

# PHOTOMASK

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EUVL19 - Best Poster paper

## Study of RLS trade-off mitigation utilizing a novel negative chemically amplified resist for high resolution patterning

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### ABSTRACT

The acid diffusion in chemically amplified resists (CARs) which are a current standard resist for semiconductor device manufacturing is a significant concern in the development of highly resolving resists. Thus, high resolution CARs are reduced the number of the acid catalytic reaction per acid by high amount of acid quencher to suppressed acid diffusion blur for remaining low line width roughness (LWR) number. Non-chemically amplified resists (non-CARs) are generally lower LWR than CARs. However, non-CARs are generally less sensitive to radiation than CARs due to lack of amplification mechanism. Recently, we proposed a negative-type resist utilizing non-CAR and CAR reactions on the same platform. This resist use radiation induced non-catalytic reactions which are polarity change of onium decomposition and radical crosslinking of radiation decomposed monomers. And also, the resist uses an acid catalytic etherification utilizing diphenyl methanol derivative and aliphatic alcohol. These combination reaction by non-CARs and CAR are expected to contribute the sensitivity improvement for high resolution resist. The synthesized resists were composed of triarylsulfonium cations as a polarity changer and radical generator, 2,2,2-trisubstituted acetophenone as a radical generator, triphenyl(4-vinylphenyl)stannane (TPSnSt) as an EUV absorption enhancer and a quencher, and 4-[(2,4-Dimethoxyphenyl)hydroxymethyl]phenylmethacrylate (ARMA) as a polymer-bound acid-reactive unit. As the result, a 25 nm HP pattern could be obtained with 2.1 nm LWR and at 160 $\mu$ C/cm<sup>2</sup>.

### Introduction

For the recent development of resist patterning, the line-and-space patterns with a half-pitch less than 15 nm have been demonstrated using a commercially available extreme ultraviolet (EUV) exposure tool (ASML NXE:3350) with chemically amplified resists (CARs).<sup>[1],[2]</sup> The number of wafer tests has also dramatically increased using a high-power EUV light source for mass production of 7nm logic node.<sup>[3]</sup> However, EUV lithography extension to sub-10 nm half-pitch (HP) node still remaining the concerns about the resist stochastic and the trade-off relationships between resolution, line width roughness (LWR), and sensitivity (RLS trade-off)

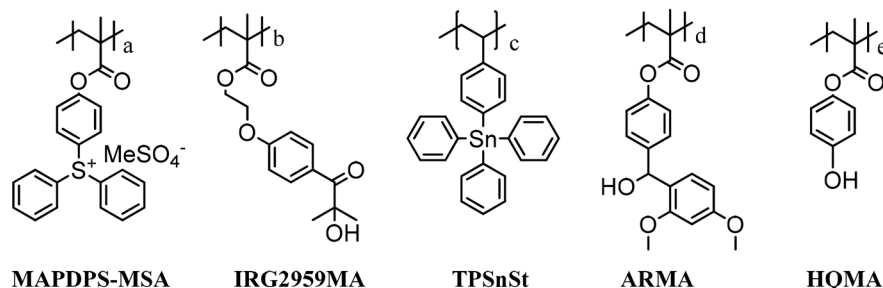


Figure 1.

TAKE A LOOK  
INSIDE:

INDUSTRY BRIEFS  
—see page 6

CALENDAR  
For a list of meetings  
—see page 7

SPIE.

# EDITORIAL

## Connecting climate with photomasks – is that even possible?

Emily Gallagher, imec

There are burdens and benefits to writing an editorial. The burden is writing something original and worth the readers' time. The benefit is the freedom to write what feels relevant. For me, that topic is climate change. I don't mean to inject politics into photomasks, but I do intend to foster thought. Climate change and photomasks became temporally connected for me when my daughter encouraged me to read a New Yorker article during the week of the 2019 SPIE Photomask Technology conference. It was written by Jonathan Franzen and had the provocative title: "What If We Stopped Pretending? The climate apocalypse is coming. To prepare for it, we need to admit that we can't prevent it." I quote two of his most disturbing points here<sup>1</sup>:

"If you're younger than sixty, you have a good chance of witnessing the radical destabilization of life on earth—massive crop failures, apocalyptic fires, imploding economies, epic flooding, hundreds of millions of refugees fleeing regions made uninhabitable by extreme heat or permanent drought. If you're under thirty, you're all but guaranteed to witness it."

"... the impending catastrophe heightens the urgency of almost any world-improving action."

Since its publication, the article has been criticized, partly because Franzen is a writer instead of a climate scientist<sup>2</sup>. Perhaps this distance from climate science is what renders his conclusions so blunt, so sticky, so immediate. To stay closer to my field of expertise, I will not weigh in on climate science, and instead consider how people who devote their working lives to the field of semiconductors – more specifically, photomask-related development – could be connected to minimizing the impact of climate change.

Humans will not willingly abandon the technology that has been developed since the industrial revolution, over two hundred years ago. Renewable energy, smart cities, green transportation, energy efficiency – all rely on semiconductors. Photomasks with high yield and lower cost is the base of lithography in semiconductor manufacturing. Developing, to indulge a personal example, EUV pellicles to increase the yield of sub-7nm node wafers helps to enable advanced-node semiconductor manufacturing. Both Samsung and TSMC have EUV lithography-based N7 offerings that offer gains in performance and reduction in power over the DUV-only process flows.<sup>3</sup>

Returning to the concept of yields, improving yield - reducing waste of any kind - reduces our impact on the planet. Innovation will be needed to propel human activity while minimizing reliance on fossil fuels. For those involved in long-term fab planning, climate change must factor into building locations and workplace practices. Investment decisions should be made with climate change in mind. Metrics related to sustainability and environmental impact should be developed and used whenever possible.

Change is essential to address climate stress and it needs to be quick and global. Political change is neither fast nor guaranteed to cross international borders. Successful companies offer a lever for change as Bill McKibben of 350.org describes in another September 2019 New Yorker article.<sup>4</sup> Individuals and the private sector will have to support difficult decisions related to climate at the city, state and national levels. As we move into this new decade, we can choose to be responsible world citizens, making informed choices in all aspects of life – photomasks and all.

1. <https://www.newyorker.com/culture/cultural-comment/what-if-we-stopped-pretending>
2. <https://www.vox.com/future-perfect/2019/9/11/20857956/jonathan-franzen-climate-change-new-yorker>
3. [https://en.wikichip.org/wiki/7\\_nm\\_lithography\\_process](https://en.wikichip.org/wiki/7_nm_lithography_process)
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Table 1.

Sample	Composition ratio (mol%)					Molecular Weight ( $M_w$ )
	MAPDPS-MSA	ARMA	TPSnSt	IRG2959MA	HQMA	
Polymer 1	27	23	30	20		13100
Polymer 2	25	23	32	20		5500
Polymer 3	22	20	23	11	24	4900

Table 2.

Sample	Acetonitrile concentration [vol%]
Polymer 1	30.0

because the performance of CARs is expected to reach their limitation.<sup>[4]</sup> The RLS trade-off problem has come to a head with the progress of pattern miniaturization. Pattern defects due to the stochastic effects (nano failure defects) markedly increase at a half-pitch of less than 15 nm.<sup>[5]</sup> The improvement of LWR and sensitivity without degrading the resolution is technically difficult because of acid diffusion and a stochastic effect.<sup>[6],[7]</sup> Therefore, some ideas for improving the sensitivity and pattern uniformity of CARs have been studied to reduce the acid diffusion length of chemical reactions and to increase EUV absorption through the incorporation of high-EUV-absorption elements to the CARs.<sup>[8]</sup>

Previously, we proposed a novel resist platform that combined two solubility change mechanisms (polarity change and radical crosslinking), named a dual insolubilization resist (DIR).<sup>[9]</sup> DIR polymers having triarylsulfonium cations and 2,2,2-trisubstituted acetophenone as side chains were designed to realize a dual insolubilization property.<sup>[9]</sup> Polymerbounded high-EUV-absorption organotin compound was also reported.<sup>[10]</sup> Moreover, chemically amplified DIR (DICAR) was reported utilizing the feature of acid generation by decomposed triarylsulfonium cation structure to increase sensitivity of DIR.<sup>[11]</sup> High resolution CARs have to be reduced the number of the acid catalytic reaction per acid by high amount of acid quencher to suppressed acid diffusion blur for remaining low line width roughness (LWR) number. On the other hand, Non-chemically amplified resists (non-CARs) are generally much less sensitive to radiation than CARs due to lack of amplification even though non-CARs generally have lower LWR and higher resolution properties compared with CARs.

DI-CAR is a negative-type resist utilizing non-CAR and CAR reactions on the same platform. This resist use radiation induced non-catalytic reactions which are polarity change of onium decomposition and radical crosslinking of radiation decomposed monomers. And also, the resist uses an acid catalytic etherification utilizing diphenyl methanol derivative and aliphatic alcohol. These combination by non-CARs and CAR are expected to contribute the sensitivity improvement for high resolution resist because an additional dissolution contrast is obtained by acid catalytic etherification after being made a negative contrast by polarity change and cross linking. Basic DI-CAR polymers were composed of triarylsulfonium cations as a polarity changer and radical generator, 2,2,2-trisubstituted acetophenone as a radical generator, triphenyl(4-vinylphenyl)stannane (TPSnSt) as an EUV absorption enhancer and a quencher, and 4-[(2,4-Dimethoxyphenyl)hydroxymethyl]phenylmethacrylate (ARMA) as a polymer-bound acid-reactive unit.

Upon exposure to EUV or an electron beam (EB), the ionic component is converted to the nonionic component through the decomposition of polymer-bounded onium cations (PBCs). The resist polymer molecules are also crosslinked through the recombination of polymer radicals, which are generated through the decomposition of polymer-bound radical gen-

erators (PBRGs) or polymer-bounded organotin compound (PBSn) upon exposure to an EB. The efficient solubility change was demonstrated by using 4-methacryloxyphenyldiphenylsulfonium methylsulfate (MAPDPS-MSA) as a PBC unit, 2-[4-(2-hydroxy-2-methylpropionyl)phenoxy]ethylmethacrylate (IRG2959MA) as a PBRG unit, triphenyl(4-vinylphenyl)stannane (TPSnSt) as a PBSn, and 4-[(2,4-Dimethoxyphenyl)hydroxymethyl]phenylmethacrylate (ARMA) as a polymer-bound acid reactivity unit (AR). As the result, a pattern size and LWR number were affected by a developer concentration of acetonitrile, and a 20 nm HP pattern could be obtained with 2.1 nm LWR and at 130  $\mu\text{C}/\text{cm}^2$  by 125keV EB. In this study, the effect of the chemical amplification on the sensitivity and dissolution selectability by acetonitrile aqueous solution were investigated.

## 2. Experimental

### A. Materials

MAPDPS-MSA was synthesized in accordance with previous patent reports.<sup>[12]</sup> ARMA, IRG2959MA, and 4-hydroxyphenylmethacrylate (HQMA) were synthesized in accordance with a conventional esterification reaction. TPSnSt was synthesized in accordance with the previous report. Polymers were synthesized in accordance with the standard solution polymerization method using dimethyl 2,2'-azobis(2-methylpropionate) (V601) as an initiator. 3-Mercapto-1,2-propanediol was applied as a chain transfer agent to synthesize Polymer 2 and 3, which is a low weight-average molecular weight ( $M_w$ ) compared with Polymer 1. After synthesis, these polymers were analyzed by  $^{13}\text{C}$ -NMR for the determination of the composition ratio, which is shown in Table 1. The molecular structures of monomers are shown in Fig. 1. Molecular weights were determined by performing gel permeation chromatography (GPC) analysis with an OHpak 806M HQ column (Shodex) using a Shodex GPC-101 system. 100 mM LiBr N,N-dimethylformamide (DMF) solution was used as an eluent at a flow rate of 1.0 mL/min and a column temperature of 70 °C. The detector was a UV detector and the monitored wavelength was 270 nm. The introduction volume was 100  $\mu\text{L}$  (full volume of sample loop). The molecular weights determined using polystyrene standards are also listed in Table 1.

### B. Verification of developer concentration efficiency

The proposed resists are a single component resist. The synthesized polymer was dissolved in the mixture of cyclohexanone, ethyl lactate, and  $\gamma$ -butyrolactone with the volume ratio of 5:4:1 for a film forming. The weight ratio of polymer and solvent was 1:35. HMDS treatment was skipped for the resist samples because Polymer 1 was highly adhesive to Si wafer without HMDS treatment. Then, the polymer solutions were spin-coated onto the surfaces of the Si wafers at 2000 rpm for 40 s to form resist films. The prebaking of the resist films was performed at 110 °C for 60 s. Polymer films with a thickness of 50 nm were obtained.

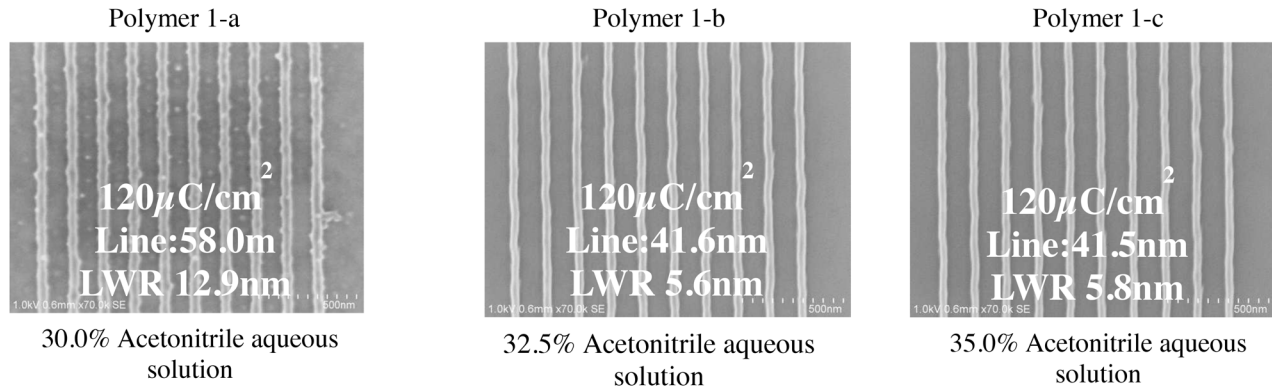


Figure 2.

The resist film was exposed to EB radiation from a 125 keV EB exposure system (Elionix ELS-F100T) with a dose from 100 to 300  $\mu\text{C}/\text{cm}^2$ . After the EB exposure, the resist film was developed with the developer for 30 s at 25 °C and rinsed with deionized water for 30 s. The delineated pattern was observed by scanning electron microscopy (SEM) (Hitachi High-Tec. S-5500). The pitch of the line-and-space patterns was 160 nm. The exposure pattern width of the lines was 25 nm. The SEM images were analyzed using line edge roughness (LER) measurement software, which measures the mean LER of an entire image.

A mixture of acetonitrile and deionized water was used as a developer. The solubility of each unexposed polymer increases with the acetonitrile concentration. The solution with the minimum concentration of acetonitrile for the complete dissolution of the unexposed polymer was confirmed as the lower limit concentration of developer for Polymer 1 (Table 2). The procedure to determine the minimum concentration of acetonitrile is as follows. The resist films were developed with the mixture of acetonitrile and deionized water for 60 s at 25 °C and then rinsed with deionized water for 30 s. The concentration of acetonitrile was increased in steps of 2.5 volume % (vol%) until the resist film was completely dissolved in the solution within 60 s.

Sample of Polymer 1 with 30, 32.5, and 35 wt% of acetonitrile aqueous solution developers were evaluated to examine the dissolution selectivity of exposed polymer.

### C. Feasibility study of high resolution EB patterning by DI-CAR

The Polymer 2 and 3 were dissolved in ethyl lactate for a film forming. The weight ratio of polymers and solvent were 1:50. A hydrophilic polymer was spin-coated at 2500 rpm for 40 s on the surfaces of Si wafers as an under-layer film to increase adhesion force of exposed polymer to the wafer surface. And then, the coated wafers were baked at 110 °C for 60s to obtain under-layer film with a thickness of 10nm. Then, the polymer solutions were spin-coated onto the surfaces of the Si wafers at 2000 rpm for 40 s to form resist films. The prebaking of the resist films was performed at 110 °C for 60 s. Polymer films with a thickness of 30 nm were obtained.

The resist films were exposed to EB radiation from a 125 keV EB exposure system (Elionix ELS-F100T) with a dose from 100 to 300  $\mu\text{C}/\text{cm}^2$ . After the EB exposure the coated wafers were baked at 110 °C for 60s, and then the resist film was developed with the developer for 30 s at 25 °C and rinsed with deionized water for 30 s. The delineated patterns were observed by scanning electron microscopy (SEM) (Hitachi High-Tec.

S-5500). The pitch of the line-and-space patterns were 50 and 40 nm. The exposure pattern widths of the lines were 25 and 20 nm. The SEM images were analyzed using line edge roughness (LER) measurement software, which measures the mean LER of an entire image. The developer for each polymer was selected 5% higher concentration of acetonitrile than lower limit concentration for polymers as shown in Table 3.

## 3. Results and Discussion

### A. Developer concentration efficiency verification

The EB patterning results for Polymers 1 with different concentration of developers are shown in Figure. 2. The patterns are obtained in all of developer condition at 120  $\mu\text{C}/\text{cm}^2$ . However, the line width and LWR of Polymer 1-a was thicker and larger than Polymer 1-b and c. Moreover, the pattern was jagged and many scams were observed. This result suggests that the lower limit concentration for unexposed polymer is very sensitive to polarity of polymer. Therefore, slight polarity differences by small number of acid diffusive reaction or solubility fluctuation from PBC composition ratio of a copolymer were faithfully transferred as a negative image to the wafer. The results of Polymer 1-b and c are much the same line width and LWR. This result indicates that the more than 2.5 vol% higher acetonitrile concentration developers were capable to ignore a slight polarity difference of polymer. The dissolution thresholds of DI-CARs are continuously adjustable to optimum condition for every polymer by changing acetonitrile concentration. Therefore, DICAR can easily adjust the composition ratio and structure of monomer unit to improve properties for EUV lithography such as increasing EUV absorption, reducing acid diffusion length and reaction ratio of catalytic and non-catalytic reaction. However, the pattern size of Polymer 1 was much thicker than the 25 nm which was a setup condition of EB exposure. One of the reasons was considered the molecular weight of Polymer 1. The molecular weight of exposed polymer becomes larger due to a crosslinking of polymer chains. The molecular weight after exposure becomes too large to obtain a high resolution pattern by using a polymer of which weight average molecular weight before exposure is 13100.

### B. Feasibility study of high resolution EB patterning by DI-CAR

Polymer 2 was synthesized a different polymerization condition with Polymer 1 by adjusting chain transfer agent and solvent. The molecular weight of Polymer 2 became less than half of the Polymer 1. Then, it was exposed by 125keV EB applying the same evaluation process of Polymer 1. As the result, a 25 nm HP pattern could be obtained with 2.1 nm LWR

Table 3.

Sample	Acetonitrile concentration [vol%]
Polymer 2	30.0
Polymer 3	35.0



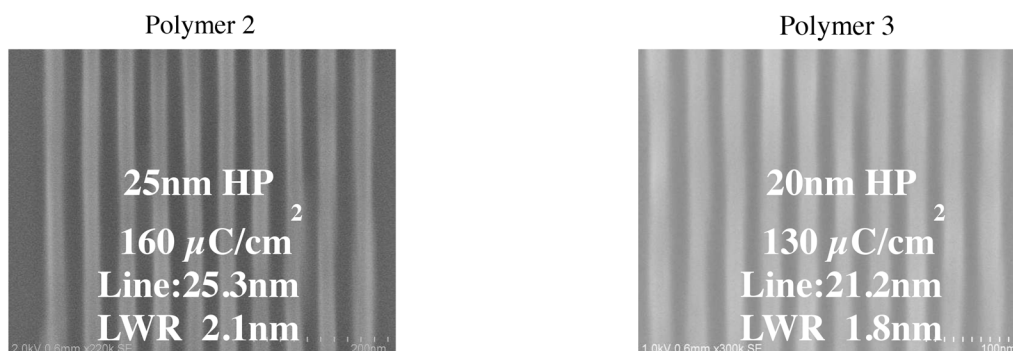


Figure 3.

and at  $160 \mu\text{C}/\text{cm}^2$  (Figure. 3). The result of 125 keV EB can convert to 50 keV that is based on the stopping power of each accelerating voltage. The sensitivity of Polymer 2 by 50keV EB was calculated approximately  $80 \mu\text{C}/\text{cm}^2$ . This result was comparable to sensitivity of chemically amplified resist.<sup>32)</sup> Furthermore, 20nm HP could be obtained with 1.8nm LWR and at  $130 \mu\text{C}/\text{cm}^2$  by modification of polymer composition ratio and content. Sensitivity of Polymer 3 was approximately 20% higher than Polymer 2 even though the pattern size was 20% smaller than the result of Polymer 2. Acid chain reaction of Polymer 3 seems effectively to obtain higher sensitivity because concentration of TPSnSt which functions as an acid quencher was lower than Polymer 2. However, LWR number was not deteriorated. Composition ratio of MAPDPS-MSA and TPSnSt in Polymer 3 was much the same. Quencher concentrations in CARs are generally lower than half molecular number of photo acid generators. Therefore, further sensitivity increases of DI-CARs are considerable to optimize the composition ratio and to modify the monomer unit. Furthermore, low LWR feature of the dual insolubilization resist is a possibility to become an effective patterning material to sub 15 nm HP patterning.

#### 4. Conclusion

The synthesized resists were composed of triarylsulfonium cations as a polarity changer and radical generator, 2,2,2- trisubstituted acetophenone as a radical generator, tetraaryltin as an EUV absorption enhancer and acid quencher, and diphenylmethanol as a polymer-bound acid reactivity unit. It has dual reactivity by non-CAR and CAR. The sensitivities of EB irradiation were comparable to CARs and LWR numbers were lower than CARs even though the resist also use acid catalytic reaction. The acid diffusion of the reaction could be controlled owing to high concentration of quencher and utilizing bimolecular reaction. These resists were not optimized a lot of things for improving resist properties. Patterning results of DI-CAR could be improved by resist optimization

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# Industry Briefs

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By **George Leopold**, EETimes

The US Military is again attempting to secure the nation's semiconductor supply chain with a handful of industrial base initiatives that include a digital twin capability that used data-driven virtualization to validate the integrity of individual device or an assembly of chips. That capability would in turn help secure devices incorporated into weapons.

<https://www.eetimes.com/military-enlists-digital-twin-technology-to-secure-chips/#>

## ■ Photonics Comes into Focus: 2020 Predictions

By **Rich Goldman**, semiwiki.com

Photonics, the technology of the future, will see solid advancement in 2020. Growth rate will be impressive, with abundant applications coming into focus. Growth will be tethered by the cleverness of engineers extending electronics, and the evolution of the photonics ecosystem. Signs of maturity are becoming more prevalent as commercial foundries join the fray and design automation matures. 2020 is the year that the commercialization of photonics comes into focus.

<https://semiwiki.com/eda/280982-photonics-come-into-focus-2020-predictions/>

## ■ CES 2020: Photonics Technologies Power Industry and Consumer Innovations

By **Optics.org**

Optics.org previews some of the new technologies on show in Las Vegas. Visitors to this year's Consumer Electronics Show, which opened on Tuesday, January 7th, in Las Vegas, NV, can witness a dazzling variety of new photonics-based gadgets – among them new TVs, wearable sensors, and numerous innovations aimed at the automotive industry.

<https://optics.org/news/11/1/5>

## ■ Trump Administration Pressed Dutch Hard to Cancel China Chip-Equipment Sale

By **Alexandra Alper, Toby Sterling, Stephen Nellis**, Technology News

The Trump administration mounted an extensive campaign to block the sale of Dutch chip manufacturing technology to China, with Secretary of State Mike Pompeo lobbying the Netherlands government and White House officials sharing a classified intelligence report with the country's Prime Minister, people familiar with the effort told Reuters.

<https://www.reuters.com/article/us-asml-holding-usa-china-insight/trump-administration-pressed-dutch-hard-to-cancel-china-chip-equipment-sale-sources-idUSKBN1Z50HN>

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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.

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**You are invited to submit events of interest for this calendar. Please send to [lindad@spie.org](mailto:lindad@spie.org).**