Radiation-Stimulated Transformation of the Reflectance Spectra of Diazoquinone–Novolac Photoresist Films Implanted with Antimony Ions

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Abstract—We measure the reflectance spectra of 1.8 μm-thick FP9120 photoresist films doped with antimony ions and deposited by centrifugation on the surface of \( p \)-type silicon wafers (\( \rho = 10 \ \Omega \ cm \)) with a (111) orientation. Implantation leads to a decrease in the refractive index of the photoresist due to the radiation cross-linking of Novolac resin molecules and a decrease in the molecular refraction and density of the photoresist. In the opacity region of the photoresist film, an increase in the reflection coefficient is observed with an increase in the implantation dose.

Keywords: lithography, radiation, substrate, photoresist, implantation, antimony, refractive index, reflection

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INTRODUCTION

The study of radiation-induced processes in polymers is of practical interest, since polymer compositions are actively used as a resist in electronic, photo, and X-ray lithography in the production of integrated circuits [1–8]. Currently, ion implantation is the primary doping method in microelectronics and nanoelectronics [9]. Increasing the degree of integration places high demands on the unit of operations that ensure masking of the ion beam. Diazoquinone–Novolac (DQN) resists play a significant role as masks in modern lithographic processes [1]. The interaction of DQN resists with far ultraviolet, X-ray, and visible radiation has been studied in sufficient detail [1]. However, the effect of ion implantation on the properties of these resists has not been studied enough, although radiation-induced processes occurring during ion implantation can have a significant impact on the quality of devices created.

The goal of the work is to study the radiation-stimulated transformation of the reflectance spectra of positive DQN resists upon the implantation of antimony ions.

MATERIALS AND METHODS

In the present work, we studied the radiation-induced processes upon the implantation of Sb\textsuperscript{+} ions into films of industrial positive photoresist FP9120, which is a composite of photosensitive O-naphthoquinonodiazide and phenol-formaldehyde resin. A photoresist film 1.8 μm in thickness was applied by an industrial process on the surface of \( p \)-type silicon wafers (\( \rho = 10 \ \Omega \ cm \)) with a (111) orientation by centrifugation at a rotation speed of 1800 rpm. Before forming the photoresist film, the silicon wafers were subjected to a standard cycle of surface cleaning in organic and inorganic solvents. The centrifuge rotation time was 40 s. After applying the photoresist to the working side of the silicon substrate, the film was dried for 50–55 min at a temperature of 88°C. The thickness of the photoresist films was controlled mechanically using a Dectak profilometer. Deviations from the average value over the plate did not exceed 1% for all the samples studied. Implantation with 60-keV Sb\textsuperscript{+} ions in the dose range of \( 1 \times 10^{15} - 5 \times 10^{16} \ \text{cm}^{-2} \) at an ion current density of \( j = 4 \ \mu \text{A/cm}^2 \) was carried out in a residual vacuum of \( 10^{-5} \ \text{mmHg} \) using a Vezuvii-6 ion-beam accelerator.

The reflectance spectra of the photoresist—silicon structures were recorded in the range of \( \lambda = 210–1100 \ \text{nm} \) using a Proscan MC-122 single-beam spectrophotometer at room temperature with a resolution of no worse than 1 nm. The reflectance spectra were measured using an attachment for measuring specular reflection, which makes it possible to change the angles of incidence of light from 15° to 90°. Before
each measurement, calibration was performed: control measurement of the intensity of light $I_0$ passing through the diaphragm without test objects at normal incidence of the light beam with respect to the diaphragm in the entire studied wavelength range. The luminous flux was regulated by means of replaceable diaphragms with different areas of the passage opening. The reflectance spectra were recorded at an angle of incidence and reflection of $20^\circ$ to the normal. It was demonstrated by atomic force microscopy that the surface relief of the film is quite smooth; the arithmetic average roughness $R_a$ of the film surface did not exceed 2 nm [3].

RESULTS AND DISCUSSION

In the reflectance spectra of the unirradiated polymer films in the transparency region of $\lambda > 290$ nm, interference bands were observed due to reflection from the photoresist–silicon and photoresist–air interfaces (Fig. 1, curve 1). With increasing wavelength, a rapid increase in the intensity of the interference bands is detected, caused by an increase in the contribution of light reflected from the photoresist–silicon interface due to a decrease in absorption in the photoresist.

In all doped samples, the intensity of the interference bands decreased near the absorption edge (in the wavelength range of $\lambda = 300–800$ nm). This effect was enhanced with an increase in the radiation dose (Fig. 1, curves 2–4). For example, at an implantation dose of $5 \times 10^{16}$ cm$^{-2}$, the interference bands appear only at wavelengths exceeding 500 nm. In the region of $\lambda > 900$ nm, we observed no significant dependence of the intensity of the interference bands on the implantation dose.

Most likely, the main reason for a decrease in the intensity of the interference bands during ion implantation is an increase in the absorption coefficient near the fundamental absorption edge, which is observed in various glassy polymers under high-energy exposure. For example, this effect was observed upon the implantation of polyimide [10–12] and polyethylene terephthalate [13] and was due to carbonization of the surface layer as a result of ion irradiation, the formation of nanoscale inclusions in the irradiated layer, and the formation of amorphous carbon, which has a smooth increase in transmittance at wavelengths from 200 to 500 nm [14].

The additional scattering caused by the ion implantation of a photoresistive film at wavelengths of 300–500 nm can be neglected, because the sizes of second-phase inclusions formed at the implantation doses used in this work do not exceed several tens of nanometers. No changes in the coefficient of reflectance from the surface of single-crystal silicon were observed during implantation in the entire investigated wavelength range. Therefore, the above effects do not significantly affect the intensity of the interference bands.

In the opacity region of the photoresist, there was an increase in the reflectance coefficient at the air–photoresist interface with an increase in the implantation dose (Fig. 1, curves 2–4). A similar effect was observed earlier upon the high-energy exposure of films of polyethylene terephthalate [15] and polyimide [10, 16]. This was caused by the radiation-induced rearrangement of the supramolecular structure of the polymer in the surface region and the relaxation of residual mechanical stress arising during production of the film [15, 17].

The implantation of Sb$^+$ ions led to a shift in the interference maxima and a change in the distance between them (Fig. 1) due to a variation in the optical length of the photoresist film upon irradiation. Based on the reflectance spectra and according to the number and position of the maxima/minima by the equation

$$2dn = m\lambda_m,$$  \hspace{1cm} (1)

where $n$ is the refractive index of the photoresistive film, $d$ is the geometric path traveled by light in the photoresistive film, $m$ is an integer or half-integer number indicating the number of wavelengths that fit in the optical-path difference, and $\lambda_m$ is the wavelength corresponding to the $m$th maximum/minimum, we calculated the dependences of $2dn$ on the wavelength $\lambda$ (Fig. 2). The dependences $2dn(\lambda)$ for all samples look like normal dispersions $dn/d\lambda < 0$.

Significant shrinkage of the photoresist during implantation was not observed. The film thickness varied within the measurement error of $\sim 10$ nm at implantation doses up to $5 \times 10^{16}$ cm$^{-2}$. These experimental results correlate with the data of [18] obtained.
by atomic–force microscopy during the implantation of a thin polyimide film by a narrow ion beam. It is demonstrated in [18] that sputtering (shrinkage) of the polyimide film is observed only at an ion fluence above $1 \times 10^{17}$ cm$^{-2}$, and even at $\Phi = 1 \times 10^{18}$ cm$^{-2}$, the shrinkage did not reach 80 nm, which is less than 4.5% of film thickness. The same result should be expected for the photoresist polymer film.

According to the Lorentz–Lorentz equation [16], the refractive index $n$ of a polymer with the molar mass $M$, substance density $\rho$, and molecular refraction $R_M$ can be determined as

$$n^2 = \frac{(M + 2R_M\rho)}{(M - R_M\rho)}. \quad (2)$$

Molecular refraction $R_M$ is an additive quantity and consists of the refractions $R_i$ of individual atoms and increments for particular types of chemical bonds (double, triple).

The refractive index may decrease during the high-energy irradiation of polymers by means of various mechanisms. It follows from Eq. (2) that an increase in the molar mass $M$ of the polymer leads to a decrease in the refractive index. Phenol-formaldehyde resins are among the oldest representatives of cross-linked polymers; however, there is no consensus on the chemical structure of the network formed by these resins [19]. This, apparently, is because the network structure can be different, depending on the course of the curing reaction.

Phenol-formaldehyde resins are polymers formed by the condensation (reaction with the removal of water) of phenol and formaldehyde, sometimes in the presence of special additives. Therefore, the degree of substitution of aromatic phenol rings in the polymer is variable and can be represented as follows:

$$\text{(I)} \quad \begin{array}{c} \text{OH} \\ \text{R} \end{array} = -\text{H}, \quad -\text{H}_{2}\text{C} \quad \text{R}, \quad -\text{CH}_{2}\text{OH}.$$ 

The network structure, as well as the average molecular weight of the polymer, can significantly change depending on the ratio of the amounts of phenol and formaldehyde used for condensation and on the curing conditions of the resin (temperature, time, mechanical stress).

When phenol-formaldehyde resins are irradiated, crosslinking reactions dominate the destruction due to the structural features of the polymer [20]. The radicals formed during the ion implantation of phenol-formaldehyde resins have different structures and reactivity, but due to reactions with macromolecules, the most thermodynamically stable phenolic- (II) and methylene-type (III) radicals remain quite quickly in the polymer volume, that is,

$$\text{(II)} \quad \begin{array}{c} \text{R} \end{array} = \begin{array}{c} \text{O} \\ \text{R} \end{array}, \quad \begin{array}{c} \text{R} \end{array} = \begin{array}{c} \text{O} \\ \text{R} \end{array}.$$ 

$$\text{(III)} \quad \begin{array}{c} \text{OH} \\ \text{R} \end{array} = \begin{array}{c} \text{C} \\ \text{R} \end{array}, \quad \begin{array}{c} \text{OH} \\ \text{R} \end{array} = \begin{array}{c} \text{H} \\ \text{R} \end{array}, \quad \begin{array}{c} \text{OH} \\ \text{R} \end{array} = \begin{array}{c} \text{O} \\ \text{R} \end{array}.$$ 

Radicals II and III are relatively stable due to delocalization of the electron density in the aromatic system; destruction reactions are not characteristic of them. A variety of recombination reactions of phenolic- (II) and methylene-type (III) radicals lead to the formation of new C–C and C–O chemical bonds and, as a result, an increase in the average molecular weight of phenol-formaldehyde resin macromolecules. The crosslinking of phenol-formaldehyde resin macromolecules under the action of radiation, as mentioned above, leads to an increase in their average molecular weight $M$, which is probably the reason for the observed decrease in the refractive index.

On the other hand, during irradiation, gas evolution occurs (mainly hydrogen and its compounds), which leads to a decrease in the density of the substance $\rho$, since, as we have found, the thickness of the photoresist film does not change significantly. Gas evolution also leads to a decrease in the molecular refraction $R_M$ due to a decrease in the contribution of
the refraction $R_i$ of hydrogen atoms. In accordance with Eq. (2), a decrease in $\rho$ and $R_M$ should lead to a decrease in $n$. These circumstances cause a decrease in the refractive index $n$ of the photoresist upon the implantation of antimony ions.

CONCLUSIONS

Thus, implantation with Sb$^+$ ions leads to a decrease in the refractive index of the photoresist due to the radiation crosslinking of Novolac resin molecules, as well as a decrease in the density $\rho$ and molecular refraction $R_M$ of the photoresist. In the opacity region of the photoresist film, the reflectance coefficient increases with an increase in the dose of Sb$^+$ implantation.

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