



Computer simulation of resist profiles at electron beam nanolithography

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ABSTRACT

In this paper, resist behavior peculiarities in nanolithography is studied. Experimental data for the development rate dependence on the exposure dose is presented and used for numerical simulation of the developed profiles at electron beam nanolithography (EBL). These data concerns the most important nanolithography organic resist – polymethyl methacrylate (PMMA), chemically amplified resist CAMP6 and for the inorganic resist hydrogen silsesquioxane (HSQ). For a study of the nonlinear resist behavior during the development process, simulated resist profiles in the case of delay effect for penetration of the developer in the fresh resist material are discussed. The results are obtained using a universal approach for computer simulation of predicted profiles. It is concluded that such an effect will decrease the average rate of development and could be observed only in the side wall shape of the developed profile.

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1. Introduction

In this paper some our results are presented aiming to prepare data and to get more understanding for the computer simulation of developed resist nanoprofiles at EBL. Next steps in nanoelectronics, being now in the range of 45 nm critical dimension of the produced microprocessors and memories, are connected to improvement and optimization of micro-structuring technologies and first of all of the electron lithography. For nanostructuring of elements with these dimensions and below, the resist thickness is 40–150 nm in order to achieve a realistic aspect ratio. There the resist-profile-relief simulation using computer models plays increasingly important role. Only correct selection of the exposure and development conditions can ensure the necessary higher resolution and the desired resist profile and dimensions. Therefore the details of the computer simulation should be reconsidered. The observed linear and nonlinear resist behavior during development [1,2] becomes more important in the field of nanolithography. But can the approach be universal for the all used resists and developers having in mind the different nature of the development process?

One-component resists directly change the molecular weight and solubility of the exposed resist volumes. Representatives of one-component positive tone resists, which are extensively used in nanolithography, are special grades of PMMA with molecular formula $[\text{CH}_2\text{C}(\text{CH}_3)(\text{CO}_2\text{CH}_3)]$. A resolution of developed PMMA patterns

bellow 10 nm of isolated features and dense array of periodic structures at a pitch of 30 nm is demonstrated [3–5]. The concentration change of the developer (to a mixture of strong dissolving agent and weak or non-solvent agents as isopropanol (IPA) or water) is a way to improve the contrast (which is important for the higher resolution) when the solubility decreases [6,7]. In the sub-10 nm region the use of development assisted with ultrasonic agitation, instead of the standard puddle development is important [8]. This increases the development rate and in this way a lower dose of exposure could be applicable ($6.4\text{--}7.5 \mu\text{C}/\text{cm}^2$ at 20 keV accelerating electron energy [6] and 200 nm thick PMMA). Rinse in IPA decreases the roughness of the developed lines [9]. Although, for the one-component resist PMMA linear behavior during development is typical feature, a nonlinear solution process has been observed [1,2].

In the case of two- or three component resists the absorbed energy modifies a radiation active component (RAC) and the post exposure heating transforms the resist solubility in treated areas by a generated agent (from RAC) through its diffusion and reactions. In the case of chemically amplified resists (CARs) catalytic reaction and repeatedly use of this agent (acid) in protection modification of polymer matrix material occur. The used development models are very academic and an experimental calibration is necessary [10–18]. An approach for using procedure waiving the need of many other experimental data, especially needed for calculation of assumed complicated processes is proposed [19,20]. This approach is based on the use of experimentally obtained characteristics of the development concerning the solubility rate R vs. the exposure dose D . In this way unification of the simulation in the case of one-component resists and in the case of multi-component resists is presented.

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Another important kind of resists is oligomer one. In the past a spin coated inorganic resist was observed as more attractive – HSQ [21,22]. The optimal doses depend on the beam energy, the desired resolution and the film thickness. Instead using a mixture of salt and alkali, development in an aqueous mixture of NaOH alkali and NaCl salt enhances the contrast. Contrast values as high as 10 in a 115 nm thick resist were achieved [23]. The contrast and the resolution also increase when the temperature of development increases up to 45 °C. For this kind of resists, similar development behavior (linear or nonlinear) can be also observed depending on the developer [24] and on the resist thickness [25] as well as on the development temperature [26].

Hence, according to the $R(D)$ dependence all resists can have linear development behavior if this dependence does not depend on the time of development and the other development conditions as well as on the resist/developer interface position in the resist depth. Probably, the more common expected case is nonlinear development behavior when the solubility rate depends on the time of development and on the resist thickness. In many cases simple dependencies between the solubility rate and the exposure dose are not applicable. Then time-dependent calculation schemes and multiciphered experimental dependencies of the solubility rate on the exposure dose are used for simulation of the developed resist profiles [19,20]. In the time-dependent calculation scheme, the passed time from the beginning of the development and/or the depth, where the corresponding evolving point (from the developed contour) is, are taken into account when the local solubility rate of this point is determined for the corresponding time step. When the experimentally obtained $R(D)$ (for the resist/developer pair) is multiciphered dependence on the dose D and on the mentioned parameters (time, depth, temperature), the part (branch) of $R(D)$, used for calculation of the local solubility rate of the every evolving point, has to be determined.

When using various couples of resist/developer the difference concerns the details' approximation of exposed or non-exposed areas removal during development. In some cases there is a surface etching process assuming movement of sharp interfaces between solid resist and liquid developing solution. One possibility is continuous movement of the resist/developer interface and another one is developed profile movement with delay time (needed for penetration of the developer in the fresh resist before starting the resist removal process from the resist-developer gel). Obtained results using an approach for computer simulation of developed profiles taking into account the delay effect are presented and development process peculiarities are considered. Data for parameters' values needed for calculation of the developed resist profile evolution are also given.

2. PMMA in nanolithography

Our experience concerning development of thin PMMA films (100 and 50 nm thick films, 950,000 Mw, development time 60 s, temperature 20 °C, developer MIBK:IPA 1:3, substrate Si, Pre-bake 170 °C, electron energy 20–30 keV) shows a lower contrast in the region of exposure doses from 30 $\mu\text{C}/\text{cm}^2$ to about 80 $\mu\text{C}/\text{cm}^2$ and an improved contrast parameter at exposure doses higher than 80 $\mu\text{C}/\text{cm}^2$ (Fig. 1). The calculated dissolution rates, using experimentally measured changes of the relative resist thickness, during the development process, at various exposure doses are different for different resist thicknesses – Fig. 1 (the electron energy is also different).

Simulation energy deposition results at the interface PMMA resist/silicon substrate for initial electron energies 20 and 30 keV (point source) are presented in Fig. 2. The symbols represent the discrete data for a radial absorbed energy for Monte Carlo (MC) calculation [15,16,27,28] while the line represents their analytical fit, using a sum of two Gaussians [16,24] (called “proximity function”). The calculated values (using MC technique [16]) of the proximity effect parameters δ_f and δ_b (the characteristic widths of the forward and the backward scattering particles), and η_E (the ratio of the energy depth dissipation of the backward scattering particles to that of the forward scattering particles) at the resist/Si substrate interface (point source) are: $\alpha = 0.05432504 \mu\text{m}$, $\beta = 2.92802 \mu\text{m}$ and $\eta = 0.1226465$ in the case of 50 nm PMMA with e-beam energy of 30 keV (Fig. 2a). For 100 nm thick PMMA at 20 keV (Fig. 2b) the corresponding parameters' values at the interface are: $\alpha = 0.0773195 \mu\text{m}$, $\beta = 1.610459 \mu\text{m}$ and $\eta = 0.3725795$. When using thin PMMA film the back scattered electrons are wider distributed and have lower amplitude in the case of higher accelerated voltage (Fig. 2). The increase of the development rates (Fig. 1) could be expected at higher exposure doses and the development rate could not change at lower doses. The development rate values are higher in the case of thicker resist layer. It could be explained by the more important role of the modified surface and interface sub-layers of the resist film, when the used resist layers are with thickness equals or less than 100 nm. In that way, the characteristics of bulk PMMA become less important than modified boundary sub-layers of the resist at nanostructure lithography using PMMA.

3. Chemically amplified resists in nanolithography

In the case of CARs time-dependent calculation scheme is the main new element in the simulation approach. The CAR-CAMP6 resist has nonlinear behavior during the development. In [20] experimental profiles in CAMP6 are explained, using time-dependent

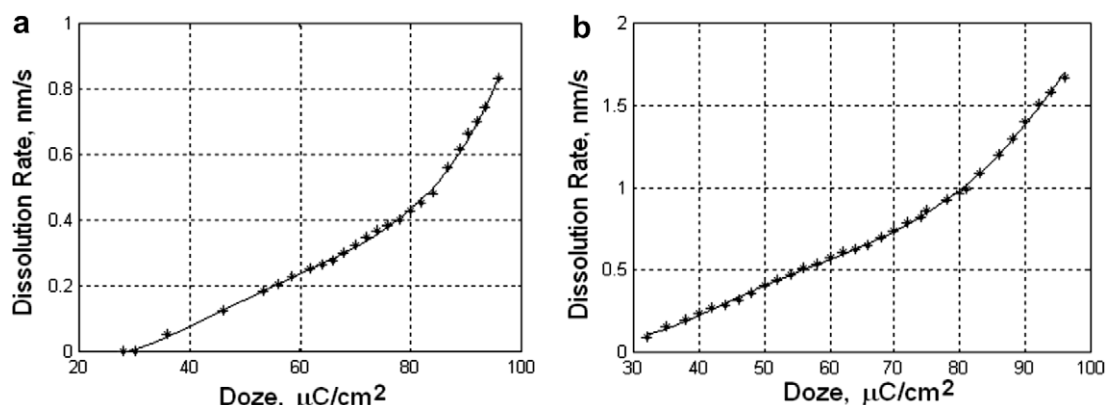


Fig. 1. Dissolution rate for PMMA (microchem) at: (a) 30 keV for 50 nm PMMA, (b) 20 keV for 100 nm PMMA.

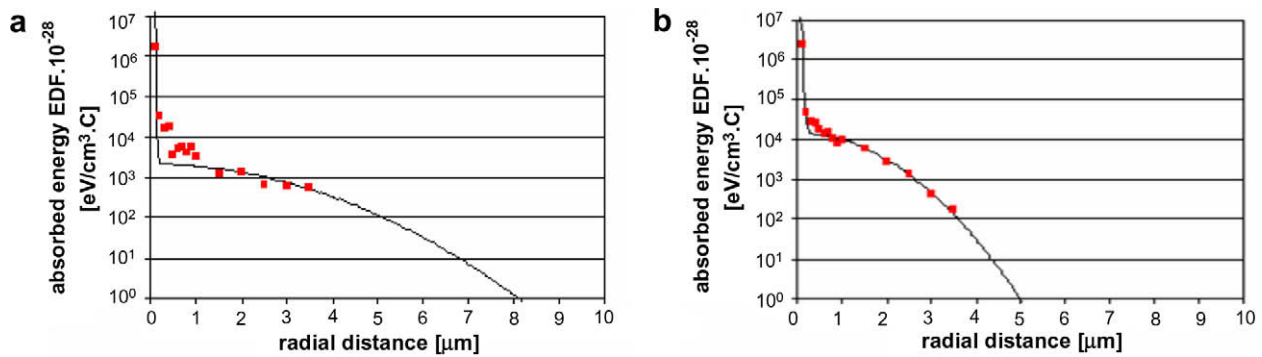


Fig. 2. Absorbed energy distribution vs. the radial distance calculated for: (a) 50 nm PMMA, 30 keV and (b) 100 nm PMMA, 20 keV at the interface resist/Si substrate. The symbols (■) present the results for MC calculation, the line – the corresponding analytical fit.

calculation scheme in simulation of the resist development and experimentally obtained multiciphered characteristics of the (average) development rate R on the dose of exposure D .

For lack of details about the nonlinear rate of development as well as about eventual delay times between the time of immersion in the developer and the time of the start of the resist development (or direct contact of the fresh resist with the developer), resist profiles in the case of delay time (which is needed for penetration of the developer in the fresh resist before starting the resist removal process from the resist-developer gel) are calculated.

Fig. 3 shows simulated resist profiles of an isolated 500 nm line at different times of development without delay effect. In this case the time-dependent scheme is not applied, because the developer very quickly penetrates in the resist and only one part of the multiciphered dependencies $R(D)$ is used.

Simulated resist profiles in CAMP6 in the case of 10 s delay time are shown in Fig. 4. The delay effect necessitates dividing resist volumes with various exposure doses where the delay time (and dissolution mechanism) is identical. Each evolving point from the developed contour advances along the normal to the profile with its local solubility rate. To determine this rate we use a time-dependent calculation scheme and multiciphered experimental dependencies of the solubility rate on the exposure dose (Table 1). Curve 1 presents the profile for 12 s after the wafer immersion in the developer. The resist/developer interface is moved during 2 s and stops its movement due to the mentioned delay time. During the delay time the developer penetrates in a surface resist layer which thickness is 80–100 nm. The developed profile keeps this position (represented by curve 1) up to 22 s from the beginning of the development. Curve 2 is a calculated profile at 25 s time of development of the exposed wafer and the removal is delayed up to 35 s from the beginning of the resist development. In

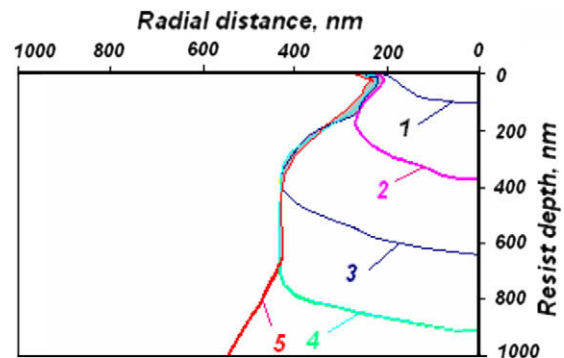


Fig. 4. Simulated resist profiles of an isolated 500 nm line for 10 s delay time at different times of development: curve 1–12 s (up to 22 s); curve 2–25 s (up to 35 s); curve 3–40 s (up to 50 s); curve 4–55 s (up to 65 s); curve 5–70 s.

consequence of such movement next profiles are calculated – curve 3 after 40 s, curve 4 after 55 s and curve 5 after 70 s (Fig. 4). It can be seen that in the case of such delay time for the penetration of the developer in the resist, the average development rate is lower and some changes of the side wall of developed lines could be experimentally observed. The features of the CAMP6 development are connected to the processes of developer penetration in the resist structure, as well as other molecular level processes and are explained in details in Ref. [19].

4. Inorganic EBL nanoresists

In Fig. 5 the normalized remaining resist thicknesses versus the exposure doses for HSQ resist and MF322 developer are presented. The two different contrast curves (Fig. 5) obtained for two different thickness of the HSQ film at one and the same developer show that HSQ-MF322 resist-developer pair has nonlinear development behavior.

5. Conclusions

In this paper the main candidates for working nano-patterning resist platform are discussed. Our data for the resist development rate dependencies on the exposure doses, needed for the computer simulation of the developed resist profiles and optimization of the electron lithography process is given.

In the paper an approach for simulation of developed profiles taking into account the delay effect and nonlinear development behavior is discussed. The simulation tools, described in the literature, are applicable only to linear solution process (solubility rate is uniform at various resist depths and developing times and is a

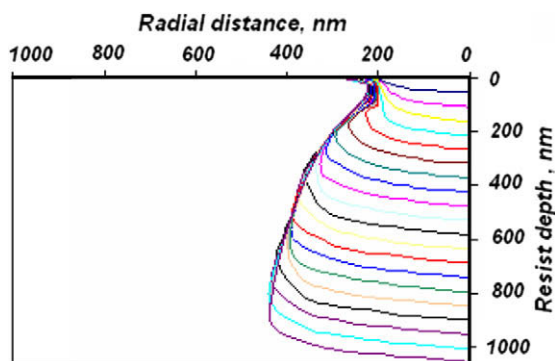
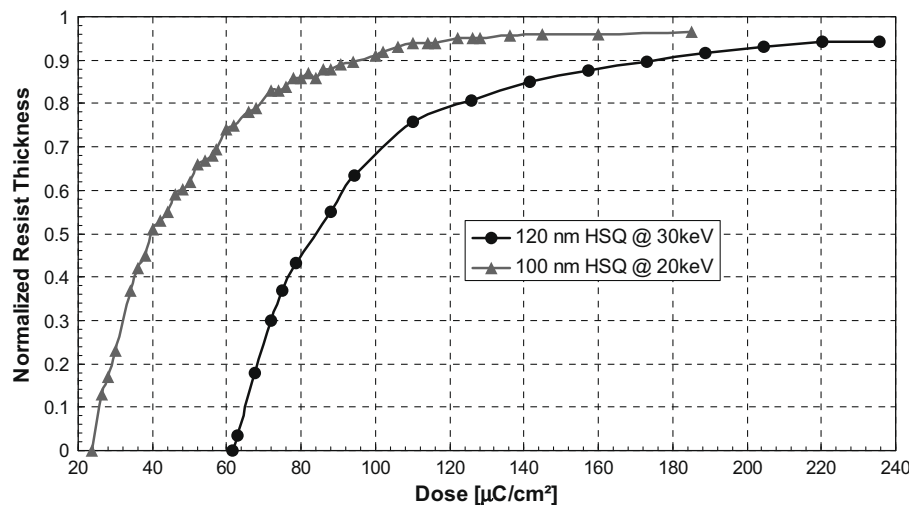


Fig. 3. Twenty simulated resist profiles ($\Delta t = 1$ s) of an isolated 500 nm line created in CAMP6 without delay effect (half the developed profiles are shown).

Table 1Evaluated dependences (using regression models) of the dissolution rate R on the exposure dose D at various times of development t for 1000 nm CAMP6 developed in OPD 262.

Parameters	Equations
D is in the range $4.5 \div 8.8 \mu\text{C}/\text{cm}^2$, $t = 15 \text{ s}$	$R = -102813.405518808108 - 52004267642035 + 142167.0066645 - 7094955037341868513 \cdot D - 84825.995315595945739978661788758 \cdot (D^2) + 28510.530606400510592897424172967 \cdot (D^3) - 5901.5392059851775643956713915221 \cdot (D^4) + 770.16977950614902453894223441137 \cdot (D^5) - 61.876802541845874295076969973777 \cdot (D^6) + 2.798542091894069835009907026354 \cdot (D^7) - 0.054571727048585807708428593202256 \cdot (D^8)$
D is in the range $4.95 \div 6.2 \mu\text{C}/\text{cm}^2$, $t = 30 \text{ s}$	$R = 16087.902418081173044563523355944 - 17028.97669942502685484722230845 \cdot D + 7163.3636397166115081558015783809 \cdot (D^2) - 1495.8434483486597413241768135557 \cdot (D^3) + 154.9219377712650030114684168368 \cdot (D^4) - 6.3592278222426436346250566590707 \cdot (D^5)$
D is in the range $4.8 \div 5.6 \mu\text{C}/\text{cm}^2$, $t = 60 \text{ s}$	$R = -172775.0700445923 + 228293.2518999999 \cdot D - 125347.0921093749 \cdot D^2 + 36600.11980468748 \cdot D^3 - 5992.939599609372 \cdot D^4 + 521.6384277343747 \cdot D^5 - 18.85189056396483 \cdot D^6$
D is in the range $4 \div 5 \mu\text{C}/\text{cm}^2$, $t = 360 \text{ s}$	$R = 26.531995 - 13.636376 \cdot D + 1.750844 \cdot D^2$

**Fig. 5.** The contrast curve of HSQ resist and MF322 developer.

function of the exposure dose only). Modeling is presented of resist profiles in the case of a resist with nonlinear and exhibited delay effect using time-dependent macroscopic characteristics of the development (the development rate vs. the exposure dose). It is shown that using changes in the side wall tilt of the developed relief, evidences for delay effect, concerning the developed profile evolution, can be searched. The nonlinear development behavior is observed for the three groups of the discussed resists and some developers and is important in the EBL of nano-dimensioned structures.

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