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### Entegris Expands CMP Filtration Technology Solutions and Research, Analytical and Manufacturing Capabilities in Taiwan

Entegris announced at the SEMICON® Taiwan tradeshow the development of a platform of CMP filtration solutions using nano-melt-blown (NMB) filtration technology, as well as the expansion of its CMP research, analytical services and manufacturing capabilities in Taiwan. These investments enable the company to further serve the growing demand for advanced CMP filtration solutions.

“CMP processes continue to grow in complexity in both the materials used and the need for greater planarity in each layer of today’s devices,” said Entegris Vice-President of the Liquid Microcontamination Control business unit, Clint Haris. “Entegris continues to invest in people, technology and facilities in Asia to introduce new solutions for the semiconductor market. As our customers produce integrated circuits with smaller feature sizes, our nanofiber technology reduces the number of defect-causing contaminants from reaching the wafer.”

The Entegris filter platform using NMB media now includes the Planargard® bulk, Solaris® point-of-tool and Planarcap® point-of-dispense families to provide contamination control solutions throughout the CMP process area. Developed and manufactured in Taiwan, the NMB media utilizes the increased porosity of the nanofibers to reduce shear stress placed upon the slurry during transport and filtration operations. These innovations result in extended filter lifetime and greater removal of defect-causing contaminants.

>> For more information please visit: Link

### SmartStack® 300 mm Contactless HWS Launch @ SEMICON Europa

Entegris launched the SmartStack 300 mm Contactless Horizontal Wafer Shipper for safer wafer handling at SEMICON Europa in early October.

"We designed an ideal solution for shipping and storing 25-lens bumped or thin wafers that offers improved safety over conventional wafer shippers," said Entegris Product Marketing Manager, Doug Moser.

"By placing the wafers on rings and removing the interleaf inserts and foam cushions, the wafers are protected from stains, imprints and scratches typically caused by these inserts. Additionally, the new design accommodates 25 wafers in one shipper, thereby increasing shipping density and lowering shipping cost 50% or more, compared with a conventional FOSB."
Future semiconductors will require new materials and new device structures, such that there will be new inherent yield-loss mechanisms from both systemic process-design interactions and random particulate defects. Both types of yield-loss mechanisms become much more difficult to control when high-volume manufacturing (HVM) is done on smaller than 22 nm-node ICs, as explained by world experts gathered at the 3rd Annual Entegris Yield Breakfast Forum, held in conjunction with SEMICON West 2015 in San Francisco.

“We really wanted to highlight the necessity of contamination control during the forum this year,” stated Entegris V.P. of Marketing, Wenge Yang, organizer and host of the annual event. “As we look to advanced nodes and the smaller geometries associated with them, the tolerance for defects shrinks as well. What may have been acceptable before becomes highly detrimental at smaller scales.”

With excellent presentations from Intel®, Lam Research®, KLA-Tencor® and Entegris on the topic, followed by a panel discussion, the forum was well-attended and well-received. Following is a summary of what was presented and covered.

Decreased Tolerance for Contamination

Dr. Archita Sengupta, Technologist and Technical Supplier-related MCSC Program Manager, Intel Corp., provided a thorough keynote address to start the event: “Enabling Global Micro-Contamination Control Collaboration for Advanced Technology Yield Enhancement.” Sengupta stated that we are already in an era of extreme process complexity due to the need to integrate a greater number of the elements from the periodic table into atomic-scale device structures. While engineering at the atomic scale, the number of possible defects increases dramatically, and there is far less tolerance for both systemic and random sources that used to be considered as noise. To control this escalating complexity, she says that a paradigm shift is required to be able to think about “clean” as having meaning only for a specific application and only as defined by some quantitative metric.

Figure 1 shows that the monitoring of trace particle defects is getting more difficult as the killer-defect size decreases, and that even in pure deionized water (DI), today’s laser particle counters (LPC) cannot reliably resolve below 20 nm particle size. Meanwhile, she said, industry leaders will soon need to be able to monitor and control 10 nm and even 5 nm particles. Metrology techniques of all types are challenged to provide sufficient sensitivity for early detection and prevention, so the OEM metrology suppliers need to engage with fabs and subsystems suppliers so the entire supply chain can be ready when multibillion-dollar fabs need to rapidly ramp new technologies.

Causes of Contamination

With new “customized, blended” materials being integrated into wet chemical processes, there are new components to be controlled, yet maintaining component assay is now insufficient. Blended chemistries introduce additional challenges such as the possibility of forming microbubbles and micelles of different phases during storage and/or transport, and such micro-phases may appear as particle defects to improperly calibrated metrology tools. As chemicals travel within any dispense system, contamination is added from leaching and/or reaction with components, and since parts-per-million (PPM) to parts-per-trillion (PPT) levels of organic impurities can degrade die yield, customized filtration and monitoring is needed to meet this “paradigm shift in defect tolerance.”

Sengupta issued a familiar call for collaboration throughout the supply chain with specific plans for quality systems to achieve “ship to control” such that fabs would ideally be “quality incident free.” From Intel’s perspective, materials suppliers must help hold responsibility for the following three critical aspects:

1. **Ship the “best” possible quality materials** by rigorous control of subsuppliers and production processes

2. **Provide aggressive “super-filtration” of chemistries** during chemical manufacturing and in shipping/dispensing

3. **Help close the metrology and analysis gap** by working with industry consortia

Contamination Control Solutions

Keith Wells, Senior Vice President of Engineering and Technology, Wafer Inspection Group at KLA-Tencor®, provided an example of the challenge in his discussion of “How to Detect Random Defectivity at 10 nm and 7 nm Nodes.” KLA-Tencor has to work closely with customers to do simulations of different, specific device layers such as gate tungsten CMP or contact liner so as to be able to model defects. In a design-rule (DR) shrink simulation of a FinFET silicon-bridge fin pattern defect, it was seen that the peak signal...
wavelength shrinks with the DR; at 14 nm DR, the peak signal is ~255 nm; at 10 nm DR, the peak is ~230 nm; and at 7 nm DR, the peak is ~190 nm. KLA-Tencor invested $100 million over many years to develop an inspection tool with wavelength range down to 190 nm in anticipation of the industry’s need for 7 nm DR.

Jim O’Neill, CTO, Entegris, discussed the role of the materials supplier in accelerating yield in a disruptive environment, and cited, as examples, the industry evolution to fluorine-free tungsten (W) sources for CVD, and the revolution to use cobalt (Co) barriers in copper interconnects. Fluorine-free tungsten is being looked at for various applications, including 3D NAND, and many of the precursors are solids that must be sublimated, so in-line filtration is needed to reduce particles flowing to the chamber. Table 1 shows Entegris’ roadmap to provide a turnkey point of use delivery of solid precursors.

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### Table 1

<table>
<thead>
<tr>
<th>Market Demand</th>
<th>Year</th>
<th>Chemistry</th>
<th>Delivery</th>
<th>Filtration</th>
<th>Monitor</th>
<th>Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine-free Source</td>
<td>2014</td>
<td>Novel</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Performance</td>
</tr>
<tr>
<td>Material Usage</td>
<td>2015</td>
<td>Novel</td>
<td>Container</td>
<td>—</td>
<td>—</td>
<td>Cost</td>
</tr>
<tr>
<td>Particle Reduction</td>
<td>2015</td>
<td>Novel</td>
<td>Container</td>
<td>In-line</td>
<td>Beta-tests</td>
<td>Yield</td>
</tr>
<tr>
<td>Process Stability</td>
<td>2016</td>
<td>Novel</td>
<td>Container</td>
<td>In-line</td>
<td>HVM</td>
<td>Cost</td>
</tr>
</tbody>
</table>

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As another example, the industry is now transitioning to the use of Co metal as barrier layers to reduce electro-migration-induced defects in the smallest of Cu dual-damascene interconnections. The integration of this new material into HVM mandates at least the need for the following new technologies: ALD/CVD precursors, precursor delivery subsystems and post-CMP and/or post-etch cleaning. For Cu-post-etch residue-removal, Entegris is working to co-optimize the filter and the chemical formulation. Per-process-optimization will be a key focus moving forward.

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**Redefining “Clean”**

During the concluding panel discussion, all presenters agreed that, at smaller geometries, defects become more threatening to yield and there are two options moving forward.

The first is to accept less yield from manufacturing due to defects (this is not, however, an acceptable option, they concluded); and second, for manufacturers to tighten collaborative efforts with suppliers to help better ensure cleaner materials that bring better performance and higher initial quality, while redoubling efforts to increase performance during in-line filtration. What it means to be clean might just start getting redefined.

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KEYWORDS: advanced, atomic, clean, contamination, control, critical, defect, Entegris, filter, HVM, integration, manufacturing, materials, node, semiconductor, yield
Yield Improvement

Entegris Announces New VaporSorb™ TRK Filter for Advanced Yield Protection in Semiconductor Lithography Processing

By Marc Venet, Product Manager | AMC Filtration Solutions - Entegris, Inc.

At advanced process nodes (sub 28 nm), the need for removing other airborne molecular contaminants (AMC) besides ammonia has become apparent. Organics have been known to cause photo adhesion problems. Acid contamination can lower yield in a number of different ways, including satellite defects resulting from acidic interaction with the TMAH developer during the development step, salt particle formation from acid base reactions and line width loss during post photo etching steps due to a loss of photoresist selectivity. Strong acids have always been fairly easy to control with standard media chemistries. More recently, weak acids have become more of a concern in causing process problems. Weak acids have proven to be much more difficult to remove and are not removed by traditional AMC filters.

Examples of weak acids include acetic and formic acids (acetate; CH₃COO⁻ and formate; HCOO⁻) and nitrous acid (nitrite; NO₂⁻). These contaminants are causing concerns regarding defects and yield in photolithography processing and can be removed by traditional AMC filters and, furthermore, may be formed from organic contamination when using traditional filter designs.

The New "Four-in-One" VaporSorb Filter

VaporSorb is a leading brand of AMC filter used in cleanroom environments and for process tools during key steps in semiconductor manufacturing. Over time, VaporSorb filters have been engineered to capture airborne organics, bases and strong acids—all in one filter. The new VaporSorb TRK has added unique material to allow it to become the first single filter to capture not only the top three core contaminant classes, but also the fourth, weak acids.

Designed specifically for photolithography coater/developer tracks, the new filter was created as a "four-in-one" filter solution to avoid the complexities of multi-filter handling and to build on the previous "three-in-one" technology. In addition, the filter retains the VaporSorb’s industry-leading service life to reduce both tool downtime and cost of ownership.

VaporSorb filters use a unique mix of materials to capture airborne molecular contaminants. The mix was improved by adding a new adsorbent to create the new four-in-one filter. In-field, end-user testing has confirmed that the filter is capable of capturing all organics, bases, strong acids and weak acids that cause wafer or equipment defects.

Field Data: Circular Void Defect Reduction

Experimental

VaporSorb TRK Filters on Lithius® PRO V-i track 22 nm process. Two identical Lithius PRO V-i tools running same process recipe:

- First tool with POR 3-in-1 filter on THC cabinet
- Second tool with Entegris VaporSorb TRK 4-in-1 filters on THC cabinet

Results

- Circular void defects (pictured) have been correlated to an as-yet-undefined environmental contaminant
- VaporSorb TRK filter consistently outperformed Positive Control condition (no RRC, POR THC filter) for circular void defectivity
- Introduction of RRC prior to photoresist dispense has proven to be an effective countermeasure. However this countermeasure:
  - Increases wafer processing time
  - Increases materials cost
- Strongest mechanism proposed suggests that contaminant is introduced to the wafer process environment through cleanroom air that is drawn into the tool.

Tool POR air filters are not capable of removing the airborne contaminant whereas VaporSorb TRK filters are removing the contaminant — see Table 1.

<table>
<thead>
<tr>
<th>Filter</th>
<th>COT</th>
<th>RRC</th>
<th>Void Defect Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>POR</td>
<td>1 × 10¹⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POR</td>
<td>Normal</td>
<td>6 × 10⁴</td>
<td></td>
</tr>
<tr>
<td>VaporSorb TRK</td>
<td>Normal</td>
<td>~2.5 × 10¹⁴</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Defect data

Field Data: Satellite and Particle Defect Reduction

Customer data from ACT 12 track in 45 nm process

Customer After Development Inspection Data

Figure 1. Circular void defect

Figure 2. Compares wafer defect data between standard 3-in-1 filter for strong acids, bases and organics with Entegris’ VaporSorb TRK 4-in-1 filter, which protects against weak acids as well. Satellite defects eliminated and particle defects dramatically reduced.
Innovation

Diffusion, a Key Parameter to Understand Contamination Phenomena in FOUPs: Part 1 — Polymer Transport Coefficients Obtention

By Paola Gonzalez Ph.D., Application Development | CEA-Leti Assignee - Entegris Europe

FOUPs are designed to hold silicon wafers securely and safely in a controlled environment, and to allow the wafers to be removed for processing or measurement tools equipped with appropriate load ports and robotic handling systems. However, contamination issues still exist in these storage containers made with porous plastics (i.e. polycarbonate, polyethertherketone, polyetherimide, etc.). These polymeric materials are well known for their ability to outgas AMC and this constitutes a significant issue with respect to wafer environmental contamination control. This molecular cross-contamination scheme has been clearly evidenced for organics and volatile acids, showing that the accumulation process (i.e. sorption) and the reversible outgassing are long-term phenomena. As sorption is governed by surface adsorption of molecules then, followed by their diffusion into polymer bulk, diffusion becomes the key parameter to understand cross-contamination mechanisms.

Experimental

Polymer thin films samples of a few cm² were set inside a low-volume reactor which is then immediately swept by a flow of HF with controlled concentration of a few hundreds ppbv in 40% humid air. The contaminated atmosphere was carried out by dilution with clean air of a 10 ppmv HF pressurized bottle. The air flow humidity was fixed at 40% and all experiments were performed at cleanroom temperature (≈25°C [77°F]).

The absorption kinetic is then obtained from different polymer samples (single exposure per sample) depending on their exposure time. Determination of the sorbed HF into the polymer samples was performed by immersion in 50 mL ultrapure hot water (UPW) overnight in an oven at 70°C (158°F). This procedure allows the HF molecules absorbed in the polymer matrix to be extracted in water in their ionic form (as fluoride ions). The analysis of fluoride in extraction solution by ionic chromatography (IC) then allowed the quantification of HF accumulated in polymer samples. Collection efficiency was controlled by consecutive extractions (three minimum). Detection thresholds of 0.2 ng/cm² and extraction efficiency more than 95% were reached.

Results

A quasi-instantaneous adsorption on a polymer surface (characterized by significant levels of HF trapped at shorter time) occurs immediately, followed by the diffusion into the material volume. This last process is the limiting kinetic factor. Then, saturation levels in polymer films were reached in about 8 days (200 h) exposure with levels of 6400 ng/cm² for PC, 7200 ng/cm² for EBM and 14,500 ng/cm² for PEI for HF at 200 ±15 ppbv. Thus PEI presents a higher solubility coefficient than PC and EBM, which are similar.

Figure 1. Sorption kinetic in polymer thin films for HF concentration in the air of 203 ppbv (±10%) From this sorption kinetics data, HF transport coefficients were determined for constant 21°C ±2°C (70°F ±36°F) and atmospheric pressure at 40% RH and are listed in Table 1. For comparison, diffusion coefficients obtained for H₂O using gas permeation method are listed too.

<table>
<thead>
<tr>
<th>HF Coefficients</th>
<th>Molecule</th>
<th>D × 10⁻¹² (cm²/s)</th>
<th>S (cm²/cmHg)</th>
<th>P 10⁻³ (cm²·cmHg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>HF</td>
<td>42 ± 16.8</td>
<td>1330 ± 0.75</td>
<td>56 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>9500 ± 0.07</td>
<td>5 ± 0.7</td>
<td>47 ± 50</td>
</tr>
<tr>
<td>PC</td>
<td>HF</td>
<td>17 ± 6.8</td>
<td>459 ± 0.17</td>
<td>7.8 ± 6.0</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>56000 ± 0.2</td>
<td>1.9 ± 0.05</td>
<td>110 ± 40</td>
</tr>
<tr>
<td>EBM</td>
<td>HF</td>
<td>3.7 ± 1.55</td>
<td>524 ± 0.44</td>
<td>1.94 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>8500 ± 0.26</td>
<td>0.32 ± 0.12</td>
<td>2.5 ± 0.4</td>
</tr>
</tbody>
</table>

Table 1. Transport coefficients determined for HF and comparison with those for water steam from permeation methods

These HF diffusion coefficients in PC, PEI and EBM are reported for the first time. These diffusion coefficients are very small in comparison with the diffusion coefficients obtained in permeation studies for the same type of polymers, but with greater solubility. Then, permeability coefficients remain similar to the ones obtained by permeation studies.

The fact that the kinetic curves follows Fick’s behavior and the same range values of permeability obtained by the sorption kinetic and permeability methodologies, validates the employed methodology and offers results at representative fab conditions (40% RH and atmospheric temperature and pressure).

Concerning HF cross-contamination in FOUPs polymers, these coefficients mean that less cross-contamination should be expected for EBM material due to its very low diffusion coefficient, followed by PC and finally by PEI (which presents the highest HF solubility, too). Then, the expectation is that by using EBM FOUPs, the contamination ability and subsequent contamination transfer to wafers will be smaller than using either PC or PEI FOUPs. This has been confirmed experimentally.

continued on the next page
Diffusion, a Key Parameter to Understand Contamination Phenomena in FOUPs: Part 2 — Coefficients Application in Numerical Simulation

By Paola Gonzalez Ph.D., Application Development | CEA-Leti Assignee - Entegris Europe

The aim of applying numerical simulation is to have better comprehension of the molecular cross-contamination phenomenon by offering complementary information (that is not experimentally reachable, such as the HF concentration profile in the polymer and its evolution depending on time). Simulation could be used to study and estimate the in-service lifetime of the FOUP and the optimal time of a cleaning process. Indeed, as microchip manufacturing technologies continue to advance and the process wafer becomes even more sensitive to the FOUP micro environment, numerical simulation could help to mimic FOUP polymer behaviors to predict and even quantify a physical phenomenon, such as AMC cross-contamination within FOUPs.

Experimental

Numerical formulation is developed for the AMC, stability and convergence studies and parameter sensibility analysis are detailed by the Entegris/CEA-Leti group. This model is reliable and we can use it with industrial conditions for the utilization of FOUPs and based on a simple polymer membrane-air model. The model has been solved numerically by Comsol® multiphysics version 3.5a (finite elements software able to solve a coupled partial differential equation).

This geometry corresponds to the near surface of the FOUP polymers. The frontier \( \Gamma_D \) represents the contamination source (i.e. just processed wafers) that diffuse through the air to be sorbed into the FOUP polymer. When no contamination occurs, the concentration is fixed at zero. In this model all the molecular movements are diffusive, both in the air \( \Omega_g \) and in the polymer \( \Omega_s \). The convective part in the air was suppressed in order to simplify the model. The air-polymer interface \( \Gamma_N \) is driven by the solubility equation \( S_i = C_i/P_i \) according to Henry’s Law.

Results

Applying diffusion (D) and solubility (S) coefficients, obtained experimentally for the polymer constituents of the FOUPs, a basic contamination case was studied and simulated.

Case of Realistic Contamination Event on a Clean Polymer

As in the sorption kinetic method described in Part 1, one polymer film is contaminated by an HF gas flow. Then, we simulate 2 hours of a film exposure into a reactor at continuous HF flow \([\text{HF}] = 2000 \text{ ppbv}\) followed by a waiting time of 100 minutes.
Product Highlight

Ultrapak® and Crystalpak® Wafer Shippers, the Gold Standard in Quality and Reliability

The Entegris Ultrapak and Crystalpak wafer shippers set, and have maintained, the industry standard for quality and reliability with their introduction over 28 years ago.

Ultrapak

Ultrapak high-purity Wafershield™ polypropylene provides a reliable 200 mm shipping box with these features:
- low inorganics
- low outgassing
- low particle generation
- naturally hydrophobic

The Ultrapak standard design features just three easy-to-use and easy-to-clean components — cover, cassette and base. This design provides integrated cantilever springs that limit wafer rotation, providing for a clean and safe shipping environment that minimizes wafer edge contamination. The Ultrapak thin wafer shippers have customized upper and lower cushions engineered for thin wafers. The Ultrapak cassette maximize automation interface and accuracy with both horizontal and vertical robotic flanges.

Crystalpak

Crystalpak’s ultrapure polycarbonate offers a dimensionally stable, clean, high-performance, reusable 200 mm shipping box with these features:
- low inorganics
- low outgassing
- low particle generation
- reusable with replaceable cushions and gaskets

Entegris molds quality into every Ultrapak and Crystalpak using state-of-the-art scientific injection molding techniques and Statistical Process Control (SPC). Ultrapak and Crystalpak products support the thin, standard, and thick wafers you need for maximum efficiency in your business.

Using the Entegris Ultrapak or Crystalpak will ensure:

- Wafer environment control
- Reliable mechanical performance
- Repeatable manufacturability

For more information, please contact your regional customer service center (refer to page 1 of this newsletter).

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