Semiconductors, Vol. 35, No. 2, 2001, pp. 226–229. Translated from Fizika i Tekhnika Poluprovodnikov, Vol. 35, No. 2, 2001, pp. 233–236.
Original Russian Text Copyright © 2001 by Kaliteevskaya, Seĭsyan.

AMORPHOUS, VITREOUS, AND POROUS SEMICONDUCTORS

Contrast Enhancement in Image Transfer via Interaction of UV Radiation with Inorganic Photoresist Films

N. A. Kaliteevskaya and R. P. Seĭsyan

Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia

Submitted June 22, 2000; accepted for publication June 22, 2000

Abstract—Photochemical transformations occurring in thin films of inorganic photoresists under UV irradiation from an excimer laser are analyzed theoretically. It is shown that the optimization of the light intensity and irradiation dose can make the transition region between the exposed and unexposed parts of a film narrower, thereby improving the image quality in photolithography. © *2001 MAIK "Nauka/Interperiodica".*

To create high-quality integrated circuits, it is necessary to achieve such a relief structure in photoresist film that the edges of all pattern features are exactly at their assigned positions and that the sidewalls are vertical. The ideal case would be a stepwise profile of the photoresist exposure. However, the light intensity profile at a desired pattern feature boundary is a "smooth function" [1], occasionally nonmonotonic, which is associated with the wave properties of light (Fig. 1). The quantitative measure of this effect is the slope of the light intensity profile in the transition region between light and dark features of the image—edge gradient dI/dx. Blurring of the exposure intensity distribution, statistical fluctuations in the photon distribution, and inhomogeneities arising in the course of chemical etching may result in the edge of a pattern element lying in a certain interval Δx around the prescribed value, which impairs the image quality [1, 2]. Studies of photochemical transformations in films of glassy semiconductors, such as AsSe and As_2Se_3, under irradiation from an excimer laser operating at 193 nm demonstrated that the irradiation dose necessary for photoresist exposure depends on light intensity [3], i.e., the process is "nonlinear." In addition, it has been established that images with a resolution comparable to the wavelength of light can be obtained [4].

The aim of this work was to study the effect of this nonlinearity on pattern formation in photolithography.

A study of the photodarkening of AsSe films under irradiation from an ArF excimer laser made it possible to develop a model quantitatively describing the process of photochemical transformations [5]. In accordance with the results obtained in [5], we assume that under the action of light the film material is transformed from the initial state I into the final state II. These states are characterized by different physical (e.g., light absorption coefficients at the wavelength of the excimer laser inducing photochemical transformations, α_1 and α_2, respectively) and chemical (e.g., solubility in a certain solvent) properties of the material. In the course of irradiation, the film material is a mixture of materials I and II. Let us denote the relative concentrations of materials I and II by, respectively, ρ_1 and ρ_2, so that $\rho_1 + \rho_2 = 1$ and the absorption coefficient of the irradiated material is expressed by

$$\alpha = \alpha_1\rho_1 + \alpha_2\rho_2 = \alpha_2 + (\alpha_1 - \alpha_2)\rho_1. \quad (1a)$$

The absorption in a layer (along the z axis) follows the Bouguer–Lambert–Beer law, so that

$$\frac{\partial I(z,t)}{\partial z} = -\alpha(z,t)I(z,t), \quad (1b)$$

where $I(z, t)$ is the local intensity and t is time.

The change in the concentration of the original material under the action of light is described by

$$\frac{\partial \rho_1}{\partial t} = -C\alpha(z,t)I(z,t)F(I)\rho_1, \quad (1c)$$

where C is the sensitivity having the dimensionality [volume] [energy]$^{-1}$. The physical meaning of the constant C is the volume of material that can be transformed from state I into state II upon absorption of unit energy. The dimensionless intensity-dependent multiplier $F(I)$ reflects the fact that the irradiation dose necessary for material exposure depends on the intensity of incident light.

Equations (1a)–(1c) constitute, together with the initial condition $\rho_1|_{t=0} = 1$ and boundary condition $I(t)|_{z=0} = I_0(t)$, where $I_0(t)$ is the incident light intensity), a system describing the photochemical transformations in films. Since the dependence of the rate of photochemical transformations on light intensity has a

threshold, we approximate the function $F(I)$, as was done in [4], by the expression

$$F(I) = \frac{1}{2}\left[1 + \tanh\left(\frac{I - I_{th}}{\delta}\right)\right], \quad (2)$$

where the parameter δ characterizes the blurring of the intensity threshold. A modeling of photodarkening in AsSe films under irradiation from an ArF excimer laser operating at 193 nm allowed us to determine that the sensitivity $C = 3 \times 10^{-3}$ cm^3/J, threshold intensity $I_{th} = 1.7 \times 10^4$ J/(cm^2 s), and blurring parameter $\delta = 8.5 \times 10^3$ J/(cm^2 s). The absorption coefficients at the excimer laser wavelength in states I and II $\alpha_1 = 0.1 \times 10^5$ cm^{-1} and $\alpha_2 = 1.2 \times 10^5$ cm^{-1}.

Upon exposure, a certain profile of the component concentrations, $\rho_1(z)$ and $\rho_2(z)$, is established in the bulk of the resist film, with the dissolution rate strongly depending on the concentration. When the development conditions (chemical composition of etchant, temperature and duration of development) are set, we can determine the threshold concentration $\rho_{1S}(z)$ separating the exposed (dissolving) and unexposed (nondissolving under the given development conditions) parts of the resist film. The material dissolves if $\rho_1(z) < \rho_{1S}(z)$, and otherwise does not. We denote the boundary position by z_S.

To calculate the concentration profile established in the photoresist bulk upon exposure, it is necessary to solve numerically the system of equations (1). However, preliminary optimization of the irradiation process parameters can be done analytically for such parameters as the concentration profile gradient at the threshold value and the slope of the isoline of threshold concentration near the sample surface.

Introducing the designation $\gamma = (\alpha_1 - \alpha_2)/\alpha_2$, we can rewrite Eq. (1c) for the surface layer of the film ($z = 0$) by separating the variables to obtain

$$\frac{d\rho_1}{(1 + \gamma\rho_1)\rho_1} = -\alpha_2 CIF(I)dt. \quad (3)$$

Integrating Eq. (3) and taking into account that $\rho_1 = 1$ at the initial instant of time, we have

$$\rho_1 = \left\{(1 + \gamma)\exp\left[\alpha_2 C\int_0^T IF(I)dt\right] - \gamma\right\}^{-1}, \quad (4)$$

where T is the duration of irradiation. In the case of a rectangular pulse of duration T_P and intensity I_P, the following concentration is established at the surface:

$$\rho_1 = \{(1 + \gamma)\exp[\alpha_2 CT_P I_P F(I_P)] - \gamma\}^{-1}. \quad (5)$$

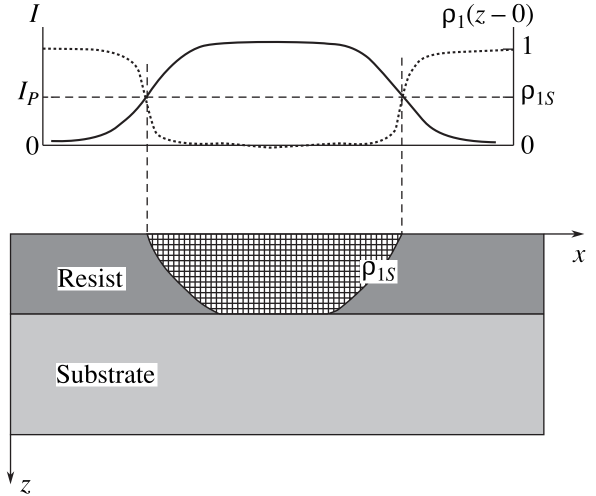

Fig. 1. Photoresist layer on substrate and light intensity profile. The line of constant threshold concentration ρ_{1S} separates the exposed and unexposed parts in the photoresist bulk. The solid line represents the spatial profile of the incident light intensity, and the dashed line, the concentration profile established at the resist surface in the course of irradiation.

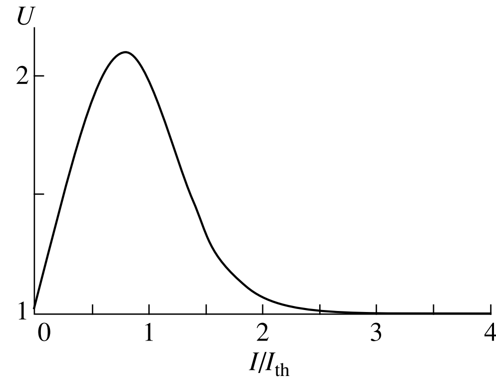

Fig. 2. Image transfer contrast enhancement as a function of light intensity.

Thus, the dose $H_P = T_P I_P$ and intensity I_P ensuring that the threshold concentration ρ_{1S} is reached at the sample surface are related by

$$\ln\left(\frac{1/\rho_{1S} + \gamma}{1 + \gamma}\right) = \alpha_2 CI_P F(I_P)T_P. \quad (6)$$

To create as sharp a boundary as possible, it is necessary that $d\rho_1/dx$ be highest around the threshold concentration ρ_{1S}. Let b be the relative edge intensity gradient (see Fig. 1)

$$b = \frac{1}{I_P}\frac{\partial I_P}{\partial x}. \quad (7)$$

Differentiating Eq. (5) with respect to the coordinate x, and using relation (7), we see that the concentration

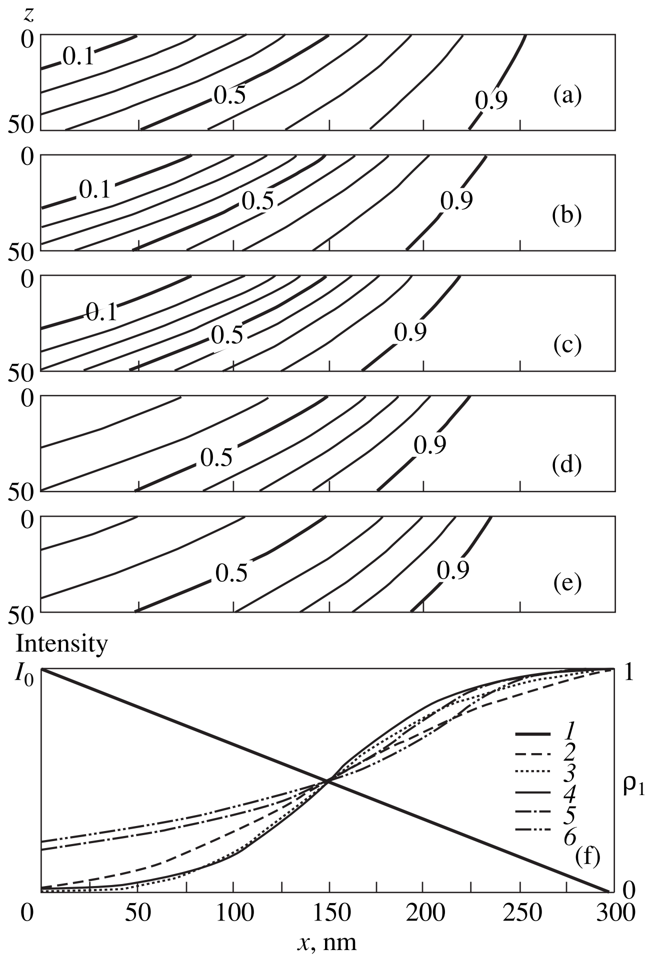

Fig. 3. (a–e) Lines of constant concentration representing concentration profiles in the photoresist bulk upon irradiation; the irradiation dose was selected in such a way that a concentration $\rho_1 = 0.5$ was established upon irradiation at the point $x = 150$ nm on the film surface; the light intensity at the point $x = 150$ nm at the film surface $I_P = I_0/2 = 0.25I_{th}$ (a), $0.5I_{th}$ (b), $0.803I_{th}$ (c), $1.5I_{th}$ (d), and $2I_{th}$ (e). (f) Spatial light intensity profile (*1*) and the dependence of the concentration ρ_1 on the sample surface at $I_P = I_0/2 = 0.25I_{th}$ (*2*), $0.5I_{th}$ (*3*), $0.803I_{th}$ (*4*), $1.5I_{th}$ (*5*), and $2I_{th}$ (*6*).

gradient is proportional to the relative edge intensity gradient with an intensity-dependent proportionality factor:

$$d\rho_1/dx = b(1+\gamma)\alpha_2 CT_P I_P \exp[\alpha_2 CT_P I_P F(I_P)] \times [F(I_P) + I_P(\partial F(I_P)/dI_P)]/\{(1+\gamma) \times \exp[\alpha_2 CT_P I_P F(I_P)] - \gamma\}^2. \quad (8)$$

Introducing the quantity

$$U = \left.\frac{(\partial\rho_1/\partial x)}{b}\right|_{\rho = \rho_{1S}},$$

characterizing the "image transfer contrast enhancement" at the surface and using relation (6), we have

$$U = U_{0\rho}(\rho_{1S}, \gamma)U_1(I_P) = (1+\rho_{1S}\gamma)\rho_{1S} \times \ln\left[\frac{1/\rho_{1S}+\gamma}{1+\gamma}\right]\left[1 + \frac{I_P}{F(I_P)}\frac{\partial F(I_P)}{\partial I_P}\right]. \quad (9)$$

For a function of the type (2), the following equation can be obtained

$$\frac{1}{F(x)}\frac{\partial F(x)}{\partial x} = \frac{2}{\exp(2x)+1}, \quad (10)$$

where $x = (I - I_{th})/\delta$.

Differentiating the right-hand part of Eq. (9) and using expression (10), we see that the concentration gradient grows to the maximum extent at an incident light intensity I_P satisfying the relation

$$\exp\left[2\frac{I_P - I_{th}}{\delta}\right]\left[1 - \frac{2I_P}{\delta}\right] + 1 = 0. \quad (11)$$

Thus, the best quality of pattern transfer can be achieved at the parameters specified by relations (6) and (11).

Figure 2 shows the intensity dependence of the pattern transfer contrast enhancement. In accordance with Eq. (11), the dependence shows a maximum at $I_P = 0.803I_{th}$. By selecting an appropriate light intensity, one can raise the concentration gradient at the boundary by more than a factor of 2.

Figure 3 presents calculated concentration profiles established in the film upon irradiation at varied light intensities. The spatial profile of the incident radiation is shown in Fig. 3f by curve *1*. In the region considered, corresponding to the boundary between the illuminated and unilluminated parts of the film, the intensity falls from the maximum value to 0. The irradiation dose was chosen for each case so that a concentration $\rho_1 = 0.5$ was established at the point $x = 150$ nm (in the middle of the region in question) upon irradiation.

Figure 3c corresponds to the optimal intensity $I_P = 0.803I_{th}$. Figures 3a and 3b correspond to intensities lower than optimal, and Figs. 3d and 3e, to those higher than the optimal value. It can be seen that the transition region separating the exposed and unexposed parts of the film is narrowest when the intensity I_P corresponds to the optimal value $0.803I_{th}$.

In addition to the intensity profile, Fig. 3f shows the dependence of the concentration ρ_1 at the surface upon the coordinate x, demonstrating a pronounced increase in the concentration gradient at the boundary compared with the edge gradient of the incident radiation at optimized light intensity and irradiation dose.

It should be noted that if the pulse pattern is other than rectangular the parameters ensuring the best image quality also change somewhat, but can be determined by numerically solving the system of equations (1).

To conclude, in the case of nonlinear photoresists, in which the rate of photochemical transformation is not directly proportional to the incident light intensity, appropriate choice of the incident light intensity and irradiation dose can make narrower the transition region between the exposed and unexposed parts, thereby improving the quality of image transfer in photolithography.

REFERENCES

1. G. N. Berezin, A. V. Nikitin, and R. A. Suris, *Optical Foundations of Contact Lithography* (Radio i Svyaz', Moscow, 1982).
2. H. I. Smith, J. Vac. Sci. Technol. B **6** (1), 346 (1988).
3. E. G. Barash, A. Yu. Kabin, V. M. Lyubin, and R. P. Seĭsyan, Zh. Tekh. Fiz. **62** (3), 106 (1992) [Sov. Phys. Tech. Phys. **37**, 292 (1992)].
4. L. G. Gladysheva, N. A. Kaliteevskaya, R. P. Seĭsyan, and D. V. Smirnov, Pis'ma Zh. Tekh. Fiz. **22** (15), 91 (1996) [Tech. Phys. Lett. **22**, 640 (1996)].
5. N. A. Kaliteevskaya and R. P. Seĭsyan, Fiz. Tekh. Poluprovodn. (St. Petersburg) **34** (7), 857 (2000) [Semiconductors **34**, 825 (2000)].

Translated by M. Tagirdzhanov