Microelectronic Engineering 86 (2009) 714–717

Contents lists available at ScienceDirect

Microelectronic Engineering

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

A simulation model for chemically amplified resist CAMP6

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ARTICLE INFO

Article history:
Received 27 September 2008
Received in revised form 11 November 2008
Accepted 11 November 2008
Available online 24 November 2008

Keywords:
Lithography simulation
Development kinetics
Chemically amplified resist
CAMP6

ABSTRACT

In this paper, a model for computer simulation of the exposure and the development of the CAMP6 chemically amplified resist (CAR) during electron beam lithography is proposed. The distribution of the absorbed electron energy in the exposed resist is determined using our Monte Carlo algorithm and computer programs. A wider resist de-protection region due to the diffusion of the exposure catalyst product (acid) during the post-exposure bake (PEB) is estimated. It lays a special emphasis upon the development process simulation. Experimentally obtained time dependent macroscopic characteristics of the development (contrast curves, the development rate vs. the exposure dose) are taken into account, aiming to avoid the need for further calibration. The proposed model demonstrates qualitative agreement with the development kinetics of the resist developed profiles for the studied CAR.

1. Introduction

Nanometer scale device fabrication rules require tight control of the developed polymer resist profile. Process simulation is a key tool for optimization of the obtained lithography results. The approaches for computer simulation of images in positive CARs are based on the use of a set of values concerning the material properties, molecular structure, concentrations of used polymer compound, energy dissipation and acid generation models, volume shrinkage and polymer stress effects during the post-exposure bake, the reaction constants such as the acid diffusion ranges and kinetics characteristics of the decomposition (catalytic de-protection) mechanisms, the parameters of developer penetration, polymer molecules dissolution and removing processes, as well as surface and interface property changes of resist solubility, etc. For practical use, the strong academic models involving majority of the listed data are too complicated, slow and need many previously provided empirical data. Nevertheless, due to variations in control parameters and batch-to-batch variations between the resist and developer used, the process parameters require the calibration of each computer simulation set [1].

The models for the calculation of the deposited energy distribution of the penetrating electrons (latent image) are based on Monte Carlo (MC) algorithms [2,3] or on analytical methods [4,5]. Development modeling of the resist profiles is sensitive to a concrete polymer and developer system [6], history of the utilized temperature processes [7], resist film thickness and various processing conditions [8] as well as to the post-exposure delay [9]. Published modeling algorithms for the simulation of profiles in chemically amplified resists consist of dependencies of coupling between diffusion and kinetic reactions; relations for nonlinear or linear diffusion as well as various development-rate models [10–11]. Surface changes of the development rate (retardation or increase) are approximated using depth dependencies of the resist solubility rate in these layers [12]. Due to these complicated and individual effects, the choice of a uniform development model and adequate process parameter set for computer simulation of the developed resist profiles in CARs is almost impossible.

In the proposed simulation model, the absorbed energy space distributions are calculated using MC algorithm for electron penetration and energy-loss calculation. Then the modification of the absorbed energy distribution as a wider distribution of de-protected polymer molecules due to diffusion and catalytic reaction of the acid during the PEB is evaluated. Experimental data, obtained as a technology base for the application of a resist-developer system, are used for simulation of the resist development. The test experiments concerning the investigated resist and developer showed nonlinear solubility process. Therefore, the simple mathematical relations between the development rate and the exposure dose for the resist profile evaluation usually used are not applicable [5]. Time-dependent calculation scheme and multiciphered experimental dependencies of the solubility rate on the exposure dose are used for an adequate simulation of the development kinetics of the resist profiles.

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doi:10.1016/j.mee.2008.11.010

2. Calculation and experimental results and discussion

E-beam exposure was applied by a 30-keV pattern generator (modified ZBA 10/1 of Carl–Zeiss, Jena, Germany) onto CAMP6 (OCG), a t-BOC protected polyhydroxysterenesulfone copolymer. To obtain the experimental development characteristics, we used resist layers 0.6–1.7 μm thick, covered with BC-5 protective coating 65 nm thick. The film thicknesses were measured using either Talystep or Dektak stylus profilometer. The process sequences for CAMP6 (OCG) resist are shown in Table 1.

To simulate the exposure of polymer resist films, we use our MC algorithm and the corresponding software tool [2,3]. This model is based on a single scattering model and a continuous slowing-down approximation, assuming the screened Rutherford elastic scattering cross-section and the Bethe energy-loss equation. The chemical composition of the resist CAMP6 is C_8H_8O, the efficient atomic number is 3.765, the atomic mass is 7.059 and the density is 1.15 g/cm^3. Radial distributions of the electron energy deposition (EDF) in CAMP6 over a Si substrate are obtained by means of the MC simulation tool following 10,000 electron trajectories from a point source (with a negligible small beam diameter) (Fig. 1). These distributions stored as arrays of numerical data are approximated by an analytical function, namely the combination of double Gaussian and exponential functions, called a "proximity function"

$$f(r)=\frac{k}{\pi(1+\eta+\nu)}\left[\frac{1}{\alpha^2}\exp\left(-\frac{r^2}{\alpha^2}\right)+\frac{\eta}{\beta^2}\exp\left(-\frac{r^2}{\beta^2}\right)+\frac{\nu}{2\gamma^2}\exp\left(-\frac{r}{\gamma}\right)\right] \quad (1)$$

The values of the parameters of this function – α, β, γ, η, ν and k are calculated using an original Monte Carlo technique [3], instead of the commonly used nonlinear least-square method. The absorbed energy space distribution (the values of the parameters α, β, γ, η, ν and k) is the basic fact that determines the characteristics of the latent image created during the electron exposure process.

In Fig. 1, the calculated radial distribution of the EDF (by MC approach, represented by the symbols ■) as well as its analytical fit (Curve 1) in the case of 200 nm CAMP6/Si with e-beam energy of 30 keV is shown as an example. The calculated values of the parameters of Eq. (1) α, β, γ, η and ν at the resist/substrate interface (point source) are α = 0.02218 μm, β = 3.0941 μm, γ = 0.37 μm, η = 1.5 and ν=0.3713.

After convolution between the real beam spot and the latent image distribution, the result is convolved with the modified distribution of the de-protected resist volume after PEB and modified (extended) latent image distribution is obtained. Curve 2 (Fig. 1) presents an example of the modified distribution for 200-nm-thick CAMP6 on Si after PEB on a hot plate at 120 °C for 60 s. The calculated parameter values, modified due to the acid diffusion [13–16], are α = 0.065764 μm, β = 3.257 μm, γ = 0.37 μm, η = 1.5 and ν = 0.3713. The diffusion spread of the latent image standard deviations is ~50–60 nm for the forward scattered electrons and 200 nm for the back scattered electrons [14,15].

Table 1
CAMP6 resist treatment sequence.

Operation	Characteristics
Wafer priming in air	HMDS/60 s
Resist spin coating and film thickness	650 nm, 6000 rpm 1000 nm, 2379 rpm
Pre-bake on hot plate in air	120 °C, 60 s
Protective layer spin coating (BC5)	65 nm, 4000 rpm
Pre-bake on hot plate in air	120 °C, 60 s
E-beam exposure	30 keV
PEB on hot plate in air, immediately after exposure	120 °C ± 2 °C, 60 s ± 5%
Development (immersion)	OPD-262 developer
Rinse	De-ionized water, 20 s
Dry spinning in air	1000 rpm, 60 s
Hard bake on hot plate in air	120 °C, 60 s

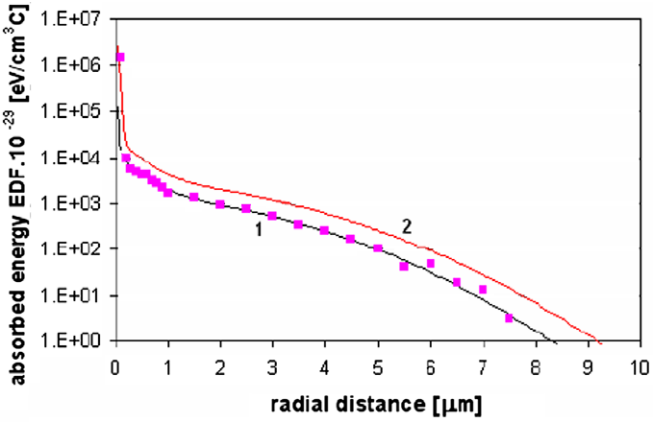

Fig. 1. Comparison of EDF(r) between MC simulation (symbols ■) and the corresponding analytical fit (Curve 1) in the case of CAMP6 on Si. The resist thickness was 200 nm and the energy was 30 keV (point source). Curve 2 – modified distribution in the case of de-protected resist volume (for 200 nm thick CAMP6 on Si) at e-beam spot dispersion 10 nm and after PEB on a hot plate at 120 °C for 60 s in air.

To simulate the development process usual calibration dependencies such as dissolution rate on the exposure dose and contrast curves could be applied instead of the exact microscopic phenomena such as the penetration of developer molecules in the resist, resist swelling, polymer chains disentanglement, transport of polymer chains and fragments through percolation or an aggregate dissolution. The algorithms for linear solution processes at lithography development are not applicable to the case of CARs with nonlinear and exhibited delay effects. The studied CAMP6 (OCG) resist has nonlinear development behavior. It also has a delay time between the time of immersion in the developer and the time of the start of the resist development. Fig. 2 presents experimental contrast curves of the studied CAR at the development of a set of resist areas exposed with doses that increased by very small increment (25 nC/cm^2). Fig. 3 shows evaluated dependencies of the respective average solubility rates on the exposure doses at various times of development. One can see a slow development rate at low exposure doses and a sharp increase of the resist removal at higher

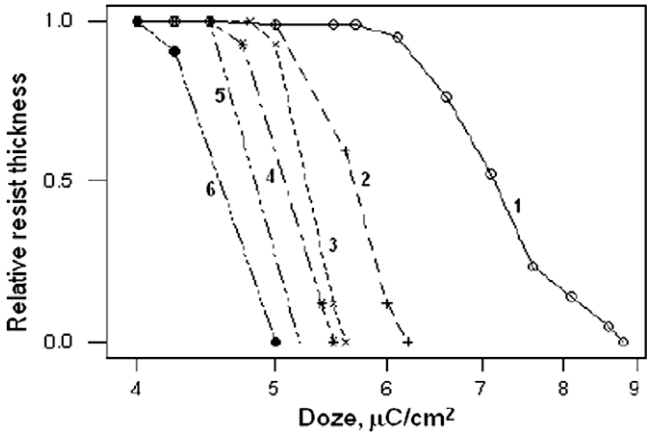

Fig. 2. Contrast curve for 1 μm thick CAMP6 (OCG) at various development times: 1–15 s; 2–30 s; 3–60 s; 4–120 s; 5–240 s and 6–360 s. Thickness loss due to the PEB is 23% and d_o = 770 nm.