Photoresist etch resistance enhancement using novel polycarbocyclic derivatives as additives

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In house synthesized mixed derivatives containing at least two carbocycles per molecule from the group of anthracenes, adamantanes and steroids with functionalized carbon chains are used as modifiers of resist properties and especially etch resistance enhancement and absorption characteristics. Etch resistance enhancement is demonstrated in oxygen, fluorine, and chlorine-containing plasmas under reactive ion etching and inductively coupled plasma etching conditions for poly(methyl-methacrylate) and a chemically amplified, positive-tone, methacrylate-based 193 nm photoresist formulation. High resolution experiments show that the proposed additives do not adversely affect the lithographic properties of the photoresists. The additive role is explained with empirical etch parameters such as the Ohnishi number and the ring parameter. © *2003 American Vacuum Society.* [DOI: 10.1116/1.1535930]

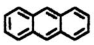
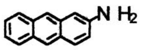
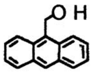
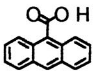
I. INTRODUCTION

Photoresists used in modern lithographic applications, such as the ones that are currently introduced in production for sub 150 nm resolution by 248 nm or 193 nm lithography, are quite complex materials that should combine a number of properties to meet the advanced patterning demands of the semiconductor industry. Appropriate absorbance at the exposure wavelength and the resistance to the plasmas used during the pattern transfer step are especially important. The latter becomes even more important as the lateral structure dimensions shrink and thin photoresist films, usually well below half a micron, are used to keep aspect ratios low and thus to facilitate lithographic processes.

Traditionally, the etch resistance properties of the resist material were obtained using phenolic polymers. This was the case for 436 nm, 365 nm and 248 nm exposures. Since novolacs and poly(4-hydroxystyrene)-based resins are highly absorbing for 193 nm light, single layer photoresist systems for 193 nm lithography are usually based on aliphatic polymers which show low absorbance, at this wavelength. However, aliphatic polymers have etching rates roughly twice as high as aromatic ones, traditionally used in previous generation photoresist systems,[1] despite the initial reactivity of aromatic polymers in the plasma environment. According to a proposed polymer etching mechanism, halogen atoms add to the double bonds first, as opposed to subtraction of hydrogen atoms from the saturated carbon bonds, and the resulting halogenated compound is less reactive than the product of abstraction.[2] The etching rate was found to be inversely proportional to the [Carbon-Oxygen] atom content of the polymer,[3] and an empirical parameter referred to as *The Ohnishi Parameter, O=(Total Number of atoms)/(Carbon-Oxygen atoms)* has been defined. The smaller the Ohnishi parameter (O) the higher the etch resistance. For example poly(4-hydroxystyrene) (PHS), a high etch resistant polymer, has O=2.43, while poly(methyl methacrylate) (PMMA), a low etch resistant polymer, has O=5. Etch resistance was also described in terms of the amount of carbon atoms present in a ring structure; an improved empirical parameter was thus defined recently as *The Ring Parameter R=(Mass of Carbon atoms in Rings)/(Total Mass of Polymer)*. The higher and closer to unity the value of R, the higher the etch resistance of the polymer.[4] For example PHS, a high etch resistant polymer, has R=0.6, while PMMA, a low etch resistant polymer, has R=0. Notice that high R values (close to unity) and small O values characterize high etching resistance.

In order to address the etch resistance problem in 193 nm, polymeric materials containing cycloaliphatic moieties, attached either to the polymer chain or as separate components, were used by most resist companies and research groups. Nevertheless, as it was first suggested,[5] another method to enhance the etch resistance of these aliphatic polymers, while keeping acceptable absorbance, can be provided by polyaromatic compounds such as naphthalene, anthracene and their derivatives. These are characterized by a red shift of the absorption band, which in simple aromatic compounds is centered around 193 nm and thus, they are more transparent at this wavelength. It has been shown[6] that anthracene loading is effective in increasing the etch-resistance, i.e., reduction of the etching rate of the PMMA by 25% is obtained at loading around 5%. In comparison addition of more than 10% w/w is required for the same etch resistance increase in

TABLE I. Reference mono-anthryl derivatives and their physiochemical properties. UV=absorbance added to the film of PMMA containing 5% of the reference additive at 193 nm for a thickness of 0.5 μm (PMMA absorbance not included). SOL=solubility at the solvents used (*=good). SUBL=temperature of sublimation from the film. ETCH RATE=Oxygen plasma etching rate in (Å/min) with additive present in PMMA in 5% w/w of the polymer (Conditions: RIE mode, 10 mTorr, 400 W power, electrode diameter 300 mm, dc bias 150 V, etching time 2 min. Etching rate of pure PMMA is 3300 Å/min under similar conditions). O.N.=Ohnishi number (the smaller the better the etch resistance) and R.P.=Ring parameter (the higher and closer to unity the better the etch resistance). O.N.(PMMA)=5, O.N.(PHS)=2.43, R.P.(PMMA)=0, R.P.(PHS)=0.6.

REFERENCE COMPOUNDS	UV 193 nm	SOL	SUBL	ETCH RATE	O.N.	R.P.	REFERENCE COMPOUNDS	UV 193 nm	SOL	SUBL	ETCH RATE	O.N.	R.P.
	0.19	*	110^{0}C	3017	2.40	0.94		0.30	*	110^{0}C	2435	1.86	0.87
	0.17	*	110^{0}C	3000	2.00	0.81		0.18	*	110^{0}C	3440	2.08	0.76

the case of adamantane (cycloaliphatic) derivatives.

Similar challenges, i.e., to enhance etch resistance using polymers or additives that have suitable absorbance at the exposure wavelength, are encountered in other wavelengths, as well as electron beam or x-ray lithography. For example, in EUV lithography at 13 nm (a strong candidate for next generation lithography) the thickness of resist films may only be in the range of 100–200 nm, requiring the highest possible etch resistance of the resist materials. The increase of etch resistance is also desirable even at longer wavelengths (e.g., 248 nm) since it allows the use of thinner resist films and thus smaller aspect ratios for high resolution patterning.

In all the above cases the use of additives can be very attractive to improve certain properties in photoresist compositions, and particularly etch resistance since it provides high versatility and allows easy preparation of different material formulations without complicated polymer synthesis or chemical modification procedures. Nevertheless, restrictions are posed by the need to fulfill a number of physicochemical requirements defined by the lithographic process: (a) The additives must be compatible with the rest of the resist components to avoid any phase separation phenomena that can lead to film property incongruity; (b) The additives should withstand the lithographic processing steps without decomposition sublimation or process-induced phase-separation phenomena; (c) The additives should not modify substantially the chemical and physical properties of the photoresist to cause deterioration of the lithographic performance.

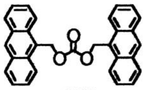
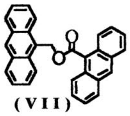
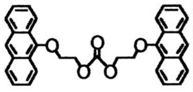
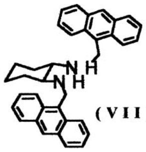
The purpose of this paper is to demonstrate novel photoresist etch resistance promoters characterized by the presence of at least two polycarbocyclic moieties in their molecule, where at least one of them is an anthracene derivative. Molecules that contain two anthracene moieties or an anthracene and a second polycarbocycle, such as adamantane, or steroid, are very useful for etch resistance enhancement. The article is organized as follows: In Sec. II the concept is demonstrated using both commercial and novel anthracene derivatives, with a discussion of their properties. In Sec. III demonstration of the etch resistance enhancement in four different plasma chemistries in inductively coupled plasma reactors is performed, and an analysis of the results with empirical parameters is presented. Finally, in Sec. IV a first attempt is made to show that the additives have no adverse effects in lithographic performance, using high resolution imaging with an "in house" synthesized new 193 nm chemically amplified, positive-tone, methacrylate-based photoresist formulation (CAPRF-3).

II. POLYCARBOCYCLIC ETCH RESISTANCE ADDITIVES

A. Proof of concept

The basic idea is to load a photoresist film with a small amount of additives 5%–15% per weight in order to increase its etch resistance, and possibly improve other properties as well. The improvement of selected physicochemical properties, defining the behavior of the additives was first tested, with the help of a standard "model" lithographic resist material. PMMA was mostly selected since it is a common, simple and well-known material and thus it can provide a universal matrix for the evaluation of the proposed additives. It has also low absorbance at 193 nm and it is characterized by low etch resistance (Ohnishi number O=5, Ring Parameter R=0). This way, the improvement obtained by loading the resist film with the synthesized additives can be easily assessed. The effect of several simple derivatives on UV absorbance, solubility, sublimation and etch resistance of the common aliphatic resist PMMA was evaluated. The commercially available anthracene, 9-anthracene methanol, 9-anthracene carboxylic acid and 2-aminoanthracene were first tested and considered as reference compounds. Table I summarizes the results and demonstrates a substantial improvement in etching resistance. More details on the use of the additives described in Table I are given in our previous publication for oxygen and sulfur hexafluoride reactive ion etching plasmas.[6]

TABLE II. Novel di-anthryl derivatives and their physiochemical properties obtained from evaluation experiments. The following explanations apply to Tables II and III. UV=absorbance added by the additive to the PMMA film at 193 nm or at 248 nm at 0.5 μm film thickness and for 7.5% weight loading (PMMA absorbance is NOT included). SOL=solubility at the solvents used (##=very bad, #=bad, ∗=good, ∗∗=very good). SUBL=temperature of sublimation from the film. ETCH RATE=Oxygen plasma etching rate in (Å/min) with additive present in PMMA in 7.5% w/w of the polymer (Conditions: RIE mode, 10 mTorr, 400 W power, electrode diameter 300 mm, dc bias 150 V, etching time 2 min. Etching rate of pure PMMA is 3300 Å/min under similar conditions). nt=not tested, O.N.=Ohnishi number (the smaller the better the etch resistance) and R.P.=Ring parameter (the higher and closer to unity the better the etch resistance). O.N.(PMMA)=5, O.N.(PHS)=2.43, R.P.(PMMA)=0, R.P.(PHS)=0.6.

NOVEL DI-DERIVATIVES	U V 193 nm	U V 248 nm	SOL	SUBL	ETCH RATE	O.N.	R.P.	*NOVEL DI-DERIVATIVES*	U V 193 nm	U V 248 nm	SOL	SUBL	ETCH RATE	O.N.	R.P.
 (V)	0.29	0.63	##	130^{0}C	nt	2.00	0.76	 (VII)	0.28	1.16	#	160^{0}C	2800	1.86	0.82
 (VI)	0.24	1.04	*	130^{0}C	3067	2.28	0.67	 (VII)	0.10	0.40	**	160^{0}C	2900	2.00	0.83

B. Novel additives as etch resistance promoters

Newly synthesized compounds[7] containing other functional groups and either two or more anthryl-moieties or one or more anthryl groups linked to polycarbocycles, such as adamantane, or steroids, were also tested and compared to known di- and poly-anthryl-derivatives. It is important that the selected additive is soluble in the solvents commonly used in the microlithography process. In the cases where poly(methyl methacrylate) (PMMA), was used as the base polymer, propylene glycol methyl ether acetate (PGMEA) and methyl isobutyl ketone (MIBK) were used as solvents. After film formation the amount of the additive sublimed during the baking cycles was tested. Evaluation of spectroscopic and etch resistance enhancement followed.

Tables II and III present the chemical structure of only a few of the newly synthesized derivatives along with their physicochemical properties. The latin numbers on the additives are denoting their synthesis number. Obviously more additives than those presented here have been synthesized, but only a few are presented here to avoid clattering the paper. As can be concluded from the results in Tables II and III this new generation of anthryl derivatives has much better physicochemical properties than any reported compounds so far (reference compounds, Table I). Sublimation temperatures are significantly enhanced. Solubility in organic solvents widely used in photoresist formulations has been also enhanced and the new chemical structure design resulted in optimized UV absorbance for the 193 nm region. Etch resistance of the new additives is large, and is reflected in their high Ring Parameter and their low Ohnishi number. Nevertheless, etch resistance increase reaches a limit, and a decrease of solubility is seen with many anthryl groups per molecule.

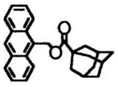
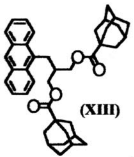
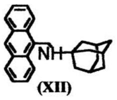
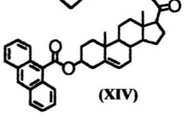
Additives containing at least one adamantane or steroid along with the anthracene are characterized as mixed. Generally, the presence of adamantane or steroid resulted in a significant improvement of absorbance at 193 nm. In particular, the very simple mixed derivative (XI), combined excellent plasma etch resistance with very good solubility, high temperature of sublimation and small UV absorbance.

III. DEMONSTRATION OF THE ETCH RESISTANCE IN VARIOUS PLASMA CHEMISTRIES AND PLASMA REACTORS

A. Etch rates in oxygen, fluorine containing, and fluorocarbon plasmas for a prototype 193 nm photoresist

In addition to the proof of concept in PMMA, the effectiveness of the novel compounds for enhancing etch-resistance was examined by loading a high-resolution 193 nm prototype photoresist CAPRF-3 (Positive Chemically

TABLE III. Novel mixed anthryl derivatives and their physicochemical properties. See explanation of symbols and conditions in Table II.

NOVEL MIXED DERIVATIVES	UV 193 nm	UV 248 nm	SOL	SUBL	ETCH RATE	O.N.	R.P.	*NOVEL MIXED DERIVATIVES*	UV 193 nm	UV 248 nm	SOL	SUBL	ETCH RATE	O.N.	R.P.
 (XI)	0.05	0.36	**	160^{0}C	2600	2.25	0.78	 (XIII)	0.17	0.45	**	160^{0}C	3100	2.50	0.69
 (XII)	0.26	0.86	**	130^{0}C	2800	2.08	0.88	 (XIV)	0.20	0.52	*	160^{0}C	2700	2.39	0.72

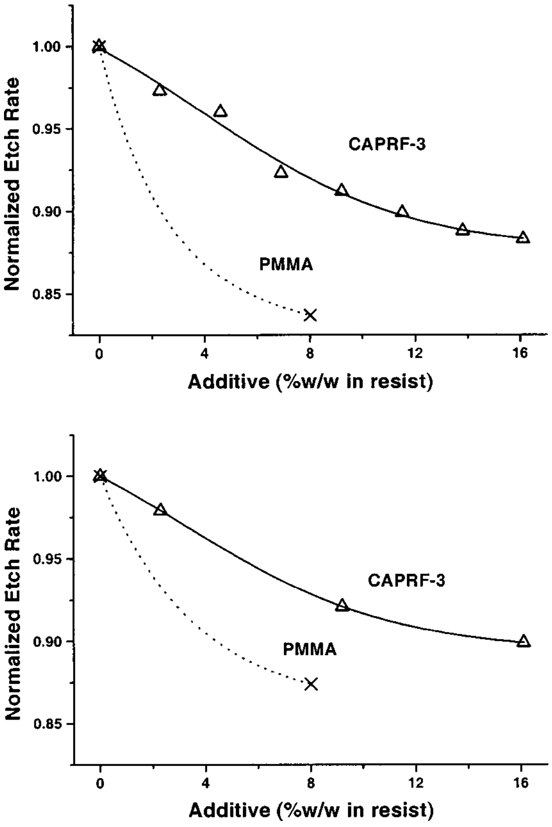


FIG. 1. Etching rates (ER) of loaded CAPRF-3 relative to pure CAPRF-3 as a function of the weight % loading content of the etch resistance enhancement additive XI (see Table III). Plasma parameters: 10 mT, top power of ICP 600 W, −100 V bias. In the same figure the etching rate of loaded PMMA relative to the pure PMMA is shown as a function of additive loading. The improvement is greater for PMMA, due to its initial etch resistance compared to CAPRF-3. (Top) Oxygen plasma, where ER(CAPRF-3)=3750 A/min, ER(PMMA)=4300 A/min. (Bottom) SF_6 plasma, where ER(CAPRF-3)=1890 A/min, ER(PMMA)=2770 A/min.

Amplified Resist Formulation) recently developed[8] in our laboratory. The resist polymer in this case was a low molecular weight methacrylate copolymer consisting of 2-hydroxylethyl methacrylate, isobornyl methacrylate, *t*-butyl methacrylate and methacrylic acid. The CAPRF-3 was a solution of the aforementioned methacrylate resist polymer and photosensitizer 3% w/w on polymer, in ethyl lactate. Etching rates of CAPRF-3 films were measured in an ICP reactor, as a function of its percentage additive content. Oxygen, sulfur hexafluoride, and trifluoromethane plasmas were used. Similar experiments were conducted for comparison purposes with PMMA. CAPRF-3 has an improved etch resistance compared to PMMA (Ohnishi number O=4.64, Ring Parameter R=0.129, compared to O=5 and R=0 for PMMA). For our test purposes we used a mixed derivative additive optimized for 193 nm lithography namely compound XI, see Table III. The variation of ER with plasma gas composition indicates a plasma chemistry-dependent etch rate for CAPRF-3.

Figure 1 depicts the results for the relative etching rates of CAPRF-3 as a function of the percentage of loading, in O_2 and SF_6 plasmas. It is observed that the loading is effective in increasing the etch resistance in O_2 and SF_6 processing plasmas, i.e., reducing its etch rate of CAPRF-3 by up 15% at a loading around 10%. In comparison the loading of PMMA induces higher etch resistance compared to the unloaded PMMA. This is because CAPRF-3 already has increased resistance as a 193 nm resist containing isobornyl in its composition. Notice the fast initial drop of the etching rate for small amounts of additive, and the subsequent quasilinear reduction. The same nonlinear initial fast reduction has been observed before, when various acrylate and cyclic (etch resistant) acrylate copolymers were synthesized.[9] The reduction observed in practice is actually better than what is shown in Fig. 1, because a heating of our samples during etching is possible. Such a heating above the glass transition temperature (T_g) could increase the etching rates of polymers with high additive content, which probably have a lower glass transition temperature due to the plasticizing effect of the organic additive.

Contrary to oxygen and fluorine containing plasmas the additives do not significantly affect etch resistance of the CAPRF-3 in CHF_3, which is already extremely high. We have measured CAPRF-3 and PHS etch rates in CHF_3 and have found them to be in the range 40–70 nm/min, analogous to the corresponding SiO_2 etch rate.

At the same time, absorbance spectra of loaded CAPRF-3 indicate that the absorbance of CAP with 10% loading is being kept at acceptable levels allowing for a CAPRF-3 thickness of up to 440 nm. Notably, most of the absorbance of the CAPRF-3 resist is due to its photoacid generator and not to compound XI (see absorbance increase in PMMA films, Table III).

B. Etch resistance in Chlorine plasmas used for polysilicon etching

The etch resistance additive XI was tested at 10% loading in CAPRF-3 resist, which was etched in a standard polysilicon gate etching recipe (main etch with $Cl_2/HBr/O_2$), in a LAM TCP reactor, in IMEC, Belgium. Table IV shows the results of etching for one minute. A large reduction of the etching rate of the experimental resist is seen.

Etch resistance enhancement in the $Cl_2/HBr/O_2$ environment is more impressive compared to the other plasma environments. This demonstrates that the use of novel anthryl derivatives as additives can be a viable and promising approach for etching resistance enhancement.

C. Discussion of the results using empirical etching parameters

The etching behavior of photoresists with and without etching resistance additives was analyzed in terms of the two known empirical parameters, namely the Ohnishi number, and the Ring Parameter. A small Ohnishi number and a large Ring Parameter signify a high etch resistance, i.e., a small etching rate. For copolymers the Ohnishi number or (the Ring Parameter) of each polymer is found and a summation based on the weight fraction of each polymer in the copolymer is done.[10] When an additive is used, the Ohnishi number

TABLE IV. Standard polysilicon-gate main-etch data of resist CAPRF-3 and CAPRF-3 loaded with additive.

Resist formulations	Initial film thickness (A)	Film thickness upon etching[a] (A)	Film thickness loss/etching rate (A/min)	Film thickness loss (%)
CAPRF-3 without additive	3200	2200	1000	31.25
CAPRF-3 with 10% additive XI (see Table III)	3420	2900	520	15.20
NRF without additive	3250	2600	650	20.00

[a] Etching time equal to 60 s.

(or Ring Parameter) is calculated based on the weight fractions of the polymer and the additive and their corresponding Ohnishi number (or Ring Parameter). In general since the additives have small Ohnishi numbers and large Ring parameters this leads to higher etch resistance. We have also used mole fractions to calculate the parameters of the copolymers and the total blend when additive is loaded, and obtained similar results.

In addition to PMMA, loaded PMMA, CAPRF-3 and loaded CAPRF-3, we also measured the etching rate of poly(4-hydroxy styrene) (PHS), partially (20%) hydrogenated PHS (h.PHS), a negative-tone (meth)acrylate-based 193 nm photoresist (NRF),[11,12] an epoxy-novolac based e-beam resist (EPR),[13] PHEMA [poly(hydroxy ethyl methacrylate)], and PHPMA [poly(hydroxy propyl methacrylate)]. NRF, and EPR are both photoresists developed in our laboratory. Table V lists relevant Ohnishi and Ring parameters. Table V clearly shows that the etch resistance additives have smaller Ohnishi and higher Ring parameters compared to the most etch resistant polymer (PHS). Thus, with addition to any polymer system etch resistance is expected to be improved.

Figure 2 shows the etching rate in RIE conditions normalized to the etching rate of PHS versus the Ring Parameter of the various loaded PMMA films. The top figure is for O_2 plasma, and the bottom for SF_6 plasma. All the commercial and novel additives described in Tables I–III, some of them at different loading (5%–15%) have been included in Fig. 2. A straight line is drawn as a best fit for the PHS, and unloaded PMMA, PHEMA, and PHPMA data. Clearly a strong super-linear reduction of the etching rate is observed versus the Ring Parameter of the film, indicating that the proposed additives can impact a high etch resistance at small loading. A similar behavior for both etchant gases is observed.

The super-linear etching rate reduction discussed in Fig. 2 for RIE conditions, has already been shown in Fig. 1 for ICP conditions. The data of Fig. 1 are redrawn in Fig. 3, together with the etching rates of other tested resist materials under ICP conditions. Figure 3 shows the normalized etching rate in O_2 (left) and SF_6 (right) plasmas versus the Ring Parameter (top) and the Ohnishi number (bottom). It is again clear that the data points for the loaded PMMA and CAPRF-3 resist are well below the line connecting the PHS and unloaded PMMA points (solid line), and a super-linear reduction of the etching rate is seen. It is quite interesting to note that the slope of the line connecting the PHS–unloaded PMMA points for O_2 plasmas is very similar to the slope observed in Cl_2 plasmas[9] (i.e., the normalized to PHS etch rate seems to be proportional to $0.42{*}\mathrm{ON}$). Notice also that for O_2 plasmas the ICP and RIE relative etching rates of

TABLE V. Ohnishi and ring parameters for some of the materials tested.

Materials/ parameters	Additive XI See Table III	PHS	NRF	CAPRF-3 with 10% additive XI	CAPRF-3	PMMA
Ohnishi O	2.25	2.43	4.92	4.35	4.64	5.00
Ring R	0.78	0.60	0.21	0.20	0.13	0.00

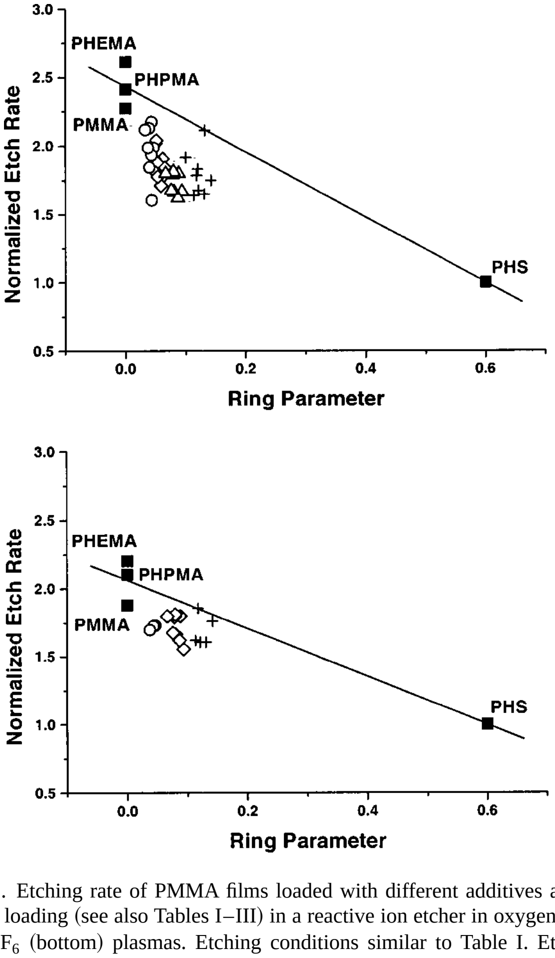


FIG. 2. Etching rate of PMMA films loaded with different additives at different loading (see also Tables I–III) in a reactive ion etcher in oxygen (top) and SF_6 (bottom) plasmas. Etching conditions similar to Table I. Etching rates have been normalized to the etching rate of PHS under similar conditions (1520 A/min and 1565 A/min in O_2 and SF_6 plasmas, respectively). A strong (super-linear) reduction of the etching rate is observed. Different symbols stand for different loading; circles 5%, diamonds 7.5%, triangles 10% and crosses 15%. Points corresponding to 15% have large scatter due to difficulty in dissolving in PMMA solution.

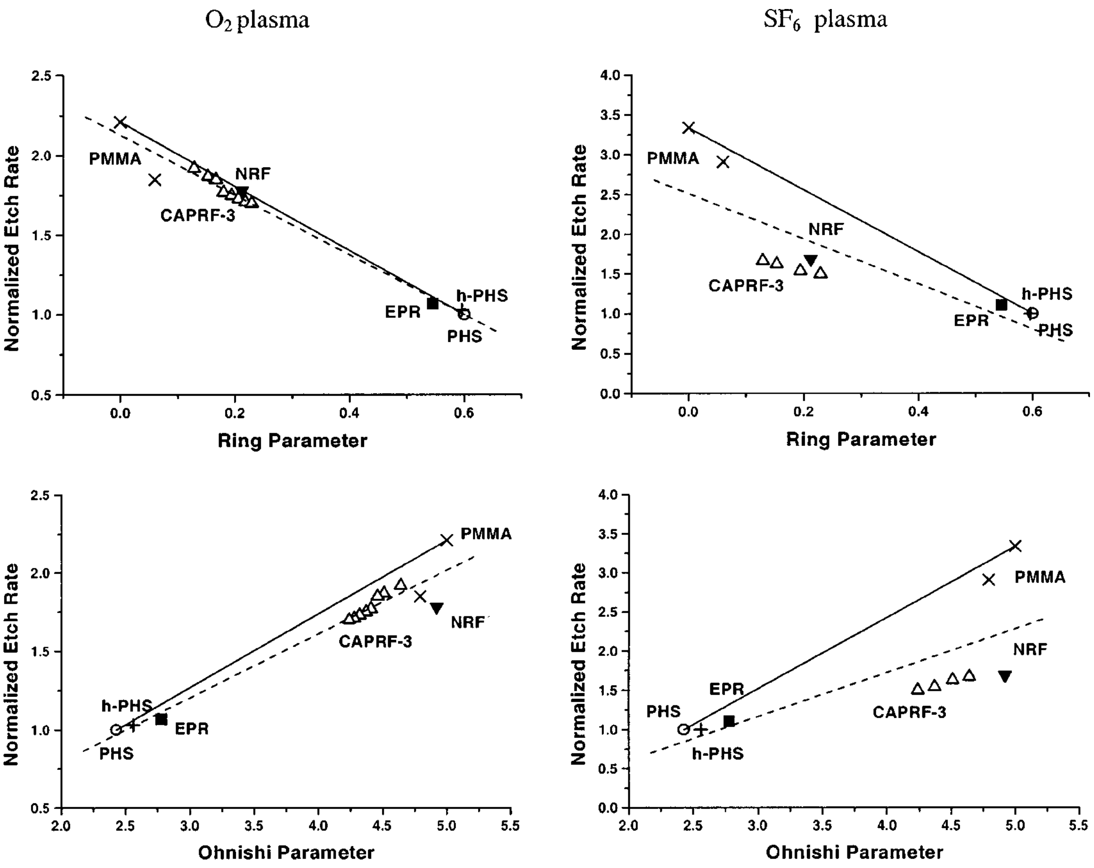


FIG. 3. Etching rate in a high-density plasma reactor in oxygen plasma (left) and SF_6 plasma (right) of various photoresist polymers normalized to the etching rate of PHS, versus the Ring Parameter (R) (top) and the Ohnishi Parameter (ON) (bottom). Multiple symbols correspond to polymers with different loading of etch resistance additives (see also Fig. 1). Solid lines connect PHS and unloaded PMMA points. Dashed lines are best fits. Conditions: Alcatel MET ICP reactor, gas flow 100 sccm, top power 600 W, bias 100 V, electrode temperature 15 °C, pressure 10 mTorr. In oxygen plasmas: Etching rate of PHS=195 nm/min. In SF_6 plasmas: etching rate of PHS=83 nm/min. Note to Fig. 3: For completeness we report the four best fits (dashed lines) for the etching rate (ER) normalized to PHS: O_2 plasmas: versus R, $ER=2.13\pm0.03-(1.88\pm0.08)R$ with regression coefficient 0.987; and versus ON, $ER=-0.02\pm0.12+(0.41\pm0.03)ON$ with regression coefficient 0.97. In SF_6 plasmas: versus R, $ER=2.51\pm0.25-(0.284\pm0.72)R$ with regression coefficient 0.81; and versus ON, $ER=-0.55\pm0.77+(0.56\pm0.18)ON$ with regression coefficient 0.73.

PMMA are very similar (around 2.5), while for ICP in SF_6 the relative etching rate of PMMA is higher (more than 3).

For CAPRF-3 after the initial super-linear etching rate reduction the data seem to be on a straight line with a smaller slope compared to the PHS-PMMA line (i.e., between 0.3 and 0.4 for the Ohnishi plot). The value of the slope approaches 0.29, as discussed for Cl_2 plasmas and for multiring polymers.[9] We have also drawn the best fit lines (dashed points) to all our data to demonstrate and predict the improvement offered by the additives, which although superlinear at small loading, might approach a linear improvement with respect to the Ohnishi or the Ring parameters at higher loading.

IV. PRELIMINARY IMAGING WITH 193 nm PHOTORESISTS LOADED WITH ETCH RESISTANCE ADDITIVES

Our experimental 193 nm acrylate-based photoresist CAPRF was used in two versions: (1) with 10% additive XI (see Table III), and 2% photo-acid generator (PAG), version CAPRF-2-10XI; (2) without additive and 3% PAG, version CAPRF-3. The two resist versions had different PAG concentrations to ensure equal absorbencies. Exposures were done with an ASML 193 nm scanner at IMEC (Belgium) with a binary mask. Preliminary results are shown in Fig. 4. The development process of CAPRF, and the resist version were not optimized, while the access time to the 193 nm scanner was limited. Thus, resist profiles were not vertical, and the patterns shown are overexposed to compensate for the nonoptimized development. Nevertheless, high resolution was obtained for both versions.

Comparison of the lithographic results of the two resist versions (with and without additive) showed no loss of resolution capability or imaging quality, at least for the level of magnification shown. Only small shifts in sensitivity and development time were observed, also caused by the different PAG content of the two versions. This is a first indication that the proposed additive can be used in photoresists for high-resolution imaging and high etching resistance. However, incorporation of the additives into a proven high-resolution optimized photoresist should be done in the future to confirm the results shown.

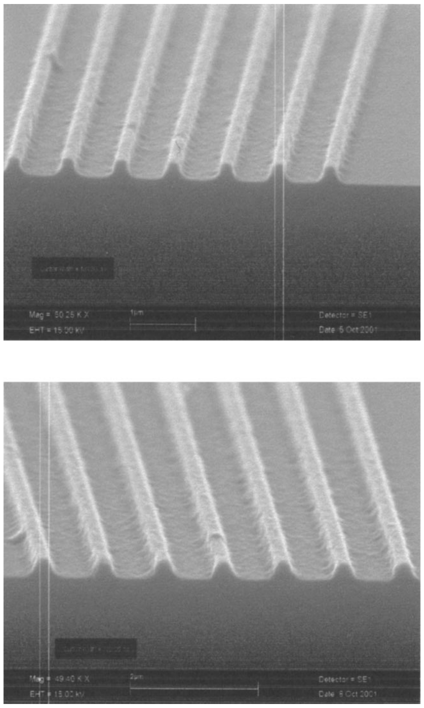


FIG. 4. SEM images of lines and spaces of CAPRF-3 resist exposed with a binary mask on an 193 nm scanner. Top: 140 nm resist lines of CAPRF-3 without additives at 2.5 mJ/cm^2. Bottom: 140 nm resist lines of CAPRF-2-10XI with 10% additive XI (see Table III) at 10 mJ/cm^2. In both cases patterns are overexposed, the development process and the resist thickness are nonoptimized resulting in novertical side-walls and some footing. However, they seem to indicate no adverse effect of the additive.

V. CONCLUSIONS

We have shown that the proposed additives can in principle be used for photoresists requiring etch resistance enhancement. The requirement for etch resistance enhancement is that the Ohnishi number of the additives is lower compared to the original photoresist, or in other terms, the Ring Parameter of the additive is higher compared to the ring parameter of the original photoresist. The advantages, which the synthesized compounds provide as resist property modifiers, are the following: (1) Sublimation is substantially reduced compared to additives with only one polycarbocycle moiety. PMMA loaded with additives has been tested up to 160 °C and no sublimation was observed; (2) etch resistance enhancement is substantial at relatively low loading; (3) absorption characteristics can be tuned by selecting suitable polycarbocyclic and functional groups; (4) compatibility with common resist materials can be achieved by selecting suitable composition and functionalization; (5) many compounds of the above family are especially suitable for use in 193 nm and EUV resists keeping tolerable absorbance at loading of 5%–10% and providing substantial etch resistance enhancement.

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