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Free-radical synthesis of narrow polydispersed 2-hydroxyethyl methacrylate-based tetrapolymers for dilute aqueous base developable negative photoresists

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Abstract

Novel (meth)acrylate tetrapolymers based on 2-hydroxyethyl methacrylate (HEMA) were synthesized via free-radical polymerization in refluxing xylene under monomer-starved conditions for use in negative photoresist formulations. 2,2′-Azobis(2-methylbutyronitrile) was used as initiator and 2-mercaptoethanol as chain transfer agent. Optimized resist formulations were obtained with a relatively narrow polydispersed ($D = 1.86$) low molecular weight copolymer ($M_n = 1677$) of 2-hydroxyethyl methacrylate (HEMA), isobornyl methacrylate (IBMA), cyclohexyl methacrylate (CHMA) and acrylic acid (AA), in a 40/30/23/7 weight ratio. A novel high-resolution single layer negative tone photoresist suitable for 193 nm and e-beam lithography that meets basic performance requirements (aqueous-base development, enhanced etch resistance, sub-0.2 μm resolution) was developed from the aforementioned (meth)acrylate tetrapolymer, the poly(2-hydroxyethyl methacrylate-*co*-cyclohexyl methacrylate-*co*-isobornyl methacrylate-*co*-acrylic acid) (PHECIMA) and a sulfonium salt photo acid generator. The key-components for the negative image formation (photoacid induced crosslinking) are the hydroxyl groups of the HEMA moieties. The swelling-free negative resist material was developed in diluted aqueous base [tetramethyl ammonium hydroxide, (TMAH) 0.26×10^{-2}N] and presented enhanced etch resistance without the use of etch resistance promoters. 0.20–0.14 μm lines were obtained upon 193 nm and/or e-beam lithography.

Keywords: 2-Hydroxyethyl methacrylate; Methacrylates; Free-radical polymerization

1. Introduction

The capability for constant evolution of both the tools and the materials used in optical lithography has established this technology as the unchallenged choice for patterning in the manufacturing of modern ICs. Moreover, near future developments in IC (integrated circuits) dimension shrinkage are also anticipated through improvement of optical lithography. Most recently, the drive toward smaller features has led to the research and development efforts in developing a production worthy 193 nm lithographic materials technology [1,2], and research efforts for 157 nm lithography have started to gain momentum. Exposure tools at 193 nm, using ArF excimer lasers as light sources, are now in production for the fabrication of 0.13–0.18 μm design rule microelectronics devices. In the resist field, quite a few positive platforms have been developed and evaluated for use in industrial environment [3]. However, limited and rather moderate results have been reported so far regarding negative resists suitable for exposure at this wavelength [4–9] despite the fact that resists of this kind may offer serious advantages for certain mask levels and pattern types [10,11]. The priority given to 193 nm positive materials explains their prominence but inherent difficulties for 193 nm negative resist design and development should be also considered and discussed.

The main challenge in designing resists (either positive or negative) for 193 nm lithography, comes from the fact that aromatic matrix resins employed in *g*-line, *i*-line and deep-ultraviolet (UV) lithography (novolacs for *g*- and *i*-lines and functionalised poly(hydroxystyrenes) or styrene–acrylate copolymers for deep-UV) are too opaque at 193 nm precluding their use in single-layer schemes at this wavelength. Moreover, the etching resistance of 193 nm photoresist candidates emerged as an issue of equal if not of greater importance, since etching resistance has traditionally been achieved through the use of aromatic moieties in the resist

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polymer [12]. Through the efforts of Ohnishi et al. [13,14], and recent considerations [15,16], it has been proposed that the key factors affecting etching resistance are the 'effective carbon content' of a material and thus high alicyclic content polymers should approach the performance of aromatic resists in plasma environments. Although certain works have shown that the introduction of limited amounts of polyaromatic additives or copolymers could substantially improve the etch resistance performance [17,18], this route was not followed by major research resist groups. Thus, in the last few years, a series of 193 nm alicyclic rich (either polyacrylates [19–23] or polyolefins [24–29]) chemically amplified resists with enhanced resist sensitivity, resolution and dry-etch resistance were reported. While highly sensitive non-chemically amplified resists would be preferred, based on process simplicity considerations, only chemically amplified resists [2,30,31] proved suitable to meet modern performance requirements.

The chemical amplification concept has proven fruitful for the design of high-resolution negative photoresists capable for 248 nm, X-ray and e-beam [32] lithography. Nevertheless, the main chemistry routes followed to develop negative materials suitable for 248 nm do not appear easily transferable to 193 nm. Thus, instead of epoxy functionalities and melamine crosslinkers used for crosslinking in previous negative systems, new approaches, such as esterification [6], transesterification [5] and pinacole rearrangement [8], have been used to overcome the difficulties posed by the need to avoid the use of phenolic resins with unacceptably high 193 nm absorbance.

Recently, our group has shown that poly(2-hydroxyethyl methacrylate) (PHEMA) crosslinks [33] upon exposure in the presence of onium salt photo acid generators, through mechanisms that involve the pendant hydroxyl groups of PHEMA. But, since PHEMA possesses a great number of pendant hydroxyl groups, this platform suffers from swelling phenomena [34] even in the case where aqueous base developers were used. In order to overcome this problem, copolymers of HEMA with other (meth)acrylate monomers, have been designed, synthesized and used for the development of negative chemically amplified resist formulations suitable for 193 nm and e-beam exposures [35]. In the present work, we report the design principles, the synthetic novelties and the characterization methodology of these novel copolymers, as well as certain lithographic results at 193 nm and e-beam of negative resist formulations. The resist polymer selected is a 4-component copolymer, consisting of 2-hydroxyethyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate and acrylic acid (PHECIMA). It was synthesized via free-radical solution polymerization and characterized. Negative resists were formulated using this polymer and an onium salt as sensitizer. We deliberately carried out our investigation with rather simple formulations and well-characterized components in order to have a better insight in complex phenomena such as those encountered in lithographic performance.

A critical part of this investigation is related to the optimization of the development process. Thus, extensive dissolution rate monitoring (DRM) studies are included and lead to swelling free development conditions using environmentally friendlier diluted (e.g. by $\times 100$) aqueous base developers than the standard 0.26N tetramethyl ammonium hydroxide (TMAH). Potential contamination from the atmospheric carbon dioxide cannot be raised as an issue of affecting the strength of these diluted base developers because the pH (=10) of carbonate buffers is significantly lower than that of diluted aqueous TMAH developers with pH $\sim$ 11 or higher (present case). The resist formulations themselves that contained hydroxyl rich, non-phenolic, polymers seem to permit such a novel development approach. These diluted base developers could be also used in other non-phenolic resist formulations (upon the necessary development process study) since no fundamental reason that might compromise the high-resolution requirements of the modern semiconductor microlithography seems to exist. These developers can be also of very important use in various emerging fields of great technological importance such as the one of (Bio) MEMS [36–40].

2. Experimental

2.1. Characterization methods, processing and exposure tools

FT-IR spectra were obtained from a Nicolet Magna 550 FT-IR spectrometer. UV–vis spectra were recorded on a Perkin Elmer UV–vis Lambda 40 and absorbance coefficients at 193 nm ($a_{193\ nm}$, μm^{-1}) were determined. Modulated differential scanning calorimetry (MDSC) analyses were performed with a Texas Instruments 2920 differential scanning calorimeter using a high temperature (600°C) cell in a N_2 atmosphere (50 ml min^{-1}) at a heating rate of 10°C min^{-1}. Gel permeation chromatography (GPC) analyses were carried out on a WATERS BREEZE 1515 series Liquid Chromatograph with a differential refractometer (WATERS 2410) as detector. THF was used as a solvent at a flow rate 1 ml min^{-1} through a guard column (Styragel® 4.6 mm I.D. $\times$ 30 mm) and a series of three Styragel HR® columns (HR5, HR4 and HR1, 5 μm particle size, 7.8 mm I.D. $\times$ 300 mm). All columns were maintained at a constant temperature of 30°C and polystyrene standards were used for the calibration. The inherent (η_{inh}) and intrinsic viscosities ([η]) at 25°C of the PHECIMA were determined for solutions in ethyl(*S*)-(−)-lactate using an Ubbelohde suspended level viscometer according to the ASTM D1601-86. The wide-angle X-ray diffraction patterns for powder specimens were obtained on an X-ray PW-1130/00 Philips diffractometer. In order to determine the equilibrium water absorption, a copolymer sample was preconditioned at 120°C in an oven for 12 h. It was subsequently placed in a desiccator where 70% relative humidity (r.h.) was maintained by means of an

oversaturated aqueous solution of $NaNO_2$ at 25°C (acc. ±0.5°C). The samples were weighed periodically. Thin films (0.48 μm) of PHECIMA and of the resist formulations (both from solutions 20%, w/w, in ethyl(*S*)-(−)-lactate) on silicon wafers were obtained upon spin-coating in a Headway Research Inc. spinner. Film thickness measurements were performed on a Sloan Technology Corporation Dektak Iia profilometer. Two hot plates HT-303D each one equipped with a digital temperature controller ATV Technologie GmbH (acc. ±0.5°C) were used for the different applied process bakes. Absorbance coefficients at 193 nm ($a_{193\ nm}$, μm^{-1}) were determined upon UV absorbance measurements at 193 nm. The refractive index (n_D) was measured using an L116B Gaertner Scientific (laser He–Ne 632.8 nm) ellipsometer.

Dissolution was monitored by an experimental dissolution rate monitor (DRM) equipped with a laser emitting at a wavelength of 650 nm. The sample (Si wafer covered with the resist layer) resides in a glass cell. The light beam from the laser source incidents almost vertically ($a \sim 5°$) on the resist surface and subsequently due to the refractive index differences between developer–resist–substrate two beams incident on the detector. One beam (A) comes from the resist surface and the second (B) from the resist–substrate interface. The total energy that incidents on the detector is monitored through a data acquisition card with high sampling rate capability. During development, resist thickness changes and therefore the optical path difference between signals A, B changes. In cases where solvent penetration is significant an intermediate layer 'wet polymer' is produced and therefore more signals are incident on the detector [41]. The detector is equipped with a narrow band filter in order to eliminate the effect of ambient light on the signal acquired.

For broadband UV exposures (220–250 nm) a Hg–Xe lamp was used. High-resolution 193 nm exposures were done in an ASML 193 nm-stepper PASS5500/900 at the facility of IMEC in Leuven (Belgium) and ST Microelectronics (Crolles, France) using a binary dark field mask. High-resolution e-beam exposures were accomplished on a 50-keV e-beam machine (Leica, EBPG-3).

Etch resistance experiments were performed in a Reactive Ion Etching (RIE) machine (ALCATEL Nextral NE 330), and in an Inductively Coupled Plasma (ICP) reactor (ALCATEL MET). Etching rates were measured by means of surface profilometry and ellipsometry, after 1-min plasma etching, and in-real time by means of in situ multi-wavelength ellipsometry. Processing conditions were 400 W power for the RIE, 800 W source power and −100 V bias voltage for the ICP, at a pressure of 10 mT in various semiconductor processing chemistries (O_2, SF_6, CHF_3).

2.2. Materials

2-Hydroxyethyl methacrylate (HEMA) (97%), cyclohexyl methacrylate (CHMA) (97 + %), isobornyl methacrylate (IBMA) (92%), acrylic acid (AA) (99%), poly(methyl methacrylate), 2-mercaptoethanol (98%), poly(2-hydroxyethyl methacrylate) (PHEMA), *p*-xylene (99 + %), petroleum ether (98%) and ethyl(*S*)-(−)-lactate (EL) (98%), were purchased from the Aldrich Chemical Company. 2,2′-Azobis(2-methylbutyronitrile) (98%) was obtained from Fluka. All materials were used as supplied. Triphenylsulfonium hexafluoroantimonate (TPSHFA, $T_{dec} > 200$°C) was used as a photo acid generator (PAG) in our resist formulations in 3–5 wt% on polymer resist. The developer used in our process was tetramethyl ammonium hydroxide solution (TMAH) 0.26×10^{-2}N. Anti-reflective coating AR®19 and a PHS-type resist, UVIII® were supplied from Shipley Company. A novolac type resist AZ5214 was provided from Clariant.

2.3. Synthesis of PHECIMA

A 250-ml round-bottom flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a N_2 inlet, a Graham condenser equipped with a cold finger using ice water as the cold trap, a dropping funnel and a heating mantle was charged with 25 g of xylene and heated to reflux. A solution of mixed monomers HEMA (41.23 g), CHMA (23.71 g), IBMA (32.61 g) and AA (7.07 g), initiator 2,2′-azobis(2-methylbutyronitrile) (3.06 g), chain transfer agent 2-mercaptoethanol (3.06 g) and 25 g of xylene, was added dropwise into the flask over a period of 3 h with stirring and heating. When addition was complete, another 0.31 g of 2,2′-azobis(2-methylbutyronitrile) was added, and refluxing was continued for 1 h. The product mixture was poured into petroleum ether (400 ml) and it was stirred for 3 h. The precipitated white solid was filtered off, washed thoroughly with petroleum ether and dried in a vacuum oven at 50°C for 24 h to obtain PHECIMA (white powder, 99.10 g, yield 99.1%).

$M_n = 1677$, $M_w = 3118$, $M_p = 2586$, $M_{z+1} = 10\,630$, $D = 1.86$, $T_g = 29.1$°C (onset temperature determined by MDSC), $T_{soft} = 70$–82°C and $\Delta H_{soft} = 0.69$ J g^{-1} (measured by MDSC), $\eta_{inh} = 0.109$ dl g^{-1}, $[\eta] = 0.062$ dl g^{-1}, $a_{193\ nm} = 0.371\ \mu m^{-1}$, $n_D = 1.461$, water uptake = 1.47% (r.h. = 70%, equilibrium after 120 h).

UV–vis: $\lambda_{max} = 190$ nm (C=O, $n \rightarrow s^*$) (film thickness = 0.50 μm).

FT-IR (cm^{-1}): 3479 (O–H stretching), 2940 (C–H stretching), 1728 (C=O, stretching), 1454 (C–O and O–H dip. coupled), 1390 (O–H dip.), 1244 (CH_2 wagging), 1160 and 1077 (C–O–C stretching), 1051 (C–OH stretching).

3. Results and discussion

3.1. Polymer design principles

Formulations based on poly(2-hydroxyethyl methacrylate) (PHEMA) and onium salts as sensitizers act as negative tone photoresists. Nevertheless, the high-resolution patterns

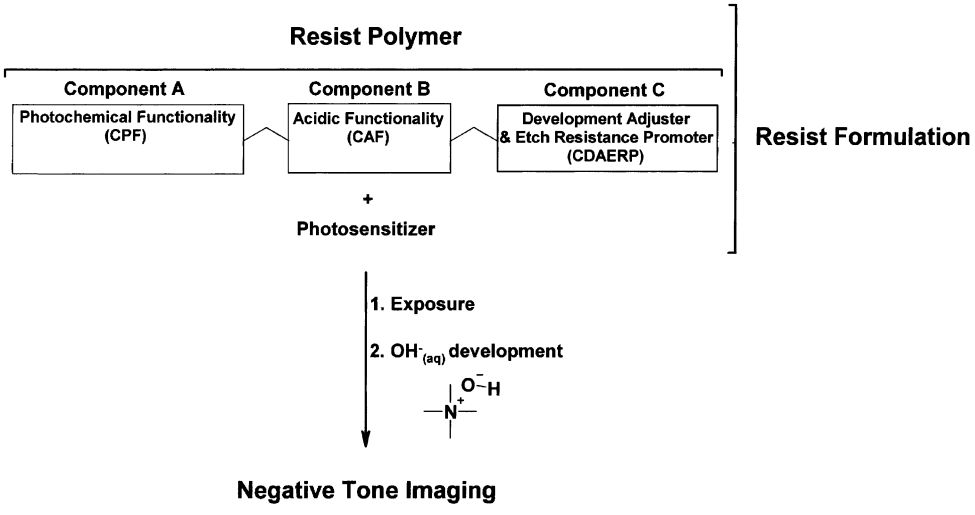
suffer from swelling phenomena that take place during the aqueous base development process step. These phenomena were attributed to the relatively high hydrophilicity of PHEMA due to its pendant hydroxyl groups. Thus, a new series of HEMA-based copolymers, which include other methacrylate monomers bearing different groups, have been synthesized. More particularly, the polymer design strategy we followed, consisted of (Scheme 1):

(a) The incorporation of pendant hydroxyethyl groups along an aliphatic polymer backbone [e.g. poly(meth)-acrylate type], that would provide the necessary photo-activated imaging functionality via acid catalyzed crosslinking reaction (e.g. transesterification, esterification, etherification) (component of photoactivated functionality, CPF). Moreover, this group is expected to enhance differentiation in aqueous base developers, amongst the unexposed (pendant hydroxyethyl groups) and the exposed (crosslinked) photoresist regions.
(b) The introduction of carboxylic groups that would afford the aqueous-base development of the uncrosslinked/non-exposed polymeric regions through neutralization reaction (component of acidic functionality, CAF). The percentage of this component needs to be rather low in order to keep the copolymer soluble in organic solvents preferred for spin coating. The use of components such as HEMA that could act synergistically in achieving aqueous base solubility, allows the percentage of the carboxylic groups to remain low as desired.
(c) The introduction of pendant aliphatic bulky groups along the polymer backbone (isobornyl, cyclohexyl, lauryl groups, etc.) that would control the penetration/diffusion of the organic base molecules (e.g. tetramethylammonium hydroxide) resulting to an effective, balanced and well controllable development. In addition, rich carbon-containing monomers is expected to enhance the etch resistance of the resist formulation by increasing significantly the carbon percentage of the polymeric matrix that is well known to be responsible for an improved plasma etch resistance [12–16] (component for development adjustment and etch resistance promotion, CDAERP).

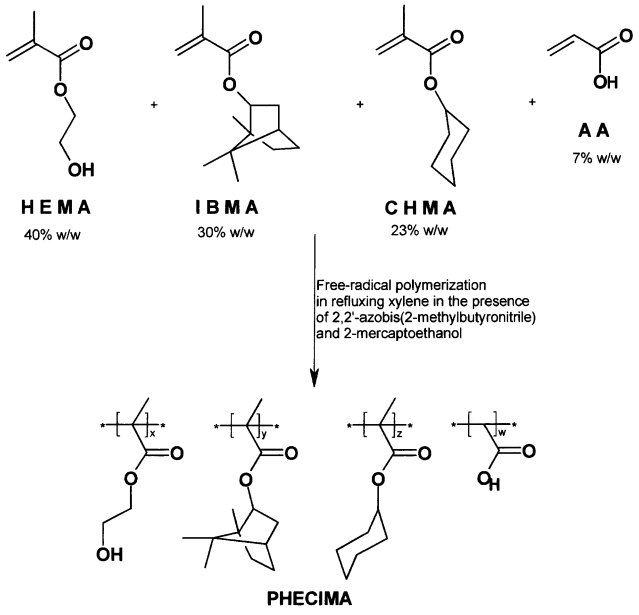
3.2. Synthesis and characterization of meth(acrylate) tetrapolymers

The solution free-radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) with other (meth)acrylate monomers at various monomers percentage weight feeds and molecular weights afforded a series of HEMA-based (meth)acrylate copolymers ($M_n = 14–92 \times 10^2$, $D = 1.70–2.45$ and $T_g = 15–67$°C), where HEMA played the role of the CPF. Either methacrylic or acrylic acid was used as CAFs and various methacrylates (e.g. methyl methacrylate, cyclohexyl methacrylate, lauryl methacrylate, isobornyl methacrylate, etc.) in different percentage weight combinations were used as CDAERPs. From a series of new-synthesized HEMA-based (meth)acrylate copolymers, few combined a controllable development without any swelling and also a promising lithographic behavior in various resist formulations. A tetrapolymer with relatively low polydispersity ($D = 1.86$), the poly(2-hydroxyethyl methacrylate-*co*-cyclohexyl methacrylate-*co*-isobornyl methacrylate-*co*-acrylic acid) (PHECIMA) was selected for use in resist development effort. This copolymer was synthesized via free-radical polymerization (monomer starved conditions) in refluxing xylene of 2-hydroxyethyl methacrylate (HEMA, 40% w/w), cyclohexyl methacrylate (CHMA, 30% w/w), isobornyl methacrylate (IBMA, 23% w/w) and acrylic acid (AA, 7% w/w) (Scheme 2).

The method applied for the free-radical polymerization of the aforementioned (meth)acrylate monomers took place under monomer starved conditions in refluxing xylene.



Scheme 1.



Scheme 2.

2,2′-Azobis(butyronitrile) was used as initiator and 2-mercaptoethanol that was used as chain-transfer agent contributed not only to an enhanced control of the synthesized copolymer's molecular weight but also helped to obtain a (meth)acrylate copolymer with relatively narrow polydispersity. An extent investigation of the role [42] of a chain-transfer agent such as 2-mercaptoethanol in the free-radical polymerization of various methacrylate monomers was carried out by Diakoumakos et al. [43,44] who have also developed, studied and proposed a modified version of the free-radical polymerization under monomer-starved conditions, characterized as free-radical separation polymerization [43,44]. That method affords (meth)acrylate copolymers of relatively narrow polydispersities ($D \sim 2$ and lower), provides excellent control of the molecular weight, severely restricts branching phenomena and also permits the use of extremely low quantities of the reaction solvent (such as those used in the synthesis of PHECIMA). Not surprisingly, PHECIMA presented relatively narrow polydispersity (Fig. 1) although it is a copolymer consisted of four (meth)acrylate monomers of quite different reactivities and also a small amount of solvent (xylene) was used for the polymerization. In other words, the results obtained in the free-radical polymerization applied for the preparation of the PHECIMA and for the series of the HEMA-based (meth)acrylate copolymers of 2–4 monomeric components such as methyl methacrylate, cyclohexyl methacrylate, lauryl methacrylate, isobornyl methacrylate, acrylic acid, methacrylic acid, etc. were in excellent agreement to those described in the free-radical separation polymerizations reported in previous work [43,44]. According to that investigation, it is strongly believed that the use of *t*-amyl peroxides, as free-radical initiators could further narrow PHECIMA's polydispersity, if desired. No study was carried

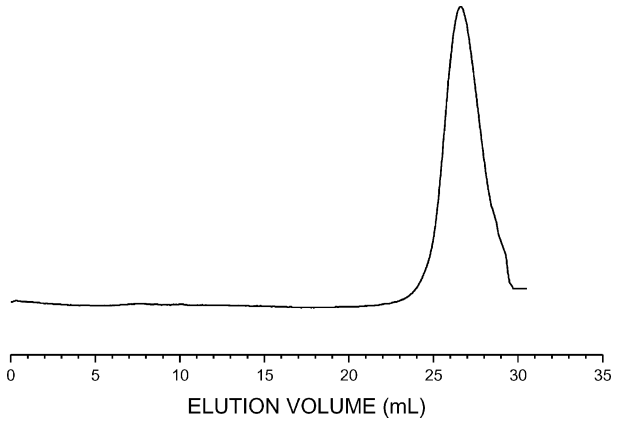


Fig. 1. Gel permeation chromatograph of PHECIMA ($M_n = 1677$, $D = 1.86$), in THF.

out regarding relative reactivity ratios of the monomers because this was out of the scope of the present work. Undoubtedly, it should be anticipated that the monomers feed ratio would in no case match exactly the monomers ratio presented in the synthesized methacrylate-based copolymers.

Fig. 2 presents a typical wide-angle X-ray diffraction pattern for a powder specimen of PHECIMA. Although the WAXS clearly shows a large amorphous halo, a strong reflection peak approximately at $2\Theta = 16.1$ and certain other peaks of considerably lower intensity at $2\Theta = 11.5$, 13.0, 38.6 and 44.6, are indicative of good packing of the oligomeric chains, resulting probably to some (very low though) degree of microcrystallinity.

The chemical composition of the PHECIMA was designed to be such that the copolymer would present substantially lower hydrophilicity than PHEMA and thus its potential to absorb water would be relatively low. In fact, water uptake measurements under controlled temperature and humidity conditions, revealed the low potential of the copolymer to absorb water. That physiochemical property was compared to that of PHEMA, in an environment

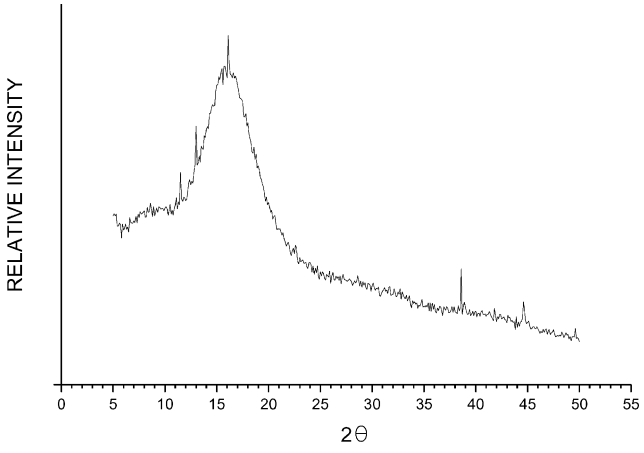


Fig. 2. Wide angle X-ray diffraction pattern of PHECIMA.

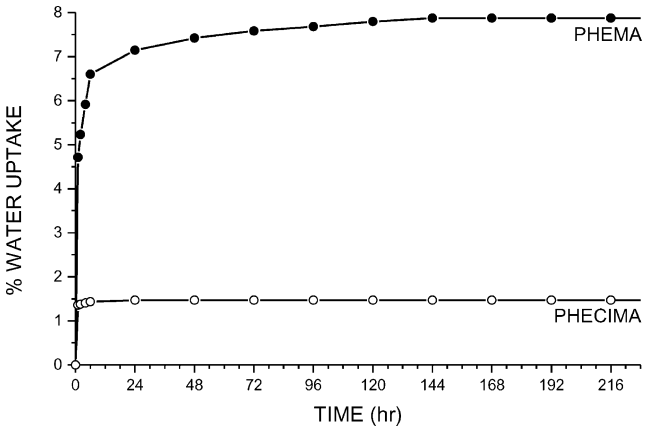


Fig. 3. Isothermal water uptake curves of PHECIMA and PHEMA.

of 70% relative humidity (Fig. 3). PHECIMA and PHEMA reached water uptake saturation upon 24 and 144 h and presented 1.47 and 7.87 wt% increase due to water uptake, respectively. These results show that the new-synthesized tetrapolymer presents almost $\times 5$ lower water uptake ability, than PHEMA.

3.3. Resist formulation and evaluation

PHECIMA and a sulfonium salt photo acid generator (PAG), triphenylsulfonium hexafluoroantimonate, were used in resist formulations for negative tone 193 nm and e-beam lithography. Negative resist formulations with PAG of either 3 (NRF3) or 5 (NRF5)% w/w on polymer (20%, w/w solution in ethyl lactate), were prepared and their lithographic behavior was evaluated. Fig. 4 presents the UV spectra of the polymer and the resist formulations NRF3 and NRF5. The absorbances at 193 nm of 0.50 μm films of the PHECIMA, NRF3 and NRF5 were 0.17, 0.57 and 0.69, respectively.

Recently, our group has shown that poly(2-hydroxyethyl methacrylate) (PHEMA) crosslinks [33] upon exposure in the presence of onium salt photo acid generators (chemical amplification mechanism). Catalyzed form the strong acid hexafluoroantimonic acid which is released into the resist film upon the exposure and subsequent decomposition [45–47] of triphenylsulfonium hexafluoroantimonate (PAG), the crosslinking is believed to proceed through mechanisms (transesterification, etherification) that involve the pendant hydroxyl groups of poly(2-hydroxyethyl methacrylate). The transesterification reaction is believed to take place amongst the hydroxyl groups and intermolecular carbonyls and the etherification (if any) amongst intermolecular hydroxyls. Due to swelling phenomena [34] this homopolymer resist platform suffered in aqueous base developers, a copolymerization approach was adopted in order to limit swelling. In the case of the newly synthesized low molecular weight HEMA-based tetrapolymers and only when HEMA's feed ratio was higher than 30% w/w, the key-components for the crosslinking and subsequent negative image formation were still the hydroxyl groups of HEMA moieties possibly via different crosslinking mechanisms such as transesterification, esterification and etherification reactions (Scheme 3). Independently of the number and specie of the other (meth)acrylate monomers mentioned here before and used in copolymerizations, no effective crosslinking was obtained for HEMA feed ratios lower than 30%, w/w. FT-IR and/or UV studies applied for determining the complex crosslinking mechanism were proven inadequate since no characteristic absorption peaks could be useful even for a qualitative evaluation of the crosslinking mechanism. Consequently, the development of a novel technique (probably based on MS principles) that will enable the in situ [48] monitoring of the HEMA-based crosslinking mechanism is suggested as a necessary tool for enlightening the dominant crosslinking reaction. Actually, this is something we are already working on and soon the outcome of a detailed work particularly focused on the photoacid induced crosslinking reactions mechanisms of PHEMA and HEMA-based copolymers, will be the subject of a forthcoming paper. At the present, what we may assume is that probably transesterification and/or esterification crosslinking processes emerge as the most probable to happen without though excluding etherification reactions from contributing to the crosslinking up to a certain (minimal though) extent. The fact that etherification is considered as rather inefficient process compared to transesterification and esterification ($K_{(\text{trans})\text{esterification}} \geqslant K_{\text{etherification}}$), and in an effort to evaluate the probability and relative percentage contribution to efficient crosslinking of each of the three aforementioned potential crosslinking reactions, we may assume that etherification's contribution (if any) to effective crosslinking should be rather minimal. The acid-catalyzed crosslinking reactions were found to result in lithographically useful imaging at a temperature range from 90 up to 110°C and for doses higher than 30 mJ cm^{-2} under 193 nm exposure (see lithographic results).

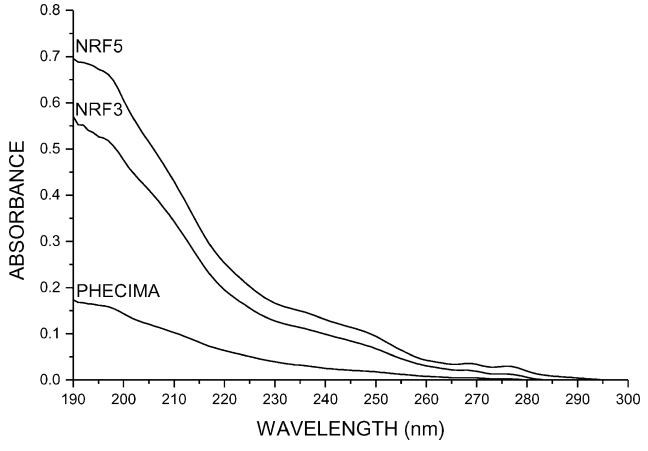
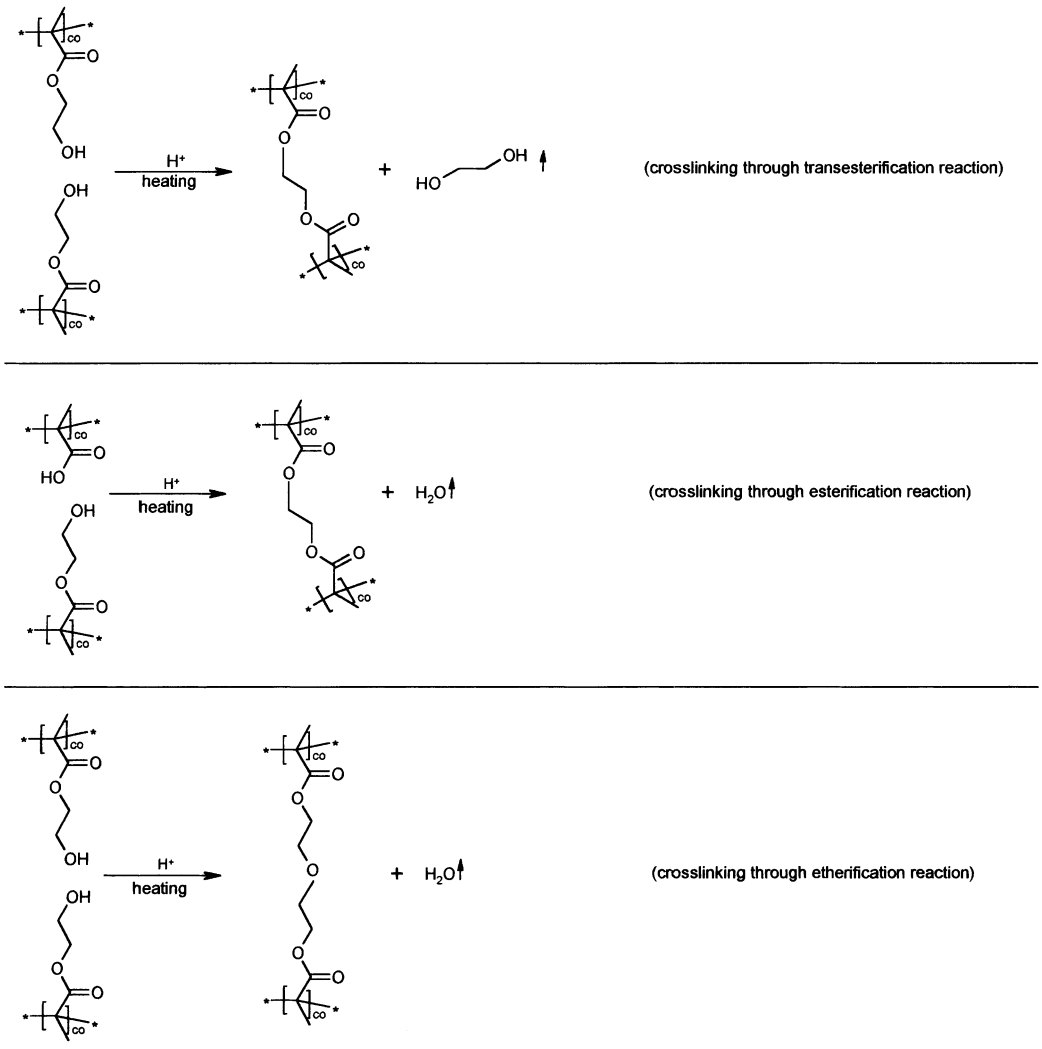


Fig. 4. UV-spectra of 0.50 μm films of the PHECIMA and the negative resist formulations NRF3 and NRF5.



Scheme 3.

The new copolymer approach was mainly adopted in order to eliminate swelling problems. Hence, the study and optimization of the development process has been one of the major tasks of the present work. Extensive experimental study was carried out by dissolution rate monitor (DRM). In all dissolution experiments aqueous solutions of TMAH of different normalities were used. As it is well known, during the development process, solvent penetration and resist dissolution are taking place and are controlled by kinetic and thermodynamic solvent/polymer interactions. The penetration rate should be substantially lower than the dissolution rate in order to obtain controllable dissolution and to avoid swelling phenomena. On the contrary, when the solvent penetration produces swelling phenomena [49,50] then patterning resolution and process latitude both decrease. From the recorded DRM signal of an unexposed 0.55 μm PHEMA film (Fig. 5) and according not only to thickness measurements but also to the pattern of the recorded interferogram, it becomes clear that there are severe swelling phenomena even in diluted TMAH solutions. More particularly, the number of fringes observed in Fig. 5, is substantially higher than the 2.5 anticipated for a film thickness of 0.55 μm; theoretically and according to the laser wavelength used in our experimental set up, every fringe represents 0.22 μm film thickness removal. At the same time the variation in the period of the sinusodial interferometric curve can lead us to the assumption that in the case of the PHEMA, gradient diffusion of the developer (dilute TMAH) into the polymeric layer leads to extend swelling and not to noticeable dissolution of the polymer. Here, it has to be stretched that even during 10 min of dissolution rate monitoring, PHEMA seems to continue to swell as no plateau region was recorded in the interferogram.

As regards negative photoresists, one of the key factors for achieving high-resolution lithographic results lays on controlling the rates between the solvent diffusion into the uncrosslinked resist's regions and the dissolution of the unexposed resist film. In the series of newly synthesized copolymers this could be controlled by controlling the percentage weight feed ratio of the more bulky, less

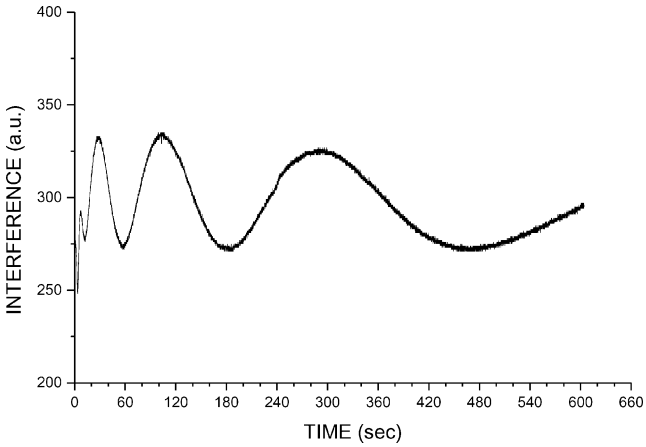


Fig. 5. DRM interferogram of a 0.55 μm film of unexposed PHEMA in TMAH 0.26×10^{-2}N.

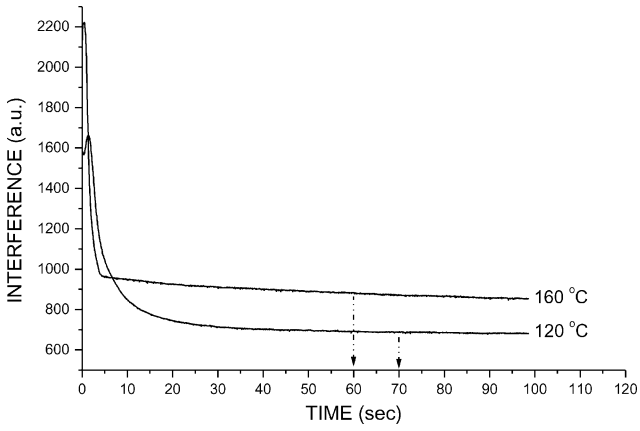


Fig. 7. Interferograms of the unexposed NRF3 upon spin casting and prebake at: (a) 120°C and (b) 160°C (solvent removal monitoring during the prebake).

hydrophilic components (CDAERP, see Scheme 1) and that of the 2-hydroxyethyl methacrylate, and (meth)acrylic acids (hydrophilic components). Certain of the new HEMA-based copolymers with unbalanced weight ratios amongst the aforementioned chemical species presented uncontrollable development resulting to poor lithographic performance. Fig. 6 presents the DRM signal of an unexposed 0.55 μm PHECIMA film in 0.26×10^{-2} and 0.52×10^{-2}N TMAH. From the recorded DRM signal and according to thickness measurements as well as to the exact match between the theoretical and anticipated number of fringes (2.5) to that of the recorded ones, it is extrapolated that there is no swelling phenomenon and that the full dissolution of the unexposed resist takes place from 32 up to 39 s, depending on the normality of the diluted aqueous base developer. The hydroxyl groups of HEMA component (see Scheme 2), which are presented in the unexposed resist regions also control base solubility. Those groups are present in the unexposed regions but are substantially reduced in the exposed regions due to the crosslinking reaction that leads to ester and ether (if any) formation. The DRM result (indication of no swelling phenomena that are attributed to PHECIMA's reduced hydrophilicity) was in excellent agreement with that obtained from the water uptake measurements of the PHECIMA (see Fig. 3).

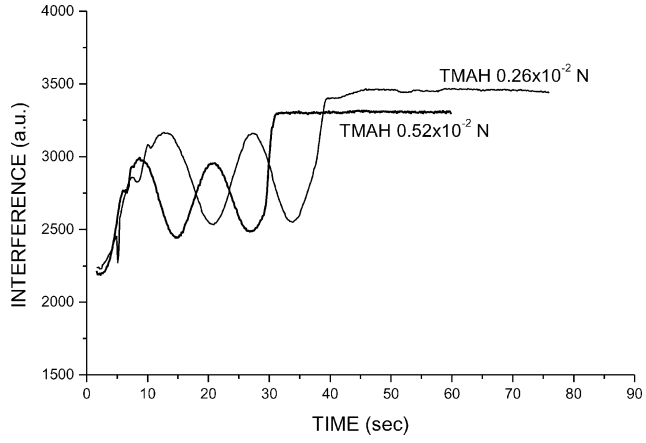


Fig. 6. DRM interferograms of a 0.55 μm film of the unexposed NRF3 in 0.26×10^{-2} and 0.52×10^{-2} N TMAH.

Recently [51,52] the interferometric method used for the dissolution study has been applied for the understanding of the phenomena that take place during the pre-exposure bake (Prebake) step of the lithographic process. For this study the interferometric apparatus is properly leveled and mounted on a hot plate. Using this set up, we have also evaluated the necessary time for removing the solvent upon spin casting of the NRF3. More specifically, temperatures of 120 and 160°C were applied and the interferogramms are shown in Fig. 7. It is obvious that the time needed for obtaining a 0.48 μm film of the NRF3 upon heating at 120 and 160°C, was about 70 and 60 s, respectively.

A typical process of the negative (meth)acrylate resist formulation consists of a prebake at 120–160°C from 1 to 2 min, a post exposure bake (Postbake) at 95–100°C for 2 min and a development in TMAH 0.26×10^{-2}N, for 70 s. Certain process studies carried out with: (a) ASML 193 nm stepper (Section 2) (dose range: 5–75 mJ cm^{-2} with a step of 5 mJ cm^{-2}) on 8″ Si-wafers coated with organic antireflective coating (AR19®) and (b) high-resolution 50-keV e-beam machine (Section 2) (dose range: 25–175 μC cm^{-2} with a step of 5 μC cm^{-2}) on 3″ bare silicon wafers. In all cases the developer dispensing was done manually. Under those conditions the development time was chosen to be 70 s. Certain typical results are presented in Figs. 8 and 9. The resist formulations (NRF3 and NRF5) tested, show good potential for high-resolution lithography in the region of 0.1–0.2 μm and it becomes evident that swelling-free development has been accomplished as anticipated from the DRM study. Nevertheless, extensive process development work is needed not only for obtaining high-density lines but also in case in which the material will undergo industrial use.

Fig. 8 presents SEM micrographs of: (a) 0.17 (1.30 μm

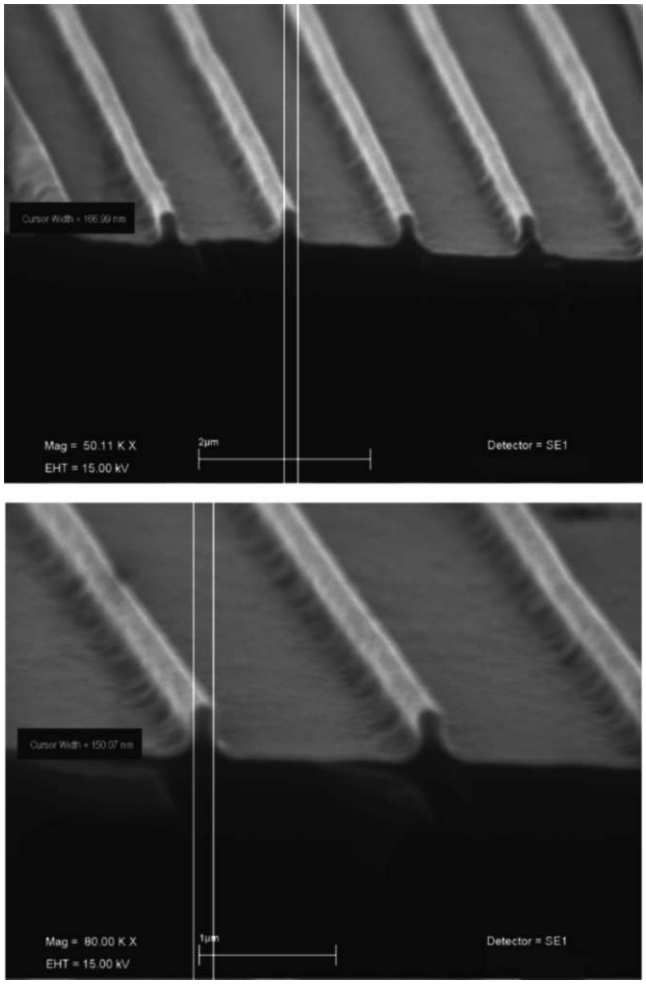


Fig. 8. SEM micrographs of 0.17 (1.30 μm pitch) (top) and 0.14 μm lines (1.54 μm pitch) (bottom) of the NRF5 obtained upon 193 nm exposure (Prebake: 120°C, 2 min, Postbake: 100°C, 2 min, dose 50 mJ cm^{-2}).

pitch) and (b) 0.14 μm lines (1.54 μm pitch) of the NRF5 obtained upon 193 nm exposure (Prebake: 120°C, 2 min, Postbake: 100°C, 2 min, dose 50 mJ cm^{-2}).

On the other hand, a quite spectacular view of resist's capabilities become eloquent by the recording of a special type of pattern used as alignment mark in optical lithography (Fig. 9). The line width is being constantly reduced from the outer to the center reaching sub 0.2 μm values.

SEM micrograph of 0.15 μm lines (0.60 μm pitch) of the NRF3 obtained upon a 50-keV e-beam exposure (PAB: 160°C, 1 min, PEB: 95°C, 2 min, dose 115 μC cm^{-2}) is presented in Fig. 10.

The performance in plasma treatment processes of negative resist formulations (NRFs), based on the novel HEMA-based (meth)acrylate tetrapolymers has been also studied. Plasma treatment has become an important industrial process not only for pattern transfer purposes but also for modifying polymer surfaces thus the interaction between reactive species from the plasma (radicals and ions) and the polymer surface attracts considerable attention [53]. In the most commonly used polymer processing plasmas (i.e.

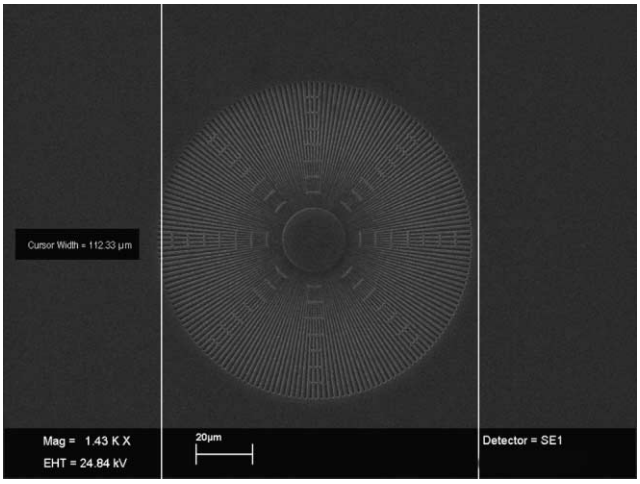


Fig. 9. SEM micrograph of a special pattern type (alignment mark) recorded with NRF3 (dose 65 mJ cm^{-2}).

oxygen- or fluorine-containing), etching of the polymer and functionalization of its surface occur simultaneously, with the balance between these two processes depending on the plasma parameters and the polymer type. The polymer design and synthetic approach that was adopted in this work for the synthesis of the PHECIMA (on which the NRFs are based) is such that the synthesized resist polymer exhibits sufficient etch resistance. This requirement is imposed by the fact that, as lithographic material, NRF3 is finally intended as a masking material during fabrication of microelectronic devices. Sufficient etch resistance, as compared to that of other (meth)acrylate-based resists that do not contain cycloaliphatic moieties (PMMA) or commercially available negative tone resists UVIII®, is obtained without the addition of specially manufactured etch resistance promoters but rather with a high cycloaliphatic content. The etching rate of the NRF3 as well as that of the PHECIMA (180 nm min^{-1}) was 0.62 of the PMMA's

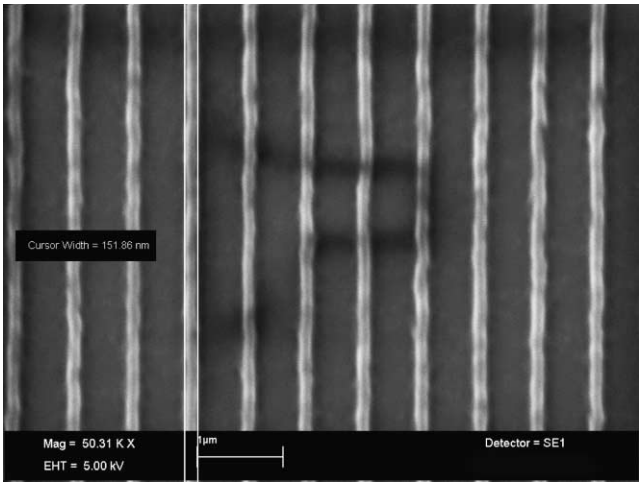


Fig. 10. SEM micrographs of 0.15 μm lines (0.60 μm pitch) of the NRF3 obtained upon 50-keV e-beam exposure (Prebake: 160°C, 1 min, Postbake: 95°C, 2 min, dose 115 μC cm^{-2}).

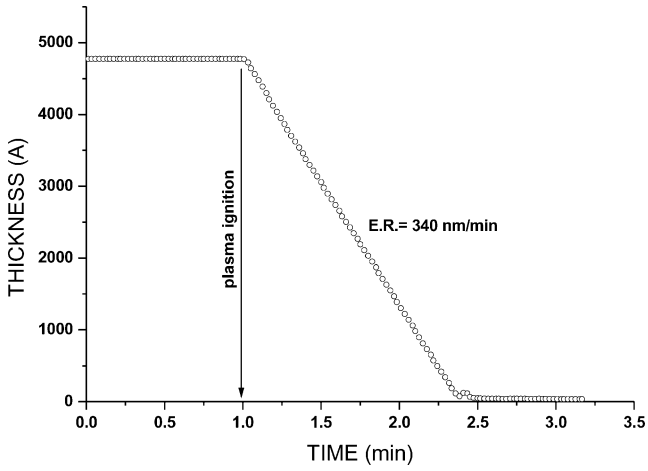


Fig. 11. Reduction of the thickness of NRF3 measured by in situ multi-wavelength ellipsometry during SF_6 plasma etching in an ICP reactor (10 mTorr, 800 W, −100 V).

corresponding value (300 nm min^{-1}). The etching rate of the NRF3 was also close to that of the PHS-type- negative UVIII® resist (Shipley Company) (171 nm min^{-1}) although the latter possesses pendant phenyl groups along the polymer backbone and it is well established that the introduction of aromatic rings into a polymer dramatically enhances its resistance to plasma [54]. Fig. 11 shows the reduction of NRF3 thickness, monitored by in situ multi-wavelength ellipsometry, during etching in SF_6 ICP plasma. The linear in time decrease of NRF3 thickness, indicates: (a) a constant rate throughout the etching process, (b) no chemical surface modification occurs during the plasma etching and (c) independence of the NRF3's etching rate by the increase of the temperature that usually takes places on the surface of the resist. Furthermore, the etching rate of the NRF3 was compared to that of a novolak type resist (AZ5214 from Clariant) in fluorine- and oxygen-containing plasmas (SF_6/CHF_3 and O_2, typically used for pattern transfer to Si/SiO_2 substrates, and for etching of low-*k* polymer-based dielectrics, respectively). As shown in Table 1, the etching rates of NRF3 were relatively comparable to those of the novolac resist [$E.R_{ADNR}/E.R_{AZ} = 1.60$, 1.56, 1.53 and 1.68 in SF_6/CHF_3(RIE), O_2(RIE), O_2(ICP) and SF_6(ICP), respectively], although the latter possesses pendant phenyl groups along the polymer backbone that are expected to dramatically enhance the polymer resistance to plasma [54]. Finally, the etch rates shown in Table 1 indicate a general trend (for both negative tone resists): they depend on the reactor type and the chemistries used, suggesting a complex resist etching mechanism.

Table 1
Etch rates of the NRF3 and AZ5214 in RIE and ICP plasma

Resist	Plasma composition			
	SF_6/CHF_3 (RIE) (nm/min)	O_2 (RIE) (nm/min)	O_2 (ICP) (nm/min)	SF_6 (ICP) (nm/min)
AZ5214	125	160	630	202
NRF3	200	250	966	340

Although, the current work showed that HEMA-based (meth)acrylate copolymers could be serious candidates amongst other 193 nm negative resist polymers as formulations similar to the NRF3 meet the resolution requirements at the 0.1–0.2 μm range, further process and material optimization needs to be undertaken in order to enhance their overall lithographic performance (e.g. sensitivity, development process steps, etch resistance, etc.). Surface imaging silylation processes based on the high number of the free pendant hydroxyl groups of the HEMA-based copolymers could permit the use of similar to the present tested negative resist formulations, for exposure at 157 nm.

4. Conclusions

(a) A series of relatively narrow polydispersed ($D \sim 2$ and lower) novel (meth)acrylate copolymers based on 2-hydroxyethyl methacrylate (HEMA) was synthesized via free-radical polymerization in solution (xylene) under monomer starved conditions. The method involved 2,2′-azobis(2-methylbutyronitrile) (initiator) and 2-mercaptoethanol as chain transfer agent, while polymerization took place in small amounts (50%, w/w on monomers) of refluxing xylene. The new synthetic approach that limits branching and also the necessary solvent amount without negatively affecting the polydispersity, can be easily applied for the preparation of relatively narrow polydispersed meth(acrylate) based copolymers [43,44].
(b) HEMA was combined with various other (meth)acrylate monomers such as methyl methacrylate, cyclohexyl methacrylate, lauryl methacrylate, isobornyl methacrylate, acrylic acid and methacrylic acid, in a wide range of percentage weight ratios. PHECIMA ($M_n = 1677$, $D = 1.86$), a typical example of the aforementioned HEMA-based copolymers, was prepared according to the aforementioned polymerization technique of 2-hydroxyethyl methacrylate (HEMA), isobornyl methacrylate (IBMA), cyclohexyl methacrylate (CHMA) and acrylic acid (AA) in a 40/30/23/7 weight ratio. The synthesized (meth)acrylate copolymers are suitable for the preparation of negative photoresist formulations and for studies on the development of novel HEMA-based swelling-free and dilute aqueous base developable materials. Both the copolymer design approach for producing swelling-free and dilute aqueous base developable photoresists as well as PHECIMA's recently introduced novel crosslinking chemistry, provide useful tools for the development of optimized resist formulations for 193 nm as well as for other wavelengths or e-beam exposure.
(c) A negative resist material formulated from the selected copolymer, PHECIMA, and a sulfonium salt photo acid generator meets the basic performance requirements of

modern industry (aqueous-base development, enhanced etch resistance, sub-0.2 μm resolution).
(d) DRM studies and lithographic results, showed that the use of dilute aqueous base developers (e.g. TMAH, 0.26×10^{-2}N) could be an attractive option to be adopted by the modern lithography and could be also proved important in emerging hi-tech fields like the Bio MEMS [37–41].

Acknowledgements

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