Volume 86, Issues 4–6 April/June 2009 ISSN 0167-9317

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MICROELECTRONIC ENGINEERING

Micro and Nano Fabrication

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The 34th International Conference on Micro- and Nano-Engineering (MNE)

September 15–18, 2008
Athens, Greece

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Microelectronic Engineering 86 (2009) 783–786

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

# Consequences of non-standard bleaching on microlithographic performance

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ARTICLE INFO

*Article history:*
Received 21 September 2008
Received in revised form 23 November 2008
Accepted 23 November 2008
Available online 4 February 2009

*Keywords:*
Optical bleaching
Resist
Process latitude
Photolithography

ABSTRACT

Photobleaching of photoresists has been at the core of high resolution relative to a particular exposure wavelength, but the accelerated advancements dictated by the sharp economic considerations of the roadmap, as well as the complexity of exposure-material-technology triad, made photobleaching a secondary subject of interest. However, the still-strong innovation in optical photolithography as well as the emergence of biomedical microdevices as a major market for microfabrication, suggest that the reconsideration of the photobleaching as a main modulator of lithographic performance is fully warranted. This study reports on the photolithography simulations which implemented a non-standard bleaching behaviour, both documented previously and hypothetical. We show that minute changes in the photobleaching behaviour can result in important changes in the performance of the lithographic process latitude, speed and resist profile.



## 1. Introduction

The advance of photolithography towards deep submicron resolution requires constant breakthroughs in the fields of equipment, materials, and technologies. Sharp economic imperatives require that this technological advancement is ruthlessly driven by the semiconductor industry roadmap, which require both dramatic improvement of present technologies [1] as well as the exploration of entirely new approaches [2]. While this planned acceleration of technological development is the key for the present healthy state of semiconductor industry, despite numerous challenges, ranging from physics to economics, the need for just-in-time alignment of the three components of semiconductor equipment, materials, and technologies often results in less-than-optimal technological solutions. Moreover, these economic imperatives appear to favour a decision chain running down from exposure equipment to materials to technologies. Consequently, much innovation in the materials and technology occurs within severe limitations. Revealingly, the photobleaching process, which is part of the photolithography cornerstone, is often addressed in the late stages of innovation, as much of the optical lithography technologies, from contrast enhancement layers to the recent double patterning, addresses the manipulation of the local optical absorption. To this end, an interesting question arises: for a photopolymer that bleaches upon exposure, and if we would be free of limitations related to the materials and exposure sources, what would be the bleaching behaviour that maximises the lithographic performance, e.g., process latitude, speed or resist profile?

This question is not so inconsequential as it looks at a first glance. First, optical lithography delivers continuously new technologies, in which the fine tuning of optical absorption is in great need. Second, it has been observed that non-standard bleaching behaviour can be exhibited by Image Reversal resists [3,4] and possibly by *all* resists at particular wavelengths [5]. Third, the micropatterning for biomedical microdevices offers the opportunity of revisiting many issues initially faced by photolithography, as their fabrication is less restrictive regarding resolution and pattern complexity, but has other critical imperatives, e.g., patterning on the very large areas.

To this end, we present here simulation results regarding the impact of actual and hypothetical bleaching processes on the lithographic performance of photopolymers.

## 2. Methodology

### 2.1. Experimental

Two photoresist systems have been used: (i) a classical, photoacid generating DNQ/novolak resist (AZ1350J) and its Image Reversal formulation, i.e., doped with imidazole derivatives; and (ii) a photobase generating resist comprising a copolymer containing O-acryloyl acetophenone oxime and a 4-acryloyl-oxybenzophenone sensitizer (AAPO). Both resists have been spin coated, dried, exposed with various energies and their respective absorption spectra have been collected. Fig. 1 represents the absorption spectra vs. exposure energy for standard DNQ resist; its Image Reversal formulation; and AAPO resist, respectively. The evolution of the bleaching of the DNQ/novolak systems (top two images) is represented in terms of transparency, while the much higher optical

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doi:10.1016/j.mee.2008.11.101

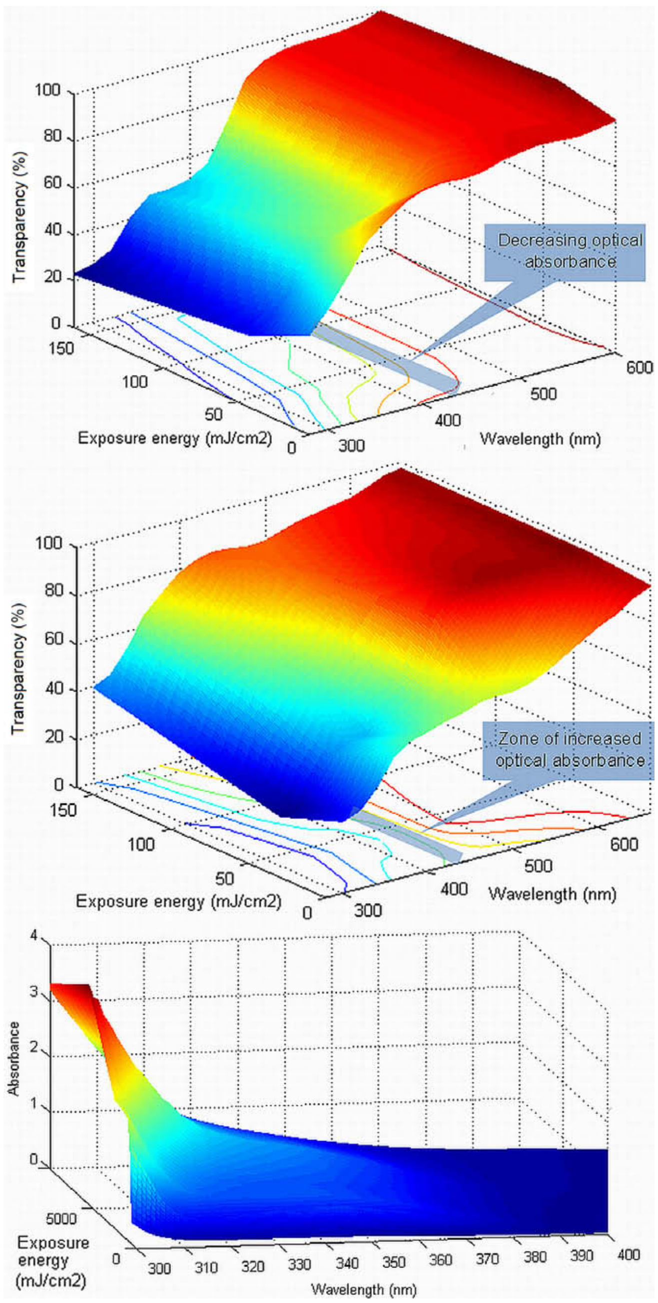


**Fig. 1.** The evolution absorption spectra for a standard (DNQ/novolak resist, top image), and two non-standard (i.e., DNQ/novolak Image Reversal formulation – middle image; and AAPO system – bottom image) bleaching processes.

absorption of AAPO recommended the representation on an exponential scale (absorbance in units, rather than %). For the DNQ/novolak system the non-standard bleaching behaviour is more apparent if one compares the evolution of transparency vs. energy as projected on the $x$–$y$ (horizontal) plane of Fig. 1. While the transparency curves (e.g., red, brown, yellow)[1] go up with exposure energy for standard resist (top image in Fig. 1), the similar curves have a pronounced dip at low exposure energies for Image Reversal resist (middle image in Fig. 1). AAPO system presents a similar behaviour (bottom image in Fig. 1), but extended throughout the whole exposure spectrum, which manifests in a saddle-like shape of the absorbance as a function of exposure energy and wavelength. More detailed information can be found elsewhere [3–5].

*2.2. Modelling and simulation*

The photolithographic process has been modelled starting from the classical modelling of photolithography process [6], which correlates the optical absorption with the Photo-Active Compound (PAC) concentration ($M$), in turn modulated by exposure energy, has been altered to account for a more general photobleaching behaviour, as follows:

$$\mathrm{Abs}(M) = B_{\mathrm{Dill}}(1 - M^E) + A_{\mathrm{Dill}} M^F \tag{1}$$

where $A_{\mathrm{Dill}}$ and $B_{\mathrm{Dill}}$ are the classical parameters in Dill et al. model [6]; and $E$ and $F$ are new modulating parameters of a general bleaching behaviour. More elaborate functions could be conceived, e.g., involving weighing the two members of the right hand side of the Eq. (1) through additional D and (1-D) parameters, but we found that Eq. (1) can account for a large span of behaviour, as presented in Fig. 2. Within this formalism, the Dill model becomes a particular case of the Eq. (1).

The simulations used an upgraded version, which implemented Eq. (1), of an open source version of PROLITH [7], i.e., PROLITH v1.4. In order to observe the pure optical impact of different bleaching behaviour no post exposure bake or any other contrast enhancement techniques have been used. The $A$ and $B$ values are those of the classical AZ1350J photoresist. The simulations were run using different bleaching behaviours, i.e., different pairs of $E$ and $F$ parameters in Eq. (1), to obtain resist profiles (example presented in Fig. 3). Also other lithographic parameters, e.g., angle of the resist profile, line at the bottom and the top of the resist have been collected and plotted against exposure energy for their respective bleaching behaviour (Fig. 4).

## 3. Results and discussion

*3.1. Non-standard bleaching systems*

Photo-induced bleaching has been responsible, in synergy with appropriate chemistry, of the high aspect ratios of the latent image in the photoresist and consequently the high resolution for a given exposure wavelength. The mathematical model of the bleaching

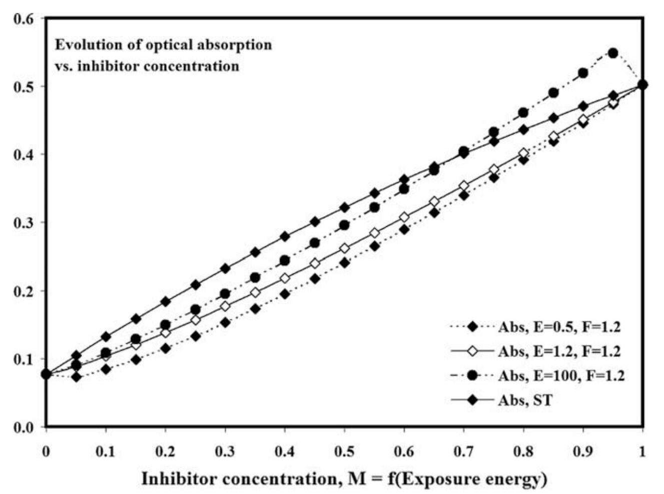


**Fig. 2.** Standard evolution of absorption with the PAC concentration ($M$) in conformity with Dills' model ($A$ and $B$ parameters as in AZ1350J photoresist) and a set of non-standard behaviours: $E$ = 100, $F$ = 1.2, similar to the Image Reversal resist (as in Fig. 1); and two hypothetical bleaching curves ($E$ = 0.5 and 1.2; $F$ = 1.2).

[1] For interpretation to colour in Fig. 1, the reader is referred to the web version of this article.

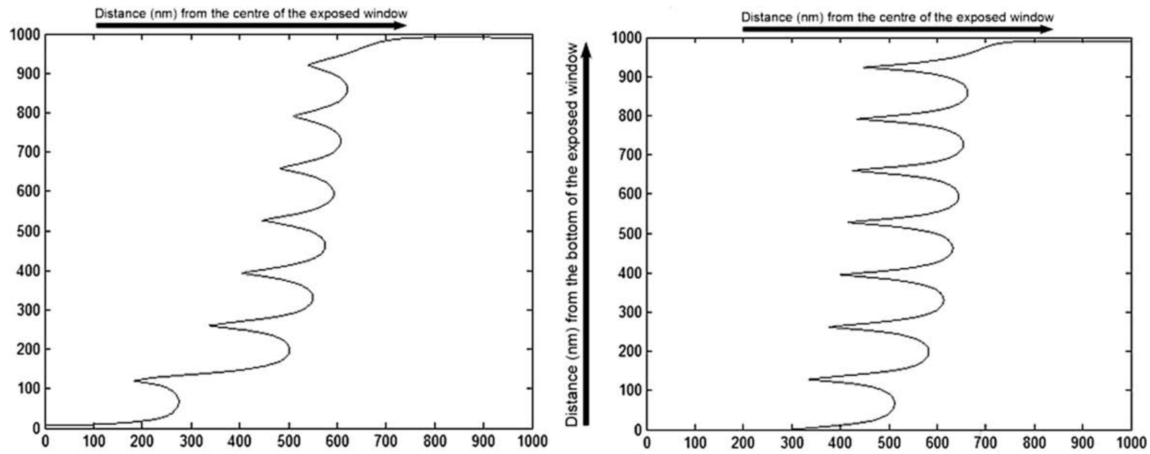


**Fig. 3.** PROLITH simulated developed resist profiles, for a standard resist (left image) and for a resist exhibiting a non-standard bleaching behaviour ($E = 100$, $F = 1.2$, cf. in Fig. 2).

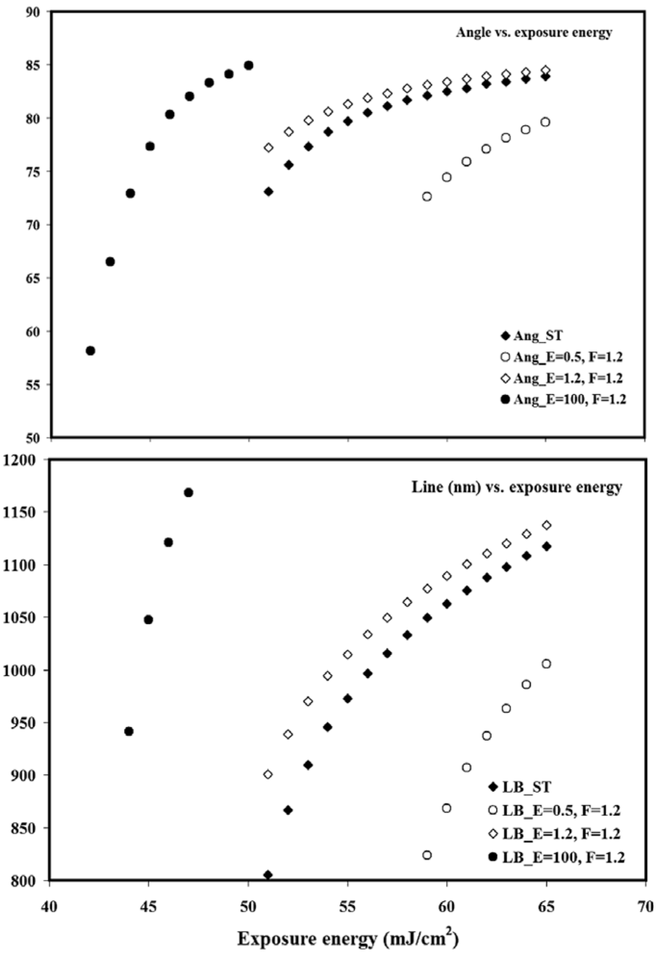


**Fig. 4.** Variation of developed resist slope (top image) and patterned line (nominal line = 1 μm) with exposure energy for various bleaching processes.

process has been elegantly described [6] in the mid 1970s and then implemented in simulation software packages, such as SAMPLE [8] and Prolith [7]. This mathematical model and simulation describe a *standard bleaching behaviour* which is specific to DNQ/novolak resists, and which consists of a monotonous decrease of the optical absorption with the decrease of the PAC concentration, which in turn decrease monotonously with the absorbed exposure energy.

We observed however long ago [3,4] that in special circumstances, Image Reversal resists exhibit a *non-standard bleaching behaviour* with beneficial effects on lithographic performance. More recently, it has been observed [5] that actually *all* resists, but at particular wavelengths not necessarily equal to exposure wavelengths, could also exhibit a non-standard bleaching behaviour. The observed non-standard bleaching behaviour consists in an *increase* of the optical absorption for low exposure energies followed by the classical monotonous decrease as in the standard model. The explanation for this behaviour can be specific, e.g., the creation of an intermediary chemical species which is more absorbent and which is further depleted by light in Image Reversal resist [4], or general, e.g., the photo-induced complex evolution of the photoresist absorption spectra containing many local absorption maxima with locations that shift during exposure [5]. For the purposes of this discussion the sources of the non-standard bleaching are however inconsequential, but it is relevant that they have been demonstrated. Fig. 1 presents the evolution absorption spectra for a standard and two non-standard bleaching processes.

Fig. 2 represents the standard evolution of absorption with the PAC concentration ($M$) in conformity with Dills' model ($A$ and $B$ parameters as in AZ1350J) and a non-standard behaviour (for $E = 100$ and $F = 1.2$) which is similar to the Image Reversal resist. For easy comparison the optical absorption values for $M = 1$ and 0, corresponding to $A$ and $B$, respectively, in the Dill model have been kept equal to those of the standard resist. Other two hypothetical bleaching curves ($E = 0.5$ and 1.2; $F = 1.2$) have been also produced. There are of course other possibilities, e.g., absorption with a maximum but always above the standard curve.

### 3.2. Impact of non-standard bleaching processes on resist profile

Fig. 3 represents the simulated developed resist profiles for a standard resist and a hypothetical one which exhibits non-standard bleaching behaviour, but which has identical optical absorption for unexposed and fully exposed resist, respectively. The resist profile for the non-standard behaviour is clearly superior in terms of slope and definition of the cleared line at the bottom of the resist. This steeper slope can be explained by the darkening of the resist on the sides of the exposed cylinder in the resist, which experience lower exposure energies at the edges of the latent image, and consequently delayed bleaching process in these regions; coupled with a quicker bleaching for higher exposure energies (Fig. 2), which accelerates the photo-induced chemistry at the centre of the image.

### *3.3. Impact of non-standard bleaching processes on process latitude and speed*

More dramatic results are revealed for the impact of non-standard bleaching on the parameters of the lithographic process (Fig. 4). The better slope of developed resist appear again when comparing the standard with non-standard, Image Reversal-like ($E = 100$ and $F = 1.2$) bleaching, and importantly these steeper slopes (∼5°) are obtained at consistently lower (∼30%) exposure energies. On the other hand, the bleaching behaviour can be modulated to reach a larger process latitude ($E = 1.2$ and $F = 1.2$) or slower lithographic process for better control ($E = 0.5$ and $F = 1.2$). It is interesting to note that minute changes in the bleaching behaviour ($E = 0.5$–$1.2$) result in important changes in the process latitude when benchmarked against the standard resist results.

## 4. Conclusions

Photo-induced bleaching in resist polymers is at the cornerstone of high resolution in photolithography, but strict economic imperatives of the roadmap make this parameter somehow embedded in material and process developments. If treated separately, the bleaching behaviour can modulate, at times dramatically, the lithography process parameters, such as speed, resist slope or process latitude. The emergence of biomedical microdevices as a major market for microfabrication on one hand, and the advanced optical nano-level lithography, in particular double patterning, offer motivations for the revisiting the issue of photobleaching for better design of lithography exposure, materials and processes. To this, end, this study demonstrates that even minute changes in the photobleaching behaviour can result in important changes in the performance of the lithographic process latitude, speed and resist profile and suggests the establishing of studies regarding non-standard bleaching behaviour as a standalone line of research.

## Acknowledgments

This study is part of the European FP6 Charged Particle Nanotechnology (CHARPAN) project. We want to acknowledge the spirited and insightful discussions with Mircea Dusa and Chris Mack and want to thank the latter for providing the PROLITH software.

## References

[1] B.J. Lin, Microelectronic Engineering 86, this issue.
[2] C.G. Wilson, Microelectronic Engineering 86, this issue.
[3] D.V. Nicolau, M. Dusa, Microelectronic Engineering 11 (1990) 557.
[4] D.V. Nicolau, M. Dusa, D. Nicolau, S. Yoshikawa, Journal Photopolymer Science and Technology 12 (1995) 187.
[5] E.P. Ivanova, J.P. Wright, D. Pham, L. Filipponi, A. Viezzoli, D.V. Nicolau, Langmuir 18 (2002) 9539.
[6] F.H. Dill, A.R. Neureuther, J.A. Tuttle, E.J. Walker, IEEE Transactions on Electron Devices ED-22 (1975) 456.
[7] C.A. Mack, Proceedings of the Society of Photo-Optical Instrumentation Engineers 538 (1985) 207.
[8] W.G. Oldham, S.N. Nandgaonkar, A.R. Neureuther, M. O'Toole, IEEE Transactions on Electron Devices ED-26 (1979) 717.