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SEMI Assessment of Proposed Alternative Photoacid Generators (PAGs)

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SEMI™ Assessment of Alternative PAGs Electronics tab of rest_pfas_appendix_e2_31101_en.xlsx https://echa.europa.eu/documents/10162/bbcd1314-31cd-ba4b-9d6c-953c542853e8 to Annex E of the Annex XV Report for the Per- and polyfluoroalkyl substances (PFAS) Restriction Proposal.

The intent of this assessment is to demonstrate that the non-PFAS PAGs proposed to be utilised at the entry into force timeframe by the Dossier Submitter are not suitable to replace the current use of PFAS PAGs.

It is the considered opinion of all lithographers consulted for this assessment that these photoacids cannot replace the PFAS acids currently used in Chemically Amplified Resists (CAR) while maintaining sufficient lithographic performance.

Benzenesulfonic acid, 4-nitro-	138-42-1
Benzenesulfonic acid, 3-nitro-	98-47-5

These photoacids will be present in typical onium salt PAGs as the following anions: Benzenesulfonic acid, 4-nitro-, ion(1-) CAS 30904-42-8, 3-Nitrobenzenesulfonate CAS 30904-40-6

The compound with CAS name benzenesulfonic acid, 4-nitro-, ion(1-) is also known as 4-nitrobenzenesulfonate. It is described as a component of an onium salt PAG in a single publication [Y. Suzuki and D. W. Johnson, Proc. SPIE 3333, 735 (1998); DOI: 10.1117/12.312350]. A second paper [M. Ikbal et al., Tetrahedron 67 (20), 3733 (2011); DOI: 10.1016/j.tet.2011.03.049] describes the formation of the free acid in a liquid phase photolysis from non-ionic precursors, which is not relevant for a lithographic assessment.

Suzuki and Johnson compare bis-t-butyliodonium 4-nitrosulfonate to the corresponding PFBS salt. Their results show that in a 248 nm resist, the 4-nitro derivative has:

a. 40% slower photospeed compared to PFBS,
b. Significantly poorer acidity/diffusivity balance, leading to significantly poorer photolithography line and space feature quality.
c. Excessive top loss.

For Bottom Anti Reflective Coatings (BARC), there are no data on use as PAGs, although it has been described as a component of a thermal acid generator [WO2023048021 A1].

3-Nitrobenzenesulfonate has acidity similar to the 4-nitro derivative. It has been described as a component of a sulfonium PAG in e-beam resists in two publications (US20030017425 A1 and WO2003007079 A1) and in two more as an iodonium salt where it has been used for e-beam lithography as a component in an antistatic laminate (JP2012226297 A, JP2012088697 A). In these publications, it is favourably compared to triflate; however, triflic acid is not a photoacid suitable for high resolution lithography. Based on the performance of the 4-nitro derivative, 3-nitrobenzenesulfonate is also not a suitable PAG for high performance CARs.

There is no experimental basis for the assertion made in Annex E that 3- or 4-nitrobenzenesulfonate-based PAGs have a "high potential for replacement at EiF." Instead, all available data point to the opposite: that these photoacids are much inferior to PFAS photoacids, and that they are not suitable for high performance photoresists.

Thiophenesulfonic acid, 5-chloro-4-nitro-	339366-40-4
Benzo[b]thiophene-2-sulfonic acid, 7-nitro-, ion(1-)	1259426-08-8

The two compounds above have been described in two companion publications [S. Liu et al., Proc. SPIE 7639, 76390D-1 (2010); DOI: 10.1117/12.846600 and US 2009/0181320A1] as anions of triphenylsulfonium PAGs in a 193 nm photoresist. No 248 nm use has been reported – it is anticipated that these anions have significant absorption at 248 nm, which is a disadvantage compared to the transparent PFAS anions.

Both photoacids are sufficiently strong to be useful in patterning 193 nm photoresists and were found to offer similar patterning quality to PFBS for 150 nm line/space (L/S) features, a dimension usually patterned with cheaper 248 nm technology. However, for typical 193 nm applications, their performance falls short of that of PFAS-based photoacids:

a. 10 and 40% slower photospeed for 70 nm L/S features

b. significantly poorer acidity/diffusivity balance, resulting in significantly poorer photolithography line space feature quality (line slimming, scumming, and top loss/rounding).
c. prohibitively high line width roughness (12.2 and 8.4 nm for 50 nm L/S)
d. significantly higher mask error factor (MEEF)

It therefore has to be concluded that while PAGs containing these photoacids might be useful as minor components in PAG mixtures for 193 nm, they are incapable of providing the same performance as PFAS-based PAGs as majority components. Their potential for PFAS PAG replacement is thus low.

2,4-Cyclopentadien-1-yl, 1,2,3,4,5-pentacyano-	869624-10-2
1,3-Cyclopentadiene-1-carboxylic acid, 2,3,4,5-tetracyano-, methyl ester, ion(1-)	46786-21-4

The two anions above have been described as triphenylsulfonium and bis-t-butyliodonium salts used in 193 nm photoresists in two companion publications [M. Glodde et al., J. Photopolym. Sci. Tech. 23 (2), 173 (2010) and US 7,655,379 B2]. The pentacyano derivative (CN5) showed slightly inferior imaging performance to PFBS for 100 nm L/S in 193 nm dry exposure, with inferior wall angle and noticeably more scumming. Photospeed was slower by 43%, although the CN5 formulation was using a higher post exposure bake (140 C vs. 120 C for PFBS). In 193 nm immersion lithography, patterning for 45 nm L/S were comparable to commercial formulations. The second anion (CN4-C1) showed similar performance. In terms of performance, CN5 and CN4-C1 could be candidates for PFAS replacements in 193 nm resists, albeit with a significant slower photospeed and a requirement for more aggressive post exposure bakes.

For the above reasons, CN5 and CN4-C1 cannot be considered to have high substitution potential for PFAS anions in PAGs.

If we make the highly unlikely assumption that non-PFAS PAGs can be developed for all needed applications, we can project the impact and timeline from sub-supplier to supplier to device manufacturer. The development of non-PFAS PAGs will require extensive research and

development between the sub-supplier and supplier. Iterative R&D will be required to produce non-PFAS PAGs which match all existing quality and performance parameters and targets. Once the PAGs have been generated, they will need to be incorporated into specific formulations to meet all customers' existing needs and process specifications. We anticipate well in excess of 100 different formulations to be generated industry wide in the EU. Even with R&D expansion, it is estimated that this process will take 5-10 years at an estimated cost of €23-56 million per material supplier customer.

Likewise, device manufacturers must each qualify a suite of new formulations from the suppliers to ensure that there is no process/technology specific impact to the device performance or yield. These multi-phased qualifications can take months to years for a single formulation depending on the complexity of the application and duration of the yield analysis activities. We expect 6-12 years for each device manufacturer to qualify a full replacement suite of materials at the cost of ~€11 million.

Even with R&D expansion, the optimistic timeline for full replacement would be 20+ years as there are not enough industry resources to qualify all materials simultaneously. It is highly probable that substitutions for many applications will be detrimental to performance and yield which would stall the progress of semiconductor innovation, computing power progress, and make some existing products incapable of manufacturing.

Additional discussion on PAG replacement can be found on page 37 of SIA PFAS Consortium report The Impact of a Potential PFAS Restriction on the Semiconductor Sector: https://www.semiconductors.org/pfas/ or attached to this Annex XV submittal.