A Comprehensive Review of EUV Resist Materials and Processing at Selete

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The Selete research and development program was started to prepare extreme ultraviolet (EUV) lithography for the manufacturing of semiconductor devices. In the past five years, Selete has evaluated more than 1000 EUV resists from resist suppliers using the small field exposure tool (SFET) which is linked in-line to a coater / developer track system under chemically controlled environments. From the results obtained, the lithographic performance of various Selete standard resists (SSRs) and optimization of related processes has been reported. Based on these, advancement in resist materials was observed to be of steady progress in terms of resolution limit, sensitivity and line width roughness (LWR). LWR reduction and pattern collapse prevention were also achieved through the application of various alternative processes. One such alternative process is the application of the aqueous solution of tetrabutylammonium hydroxide (TBAH) instead of the conventional tetramethylammonium hydroxide developer. TBAH was found to be most effective in the suppression of resist film swelling which causes pattern collapse. Alternative rinse solutions evaluated and utilized have also allowed improvements in LWR reduction and pattern collapse. Meanwhile, EUV resist outgassing, which is also a concern for the effective application of EUV lithography, was quantified and analyzed. Analysis results have shown that protecting group and photo-acid generator components of EUV resists are the main source of such outgassing during exposure. Moreover, for fundamental research, a new approach using high speed atomic force microscopy in the *in situ* analysis of resists during the dissolution and rinse processes is presented. The results obtained with this method supported a number of previous assumptions about resist dissolution and rinse mechanisms which presented potential pointers for use in next-generation lithographic applications.

Keywords: EUV lithography, resolution limit, sensitivity, LWR, dissolution, rinse

1. Introduction

Extreme ultraviolet (EUV) lithography is a leading technology for the manufacture of semiconductor devices as small as the 22nm node and beyond^[1]. At present, EUV resist sensitivity and resolution limits continue to be improved but line width roughness (LWR) still remains a difficult issue^[2]. To provide possible solutions, there is a trend in individual and collaborative efforts between research consortiums, universities, and resist material developers on the investigation of new EUV resist platform and material designs^[3-9]. This is also true for the conceptualization and application of alternative resist processes which have shown significant potential as pattern sizes become smaller^[10-13]. In the last five years, Selete

has been actively advancing EUV lithography (EUVL) as the next lithographic technology for semiconductor manufacturing.

In this article, a comprehensive review of the Selete research program on EUV resist material and processing is presented. The lithographic performance of the Selete standard resists (SSRs) and an update on the latest high performance materials developed is also discussed. Furthermore, investigative work on EUV resist outgassing analysis, application of non-conventional resist processes such as alternative developer and rinse solutions, and the latest results for fundamental research on *in situ* analysis of the dissolution and rinse behavior of EUV resists is reported.

2. EUV resist benchmarking and Selete standard resists

In order to meet the stringent requirements in resolution limit, sensitivity, and LWR for the manufacture of semiconductor devices, Selete has evaluated more than 1000 EUV resists (from various resist suppliers) using the 0.3NA small field exposure tool (SFET)^[2]. Annular illumination condition ($\sigma_{\text{outer}} = 0.7$, $\sigma_{\text{inner}} = 0.3$) is applied for these evaluations. However, for enhanced imaging experiments of 30nm lines and spaces (L/S) and below, the x-slit^[2] illumination with direction parallel to the incident beam is applied. The SFET has a magnification of 1/5 and an exposure field of $0.2 \text{ mm} \times 0.6 \text{ mm}$ in size.

Using this exposure tool, the lithographic performance of poly(hydroxystyrene) (PHS) and acryl-based polymer resists, low molecular resists (targeted for LWR reduction), and a number of other resist resin platforms were investigated. Moreover, variations of chemical formulations involving photo-acid generators (PAGs), quenchers, photosensitizers, etc. were performed. Based on these results, SSRs were selected for further application in test device production^[2]. [Fig. 1]

Looking back, on July, 2007, the SSR1^[14] was released as an evaluation resist for checking and maintaining the SFET performance. For this resist, a 40nm L/S resolution limit, 13.4 mJ/cm^2 sensitivity (at 45nm L/S) and 7.6nm LWR (at 45nm L/S) was obtained.

Around the same time, the high-resolution limit SSR2^[14] was also evaluated. For this resist, a 28nm L/S resolution limit, 17.4 mJ/cm^2 sensitivity (at 32nm L/S) and 10.3nm LWR (at 32nm L/S) was obtained.

was achieved.

In 2008, the SSR3^[15] was released with a 25nm L/S resolution limit, 13.1 mJ/cm^2 sensitivity (at 32nm L/S) and 6.7nm LWR (at 32nm L/S) lithographic performance. The SSR3 was utilized for the evaluation of 3x-nm test device manufacturing. During this time, the lithographic performance of the SSR3 was best among available EUV resists.

In September, 2009, the SSR4 and SSR5^[16] was made available. For the SSR4; a 28nm L/S resolution limit, 12.4 mJ/cm^2 sensitivity (at 32nm L/S) and 5.5nm LWR (at 32nm L/S) lithographic performance was obtained. With a comparatively improved shelf-life and minimal defects, better test device yield was achieved. Pattern collapse at very narrow pattern sizes was an issue but this was solved with the application of alternative resist processes (discussed in later chapters). After optimizations, improved resolution limit of 24nm L/S was attained^[2].

The SSR5 was prepared in parallel with the SSR4, in case the pattern collapse issue was not resolved. For this PHS based resist, a lithographic performance of 26nm L/S resolution limit, 10.7 mJ/cm^2 sensitivity (at 32nm L/S) and 7.5nm LWR (at 32nm L/S) was obtained. The sensitivity of the SSR5 satisfies the requirement for EUV resists.

On September of 2010, the SSR6 and SSR7^[2] were released. The SSR6 was originally developed for application in test devices below 28nm L/S. This was confirmed with resolution limits reaching pattern modulation even at 22nm L/S, with conventional resist processes. Moreover, higher

Resist name	SSR1	SSR2	SSR3	SSR4	SSR5	SSR6	SSR7
Resolution (nm L/S)	40	28	25	28	26	24	28
LWR (nm) @ 32nm L/S	7.6 @ 45nm L/S	10.3	6.7	5.5	7.5	5.7	5.7
Sensitivity (mJ/cm^2) @ 32nm L/S	13.4 @ 45nm L/S	17.4	13.1	12.4	10.7	14.6	18.1
Top-down image @ 32nm L/S
Cross-section image @ 32nm L/S

Fig.1 Lithography performance of Selete standard resists (SSRs).

etching resistance was attained in comparison with previous SSRs. Lithographic performance was achieved at 24nm L/S resolution limit, 14.6mJ/cm² sensitivity (at 32nm L/S), and 5.7nm LWR (at 32nm L/S). [Fig. 2]

Lastly, for the SSR7, a lithographic performance of 24nm L/S resolution limit, 18.1mJ/cm² sensitivity (at 32nm L/S), and 5.7nm LWR (at

32nm L/S) was achieved. Significantly high etching resistance was confirmed with this fullerene-based low molecular resist, thus, providing high yield. It is also noteworthy that the SSR7 is the first low molecular EUV resist utilized for 3x-nm test device patterning. [Fig. 3]

From these results, it is clear that improvements in resolution limit and sensitivity have been achieved through the years, however there is still a need to reduce LWR to meet the targets^[1]. [Fig. 4]

Fig. 2 Pattern cross-section profiles of SSR6 using the x-slit illumination condition.

Fig. 3 Pattern cross-section profiles of SSR7 using the x-slit illumination condition.

3. Alternative resist processes

As discussed in the previous chapters, in the lithographic targets required for EUV resists, LWR is viewed as one of the most difficult to attain. To provide new answers to this issue, various researches in resist material improvement are being performed. However, taking the material approach is starting to become more difficult as pattern sizes reach molecular levels smaller than currently available polymers. Moreover, in the past few years, pattern collapse at fine sizes has also limited the resolution limit of high-performance resists^[17].

Another approach being considered to provide possible solutions is through the application of non-conventional resist processes^[2, 10, 11]. Early works in Selete have shown the applicability of the 0.26N aqueous tetrabutylammonium hydroxide (TBAH) solution as an alternative to the commonly available tetramethylammonium hydroxide (TMAH) developer^[10]. Moreover, a number of aqueous rinse solutions have also shown similarly promising results^[2]. Improvements in

(a) Sensitivity - resolution

(b) Sensitivity - LWR

Fig. 4 The resolution-sensitivity-LWR trade-off of the SSRs; (a) the relationship between the sensitivity and ultimate resolution, (b) the relationship between the sensitivity and LWR.

resolution limit due to the minimization of pattern collapse for some resists were attributed to the minimization of capillary force occurring between very narrow L/S patterns during dissolution and rinse. Also, LWR reduction through the rinse process depending on the resist platform has been reported^[2].

The latest reports have shown that a combination of alternative developer and rinse solutions show optimal results in the reduction of pattern collapse and minimization of LWR. Utilizing the SSR4 at optimal bake conditions, an experiment was carried out using the TBAH developer in combination with a rinse solution N of low surface tension. The SSR4 is known to have pattern collapse issues at very narrow pattern sizes, which was then presumed to be due to significant resist film swelling during dissolution^[17]. To further emphasize the effect of these alternative processes on pattern collapse, the SSR4 was also set at a comparatively higher aspect ratio at a film thickness of 80nm.

As a result, 26nm L/S pattern of 80nm film thickness and aspect ratio of over 3 was obtained using a combination of the TBAH developer and rinse solution N. Improvements obtained here were

attributed to the suppression of resist film swelling. This was viewed as the effect of minimized resist uptake of the TBAH developer which is of higher molecular weight in comparison to the TMAH. Also, another factor considered is the reduction of capillary force due to the low surface tension introduced by the solution N during rinse process. [Fig. 5]

To summarize, further progress can be expected through the optimization of the developer and rinse solutions to the presently available resist materials. These results show the potential of these alternative processes in mitigating pattern collapse and LWR.

4. EUV resist outgassing

Resist outgassing is considered an EUVL-specific issue^[18]. Resist outgassing also exists in other lithographic technologies but needs special consideration in EUVL where exposure tool systems are kept in significantly clean ultra-high vacuum conditions to maintain a high EUV light intensity at wafer surface. Thus, intensity loss due to mirror contamination from resist outgassing needs to be minimized or eliminated.

L/S (nm)	35	32	30	28	26
TMAH @ D.I.W.					
TBAH @ D.I.W.					
TMAH @ Rinse N					
TBAH @ Rinse N					

Fig. 5 Mitigation of pattern collapse with the combination of alternative developer and rinse solution.

To gain a deeper understanding of EUV resist outgassing and develop outgassing control techniques, various research groups^[18-20] have taken steps in its analysis and quantification. In resist outgassing quantification, the pressure rise and gas chromatography mass spectrometry (GC-MS) measurement methods are typically utilized. The GC-MS method has also been reported to provide comparatively accurate results in the identification of resist outgassing components^[18].

In 2006, Selete initiated resist outgassing studies to establish a system of screening EUV resists prior to exposure evaluations at the exposure tool^[21]. The main goal was to understand resist outgassing mechanisms for the development of low-outgassing high performance EUV resists. More than 400 resists have been analyzed (using the pressure rise method)^[18]. The results of which, have been beneficial in maintaining an effective and clean EUV exposure tool.

On resist outgassing component analysis and characterization using the GC-MS a total of more than 40 resists (including the SSRs mentioned in the previous chapter) were investigated^[18] [Fig. 6]. Moreover, based on results utilizing model resists, majority of the resist outgassing released during EUV exposure came from protecting group and PAG components of the resists. Possible outgassing components of concern are isobutene (from the protecting group), benzene and diphenylsulfide (both from the PAG)^[18] [Fig. 7]. These results show that for the development of

Fig. 6 Resist outgassing amounts of more than 40 resist samples determined by GC-MS at exposure dose of 30mJ/cm².

low-resist outgassing resists, careful consideration of the protecting group and PAG formulation is necessary.

5. Dissolution characterization

The characterization of the resist dissolution process after exposure has been continuously investigated in search for new ideas in the optimization of resist materials and processes^[22-23]. Methods such as the quartz crystal microbalance (QCM)^[24] and dissolution rate monitors^[25] provide information that can help define the behavior of a resist film during the dissolution process. A visual observation of the actual pattern formation of resists during dissolution may provide some answers and new pointers in further improving resist performance.

As we have recently reported, focusing on the 32nm isolated line (I/L) pattern, a visual observation of the actual pattern formation of resists during dissolution was realized with the application of high speed atomic force microscopy (HS-AFM) [26-28]. The system (Nano Live Vision by Research Institute of Biomolecule Metrology) is equipped with highly sensitive, ultra-fast cantilever and AFM scanning capabilities. Utilizing the HS-AFM, an *in situ* resist dissolution analysis method was established.

Initial results have shown the variation in the dissolution characteristics depending on the resist platform and type of developer utilized. A difference in the amount of resist swelling and grain size were observed during the dissolution of various types of EUV resists. An analysis of dissolution characteristic differences between

acryl-based polymers of various PAG configurations (PAG-blended, PAG-cation bound and PAG-anion bound) was also performed. Based on the results, resist film swelling of an acryl-based polymer resist during dissolution was found to be significantly minimized by bounding the PAG-anion to the polymer structure [28].

Latest results have also shown that with this method, the *in situ* analysis of resists during the rinse process (after development) is possible [28].

Utilizing an acryl-based polymer resist an analysis of the line size variation of the 32nm I/L during the rinse process using de-ionized (D.I.) water was performed. Based on results obtained, the occurrence of line size narrowing and afterwards, line size swelling during rinse process was confirmed. [Fig. 8]

The acryl-based resist has been understood to

Fig. 8 The *in situ* analysis results for an acryl-based resist during the standard rinse process using D.I. water.

Fig. 9 The line size variation of the 32nm I/L during the rinse process using;
(a) D.I. water, (b) Alternative rinse solution.

exhibit significant swelling properties during dissolution in the developer solution. This is especially true in the exposed area of the resist surface. These results suggest that even after pattern formation of the 32nm I/L during the dissolution process, some form of swelling continues to occur in the pattern's side walls. During the rinse process, a total replacement (or absence) of the developer solution allows this swelling side wall to shrink and, in effect, cause line size narrowing. However, after a certain period of immersion in D.I. water, the acryl-based resist again exhibits swelling, which is assumed to be due to water or rinse solution uptake.

The same process was performed using an alternative aqueous rinse solution. The rinse solution utilized has been tuned with a surfactant additive to prevent resist film swelling and consequently, pattern collapse. The same line narrowing phenomena during rinse process was observed. However, line size swelling afterwards was found to be minimal, in comparison to the results obtained with the D.I. water rinse process [Fig. 9].

To summarize, these results have shown the potential of the HS-AFM as a method of analyzing not only the dissolution characteristics of resists but also its behavior during the rinse process.

6. Summary

The Selete EUV research and development program ended on March 31, 2011. This last five years has seen the development of EUV resists materials and processes in preparation for the manufacture of 22nm node and beyond.

With a total of more than 1000 EUV resists evaluated and optimized, SSR1-SSR7 were selected. Moreover, to further optimize the performance of these SSRs, the conceptualization and actual application of alternative developer and rinse processes were developed and utilized.

Meanwhile, for EUV resist outgassing, a screening and component analysis method was established and utilized. Applying this on model resists, the main source and mechanism of resist outgassing and its components were identified.

From dissolution characterization studies made, an *in situ* resist dissolution analysis method using the HS-AFM was established. Initial investigations, which are the first of its kind, have shown the potential of the HS-AFM as a method of analyzing not only the dissolution characteristics of resists but also its behavior during the rinse process.

EUV lithography is on its way from a laboratory curiosity to semiconductor fabrication technology. Resists will continue to play a major role in its realization. Thus, the research continues for new resist materials / designs and effective processes, as lithographic targets move forward in the manufacture of smaller, next generation semiconductor devices.

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