To bake or not to bake... : the role of prebake in the EUV resist process

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ABSTRACT

In photoresist processing a prebake is traditionally used after coating the photoresist on a wafer to drive off solvents in the resist, resulting in a more stable film. In comparison to other stages of the lithography process (e.g. the conditions of exposure and post-exposure events), limited attention is paid in the prebake optimization for the EUV application. In this work, investigation is done to clarify its role for the case of chemically amplified resists (CAR). Compared to the earlier DUV application, this resist is used at significantly smaller thicknesses and has a significantly different composition in terms of photo acid generator (PAG) and quencher types and concentration.

In a first screening, a commercial CAR material – coated on Si – was investigated towards contrast changes at different prebake temperatures. It was found that lower temperature can result in adhesion failure when substrate conditions are not optimized for adhesion. With proper adhesion promotion however, it was found that prebake temperature could be lowered significantly or even omitted, without clear change in contrast. Using model resists in combination with residual gas analysis (RGA), it was found that the use of photo-decomposable quencher could be responsible for maintaining contrast to lower bake temperatures. In a second investigation, an assessment towards outgas risk was done when using resists at lower prebake temperatures in EUV scanner environment. Finally, the printability of commercial CAR was tested on the NXE3400 EUV scanner at different prebake temperatures. This was done by coating the CAR on two available underlayer materials: spin-on-glass and deposited underlayer. Results show that the prebake temperature could be reduced or even omitted without a clear deterioration in process window, line edge roughness and defectivity. It was found that proper choice of underlayer material could even improve slightly the printing performance at lower prebake condition.

Keywords: EUV lithography, photoresist, chemically amplified resist, prebake, softbake, PAB, underlayer, contrast.

1. INTRODUCTION

Traditionally a prebake is used in lithography after coating the photoresist on a wafer to drive off solvents from the resist, resulting in a more stable film [1]. This process is also called softbake or post-apply bake (PAB). In comparison to other stages of the lithography process (e.g. post-exposure events like post-exposure bake or developer), limited attention is paid in the prebake optimization, and often the general guideline is used to maximize the prebake conditions to remove the solvent, taking however in mind the limits to prevent changes in the resist polymer and diffusion of critical photo-components, like PAG and quencher in the example of a chemically amplified resist (CAR). The few investigations were mostly done for lithography technologies where relative thick photoresist was used [2], however entering the era of EUV lithography this could be significantly different. EUV film thicknesses are in the order 15-50 nm which is rather comparable to the size of the involved resist molecules and their diffusion lengths. Therefore, solvents should be able to escape the film much easier than in thicker technologies. As a result, it could be claimed that a prebake might become less critical in the EUV case, provided that any residual solvent outgassing should not be a concern for the scanner environment. Besides its impact on the solvent, the prebake could also result in diffusion or aggregation events of critical photo-components (PAG and quencher). This could distort the resist contrast and could result in resist profile and/or increase linewidth roughness changes. Such effects have been observed also when different kinds of underlayer (UL) materials are combined with a CAR [3-4], therefore prebake could be an additional dimension in the parameter space that is able to change the printability and/or defectivity. Finally, by applying low or high prebake temperature, the cohesive forces

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between resist and underlying substrate could be altered, which can have an impact on adhesion and defectivity. The impact of prebake temperature on all these items will be discussed below, with focus on the CAR.

2. CHEMICAL EVALUATION AND CONTRAST CURVES OF CAR-ON-SI

In this section the impact of prebake temperature was evaluated using the EUV Tech outgas tool at imec. This experimental set-up was introduced at imec for resist outgas qualification and can used for the exposure of contrast curves at EUV wavelength and for measurement of outgassing by residual gas analysis (RGA) [5]. These functionalities were used for an initial screening of the of prebake temperature on CAR. The CAR materials involved in this part are on one hand side a commercial resist and on the other hand on model resists (with known details of chemistry).

2.1 Prebake dependency of commercial CAR.

In the investigation first a commercial CAR material was investigated, which was standard available on the NXE3400 EUV cluster and having 32nm pitch printing capability.

The contrast curves for this material at different prebake temperatures when coating directly on Si, are shown in Fig. 1(a). For the standard prebake of 130 °C, the contrast curve shows a slope at the solubility switch, which is related to resist contrast [6]. For a higher temperature of 150 °C this slope does not change significantly, only a small shift of the curve to lower dose is present. For lower than standard prebake temperatures a much steeper slope is observed in the contrast curve, quasi-independent of the prebake temperature and even in the case where no prebake is applied. More detailed microscope inspection of the wafers at lower prebake temperature shows however a signature of film delamination when dose is sufficiently high (see picture inset of Fig. 1(a)). At the lower dose where film thickness shows a gradual decrease in the curve, the film is merely intact and only local film delamination is observed at the edges of the exposed region, while at higher dose the film is fully delaminated. When the prebake is at standard 130 °C or higher, no delamination is observed. The delamination seems to point out a first important property that is affected by the prebake temperature, namely adhesion to the underlying substrate.

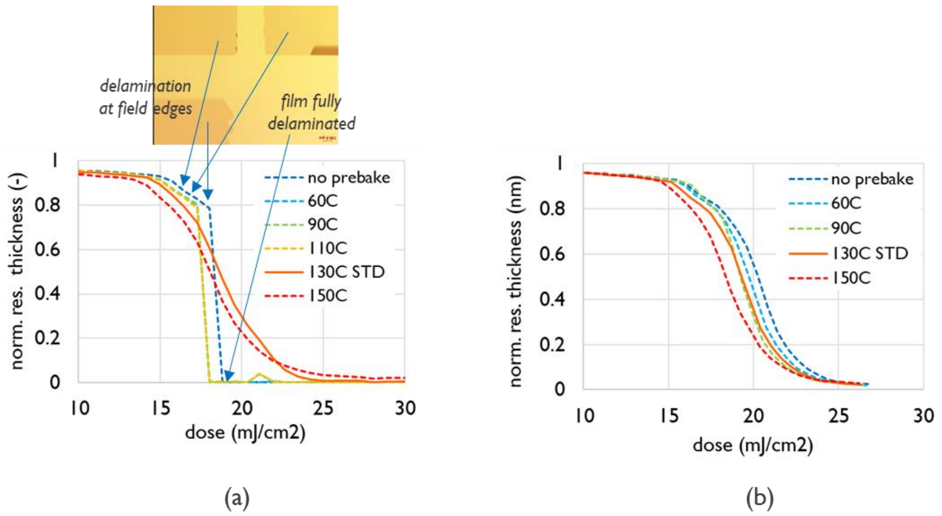

Figure 1: Contrast curve evaluation of the commercial CAR: (a) evaluation without HMDS prime; the picture onset illustrates that in this case film delamination was affecting the contrast curve result; (b) evaluation with HMDS prime shows that a minor difference in contrast is for lower than standard prebake temperatures.

Important to note in this context is that adhesion on Si can be altered by a proper adhesion promotor, for example a well-known method used on Si is a treatment with HMDS (hexa methyl disilazane). When such a treatment is done prior coating the commercial CAR, the contrast curve shape at lower prebake temperatures is very similar to that at the standard 130 °C temperature. Since the small changes in contrast and sensitivity could be within the dose control error of the EUV Tech outgas tool, a more detailed and accurate testing was done on the NXE3400 EUV scanner to explore the feasibility of this material towards printing at lower prebake temperatures, which will be described in Section 4.

2.2 Prebake investigation on model CAR materials

To understand the rather insensitive response of the contrast curve of the commercial CAR for different prebake temperatures, the contrast curve was also evaluated for selected model resists. The results are summarized in Fig. 2.

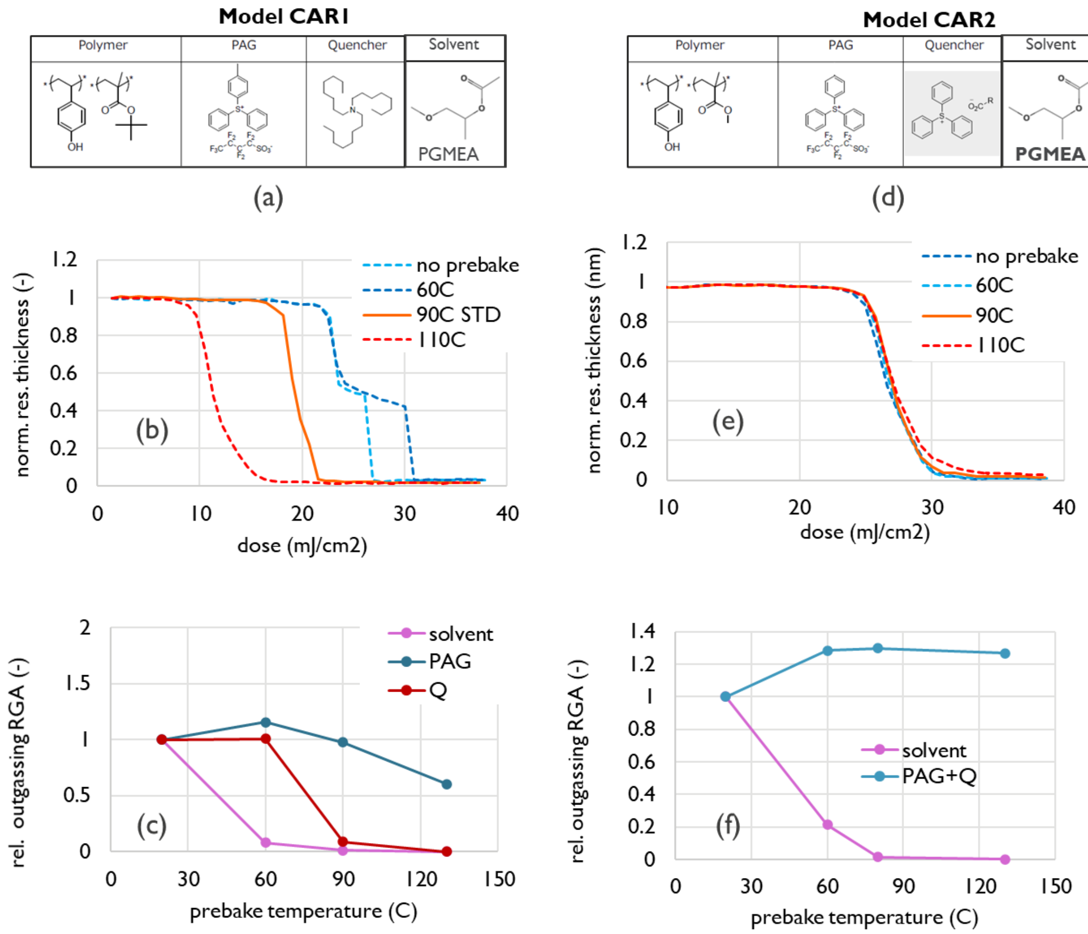

Figure 2: (a-c) chemical formulation, prebake dependency of contrast curve and outgassing for older type model EUV resist with amine-based quencher; the contrast of this material is highly sensitive to prebake variations; (d-f) chemical formulation, prebake dependency of contrast curve and outgassing for newer type model EUV resist with photo-decomposable quencher; this material is much less sensitive to prebake variations.

A first model resist that is investigated has chemistry as indicated in Fig. 2 (a). Although this formulation is still quite simple and probably closer to a commercial DUV CAR than an EUV CAR, it had proven its usefulness in earlier work [7]. The result of contrast curve measurement of this resist on HMDS primed Si is given in Fig. 2 (b) for the different prebake temperatures applied. In contrary to the commercial CAR material of section 2.1, the contrast curves are now very dependent on the prebake temperature. For prebake temperatures lower than standard (90 °C), the resist shows a decrease in sensitivity (which is even more pronounced in the lower half of the film) while for higher prebake temperatures, the sensitivity is increased significantly. To understand the chemical reactions involved at the different prebake temperatures, RGA is used to analyze the outgassing of the different components during EUV exposure. The masses from the RGA spectrum that were used to detect resp. the solvent, PAG and quencher were 72amu, 78amu, and 254amu. The result of this component outgassing as function of prebake temperature is shown in Fig. 2 (c), where the outgassing is normalized to the case without any prebake. This graph shows that solvent outgassing decreases rapidly with prebake temperature. At 60 °C solvent outgassing is reduced to about 10% of its original state (no prebake), while at 90 °C and higher, the RGA signal for solvent is only around 1% or less. For PAG there is a less clear trend (the lower amount of PAG measured at 130 °C prebake could be due to a degree of polymer densification), but clearer is the distinct decrease of quencher signal from prebake 60 °C to 90 °C. This suggests that quencher material is volatile at higher prebake temperatures. The behavior of quencher outgassing explains in large amount the variability observed in the contrast curves. Comparing the case of no prebake to that prebake at 60 °C, the main difference is likely only the removal of solvent from the film. The large shoulder in the lower part of the contrast curve suggests further on an accumulation of quencher material in the lower part of the film. When the film is prebaked at 90 °C, the RGA suggests that part of the quencher is removed from the film, with possible redistribution of the (remaining) quencher, which makes the slope of the contrast curve straighter. Further increase of bake to 110 °C (or 130 °C) results in more quencher removal, which shifts the contrast curve to lower doses.

This evaluation with the first model resist shows that the prebake temperature can be critical for the chemistry platform using this older type of quencher. Since the commercial CAR was less sensitive to prebake variations, it suggests that the type of quencher in the newer material is significantly different, for example of a photo-decomposable quencher type, which is believed to be used in more recent EUV CARs. To test this, a new model CAR is evaluated with chemistry depicted in Fig. 2 (d). The main difference is the replacement of the amine-based quencher to a photo-decomposable quencher. Note that the molecular structure of this quencher has similarity with the PAG, both have the same cation structure, which upon exposure will result in similar decomposition. As a result of the similar reaction mechanisms, the RGA outgassing analysis depicted in Fig. 2 (f) cannot distinguish anymore between PAG related and quencher related outgassing, but it shows that its “total” outgassing is unchanged over the range of investigated prebake temperatures. The solvent removal is fairly in line with the first model resist, i.e. at 60 °C prebake temperature there is only ~20% solvent remaining, and is almost completely disappeared at 80 °C. More relevant to printing performance is the response of the contrast curves at different temperatures (Fig. 2. (e)), which show very minor differences. Together with the commercial CAR investigated in Section 2.1 this suggests opportunities to use significantly lower prebake temperature for currently available CAR chemistries, in particular ones containing photo-decomposable quenchers.

3. OUTGAS ASSESSMENT FOR LOW PREBAKE TEMPERATURE CONDITIONS

The previous screening suggested that the prebake temperature could be significantly decreased without implication to resist contrast, including the possibility to omit the prebake. This could however result in larger solvent outgassing during exposure in the EUV scanner, therefore this needs an assessment in what amount this can be a risk for the EUV scanner.

Resist outgassing of CAR and its potential impact on scanner contamination has been investigated in detail in the past and required initially a test protocol with a specification on the maximum allowable cleanable and non-cleanable contamination [5]. After detailed evaluation, no real contamination concern could be found for regular CAR chemistries, and therefore the requirement for testing CAR was stopped in 2015. Note that – at the supplier recommended prebake – the outgassing is then mostly generated by decomposed PAG/quencher, and room-temperature deprotection of the polymer (all are expected to by hydrocarbon). A typical outgas risk assessment of a material with unknown chemistry can be done also using RGA and by summing up the measured outgas rates in different mass ranges, for example range amu1-50 for low molecular mass structures, amu51-100 for medium structures, and amu101-200 for high molecular mass structures. In addition, it is known that higher molecular masses will contribute more to contamination than the lower molecular masses [5].

Having this in mind, the prebake related outgas risk assessment was done for the commercial CAR and for the model CAR with photo-decomposable quencher and results are shown in resp. Fig. 3 (a) and (b). At the standard prebake of these materials (resp. 130 °C and 90 °C), the outgas spectrum consists of a combination of the three mass ranges, mostly low and medium category masses. When evaluating the lower prebake temperatures, the figure shows that only the fraction of low molecular mass is increased, which suggests a low contamination risk. Moreover, the figure shows also that a low prebake at 60 °C gives an outgas spectrum close to that of the standard prebake.

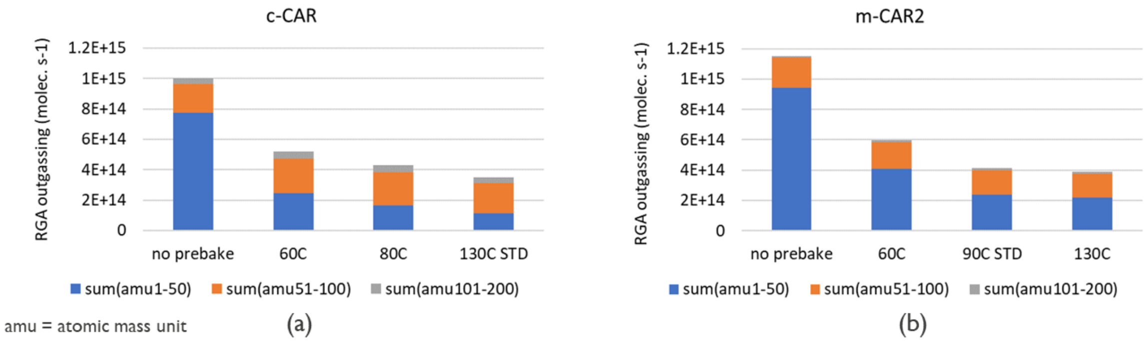

Figure 3: Outgassing as function of prebake temperature where masses from outgas spectra are grouped in three categories : low molecular mass amu1-50, medium molecular mass amu51-100, and high molecular mass amu101-200; (a) result for commercial CAR; (b) result for model CAR with photo-decomposable quencher. In both cases the increase in outgassing for lower prebake temperatures is solely due to low molecular mass contribution and is fairly limited for a low temperature prebake of 60 °C (compared to standard prebake temperature).

4. CONTRAST, CD PROCESS WINDOW AND DEFECTIVITY ON NXE3400

In the initial screening above, it was found that the contrast of the commercial CAR remained fairly constant when decreasing the prebake temperature significantly, which would suggest similar printing performance. In this section this was evaluated in more detail on NXE3400. To be in line with regular patterning where an underlying stack is included, the CAR prebake investigation was done on two available UL materials : a spin-on-glass/spin-on-carbon (SOG/SOG) stack and a deposited UL.

4.1 Prebake investigation of CAR on SOG/SOC

In a first evaluation, the commercial CAR from section 2.1 was investigated on NXE3400 and applied on a SOG/SOC stack of resp. 10nm and 65nm thickness. Results of this evaluation are summarized in Fig. 4. In a first experiment, a contrast curve was made on the SOG/SOC for the case of standard prebake and the case where the prebake was omitted. As can be seen, the two curves showed almost perfect overlap, which would suggest very similar CD printing performance. This was confirmed by the NXE3400 exposures of 32nm pitch line/space patterns. The CD process window was found to be very similar, with comparable failure mechanisms at edge of process window as observed in SEM. As an example, the exposure latitude is shown in Fig. 4 (b), showing no clear differences amongst the different prebake conditions. Also, defectivity results given in Fig. 4 (c) show similar cliffs for resp. line breaks and bridges for the two prebake temperatures tested. Further on, the unbiased line-edge-roughness (LER) was found to be very similar also.

4.2 Prebake investigation CAR on deposited UL

In a second evaluation, the commercial CAR was applied on deposited UL. Two thicknesses of resp. 10nm and 5nm were tested of this material. This NXE3400 testing was based on contrast curve only and results are shown in Fig. 5. In Fig. 5 (a) an overview of all contrast curve measurements is shown for the different prebake temperature and thicknesses involved. Unlike the case of SOG, there is a noticeable change in the curves amongst the range of prebake temperature. For further analysis and quantification, the contrast curves for the 10nm deposited UL are plotted normalized in Y and scaled in log(dose) in X-axis (Fig. 5 (b)), which is the typical representation for analyzing the contrast as linear slope. As can be seen, the contrast is identical for prebake conditions, however with decreasing prebake temperature, the sloped part of the curves shifts to lower doses. So, with this UL a small benefit of applying lower prebake temperature is observed, i.e. the sensitivity of the CAR material is increased. This shift in sensitivity is shown more clearly in Fig. 5 (c) by plotting the dose-to-clear of the CAR with the prebake temperature. In this graph also the result on a 5nm deposited UL is included for two selected prebake temperatures. It shows that the sensitivity is not affected by the UL thickness, with identical trend for the different temperatures applied. Although not yet investigated in more detail, this suggests that a process optimization is possible by adjusting the prebake temperature, but likely this is UL and photoresist dependent.

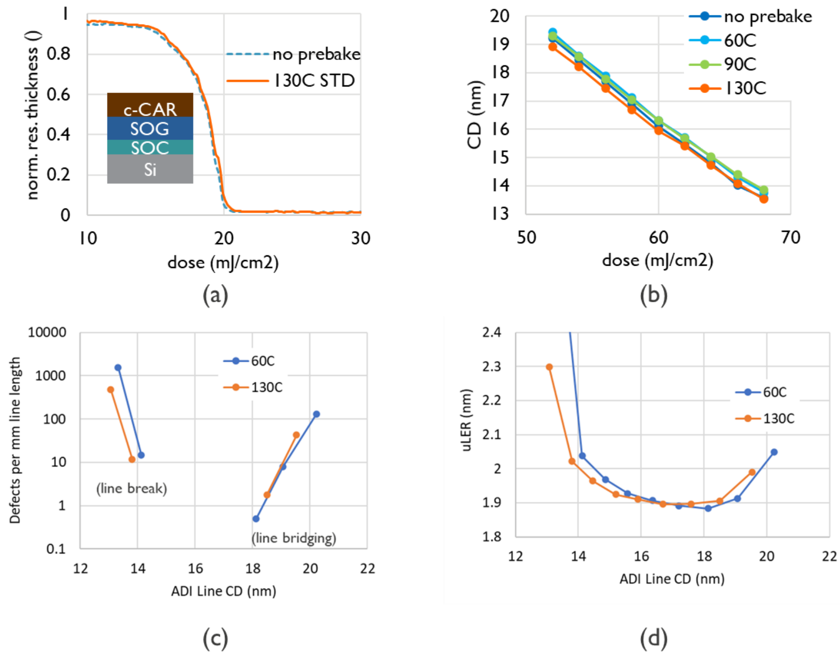

Figure 4: Prebake investigations of the commercial CAR on SOG/SOC done on NXE3400: (a) contrast curve, (b) exposure latitude for 32nm pitch features, (c) stochastic defectivity, and (d) unbiased LER. All show no clear changes of printing performance towards lower prebake conditions.

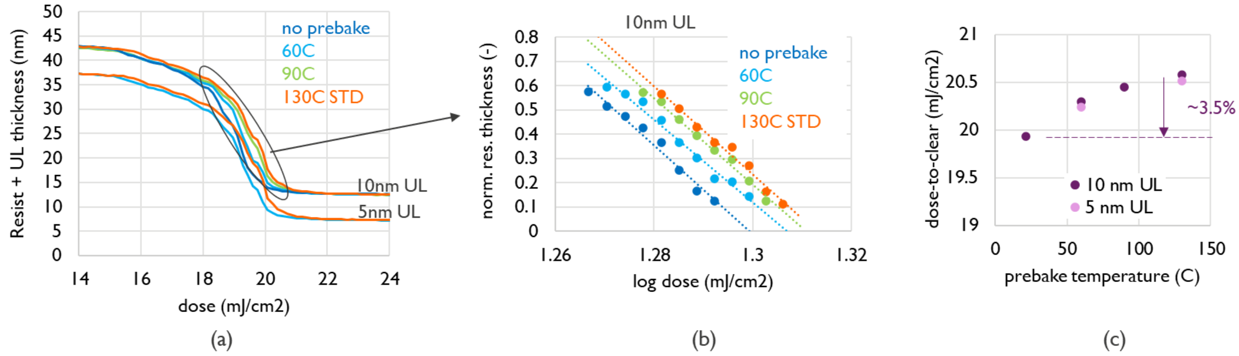

Figure 5: Prebake investigations of the commercial CAR on deposited UL done on NXE3400: (a) contrast curve on resp. 10nm and 5nm UL, (b) resist contrast analysis for 10nm UL, and (c) dose-to-clear versus prebake temperature. By reducing the prebake temperature a small increase of CAR sensitivity can be obtained which is independent of the UL thickness.

5. SUMMARY AND CONCLUSIONS

In this paper, the impact of prebake temperature has been investigated for EUV CAR materials.

In a first screening, the resist contrast of a commercial CAR material was investigated at different prebake temperatures after coating on Si. It was found that lower temperature can result in adhesion failure when substrate conditions are not optimized towards adhesion. However, with proper use of adhesion promotor (like HMDS or use of underlayer) the prebake temperature could be lowered significantly or even omitted, without clear change in contrast. Using residual gas analysis (RGA) in combination with model resists, it was found that the use of photo-decomposable quencher could be responsible for that. In a second investigation, an assessment towards outgas risk was done for using such resists at lower prebake temperatures, showing that lower prebake temperatures are only affecting outgassing of low molecular weight. Finally, the commercial CAR was evaluated on the NXE3400 EUV scanner for printability changes at different prebake temperatures. This was done by applying the CAR on two available underlayer materials : SOG/SOC and deposited underlayer. In both cases, it was found that the prebake temperature could be reduced or even omitted without a clear deterioration in process window, line edge roughness and defectivity. It was found that proper choice of underlayer material could even improve slightly the printing performance at lower prebake condition.

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