A Novel Platform for Production-worthy ArF Resist


Process Development Team, Semiconductor R&D Center, Samsung Electronics Co., Ltd.
San #24, Nongseo-Ri, Kicheung-Eup, Yongin-Si, Kyungki-Do, Korea
*Shipley Company, Inc., 455 Forest Street, Marlboro, MA 01752

ArF lithography, in combination with chemically amplified resists, has been investigated as one of the most promising technologies for producing patterns below 100 nm. In considering the polymer matrix for 193 nm photoresist applications, factors such as sensitivity, transparency to 193 nm radiation, adhesion to substrate, dry etch resistance, ease of synthesis, and availability of monomers are very critical. In these respects, remarkable progress has been made in development of ArF resist material. Polymers of acrylic and methacrylic esters show good imaging performance at 193 nm, but have insufficient dry-etch resistance under oxide or nitride etch condition. On the other hand, cyclic olefin-maleic anhydride (COMA) alternating copolymers exhibit good dry etch resistance, but have poor resolution capability. We previously reported a new platform, based on a vinyl ether-maleic anhydride (VEMA) alternating polymer system, that demonstrated both good resolution and high dry etch resistance.

In this paper, VEMA systems with improved lithographic performance are presented. The new platform (VEMA) showed good performance in resolution, depth of focus (DOF), iso-dense bias, and post-etch roughness. With conventional illumination (NA=0.6, sigma=0.7), 120 nm dense line/space patterns with 0.4 µm DOF were resolved. And 90 nm L/S patterns 0.6 µm DOF were resolved with off-axis illumination (NA=0.63). Another important factor to be considered for the dry-etch process is post-etch roughness. In the case of VEMA system a clean surface was observed after etch under oxide, nitride, and poly conditions. The VEMA resist system is regarded as one of the most production-worthy material for real device manufacture.

Keywords: Photoresist, chemically amplified resist, ArF, lithography, VEMA.

1. Introduction

In previous years ArF lithography was discussed as being one of the most promising technologies for producing patterns below 150 nm. In this past year it has become clear that with further improvements in KrF resist technology with the latest more capable resists and improved lithographic exposure tools and processes, (increasing NA, RET, etc.) the implementation of ArF lithography in production will be pressed to 100 nm and below. Last year at this conference we introduced our VEMA resist system as being a solution for imaging at the 130 nm node. In light of the continued improvements of KrF technology we have improved the capability of our ArF resist. In previous papers, the importance of factors such as sensitivity, transparency to 193 nm radiation, adhesion to substrate, ease of synthesis, and availability of monomers have been well outlined in considering suitable matrix polymers for ArF photoresist applications. As outlined in the early papers of this series, the VEMA material set meets these basic requirements.

In this paper we will focus on recent experiments exploring the imaging and pattern transfer capability of our VEMA resist technology for 100 nm and below. Issues such as line slimming, and etch resistance that we have been studying in preparation of this technology for true device manufacturing will be discussed. This is of great importance as in our studies of first generation ArF methacrylate based resists, which still providing promising imaging performance at

Received April 10, 2001
Accepted May 25, 2001
193 nm, continue to have insufficient dry-etch resistance to fluorine-based gas chemistries. Considering that as target dimensions are reduced to sub100 nm and the NA of exposure tools are increased, resist film thickness will be continually reduced, and a greater burden will be placed on the resist material in providing sufficient etch resistance. To meet the current requirements, at an absolute minimum, ArF single layer resists must have equivalent dry etch resistance to state of the art KrF resists. In the future as target CD's approach 70 nm (and possibly even below) further improved etch resistance will be required. Data will be presented that will demonstrate the capability of VEMA resists in achieving these goals. With the implementation of resists into production, materials need to have etch capability in varying etch chemistries. We will discuss recent studies we have carried out comparing various resist chemistries and how they respond to these different required resist chemistries.

2. Experimental

2.1. Materials

Radical initiator, 2,2'-azobisisobutyronitrile (AIBN), was purchased from the Aldrich Chemical Co., and recrystallized in ethanol prior to use. Maleic anhydride (MA), and alkyl vinyl ethers were purchased from the Aldrich Chemical Co. and used without further purification. Acrylates having alicyclic leaving groups were synthesized by one-step reaction of Grignard reagents with acryloyl chloride.

The chemical structures of poly(VE/MA-tA) are shown in Fig. 1. Alkyl vinyl ethers are either linear or cyclic, R3 is an acid-labile alicyclic groups. Polymers were synthesized by free radical polymerization. Typically, the monomers were mixed at the appropriate ratios and dissolved in tetrahydrofuran (THF). Free radical initiator was added to the monomer solution. The solutions were then heated to 65°C and refluxed for 24 hours. Polymers were then isolated by precipitation in isopropyl alcohol, filtered and dried at 50°C under vacuum.

2.2. Polymer Characterization

1H-NMR spectra were obtained with a Bruker AC 300 MHz instrument. Visible absorption spectra were measured with a Jasco V560 spectrometer, and FT-IR spectra were obtained from a Nicolet Magna 550 instrument. The weight-average molecular weights (Mw) and polydispersities were determined in THF solvent with a Hewlett-Packard 1050 GPC, calibrated with polystyrene standards. Thermal properties were analyzed using a Polymer Laboratories STA 625 at a heating rate of 10°C/min.

2.3. Lithography & Etch

Suitable Photo Acid Generators (PAGs) were purchased from various suppliers and used as received. Resists were formulated by dissolving the polymer (12-15 wt%), the PAG and a base additive in propylene glycol monomethyl ether acetate (PGMEA) or other suitable resist solvent, the resist solutions were then filtered with a 0.2µM Teflon membrane filter. Resists were coated to yield 250-350 nm thick films on substrates and soft-baked at 120-140°C for 90 seconds. Lithographic exposures were carried out on an ISI 193 nm micro-stepper, NA 0.6 or an ASML PAS 5500/950, NA 0.63. Exposed resists were baked at 110-140°C for 90 seconds on a hot-plate and developed with 0.26N (TMAH) aqueous solution for 60 sec. Dry-etching was carried out in the appropriate RIE system (e.g. Rainbow 4500: CF4/CHF3/Ar=10/10/300 sccm, 700 W, 150 mTorr, 120 sec).

3. Results and discussion

The design concept and polymer properties for our VEMA polymers have been outlined and discussed elsewhere.9,10 The general polymer concept for our VEMA system is outlined in Fig. 1. When compared to other available polymer chemistries for ArF resists the key issues that this design improves upon are high Tg, inorganic substrate adhesion, transmittance, polymer yield, dry etch resistance, metal contamination and ease of polymerization.

![Fig. 1. VEMA (Vinyl Ether Maleic Anhydride) polymer system, R1 = vinyl ether functional group, R2 = alkyl functional group, R3 = alicyclic leaving group.](image)

3.1 Etch Resistance

In Fig. 2, normalized oxide etch rates are presented for various ArF resist chemistries compared to a commercial KrF resist. As
previously reported VEMA based resists perform better than other ArF resists when tested under these conditions. This past year we have further optimized the materials etch resistance to levels that exceed the etch resistance of KrF resists by ~10%, further improvement pathways remain available to increase the etch resistance even further. This data is also presented in Fig. 2. This data is representative for the actual resists used for lithographic evaluations discussed later in this paper.

Previously VEMA based resists have been shown to exhibit better patterned etch behavior particularly when compared to methacrylate based resists. Studies have recently been extended to other etch chemistries that will be required for full implementation of ArF resists for device manufacture. Three types of etch chemistries were investigated, polysilicon, oxide and nitride. In Fig. 3, we present data for three resist chemistries, a commercial KrF resist, a VEMA based resist and finally an acrylate based resist, following blanket exposure to the three different dry etch chemistries. From this data it is clear that the polysilicon etch is the least aggressive and as will become clear the least discriminating of the etch chemistries as all resists have comparable performance (both etch rate and roughness) when tested under this condition. It is likely that this is the reason for some of the confusion with regards to ArF resist etch performance in early work where most comparisons were made using this condition. Under oxide etch conditions the first obvious discrimination between the resists is observed in the relative etch rates, with the acrylate based resists etching up to 40% faster than VEMA or KrF resists. Although, as was shown in Fig. 2, some improvement has been made in the oxide etch rate for more advanced acrylate resists where rates are at times only ~20% faster than VEMA or KrF. However, on closer inspection of the blanket processed wafers etch roughness becomes evident as the key second difference under this more aggressive condition.

The final etch chemistry investigated was nitride. Under this condition the discrimination between the materials was immediately apparent as the surface roughness of the blanket processed wafer was so severe that the post dry etch thickness for the acrylate material was not measurable and so the etch rate cannot be reported. In the case of VEMA it has equivalent performance to the KrF resist standard in both etch rate and smoothness.

In device manufacture it is important to have smooth pattern transfer into the substrate as etch roughness as discussed above can be transferred into the substrate in two different but very different insidious ways. The first can be described as LER amplification, this results from inhomogeneous etch rates along the resist sidewall increasing the level of LER transferred to the substrate. The second failure mode is a pitting or breakthrough that occurs in the un-exposed areas where as a result of the inhomogeneous etching some areas of film get etched faster with the underlying substrate getting pitted or damaged. If present, these problems readily becomes evident after resist strip. To address this issue we tested our VEMA resist using a currently implemented 248 nm manufacturing process. In Fig. 4 we show pictures for a VEMA resist following wet develop, dry etch, and finally after resist strip. It is clear that, from both end-on and tilted SEM view, clean pattern transfer has occurred and no damage to the underlying substrate was evident.

![Fig. 2. a) Etch rates of various ArF resist normalized to KrF resist under silicon oxide etching condition, b) Etch rate tuning of VEMA (Vx-z) resists, normalized to KrF under oxide etching.](image-url)
3.2 Line slimming

Line slimming has been a key challenge for ArF resist technology. Device manufacturers, SEM tool makers and resist suppliers have done a great deal of work in the past year in beginning to understand and deal with this problem. In Fig. 5, data is presented for an acrylate based system. In this experiment various SEM measurement parameters such as magnification, beam power, and number of measurements were tested. It is clearly evident that acrylate systems have a line slimming problem under all conditions, however some learning was made. The most change was observed for settings that used higher magnification and beam powers, with an early rapid slimming occurring. For acrylates, this early rapid slimming can be ameliorated in two ways. Firstly, by reducing the magnification, the rate of early slimming is reduced, however this strategy was only successful for a shorter number of measurement times as it was observed that eventually the absolute line slimming reaches levels equivalent to that observed at higher magnification. The second and more successful method was to reduce the beam power, in this case the absolute level of slimming was reduced ~ 38 %, the main feature remaining was the early rapid onset. The next step in our studies was to study the effect of resist chemistry.

In Fig. 6 data is presented for three different resist chemistries, an ESCAP based KrF resist, an acrylate based ArF resist and finally our VEMA based resist. Compared to the experiment just discussed the goal of this experiment was to stress the resist capability particularly in the early onset area, so we increased the test magnification to 100KX while holding the beam power at 400eV. Also instead taking and reporting the number of measurements, in this case the time the beam was held on before measurement was made is reported. The acrylate resist again performed rather poorly with over 20 nm of line slimming occurring. However both the KrF and VEMA based resists perform much better, with no early onset occurring with either of these resists. In Table I slimming rates were calculated for what may in fact be two different chemical events. It was found that all the resists suffer from the slower line slimming which occurs at a rate of ~0.21 nm/sec, however only the acrylate based resist suffers from the first fast rate which is calculated at 1.36 nm/sec. It is our belief that the fast rate is a result of the resist backbone chemistry and in the case of acrylate materials may prove irresolvable. This is a key advantage for our VEMA technology and one of the key reasons for pursuing this material when compared to other available chemistries.

Fig. 3. Surface roughness of different resist types following poly, oxide and nitride etching.

Fig. 4. Contact hole etching of VEMA resist, no evidence of pitting or surface damage after oxide etching was observed, target oxide depth 300nm.

Fig. 5. Line slimming for an acrylate platform using different SEM conditions (KLA 8100 SEM).

Fig. 6. Line slimming for an acrylate platform using different SEM conditions (KLA 8100 SEM).
3.4 Dissolution contrast

In Fig. 7 dissolution contrast data are presented for our VEMA resist. In going from V2 to V5 we have optimized both the polymer and the resist formulation. The key changes between the two resists are transparency, quencher loading, polymer blocking level and molecular weight. The $R_{\text{min}}$, $R_{\text{max}}$ and $\tan \phi$ values are also reported in Fig. 7. From analysis of the dissolution contrast data a number of key features stand out. Firstly as expected the $R_{\text{min}}$ was reduced which is expected to reduce film loss. The $R_{\text{max}}$ was increased which should lead to improved resolution and help in clearing out any scum between the resist lines and in combination with the lower $R_{\text{min}}$ lead to improved profiles. Overall the higher contrast should improve dense line resolution. This is clearly evident from the SEM pictures that are also shown in Fig. 7. Further lithographic evaluation of this material is shown later in this paper. Further formulation optimization have been carried out to improve the roughness evident on the top of the resist lines however the dissolution contrast data was not available in time for this paper, however some of the preliminary lithographic data is presented in the next section.

3.5 Lithographic Performance

In Fig. 8(a) the masking linearity for a recent VEMA based formulation (V6) is shown for dense lines and spaces. This is the improved dissolution contrast material described above with a solvent change. This change has led to a slight improvement in resolution performance however significant roughness was still observed on the top of the patterned lines well into the unexposed region. However this formulation was readily capable of 100 nm 1:1 L/S performance with a wide depth of focus margin as shown in Fig. 8(b). In Fig. 8(c) the masking linearity is shown for the 1:1.5 L/S pairs, in this case well below 100 nm resolution was resolved, sizing is shown for the 90 nm L/S however it is clear that this resist is capable of even smaller feature sizes. A focus latitude plot for 110 nm 1:1 L/S for this formulation is shown in Fig. 9 using annular illumination. In Fig. 10 focus latitude plots are shown for 100 nm 1:1.5 L/S using conventional illumination.

Fig. 7. Comparison of dissolution contrast and resolution performance at 110 nm L/S for recent improvements in VEMA resists.

3.6 Lithographic Performance

In Fig. 8(a) the masking linearity for a recent VEMA based formulation (V6) is shown for dense lines and spaces. This is the improved dissolution contrast material described above with a solvent change. This change has led to a slight improvement in resolution performance however significant roughness was still observed on the top of the patterned lines well into the unexposed region. However this formulation was readily capable of 100 nm 1:1 L/S performance with a wide depth of focus margin as shown in Fig. 8(b). In Fig. 8(c) the masking linearity is shown for the 1:1.5 L/S pairs, in this case well below 100 nm resolution was resolved, sizing is shown for the 90 nm L/S however it is clear that this resist is capable of even smaller feature sizes. A focus latitude plot for 110 nm 1:1 L/S for this formulation is shown in Fig. 9 using annular illumination. In Fig. 10 focus latitude plots are shown for 100 nm 1:1.5 L/S using conventional illumination.

---

Table I: Comparison of resist line SEM slimming rates, S platform is acrylate based, V platform is VEMA based and UV210 is KrF escap based resist. (KLA 8100, 50% threshold, beam at 400eV, 100KX.)
At this point in our studies LER of the resist was the key parameter still to be improved. It was found that by optimizing the resist formulation in combination with a BARC optimization that the LER was reduced while also improving the resist profile, data for this optimized system is presented in Fig. 11. It is often asked how profile and LER compare to current KrF resists and so in Fig. 12 120 nm 1:1 L/S features are shown for the optimized VEMA resist along with data for a state of the art KrF resist. As can be seen LER and profile is comparable for both processes, a more rigorous measurement analysis is underway.

Finally, in optimizing this resist for dense L/S applications, the effect of optical illumination settings has been investigated. It has been observed that dipole settings give excellent performance with regards to resolution and process window. Some preliminary results are shown in Fig. 13. 100 and 90 nm 1:1 L/S pairs were readily resolved with close to a micron depth of focus in the case of 90nm 1:1 L/S and more than a micron in the case of 100 nm 1:1 L/S pairs. Considering that this was obtained on a 0.63 NA scanner and as ArF is expected to go into full production on higher NA tools this is a very encouraging result.

Fig. 8. Lithographic performance of V6 photoresist, (a) 1:1 L/S, (b) 1:1.5 L/S, (c) 100 nm 1:1 L/S, process conditions: 820Å AR19 (215°C/90sec.), FT = 3,300Å, SB = 120°C/60sec. Proximity, ASML /900 (0.63NA, 0.87/0.57σ), Binary mask. Exposure energy 18 mJ/cm², PEB = 120°C/60sec. Proximity. 0.26N, 60sec. SP.

Fig. 9. Focus Latitude plot for 110 nm 1:1 L/S for VEMA photoresist, process conditions: 820ÅAR19 (215°C/90sec.), FT = 3,300Å, SB = 120°C/60sec. Proximity, ASML /900 (0.63NA, 0.87/0.57σ), Binary mask, Exposure energy 18 mJ/cm², PEB = 120°C/60sec. Proximity, 0.26N, 60sec. SP.
3.6 PED dependency & PEB sensitivity

In Fig. 14 the PED dependency of our VEMA resist is presented. Up to 60 minutes delay was observed with no change in CD. In the case of this test, imaging was carried out on an ISI micro-stepper where the amine levels are controlled to 2 ppb or less. Following delay the wafers were manually transferred to a track with similar levels of amine control, some exposure to higher amine levels was unavoidable during the manual transfer between the tools.

In Fig. 15, PEB sensitivity data is presented. For the tested VEMA resist, values of 5.4 nm/°C were recorded when averaged for 130 1:1 L/S and isolated lines. This is a promising result for a non-methacrylate based system, however further formulation improvement will be required in reducing this to the target value of 3nm/°C.

4. Conclusions

In conclusion, the VEMA resist system, which was recently designed and introduced as a single-layer resist for 193nm lithography has undergone further improvements in the last twelve months.

This resist shows a high dry-etch resistance and good lithographic performance

- Resolution 100nm L/S (1:1 dense) (0.63NA, 0.87/0.57σ); 90nm L/S (1:1 dense) (dipole illumination)
- DOF : > 0.7 um (@100nm L/S)
- Etch resistance : 1.02 times to KrF resist
- PED : > 60 min (@ 2ppb NH₃)
- SEM slimming : equivalent to KrF

It is our opinion that this resist is a very promising candidate for the manufacture of sub-130 nm devices and may even be extended to below 100 nm once higher NA ArF exposure tools become available this year.
Fig. 13. Lithographic performance of optimized VEMA photoresist for dense applications, process conditions: FT = 3,300Å, SB = 120°C/90sec. Proximity, ASML/900 (0.63NA, Dipole illumination), Binary mask, PEB = 120°C/60sec. Proximity, 0.26N, 60sec. SP.
Fig. 14. PED dependency, environmental condition 2 ppb in stepper and track, off-line between stepper & track, process conditions: FT = 3,300Å, SB = 120°C/60sec, ISI ArF micro-stepper (0.6NA, OAI), Binary mask, PEB = 120°C/60sec, Develop 0.26N 60sec. SP.

Fig. 15. PEB sensitivity for 130 nm 1:1 L/S and isolated lines, process conditions: 820ÅBARC, FT = 3,300Å, SB = 120°C/60sec, ISI ArF micro-stepper (0.6NA, 0.7η), Binary mask, PEB = as indicated °C/60sec, Develop 0.26N 60sec. SP.

References