Determination of the Radiation Efficiency, Contrast and Sensitivity in Electron and Ion lithography

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Abstract

Knowledge of the solubility rate dependence on exposure dose *S(D)* gives possibility to estimate the values of the radiation efficiency, sensitivity and contrast characteristics in electron and ion lithography. The idea for interconnection between the sensitivity and the contrast characteristics for an arbitrary combination of resist and developer (i.e. at a given molecular weight, resist density and radiation efficiency of the charged particles) is a base for the sensitivity optimisation in order to achieve the required contrast at chosen development conditions. The contrast parameter value γ_s (related to the traditionally used contrast parameter γ_d) is determined by the slope of the dependence *S(D)* of the resist solubility rate *S* on the average exposure dose *D* .

1 Introduction

Microstructures for nano-electronics and photonics with critical dimensions in the order of 30 nm – 150 nm will be mastered during the next years. Electron and ion lithographies are the techniques, which meet the requirements of the challenge for further electron devices miniaturization. The quantitative estimation of the resist modification parameters [1] is an important step at optimisation of the electron and ion lithographies exposures and of the connected development processes.

The solubility rate changes upon irradiation due to the cross-linking or the scission of the polymer molecules of the resist layer. After a proper development process by suitable solvent (developer) relief microstructure in the resist layer can be observed. During the development process, the irradiated areas for the positive and opposite-the non-irradiated areas – for the negative resists are removed. The solubility rate variation of the irradiated spots depends on the used exposure dose. The sensitivity of the polymer resist to the radiation (with the electron and ion beams) is measured as the minimal dose D_0 for the development process of the exposed image. The resist sensitivity is determined by the radiation efficiency of irradiated particles that can be characterized by the mean number of chemical events (chain scission or destruction) per one unit (namely electron-volt) of the absorbed energy. In the field of high-resolution electron beam and ion beam lithography it is very important to characterize the developed profiles in the resist. and that can be done by the contrast parameter. The contrast parameter γ_d is defined for the remaining thickness of the utilised resist layer for given time and used dose D_0 by the dose interval between the initial exposure dose D_I (at which a start of development can be observed) and the mentioned dose D_0 (for full development of studied resist thickness). The value of the contrast parameter γ_d at the removed normalised thickness can be calculated from the relation $\gamma_d = [lg\ (D_I/D_0)]^{-1}$

Sensitivity and contrast values have been calculated experimentally for some average molecular weight of the used resist (measured for example in a.u.) and for a chosen developer. Data for the sensitivity D_0 and for the contrast γ_d of PMMA in the case of electron sub-micron lithography are given in [2,3]. The effect of the developer and the development conditions on these parameter values are discussed. A similar effect of the used developer on the contrast value γ_d for electron lithography of Amil Acetate layers is shown in [4] and in the case of PMPS & Novolak in [5]. In addition in the ref. [6, 7] data for the sensitivity and for the contrast γ_d in the case of some ion beam resists are given. Generally, the resist sensitivity of the polymer resists at the ion exposure is higher than for electron exposure [1,8]. The comparison is not precise due to the different conditions and the peculiarities of the figures of merit used. The sensitivity and the contrast are described usually as independent properties. Recently a definition of another contrast parameter $\gamma_s = (\Delta S/\Delta D)$ as the slope of the solubility rate dependence on the exposure dose $S(D)$ at a given exposure dose (i.e. sensitivity D_0) was accepted. Then these parameters γ_s and D_0 for a resist-developer combination are mutually connected [9,10].

Chemically amplified resists (CARs) are the most suitable candidates for future direct writing since they provide high resolution and high sensitivity. In CARs, acid is generated by the sensitiser during exposure which catalyse the necessary reaction for solubility change during post exposure bake (PEB) and thus alters the latent resist image after exposure. Modified sensitivity and contrast parameters for these resists can be evaluated. An acid diffusion coefficient as additional resist parameter can be evaluated too, using the time evolution curve $L(t_{PEB})$ of the image dimension L at different PEB conditions (t_{PEB} (s), T_{PEB} (^{0}C)) [11].

In this work an approach for calculating the radiation efficiency and the contrast characteristics for an arbitrary couple of a positive resist – developer in the field of electron and ion lithography is proposed. The approach is based on the theoretical approximation of the experimental dependence of the resist solubility rate S on the adsorbed energy of the irradiating charged particles beam in the resist. The methodology for evaluation of the radiation efficiency, contrast parameters at a radiation dose D (i.e. sensitivity D_0), uses Monte-Carlo calculation technique. The presented examples of evaluated contrast values and radiation efficiency values are for electrons or for various ions and at different energies.

2 Theoretical background and evaluation results

The evaluation of the resist parameters is based on the knowledge of the solubility rate S as a function of the exposure dose D. The resist solubility rate can be evaluated by the following empirical formula:

$$S = Ro + B \big/ \overline{M_f}^{\,A} \quad , \qquad (1)$$

where $\overline{M_f}$ is the average polymer molecular weight after radiation, and R_0, B and A are constants for a given resist-developer couple. The parameter R_0 has a physical meaning (the starting solubility rate), and A is the power coefficient. The molecular weight $\overline{M_f}$ depends on the radiation efficiency g and on the exposure dose D as well as from original molecular weight M_n. Then [13] the solubility rate S will be:

$$S = R0 + B\,[(1/Mn) + (gED/\rho NA)]A\,, \qquad (2)$$

where E is the adsorbed energy in the resist , ρ is the resist density, N_A is Avogadro's number, g is the radiation efficiency.The curve $S/S_0(D)$ can be used instead of $S(D)$ (where S is the resist solubility rate after the exposure and S_0 is this rate without exposure). In the ion irradiation case, E presents the electronic and the nuclear components of the absorbed energy. According to [16] electronic stopping power is responsible for polymer modification. Some examples of evaluated coefficients values R_0 ,B and A for PMMA resist from eq. (1) and (2) are given in Table 1.

Table 1. The solubility rate parameters (eq. 1) for PMMA and for various developers at electron irradiation:

Solvent	R_0 (A/min)	B (A/min)	A	References
MIBK:IPA 1:1	0	$3{,}34.10^{6}$	1.5	[15] , [13]
IPA	0.008	6.10^{21}	5.31	[9] , [13]
MIBK	84	$3{,}14.10^{8}$	1.3	[14]
MIBK:IPA 1:1	0	$3{,}14.10^{8}$	1.19	[14]
MIBK:IPA 1:3	0	$3{,}14.10^{8}$	3.86	[14]

It can be found that the contrast parameter γ_s is related to the traditionally estimated contrast parameter γ_d. An example of the contrast parameter values γ_s calculated for the electron exposure of PMMA and for one of the developers is shown in Table 2. One can see a high sensitivity D_0 at a low contrast value γ_d and a high contrast value γ_d at lower sensitivity D_0.

Table 2. Contrast γ_s and sensitivity D_0 for PMMA at one of developers (MIBK:IPA mixed in ratio 1:1-see Table 1) for electron irradiation.

D_0 [C/cm^2]	2.10^{-5}	1.10^{-4}	$5.5\ .10^{-4}$
γ_s [A.cm^2/min.C]	0.001	0,3	2,8

The value of the radiation efficiency g, is specific for every chosen material and scanning particle. In Table 3 the radiation efficiency values are presented for various ions and for a wide range of energies, as they was evaluated on the base of the relation (2) by experimental data in ref.[13].

Table 3. The radiation efficiency values for PMMA (ion beam lithography).

Ion	Ion energy (keV)	PMMA thickness (μm)	g (eV^{-1})
Li	50	0.4	$1.7x10^{-2}$
Ga	50	0.15	$2.3x10^{-2}$
Li	60	0.4	$1.7x10^{-2}$
H	60	0.4	$0.6x10^{-2}$
Be	200	1.5	$0.993x10^{-2}$
Si	200	0.7	$0.6x10^{-2}$

3 Conclusions

The correct selection of the exposure and the development conditions in order to ensure the necessary resolution and the resist contrast is the general task of the nano-image's technology designer. Using the presented approach – on the base of the knowledge on the dependence S(D) of the solubility rate on the exposure dose - the contrast parameter and the sensitivity can be optimized at chosen development process parameters like: developer, development temperature, development time at a given resist thickness and polymer material characteristics.

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