Image Formation in Electron Projection and E-beam Direct Write Lithography Resists


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We have demonstrated that current DUV resist platforms can be optimized to develop new EPL resists and that these new resists have a greater degree of freedom in their design than their optical counterparts. Free from the constraints of optical lithography, we have been able to use high levels of PAG that would be too strongly absorbing at DUV, and produce resists that are 3 to 10 times more sensitive than UV6. Monte Carlo simulations of these phenolic resists indicate that the 100 KeV electrons will travel straight through the film, leaving straight sidewalls, as verified by SEM cross sections of EPL-optimized resists. Recent work indicates that a new set of formulations will enable even better sensitivity than initial EPL resist requirements. The image formation process for an e-beam exposure on a positive chemically amplified resist has been simulated using discrete models from exposure through development. A ‘percolation network formation for diffusion-reaction development’ model for chemically amplified resists was used to compare simulation results with experiment for 45 nm contact hole arrays, showing excellent agreement. Ionization statistics show that most of the secondaries generated in the resist have energies well below 100 eV, peaking at around 10 eV. At these low energies impact ionization or plasmon generation are not possible, which means other types of interactions between secondary electrons and PAG come into play for photo-acid generation. This is consistent with a “scavenging” interaction described in the literature. Photoacid diffusion, solubility range and threshold have been identified as contributors to sidewall roughness, though further study is warranted.

Keywords: EPL, resists, Monte Carlo, simulation.

1. Introduction

Direct write e-beam lithography (DW) in chemically amplified resists is capable of very high resolution (<40 nm) [1,2], however, the throughput of direct write approaches have limited their use to the manufacture of masks and other low throughput applications. Electron projection lithography systems (EPL), such as SCALPEL and PREVAIL, combine the high-resolution capability of e-beam lithography with the high throughput characteristics of a projection system and is now a viable candidate for imaging sub-130 nm features on wafers. In order to meet the stringent requirements for Next Generation Lithography (NGL), an EPL imaging approach must include resists capable of printing sub-100 nm features (50-100 nm dense lines) with high sensitivity (5-10 µC/cm² at 100 KV), broad process latitude and low line edge roughness. In most chemically amplified systems, a tradeoff exists between sensitivity and resolution since many formulation or process variables that improve sensitivity (e.g. high PEB temperatures,
long acid diffusion path lengths, and low base levels) limit resolution. Another difficult requirement common to all new technology resists is the low line edge roughness. In order to be able to develop new materials that comply with this requirement a deeper understanding, down the molecular level, of all the processes involved in the image formation is needed.

The objective of this paper is to describe in detail the image formation process in e-beam resists and show how this understanding can aid in the development of resists optimized for EPL. We also wish to highlight the resist technology advantages for EPL, such as that resists can be derived from current phenolic chemically amplified platforms. This lifts the requirement of developing new base materials, unlike fluorine-based polymers for 157 nm lithography and ultra thin films for EUV. An additional advantage of EPL technology is the freedom from transparency constraints that burden optical-technology resist platforms. This allows for the use of high levels of photoacid generators not possible in resists used for optical lithography. Electrons with 100 KeV energies traverse resist films quite easily with very few inelastic events, and therefore do not suffer from opacity limitations. Monte Carlo simulations of the e-beam exposure process are used to determine the level of interaction of high energy electrons with PAG and polymer and have shed further insight to the image formation process in resists.

In previous work, positive tone chemically amplified resist, UV6 (Shipley), was used as a reference material and evaluated by SCALPEL. A first round of experiments was aimed to increase sensitivity and contrast over UV6 by modification of the base resin and by increasing PAG loading [3]. In Figure 1, we show SEM micrographs of the DUV imaging capability of UV6 and two of the candidate formulations for imaging using SCALPEL. These new resists show an improvement in DUV sensitivity by better than a factor of 3. However, the non-vertical sidewall profiles of EPL resist candidates demonstrate limitations in DUV imaging of resists with heavy PAG loading. Because there is more optical absorption of the resist due to higher PAG concentration, the dose profile as a function of depth in the resist is non-uniform. When exposing with the SCALPEL tool, the optimized resists maintained the increased sensitivity over UV6 [3] and exhibited straight sidewalls. Figure 2 shows cross sectional SEM micrographs for XP9947A, showing no opacity effects, i.e. sidewalls are straight, even though PAG levels are higher and the PAGs are stronger than encountered for DUV resists.

The lithographic performances of poly-hydroxystyrene based photoresists, such as the positive tone EP-004 and negative tone EN-009 chemically amplified resists (Tokyo Ohka Kogyo), have been characterized for the SCALPEL exposure system [4,5] as well. Further optimization of EP004 and XP9947A yielded a new family of resists with sensitivities below 5 µC/cm² at 100 KV and sub-100 nm resolution, Fig. 3. These results are from direct write prescreening experiments using a JEOL 9300 100 KV exposure tool and show that current EPL resist technology is in place to meet lithographic performances needed for future generations of devices.

![Figure 1. DUV imaging capability of UV6 (left) and two positive tone SCALPEL resist candidates, XP9947A (middle) and XP9948B (right). Pattern shown is 200 nm dense lines and spaces. Film thickness is 400 nm.](image)
2. Image formation modeling

As new advances in resist development in e-beam based lithography progress, understanding of interactions of the resist with the incident beam is necessary. For this purpose a 3-dimensional Monte Carlo code, LESiS [6-8], has been used for simulating the exposure of commercially available resists [3,4,9]. The code simulates the ionization of materials exposed to high-energy electrons. In this manner, discrete energy loss events can be tracked as the incident and secondary electrons travel through the resist. Required input data for this type of simulation is the atomic composition of the resist. The model assumes single scattering events so that molecular structure data is not necessary. Resist composition data will not be disclosed in this paper since it is proprietary information of the resist vendor. Simulations were run for UV6, X9947A and XP2001B at the imaging doses specified for sub 120 nm features. With this data detailed information can be obtained on the ionization of each of the different resist components. In an attempt to further understand the role of the PAG in the exposure process, relative dose absorption data was obtained for these materials for both DUV and 100 KV electron exposures. The DUV data was measured with a photo-spectrometer and the high-energy electron data was obtained using the Monte Carlo code [3]. The results are illustrated in Fig. 4. The extra loading of PAG and modification of PAG type increases PAG DUV absorption such that it is almost equivalent to that of the polymer. It is clear that the PAG has a significant role in the absorption process of the incident energy. However, the Monte Carlo results for 100 KeV electron exposures show that the PAG absorbs less than 5% and the polymer absorbs more than 95% of the deposited energy via ionization for all samples studied [3]. This means that dose absorption, via ionization, by the PAG alone can not explain the greater than 3-fold improvement in sensitivity found in the optimized resists, and that there are other underlying interactions between the polymer and the PAG that need to be considered. Recent experimental work [10] has found that during e-beam exposure the PAG interacts significantly with the surrounding organic matrix by scavenging the secondary electrons originated from the matrix ionization.
In order to study in more detail the image formation process using high-energy electrons, the exposure of an array of 45 nm contact holes was simulated and compared to experimental results. In Figure 5 we show 50 nm and 45 nm contact holes patterned using the JEOL 9300 100 KV e-beam tool.

**Figure 4.** Relative dose absorption as a function of resist component (Polymer or PAG). *(Left)* Data taken using DUV spectrometry. *(Right)* Simulation results using a binary impact ionization model for 100 KeV electron beam exposure. The scale for PAG absorption data (right side) has been magnified by 10.

**Figure 5.** Examples of sub-50 nm contact holes exposed in a DUV resist using 100 KV e-beam lithography.

**Figure 6.** Simulation of exposure of four 45 nm contact holes using a stack of 400 nm DUV resist, 500 nm of SiO2 and 500 nm Si substrate. Plot is map of deposited energy from incident 100 KV electrons and its secondaries. Dose contour plot at 1/e the maximum dose level.
using 400 nm of DUV resist and a dose of about 128 µC/cm². The simulated exposure considered 400 nm of DUV resist over 500 nm of SiO₂ and 500 nm of a silicon substrate. In Figure 6 an energy deposition map showing a 1/e normalized threshold dose level is plotted. This simulation shows the location and intensity of all discrete energy loss events that occur during exposure. It is clear that there is a population of secondary electrons that do expose regions in between design locations.

**Figure 7.** Energy loss distributions in resist due to ionization processes. Plasmon losses were left out of plots but included in exposure simulation. (Left) Total energy loss, \( \Delta E \), (Right) Kinetic energy of secondary electron after ionization, \( \delta E_{\text{kinetic}} \).

**Figure 8.** Atomic ionization statistics of e-beam exposure of a DUV resist. (Top) Histogram of ionization events per element, where C, H and O dominate. (Bottom) Histograms of atomic level ionization for C and O, showing dominant valence electron ionization and significant L-shell ionization.
Figure 9. Image formation sequence for 45 nm contact hole array exposed using 100 KV electrons in a DUV resist. (Top-left) Map of PAG generation locations due to discrete energy losses of incident electrons and secondaries. (Top-right) Map of catalytic reaction locations due to diffusion of PAG, so called “amplification effect”. (Bottom-left) Contour level of solubility after forming solubility network. (Bottom-right) Cross section view of developed resist after developer removes material from soluble regions.

Figure 10. Comparing simulation result with cross section SEM micrograph of a 45 nm contact hole exposed in a DUV resist.
An analysis of energy loss statistics in the DUV resist reveals that most energy losses are well below 100 eV, and that the kinetic energy of the generated secondaries are also well below 100 eV, peaking at around 10 eV. This is significant in that most Monte Carlo codes that simulate electron energy losses in materials cannot track such low energy electrons. It is unclear how do these low energy electrons would interact with a PAG molecule. The energy is too low for impact ionization or plasmon generation. But this statistical result is still consistent with the “scavenging” picture that has been postulated by Tagawa et al [10]. The origin of these secondaries can be identified by further analysis of the data. In Figure 8 we show that about 99% of the ionization events occur in elements that dominantly come from the polymer resin, i.e. C, O and H. This figure also shows that the L-shell and valence electron ionizations occur in C and O significantly more than K-shell ionizations. It is unclear though how do such ionizations affect the polymer backbone. This is beyond the scope of this work.

Besides the exposure and ionization processes, the image formation process includes the photoacid generation process, the amplification process though the diffusion of the photoacid, the spatial effect of the catalytic reactions generated by the photoacid, the degree of solubility change and then the development and rinse processes. This model is known as a ‘percolation network formation for diffusion reaction development’ model [9]. An exercise of this model is shown in Figure 9. Here the image formation sequence for 45 nm contact hole array exposed using 100 KV electrons in a DUV resist is illustrated in four steps. In Figure 9 (top-left) a map of photo-acid generation locations due to discrete energy losses of incident electrons and secondaries shown; (top-right) a map of catalytic reaction locations due to diffusion of photo-acid, so called “amplification effect”; (bottom-left) 3-D contour level of solubility after forming solubility network; (bottom-right) a cross section view of developed resist after developer removes material from soluble regions. The photo-acid was let to diffuse randomly with a range of 32 nm (3σ), in 150 hops and with a 63% probability of creating a de-protection site. The deprotection site was modeled to affect the solubility of a region of about 15 nm (3σ), using a gaussian convolution method [9] and a solubility threshold was set at 25% of maximum solubility. No attempt has been made to simulate polymer-developer interactions such as swelling or gel-permeation layers, nor has the polymer morphology been included. However, when the final result is compared to experiment in Figure 10 excellent agreement is observed, including sidewall roughness. During the simulation work, it was found that the range of photoacid diffusion significantly affects the sidewall roughness of the exposed feature. Other significant factors are the solubility range and the solubility threshold. A more systematic study of the effect of these parameters to sidewall roughness will be performed in future work.

3. Summary and conclusions

We have demonstrated that current DUV resist platforms can be optimized to develop new EPL resists and that these new resists have a greater degree of freedom in their design than their optical counterparts. Free from the constraints of optical lithography, we have been able to use high levels of PAG that would be too strongly absorbing at DUV, and produce resists that are 3 to 10 times more sensitive than UV6. Monte Carlo simulations of these phenolic resists indicate that the 100 KeV electrons will travel straight through the film, leaving straight sidewalls, as verified by SEM cross sections of EPL-optimized resists. Recent work indicates that a new set of formulations will enable even better sensitivity than initial EPL resist requirements. The image formation process for an e-beam exposure on a positive chemically amplified resist has been simulated using discrete models from exposure through development. A ‘percolation network formation for diffusion-reaction development’ model for chemically amplified resists was used to compare simulation results with experiment for 45 nm contact hole arrays, showing excellent agreement. Ionization statistics show that most of the secondaries generated in the resist have energies below 100 eV, peaking at around 10 eV. At these low energies impact ionization or plasmon generation are not possible, which means other types of interactions between secondary electrons and PAG come into play for photo-acid generation. This is consistent with a “scavenging” interaction described in the literature. Photoacid diffusion, solubility range and threshold have been identified as contributors to sidewall roughness, though further study is warranted.
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References: