Carborane-Based Photoacid Generators:
New Superacids For 193 nm and EUV Lithography

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Photogenerated carborane superacids have been found to be effective as catalysts for chemically amplified resists in 193 nm and EUV. It was found unexpectedly that despite the documented high acid strength of the 1-carboranes, the photospeed of resist formulations containing them was significantly lower than that of corresponding perfluoro-substituted sulfonic acids. This behavior is attributed to the high stability of the intermediate carbocation/acid anion complex, which for perfluoroalkane sulfonates is a transition state but an isolable intermediate for the 1-carboranes. The long residence time of the carborane acid catalyst in this intermediate reduces its availability and causes the lower photospeed; at the same time, this phenomenon leads to lower diffusion rates as a result of the immobility of the bulky intermediate complex. Coupled with the high transparency of carborane anions in EUV, it is expected that the use of carborane PAGs for EUV formulation optimization will offer new opportunities to escape the photospeed/resolution/LER triangle trade-off that has limited progress in EUV photoresists.

Keywords: carbornen, photoacid generators, superacids, EUV lithography, 193 nm lithography, perfluoroalkane sulfonate, mesitylen oxide

1. Introduction

The design of chemically amplified resists requires the use of acids which combine high acid strength with low nucleophilicity of the conjugate anion. In the case of the dominant 193 nm photoresist platform, based on tertiary alkyl esters and lactone monomers, these requirements are particularly exacting: this type of polymer matrix exhibits far weaker interaction with and stabilization of the catalytic protons than the phenolic matrices used for 248 nm, and in this platform many acids which are widely used in 248 nm resists are therefore too weak (e.g. camphorsulfonic acid) or too volatile (e.g., triflic acid) to be effective catalysts. Furthermore, the tertiary alkyl cleavage groups used in 193 nm, such as, e.g., 2-methyladamantanane or ethylcyclopentane, are almost as susceptible to SN1-type recombination reactions between the cationic intermediate and the acid anion as the ESCAP-type, t-butyl ester based chemistry used in 248 nm. Such reactions lead to catalyst loss and low turnover numbers in the catalytic chain, resulting in low photospeeds. Together, these twin requirements have greatly limited the type and number of acids available for 193 nm resist design, initially shrinking it down to the perfluoroalkanesulfonic acids with chain lengths of C4 or more, and with the environmentally motivated, voluntary industry restrictions on PFOS, basically reducing it to nonaflates. More recently, through the work of researchers at 3M and others, CH-and NH-acidic superacids containing short-chain perfluorosulfo groups have been introduced which have expanded the design options for PAGs.

The same types of perfluorinated acids are also used in EUV, where they have the disadvantage of adding substantial absorbance to the resist. In EUV, the absorbance events occur in the inner shells of atoms, and the absorbance of the film is no longer determined by chemical structures, but entirely by the film's atomic composition. Fluorine has a high inelastic X-ray scattering cross section (f2 factor), and thus leads to increased film absorbance. Ideally,
counterions for EUV will not contain elements with high $f_2$ factors.

A second drawback lies in the recently discovered photochemical decomposition reaction of perfluoroalkane sulfonates\(^5\) to yield $\text{SO}_2$, $\text{HF}$, and other fragments (Scheme 1). This reaction has been studied in 193 nm, where it leads to substantial outgassing of reactive compounds. While no studies have yet been reported on the perfluoroalkysulfonyl-substituted methide and imide PAGs, one would expect that a similar mechanism will be operative for these compounds. Additionally, for EUV, one would expect that the impact of this reaction will be substantially more severe: at 193 nm, the level of outgassing is mitigated by the high transparency of the perfluoroalkane sulfonates at that wavelength, whereas for EUV, both direct absorption events and exposure by secondary electrons should lead to much higher reaction rates.

As the above discussion shows, there is a need to develop new non-fluorinated superacids with low nucleophilicity for both 193 nm and EUV lithography. The chemical literature contains a number of potential candidates; of these, this paper will report on the use of 1-carboranes as catalysts for chemically amplified photoresists. The superacid properties of 1-carboranes have been well characterized in the literature;\(^6\) additionally, the $f_2$ factor of boron is two times lower than that of carbon, seven times lower than that of oxygen, and eleven times lower than that of fluorine (see Fig. 1), which makes the 1-carboranes particularly attractive as highly transparent photoacids in EUV lithography. It should be noted that during the course of this study, the same suggestion has independently been made by R. Meagley of Intel.\(^3\)

### 2. Carborane Acid Chemistry

The carborane clusters are prime examples of sigma-aromatic structures. They contain delocalized 3-center bonds between the boron atoms which for the parent anion $\text{CB}_{11}\text{H}_{12}^-$ ($\text{CBP}$) and the closely related,

![Scheme I: Photochemical decomposition of perfluoroalkane sulfonates. Decomposition products in boxes have been identified by mass spectroscopy.](image-url)
charge-neutral di- or o-carborane $\text{C}_2\text{B}_{10}\text{H}_{12}$, add up to $2n+2$ bond electrons, thus obeying Hückel's rule. Consequently these compounds exhibit high thermal stability and extraordinary chemical inertness to acids, bases and oxidants. The closo-carboranes are not bioreactive and have about the toxicity of sodium chloride. As opposed the non-cluster boron hydrides, the B-H bonds in carboranes are only very mildly hydridic and do not react with nucleophiles such as water; instead they are amenable to electrophilic substitution reactions similar to the hydrogens in benzene.

The parent icosahedral closo-carborane $\text{CB}_{11}\text{H}_{12}$ (CBP, Fig. 2) was first synthesized in 1967; improved syntheses were developed in the mid-1980s by Czech researchers who also showed that halogenation proceeds very selectively to yield first 7,8,9,10,11,12-hexasubstituted derivatives (see Fig. 2) and, under more reactive conditions, complete undeca-substitution.

Since closo-carboranes completely lack both $\pi$ electrons and lone pairs, they have a very large HOMO-LUMO gap and are therefore very weakly coordinating ions and exceedingly weak nucleophiles. At the same time, the conjugate acids of the 1-carboranes derived from CBP are Brønsted superacids with acid strengths that exceed that of perfluoroalkyl sulfonic acids. The best way to understand their high acid strength is to look at their counterions are such extraordinary weak bases.

The acid $\text{CB}_{11}\text{H}_{13}$ (CPBH) can be isolated in pure form as a white solid from the silylium salt by the reaction

$$\text{Et}_3\text{Si}^+ (\text{CB}_{11}\text{H}_{12}^-) + \text{HCl} \rightarrow \text{CB}_{11}\text{H}_{13} + \text{Et}_3\text{Si-Cl}$$

Calculated gas phase acidities for carborane acids have ranked them the strongest of any isolable acid, but, as usual, conversion of the calculated $G$ values to actual condensed phase acidities is problematic. Triflic acid has a value of -14.1 on the $H_0$ acidity scale, and HFSO$_3$ a value of -15.1. The NH-acidic superacid HN(SO$_2$CF$_3$)$_2$ comes in noticeably lower at -12.1. Using the protonation of benzene as a guide, triflic acid does not protonate benzene, and the strongest known liquid acid, HFSO$_3$, does so only partly. In contrast, CBPH forms the benzenium salt $\text{C}_6\text{H}_7^+$ already in dilute solutions; the salt can be crystallized and is stable until 150 $^\circ$.

Based on the $^{13}$C NMR shift on protonation of

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**Figure 2:** Structures of icosahedral closo-carborane anions used in this study. Parent anion $\text{CB}_{11}\text{H}_{12}$ CBP, undecamethyl derivative CBM11, hexachloro derivative CBC6, hexabromo derivative CBB6, hexaiododerivative CBI6 (all hexasubstitutions in 7,8,9,10,11,12-positions).
mesityl oxide (Table 1) or the shift in $\nu_{\text{NH}}$ frequencies of tri-octylammonium salts (Table 2), all hexasubstituted 1-carboranes are significantly stronger acids than the ones that have until now been used in photolithography. Based on the change in $\nu_{\text{NH}}$ frequencies, symmetrical undeca-substitution reduces acid strength, and the undecamethyl-substituted derivative used in this study is one of the weakest of the carborane acids.

While the 1-carboranes show low absorbance at EUV wavelength, they do not appear to be fully transparent at 193 nm. UV spectra of their alkali metal salts in solution show a rapidly rising absorption below 200 nm. Acceptor substitution seems to exert a hypsochromic shift on the onset of the 1-carborane absorption, whereas donor substitution causes a bathochromic shift (see Table 3). The picture is complicated by the fact that some substituents, such as bromine, can contribute absorptivity of their own at 193 nm. Overall, the hexachloro derivative is the most transparent 1-carborane among the ones studied.

The al-carboranes $C_5B_{10}H_{12}$ are not superacids and cannot be used in chemically amplified systems. However, it should be noted that they have been used as pendant groups in polymers for EUV lithography, taking advantage of the low $f_2$ factor of boron to design less absorbing EUV photoresists.

3. Experimental Section

CBP was purchased as the potassium salt and CBC6, CBB6, and CBM11 were purchased as their cesium salts from Katchem Ltd., E. Krasnhořské 6, 110 00 Praha 1, Czech Republic (www.katchem.cz), and used without further purification. Photoacid generators (PAGs) were prepared as the triphenylsulfonium or bis-(t-butylphenyl)iodonium salts using metathesis reactions from the corresponding bromides or acetates in dichloromethane/water. Photoresists were formulated in methylhydroxyisobutyrate (MHIIB) for a film thickness of 120 nm using a 193 nm photoresist resin of the general formula

$$\text{R}_1\text{H~CHO~R}_3$$

where $R_1$ is hydrogen or methyl, $R_2$ is a lower alkyl group, and $R_3$ is a large, non-polar unit.

Formulations either employed carborane PAGs only or mixtures of carborane PAGs with others.

Table 3: UV absorbance of 1-carborane salts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorptivity at 193 nm (L/(g cm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^+$ CPB$^-$</td>
<td>10.76</td>
</tr>
<tr>
<td>Cs$^+$ CBC6$^-$</td>
<td>3.36</td>
</tr>
<tr>
<td>Cs$^+$ CBB6$^-$</td>
<td>6.01</td>
</tr>
<tr>
<td>Cs$^+$ CBM11$^-$</td>
<td>75.10</td>
</tr>
<tr>
<td>(Bis-t-butylphenyl)-iodonium CBP$^-$</td>
<td>99.7</td>
</tr>
<tr>
<td>(Bis-t-butylphenyl)-iodonium nonaflate</td>
<td>88.9</td>
</tr>
</tbody>
</table>
including perfluoroalkanesulfonates. Typical PAG loadings were of the order of 115 \( \text{moles per gram polymer} \). Bases were added at about 30\% molar ratio to the PAG in order to pre-poison the resists. All resists were coated on organic bottom antireflective coatings. Softbakes were standardized at 100 C/60 sec, and post exposure bakes at 110 C/60 sec.

193 nm exposures were carried out on a Nikon S306D scanner with numerical aperture (NA) of 0.85 using a 6\% half-tone phase shift mask and either Y-dipole or 2/3 annular illumination, as indicated. For EUV exposures, the samples were diluted down with MHIB to a target film thickness of 70 nm in order to minimize line collapse. EUV interference lithography (IL) exposures were carried out using the Swiss Light Source beamline at the Paul Scherrer Institute in Villingen, Switzerland. In this interference lithography setup, EUV photons are transmitted through a silicon nitride membrane and are diffracted by gratings on each side of the direct beam stop. Doses were measured on the mask and were divided by a factor of 3 for 50 nm features, and by higher factors for smaller ones.

4. Lithographic evaluations

4.1 Results with 193 nm exposure

Initial experiments were carried out with TPS\(^+\) CBP\(^-\) as PAG. Due to the high acid strength of the carboranes, we expected to find increased photospeeds. However, compared to a reference formulation containing conventional PAGs, an equivalent formulation using only TPS\(^+\) CBP\(^-\) as PAG was found to be exceedingly slow: it did not open at more than twice the dose of the reference resist, which put it out of the range that could comfortably be imaged without incurring lens heating. If one third of the PAGs in the reference resist was replaced with TPS\(^+\) CBP\(^-\), photospeed increased more moderately by about 33\% (Figure 4), while other resist properties remained basically unchanged. Further work on a variety of mixed formulations showed that it was indeed possible to replace up to 50\% of conventional PAGs in a formulation without deterioration of properties except for an increase in exposure dose.

When formulations were prepared at lower film thickness (70 nm) for the EUV experiments, the resists were initially tested in 193 nm exposures. At the lower film thickness, the conventional reference formulation was found to be exceedingly fast, whereas the CBP\(^-\) containing formulation now imaged at 71 mJ/cm\(^2\). CBB6 and CBM11-containing resists were faster, imaging at 32 and 24 mJ/cm\(^2\), respectively (Fig. 5 and Table 4). DOF, exposure latitude, and LWR were comparable for all three formulations using only carborane-based PAGs, and they were comparable to that of the reference formulation at higher film thickness.

4.2 Results with EUV exposure

In EUV, the reference formulation containing
5. Discussion

The large difference in photospeed and the other differences in performance measures seen for the carborane PAGs were contrary to our initial expectation that higher acid strength would also lead to higher photospeed. Since the high acid strength of carboranes has been measured by independent methods, the root cause of the performance difference must have other origins. The combination of lower sensitivity and higher LER observed in EUV pointed towards differences in the diffusion behavior. Very low diffusivity of the carborane acids could indeed generate just such a combination.

To gauge the diffusivity of the carboranes, we first investigated their geometrical aspects. To this purpose, models of various acids were constructed using the Hyperchem molecular modeling software.
Figure 7: Performance of reference formulation in EUV II exposure. 32.5 nm target linewidths were resolved with a dose of 49.2 mJ/cm², and 30 nm target linewidth with an overdose of 56.3 mJ/cm² (all doses at mask plane). Corresponding dose in resist at 50 nm is 13 mJ/cm².

and their geometries were optimized by semiempirical calculations (PM3). The largest horizontal and vertical dimensions were then determined from the model, and combined in the cross section numbers of Table 5.

Table 5: Cross sectional profiles of photoacids

<table>
<thead>
<tr>
<th>Anion</th>
<th>largest vertical [Å]</th>
<th>largest horizontal [Å]</th>
<th>X-section [Å²]</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>triflate</td>
<td>3.1</td>
<td>2.6</td>
<td>8.0</td>
<td>0.3</td>
</tr>
<tr>
<td>nonflate</td>
<td>7.6</td>
<td>2.6</td>
<td>19.8</td>
<td>0.7</td>
</tr>
<tr>
<td>CBr7H12O</td>
<td>5.6</td>
<td>5.0</td>
<td>27.9</td>
<td>1.0</td>
</tr>
<tr>
<td>C6H5O4S</td>
<td>5.6</td>
<td>5.1</td>
<td>28.2</td>
<td>1.0</td>
</tr>
<tr>
<td>PFOS</td>
<td>11.0</td>
<td>2.6</td>
<td>28.5</td>
<td>1.0</td>
</tr>
<tr>
<td>CBr7H8Cl6</td>
<td>6.1</td>
<td>5.9</td>
<td>36.3</td>
<td>1.3</td>
</tr>
<tr>
<td>CBr7H8Br6</td>
<td>6.3</td>
<td>6.1</td>
<td>38.4</td>
<td>1.4</td>
</tr>
<tr>
<td>CBr7H8I6</td>
<td>6.5</td>
<td>6.6</td>
<td>42.6</td>
<td>1.5</td>
</tr>
<tr>
<td>C12B11H24+</td>
<td>6.8</td>
<td>7.2</td>
<td>49.3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The parent carbaborane CBP is about the same size as PFOS or camphorsulfonic acid, while the more highly substituted carbaboranes are substantially bigger. CBP (CBr7H12) is noticeably smaller than CBB6 (CBr7H8Br6) and CBM11 (C12B11H24+), yet the observed photospeeds go in the opposite direction. We therefore exclude geometric arguments as the main reason for the observed differences.

It is well known that due to their nonoxidizing nature and low nucleophilicity, carbaborane anions can greatly stabilize otherwise unstable counter cations, such as protonated benzene or t-butyl cations. The salts of carbaborane acids with benzene and t-butyl cation have been isolated preparatively and characterized by NMR or X-ray crystallography. This behavior is markedly different from that of perfluoroalkane sulfonic acids, which show no measurable equilibrium concentration of protonated benzene and whose t-butyl salts decompose very rapidly with formation of isobutene. The complex formed from perfluoroalkane sulfonic acid and a tertiary cation, such as methyl adamantly cation, is therefore a transition state, whereas the carbaborane salt is an intermediate.

Fig. 8 schematically shows the energy profile along the reaction coordinate for the two cases. For perfluoroalkane sulfonic acid (Fig. 8, left), the catalytic acid spends only a minimal amount of time in the vicinity of the transition state; it is soon regenerated and can diffuse onto the next reaction site. Carbaborane salts are stable intermediates, and the rate of regeneration of the acyl catalyst is now restricted by the decomposition rate of the salt (Fig. 8, right). Since carbaborane acids are strong enough to protonate benzene, there will not only be aliphatic cation salts but also aromatic ones. Fig. 8 alludes to this by showing structures not only for an adamantyl CBB6 salt but also for a protonated benzene-CBB6 σ-complex. We suggest that it is this difference in stability of the salts that underlies the observed behavior between carbaborane and perfluoroalkane sulfonate PAGs.

Can this hypothesis also provide a rationale for the observed catalytic activity within the series of carbaborane PAGs? We propose that in the case of the weakest acid, CBM11H, the acid strength is sufficiently low to allow more rapid decomposition of the complex, whereas for the hexahalogenated acids CBC6H and CBB6H, the cation complexes are more stable but the high acid strength leads to higher reaction rates. This leaves CBPH with medium acid
strength and reaction rate at the minimum in catalytic activity.

The high stability of the intermediate complex formed by the carborane acids has important implications for their use in high resolution lithography. There have been concerns that resist chemists will not be able to extend the chemically amplified resist concept to smaller features (below 30 nm or so) due to excessive diffusion blur. The intermediate complex formed by the carborane acids is very large and can be assumed to be rather immobile. Carborane acids will therefore have intrinsic low diffusivity. For EUV, they offer the additional advantage of low absorbance: adding carborane PAGs to a resist film actually reduces the absorptivity. Even when assuming constant film density (a conservative assumption), CPB” anion itself has half the X-ray scattering cross section of a photoresist resin and one fifth that of perfluoroalkane sulfonates. With carborane PAGs, formulators will be able to greatly increase the PAG concentration while concurrently lowering the absorbance and maintaining low diffusivity. It may thus be possible that the use of carborane PAGs in EUV will make it feasible to find an improved operating point in the critical triangle formed by dose, resolution, and line edge roughness.

6. Conclusion

Photogenerated carborane superacids have been found to be effective as catalysts for chemically amplified resists in 193 nm and EUV. It was found unexpectedly that despite the documented high acid strength of the 1-carboranes, the photospeed of resist formulations containing them was significantly lower than that of corresponding perfluoro-substituted sulfonic acids. This behavior is attributed to the high stability of the intermediate carbocation/acid anion complex, which for perfluoroalkane sulfonates is a transition state but an isoeable intermediate for the 1-carborane acids. The long residence time of the carborane acid catalyst in this intermediate reduces its availability and causes the lower photospeed; at the same time, this phenomenon leads to lower diffusion rates as a result of the immobility of the bulky intermediate complex. Coupled with the high transparency of carborane anions in EUV, it is

Fig. 8: Schematic reaction diagrams for perfluoroalkane sulfonic acids (left) and carborane acids (right). In the case of the carborane acids, the ionic complex is not a transition state but an intermediate with appreciable stability.
expected that the use of carborane PAGs for EUV formulation optimization will offer new opportunities to escape the photospeed/ resolution/LER triangle trade-off that has limited progress in EUV photoresists.

7. Acknowledgements

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8. References


5) R.R. Kunz, MIT Lincoln Labs, *private communication*.

6) For general references on carborane chemistry and properties, see:


10) Depending on their orientation, the more linear molecules triflate, nonaflate and PFOS have different diffusional cross sections. It could be argued that it is not appropriate to use the maximum cross section for comparison purposes. However, the longitudinal cross sections are identical for the three molecules, which most certainly does not correlate with their observed diffusion behavior.