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Unraveling the role of photons and electrons upon their chemical interaction with photoresist during EUV exposure

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ABSTRACT

The interaction of 91.6 eV EUV photons with photoresist – in particular chemically amplified resist (CAR) – is different than exposure at 193 nm and 248 nm wavelengths. The latter is understood well and it is known that photons interact with electrons in the resist's molecular valence orbitals (for chemically amplified resist (CAR) the photon interacts with the photo acid generator (PAG), which leads to a deprotection reaction on a polymer after a thermal catalytic reaction during a post-exposure-bake.). At EUV however, more steps are involved in the radiolysis process between the absorption of the photon and the final chemical modification. These are related to the generation of primary electrons and their decay to lower energy secondary electrons, and most of this steps are not well understood.

In this paper, the reaction products from EUV and low energy electron exposure are examined using Residual Gas Analysis (RGA), which measures and analyzes the outgassing products related to the ongoing reactions.

This investigation is applied firstly on a model CAR where details of the resist chemical constituents were known prior to testing. The measurement not only resolved information on the expected acid related reactions from the PAG and protection groups, but also exhibited direct scission reactions of the polymer, where some of them lead to polymerization reactions. Moreover, the measurement quantifies the balance between the different ongoing reactions, which were confirmed by contrast curve measurements.

Based on learnings on the model resist, applied the measurement technique to commercial resists, where actual resist chemistry composition is not known. Despite that, it was found that information could be deduced to distinguish between acid related ongoing reactions and direct scission of reaction on the base polymer and quantify their relation. Moreover, different generations of commercial resists based on similar chemistry platform were investigated, which revealed that improvements in printing performance could be explained by PAG reaction yield increase.

Keywords: EUV lithography, CAR, photoresist chemistry, RGA, photons, secondary electrons.

1. INTRODUCTION

Optimizing photoresist performance is one of the key challenges for high volume manufacturing (HVM) based on extreme ultraviolet (EUV) lithography. Compared to the lithography at DUV wavelength where direct absorption of a photon leads to the desired chemistry and is well understood, absorption of 91.6 eV photons with photoresist leads to subsequent reactions via interaction with the cascade of low energy electrons whose energy resonates with the molecular components that constitute the resist. In DUV lithography, most resist chemistries are based on chemically amplified resists (CAR), consisting of a polymer with protection groups (PG), blended with photoacid generator (PAG), quencher (Q), and solvent. Its photochemistry in DUV is well understood, and based on molecular interaction between photon and resist [1,2]. In particular, the photon is absorbed by the PAG, which results in its decomposition and generates acids. This in turn is the starting point for the polymer deprotection, which makes the exposed resist soluble for the developer after a thermal catalytic reaction during the post-exposure bake. The primary role of the quencher in these situations is to minimize the acid blur at the edge of the exposed region and improve line edge roughness (LER).

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In EUV lithography, CAR based resist chemistry is still one of the main candidates for HVM, however the interaction of 91.6eV photons with the resist is much less understood than in DUV [3]. At this high energy, photons are first absorbed locally by the core electrons of the atoms that make up the molecular components of the resist and do not react directly with the valence orbitals of the molecules until electrons that are generated during the cascade of electron spawning photoionization ionizations events are of resonant energy with those molecular orbitals. The main energy conduit here begins with the resist polymer [4] since it provides the majority of absorption targets for photon interaction with core level electrons – atomic orbital localized, resulting in higher energy primary electron [5]. The initial photon could therefore result in the generation of several secondary electrons at lower energy [6-8] that eventually enable chemical modifications, e.g. decomposition of the PAG [9] or bond scission that leads to crosslinking between molecular components.

In addition to the complexity of the photon-resist interaction, the CAR composition itself is a complex composition of many materials. Although they are essentially a combination of polymer where PAG and quencher is added, commercial CARs can be based on various polymer platforms with different types of PAG and quenchers in various concentrations. Moreover, absorbing units, sensitizer materials, and additives can be included to improve the printing and profile performance of the critical dimension. Since the individual material components and compositions are proprietary information, it is very hard to predict the detailed photon-matter interaction in this case.

Since the actual photon and electron processes inside the CAR are very complex, it can be an alternative approach to investigate the results of the reactions and not the steps to get to a certain reaction. This approach was used in this paper and is based on measuring the outgassing species generated by the resist as the result of chemical reactions inside the resist upon exposure.

In this paper, we describe such a methodology to identify reactions by measuring and analyzing outgassing species by Residual Gas Analysis (RGA). This measurement on CAR is done with EUV exposure or with exposure of low-energy electrons. Note that this RGA approach can potentially have the disadvantage not to detect the reactions in the resist if they do not result in escaping volatile reaction products. On the other hand, this approach has the potential to detect not only the reactions that are expected to occur (e.g. PAG and acid related), but also any other reaction that is ongoing and leading to volatile reaction products. In this work, the RGA based measurements are compared to EUV contrast curves.

The measurement method is first applied to a model resist of which the chemical constituents is known, and where the goal is to understand and quantify the ongoing reactions. Based on this learning, the method has been applied also on commercial CARs. Although chemical details in this case are unknown, the goal is to check for changes in reaction for materials that have different printing performance.

2. METHODOLOGY

In this work, CAR based materials are investigated with RGA upon exposure with either EUV or with low energy electrons. In this section, it will be described how the chemical yield of reactions can be calculated by such measurement.

2.1 RGA measurement

Residual Gas Analysis is a method that uses mass spectroscopy to measure the vacuum quality of chambers and to detect traces of species in low pressure environment due to e.g. material outgassing [10-12]. Its measurement is based on the ionization of the molecular species, and the subsequent analysis of the fragmented masses. It is important to note that each molecule will always fragment in a unique way, therefore the intensity spectrum versus mass will always be very similar, independent of RGA hardware and chamber geometry. An example of a measured spectrum of isobutene is shown in Fig. 1. As consequence of the unique species-specific spectrum, one can consult mass spec libraries for species identification (e.g. from NIST Chemistry Webbook [13]) to identify the molecular structure of an outgassed species based on experimentally obtained spectra. Also, once the type of an outgas species is known, one can limit the data collection to a single mass, e.g. in order to benefit from a faster acquisition time.

Another advantage of RGA is that the measured intensity can be converted to molecules/(cm² s), taking into account tabulated or measured parameters, such as fragmentation factor, ionization cross-section, pressure, and pumping speed.

So in this way the measured RGA intensity on a certain mass can be converted to the number of outgassed molecules/(cm² s) of that species, and therefore related to the number of ongoing reactions where that species is formed.

When the resist related reactions are generating more than one species, the resulting RGA spectrum will be a superposition of many spectra, and can be more complicated. However, in many cases, interpretation on the number of parallel reactions is in many cases still possible, in particular if the resist is supplied in different formulations (e.g. polymer only, polymer+PAG, polymer+PAG+quencher).

Figure 1. Example RGA spectrum of isobutene, measured by leaking the species in the chamber with the RGA. In this case the species fragmentation results in high intensities at mass 27, 39, 41, and 56 amu. Note that highest mass in spectrum (in this case 56 amu) is typically close to the molecular weight of the species.

2.2 Experimental measurement of the chemical yield

As indicated above, the RGA-based measurements are made during either EUV or low energy electron exposures, in order to explore the ongoing reactions upon irradiation. Depending on the exposure source, the interaction volume will be significantly different. For EUV exposure, the photons are expected to be absorbed through the full resist thickness, therefore the measured reactions will come from the full resist layer. Injection of low energy electrons is expected to generate reactions only at the top surface, since these electrons are known to have small penetration depth in solids due to their limited inelastic mean free path [3].

In the experiments, the RGA measurements and exposures are done in a tool previously used for resist outgas qualification [14]. This tool can expose a 200 mm resist coated wafer either by EUV photons or by electrons. For the EUV exposure, an Energetiq EQ-10 source is integrated in the tool, supplying 10W/2πsr EUV irradiation into the system. This light is filtered by a Zr spectral purity filter (SPF), and reflected by a multilayer (ML) mirror and grazing incidence mirrors towards the wafer. Spot size on wafer is ~10mm² and the power density is ~4 mW/cm². For electron based exposures a low-energy electron gun ELG-2 from Kimball Physics has been installed, which supplies electrons with energies from 1eV to 2keV. For the results reported in this paper, the energy range 2-80 eV was mostly used. RGA measurements in the outgas tool were done with a Pfeiffer QMG422 mass spectrometer, which can measure over a broad atomic mass unit (amu) range of 1 to 512 amu. It is found that CAR related RGA intensity spectrum is typically found below 300 amu, therefore full spectrum measurements are typically limited to that range.

Once the masses of the species that are representative for the studied chemistries are identified, it is possible to do fast RGA acquisition on these masses while simultaneously exposing the resist wafer in scanning mode. In Fig. 2 this is schematically illustrated for the EUV exposures, and shown that from line to line the EUV intensity is increased at constant scan speed. A reference scan without exposure ('no exp') is used as reference for RGA, while in between the lines the exposure is interrupted. The measured RGA signal for one mass during this exposure scheme is shown in Fig. 2 (a), where a mass representative of a PAG fragment is taken as an example. It can be seen that the RGA detects a clear signal at the lowest dose. It can also be observed that from line to line when the EUV exposure is stopped in between the lines, the signal drops significantly, but that this local minimum is slightly increasing in time due to residual outgassing of earlier exposed resist or limitation in pumping away the species. In order to have a single output for each exposure dose condition, it was considered that the incremental increase ΔQ at the start of a line exposure is a good measure for the impact that this EUV dose has on chemical reactions, and this value will be called the chemical yield for this species. As indicated earlier, this RGA increment can be considered proportional to the number of molecules/(cm² s) that were

generated by the reactions (when taken into account the fragmentation factor). In Fig. 2 (c), this chemical yield (in this example for PAG dissociation reaction) is plotted as function of the dose.

Note that when the resist wafer is fully exposed after the RGA testing, a post-exposure bake (PEB) and development of the wafer can be performed, making it possible to relate the radiolysis products between exposure to EUV to the dose-to-clear (D2C). In Fig. 2 (c) this is indicated in the plot with the red box.

Figure 1. Details of the measurement procedure : (a) schematic representation of RGA measurement with simultaneous EUV scanning. Each line is exposed at constant scan speed, but EUV intensity is changed from line to line; (b) time registration of RGA signal at a mass related to PAG; (c) chemical yield of PAG (as defined by the incremental RGA increase at start of a line scan) as function of EUV dose exposed.

Besides the exposure with EUV (as illustrated in Fig. 2 (a)), it is possible to combine the RGA measurements with low energy electron exposures. A preliminary version of this methodology was described earlier [15] and is now more refined. The exposure sequence is very similar to that of Fig. 2 (a), but low energy electron (2-80 eV) exposures are used instead of EUV exposures. In this case electron energy is changed from line to line at constant electron current (number of electrons). For such an experiment, similar chemical yield results can be obtained, which will be discussed below.

2.3 Materials

In this work, the investigation is focused on chemical reactions of CAR materials. First, a model CAR material was used with chemical composition as shown in Fig. 3. This chemistry is similar to an ESCAP resist from 248nm lithography, but has shown good printing performance under EUV (dense line-space pattern with a resolution of 18nm half-pitch at $\sim 27\text{mJ/cm}^2$). In order to facilitate the interpretation of the chemical reaction observed by RGA outgassing, the material was provided in different formulations: polymer-only, polymer+PAG, polymer+PAG+Q.

Figure 3. Model CAR material used in the investigation on CAR chemical reactions. Besides the full composition polymer+PAG+Q, it was also provided in more simple compositions polymer+PAG and polymer-only.

Second, in addition to the model resist, commercial resists were explored. For these the details of their formulation was unknown, however, some materials were also supplied in more simple formulations, e.g. polymer-only.

3. RESULTS

Equivalent to DUV lithography, where the majority of absorbed photons are expected to photochemically convert PAG to acid, the ideal scenario in EUV for the CAR is that all the secondary electrons generated by the photons and of resonant energy are used for acid formation only. However that is the ideal and may not be reality. In this section, the RGA based method is applied to identify all the reactions that are actually taking place in the resist. This is done first on the open model resist of Fig. 3, but also on commercial resists with unknown formulations.

3.1 Model CAR material

3.1.1 Full spectrum RGA measurement

Given the model resist with chemistry as shown in Fig. 3, the expected reaction products to be measured by RGA upon exposure with EUV are (molecular mass of full species is given between brackets) :

- From decomposition of the PAG cation : benzene (amu78), toluene (amu92), di-phenyl sulfide (amu186), phenyl p-tolyl sulfide (amu200)
- From acid-related deprotection of polymer (from carboxyl group) : isobutene (amu56)

Experimental RGA full spectrum testing confirmed that these species are present in the outgassing, however also CO₂ (amu44) is found. Since the model resist was also provided in polymer-only composition, RGA testing on this sample revealed the CO₂ outgassing in similar intensity, but with isobutene at lower intensity suggesting deprotection without acid catalysis. So, this result confirms (or suggests) that scission reactions from EUV exposure on the polymer chain occurs [16], and in this particular case, as proposed on Figure 4, scissions on the carboxyl group that are related with a PG-scission, and a CO₂-scission. The PG-scission seems to be a similar reaction result as that of the acid-related deprotection (when PAG is present), but as it was observed for polymer only formulation, it means it is likely caused by resonant energy 2nd electrons.

Figure 4. Schematical representation of the scission reactions that are observed when exposing the polymer-only model resist with EUV.

Figure 5. Contrast curve comparison of the model resist (with chemistry as shown in Fig. 3), exposed with either 248nm or EUV. Dose-to-clear is very close, however at high EUV dose, the resist shows polymerization issues (non-solubility), which are not present in 248nm

The CO₂-scission is then a subsequent scission of the remainder of the carboxyl group on the polymer main chain. It can be expected that this CO₂ scission could have significant impact on the over-all polymer properties. On one hand, it is

known that if this CO₂ scission is leaving a carbon radical in the polymer chain, then different polymer chains can start to cross-link [16], potentially leading to an insoluble crosslinked network if a lot of these reactions take place. On the other hand, since the hydrophilic unprotected carboxyl group on the polymer chain is driving the dissolution in aqueous solvent, the absence of that group due to scissions is expected to influence the solubility switch of the polymer, potentially deteriorating it. So, these two mechanisms induced by the CO₂-scission are expected to deteriorate the solubility of exposed polymer.

An easy way to demonstrate that these two mechanism are playing a significant role is to perform a contrast curve with a large range of EUV dose. In fig.5, a dose to clear around 10mJ/cm² is observed, but if with a continuous increase of the dose up to more than 1000mJ/cm², the resist is showing evidence of non-solubility, which is likely a result of the CO₂ based polymerization. Surprisingly, this is not the case if we perform a similar contrast curve using 248nm exposure, where the first D2C is observed at a similar dose (comparison within experimental error), but no insolubility is observed at high dose. In order to understand this difference, we performed low energy electron measurement.

3.1.2 Low energy electron induced chemical yield

In addition to the full RGA spectrum measurements, low energy electron testing has been done on the different model resist formulations. As explained above, the resist is scanned and exposed with selected electron energy in between 1-80 eV, while simultaneously (fast) RGA acquisition is done on the specific masses related to reaction products. In this way chemical yield can be obtained as function of the electron energy. Since the low energy electrons are injected in the resist from outside, the interpretation of electron-matter interaction and the ongoing reactions is much more complex especially for very low energies 1-10eV [17], however, this kind of measurements seem in particular interesting to determine the electron activation energy for a reaction, i.e. the minimum electron energy required to observe a significant reaction response [15].

Results of these measurements are summarized in Fig. 6. This plot is a combination of measurements done on polymer-only, and on the polymer+PAG composition of the model resist. As discussed below, the two reactions that were observed on polymer-only formulation are the electron scission reaction on the protection group and the CO₂ group. As can be seen in Fig. 6, these scission reactions start to increase significantly at ~12 eV and ~15 eV respectively. These energies are significantly larger than the energy of 248 nm (~5 eV) or 193 nm (~6.5 eV), which could explain why these kinds of scission reaction are not present at these wavelengths. The sample containing PAG permitted to determine the activation energy for PAG decomposition, at ~5 eV, which is in line with 248 nm exposure where similar energy is used, allowing PAG activation.

Figure 6. Results of chemical yield measurements using low energy electron exposures.

Also visible in Fig. 6, the response of chemical yield as function of electron energy is fairly linear when energy is higher than the activation energy. It needs further investigation how to interpret this trend, since a lot of parameters play a role here. Firstly, the resist volume where reactions occur using low energy electrons is localized very close to the top of the

resist layer, but the penetration depth is depending on the electron energy due to differences in mean free path. Therefore, higher energy electron interacts with a larger volume, potentially triggering a larger chemical response. Also, one electron injected in the resist at energy of e.g. 50 eV might not induce direct chemical reactions, but will generate a number of lower energy daughters that will be able to trigger chemical response.

3.1.3 EUV photon induced chemical yield and contrast curves

As is shown so far, the interaction of EUV photons with the model CAR resist is a combination of PAG decompositions and acid related reactions on one side, and on the other side electron scission reactions of which some of them can cause polymerization. In this section, the balance of all of these reactions upon exposure with EUV will be investigated, and their relation to their characteristic contrast curve.

The starting point in the investigation is the polymer-only formulation of the model resist, on which RGA chemical yield measurements were done according to the method of Fig. 2. As indicated above, this involves only PG and CO₂ scission reactions, and the chemical yield of these reactions as function of EUV dose is given in Fig. 7(a). As expected, there is an increasing trend for both of them as function of dose. Fig. 7 (b) shows the ratio of CO₂ yield to PG yield is very constant (~ 0.2) over a fairly large dose range. This suggests that it can be assumed that scission based reaction on the polymer will always be proportional, even when PAG and/or Q are added to the polymer. So for this polymer, every observed CO₂ scission should always go together with approximately 5 PG reactions.

Figure 7. EUV induced chemical yield results for the various compositions of the model resist; (a) chemical yield for polymer-only shows increasing trend for scission reactions as function of dose; (b) the ratio of scission reaction is fairly constant over dose, per CO₂ scission there are $\sim 5\times$ PG scissions; (c) repeat of plot (a) in smaller dose range; (d) EUV induced chemical yield for polymer+PAG; the expected fraction of PG-scission by calculation out of the CO₂, is added in the plot; (e) EUV induced chemical yield for polymer+PAG+Q; for (d) and (e) the dose conditions that result in dose-to-clear are marked by D2C.

When PAG is added to the polymer, the chemical yield of the CO₂ scission is comparable to that of polymer only, as can be seen by comparing Fig. 7 (d) (polymer+PAG) to Fig. 7 (c) (polymer-only adjusted in scale). Obviously, there is now also chemical yield for the PAG decomposition reaction, as well as a high chemical yield for PG. This chemical yield for

PG is expected to be a combination of acid-related deprotection combined with scission reactions on the polymer. Assuming the 5x ratio between the CO₂ scission and the PG scission, it is possible to calculate the expected chemical yield for the PG scission, and compare this to the measured total PG. This calculation suggest that ~85% of the detected deprotections are related to acid-related deprotections, while ~15% are related to direct scission.

When in addition quencher is added, the chemical yield for the various reactions are as shown in Fig. 7 (e). The behavior as function of dose is similar for PAG and for CO₂, but the measured total PG is significantly lower, which is consistent with a portion of the acid produced is quenched by the quencher before being able to react with the PG. Therefore the ratio of acid related PG deprotections to electron PG scissions is now changed to ~60%/40%. Since the EUV tested wafers can get further PEB and development afterwards, the chemical yield of the different conditions can also be compared at similar D2C imaging condition. At dose to clear, the absolute amount of reactions for PAG, CO₂, and total PG are higher for polymer+PAG+Q than for the polymer+PAG.

Complementary to the RGA based information gained, contrast curve measurement are done on the different compositions of the model resist, which enables to understand how the chemical yields result in simple imaging performance after PEB and development. The results of these tests are shown in Fig. 8.

The characteristic contrast curve for the polymer-only sample is in agreement with the observed PG-scission based deprotection process : at sufficiently high EUV dose (~200 mJ/cm² in this case), there is sufficiently PG-scission to develop the polymer (note that there is no impact of PEB here). However, at slightly higher EUV dose of ~300 mJ/cm², there is already first signs of insolubility issues due to CO₂-based polymerization described earlier. When PAG is added to the polymer, the contrast curve shows the expected high sensitivity of the resist (dose-to-clear less than 2 mJ/cm²), yet the polymerization at high dose starts at same dose as for polymer-only. This in line with the RGA observations, and confirms that solubility issues are not influenced by the PAG. When quencher is added, the sensitivity of the materials decreases, and similarly the polymerization dose is fairly in line with the other samples.

Figure 8. EUV contrast curves for the different compositions of the model resist (see text)

3.2 Commercial CAR materials

In addition to the model resist, a number of commercial CAR formulations were investigated in a similar way. Although these commercial resists are expected to be of the type polymer+PAG+Q, the exact chemistry could be much more complicated, due to incorporation of absorbing units, polymer-bound PAG, photo decomposable base quenchers, sensitizers, etch-resistant functional groups, etc. [18] Moreover, the details of the chemistry of all materials involved in proprietary information, therefore the RGA spectrum from the full commercial resist, is typically difficult to interpret.

However, it is helpful for the interpretation, if the commercial resist is provided in minimum two versions :

- Polymer-only : in most cases this will reveal the scission based reactions, that possibly can lead to polymerization
- Full resist : by subtraction of the polymer only reactions, the acid related reactions will become more clear.

The provision of any additional composition (e.g. polymer with PAG only) will off course help further the interpretation.

An example of the RGA interpretation of ongoing reactions in a commercial resist is given in Fig. 9. This resist was provided in three versions : polymer-only, polymer+PAG, and full resist formulations. In the upfront full spectrum analysis of the three resist compositions, it was found that besides a clear PAG decomposition and acid related PG deprotection, the polymer-only also showed evidence of direct PG-scission and CO₂-scission.

As can be seen in Fig. 9, the chemical behavior of the ongoing reactions is fairly in line to what is observed with the model resist in Fig. 7 (c-e). For the polymer only (Fig. 9 (a)), there is a fairly proportional increase of the chemical yield observed both for the electron PG-scission as well as for the CO₂-scission reaction product. By adding PAG, the PAG decomposition reaction becomes clear, as well as an increase of the (mostly acid related) PG reactions (Fig. 9 (b)). For the full resist (Fig. 9 (c)), the CO₂ and the PAG reactions are fairly similar as for the polymer+PAG version, however there are much fewer PG reactions. Since the dose-to-clear for this version is significantly higher than the polymer+PAG version, it is likely due to quenching reactions.

Figure 9. Chemical yield results for the commercial resist provided in three compositions. Note that although the chemistry of the commercial resist is unknown and expected to be significantly different to the model resist of Fig. 7, the trends in most reaction yields are very similar.

Since the RGA based analysis on this commercial resist provides fairly similar interpretation as for the model resist, it was decided to test if the RGA analysis would also reveal changes in chemical reactions between different generations of commercial resist based on similar chemistry. This test was done on three commercial CAR materials (called resp. CAR1, CAR2, and CAR3, all from same supplier), which seem to have similar chemistry in terms of PG and PAG, based on RGA spectra analysis. Moreover, these commercial resist formulations were imec champion NXE performing resists in 2012, 2015, and 2017 respectively. Similar as for the commercial resist of Fig. 9 (c), it was possible to evaluate the number of PAG reactions at dose-to-clear, as well as the number of CO₂-scissions at dose-to-clear. The former is expected to have beneficial impact on the printing performance (acid formation), while the latter less (polymerization).

The result of this comparison at dose-to-clear is shown in Fig. 10. Towards PAG reactions, the three generations of resists show a large increase in the number of PAG-reactions. For CAR2, this increase is about 5x compared to CAR1, while for the more recent CAR3, the number of PAG reactions is more than 10 times higher than for CAR1. On the other hand the chemical yield for the CO₂ polymerization reaction is not changing that much from one resist generation to another. In conclusion even without direct knowledge of the formulation changes throughout the three generations of commercial resists, the RGA based method is able to quantify improvements in the main reactions as well as side reaction.

Figure 10. Chemical yield results for the commercial resist provided in three compositions.

4. SUMMARY AND CONCLUSIONS

In this paper, a characterization technique to investigate the chemical interaction of photons and electrons is discussed. The method uses direct measurement of the reaction products of the chemical interaction. This approach is based on Residual Gas Analysis (RGA), which measures and analyzes the outgassing products related to the ongoing reactions upon exposure. This measurement is thus combined with either EUV exposures or low energy electron injections, to get as much as possible information on the ongoing reactions.

This method was used firstly to investigate a model CAR where the resist formulation were known, and where the material was supplied in different compositions, e.g. polymer-only, polymer+PAG, and polymer+PAG+Q. The measurement not only resolved information on the expected acid related reactions from the photo acid generator (PAG) and protection groups, but also revealed that EUV induced secondary electrons can do direct scission reactions on the polymer, where some of them can lead to polymerization reactions, resulting in insolubility. Moreover, the measurement can quantify the ratio between the different ongoing reactions, which could be confirmed by contrast curve measurements.

Based on learnings on the model resist, the measurement technique has also been applied on commercial resists, where actual resist chemistry composition is not known. Despite this fact, it was found that valuable information could still be deduced to distinguish between acid related ongoing reactions and direct scission of reaction on the base polymer and to quantify their relation. Moreover, different generations of commercial resists based on similar chemistry platform were compared, which revealed that improvements in printing performance could be correlated with a quantified increase of PAG reaction yield, with a fairly constant polymerization reaction yield.

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