GENERATION OF POWER MEGASONIC ACOUSTIC WAVES IN SUPERCRITICAL CO_2

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A new power acoustic transducer was developed for surface cleaning in supercritical CO_2 and is disclosed here [1]. Celerity of sound was measured in CO_2 under pressure between 1 and 25 MPa and temperature between 293 and 311 K. Acoustic boundary layer thickness and wavelength were calculated. It was shown that acoustic boundary layer thickness is 4 times smaller and wavelength 10 times shorter than in water. Influence of its acoustic activation of supercritical CO_2-based fluid on wafer cleaning was illustrated for two different applications: particle contamination removal (mechanical effect) and ionic contamination removal (sonochemical effect). It was observed that acoustic power increases particle removal for particles bigger than the calculated acoustic boundary layer. This demonstrates the transmission of mechanical energy to the surface of the wafer, as observed in classical liquids. Ionic contamination removal was also enhanced, demonstrating sonochemical activation.

INTRODUCTION

Power acoustic generation in liquids is now commonly used for surface cleaning and finds many applications in process engineering, i.e. atomization, cell lysing or sonochemistry. The ultrasonic frequencies implemented are generally in the range of 20 to 130 kHz.
In the semiconductor industry, higher frequency transducers have been developed for surface wafer cleaning to meet requirements for very small particle size to remove and high fragility of patterns to be cleaned. These transducers work in megasonic frequencies, in the range of 800 kHz to 2 MHz.

Two parameters have a great influence on the phenomena participating to particle removal in megasonic surface cleaning (streaming, micro-streaming, pressure gradient, drag forces): the acoustic boundary layer thickness δ and the acoustic wavelength λ. The smaller they are the higher efficiency is obtained. The acoustic boundary layer thickness is the distance from substrate where the wall effect is not detected. It can be calculated with the following equation [2]:

$$\delta = \left(\frac{\mu}{\rho \cdot \pi f} \right)^{1/2}$$

M: dynamic viscosity (kg/m.s)
ρ: density (kg/m^3)
f: transducer frequency (Hz)

The acoustic wavelength is obtained with the following formula:

$$\lambda = \frac{C}{f}$$

C: velocity of sound (m/s)
f: transducer frequency (Hz)

The goal of this study is to quantify the value of these two parameters in SC CO_2 for a megasonic transducer and to evaluate the interest of power megasonic activation in CO_2.

POWER ACOUSTIC WAVES GENERATION UNDER HIGH PRESSURE

Different studies demonstrated the interest of power ultrasonics generated in liquid or supercritical CO_2 for extraction or polymerization processes [3] [4]. Cavitation in liquid and supercritical CO_2 was also highlighted at a frequency of 20 kHz [5].
Systems used to transmit acoustic power to the fluid are generally resonating probes called sonicators, fixed through the walls of the pressure vessel. These systems are efficient at low frequency, but do not work for higher ones. In another system, a piezoelectric transducer was placed directly inside the pressure vessel, but the presence of chemical additives in carbon dioxide for cleaning application would corrode the transducers and contaminate the parts.

In order to insulate piezoelectric actuators from cleaning fluid, a sealed sonic box was developed and placed in a dedicated high pressure cleaning chamber, as described in figure 1. Similar to standard immersible transducers, the sonic box is filled with an incompressible fluid to avoid deformation of the vibrating membrane. The three piezoelectric crystals have a resonance frequency of 1.4 MHz, and the power of the system is 100 W.

This transducer was placed in a tool dedicated to silicon wafer cleaning in CEA-LETI (Grenoble, France) [6]. Its resistance to pressures up to 30 Mpa was verified and it was not damaged by emergency venting (pressure drops of 1 to 5 Mpa / sec).

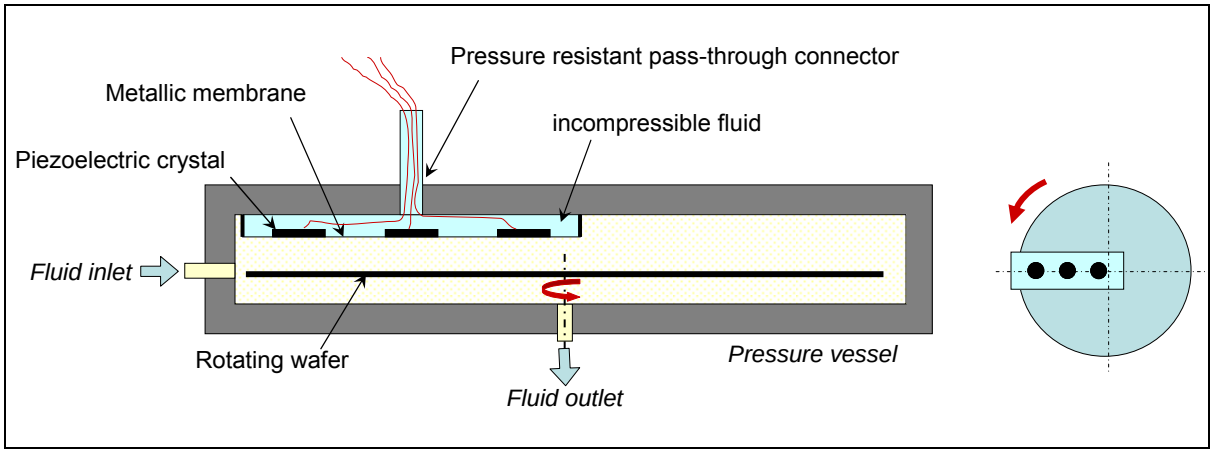


Fig. 1: Megasonic transducer inside the cleaning vessel

EXPERIMENTS

Sound velocity measurement in dense carbon dioxide

In order to determinate the wavelength λ of the acoustic waves generated by the 1.4 MHz power transducer in SC CO_2, velocity of sound should be measured. For that purpose, a dedicated acoustic system was built, working at 40 kHz. As described on figure 1, this system is constituted of two piezoelectric transducers, one emitter and on receiver, with a fixed distance between them. A pulse is generated by the emitter with a signal generator and an oscilloscope records simultaneously pulse emission and reception. This system was placed in a pressure vessel. Emission and reception signals were recorded at different pressures and temperatures.

Impact of Power Megasonics in SC CO_2 trough wafer surface characterization

Cleaning equipment used for experiments is described on figure 3. Acoustic power and wave train length of the transducer are tunable. For all the experiments the power is adjusted to the maximal value of 100 W and wave train length to the minimal value corresponding to a 160 Hz wavelength emission.

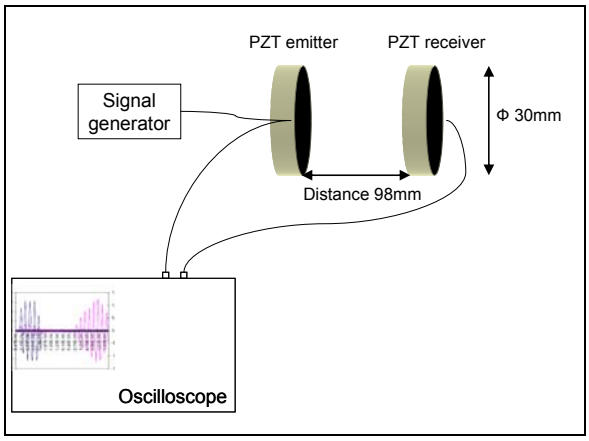


Fig. 2: Acoustic system for sound velocity measurement.

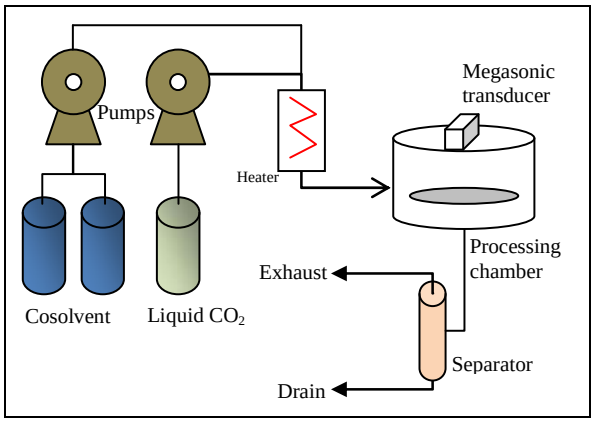


Fig. 3: Basic components of the SC CO2 cleaning equipment.

Impact of megasonic energy in SC CO_2 was studied through the measurement of particles contamination brought by the process and metal decontamination on 200 mm silicon wafers. Experiments are described in table 1.

Added particles onto the wafer were determined by KLA Tencor Surfscan SP1 measurement system. The results are given with an accuracy of 5 %.

In metal removal experiments, 200 mm silicon wafers were dipped in copper-dissolved baths. The resulting copper concentrations on the wafer were about 10^{13} at.cm^{-2}. Supercritical CO_2 cleaning was performed with a 5% additives solution during two minutes. Fluorhydric acid was chosen to etch the native silicon oxide (17 Å) at the Si wafer and consequently to remove the contamination located at the surface. Nine points mapping of Total Reflection X-ray Florescence analyses were performed before and after process to determine metal concentrations in order to calculate the remaining copper.

Processing conditions	T (K)	P (Mpa)	Additives
Particles contamination	353	15	-
	293	6	-
Metal decontamination	353	15	HF 0.05 V%

Table 1: Cleaning processes used for megasonic activation evaluation. Additive concentration given is volume concentrations in ethanol.

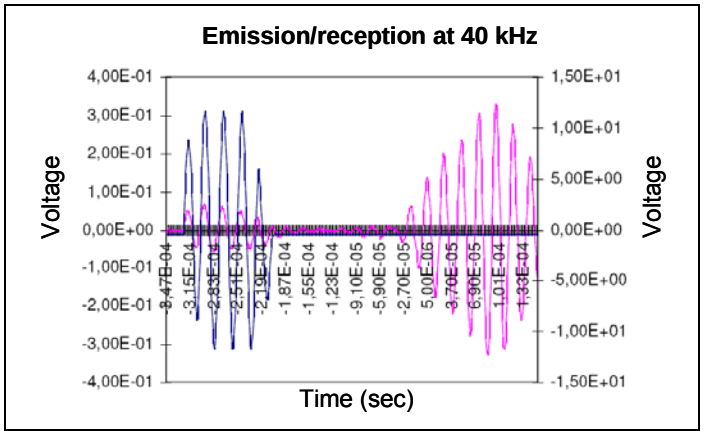


Fig. 4: Emission (blue) and reception (violet) in supercritical CO_2, as recorded by oscilloscope

RESULTS AND DISCUSSION

Sound velocity measurement in dense carbon dioxide

The emission and reception signal recorder by the oscilloscope is presented on figure 4. Elapsed time between them is defined by overlying these two signals.
Measurements and values deduced are presented in table 2 and illustrated on figures 5a and 5b.

Pressure (Mpa)	Temperature (K)	Sound velocity (m/s)	Acoustic Boundary layer thickness @ 1.4 MHz (µm)	Wavelength @ 1.4 MHz (µm)
1.0	286	225	0.415	161
2.0	286	229	0.285	164
4.0	286	212	0.200	151
6.2	286	331	0.144	236
6.9	286	322	0.145	230
7.5	286	343	0.146	245
10.0	287	371	0.146	265
14.0	288	425	0.148	304
20.0	289	459	0.156	328
25.0	289	492	0.163	351
7.3	297	183	0.142	131
7.5	301	173	0.138	124
7.5	***303***	***138***	***0.135***	***99***
7.5	306	190	0.146	136
10.0	309	209	0.141	149
14.9	311	277	0.143	198
20.0	311	364	0.147	260
25.0	311	457	0.151	326
Water		**1500**	**0.480**	**1070**

Table 2: sound velocity measurements at 40 kHz in carbon dioxide and calculation of acoustic boundary layer and wavelength for a 1.4 MHz transducer. Comparison with water at room pressure and temperature

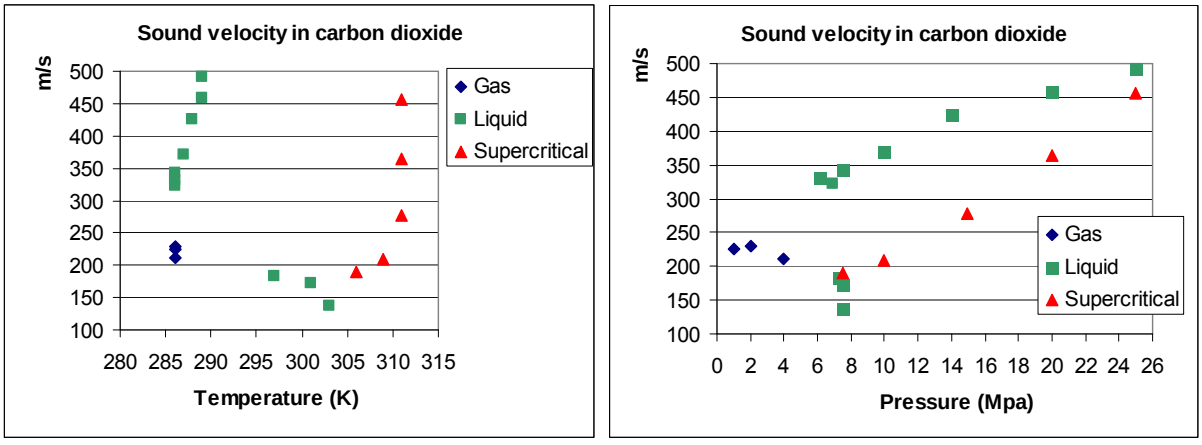
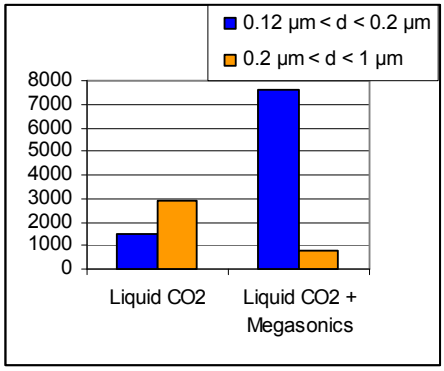


Fig. 5a and 5b : Sound velocity in carbon dioxide as a function of temperature and pressure

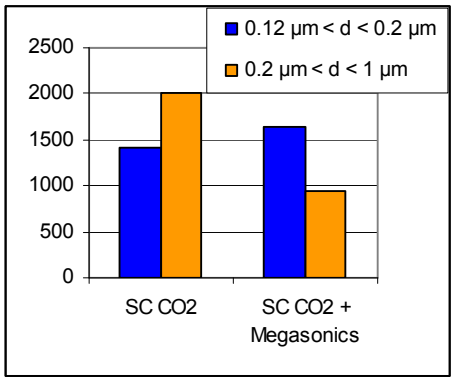
Velocity of sound is very low in dense carbon dioxide compared to classical liquids, even for equivalent densities (e.g. 1500 m/s in water). As expected, the lowest sound velocity was observed at the vicinity of the critical point, a value as low as 138 m/s was measured. Moreover, in dense carbon dioxide and at 1.4 MHz, calculated thickness of the acoustic boundary layer is 3 to 4 times lower than in water (. Acoustic wavelength is as much as 10 times lower than in water. These values highlight

better fluid properties for particles removal in SC CO_2 than in water.

Impact of Power Megasonics in SC CO_2 trough wafer surface characterization



(a)



(b)

Fig. 6: Added particles after a process in liquid CO_2 (a) and in supercritical CO_2 (b).

In order to highlight the influence of power megasonic activation for surface cleaning applications, the efficiency of the power acoustic transducer was evaluated for two different applications concerning silicon wafer processing:

- Particle contamination added by process equipment on wafer ;
- Atomic copper contamination removal.

Particle contamination

Processing equipment used for the tests has a high particle-added contamination level, despite of efforts to reduce it. These particles are transported by either liquid or supercritical fluid during the process. Even if this contamination is a real issue for semiconductor applications, it was used here to highlight the many differences observed with or without megasonic activation. The number of added particles after the different processes is presented

The number and size distribution of added particles depend on the fluid state and the megasonic activation and reveal a critical diameter of 0.2 µm. Indeed, with megasonic activation particle contamination is more important below 0.2 µm and reduced above 0.2 µm. As calculated for the processing conditions, in liquid and supercritical carbon $\boldsymbol{\delta}$ is about 0.15 and 0.14 mm. As a comparison, the hydrodynamic boundary layer, depending on stream velocity in the processing vessel [7], is 2µm. As illustrated in figure 7, drag forces gradient in the vicinity of the substrate surface is thus considerably increased by the reduction of the boundary layer. For this reason particles with a diameter higher than this acoustic boundary layer are easily removed from the surface. On the contrary, acoustic activation can bring small particles closer to the surface, where they are trapped by attractive forces.

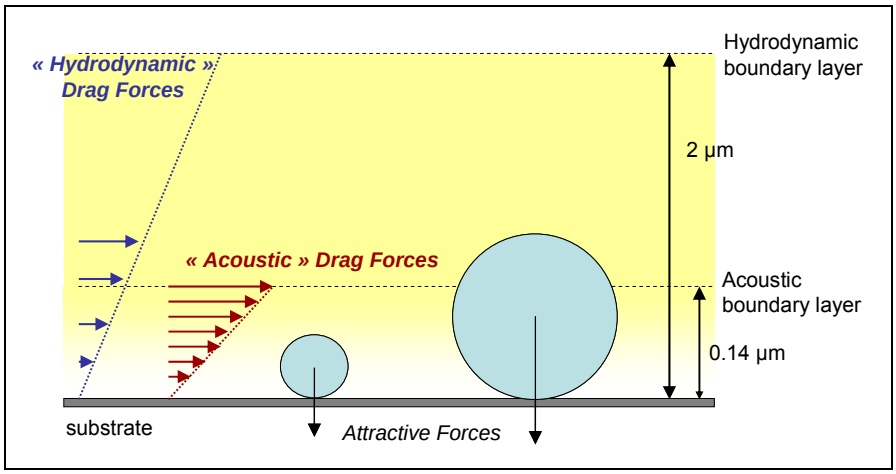


Fig. 7: Modification of drag forces gradient near substrate with acoustic activation.

Atomic copper contamination

The data obtained are illustrated on figure 6 and show that only processes with megasonics and additives are efficient to remove metal contamination. It appears that this supercritical cleaning solution is efficient only with megasonic activation, illustrating the sonochemical effect of the acoustic streaming.

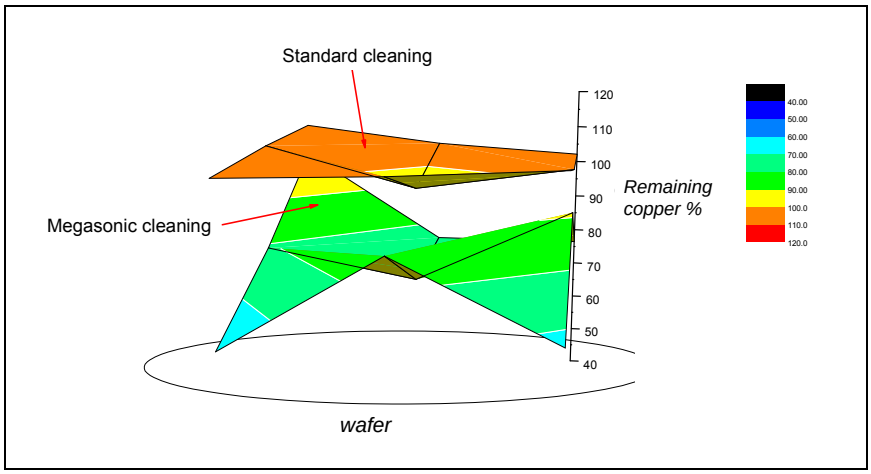


Fig. 6: Residual copper contamination with / without megasonic activation.

CONCLUSION

This preliminary study showed that with a low viscosity, high density and with good acoustic and thermal coupling, supercritical carbon dioxide is a fluid particularly adapted for high-frequency power acoustic generation. The resulting very thin boundary layer should find applications in cleaning and nanotechnologies such as powder processing.
The power acoustic transducer demonstrated its ability to work in a supercritical environment and its design can be adapted to other geometries, depending on process needs. Higher frequencies up to 5 MHz can be also implemented.

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