

Post Etch Treatment Optimization for Contact Etch

Jian Chen, Sheng Wang, Yan Wang, Zhidong Wang, Wutao Tu, Haiyang Zhang*

Technology R&D, Semiconductor Manufacturing International Corp. Pudong New Area, Shanghai, P. R. China 201203.

* Corresponding author. Email: Steven_Z@smics.com

Manuscript submitted August 17, 2021; accepted December 28, 2021.

doi: 10.17706/ijmse.2022.10.1.10-17.

Abstract: As the critical dimension (CD) of transistor scaling down to 14nm and below, contact etch has encountered big challenges due to the balance of CD shrink and contact open. Polymer richer etch process has to be used for much larger CD shrink gap from litho. to etch and higher selectivity requirement. However, this heavier polymer process will easily lead to metal void or block the metal formation in subsequent metal deposition step. In-situ post etch treatment (PET) is therefore widely used after contact etch process to help remove the polymer residues. PET can effectively enlarge the process window. This paper focuses on the N₂/H₂ PET process optimization with uniform design DOE for N₂/H₂ ratio, and aims to find the most efficient polymer removal N₂/H₂ PET. XPS and FTIR are adopted to characterize the C-based polymer on wafer surface. C atom% measured by XPS is then utilized as the polymer amount index. With this method, we can quantitatively analyze the polymer removal efficiency. It is found that N₂/H₂ ratio has huge effects on the polymer removal efficiency, N₂/H₂ =1.07 is the predicted as the most efficient polymer removal ratio. The DOE model is validated by inline DVC (dark voltage contrast) count data. Our DOE results can act as a guideline for the PET optimization.

Key words: Post etch treatment, contact etch, N₂/H₂, DOE.

1. Introduction

As the critical dimension (CD) of transistor scaling down to 14nm and below, contact etch become more and more challenging due to large CD bias and high selectivity to hard mask [1]-[3]. Contact etch with rich polymer has to be used in order to achieve large CD shrink and high selectivity, however, this polymer rich process has high contact open risk once the polymer residues do not removed completely by the wet clean process [4], [5]. To enlarge the contact open and wet clean window, post etch treat (PET) is embedded widely in contact etch process. PET with N₂/H₂, H₂, CO₂, Ar and NH₃ et al, are reported to help remove the C-F polymer produced in contact etch [6], [7]. Among them, N₂/H₂ is the most common used PET in contact etch. Forming gas (N₂/H₂) with 4% H₂ is a classic ratio for the polymer remove. However, the N₂/H₂ ratio effects on the polymer removal efficiency has not been systematically studied yet.

Below 14nm node, LELE (litho./etch/litho./etch) is adopted in contact patterning as the contact pitch scaled to the limitation of DUV photography. An ESL (etch stop layer) is needed to make different masks etch stop at the same layer. Subsequently, a LRM (liner removal) process is used to open the ESL, forming a hole or trench contact. LRM is a polymer heavy process since it must have high selectivity to the above layers. A typical LRM process is shown in Fig. 1(a). In order to open the ESL layer and achieve high selectivity to oxide, polymer is deposited on SiO₂ surface to protect SiO₂ and decrease the SiO₂ etch rate

during ESL etch. In-situ PET is adopted to remove the polymer residue post LRM. To quantitatively characterize the polymer removal efficiency of PET, we designed an offline process to mimic this inline process as shown in Fig. 1(b). We used a bare wafer with SiO₂ film on the surface to run the LRM first, and then different PET conditions were processed. XPS was used to characterize the element content on the surface, C atom% post PET was used as the polymer removal efficiency index. With this method, we can quantitatively analyze the PET capability.

The well-known orthogonal DOE has been widely utilized and proved to be useful in optimizing a specific process. Based on our quantitatively index, in this paper, we investigated the N₂/H₂ ratio effects on the polymer removal efficiency with uniform design DOE method, and figured out the best ratio for contact etch PET.

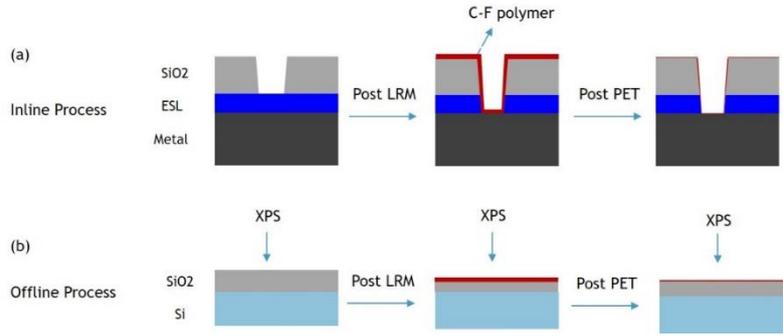


Fig. 1. Inline and offline process flow.

2. Experiments

Three parameters were selected as the experimental variables including N₂ flow, H₂ flow and time. The lower and upper limits were shown in Table 1.

Table 1. PET DOE Factors & Experimental Specification

No.	Parameters	Level	Lower limits	Baseline	Upper limits
1	N ₂ flow	2	X4	X2	X1
2	H ₂ flow	2	Y2	Y1	Y4
3	Time	2	Z1	Z2	Z3

A 2-level and 3-factor optimal design was selected for the DOE. Considering the reliability of DOE model, two center points were introduced in DOE table as shown in Table 2. Total 12 runs followed the randomization running orders for PET experiment.

Table 2. PET DOE Experiment Table

Runs	N ₂ flow (sccm)	H ₂ flow (sccm)	Time (s)
1	X1	Y1	Z1
2	X1	Y2	Z2
3	X2	Y1	Z2
4	X3	Y3	Z1
5	X1	Y2	Z3
6	X4	Y1	Z3
7	X4	Y1	Z1
8	X1	Y1	Z3
9	X4	Y4	Z3
10	X2	Y1	Z2
11	X4	Y4	Z1
12	X1	Y3	Z1

All the experiments in this paper were performed on commercial CCP etcher. LRM process was performed with $\text{CH}_2\text{F}_2/\text{H}_2$ mix gases, which showed high selectivity to SiO_2 . N_2/H_2 PET with various ratios were then processed in the same chamber.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a Nova VeraFlex II in-line XPS system using a Mg anode (photon energy 1253.6 eV) scanning C1s (286 eV), N1s (401 eV), O1s (535 eV), F1s (688 eV) and Si2p (106 eV) regions. XPS characterizations were performed post SiO_2 deposition, post LRM and post PET.

Fourier Transform Infrared Spectroscopy (FTIR) was used as a nondestructive technique to obtain the information about the properties of the polymer layer, including the types of chemical bonds, and the relative content.

DVC (dark voltage contrast) is one method to monitor contract failure after metal CMP process. By comparing the inline DVC counts with different PET conditions, we can validate the offline DOE model.

3. Results and Discussion

3.1. Polymer Analysis Post LRM

LRM process is designed to etch the ESL and have high selectivity to SiO_2 . The high selectivity is achieved by the C-F polymer thickness difference deposited on ESL and SiO_2 . Much thicker C-F polymer formed on SiO_2 surface compared to ESL surface, the C-F polymer layer serves as a barrier for chemically active fluorine species, which lead to much lower etch rate of SiO_2 than ESL [8], [9]. FTIR analysis confirmed the C-F polymer on SiO_2 surface. As shown in Fig. 2, after LRM etch, an obvious sharp peak was observed at $\sim 1105 \text{ cm}^{-1}$, which is attributed to the F-C-F symmetric stretching. Meanwhile, Si-O symmetric stretching peak at $\sim 1030 \text{ cm}^{-1}$ decreased, indicating that LRM etch produced a thick C-F polymer layer on SiO_2 surface.

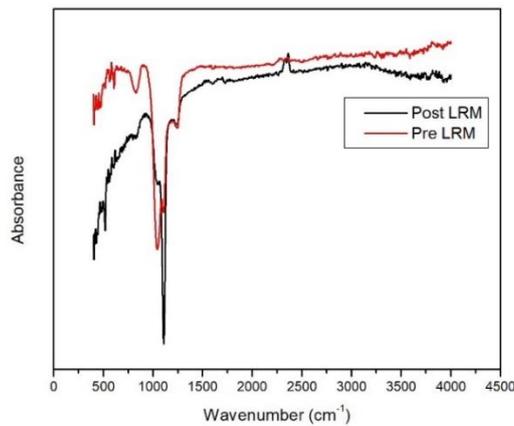


Fig. 2. FTIR spectra of post-LRM.

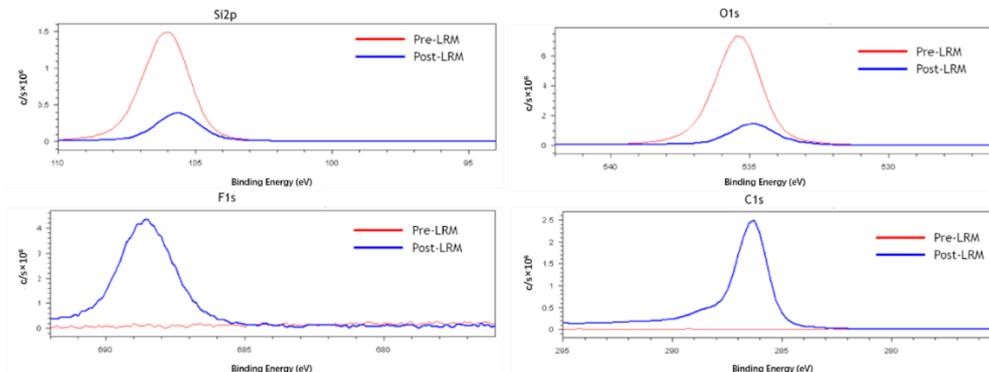


Fig. 3. XPS spectra pre- and post- LRM.

In order to quantitatively analyze the polymer content on the surface, XPS was used to analyze the surface element content. Fig. 3 and Table 3 showed the XPS results of SiO₂ surface pre- and post- LRM. The C and F levels were 0.21 and 0.02 atomic% pre-LRM, and increased to 62.65 and 6.77 atomic% post-LRM, indicating that a C-F polymer layer was formed after LRM etch on the SiO₂ surface. With this method, we can quantitatively characterize the polymer removal ability of PET by comparing the C atomic% change pre- and post-PET.

Table 3. XPS Element Analysis pre- and post- LRM

Condition	Si-O (Atomic%)	O1s (Atomic%)	F1s (Atomic%)	C1s (Atomic%)
Pre-LRM	28.51	70.75	0.02	0.21
Post-LRM	10.31	20.15	6.77	62.65

3.2. PET DOE Results

We conducted the 12 PET DOE runs after LRM etch with a randomization order. All the XPS data were collected and C atomic% were shown in Table 4.

Table 4. PET DOE Experiment Table and Results

Runs	N ₂ flow (sccm)	H ₂ flow (sccm)	Time (s)	C1s (Atomic%)
1	X1	Y1	Z1	41.58
2	X1	Y2	Z2	26.46
3	X2	Y1	Z2	4.37
4	X3	Y3	Z1	46.34
5	X1	Y2	Z3	3.87
6	X4	Y1	Z3	50.63
7	X4	Y1	Z1	62.07
8	X1	Y1	Z3	1.17
9	X4	Y4	Z3	47.02
10	X2	Y1	Z2	3.74
11	X4	Y4	Z1	61.98
12	X1	Y3	Z1	46.26

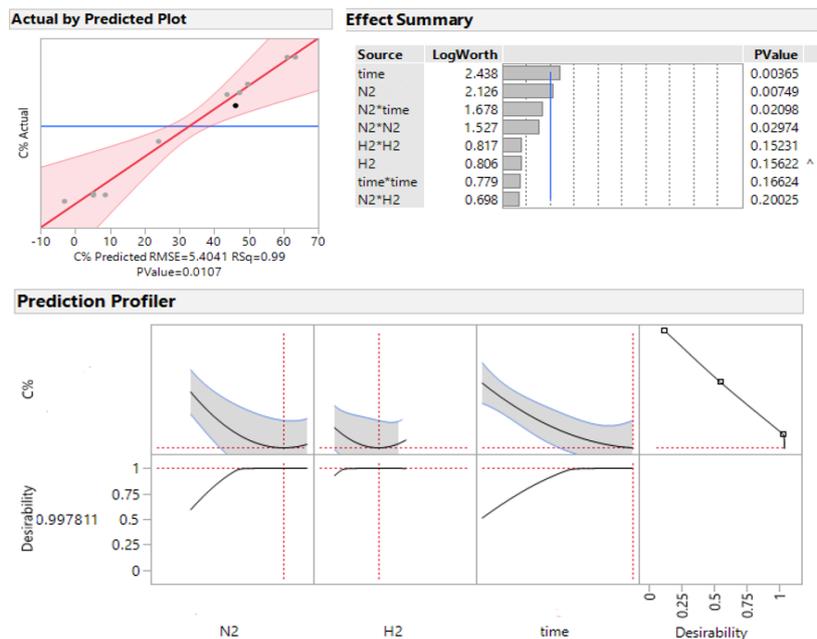


Fig. 4. DOE experiments fitting results.

A response surface model was fitted in the DOE analysis. Fig. 4 showed that the predicted model matched well actual performance, R square = 0.99. After parameter screening, time, N₂ flow, N₂ flow*time and N₂ flow*N₂ flow are identified as the main parameters that can significantly affect the polymer clean ability (P value<0.05). Time and N₂ flow are the two most significance parameters (P value <<0.05), which means that N₂ plays crucial roles in C-F polymer removal. As N₂ flow increases, the C atomic% decreases firstly and then increase again, meaning that there is a best ratio for polymer removal. From the DOE analysis, the predicted best N₂/H₂ ratio is 1.07/1.

3.3. PET Polymer Removal Kinetics

After screened out the best N₂/H₂ ratio, we further studied the polymer removal kinetics of this condition (N₂/H₂=1.07/1). As shown in Fig. 5, both C and F element decreased rapidly during the first 15s, and then decreased to steady status. C atomic% decreased to ~0.25 at around 60s and then did not change any more even increase time to 260s. This matched the -CN group signal collected in equipment OES with inline wafer. The offline XPS and inline OES suggested that N plasma helps clean the C-F polymer by breaking the long chain C-F and C-C bond to form small molecular with C-N bond.

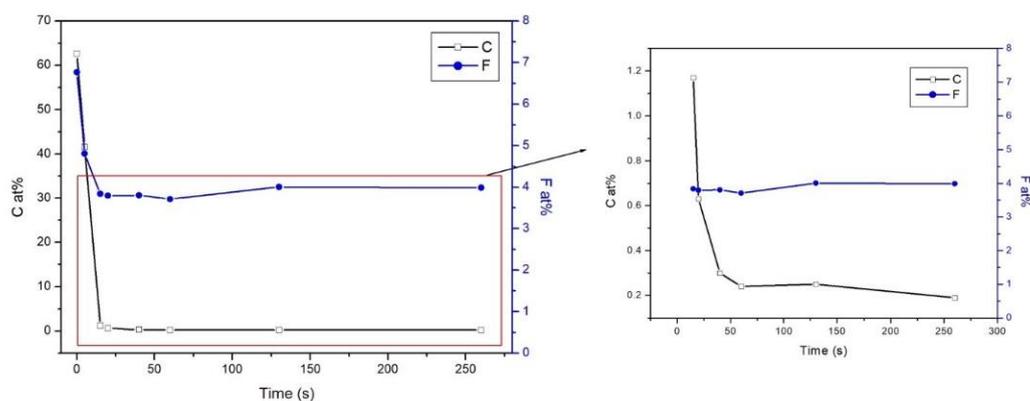


Fig. 5. C atomic% and F atomic% versus time.

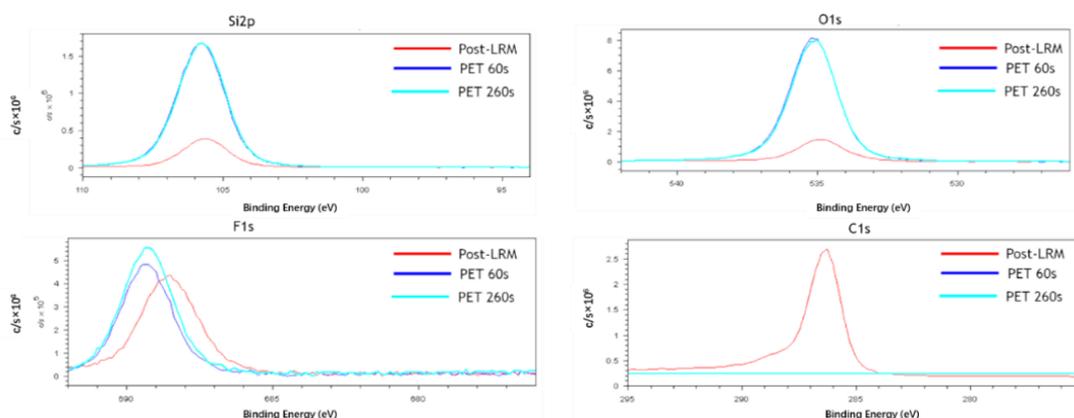


Fig. 6. XPS spectra post LRM and post PET.

It was noticed that the F element on the surface did not reduce to a very low level even with long time N₂/H₂ PET. As shown in Fig. 6, the peak position of F1s shifted from 688.5 to 689.5 eV, indicating that the chemical bond changed after PET. Since C has been completely removed from the surface, the remaining F1s signal should not come from the C-F polymer. LRM could etch some SiO₂ before the C-F polymer accumulated to a certain thickness to protect the SiO₂ surface. This etching progress is mainly done through the F-containing species (CF₂ radicals, CH₂F⁺ ions, F atoms) from the HFC- containing plasma in LRM.

Therefore, the F1s signal after PET might come from the Si-F bond on the SiO₂ surface, resulting from the LRM process.

3.4. Inline Validation

DOE optimized PET condition 40s and 60s were selected to validate the DOE model and the kinetics, w/ BSL condition 60s as reference. DVC results were collected as the evaluation criteria. As shown in Fig. 7, DOE optimized condition 60s achieved much better DVC performance compared to BSL condition 60s. DOE optimized condition 40s still had high DVC, indicating that some polymer residue still remained after 40s PET, which matched the polymer removal kinetics.

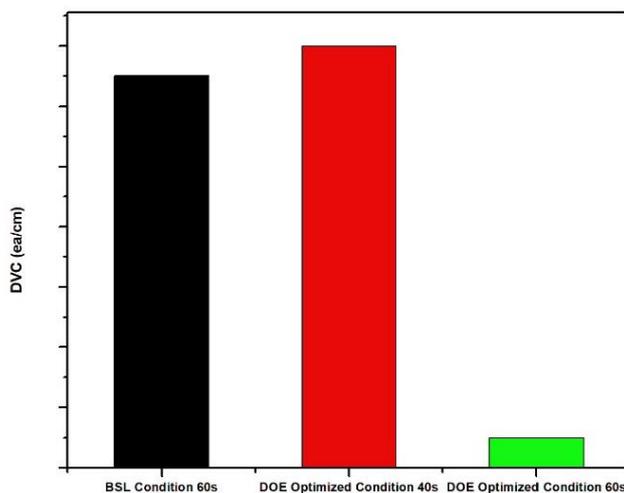


Fig. 7. DVC results of different PET conditions.

4. Conclusions

An offline process flow was developed to quantitatively study the polymer clean ability of PET. C atomic% measured by XPS could act as an index of the polymer remaining on the surface. Effects of N₂ flow, H₂ flow and time on the polymer removal efficiency were studied with orthogonal DOE experiments. It was found that N₂ flow and time are the two most significant factors. The best N₂/H₂ ratio is ~1.07/1. In our experiment, the C-F polymer was removed rapidly during the first 15s, and then slowly decreased to flat. F element could not be removed completely due to Si-F bond formed by LRM process. These offline studies acted well as guideline for the PET optimization and has been proven to greatly improve the inline DVC performance.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Jian, Sheng and Haiyang concuted the research; Yan, Zhidong and Wutao analyzed the DOE data; Jian wrote the paper; All authors had approved the final version.

Acknowledgment

The authors acknowledge Mr. Li of Measurement & Metrology department from SMIC technology research and development center for technical assistance and useful discussions during the course of this work. This project is supported by the Shanghai “Phosphor” Science Foundation, China (Grant No. 20QB1406500).

References

- [1] Radisic, D., *et al.* (2019). Plasma etch selectivity study and material screening for Self-aligned Gate Contact (SAGC). *Advanced Etch Technology for Nanopatterning VIII*, 10963, 109630P.
- [2] Chew, S-A., *et al.* (2018). Replacement metal contact using Sacrificial ILD0 for wrap around contact in scaled FinFET technology. *IITC*.
- [3] Demuyne, S., *et al.* (2007). Novel patterning shrink technique enabling sub-50 nm trench and contact integration. *Semiconductor Manufacturing*.
- [4] Xu, R. H., *et al.* (2020). The solution of contact open and short. *CSTLC*.
- [5] Wang, X. P., *et al.* (2011). Highly Selective etching solutions for advanced logic technologies. *CSTLC*.
- [6] Huang, J. Y., *et al.* (2015). The optimization of post etch treatment for contact etch process. *CSTIC*.
- [7] Posseme, N., *et al.* (2009). In situ post etching treatment as a solution to improve defect density for porous low-K integration using metallic hard masks. *IITC*.
- [8] Buzi, L., *et al.* (March 23, 2020). Hydrocarbon layer formation and removal studies on SiN films etched in halogen/hydrofluorocarbon plasmas. *Proceedings of SPIE 11329*.
- [9] Hsiao, S-N., *et al.* (2021). Selective etching of SiN against SiO₂ and poly-Si films in hydrofluoroethane chemistry with a mixture of CH₂FCHF₂, O₂, and Ar. *Applied Surface Science*, 541, 148439.

Copyright © 2022 by the authors. This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited ([CC BY 4.0](https://creativecommons.org/licenses/by/4.0/)).

Jian Chen was born in China in 1989. He received his Bachelor's degree in material science and engineering from Tong Ji University in Shanghai in 2008 and a master degree in applied chemistry from Peking University in Beijing in 2015.

He joined Semiconductor Manufacturing International (SMIC) Corporation in 2018. He is now working in the R&D/Etch group. He was responsible for metal gate related plasma etch development. He has published over 5 articles and applied more than 30 patents.



Sheng Wang was born in Zhejiang, China in 1986. He received the B.S., M.S. and Ph.D. degrees in physics from Zhejiang University, Hangzhou, Zhejiang, P. R. China, in 2008, 2011, and 2016, respectively.

He has been working in R&D/Etch group of Semiconductor Manufacturing International (Shanghai) Corp since 2016. His work mainly focuses on the development of contact plasma etch process for semiconductor manufacturing from 28nm technology node to sub14nm node.

Yan Wang was born in Jiangsu, China in 1982. He received PhD degree on condensed matter physics in Peking University in 2009.

He has been working in SMIC(Shanghai) since 2013. He holds over 50 patents on semiconductor technology. His work mainly focuses on the plasma etch of the silicon-based material for semiconductor manufacturing from 28nm technology node to FinFET technology node.

Dr. Wang was granted the title of Shanghai rising star and Shanghai top young talents in 2017 and 2020, respectively.



Zhidong Wang received the B.S. and the M.S in material and science from Wuhan University and Technology, China, in 2003 and 2005, respectively.

She is a Member of Technical Engineer in R&D of Etch department, Semiconductor Manufacturing International (Shanghai) Corp.

Zhidong Wang joined as a process engineer in Semiconductor Manufacturing International (Shanghai) Corp, P. R. China in 2005 and joined R&D of Etch department in 2016. From 2016, she is involved in 14nm and advanced technology on inter connection of etch process.



Wutao Tu received his B.S. and M.S. degrees from Huazhong University of Science and Technology, Wuhan, China, and the Ph. D. degree in from Tsinghua University, Beijing, China, in 2016, all in Materials Science and Technology.

Since July, 2016, he has been with R&D group of Semiconductor Manufacturing International (SMIC) Corp. He was a senior engineer in metal etch processes and cleaning processes development.

Dr. Tu is the program leader of the Shanghai “Phosphor” Science Foundation (20QB1406500).



Haiyang Zhang, received his B.S., M.S. and 1st Ph.D. degrees from Peiyang University, Tianjin, China, in 1997, and 2nd Ph. D. degree in advanced process control of dry etching process from University of Houston, Texas, USA, in 2002, all in chemical engineering.

Since May 2004, he has been with R&D/Etch group of Semiconductor Manufacturing International (SMIC) Corp. He spent more than 17 years on start-up, development, optimization and transfer of logic related etch processes from 90nm node to sub14nm node. Currently he is the author and/or co-author of 700+ issued patents, and 80+ dry etching related technical papers.