A. Project Title and Date:

Elimination of PFOS and PFOA in IBM Semiconductor Manufacturing Processes and Development of PFAS-Free PAGs

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B. Primary Sponsor:

International Business Machines (IBM) Corporation Microelectronics Division

C. Contact person:

Rao Varanasi
IBM Corporation
2070 Route 52, Hopewell Junction, NY 12533
Email: varanasi@us.ibm.com
Phone: (845) 894-7787

D. Contributors:

Laird MacDowell, Brennan Brown, Chip Whiting, Ruma Kohli
IBM Corporation
1000 River St.
Essex Junction, VT 05452

Rao Varanasi, Sen Liu, David Speed, Richard Kaplan, Narayan Ayengar, Scott Danskin
IBM Corporation
2070 Route 52
Hopewell Junction, NY 12533

The International Business Machines (IBM) Corporation Microelectronics Division has eliminated all known applications of PFOS (perfluorooctanesulfonate) and PFOA (perfluorooctanoate) from its US semiconductor manufacturing operations. These compounds are classified as PFAS (perfluroalkylsulfonates) and PFAC (perfluoroalkylcarboxylates). The effort was completed in January 2010, and this accomplishment places IBM in a worldwide leadership role as the first US semiconductor manufacturing company to eliminate these environmentally persistent and bioaccumulative compounds.

This application is submitted for consideration under Focus Area 3: Industry Sponsor for the Design of Greener Chemicals; it is not eligible for either the small business or academic award.

The IBM Microelectronics Division operates two semiconductor fabricators (fabs) in the United States: a 200-mm wafer fab located in Essex Junction, Vermont and a 300-mm wafer fab located in Hopewell Junction, New York. Both fabs conducted multi-year qualifications of substitute manufacturing process chemicals to eliminate use of both PFOS and PFOA compounds, primarily used as surfactants in etch and lithographic chemicals. As of January, 2010, all semiconductor products that were manufactured at these fabs were without the use of any PFOS or PFOA compounds. IBM semiconductor products are used in IBM products and multiple consumer products. As a continuation of this effort, in February 2010, IBM researchers announced the development of a PFAS-free photoacid generator (PAG) chemistry for use in 193-nm photoresists.

Abstract

In 2002, the United States Environmental Protection Agency (EPA) placed restrictions on new applications for PFOS compounds due to scientific evidence showing that PFOS was persistent and bioaccumulative in the environment. Use of PFOS compounds were permitted for “use as a component of a photoresist substance, including a photo acid generator or surfactant, or as a component of anti-reflective coating, used in a photolithography process to produce semiconductors or similar components of electronic or other miniaturized devices”, since the semiconductor manufacturing industry had demonstrated limited release and exposure. In 2006, IBM issued a Corporate Directive to eliminate all uses of PFOS and PFOA in manufacturing processes by 2010 in order to help reduce the environmental impact of these compounds.

The IBM fabs engaged in the replacement of the PFOS surfactant in buffered oxide etch (BOE) chemicals by working with the chemical suppliers to first identify and then qualify a non-PFOS surfactant replacement. In 2008 both fabs completed the replacement of the PFOS surfactant in BOE chemicals with a four carbon chain fluorocarbon–perfluorobutane sulfonate (PFBS)– which the EPA has deemed less of a concern for the environment than the corresponding PFOS compounds.

Both IBM fabs targeted replacement of specific photoresists and antireflective coatings (ARCs) that contained either PFOS or PFOA used as a surfactant or as a photoacid generator (PAG) in photoresist. After several years of conducting IBM product qualifications, both fabs completed the qualification and conversion to non-PFOS/PFOA photochemicals by January, 2010. The total amount of PFOS/PFOA compounds eliminated from IBM’s semiconductor processes was in the

order of 140 kgs per year. Total estimated PFOS consumption for worldwide semiconductor industry is 8000 kgs per year. To the best of our knowledge, IBM is the only company in the world to completely eliminate PFOS and PFOA compounds from semiconductor manufacturing. IBM researchers have also developed PFAS-free PAGs for use in both dry and immersion 193-nm photolithography in semiconductor manufacturing, with equivalent performance in 45-nm and 32-nm semiconductor technology.

Phase I: PFOS Elimination Project Details

1. PFOS Regulatory History

In 2002, the United States Environmental Protection Agency (EPA) published a PFAS Significant New Use Rule (SNUR) for 13 PFOS chemicals, followed by a supplemental SNUR for 75 additional chemicals, due to scientific studies showing the compound was Persistent, Bioaccumulating and Toxic (PBT) to mammalian species. The Final PFAS SNUR published on December 9, 2002 (Federal Register / vol.67, No. 236) granted an exemption for the use of PFOS compounds in photoresists and antireflective coating chemicals used for semiconductor lithography applications since the PFOS usage volumes are very low, tightly-controlled, and involve minimal release to the environment. However, use of PFOS in buffered oxide etch chemicals used for semiconductor applications did not receive an exemption due to higher volumes of PFOS entering the waste stream.

In March 2006, the EPA proposed adding to the SNUR the remaining 183 PFAS chemicals with a carbon chain length of 5 or higher not already covered by the existing PFAS SNUR. Consistent with IBM's environmental policy objectives, IBM made a commitment to transition away from PFAS, PFOS and PFOA materials. IBM prohibited the new uses of PFASs with five or more carbon atoms in the alkyl chain, PFOS and PFOA after January 1, 2007, and committed to eliminate all existing uses of PFOS and PFOA by 2010.

Furthermore, in May 2009, PFOS was classified as Persistent Organic Pollutant (POP) as part of the United Nations sponsored Stockholm Convention based on its environmental characteristics. PFOS has been placed in the Annex B of the Stockholm Convention which includes an exemption for "acceptable purposes": photo imaging, photo-resist and ARCs for semiconductors.

IBM communicated to its customers and the public its plans to eliminate PFOS due to both the EPA ruling and the listing of PFOS as a POP.

2. Semiconductor Process Chemical Descriptions

Both PFOS ($C_8F_{17}SO_3$) and PFOA ($C_7F_{15}CO_2$) were used primarily as surfactants to reduce the liquid surface tension for better "wetting" of the substrate surface allowing for resolution of fine geometric features on silicon wafers. These chemicals have the following advantageous properties: very low concentrations are required, non-ionic, low foaming, tolerance of severe acidic and basic conditions, and resistance to degradation under high temperature exposure.

BOEs consist of an aqueous mixture of hydrogen fluoride (HF) and ammonium fluoride (NH_4F) with an added surfactant for surface tension reduction. IBM uses three different concentrations of this strong acid/base mixture for selective etching of silicon dioxide films to define circuit patterns.

Photoresists are used to create circuit patterns on silicon wafers by passing light of a specific wavelength through a photomask and then developing the unexposed areas with an alkaline developer. In addition to being used as a surfactant, PFOS was also used as a PAG in both 248-nm and 193-nm photoresists, which required a super acid to catalyze the polymer cross-linking process as a result of UV light exposure.

Two types of ARCs are used to enhance the photolithographic process. Bottom-ARCs (BARCs) are applied to the silicon wafer to absorb reflected light during exposure of the subsequent photoresist layer to prevent both destructive interference and “reflective notching” of the sidewalls of the photoresist film. BARCs are typically composed of a polymer, an acid or thermal acid generator, a cross-linking agent and a surfactant which are all dissolved in a base solvent. Top-ARCs (TARCs) are applied to cross-linked photoresist films to suppress the swing amplitude of the photoresist and improve the critical dimension uniformity. TARCs typically consist of an acidic polymer and a surfactant dissolved in DI water. PFOS and PFOA compounds were used as the surfactant in TARCs and BARCs to reduce both surface tension and control the refractive index.

3. Replacement of PFOS in Buffered Oxide Etch (BOE) chemicals

Following several years of evaluations to determine the optimum candidate to replace PFOS surfactant, a four carbon chain fluorocarbon PFBS ($C_4F_9SO_3$) surfactant from 3M Company was selected as the optimum replacement. 3M determined that PFBS is a suitable replacement for PFOS due to low ecotoxicity and bioaccumulation potential and that it is not classified as a PBT chemical under EPA policy. The 3M PFBS surfactant is named Novec ™ 4200 and consists of 25% ammonium fluoroalkylsulfonamine in water. IBM began product qualifications of the Novec ™ 4200 in three different BOE chemicals in 2005 and completed all qualifications by 2008.

The 200-mm fab found that the shorter chain length of the PFBS surfactant allowed easier passage through the point of use chemical filters resulting in a more consistent surface tension during the BOE etch process. This stability resulted in higher semiconductor product yield on some products and reduced chemical usage associated with conditioning the BOE point of use filters. The PFBS surfactant replacement did not add additional cost to the BOE chemical.

The IBM 200-mm fab was awarded the 2008 Vermont Governor’s Award for Environmental Excellence and Pollution Prevention for the elimination of PFOS in buffered oxide etch chemicals. The US based suppliers of BOE chemicals report that all customers have converted to PFBS surfactant versions and credit IBM with taking a leadership role in the conversion away from PFOS surfactant.

4. Replacement of PFOS and PFOA in photoresists and ARCs

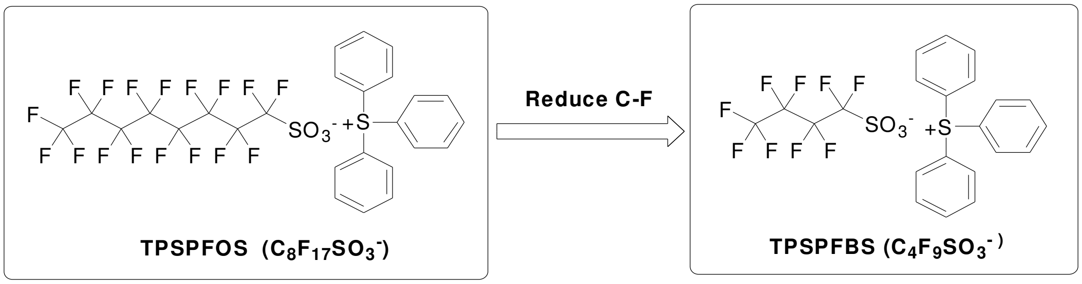
The 200-mm fab conducted 45 separate qualifications to replace eight different photochemicals with non-PFOS/PFOA versions and the 300-mm fab conducted 17 separate qualifications to replace six photochemicals with non-PFOS/PFOA versions

A. Photoresist PFOS/PFOA Replacement Details

Several years ago IBM qualified a process called "wafer prewet" in which a solvent mixture consisting of 70% gamma-butyrolactone and 30% N-butyl acetate is applied to the wafer surface to "wet" the substrate prior to application of photoresist or BARC. This unique mixture of a polar and non-polar solvent allowed for removal of the surfactant in photoresists and BARC's due to superior wetting of the substrate surface. Use of this solvent blend allowed for a significant reduction in the photoresist and BARC coating volumes reducing waste and saving chemical cost. IBM filed patent BUR920010147US2.for the coating volume reduction benefits of this solvent mixture. The supplier of a 248-nm photoresist provided samples in which the PFOS surfactant was removed from the formulation and both fabs qualified the "non-surfactant" version of the photoresist with use of a prewet solvent.

The qualification of a replacement for photoresists with a PFOS PAG was more challenging since it required a change to a different photoresist, in some cases from another supplier, and the qualification process was demanding. A 193-nm photoresist used by both fabs contained a PFOS PAG and each fab conducted extensive qualifications of different photoresists with a PFBS PAG, all of which were successful.

Figure 1: PFOS PAG Replacement chemistry



B. Antireflective Coatings PFOS/PFOA replacement details

The 248-nm and 193-nm BARCs used in both fabs that contained a PFOS surfactant were replaced with non-surfactant versions. The ARC film thickness is much less than for photoresist so there was no degradation of film quality converting to non-surfactant versions of these BARCs.

The replacement of 248-nm and 193-nm aqueous TARCs had additional challenges since a solvent prewet process was incompatible. The PFOS or PFOA surfactant controled both the refractive index of the TARC and the liquid surface tension. The PFOS surfactant in the TARC was replaced with a non-fluorocarbon surfactant ethoxylated acetylenic diol which required adjustments in the spin coating wafer application recipe in order to provide equivalent performance.

Phase II: Development of new PFAS-free compounds for use in 193 nm lithography

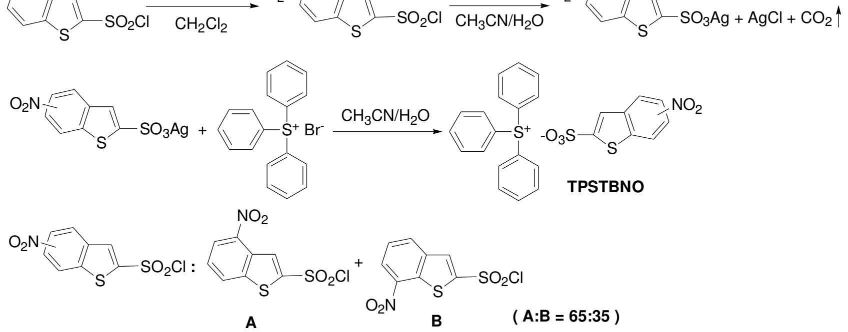
Researchers with the IBM Semiconductor Research and Development Center (SRDC) announced in February, 2010 new PFAS-free compounds for use as PAGs in 193-nm photoresists, replacing the use of PFAS compounds. This materials innovation effort was the next step after the replacement of PFOS PAG with PFBS (C4) and shorter chain length sulfonate PAGs. The key challenges with replacing the use of PFAS PAGs were the requirements for super acidity, high contrast, 193 nm optical transparency and compatibility with dry and immersion lithography. This new suite of compounds is the industry's first PFAS–free PAGs for 193-nm lithography chemicals with the following attributes: 193 nm optical transparency, thermal stability, soluble in photoresist formulations and compatible with immersion lithography. The SRDC team focused on the design and synthesis of two classes of PFAS-free PAGs for 193-nm lithography.

Class I: **PFAS-free PAGs based on heteroaromatic sulfonates** : Due to the super acidity of PFAS compounds, these perfluoro carbons are well adopted in the 193-nm lithography materials. Therefore, it was quite challenging to design alternative PFAS-free materials that can maintain super acidity at molecular level without the presence of a carbon-fluorine bond.

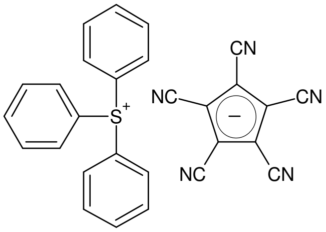
The initial design of non-fluorinated aromatic sulfonate PAGs failed since these could not provide sufficient super acidity from the high delocalization energy of the aromatic ring under 193-nm radiation. Thus, heteroaromatic thiophene ring structures with lower delocalization energy became attractive for 193-nm PAG anion design in combination with their convenience and flexibility in synthesis.

To further enhance photo-generated superacid strength, a strong electron withdrawing nitro group was incorporated which enabled an even more effective delocalization of the negative charge onto thiophene by inductive and resonance effects, thus substantially enhancing the resultant acid strength. As such, nitro-substituted thiophenesulfonate PAGs (Class I) were designed and synthesized with optimized thermal stability. Their size and shape were modified by incorporating a fused benzene ring into the heteroaromatic anion to tune PAG diffusivity.

Figure 2 : The synthetic procedure and chemical structure of Class I PFAS-Free PAG TPSTBNO



Class II : **PFAS-free PAGs based on pentacyanocyclopentadienides** :
Pentacyanocyclopentadienide (CN5) compounds were designed as a class of non-traditional ionic PAGs for 193-nm lithography since they do not contain any sulfonates and still maintain superacidity. In this approach, nucleophilicity, tendency of coordination and proton affinity are very small, as a protonation of the ring would break up the aromaticity and the negative charge is very delocalized due to the electron-withdrawing cyano groups. Therefore, the super photo-generated acidity from CN5 anion was achieved.
Fig 3: Chemical structure of triphenylsulfonium substituted CN5 photoacid generator in Class II, TPSCN5:



TPSCN5

Commercialization status

The lab scale synthesis of these two classes of PFAS-free PAGs was demonstrated. These PAGs have low toxicity according to an ocular toxicology test. PBT simulation based on EPA Profiler also predicted that these PFAS-Free PAGs are of lower persistency and bio-accumulativity concerns when compared with PFAS PAGs. The lack of electron negative and robust C-F bonding in the resulting sulfonates may contribute to the reduced persistency, bio-accumulativity and toxicity of PFAS-free PAGs.

Table 1: EPA PBT Profiler Simulation Results

Anion	Persistency				Bioaccumulation	Toxicity
	HL water (Day)	HL soil (Day)	HL sediment (Day)	HL air (Day)	Bioconcentration Factor (BCF)	Fish ChV (mg/L)
CN5	38	75	340 (0%)	54	3.2	n.a.
TBNO	38	75	340 (0%)	20	3.2	27000
$CF_3SO_3^-$	38	75	340 (0%)	120	3.2	21000
$C_2F_5\ SO_3^-$	60	120	540 (0%)	120	3.2	4000
$C_3F_7\ SO_3^-$	60	120	540 (0%)	120	3.2	720
$C_4F_9\ SO_3^-$	180	360	1600 (0%)	120	3.2	130
$C_5F_{11}\ SO_3^-$	180	360	1600 (0%)	120	3.2	21
$C_6F_{13}\ SO_3^-$	180	360	1600 (3%)	120	3.2	3.5
$C_7F_{15}\ SO_3^-$	180	360	1600 (18%)	120	5.6	0.57
$C_8F_{17}\ SO_3^-$	180	360	1600 (48%)	120	56	0.09

Low concern

Medium concern

High concern

Once incorporated in photoresist formulations, they also demonstrated compatibility with both dry and water immersion exposure conditions. Under 32-nm node process conditions, the lithography performance of the PFAS-free PAGs was comparable to that of PFAS based commercial 193 nm photoresists.

IBM was issued two patents (US 7655379, US 8034533) for this work. IBM is actively presenting this material innovation to semiconductor chemical industry and making it accessible to scientific community both domestic and world-wide. Some examples of IBM's outreach about this innovation include:

- Publicized Green Chemistry innovation of PFAS-free photoacid generators Class I at SPIE-the International Society for Optics and Photonics conference of Advanced Lithography in San Jose, California; (*SPIE* 7639 76390D, 2010)
- Released the same innovation to public via EE Times: http://www.eetimes.com/electronics-news/4087901/IBM-says-litho-chemical-better-for-environment
- Presented PFAS-free photoacid generator Class II at the 27th International Conference of Photopolymer Science and Technology in Chiba, Japan. (*J. Photopol. Sci. Tech.* 23 (2), 173, 2010)
- Showcased PFAS-free Green Chemistry innovation at EPA Region 2 workshop on Green Chemistry in September 2011.

IBM is also pursuing technology transfer opportunities and is willing to share the technical details with chemical companies interested in commercialization of these PFAS-free PAGs for a wider range of applications and enable the elimination PFOS, PFOA and PFAS compounds with environmental and health concerns.

Conclusion

IBM's PFOS and PFOA elimination epitomizes pollution prevention and is exemplary of IBM's commitment to environmental leadership in chemical substitution and the use of environmentally preferable materials and substances. The project involved thousands of man-hours over an eight year time period. Due to IBM's leadership position and collaborative efforts with chemical suppliers, many of these non-PFOS/PFOA formulations are now available throughout the world for other semiconductor manufacturers to use. IBM is also pursuing commercial availability of newly developed PFAS-free PAGs for use in 193-nm photoresists.