectral Sound Field Parameters in Ultrasound Cleaning Baths using Piezo-electrical Hydrophones and Optical Fiber Tips", IEEE Ultrasonics Symposium, 2006, 1051-0117/06 pg 1433-1436
- [12] T.G. Leighton "The Acoustic Bubble: chapter 4 and 5, Academic press 1997

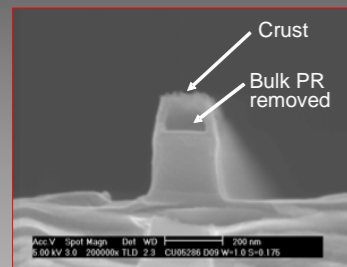
Introduction:

Solvent chemicals are widely used in the removal of chemically amplified photo-resist in advanced packaging and being researched in the back end of line as a method in preserving the low k from plasma damage and in the front end for both memory and logic metal gate steps to prevent corrosion, non-selective etching and dopant loss. Internal data shows Megasonic agitation can enhance polymer removal without complete dissolution for various solvent chemicals in the major process steps such as BEOL, FEOL and far BEOL such as BUMP and TSV steps.

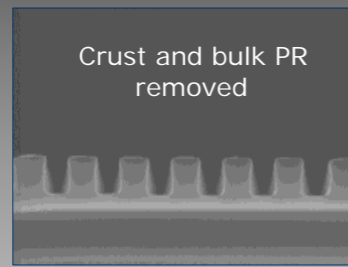
Experimental: PR patterned bare Si wafers scans performed using an SP2, patterned wafers used SEMVision, KLA 2800, Leica 3300, the photoresist was 248nm positive resist, Boron doping, and BARC from Brewer Science, JSR thick negative resist and the removal took place on the Akrion Velocity Cleaning platform using the Goldfinger Megasonic.

BEOL -photoresist and BARC removal

Crusted PR Removed



No Megasonic



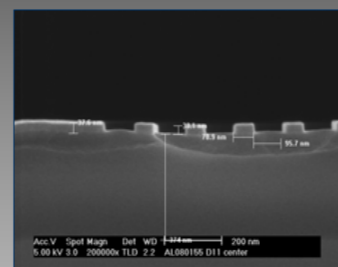
With Megasonic

Applying Megasonic energy to chemical processes like photo resist removal show an impact to the chemical alone process. This is allowing researchers to extend existing cleaning.

BARC Removed



No Megasonic



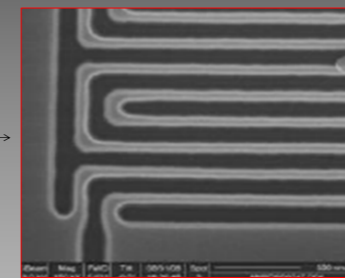
With Megasonic

•Tests for 3 minutes of chemical application time at 50 degrees Celsius
•Damage free results confirmed at 90, 50 and 30nm structures at 10 Watts of applied power

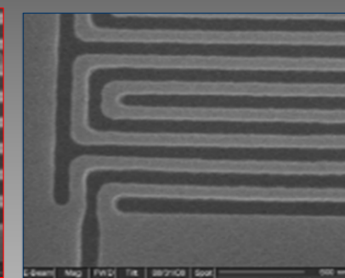
BARC and photoresist was removed on blanket and patterned wafers allowing good electrical yield for ELK at 50nm trench and exceeding the lifetime requirement for pilot production entry.

ELK post trench etch all wet flow vs baseline flow

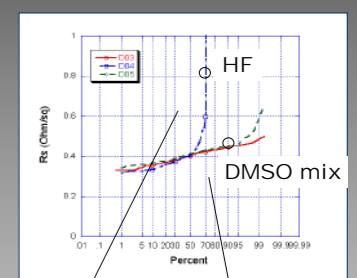
post TiN hard mask open



HF Baseline

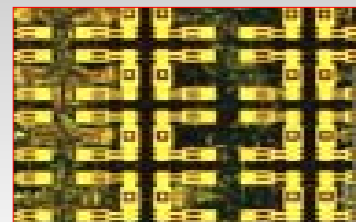


Meg + DMSO Mix

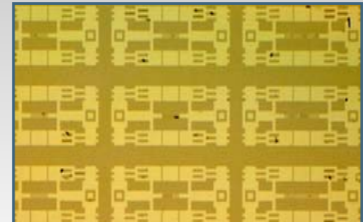


No meg Solvent meg

FEOL -photoresist removal



NMP, no Meg

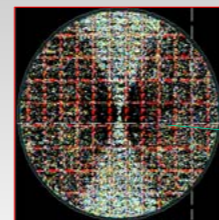


NMP, 10 Watts Meg

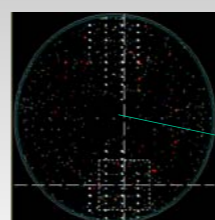
Pure NMP at 120C for 15 min versus 5 min megasonic chemical assisted removal at 45C and 10W = 0.3W/cm² removing 5keV, E15/cm² implanted photoresist at a 45 degree angle

High I/I ranged from 40keV to 2keV at E15/cm², megasonic energy allowed the photoresist to be removed better than the chemical itself with 2 and 5keV yielding equivalent levels of clean to an oxygen plasma ash.

Megasonic assisting NMP Solvent



at cavitation threshold

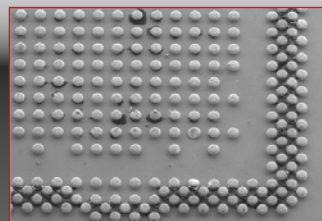


above cavitation threshold

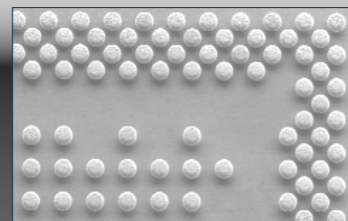
low power removal test just above cavitation threshold vs 10W = 0.3W/cm² meg on power for a densely patterned photoresist at 7 degree implant angle with 5keV, E15/cm² implanted energy

BUMP – Thick photoresist removal

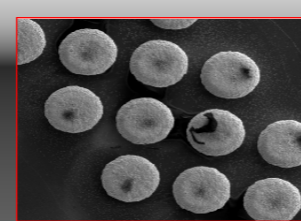
JSR TH-151N (JSR Negative photoresist), 50um



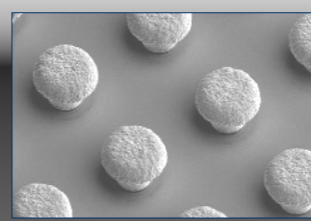
2.5 min chemical technology



Megasonic assisted chemical



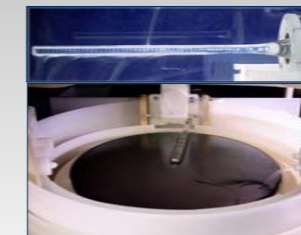
2.5 min chemical technology



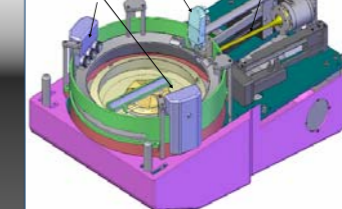
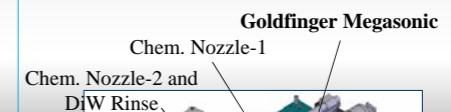
Megasonic assisted chemical

Overall the optimized process yielded consistent removal of 50um of JSRTH151N in 2 minutes on a single wafer tool vastly improving the chemical only technology results

Goldfinger™ Megasonic



Chemical Nozzle-1



Akrion Cleaning Technology

Applications

- FEOL**
 - PR strip
 - Post CMP clean
 - Post SAC etch clean
 - Pre Litho F/B clean
- BEOL**
 - BARC / PR strip
 - Post RIE trench clean
 - Post Via RIE clean
 - Post CMP clean
- Far BEOL**
 - BUMP strip
 - TSV PR strip

Conclusion:

The implementation of a megasonic assisted all wet process flow in the Cu dual damascene has provided good yielding structures and longer lifetime than in process flows with dry ash.

Even at very low applied megasonic powers the removal capacity of pure NMP solvent is radically improved for photo-resist removal in the FEOL

Implementation of megasonic agitation has allowed BUMP removal chemical technologies the ability to process advanced packaging technology on a single wafer tool.

References:

- [1] P. W. Mertens, G. Vereecke and R. Vos, "Post Ion-Implant Photoresist Removal for Front-End-Of-Line Applications", Semiconductor Fabtech, 31, 86 (2006)
- [2] C. Franklin "Using Megasonic Agitation to Extend Chemical Cleans for Nano Technology" joint acoustic society of American, the European Acoustics Association and the Société Française d'Acoustique, Paris France, June 30 (2008).
- [3] S.Cohen: Studies of the Relationship Between Megasonics, Surface Etching, and Particle Removal in SC1 Solutions (Mat. Res. Soc. Symp., 13 1995, 386).
- [4] CRC handbook 64th edition pg. E70-74
- [5] www.otrain.com/OTI_MSIDS(IP)WMAP
- [6] Dario L. Goldfarb, High pressure sonoelectrochem - soft cavitation under CO₂, J.Phys. Chem. July 1998
- [7] Cuiling Gong and Douglas P. Hart. Ultrasound Induced Cavitation and Sonochemical Yields, Journal of Acoustic Society of America, 1998
- [8] between cavitation threshold and dissolved air in the MHz Range, Jpn J. Appl Phys, May 1998

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