POST-CMP CLEANING OF HYDROPHILIC AND HYDROPHOBIC FILMS USING AQUEOUS ASSISTED CO\(_2\) CRYOGENIC CLEANING

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ABSTRACT

This paper describes the use of a hybrid cleaning consisting of a combination of CO\(_2\) cryogenic cleaning technology with conventional wet cleaning for post chemical mechanical polishing (CMP) cleaning at 0.13 \(\mu\)m technology node and lower. Following CMP, the aqueous enhanced cryogenic cleaning is performed to remove the sub 0.3 \(\mu\)m particles from surfaces with greater efficiency than is presently possible with wet cleaning only. The films investigated in this work were TEOS, Coral, SiLK and SiC. The TEOS wafers were polished with Cerria slurry while colloidal silica slurry was used to polish the other wafers. Post CMP cleaning of the wafers consisted of wet cleaning, followed by spin rinse drying and CO\(_2\) cryogenic cleaning. The results indicate that more than 50% of the light point defects (LPD) larger than 0.2 \(\mu\)m left after aqueous cleaning and drying were removed by cryogenic cleaning. There was no change in bulk or surface chemical properties of the two low \(k\) films investigated as measured by FTIR and XPS. The film roughness, measured by AFM, did not show an increase. Cryogenic cleaning was therefore found to enable aqueous cleaning in removing slurry particles while maintaining the critical film properties.
I. INTRODUCTION

Global planarization of dielectrics and metals is best done by CMP with the aid of slurries. The post CMP cleaning requirements include: 1) removal of chemical additives which are part of the slurry composition such as organic acids, corrosion inhibitors, passivators, and surfactants, 2) the chemical reaction by-products of CMP, and 3) the slurry particles. All of these contaminants must be removed prior to the next step in the IC fabrication process.

The current cleaning method in post CMP is aqueous based wet cleaning which adequately addresses first two of the three cleaning requirements outlined above. However, it is limited by the boundary layer thickness and the reduced wetting of hydrophobic films in removing small particles. The boundary layer due to fluid flow can be reduced by the use of acoustic excitation, however, the reduction in the boundary layer even with the addition of megasonics is insufficient for effective removal of sub 0.3 μm particles such as those of the slurry [1,2]. Hence, to effectively remove the small slurry particles after CMP, a new form of cleaning is investigated, not constrained by the boundary layer thickness of the cleaning fluid or its surface tension, to augment the wet cleaning for complete and effective post CMP cleaning. Carbon dioxide (CO\(_2\)) cryogenic is one such cleaning technology which if used in conjunction with wet cleaning, can address all the cleaning requirements for post CMP cleaning, and especially remove the particulate contamination with greater efficiency than is possible with the conventional wet cleaning only.

II. MECHANISM OF CRYOGENIC CLEANING

In cryogenic cleaning liquid CO\(_2\) at a pressure of 850 psi and 25C from a purified source is made to expand through a specially designed nozzle intended to make the expansion a constant enthalpy process. The expansion of liquid CO\(_2\) through the nozzle creates solid and gaseous CO\(_2\) in a highly directional and focused stream. There are three mechanisms by which surface cleaning is done: 1) momentum transfer by the cryogenic particles to overcome the force of adhesion of slurry particle to wafer
surface, 2) drag force of gaseous CO\textsubscript{2} to remove the dislodged particle off the surface of the wafer, and 3) the dissolution of organic contaminants by liquid CO\textsubscript{2} formed at the interface of the cryogenic particle and the wafer surface.

The flow of gas over the wafer surface creates a boundary layer through which the cryogenic particles have to travel to arrive at the wafer surface and the contaminant particle to be removed. During the flight through the boundary layer, their velocity decreases due to the drag force on them by the gaseous CO\textsubscript{2} in the boundary layer. The relaxation time is given as:

\[ \tau = \frac{2r^2 \rho_p C_c}{9\eta} \]  

where:

- \( r \) is the radius of the cryogenic particle
- \( \rho_p \) is the density of the cryogenic particle
- \( \eta \) is the viscosity of the CO\textsubscript{2} gas
- \( C_c \) is the Cunningham slip correction factor

The velocity of a cryogenic particle decreases to 36% of the initial velocity if it takes a time equivalent to one relaxation time [3-5] to cross the boundary layer. The relaxation time increases for larger cryogenic particles, implying, that they can cross the boundary layer with greater fraction of their initial velocity. It has been shown in [4] that based upon this physical model of cryogenic cleaning, the boundary layer does not pose a limit on the efficiency of sub-micron and nano particle removal in CO\textsubscript{2} cryogenic cleaning.

### III. EXPERIMENTAL DESCRIPTION

Blanket TEOS, SiLK, Coral, and SiC wafers were first scanned using KLA-Tencor’s SP1 to determine their quality. Wafers without scratches were chosen for these experiments and polished on an IPEC polisher. The TEOS wafers were polished using EKC STI2100™ Cerria slurry as would be used in shallow trench isolation (STI) fabrication process. The BEOL films Coral, SiLK and hardmask SiC were polished
using colloidal silica MicroPlanar CMP 9000™ series slurry from EKC Technology. Following polishing, the TEOS wafers were cleaned in a single wafer SSEC cleaner with a megasonic wand while the Coral, SiLK and SiC wafers were cleaned in a two station brush assisted OnTrak cleaner. Some wafers were cleaned with basic cleaner LPX-100, from EKC Technology, while others with DI water only. The wafers were then dried in a spin rinse dryer after which they were measured for particles using the SP1. Cryogenic cleaning with ATS EcoSnow’s WaferClean1600™ was next done, four to thirty hours after drying the wafers. The wafers were then measured for surface particle using the same recipe as the pre-measurements, from which the particle removal efficiency was determined. Film characterization of SiLK, Coral, and SiC were also done to determine the impact of the cryogenic cleaning on film structure, surface film composition and roughness. The section below describes the results of these experiments.

**IV. RESULTS AND DISCUSSIONS**

Figures 1 and 2 below show the cleaning efficiency for TEOS wafers polished with Cerria slurry. The six wafers in figure 1 following polishing were cleaned using LPX-100 whereas those in figure 2 were cleaned only with DI water with no other chemicals added to it. An average of 82% of the LPD’s left after aqueous clean with LPX-100 and dry was removed by cryogenic cleaning. In three of the six wafers the removal efficiency was greater than 90% and final LPD count of as low as 21 was obtained on the wafer surface. The DI clean sequence in figure 2 indicated that on an average of 98% of LPD’s left after the aqueous clean and spin rinse dry was removed by cryogenic cleaning.
Figures 3 and 4 show the results of polishing and cleaning Coral, a carbon doped oxide low k film, and SiLK, a spin-on organic dielectric film using the aqueous and cryogenic cleaning sequences. All three Coral wafers showed reduction of greater than 58% of LPD, by CO\textsubscript{2} cryogenic cleaning, left after the aqueous cleaning and drying. The SiLK wafers in figure 4 had very high, >35,000, LPD on them after un-optimized aqueous cleans consisting of DI water and LPX-100 with brush assistance. It is believed that many of these defects were a result of water stains formed during drying of hydrophobic films. The cryogenic cleaning was able to remove more than 62% of these defects. Thus more than half of the defects left behind after an aqueous cleaning can be removed by cryogenic cleaning even when the cryogenic cleaning is preceded by spin rinse drying and is done in some instances 30 hours after the aqueous clean and dry.
Figure 3. Silica particles on Coral before and after cryogenic clean in an aqueous and cryogenic cleaning sequence.

Figure 4. Silica particles on SiLK before and after cryogenic clean in an aqueous and cryogenic cleaning sequence.

Measurements on both spin-on organic SiLk and CVD deposited CDO Coral wafers were done to determine any changes in bulk and surface film properties. Figures 5 and 6 show the FTIR measurement results on Coral and SiLK wafers respectively. There appeared to be no change in the spectrum for both types of low k films before and after cryogenic cleaning. Thus the FTIR measurements indicated no change in the bulk properties of the film as a result of the cryogenic cleaning.

The surface characterization of SiLK film was done using XPS to determine if chemical change has taken place due to the cryogenic cleaning. The results indicate that there were only two elements Carbon and Oxygen detected on the film surface. The atomic composition of Carbon was 97.96% +/- 0.14% before cryogenic cleaning and 97.86% +/- 0.12% after, or no significant difference at 95% confidence level. The Oxygen atomic compositions before and after cryogenic cleaning were 2.04% +/- 0.14 and 2.14% +/- 0.12%, respectively, again indicating no significant difference. High energy XPS of the Carbon and Oxygen peaks showed no shift in their positions before and after cryogenic cleaning indicating no change in the bond structure. Thus neither
the elemental composition nor the chemical bonding changed as a result of cryogenic cleaning.

![Figure 5. FTIR spectra of Coral film](image1)

![Figure 6. FTIR spectra of SiLK](image2)

Figure 7 shows the results of polishing and cleaning of CMP hardmask SiC film. The blanket SiC wafer was polished using silica slurry after which it was wet cleaned and dried following which it was further cleaned cryogenically. The results indicate that 68.2% of the LPD larger than 0.2 µm left on the wafer surface after the aqueous clean and dry were removed by the cryogenic cleaning.

The roughness of SiC was also measured using AFM to determine if the cryogenic cleaning process induced surface roughness of the film. Figures 8 and 9 show the 10 µm x 10 µm AFM scans of the SiC as-deposited and after the hybrid aqueous and cryogenic cleaning respectively. The RMS roughness of the as-deposited film measured at the center was 1.35 Å while the film after cleaning had a roughness of 0.96Å.
V. SUMMARY

Post CMP cleaning consisting of a combination of conventional aqueous cleaning with CO$_2$ cryogenic cleaning results in better cleaning than aqueous. Cryogenic cleaning was seen to remove more than half the LPD, greater that 0.2 µm,
left after the aqueous clean and dry from hydrophilic and hydrophobic films used in the integrated circuit manufacturing process. This was possible even when the wafers were dried and significant time elapsed prior to the cryogenic cleaning. Thus a sequence of aqueous and CO\(_2\) cryogenic cleaning should be investigated for post CMP cleaning for device fabrication at 130 nm technology and lower.

**VI. Bios**

**Souvik Banerjee**, Ph.D. is the Chief Scientist at ATS EcoSnow Systems Inc. where he is responsible for directing the R&D of the company in the area of surface preparation in integrated circuit manufacturing process. Before joining EcoSnow, he was a Senior Process Engineer at Novellus Systems working on development of advanced surface preparation in semiconductor device fabrication. His work involved development of new cleaning technologies for back-end-of-line post etch residue removal applications. Prior to joining Novellus, he was a Research Engineer at Komag where he worked on post-CMP cleaning, evaluation of cryogenic cleaning for removal of polymeric particles, and process control. His Ph.D. research were in the areas of particulate charging, transport of charged particles, and particle adhesion to surfaces. He received the Maurice K. Testerman award in 1994 given for outstanding research from the University of Arkansas from where he obtained his Ph.D. He has authored several papers on post CMP cleaning, particle charging, and adhesion of particles to surfaces. He has filed 5 patents on supercritical fluid cleaning development and 3 on cryogenic cleaning. He taught the UC Berkeley Extension “Cleaning Technology for Integrated Circuit Manufacturing” course in 2001 along with other professionals from the semiconductor industry.

**Harlan F. Chung** is a senior application scientist at Eco-Snow Systems, where he is responsible for the development, design, and application of CO\(_2\) cleaning processes for the MR head and semiconductor industries. He has 30 years of experience in the fields of semiconductor materials growth and process development. The author of 20 plus articles
on materials growth and process development and the holder of three patents, he received his BA in biochemistry from the University of California, Berkeley.

**Andrea Via** is an applications engineer at ATS EcoSnow Systems Inc. where she is responsible for the development, design, and application of CO₂ cleaning processes for the MR head and semiconductor industries. Before joining EcoSnow, she was a Process Engineer at JDS Uniphase working on development of cleaning lines and inspection criteria for optical filters. Prior to joining JDS Uniphase, she was a Process Engineer at Sola Optical, where she was responsible for the implementation, process control, and process transfer of the hardcoating lines used to coat eyeglass lens. She received a BS degree in Chemistry from the University of California, Davis.

**Robert J. Small**, Ph.D., is the technical director of the CMP group at EKC Technology. He is involved in developing new chemistries for post CMP cleaning, CMP chemistries and post etch residue removal. Bob has BS from Norwich University, an MS from Texas Tech University, and a Ph.D. in organic photochemistry from the University of Arizona. He received the first Technical Catalyst Award from First Chemical Corp in 1994. He has authored or co-authored nearly 100 articles and presentations including BEOL, post clean treatment, post CMP and CMP processes. He holds more than nineteen U.S. and foreign patents and has ten submitted U.S. patent applications. (Small can be reached at 510/784-5846, bsmall@ekctech.com).

**Cass Shang**, has been an R&D chemist at EKC Technology since 1998. Her research focus for the R&D CMP group is developing new CMP slurries and optimizing CMP processes. She has also worked on copper contamination control during the CMP process. Shang has a BS in chemical engineering from Beijing University, an MS in environmental and surface analysis from University of Colorado. She has coauthored 12 papers related to metal CMP and post CMP cleaning. (Shang can be reached at 510/670-1478, Cass_Shang@ekctech.com).
VI. REFERENCES


