

## Review Article

Takahiro Kozawa\*

# Resist material options for extreme ultraviolet lithography

DOI 10.1515/aot-2015-0028

Received April 1, 2015; accepted June 16, 2015; previously published online July 8, 2015

**Abstract:** Owing to the worldwide efforts, the development of extreme ultraviolet (EUV) lithography has significantly progressed during the past decade. The resolution of chemically amplified resists has reached sub-16-nm region. From the viewpoint of the extendibility of EUV lithography, the development of resist materials capable of resolving sub-10-nm is an urgent task. In this review, the resist material options for EUV lithography are discussed on the basis of the EUV sensitization mechanisms after reviewing the problems for the sub-10-nm fabrication.

**Keywords:** extreme ultraviolet lithography; line edge roughness; resist; sub-10-nm.

## 1 Introduction

The development of extreme ultraviolet (EUV) lithography has been significantly progressed [1–3]. Although the source power has been the most critical issue, it has been rapidly improved in 2014. A 90-W source operation in a fab site has been reported [4]. With the progress in the development of EUV sources, the demand for the improvement of resist performance became increasingly strong. The resist materials were ranked second in the focus area for the realization of EUV lithography issued by the steering committee of EUV symposium in 2014. The wavelength of the EUV exposure tool is 13.5 nm, which is 1/14 of the wavelength of the current mainstream exposure tool, the ArF excimer laser. A significant

improvement in the resolution has been expected for EUV lithography because of the reduction in the wavelength. The resolution of EUV lithography with chemically amplified resist processes has already reached the sub-16-nm region [5, 6]. The focus of the resist development is shifting to the 11-nm half-pitch node. Also, a sub-10-nm (single nano) half-pitch fabrication has recently attracted much attention from the viewpoint of the extendibility of EUV lithography.

A highly sensitive resist, called a chemically amplified resist [7, 8], has been used in the high-volume production of semiconductor devices. Even in the sub-10-nm high-volume production, the mechanism of chemical amplification is still attractive from the viewpoint of productivity. However, the diffusion of acid molecules is a significant concern, as is often pointed out [9, 10]. Also, the range of secondary electrons is another concern for the radiation capable of ionizing molecules, such as EUV radiation [11, 12]. Figure 1 shows the schematic drawing of chemically amplified resist process. The role of resist materials is the conversion of optical images to real binary images used for device fabrication. On the other hand, the role of photons is the transfer of the information recorded on a mask and the energy required for the chemical change of resist materials. In the conversion process, the energy of photons is absorbed by resist materials. Using the absorbed energy, an acid image is generated through the decomposition of acid generators (photosensitive compounds). With the supply of thermal energy, the acids catalyze the deprotection of the resist polymer, the polar groups of which are partially protected with nonpolar groups. A resist image is obtained by developing the chemical image generated through the acid-catalytic reaction. The resist performance is basically determined by the efficiency of this conversion process.

For the realization of sub-10-nm half-pitch fabrication, the stochastic effects such as line edge roughness (LER) is a serious concern. It has been reported that LER is expressed using the chemical gradient  $dm/dx$  as [13]

$$\text{LER} \approx \frac{f_{\text{LER}}}{dm/dx}. \quad (1)$$

\*Corresponding author: Takahiro Kozawa, The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan, e-mail: kozawa@sanken.osaka-u.ac.jp

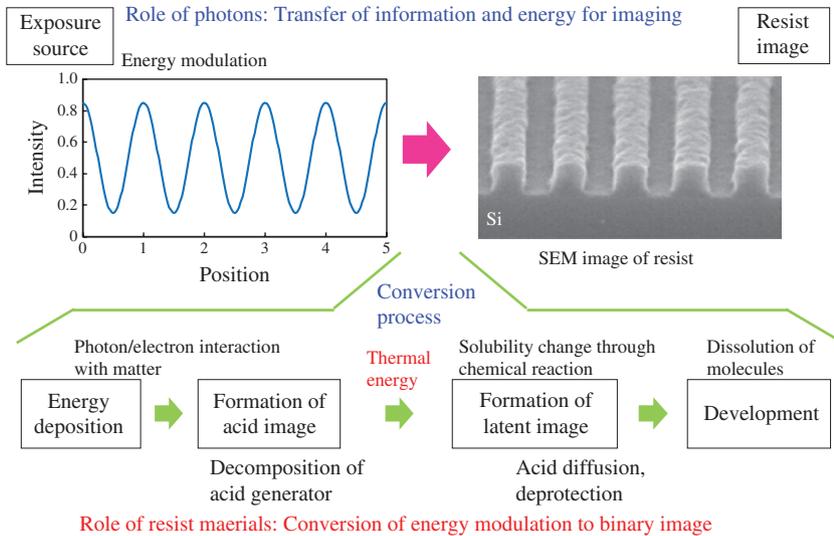
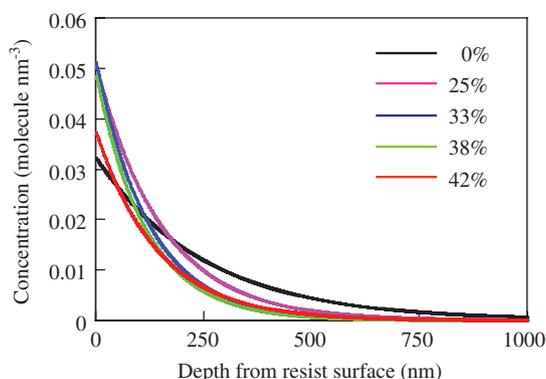


Figure 1: Schematic drawing of chemically amplified resist process.

Here,  $x$ ,  $f_{\text{LER}}$ , and  $m$  are the distance in the direction vertical to line patterns, the proportionality constant (development factor) and the normalized protected unit concentration, respectively. The main factors that determine the chemical gradient are the exposure dose (sensitivity) [14], the optical image quality such as contrast [15] and half-pitch (resolution) [16], the absorption coefficient of the resist [17], the quantum efficiency of acid generation [17], and the effective reaction radius for deprotection [18]. The effective reaction radius for deprotection represents the efficiency of acid catalytic chain reaction in chemically amplified resists. The development factor is related to the dissolution kinetics and morphology change during rinse and dry processes, including the fluctuation of the number of protected units connected to a polymer molecule [19]. Among these factors, it is well known that the relationships between resolution, LER, and sensitivity are trade-offs [20, 21]. These tradeoff relationships are the most serious problems in the development of resist materials. Also, these relationships indicate that the potential performance of chemically amplified resists is mainly determined by the absorption coefficient, the quantum efficiency of acid generation, the effective reaction radius for deprotection, and the development factor. In other words, the increase in the efficiency of conversion process is essentially required for the improvement of resist performance. This is also true for the improvement of resolution. A significant improvement in the efficiency of conversion process is required for the realization of sub-10-nm fabrication.

## 2 Absorption (energy deposition on resist material)

In the energy range of ionizing radiations such as EUV, the energy of photons (or particles) is mainly absorbed by resist polymers because the molecular selectivity of photoabsorption is largely lost in this energy range and because the resist polymer is the main constituent of the resist. This fact means that an efficient reaction mechanism for the sensitization of photosensitizers is required for the development of highly sensitive resists even if the energy of photons is not directly absorbed by the photosensitizers. The energy deposited on the resist polymer should be efficiently used for the acid generation in chemically amplified resists. The reaction mechanism is later explained. The increase in the absorption coefficient of the polymer is anyway an effective method for the development of high performance resists for ionizing radiation [22]. This is a stark contrast to the resist design for deep UV light. The absorption coefficient of current resist polymers is approximately  $4 \mu\text{m}^{-1}$  [23]. Although the increase in the absorption coefficient is limited by the sidewall degradation (the increase in the angle of resist sidewall), there is a significant room for the absorption enhancement [24]. A typical atomic element with large EUV-absorption cross section is fluorine [25]. Figure 2 shows the effect of fluorine content on acid concentration in resist films [26]. By increasing the fluorine content, the acid concentration near the film surface can be increased. Metal-containing resists have recently attracted much attention from the



**Figure 2:** Depth distribution of acid concentration generated in resist films with an EUV exposure dose of  $5 \text{ mJ cm}^{-2}$ . The numerical values in % in the graph denote the percentage weight of fluorine atoms per polymer molecule.

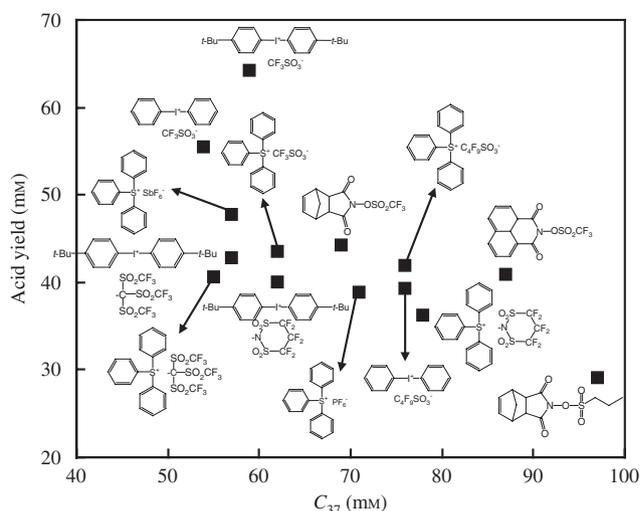
viewpoint of absorption enhancement [27, 28]. The metal-containing resists also have an advantage in the etching durability.

### 3 Radiation-induced reaction (acid generation)

In chemically amplified EUV resists, the acids are generated through radiation-induced reactions. The energy of EUV photons is mainly used for the ionization of polymer molecules, that is, the charge separation between radical cations (mainly polymer radical cations) and electrons. In the acid generation processes, the electrons (negatively charged species) are converted to the counteranions of acids. On the other hand, the polymer radical cations (positively charged species) are converted to the protons of acids. The quantum efficiency of acid generation has been evaluated to be 2–6 [29, 30].

#### 3.1 Anion generation

Upon exposure to EUV radiation, the acid generators are decomposed through the dissociative electron attachment with thermalized electrons and produce the anions of acids. Figure 3 shows the relationship between  $C_{37}$  parameter and acid yield generated in poly(4-hydroxystyrene) (PHS) films with 5 wt% acid-sensitive dye (Coumarin6) and 0.4 M acid generators [31]. The yield of anions corresponds to that of acids in PHS films because the radical cations of PHS are efficiently deprotonated [32].  $C_{37}$  is a parameter, which describes the reactivity of chemical



**Figure 3:** Relationship between  $C_{37}$  parameter and acid yield generated in PHS films with 5 wt% acid-sensitive dye (Coumarin6) and 0.4 M acid generators.

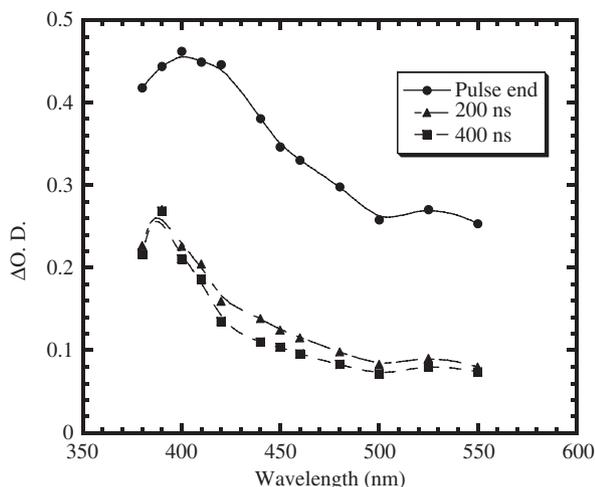
compounds with presolvated electrons generated in a solution.  $C_{37}$  of acid generators evaluated in tetrahydrofuran solution represents the reactivity of acid generators with the thermalized electrons before solvation. A small value of  $C_{37}$  indicates high reactivity. Figure 3 indicates that  $C_{37}$  well correlates to the acid yield generated in solid PHS films dispersed with acid generators. The acids are efficiently generated in typical resist polymer films despite the random energy deposition. A reason for the efficient acid generation is that the thermalized electrons react selectively with acid generators. The increase in the reactivity of acid generators with thermalized electrons is effective for the enhancement of resist sensitivity. The quantum efficiency of acid generation in chemically amplified EUV resists depends on the acid generator concentration [29, 30]. The quantum efficiency increases with the acid generator concentration and shows the tendency of saturation in the high concentration region of acid generators because its maximum value is basically limited by the number of secondary electrons generated by single EUV photon [29]. Beside the contribution to the acid generation, the acid generators play an important role in the suppression of resolution blur by replacing the mobile thermalized electrons with immobile anions [12]. The concentration of 0.2–0.3 mol  $\text{dm}^{-3}$  (approximately 10 wt% in a TPS-Tf equivalent) is required to avoid a serious resolution blur in chemically amplified EUV resists. This is a reason why EUV resists require a higher concentration of acid generators than KrF and ArF resists [12]. With the reduction in feature size, the increase in acid generator concentration is essentially required not only to meet the sensitivity

requirement but also to meet the LER requirement, particularly, in the sub-10-nm resolution region [33]. However, the increase in acid generator concentration is not an easy task because an increase in acid generator concentration generally degrades the dissolution kinetics of resist materials. Also, the increase in the concentration of small molecules such as acid generators is likely to decrease the activation energy for acid diffusion. The decrease in the activation energy for acid diffusion leads to the decrease in the effective reaction radius for deprotection. The segregation of acid generators to the interfaces [34] and the inhomogeneous distribution of acid generators due to the aggregation are also problems. A polymer, to which the acid generators are bound through a covalent bond, is being developed to circumvent these problems [35–37].

### 3.2 Proton generation

Although the anions of acids are generated through the reaction of acid generators with thermalized electrons, the generation of protons is necessary for the acid generation. Upon the exposure to KrF or ArF excimer laser, the protons are generated mainly from the acid generator molecules [38]. However, the origin of the positive charge of protons is that of radical cations generated through the ionization in EUV resists. In the case of PHS, a typical backbone polymer for chemically amplified EUV resists, the protons are generated through the PHS radical cations. Figure 4 shows the transient absorption spectra obtained in the pulse radiolysis of 100 mM PHS-benzonitrile solution, monitored at the pulse end, and 200 and 400 ns

after the electron pulse [39]. Note that the spectrum at the pulse end largely overlapped with the transient absorption spectra of solvent intermediates. An absorption peak observed at the wavelength of 390 nm at 200 and 400 ns after the pulse is due to a phenoxy radical of PHS [39, 40]. The decaying absorption from 400 to 550 nm is due to a radical cation of PHS [39]. The protons are generated in PHS films when the radical cation of PHS is decomposed to the phenoxy radical of PHS. The efficiency of deprotonation depends on the molecular structures. A hexafluoroalcohol is also an effective proton source [41]. The acid generation mechanisms in the absence of an effective proton source such as the phenol units of PHS have been also investigated [42]. As an example of such case, the following mechanism has been reported for a triphenylsulfonium salt. The triphenylsulfonium salt is decomposed through the dissociative electron attachment to generate a diphenyl sulfide, a phenyl radical, and an anion. The positive charge generated through the ionization is transferred to diphenyl sulfide. The radical cation of diphenyl sulfide reacts with a phenyl radical to generate a proton. Thus, a proton generation mechanism should be designed in the chemically amplified EUV resists. The proton yield has been estimated to be less than the anion yield in current chemically amplified EUV resists because of the inefficiency in the conversion process of radical cations to protons. In other words, the proton yield has limited the quantum efficiency [43]. The increase in proton generation efficiency is an important issue in the design of next-generation materials [44].



**Figure 4:** Transient absorption spectra obtained in pulse radiolysis of 100 mM PHS solution in benzonitrile. The sample was deaerated by  $\text{SF}_6$  bubbling before irradiation.

## 4 Acid catalytic chain reaction

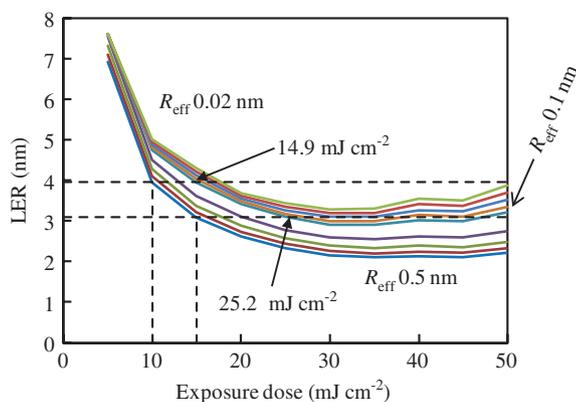
The efficiency of acid catalytic chain reaction in chemically amplified resists is expressed using an effective reaction radius for deprotection. The effective reaction radius corresponds to the efficiency of deprotection per unit acid diffusion length. We have investigated the effective reaction radius for deprotection in state-of-the-art resists on the basis of sensitization and reaction mechanisms of chemically amplified EUV resists. The effective reaction radius for deprotection was 0.06–0.16 nm [19, 45–48]. The effective reaction radius should be increased for the improvement of resist performance because the chemical gradient increases with the effective reaction radius for deprotection. However, the fluctuation of protected unit distribution expressed by the standard deviation of the number of protected units connected to a polymer molecule after PEB also increases by increasing the effective

reaction radius [49]. The effective reaction radius of 0.4 nm is a reasonable target of the resist development [49]. The effective reaction radius for deprotection can be increased by decreasing the activation energy for deprotection and/or by increasing the activation energy for acid diffusion. For the increase in the activation energy for acid diffusion, the increase in anion size, anion-matrix interaction, and polymer  $T_g$  is a general measure.

## 5 Termination of chemical reaction

In the early stage of development, chemically amplified resists did not contain quenchers; therefore, the resolution blur caused by the acid diffusion has been a significant concern [9, 10]. By adding basic compounds, called quenchers, the acid catalytic chain reactions induced in chemically amplified resists have been controlled. Initially, it was reported that the addition of quenchers improves the stability of resist performance in the presence of the airborne basic compounds [50, 51]. Later, it was reported that the addition of quenchers improves the resolution [52–54]. Since then, quenchers have been used to enhance the resolution.

The effects of the efficiency of neutralization on the resist performance were investigated using a simulation on the basis of the reaction mechanisms of chemically amplified resists. Figure 5 shows the exposure dose dependence of LER estimated from the chemical gradient [55]. With the increase in the effective reaction radius for neutralization, LER decreased. To obtain the same LER

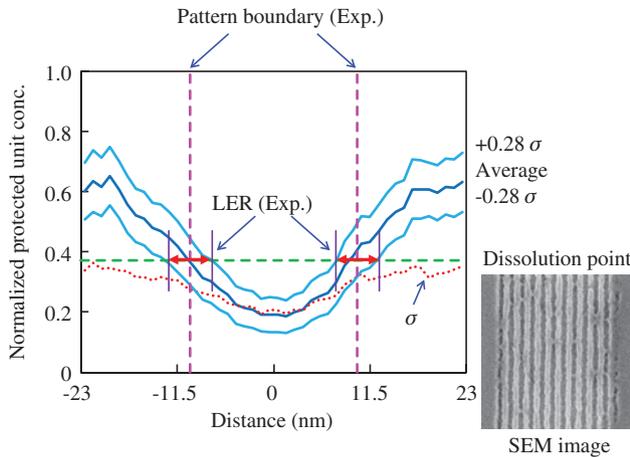


**Figure 5:** Exposure dose dependence of LER. LER was estimated from the chemical gradient. The proportionality constant between LER and chemical gradient was assumed to be 0.2. The effective reaction radius for neutralization ( $R_{\text{eff}}$ ) was changed from 0.02 to 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4, and 0.5 nm. The quencher concentration, PEB time, and dissolution point were optimized for each exposure dose to maximize the chemical gradient at the intended boundary.

obtained using the resist with a 0.5-nm effective reaction radius upon exposure to 10  $\text{mJ cm}^{-2}$ , the required exposure dose was 14.9  $\text{mJ cm}^{-2}$  for the resist with a 0.1-nm effective reaction radius. Similarly, to obtain the same LER obtained using the resist with a 0.5-nm effective reaction radius upon exposure to 15  $\text{mJ cm}^{-2}$ , the required exposure dose was 25.2  $\text{mJ cm}^{-2}$  for the resist with a 0.1-nm effective reaction radius. This indicates that the efficiency of quenchers is important not only for the resolution enhancement and LER reduction but also for the sensitivity improvement. The efficiency of the termination of chain reaction strongly affects the resist performance for the resist, which utilizes the chemical amplification mechanism. The high performance of chemically amplified resists owes the high efficiency of acid-base neutralization [55]. Because the acid catalytic chain reaction is not the only solution for chemical amplification, the other mechanisms such as radical chain reaction [56] can be considered. In such case, we have to simultaneously consider the efficient termination mechanism equivalent to the acid-base neutralization.

## 6 Development and rinse

The proportionality constant  $f_{\text{LER}}$  (development factor) in eq. (1) has been estimated to be 0.14–0.31 for state-of-the-art resists [19, 45–48]. The development factor is related to the fluctuation of the solubility of the polymer molecule. Figure 6 shows the distribution of protected units at half the height of resist patterns after PEB and the corresponding SEM image [19]. The line marked ‘Average’ represents the average protected unit concentration after PEB. The dotted line marked ‘ $\sigma$ ’ represents the standard deviation of the number of protected units connected to a polymer molecule after PEB, normalized by the initial number of protected units per polymer molecule before PEB. The lines marked ‘Ave.  $\pm 0.28 \sigma$ ’ are the protected unit concentrations after adding 0.28  $\sigma$  to and subtracting 0.28  $\sigma$  from the average protected unit concentration, respectively. The double-sided arrows represent LER, evaluated from the SEM image shown in Figure 6. The vertical dashed lines represent the boundaries between lines and spaces, also evaluated from the SEM image. The horizontal dashed line is the estimated threshold of protected unit concentration for the dissolution of resist polymer. The protected unit concentration fluctuates with the standard deviation shown in the graph, which depended on the position in the horizontal direction vertical to the line pattern. The  $\pm 0.28 \sigma$  fluctuation corresponds to LER in the case of the resist shown in Figure 6. The fluctuation in the protected



**Figure 6:** Distribution of protected units at half the height of resist patterns. The protected units of the polymer before PEB were randomly distributed. The vertical axis represents the number of protected units per polymer normalized by its initial value. The half-pitch was 23 nm. The exposure dose was 16.0 mJ cm<sup>-2</sup>.  $\sigma$  was normalized by the initial number of protected units per polymer. The experimental line width and LER and an SEM image are also shown.

unit concentration causes a shift in the crossing point of the latent image with the dissolution threshold. Thus, the proportionality constant  $f_{\text{LER}}$  in eq. (1) increases with the protected unit fluctuation  $\sigma$  and with the factor of  $\pm 0.28$  (dissolution factor). The dissolution factor is considered to depend on the size of dissolution unit (e.g. the molecular size and the degree of aggregation) and dissolution kinetics. However, their details are still unknown. Because such relationship was evaluated using 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution, the possibility of the reduction of  $f_{\text{LER}}$  or dissolution factor cannot be excluded. Recently, the direct observation method of development and rinse processes was enabled using a high-speed AFM [57, 58]. The details of development and rinse processes are currently being investigated.

## 7 Summary

The performance of chemically amplified resists has significantly improved during the past decade despite the trade-off relationships among resolution, LER, and sensitivity. The resolution has reached sub-16-nm half-pitch region. However, the tradeoff relationships are still the most serious problem for the development of resist technology capable of resolving sub-10-nm features. The strategy of material design is the enhancement of chemical gradient [the denominator of the right-hand side of eq. (1)].

The chemical gradient can be enhanced by increasing resist absorption, the quantum efficiency of acid generation, and the effective reaction radius for deprotection. The reduction in LER through the improvement of resist process after PEB basically corresponds to the reduction in  $f_{\text{LER}}$  [the numerator of the right-hand side of eq. (1)].  $f_{\text{LER}}$  can be reduced by decreasing the protected unit fluctuation and the dissolution factor. Because the details of the dissolution mechanisms from the narrow region is particularly important in the next-generation resist materials. The chemically amplified resists are still the most promising materials for sub-10-nm fabrication owing to the efficient termination mechanism of the chemical reaction.

## References

- [1] H. Kinoshita, K. Kurihara, Y. Ishii, and Y. Torii, *J. Vac. Sci. Technol. B* 7, 1648 (1989).
- [2] S. Wurm, *Jpn. J. Appl. Phys.* 46, 6105 (2007).
- [3] D. Simone, A. M. Goethals, F. Roey, T. Zheng, P. Foubert, et al., *J. Photopolym. Sci. Technol.* 27, 601 (2014).
- [4] A. Yen, presented at SPIE 9428 (2014).
- [5] K. Sakai, M. Shiratani, T. Fujisawa, K. Inukai, K. Sakai, K. et al., *Photopolym. Sci. Technol.* 27, 639 (2014).
- [6] S. Tarutani, H. Tsubaki, T. Fujimori, H. Takizawa, and T. Goto, *J. Photopolym. Sci. Technol.* 27, 645 (2014).
- [7] H. Ito and C. G. Willson, *Polym. Eng. Sci.* 23, 1012 (1983).
- [8] H. Ito, *Microlithography/Molecular Imprinting* (Springer, Heidelberg, 2005) *Adv. Polym. Sci. Ser.*, Vol. 172, p. 37.
- [9] J. Nakamura, H. Ban, K. Deguchi, and A. Tanaka, *Jpn. J. Appl. Phys.* 30, 2619 (1991).
- [10] L. Schlegel, T. Ueno, N. Hayashi, and T. Iwayanagi, *J. Vac. Sci. Technol. B* 9, 278 (1991).
- [11] T. Kozawa, S. Tagawa, H. B. Cao, H. Deng, and M. J. Leeson, *J. Vac. Sci. Technol. B* 25, 2481 (2007).
- [12] T. Kozawa, S. Tagawa, and M. Shell, *J. Appl. Phys.* 103, 084306 (2008).
- [13] T. Kozawa, H. Oizumi, T. Itani, and S. Tagawa, *Appl. Phys. Express* 3, 036501 (2010).
- [14] T. Kozawa and S. Tagawa, *Jpn. J. Appl. Phys.* 48, 106504 (2009).
- [15] T. Kozawa and S. Tagawa, *J. Photopolym. Sci. Technol.* 22, 51 (2009).
- [16] T. Kozawa and S. Tagawa, *Appl. Phys. Express* 2, 056503 (2009).
- [17] T. Kozawa, *J. Photopolym. Sci. Technol.* 25, 625 (2012).
- [18] T. Kozawa and S. Tagawa, *Jpn. J. Appl. Phys.* 49, 06GF02 (2010).
- [19] T. Kozawa, J. J. Santillan, and T. Itani, *Appl. Phys. Express* 6, 026502 (2013).
- [20] G. M. Gallatin, *Proc. SPIE* 5754, 38 (2005).
- [21] D. Van Steenwinckel, R. Gronheid, F. Van Roey, P. Willems, and J. H. Lammers, *J. Micro/Nanolithogr. MEMS MOEMS* 7, 023002 (2008).
- [22] T. Kozawa, S. Tagawa, H. Oizumi, and I. Nishiyama, *J. Vac. Sci. Technol. B* 24, L27 (2006).

- [23] N. N. Matsuzawa, H. Oizumi, S. Mori, S. Irie, S. Shirayone, et al., *Jpn. J. Appl. Phys.* 38, 7109 (1999).
- [24] T. Kozawa, K. Okamoto, J. Nakamura, and S. Tagawa, *Appl. Phys. Express* 1, 067012 (2008).
- [25] B. L. Henke, E. M. Gullikson, and J. C. Davis, *At. Data Nucl. Data Tables* 54, 181 (1993).
- [26] H. Yamamoto, T. Kozawa, S. Tagawa, H. Yukawa, M. Sato, et al., *Appl. Phys. Express* 1, 047001 (2008).
- [27] J. Jiang, S. Chakrabarty, M. Yu, and C. K. Ober, *J. Photopolym. Sci. Technol.* 27, 663 (2014).
- [28] J. Passarelli, M. Sortland, R. D. Re, B. Cardineau, C. Sarma, et al., *J. Photopolym. Sci. Technol.* 27, 655 (2014).
- [29] R. Hirose, T. Kozawa, S. Tagawa, T. Kai, and T. Shimokawa, *Appl. Phys. Express* 1, 027004 (2008).
- [30] C. D. Higgins, C. R. Szmanda, A. Antohe, G. Denbeaux, J. Georger, et al., *Jpn. J. Appl. Phys.* 50, 036504 (2011).
- [31] K. Natsuda, T. Kozawa, K. Okamoto, A. Saeki, and S. Tagawa, *Jpn. J. Appl. Phys.* 48, 06FC05 (2009).
- [32] H. Yamamoto, T. Kozawa, A. Nakano, K. Okamoto, Y. Yamamoto, et al., *Jpn. J. Appl. Phys.* 43, L848 (2004).
- [33] T. Kozawa, J. J. Santillan, and T. Itani, *Jpn. J. Appl. Phys.* 53, 106501 (2014).
- [34] T. Fukuyama, T. Kozawa, S. Tagawa, R. Takasu, H. Yukawa, et al., *Appl. Phys. Express* 1, 065004 (2008).
- [35] R. D. Allen, P. J. Brock, Y. H. Na, M. H. Sherwood, H. D. Truong, et al., *J. Photopolym. Sci. Technol.* 22, 25 (2009).
- [36] J. W. Thackeray, V. Jain, S. Coley, M. Christianson, D. Arriola, et al., *J. Photopolym. Sci. Technol.* 24, 179 (2011).
- [37] S. Tarutani, H. Tamaoki, H. Tsubaki, T. Takahashi, H. Takizawa, et al., *J. Photopolym. Sci. Technol.* 24, 185 (2011).
- [38] J. L. Dektar and N. P. Hacker, *J. Am. Chem. Soc.* 112, 6004 (1990).
- [39] A. Nakano, T. Kozawa, K. Okamoto, S. Tagawa, T. Kai, et al., *Jpn. J. Appl. Phys.* 45, 6866 (2006).
- [40] E. J. Land and G. Porter, *Trans. Faraday Soc.* 59, 2016 (1963).
- [41] H. Yamamoto, T. Kozawa, K. Okamoto, A. Saeki, S. Tagawa, et al., *J. Vac. Sci. Technol. B* 24, 1833 (2006).
- [42] Y. Komuro, H. Yamamoto, K. Kobayashi, Y. Utsumi, K. Ohomori, et al., *Jpn. J. Appl. Phys.* 53, 116503 (2014).
- [43] H. Yamamoto, T. Kozawa, A. Nakano, K. Okamoto, S. Tagawa, et al., *Jpn. J. Appl. Phys.* 44, 5836 (2005).
- [44] T. Kozawa, J. J. Santillan, and Toshiro Itani, *Jpn. J. Appl. Phys.* 53, 116504 (2014).
- [45] T. Kozawa, H. Oizumi, T. Itani, and S. Tagawa, *Jpn. J. Appl. Phys.* 49, 066504 (2010).
- [46] T. Kozawa, H. Oizumi, T. Itani, and S. Tagawa, *Jpn. J. Appl. Phys.* 49, 116505 (2010).
- [47] T. Kozawa, H. Oizumi, T. Itani, and S. Tagawa, *Jpn. J. Appl. Phys.* 50, 076503 (2011).
- [48] T. Kozawa, H. Oizumi, T. Itani, and S. Tagawa, *Jpn. J. Appl. Phys.* 50, 126501 (2011).
- [49] T. Kozawa, J. J. Santillan, and T. Itani, *Jpn. J. Appl. Phys.* 54, 036507 (2015).
- [50] Y. Kawai, A. Otaka, A. Tanaka, and T. Matsuda, *Jpn. J. Appl. Phys.* 33, 7023 (1994).
- [51] K. Asakawa, T. Ushirogouchi, and M. Nakase, *Proc. SPIE* 2438, 563 (1995).
- [52] T. Ushirogouchi, K. Asakawa, M. Nakase, and A. Hongu, *Proc. SPIE* 2438, 609 (1995).
- [53] T. B. Michaelson, A. R. Pawloski, A. Acheta, Y. Nishimura, and C. G. Willson, *Proc. SPIE* 5753, 368 (2005).
- [54] W. D. Hinsberg, F. A. Houle, M. I. Sanchez, M. Morrison, G. M. Wallraff, et al., *Proc. SPIE* 3999, 148 (2000).
- [55] T. Kozawa, J. J. Santillan, and T. Itani, *Jpn. J. Appl. Phys.* 53, 06JC02 (2014).
- [56] M. Shirai, K. Maki, H. Okamura, K. Kaneyama, and T. Itani, *J. Photopolym. Sci. Technol.* 23, 687 (2010).
- [57] J. J. Santillan, K. Yamada, and T. Itani, *Appl. Phys. Express* 7, 016501 (2014).
- [58] J. J. Santillan and T. Itani, *Jpn. J. Appl. Phys.* 52, 06GC01 (2013).



**Takahiro Kozawa**

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan,  
[kozawa@sanken.osaka-u.ac.jp](mailto:kozawa@sanken.osaka-u.ac.jp)

Takahiro Kozawa is a Professor of the Institute of Scientific and Industrial Research (ISIR), Osaka University. He received his BS and MS degrees in Nuclear Engineering from the University of Tokyo and a PhD degree in Chemical Engineering from Osaka University in 1990, 1992, and 2003, respectively. His work is mainly focused on beam-material interaction and beam-induced reactions in resist materials.