

Adhesion of Diazoquinone–Novolac Photoresist Films Implanted with Boron and Phosphorus Ions to Single-Crystal Silicon

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Received July 24, 2019; revised July 24, 2019; accepted August 12, 2019

Abstract—The effect of ion implantation on the specific energy of delamination of FP9120 diazoquinone–novolac photoresist films deposited on single-crystal silicon wafers has been studied. It has been found that during the implantation of boron and phosphorus ions, ester crosslinks between hydroxyl groups on the surface of an oxide layer of the silicon wafer and the carboxyl groups of 1-H-indene-3-carboxylic acid grafted to the polymer are formed at the photoresist–silicon interface, thereby leading to an increase in the specific energy G of film delamination from the substrate. This effect is observed far beyond the ion range, being more pronounced in the case of implantation of phosphorus ions.

Keywords: diazoquinone–novolac photoresist, ion implantation, adhesion, silicon

DOI: 10.1134/S0018143920010129

INTRODUCTION

Interest in studying processes induced by ion bombardment in polymer materials is due to the need to develop new materials for space technology, electronics, and medicine [1]. Ion implantation makes it possible to modify the physicochemical and biological properties of the surface layers of polymers over wide ranges [2]. This opens up new possibilities for the practical use of polymeric materials.

Ion implantation is widely used in modern electronics for the high-precision control of dopant concentrations in semiconductor materials. Diazoquinone–novolac resists, which are composites of photosensitive *o*-naphthoquinone diazide and phenol–formaldehyde resin, play an important role as masks in submicron and nanolithography processes [3, 4]. The interaction of photoresists with ultraviolet and visible radiation and X-rays has been studied in sufficient detail, while the processes induced by ion irradiation were almost not studied despite the fact that they can have a significant effect on the quality of the devices developed [3].

One of the most important characteristics of photoresist films is their adhesion to a single-crystal silicon substrate. Previously, Brinkevich et al. [4] found that Sb ion implantation can significantly change the physicochemical properties of diazoquinone–novolac films at the interface with a silicon substrate. The aim of this work was to study the effect of the implantation of B⁺ and P⁺ ions on the adhesion of

FP9120 diazoquinone–novolac photoresist films to single-crystal silicon.

EXPERIMENTAL

The FP9120 positive photoresist films 1.0 and 1.8 μm thick were deposited onto the surface of Si by centrifugation [5]. The KDB-10 single-crystal (111) silicon wafers (100 mm in diameter) were used as substrates. The thickness h of a photoresist film depended on the rotation speed, and it was 1.0 or 1.8 μm at the rotation speed $v = 8300$ or 2900 rpm, respectively. The photoresist film thickness was monitored at five fixed points located on two mutually perpendicular diameters on each wafer using an MII-4 microinterferometer.

Implantation with B⁺ (the energy $E = 100$ keV) and P⁺ ions (energy, 60 keV) in a dose range of 5×10^{14} – 1×10^{16} cm⁻² was carried out at the ion current density $j = 4$ μA/cm² and a residual pressure of no higher than 10^{-5} torr using a Vezuvii-6 ion-beam accelerator.

Indentation was carried out at room temperature on a PMT-3 instrument according to a standard procedure [6]. A diamond tip as a tetrahedral pyramid with a square base and the apex angle $\alpha = 136^\circ$ was used as an indenter. The indenter load (P) varied in a range of 1–100 g. The loading duration was 2 s, and an exposure under load was 5 s. The specific energy of film delamination (G) was calculated from the following equation, which is widely used to study various polymer films on glass substrates [7, 8]:

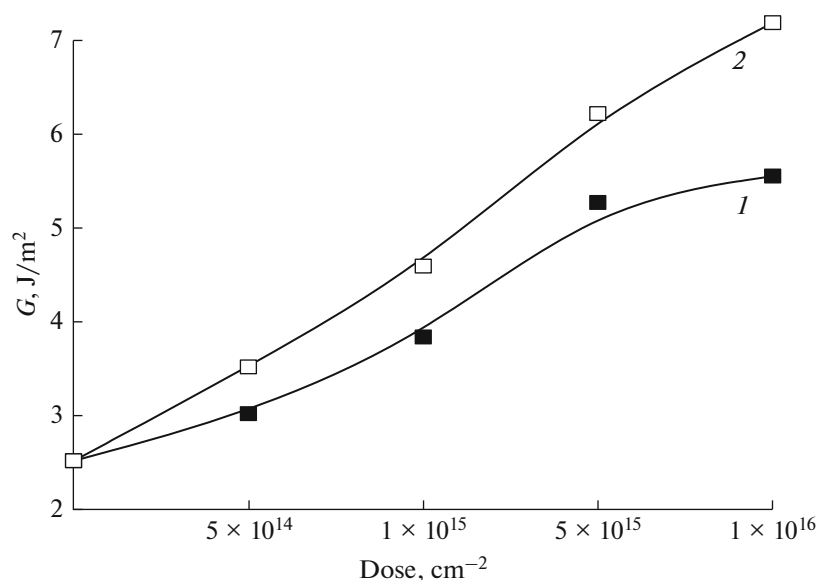


Fig. 1. The dose dependence of the specific delamination energy G for a polymer film of a 1.0 μm thickness measured at a load of 50 g on the implantation of (1) boron and (2) phosphorus ions.

$$G = \frac{0.627H^2h(1-\nu^2)}{E(1+\nu+2(1-\nu)Hl^2/P)^2}, \quad (1)$$

where h is the film thickness; ν is Poisson's ratio (a value of 0.3 was used); E is Young's modulus (8 GPa for the test film); P is the indenter load; and l is the delamination crack length. The measurement was carried out based on at least 50 prints at each load with the processing of the results by mathematical statistics methods [9].

RESULTS AND DISCUSSION

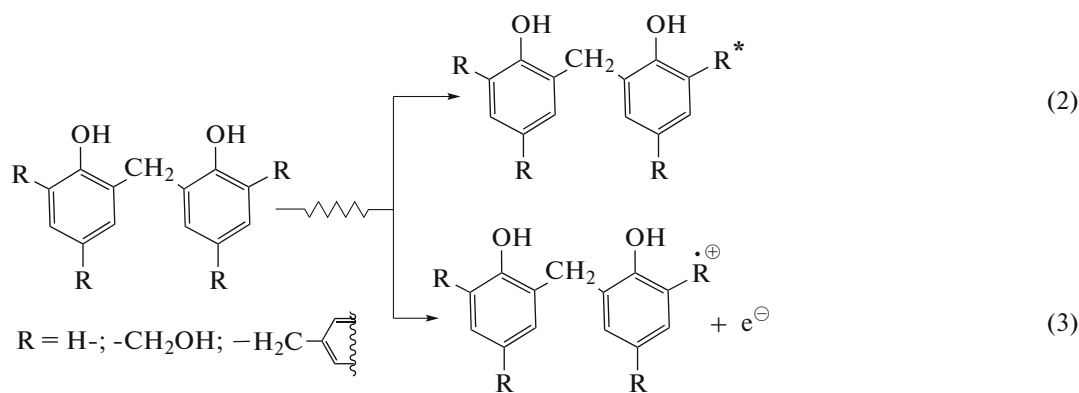
Equation (1) is applicable if the indenter penetration depth in the photoresist–silicon structure substantially exceeds the film thickness. In our case, for a photoresist film 1 μm thick, this condition was satisfied at loads above 20 g, when the indenter penetrated the silicon substrate to a depth of $>4 \mu\text{m}$. For this reason, the effect of ion implantation on the adhesion properties of the photoresist to silicon was studied at loads of 50–100 g, when the lateral component of load was predominant and the dispersion of the measured values of G was small (no higher than 10%).

The implantation of B^+ and P^+ ions led to an increase in the specific energy G of film delamination (Fig. 1); in this case, the growth of G on the implantation of phosphorus ions (Fig. 1, curve 2) was faster than that on the implantation of boron (Fig. 1, curve 1). Note that an increase in the microhardness of a polymer film near the photosensitive polymer–silicon interface upon ion implantation, which can be interpreted as the enhanced adhesion of the polymer film to silicon, was also observed previously [10].

The thickness of diazoquinone–novolac films was greater than the projected path R_p of phosphorus ions calculated using the SRIM-2010 program (www.srim.org), which was 96 nm at an energy of 60 keV used in this work, by a factor of >10 . For boron ions, R_p was ~ 400 nm. Thus, the experimental data indicate that the modification of the physical properties (and, accordingly, the structure) of the diazoquinone–novolac resist upon ion implantation occurs far beyond the ion implantation region.

To explain the experimental data, it is necessary to take into account the specific features of the molecular and supramolecular structures of the polymer. The action of high-energy ions on a phenol–formaldehyde resin leads to the excitation (reaction (2)) and ionization (reaction (3)) of macromolecules. The possibility of nuclear deceleration of phosphorus and boron ions in the sample should also be taken into account. The direct action of high-energy ions on the nuclei of polymer atoms leads to their knocking out of macromolecules, which manifested itself in the destruction and carbonization of phenol–formaldehyde resin along ion tracks.

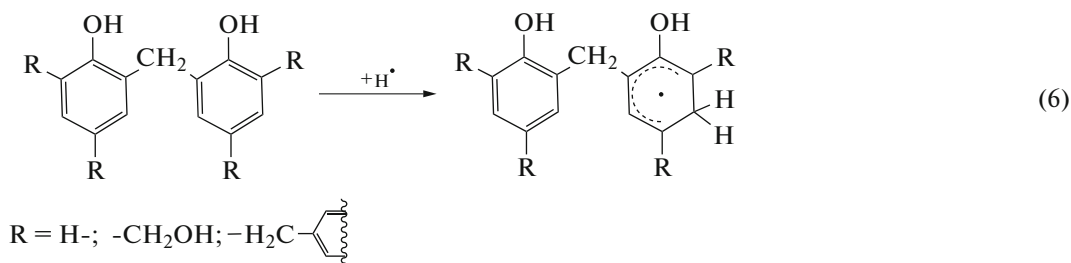
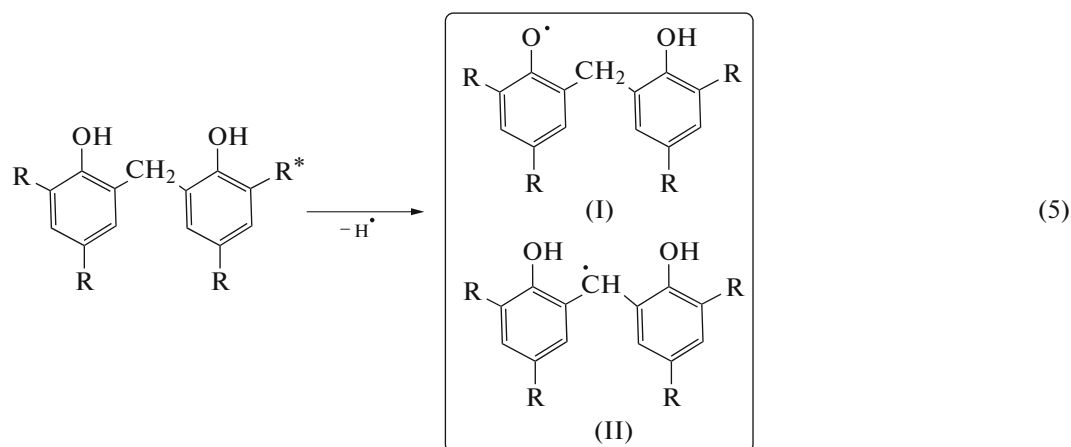
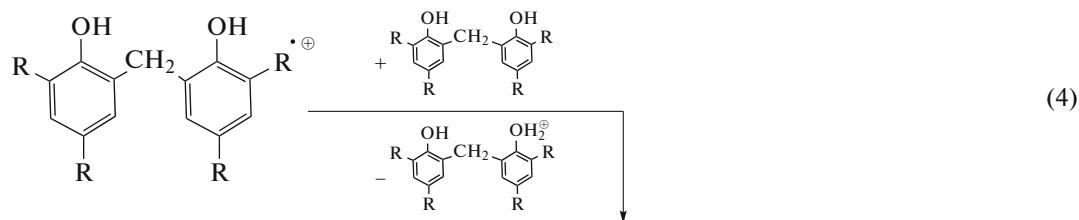
The main feature of the radiation chemistry of phenols, as compared with the conversion of most other organic compounds, in particular, aliphatic alcohols [11–13], is their high radiation resistance. Low radiation–chemical yields of the formation of radiolysis products are related to relatively short lifetimes of ion pairs and high yields of excited states, which are quite stable and less prone to fragmentation reactions due to energy distribution over conjugated π bonds, [14].

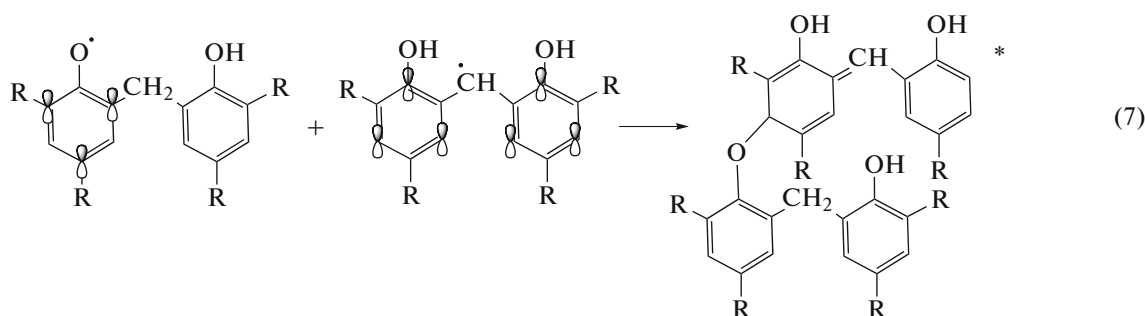


The homolytic transformations of phenol–formaldehyde resin can induce various ion–molecule reactions, for example, reaction (4), the decomposition of excited molecules according to reaction (5), and radical–molecule reactions, for example, (6). As a result, radicals of phenoxy (I) and methylene (II) types are predominantly formed; they exhibit thermodynamic stability due to spin density delocalization in the aromatic system. Therefore, the dominant mechanism of decay of phenol–formaldehyde resin radicals is recombination with the formation

of covalent crosslinks between polymer chains [4], for example, due to reaction (7).

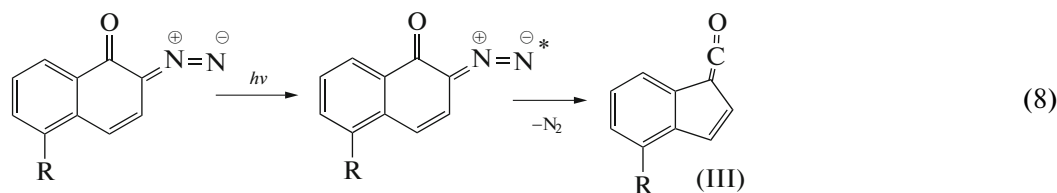
The formation of a new chemical bond upon the recombination of radicals leads to an energy release of 3.9–4.4 eV, which is distributed in the form of excitation energy over the polymer macromolecule. The presence of long molecular chains in the structure of phenol–formaldehyde resin can facilitate energy transfer from the range of ions to relatively long distances, especially, if the excess energy is insufficient for the decomposition of molecules into radicals by reaction (5).



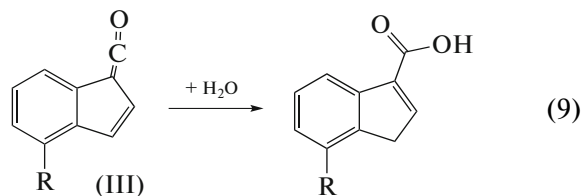


Two energy transfer mechanisms through atomic vibrations (elastic waves) and through the electronic subsystem of molecules can occur in polymers [15–18]. In our opinion, the transfer of excitation energy to the photoresist–silicon interface under conditions of ion implantation mainly proceeds according to the former mechanism. An increase in excess energy on polymer macromolecules near the interface due to the interference of elastic waves is possible; as a result of this, free radicals can be formed with the subsequent chemical modification of a near-surface layer of the photoresist.

However, the main reason for the observed increase in the adhesion of the FP9120 phenol–formaldehyde photoresist to silicon after ion implantation consists in processes with the participation of its photosensitive component, *ortho*-naphthoquinone diazide. This compound chemically grafted to phenol–formaldehyde resin is capable of absorbing UV radiation with an energy of 2.8–4.0 eV; as a result of this, it passes into an excited state [3]. The subsequent decomposition (deazotization) by reaction (8) leads to the formation of highly reactive ketene (III).



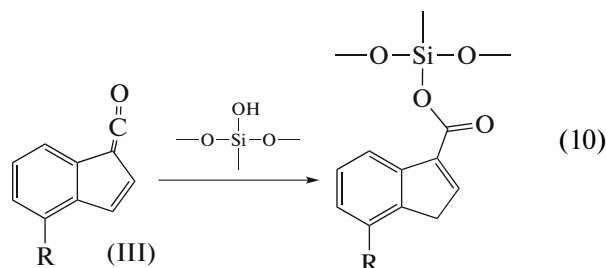
After drying, the photoresist film contains a small amount of water (~1 wt %). Therefore, under photolithography conditions, the ketene adds water in accordance with reaction (9) to be converted into 1-H-indene-3-carboxylic acid, which increases the solubility of phenol–formaldehyde resin in 0.1–0.3 M aqueous solutions of NaOH and other alkaline etching agents [4].



Under ion implantation conditions (a residual pressure of 10⁻⁵ Torr), water is completely removed from the polymer, and reaction (9) cannot proceed. On the other hand, phenol–formaldehyde resin macromolecules can transfer excitation energy to *ortho*-naphthoquinone diazide to cause the formation of ketene (III). This is facilitated by the fact that an energy of <4 eV is insufficient for the occurrence of homolytic destruction reactions similar to reaction (5). Therefore, such a low-energy excitation can freely

move along the polymer macromolecule, regardless of whether it was formed upon the action of corpuscular radiation on the polymer (reaction (2)), due to the recombination of radicals (reaction (7)), or the neutralization of oppositely charged ions.

When a photoresist was implanted with Sb⁺ ions, the interaction of ketene (III) with the OH groups of phenol–formaldehyde resin in the bulk of the polymer led to the formation of ester crosslinks, which was manifested in an increase in the microhardness and embrittlement of the resistive film [4]. The occurrence of a similar reaction with the participation of hydroxyl groups on the surface of a silicon wafer (reaction (10)) may be responsible for the observed increase in the adhesion of the photoresist to the substrate.



Thus, the formation of ester crosslinks between hydroxyl groups on the surface of the oxide layer of a silicon wafer and the carboxyl groups of 1-H-indene-3-carboxylic acid according to reaction (10) leads to an increase in the specific energy G of polymer film delamination.

The found differences in the properties of photoresists implanted with P^+ and B^+ ions should be considered individually. In the case of phosphorus ions, a more pronounced increase in adhesion to the silicon substrate was observed at a lower absorbed dose. This experimental fact is related to a small contribution of nuclear retardation, which is no greater than 10–15% of electronic retardation, upon the implantation of B^+ . This is significantly lower than that upon phosphorus implantation, for which losses due to nuclear (about 40%) and electronic (~60%) retardations are comparable [2]. In addition, linear energy transfer—radiation energy lost per unit path length in the sample—is significantly smaller upon implantation with boron ions. On the one hand, this leads to a lower energy of elastic waves upon B^+ implantation (than that upon the introduction of phosphorus ions) and, accordingly, a smaller amount of energy transferred to the photoresist—substrate interface. On the other hand, higher linear energy transfer values in the case of phosphorus are responsible for a higher probability of the recombination of ions and radicals along the particle track. As a consequence, the yields of electronically excited states of macromolecules, which ultimately cause the deazotization of *ortho*-naphthoquinone diazide with the formation of ester crosslinks at the polymer—silicon interface, are significantly higher.

CONCLUSIONS

In the course of the implantation of boron and phosphorus ions, ester crosslinks between hydroxyl groups on the surface of the oxide layer of a silicon wafer and the carboxyl groups of 1-H-indene-3-carboxylic acid are formed near the photoresist—silicon interface. This leads to an increase in the specific energy G of polymer film delamination. The above effect is observed far beyond the range of ion paths, and it is more pronounced upon the introduction of P^+ .

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Translated by V. Makhlyarchuk