Ultra-sensitive EUV resists based on acid-catalyzed polymer backbone breaking

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Abstract

The aim of the current work was to develop new sensitive polymeric materials for lithographic applications, focusing in particular to EUV lithography, where the main polymer chain is cleaved under the influence of photogenerated acid. Resist materials based on the cleavage of polymer main chain are in principle capable to create very small structures, to the dimensions of the monomers that they consist of. Nevertheless, in the case of the commonly used non-chemically amplified materials of this type issues like sensitivity and poor etch resistance limit their areas of application, whereas inadequate etch resistance and unsatisfactory process reliability are the usual problems encountered in acid catalyzed materials based on main chain scission. In our material design, the acid catalyzed chain cleavable polymers contain very sensitive moieties in their backbone while they remain intact in alkaline ambient. These newly synthesized polymers bear in addition suitable functional groups for the achievement of desirable lithographic characteristics (thermal stability, acceptable glass transition temperature, etch resistance, proper dissolution behavior, adhesion to the substrate). Our approach for achieving acceptable etch resistance, a main drawback in other main chain cleavable resists, is based on the introduction of polyaromatic hydrocarbons in the polymeric backbone, whereas the incorporation of an inorganic component further enhances the etch resistance. Single component systems can also be designed following the proposed approach by the incorporation of suitable PAGs and base quencher molecules in the main chain. Resist formulations based on a random copolymer designed according to the described rules evaluated in EUV exhibit ultrahigh sensitivity, capability for high-resolution patterning and overall processing characteristics that make them strong candidates upon further optimization.

Keywords: EUV lithography, Photoresist, Scissionable polymeric resists, Ultra-sensitive photoresists

1. INTRODUCTION

The continuous need for dimensions reduction in integrated circuits and the expansion of applications in the broader field of micro-nanosystems lead to the quest for new lithographic technologies capable of addressing the demands of the high-volume manufacturing. The development of exposure tools that have ever-shorter wavelengths constitutes one of the major trends in lithography, in the effort of achieving mass production of devices with sub-20nm and even sub-10nm feature sizes. In this context, extreme UV lithography (EUVL) at a wavelength of 13.5nm is the main candidate for next-generation lithography technology [1-3]. However, EUV lithography requires high-performance photoresists with high sensitivity ($<20\text{mJ}/\text{cm}^2$) to enable high throughput in high volume manufacturing environment. The well-known trade-off in optimizing sensitivity, roughness and resolution (RLS tradeoff) continues to pose huge challenges towards acceptable EUV lithographic resists. Until now, chemically amplified resists (CARs) have been mainly used in EUVL since they have the advantage of compatibility with mature manufacturing. But issues such as low resolution and sensitivity, and high line edge roughness (LER) make these EUV resists to be still far from manufacturing requirements. On the other hand, metal-containing resists have attracted substantial attention in recent years [4, 5]. The metal oxide resists though are not yet as sensitive as desired, while nanoparticles cause resolution and roughness problems. Thus,

although metal containing resists utilize novel patterning mechanisms and smaller building blocks, RLS trade-off is still hindering performance. In addition, due to the relatively short history of the metal resists, their integration into high volume manufacturing requires tedious efforts in resist material optimization and risk management [6-8].

Under the aforementioned status for the research and development in EUV lithography, in the recent decade, researchers have been developing novel photoresists using acid labile groups incorporated into polymeric or molecular materials exploiting the chemical amplification mechanism [9-11]. Most polymers used today in photoresist formulations work with the mechanism of a side group deprotection and thus have limitations towards the further reduction of the formed structure dimensions since their LER is related to the size of the polymer chain [12,13]. Moreover, in lithographic materials that make use of polymer network formation mechanisms additional risks are encountered in the fabrication of small patterns related to their tendency for swelling during development [14]. On the other hand, molecular glasses have emerged as an alternative to traditional polymeric resists but they have not yet been proven to exhibit consistently superior resolution or reduced LER compared to polymer resists [15]. Taking into account the above limitations, it is well-justified the investigation of resist materials in which the lithographic imaging is based on the cleavage of the polymer main chain, since such materials could in principle be capable to create very small structures, to the dimensions of the monomers they consist of. Polymethyl methacrylate and other methacrylic polymers (ZEP) have been widely used as e-beam resist showing capabilities for structures below 10 nm feature sizes [16,17]. Nevertheless, in the case of the commonly used non-chemically amplified materials of this type issues like sensitivity and poor etch resistance limit their areas of application, whereas inadequate etch resistance and non-satisfactory process reliability are the usual problems encountered in acid catalyzed materials based on main chain scission [18,19].

In this work, we tried to apply the main chain scission mechanism of polymeric materials to develop photoresists capable for EUV lithography. To the best of our knowledge, there are no reports demonstrating the applicability of this approach for making fine patterns below 100 nm half-pitch (hp) with EUV by developing a photoresist based on backbone acid-scissionable polymers, which exhibits acceptable etch resistance for transferring the created pattern into another layer. In our case we have designed a chemically amplified resist in which the imaging chemistry depends on the acid catalyzed breaking of the polymeric backbone. These polymers are expected to give extremely low molecular weight compounds with monomer size following the influence of the photogenerated acids. Furthermore, these polymers show high sensitivity which meet the sensitivity requirements posed for EUV technology. The monomers used in polymer synthesis have been properly selected to enhance the etch resistance of the photoresist, to control the absorption of the polymer at 13.5 nm and to tune the Tg of the polymer into acceptable for lithographic applications values. Overall, the approach we introduce targets at innovations to improve LER, etch resistance, thermal resistance, and sensitivity, which are essential in next generation semiconductor manufacturing processes. In this paper, we present results demonstrating the applicability of the acid catalyzed backbone breakable polymers as photoresist components, on the basis of both, fundamental studies for synthesis and characterization, and lithographic performance studies using EUV exposure.

2. EXPERIMENTAL

2.1 Materials

All solvents and reagents were purchased from Sigma or Alfa Aesar and were of analytical or HPLC grade. Tetrahydrofuran (THF) was distilled three times from potassium. The monomers were passed over a column of basic alumina to remove the inhibitors and protonic impurities.

2.2 Polymer synthesis and characterization

Polymer synthesis was carried out by catalyzed stepwise addition of the monomers. Predetermined amounts of the monomers were dissolved in anhydrous tetrahydrofuran in a concentration of 1.0 M. A catalytic amount was then added, and the solution was allowed to stir at room temperature. After 24 h, the polymerizations were stopped with triethylamine and then the polymers were precipitated into cold hexanes. The solid was then dried in vacuo overnight. Gel permeation chromatography was carried out using a Waters system equipped with an ultraviolet and refractive index detector and mixed D and E columns. The molecular weights and the molecular weight distributions of the polymers were determined using PS standards with THF as an eluent at 40 °C and a flow rate of 1 ml min⁻¹. NMR studies were carried out on a Bruker Advance DPX 300 NMR Spectrometer (300 MHz). Thermogravimetric analysis was performed using a Perkin Elmer pyris diamond TG/DTA instrument with a heating rate of 10 °C/min under dry nitrogen

atmosphere. Glass transition temperatures were measured on a Perkin Elmer diamond DSC instrument using repeated heat/cool cycles at 10 °C/min between -50 and 150 °C.

2.3 Preparation of thin films and lithographic evaluation

Si substrates (100) were cleaned by sonication in acetone and isopropanol for 5 min each, dried under a N₂ gas flow and baked for 2 min at 120°C in an ambient atmosphere to remove any residual IPA. The polymer was dissolved in propylene glycol methyl ether acetate at room temperature to yield 5.0 wt% polymer solutions. Then, the photoacid generator Triphenylsulfonium triflate or N-Hydroxynaphthalimide triflate was added to the solution at a concentration of 5 wt% with respect to the polymer. Photoresist thin films were fabricated by spin-coating a polymer solution at 2000 rpm for 60 seconds. Prior to spin-coating, the silicon substrates were primed 2 times by spin-casting propylene glycol methyl ether acetate (4000 rpm, 60 seconds). After spin-coating, the photoresist thin films were baked for 2 min at 100 °C on a hotplate to remove any residual propylene glycol methyl ether acetate. The film thickness was determined by ellipsometry (Gaertner L116B spectroscopic ellipsometry) at an incidence angle of 70°. SEM images were obtained using a JEOL JSM -7401f FESEM with a thin layer of Pd sputtered on top of the film. FTIR spectra (resolution 4 cm-1) were recorded using a Bruker Tensor Fourier Transform IR spectrometer. Optical lithography at EUV wavelength was carried out at the XIL-II beamline of the Swiss Light Source synchrotron [20]. Post exposure baked (PEB) was at 50 °C for 30 s, and they were developed using aqueous 0.26N tetramethylammonium hydroxide (TMAH) solution (30 s). The oxygen plasma etch resistance experiments were carried out in a reactive ion etcher NE330 tool.

3. RESULTS AND DISCUSSION

3.1 Polymeric material design, synthesis and characterization

Figure 1 shows the structure of the designed random copolymers synthesized by polycondensation reactions. The monomers were selected in the direction to improve specific properties of the final random copolymers. Random copolymers consisted of about 85 % of the monomer R1, about 10% of the monomer R2 and about 5% of the monomer R3. Monomer R1, which is the main component of the random copolymer, gives properties such as glass transition temperature control, improved surface adhesion, solubility, etch resistance and compatibility with other substances. Monomer R2 was selected to improve the compatibility between the random copolymer and the photoacid generator. Finally, the monomer R3 is a monomer containing an inorganic complex that can regulate the absorption in the EUV regime and further increase the etch resistance of the random copolymer. Furthermore, every monomeric unit in the random copolymer contains an acid labile bond.

Figure 1: Chemical structure of the random copolymer.

The molecular weights of the random copolymer were measured by GPC and listed in table 1. The measured molecular weight is about 8000 (M_n) with a polydispersity of about 1.8. The molecular weight is not very high but suitable for a resist material.

Table 1: Characteristics of the random copolymer

Polymer	M _n	M _w	M _w /M _n	T _g (°C)	T _d (°C)
Random copolymer	8300	15000	1.8	91	220

To estimate the stability of the resist pattern, the T_g of the random copolymer was measured, shown in Table 1. This is an acceptable T_g value for a resist candidate polymer because it is not so high to need extent PEB and it is not so low to induce pattern collapse after the development. According to these data the synthesized random copolymer demonstrated high thermal stability, and was considered as capable for high-performance photolithography applications. The T_d value shown in Table 1 was obtained from the TGA.

3.2 Imaging chemistry

The acid labile bonds can be cleaved by the protons generated by the photoacid generators. When the proton generation takes place upon the irradiation, the acid labile bond is cleaved leading to the production of small hydrophilic products which are removed by the developer. To investigate the acidolysis activity, the film of the random copolymer containing 3% of TPS-Tf and 0.15% aminoanthracene as base quencher was exposed to low pressure Hg light (254 nm) with the exposure dose of about 20 mJ/cm² and then baked at 80 °C for 2 minutes.

Figure 2: Main chain scission mechanism of the random copolymer after the influence of the photogenerated acid.

In Fig. 3 IR spectra of the random copolymer films with 3% TPS-Tf photoacid generator and 0.15% aminoanthracene, are shown. Line 1 corresponds to the random copolymer film after the soft bake on a hotplate for 5 minutes at 100 °C, whereas the line 2 spectrum was taken after the exposure of the film at a dose of 20 mJ/cm² with 254 nm light. Line 1 and line 2 do not display significant differences indicating that the main chain scission is does not occur by the generation of the acid after the irradiation. After the PEB (line 3) at 80 °C for 2 minutes, the dominating absorption peak is that of the hydroxyl moieties produced during decomposition, at 3100–3600 cm⁻¹ wavenumbers. This finding demonstrates that the acidolysis reaction at 80 °C is surprisingly rapid and can result in a very high dissolution rate difference between the exposed and the unexposed areas.

Figure 3: FT-IR spectra of random copolymer film containing 3% TPS-Tf and 0.15% aminoanthracene. Line 1 corresponds to the film after the soft bake at 100 °C for 5 minutes, 2: after the irradiation with 254 nm light and 3: after the post exposure bake at 80 °C for 2 minutes.

3.3 Lithographic and etch resistance properties

Random copolymer thin films containing 5% of TPS-Tf photoacid generator and 0.25% aminoanthracene were created by spin casting and baked on a hotplate for 5 min at 100 °C to remove the remaining PGMEA solvent. Then, the films were exposed with EUV light (13.5nm) at different doses. After the exposure, PEB was carried out at 60 °C for 2 minutes and the development is done in tetramethyl ammonium hydroxide solution (0.26 N for 60 sec). The contrast curve obtained by the aforementioned process is shown in Figure 4. Under these conditions, the dose-to-clear is about 4.5 mJ/cm². It is obvious that this resist shows very high sensitivity with very good contrast.

Figure 4: Contrast curve for the random copolymer photoresist system (EUV exposure, process details in text).

The etch rates measured in oxygen plasma for polymethyl methacrylate, AZ commercial novolac photoresist and our random copolymer based films are presented in Figure 5. The pressure of the oxygen gas was 10 mTorr in 400 W power; these etch conditions are typical for an oxygen RIE process. The etch rate of the random copolymer (RCP) based film is distinctly better than Polymethyl methacrylate and it is comparable with a commercial novolac photoresist film (AZ3214). The performance of the films in He/H₂/C₄F₈ plasma is also shown, where a ~1/10 selectivity to SiO₂ is demonstrated.

Figure 5: Etch resistance of the backbone breakable random copolymer (RCP) photoresist system.

3.4 Lithographic evaluation

Processing and lithographic performance of the backbone breakable photoresist is given below. Several lithographic conditions have been checked resulting to those listed in Table 2.

Table 2: Process conditions used for the photoresist.

Process step	Process conditions
Wafer prime	Hotplate, 10 min at 170 °C and two times spin casting PGMEA prior to polymeric solution
Post Applied Bake (PAB)	100 °C for 5 min in a hotplate
Film thickness	>50 nm
Exposure	EUV XIL-II beamline of the SLS synchrotron
Post Exposure Bake (PEB)	60 °C for 120 s in a hotplate
Development	0.26 N Tetramethyl ammonium hydroxide solution (TMAH) 60 s
Rinse/dry	Deionized water 20 sec /nitrogen dry

The resist was very sensitive even with 2.5 % w/w photoacid generator and 0.15% aminoanthracene as the base quencher with low amplification process (only 60 °C post exposure bake). Figures 6 and 7 show lines with 25 nm width produced with EUV doses in the range of only 1 mJ/ cm² following the process provided in Table 2. The film thickness was about 80 nm and the line/space ratio was 1/4. In order to achieve even smaller dimensions, the amount of the aminoanthracene was increased to 0.5 % and the film thickness was reduced to 50 nm. Figures 8, 9 and 10 show patterns produced in random copolymer thin films by EUV exposure with doses of 4, 3.5 and 3 mJ/cm² respectively baked at 60 °C and developed in aqueous TMAH solution. The line/space ratio is 1/3, 1/4 and 1/1 for the figures 8, 9, and 10 respectively.

Figure 6: Line/space patterns of 100 nm pitch and 25 nm CD.

Figure 7: Line/space patterns of 100 nm pitch and 25 nm CD.

Figure 8: Line/space patterns of 80 nm pitch and 22 nm CD.

Figure 9: Line/space patterns of 80 nm pitch and 20 nm CD.

Figure 10: Line/space patterns of 30 nm half-pitch.

4. CONCLUSIONS

A random copolymer containing acid-cleavable bonds along the main chain has been synthesized through step wise polymerization. Their molecular and physicochemical properties have been measured via various characterization methods. Resist films based on the synthesized polymer have shown satisfactory etch resistance, due to the high aromatic moiety content and to the inorganic components of the polymer. The sensitivity of this polymer is very high and the high values of T_g maintain the polymeric thin film untouched in the exposure step as it is indicated by IR spectroscopy. The main chain of the polymer steadily chopped in the post-exposure bake step in which the photogenerated acid can easily

penetrate into the polymeric matrix. Resist formulations based on the synthesized random copolymer were exposed to EUV radiation (at 13.4 nm) exhibiting a high potential for industrial applications. A characteristic contrast curve (figure 4) shows that the resists are ultra-high sensitive ($\sim 0.5 \text{ mJ/cm}^2$ using 5% PAG and 0.25% quencher) with satisfactory contrast, whereas they also showed very good etch resistance (1/10 selectivity to SiO_2). Imaging experiments using EUV lithography have demonstrated capability for 25 nm (figure 6) 1:4 lines and 22 nm (figure 8) 1:3 lines, 20 nm (figure 9) 1:4 lines and 30 nm (figure 10) 1:1 lines with high sensitivity $< 4 \text{ mJ/cm}^2$ using 2.5 % PAG and 0.15% quencher.

5. ACKNOWLEDGMENTS

The evaluation of the resists has been funded from the EU-H2020 Research and Innovation program under Grant ID-207 NFFA-Europe.

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