Real time analysis of the Haze environment trapped between the pellicle film and the mask surface

Jaehyuck Choi, Yongjin Cho, Sunghun Ji, Byung Cheol Cha, Sung Woon Choi, and Woo Sung Han, Photomask team, Samsung Electronics. Co. Ltd.; Seungyeon Lee, Samsung Advanced Institute of Technology, San #24 Nongseo-Ri, Giheung-Eup, Yongin-City, Gyeonggi-Do, Korea 449-711

ABSTRACT

With the use of 193nm lithography, time-dependent haze problem has become a critical issue for semiconductor industry. The understanding of the conditions that create haze defects is very crucial for the future development of haze-free cleaning processes. The gaseous environment trapped between the pellicle film and the mask surface triggers photochemical reaction under laser exposure, which could result in the formation of killer (printable) defects on the mask surface. Therefore, the real time analysis of the haze environment in the trapped space could provide essential clues to the characterization of haze defect growth mechanism. This fundamental study can be applied to the invention of real-time monitoring tools for the defect growth progress on the mask surface as well as the development of haze-free cleaning processes. Here, we propose a method to analyze the gaseous space trapped between the pellicle film and the mask surface that creates a highly reactive environment.

1. Introduction

Time-dependent haze defects have been a serious subject in 193 nm lithography since they grow much faster under such a higher energy dose compared to that of previous longer wavelength lithography.1 Many endeavors have been made on the examination of the haze defects on the mask surface using various tools such as IC-MS, TOF-SIMS, Raman and FTIR Spectroscopy.1,4 Most of them are
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<th>19.0 kV</th>
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<td>Quartz etch profile with straight sidewalls and no micro-trenching</td>
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<th>19.0 kV</th>
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EDITORIAL

1986-2006: A Brief History of the Photomask Industry

Ken Rygler, President, Rygler and Associates, Inc.

September 19 is an important date to me. It happens to be my birthday but it also happens to be the birth date of something I started and helped build. On September 19, 1986 the DuPont Company entered the photomask business and helped change the face of this industry.

The world and the semiconductor industry were very different places in 1986. PCs used an 8088 and 1 MB of DRAM, Argentina won the World Cup (without any headbutting), the Red Sox found yet another way to lose the World Series, and Japanese semiconductor producers were beginning to dominate DRAM and the rest of the semiconductor industry.

As for photomask production, there were many, many captive and merchant mask operations (I never got comfortable with being a “shop”). DuPont’s entry strategy was predicated on the change from optical pattern generators to e-beams, and related increases in cost for metrology and inspection equipment. We believed this order of magnitude increase in capital intensity would force a consolidation of the merchant producers. In addition, it would drive companies with internal mask making operations to rethink making such investments, when presented with an opportunity to procure photomasks from a global, technically competent, dependable company like DuPont.

And, indeed, over the next two decades, the photomask industry underwent a dramatic consolidation, which has resulted in three or four merchants owning over 90% of the merchant market. Adding the five or six major captives to these merchants, and you’ve got well over 95% of the total market. The number of photomask manufacturers has declined by about an order of magnitude.

In the first decade, the key success drivers were service and cost. Proximity to customers mattered, and, over time, most successful companies followed DuPont’s lead by trying to establish global manufacturing and distribution. With the advent of the subwavelength era at 180nm, technology became an important driver.

Things began to change as we approached the new millennium. Design costs and mask costs conspired with the 2000-2001 collapse to severely reduce ASIC starts. Companies like Agere and LSI Logic, which consumed loads of photomasks, went fabless, turning to foundries like TSMC with captive mask operations, significantly reducing the merchant ASIC mask market. The 20 year captive to merchant shift not only came to an abrupt halt, but perhaps reversed itself with Micron Technology’s decision to build a captive mask operation. Merchant photomask companies were forced to buy wildly expensive new mask writers and inspection tools, creating excess capacity, while competing for a shrinking merchant mask market. Global expansion reversed itself as merchant photomask companies began closing sites and consolidating their operations. Consolidation reached a high point (so far) with Toppan’s acquisition of DuPont Photomasks.

What’s next? Extrapolating the past can be misleading but this much seems clear. Fewer semiconductor producers can afford $3B fabs and $1B/node R&D bills. Fewer devices can afford $30M+ design costs and $3M+ mask costs. Standard and programmable products and very high volume SoCs will rule. Other merchant to captive moves may emerge, as mask technology is increasingly viewed as a differentiator. Mask unit volume will decline, while revenues may not, depending on ASPs. Even with ever-increasing complexity, we learned the hard way the devastating effect excess capacity can have on mask ASPs and profitability.

Merchant photomask makers will need to develop new skills and approaches to succeed in the 21st century. Simply having lots of money to buy expensive tools and raw materials, and chemistry and chemical engineering expertise, won’t be enough. A deeper understanding of semiconductor lithography, EDA, mask design, DFM/DFY challenges, and creative business models to deal with a declining unit market and stronger/fewer customers/customer consortia, will be required.

None of my 20 years in and around the mask industry were easy. But the next 20 may make the last 20 look like a walk in the park. It took the Red Sox nearly 20 years to recover from their devastating 1986 loss, but they finally did, which gives us all hope.
Continued from cover.

Figures 1-3 are not included in the text. Figure 1 shows a schematic drawing of a mask with pellicle on it. When the UV laser is applied on the mask, it creates a high energy environment in the space trapped between the pellicle film and the mask surface. This haze environment triggers photochemical reactions that could possibly induce haze defect formation on the mask surface.

Figure 2 is a schematic drawing of the haze accelerator. The laser beam is applied to the mask located inside the chamber through a relatively simple optical system.

Figure 3 is a real image of the gas analyzer used for gas analysis. The gas analyzer consists of an inlet system and a quadrupole mass spectrometer. The gas sample inserted through the inlet system reaches the mass spectrometer where it is analyzed.

Figure 4 shows TOF-SIMS surface mapping of various ions on the mask surfaces without laser exposure (Sample 1) or with exposure (Sample 2). Surface mapping for the sample 2 exhibits higher concentration of fluorine ions and compounds, and hydrocarbon around the spot irradiated by laser.

2. Experiment

Sample Preparation
ArF PSM masks with test pattern were cleaned by conventional SPM/SC-1 cleaning processes. Haze acceleration test was performed for mask samples prepared as above under atmosphere of 80% N₂ and 20% O₂ and humidity of 45%. Repetition rate was 150 (Hz) and energy density was 6 (mJ/cm²/pulse). The spot size of the laser beam was 5 mm by 5mm. Schematic drawing of the haze accelerator is shown in Fig. 2.

TOF-SIMS Analysis
ArF PSM mask sample with laser exposure under haze accelerator (Sample 1) and mask sample without laser exposure (Sample 2) were analyzed using TOF-SIMS. ION-TOF 5 with ion beam source of Au has been used for the scanning of the area of 9 cm by 9 am on each mask sample.

Gas Analysis
Micro syringe was injected into the pellicle through a vent hole in order to extract gas trapped between the pellicle film and the mask surface focusing on direct chemical composition analysis of the haze defects formed on the mask surface qualitatively or quantitatively.

UV laser applied on the mask with pellicle creates a high energy environment in the space trapped between the pellicle and the mask surface (Fig.1). This environment is filled with outgassed chemicals from pellicle materials and highly reactive oxygen radicals and ozone produced during the laser exposure, creating an ideal nest for photochemical reactions that could possibly induce the haze defect formation on the mask surface. Therefore, it is very essential to investigate the haze environment in order to understand how the photochemical environment is participating in various surface reactions towards haze defect formation on the mask surface during the exposure. This information could not only shed light on the study of haze defect growth mechanism but also be inversely applied to the development of real-time monitoring tools for the defect growth progress on the mask surface in real scanner systems. In this paper, we propose a simple method to analyze the gaseous space trapped between the pellicle film and the mask surface that creates a highly reactive environment.
Reaction Mechanism (ASML)

\[
\text{DUV Light} \quad \text{H}_2\text{O} \quad \text{NH}_3
\]
\[
\text{SO}_2 \xrightarrow{\text{hv}} \text{SO}_3 \xrightarrow{} \text{H}_2\text{SO}_4 \xrightarrow{} (\text{NH}_4)\text{SO}_4
\]
overall reaction:

\[
\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4
\]

Figure 6. Ammonium sulfate haze defect formation mechanism proposed by ASML. H\textsubscript{2}O is known to play an important role in the reaction as catalytic species. This mechanism explains why H\textsubscript{2}O is consumed in the process of haze defect growth.

Table 1. Chemical composition changes of environmental components in the space trapped between the pellicle film and the mask surface as a function of exposure time. H\textsubscript{2}O and Ar are decreasing but CO\textsubscript{2} is increasing with exposure time.

<table>
<thead>
<tr>
<th></th>
<th>H\textsubscript{2}</th>
<th>H\textsubscript{2}O</th>
<th>N\textsubscript{2} (+CO)</th>
<th>O\textsubscript{2}</th>
<th>Ar</th>
<th>CO\textsubscript{2}</th>
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<tbody>
<tr>
<td>0h pellicle</td>
<td>0.011152</td>
<td>1.276992</td>
<td>76.287195</td>
<td>21.442555</td>
<td>0.874245</td>
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<tr>
<td>3h pellicle</td>
<td>0.011207</td>
<td>1.104140</td>
<td>75.959879</td>
<td>21.937996</td>
<td>0.867739</td>
<td>0.118980</td>
</tr>
<tr>
<td>6h pellicle</td>
<td>0.010615</td>
<td>0.932802</td>
<td>76.036448</td>
<td>22.028271</td>
<td>0.867400</td>
<td>0.124559</td>
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surface. The volume of the gas extracted each time was 2 ml. The extracted gas was inserted into the gas analyzer that consists of inlet system and quadrupole mass spectrometer (Fig.3)

3. Result and Discussion

TOF-SIMS surface mapping of fluorine ions for the mask sample exposed under a haze accelerator exhibits a concentric circle where it shows higher concentration of fluorine near the center of the spot irradiated by laser (Fig.4). This indicates that fluorine ions are outgassed from pellicle materials and deposited on the mask surface during the exposure, increasing with laser intensity. Moreover, the fluorine ions outgassed from pellicle materials interact with other chemicals such as oxygen, carbon or even with silicon on the mask surface to make other fluorine compounds on the surface, which could not be observed for the mask sample without exposure. In addition, the mask with exposure shows higher concentration of hydrocarbon compared to the mask without exposure. This signifies that hydrocarbons are also outgassed from pellicle materials and deposited on the mask surface during the exposure.

In order to double check whether those chemicals are truly coming out from the pellicle materials, we analyzed a pellicle film using TOF-SIMS. As can be seen in the Fig.5 (a), fluorine, carbon, oxygen and the compound of CFO were detected to confirm that they are originated from the pellicle film. This result coincides with the data of pellicle polymer composition provided by the vendor (Fig.5 (b)). (a)(b)

We further investigated the gaseous haze environment using gas analyzer. The gas analysis shows that H\textsubscript{2}O and Ar are decreasing but CO\textsubscript{2} is increasing with exposure time (Table 1). The reason why H\textsubscript{2}O is decreasing with exposure time could be explained as follows. In many haze defect growth mechanism including specially that of ammonium sulfate, moisture is known to play an important role in the defect growth reaction as catalytic species\textsuperscript{6} (Fig.6). Therefore, more H\textsubscript{2}O are expected to be consumed as the defect growth is progressed under exposure. The fact that CO\textsubscript{2} is increasing with exposure time could be understood based on that CO\textsubscript{2} is also outgassed from the pellicle film subject to the laser exposure. However, it is not clear at this moment why Ar is decreasing with exposure time and it might need further careful examination.

Since we observed higher concentration of fluorine and its compounds deposited on the mask surface (Figure 4), we expected to detect fluorine from the gas analysis. To the contrary to our expectation, we did not observe any fluorine ions or compounds from this
analysis. This might be due to that fluorine ions are so reactive that they interact with chemicals on the mask surface right after they are outgassed from the pellicle film. It could be also possible that fluorine is outgassed as compounds rather than ions and the amounts of these compounds are below the detection limit of the gas analyzer we currently have.

For this work, we did not apply the laser exposure until visible haze defects are made on the masks surface. This is because we want to see if we could detect any change even in the early stage before defects are visibly created. Currently, we are working on applying laser exposure until visible defects are actually made on the mask surface, in which we might be able to detect more significant chemical component changes or production of new chemical species such as fluorine. It is believed that this new information will give a better idea on the haze defect study.

4. Conclusion

In this work, we have analyzed the mask surface and the gaseous environment trapped between the pellicle and the mask. We observed that fluorine ions and hydrocarbons are outgassed from the pellicle materials and then deposited or interact with other chemicals to make various compounds on the mask surface during laser exposure. Gas analysis shows that chemical compositions of H$_2$O, CO$_2$, and Ar are changing with exposure time. This fact can be further applied not only to the study of haze defect growth mechanism but also to the development of real-time monitoring tools for the defect growth progress on the mask surface.

5. References

5. Personal communications with B. J. Grenon and J. Gordon.
6. Personal communications with ASML scientists.
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Industry Briefs

- **Building on Its Decade of Leadership in China, Toppan Photomasks Expands Shanghai Site**

Toppan Photomasks, Inc. plans to expand its Shanghai facility, adding capacity to produce photomasks used to manufacture semiconductor devices with 180nm design rules, and additional lithography and inspection capacity for 250nm-and-above products.

The expansion, the fourth since the company opened the facility in 1996, will add clean room space and enhanced process, inspection, and repair capabilities to supply current demand and forecasted growth in China’s increasingly vital market. The factory, which has tripled its output since opening, currently produces photomasks for geometries down to 250nm. The fast-track project is expected to make the expanded clean room available in the third quarter of 2006, and to ramp additional capacity and capabilities in the fourth quarter.

- **Photronics Hosts Grand Opening Ceremonies in Shanghai, China**

Photronics, Inc. (Nasdaq:PLAB), a worldwide leader in supplying innovative imaging technology solutions for the global electronics industry, announced ceremonies were being held to commemorate the grand opening of the Company’s semiconductor photomask manufacturing facility. Semiconductor manufacturing customers, government officials and local community leaders joined members of the Photronics management team to tour this newly constructed photomask fabrication facility and meet with members of Photronics’ local manufacturing and sales organization. Located in the Zhangjiang Semiconductor Industrial Park, the facility is the first merchant photomask fabrication facility to be brought on-line in the Shanghai region for more than a decade. Production at the facility will be initiated in the fourth quarter of this year.

- **Photronics Slashes Revenue Forecast; Cites FPD Shortfall**

Dylan McGrath, EE Times

Blaming a shortfall in flat panel display (FPD) photomask orders, U.S. mask maker Photronics Inc. said it has revised its quarterly guidance downward. The company said it expects to report quarterly revenue of $106 million to $107 million for the three-month period ended July 30, down from original expectations of $119 million to $124 million.

Photronics (Brookfield, Conn.) said fiscal third quarter earnings are expected to be between 9 and 11 cents per diluted share. The company said its revised earnings-per-share guidance excludes the impact of previously announced restructuring charges associated with the consolidation of its operations in North America.

Photronics said it experienced a slower-than-expected demand for FPD mask technology and services in both the Korean and Taiwanese regions. The company said believes that the impact of current market dynamics will short-term, and that FPD design activity continues to be focused on leveraging new manufacturing capability coming on line from Generation 7 and Generation 8 facilities in Korea and Taiwan.

- **Vistec Seeks Acquisitions, Sets Up in Silicon Valley**

Mark LaPedus, EE Times

Once the self-proclaimed “orphan” of the IC equipment business, upstart Vistec Semiconductor Systems GmbH, has finally put down roots, established a product focus and is on the acquisition path.

Vistec (Wetzlar, Germany), formerly known as Leica Microsystems GmbH, next month plans to move its U.S. branch office from Chantilly, Va., to Fremont, Calif. The company’s sales and support unit will also relocate to California in an effort to get closer to its customer base.

Also part of its strategy, Vistec is seeking acquisitions to sustain its future growth, said Papken Der Torossian, chairman of the semiconductor equipment firm. “We are looking for new opportunities and acquisitions,” Der Torossian said in an interview at last week’s Semicon West trade show here.

After getting lost in the shuffle, Vistec is back on the growth path. The privately-held supplier of metrology and electron beam equipment projects that its sales will hit $160 million in 2006, up from $130 million in 2005.

The company remains upbeat despite signs of an industry decline. “We haven’t seen a slowdown,” said Der Torossian.

It has been a wild ride for Vistec. For years, the company had been the under the umbrella of Germany’s Leica Group, a market leader in cameras, microscopy, pathology diagnostics and surgical microscopes.

Then, the company decided to divest its fab-tool unit. In July of 2005, diversified conglomerate Danaher Corp. entered the semiconductor equipment and other markets by announcing that it had acquired Leica Microsystems from LM Investments for about €450 million euros ($550 million). Part of the deal included Leica’s chip equipment unit.

More recently, the company changed its name to Vistec and hired industry veteran Der Torossian. Vistec got a new lease on life and regained some stability under the auspices of Golden Gate Capital, said Gerhard Ruppik, general manager of Vistec’s Semiconductor Systems Division.
About the BACUS Group
Founded in 1980 by a group of chrome blank users wanting a single voice to interact with suppliers, BACUS has grown to become the largest and most widely known forum for the exchange of technical information of interest to photomask and reticle makers. BACUS joined SPIE in January of 1991 to expand the exchange of information with mask makers around the world.

The group sponsors an informative monthly meeting and newsletter, BACUS News. The BACUS annual Photomask Technology Symposium covers photomask technology, photomask processes, lithography, materials and resists, phase shift masks, inspection and repair, metrology, and quality and manufacturing management.

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