Electronic Conductivity in a $\text{P}^+$-Ion Implanted Positive Photoresist

A. N. Oleshkevich*, N. M. Lapchuk*, V. B. Odzhaev*, I. A. Karpovich*, V. S. Prosolovich*, D. I. Brinkevich*, and S. D. Brinkevich*  

*Belarus State University, Minsk, 220030 Belarus  
**e-mail: Oleshkevich@bsu.by  
**e-mail: Odzaev@bsu.by

Received May 17, 2019; revised May 22, 2019; accepted June 4, 2019

Abstract—FP-9120 positive photoresist films 1.8 $\mu m$ thick implanted with boron and phosphorus ions deposited onto the surface of KDB-10 single-crystal (111) silicon wafers by centrifugation are investigated by their conductivity and electron spin resonance measurements. It is shown that the $\text{P}^+$ ion implantation leads to the formation of a layer with an electronic conductivity of about $10^{-9}$ $\Omega^{-1}$ cm$^{-1}$. At a phosphorous implantation dose of $6 \times 10^{15}$ cm$^{-2}$, the electron spin resonance spectrum contains a narrow isotropic line with a $g$ factor of 2.00654 and a width of 3.83 G, which is most likely related to the formation of phenoxy radicals. As the implantation dose increases to $1.2 \times 10^{16}$ cm$^{-2}$, a line with a $g$ factor of 2.00264 and a width of 3.96 G is detected in the electron spin resonance spectrum, which is caused by unpaired electrons delocalized according to the $\pi$-polyconjugated system.

Keywords: photoresist, implantation, electronic conductivity, electron spin resonance, phenoxy radicals

DOI: 10.1134/S1063739719060076

INTRODUCTION

Polymers are widely used to protect discrete and integrated electronic devices against external factors and have, as a rule, good insulating properties, which ensure electric charge accumulation in the polymer exposed to electromagnetic and penetrating radiation. At a certain critical value, an electrical breakdown can occur, which can cause a failure in the operation of individual electronic circuit components and the entire device [1, 2]. When choosing materials for compensating the induced charges, it should be taken into account that most polymer materials (polyimide, polytetrafluoroethylene, polystyrene, etc.) are hole dielectrics, while the charge drain requires materials with electronic conductivity. In such materials, the injection currents which allow charges to efficiently drain from a dielectric to metal elements (outputs) can be induced [3].

Ion implantation is one of the main methods for forming device structures. It can be used to create both surface and buried layers with different conductivities [4, 5]. Since polymer photoresists are widely used in electronic production and the main material in manufacturing semiconductor devices is silicon, the possibility of using ion implantation to form layers with electronic conductivity was studied on commercial FP-9120 photoresist films deposited by centrifugation onto silicon wafers. It is important that this photoresist is based on phenol formaldehyde resins with strong radiation resistance [6].

The aim of the study is to investigate the possibility of creating a diazoquinone-novolak FP-9120 photoresist layer with the controlled electronic conductivity using ion implantation.

EXPERIMENTAL

Films 1.8 $\mu m$ thick of an FP-9120 positive photoresist, which is a composite of the photosensitive ortho-naphthoquinondiazide and phenol formaldehyde resin, were deposited onto the Si surface by centrifugation at a centrifuge speed of 2900 rpm. The substrates were KDB-10 single-crystal silicon wafers 100 mm in diameter with the (111) orientation. Before the formation of a photoresist film, the silicon wafers were subjected to conventional surface cleaning in organic and inorganic solvents. The rotation time of the centrifuge was 40 s. After depositing the photoresist onto the working side of the wafer, the latter was dried for 50–55 min at a temperature of 88°C. The photoresist film thickness was controlled with an MII-4 microinterferometer at five fixed points lying on two mutually perpendicular diameters on each wafer.

The film’s conductivity was measured by the van der Pauw method. Electric contacts to the implanted photoresist side were formed from an epoxy-based conductive silver paste (CSP). The contact diameter was not more than 1 mm. For the convenience of measurements, copper wires were inserted into the contacts during the polymerization of the CSP.

The ESR spectra of the photoresist were recorded on a RadioPAN SE/X-2543 radiospectrometer with
The ESR spectra of the initial unirradiated photoresist film (Fig. 1), as during implantation with P+ and B+ ions in the dose range of \( D = (6 \times 10^{14} - 1.2 \times 10^{15}) \text{ cm}^{-2} \), contained no absorption lines.

As the phosphorous ion implantation dose increases to \( 6 \times 10^{15} \text{ cm}^{-2} \), a narrow isotropic line with a \( g \) factor of 2.00654 and a width of 3.83 G arises in the ESR spectrum (Fig. 2). The detected line is symmetric; the ESR line’s asymmetry parameter is \( a/b = 1 \), where \( a \) and \( b \) are the amplitudes of the low- and high-field spectral areas of the first derivative of the absorption line. As shown in [7], the detected ESR line originates from the Si–O–C-type paramagnetic centers, which can form at the photoresist–substrate interface.

At an implantation dose of \( 1.2 \times 10^{16} \text{ cm}^{-2} \) (Fig. 3), the line with a width of 3.96 G and a \( g \) factor of 2.00264, which is similar to the \( g \) factor of a free electron occurs in the ESR spectrum. It is most probable that this paramagnetic center is caused by unpaired electrons delocalized according to the \( \pi \)-polyconjugated system. The value \( g = 2.0027 \) typical of the paramagnetic centers detected in coals and neutron-irradiated diamonds and corresponds to the broken carbon bonds [8].

To explain the obtained experimental data, we need to take into account that ion irradiation stimulates a complex set of physical and chemical processes that noticeably affect the polymer structure and composition. For light ions (e.g., B+), the main mechanism of the ion drag in a target is the interaction with

---

**RESULTS AND DISCUSSION**

After ion implantation, the conductivity of the photoresist film increased to over \( 10^{-9} \text{ } \Omega^{-1} \text{ cm}^{-1} \) for both phosphorous and boron. Its growth by about an order of magnitude is observed at the initial dose of \( 6 \times 10^{14} \text{ cm}^{-2} \). These experimental data show, according to the concept of the nanoconductivity of the dielectrics [2], the possibility of creating multilayer coatings with the controlled electrical conductivity of the layers by choosing appropriate implantation modes or using focused ion beams to form conducting channels for the relaxation of the static electric charge.

The ESR spectra of the initial unirradiated photoresist film (Fig. 1), as during implantation with P+ and B+ ions in the dose range of \( D = (6 \times 10^{14} - 1.2 \times 10^{15}) \text{ cm}^{-2} \), contained no absorption lines.

As the phosphorous ion implantation dose increases to \( 6 \times 10^{15} \text{ cm}^{-2} \), a narrow isotropic line with a \( g \) factor of 2.00654 and a width of 3.83 G arises in the ESR spectrum (Fig. 2). The detected line is symmetric; the ESR line’s asymmetry parameter is \( a/b = 1 \), where \( a \) and \( b \) are the amplitudes of the low- and high-field spectral areas of the first derivative of the absorption line. As shown in [7], the detected ESR line originates from the Si–O–C-type paramagnetic centers, which can form at the photoresist–substrate interface.

At an implantation dose of \( 1.2 \times 10^{16} \text{ cm}^{-2} \) (Fig. 3), the line with a width of 3.96 G and a \( g \) factor of 2.00264, which is similar to the \( g \) factor of a free electron occurs in the ESR spectrum. It is most probable that this paramagnetic center is caused by unpaired electrons delocalized according to the \( \pi \)-polyconjugated system. The value \( g = 2.0027 \) typical of the paramagnetic centers detected in coals and neutron-irradiated diamonds and corresponds to the broken carbon bonds [8].

To explain the obtained experimental data, we need to take into account that ion irradiation stimulates a complex set of physical and chemical processes that noticeably affect the polymer structure and composition. For light ions (e.g., B+), the main mechanism of the ion drag in a target is the interaction with
the bound electrons of the target, i.e., electron deceleration [4]. Collisions with nuclei (nuclear deceleration) make a significant contribution only at low energies at the end of the ion path and lead to the atomic displacement, formation of disturbed regions, and, then (at high doses), to the formation of an amorphized carbon layer. During electron deceleration, the target molecules are excited and ionized, which eventually leads to the break of chemical bonds and the formation of radicals, as well as positively charged ions and electrons. In solid polymers, the contribution of the primary ionization of the molecules is dominant; it accounts for more than half of the energy lost during electronic deceleration (according to some reports, up to 80%) [9]. Electrons are quite mobile and can move over distances of about 100 nm, exciting the target atoms and forming latent tracks [4, 9].

Although the phenol formaldehyde resins contained in the photoresist are among the oldest cross-linked polymers, a lack of consensus remains on the chemical structure of their network. This is apparently due to the fact that the network structure depends on the course of the hardening reaction [10].

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

\[ R = \text{H}_2\text{C}-\text{CH}_2\text{OH}, \]
\[ \text{H}_2\text{O}, \]
\[ \text{H} \]

Therefore, the network structure, as well as the average molecular weight of a polymer, can strongly change, depending on the ratio between the phenol and formaldehyde used for condensation, as well as the resin hardening conditions (temperature, time, and mechanical impact).

The phenol formaldehyde resins on which the FP-9120 photoresist are based are, like all polymers with aromatic
rings, more radiation-resistant than aliphatic polymers, e.g., polyethylene or polypropylene, which is due to the features of their radiation-chemical transformations.

Under implantation of the photoresist with B\(^+\) and P\(^+\) ions, the ions and free radicals form along the charged particle tracks. Due to the set of ion-molecular and radical-molecular reactions in phenol formaldehyde resins, mainly thermodynamically stable radicals of the phenolic (II) and methylene (III) types will be formed. However, several days after irradiation, we did not detect these radicals in the samples implanted with B\(^+\) or in those implanted with P\(^+\) by the ESR in doses of up to \(6 \times 10^{15}\) cm\(^{-2}\). These intermediates probably vanish sufficiently fast during the biradical reactions, mainly with the formation of new chemical bonds.

The type-(II) and (III) radicals are relatively stable due to the delocalization of the electron density according to the aromatic system. The destruction reactions are not typical of them; a key role is played by various recombination reactions, which leads to the formation of new C–C and C–O chemical bonds. In addition, these radicals can effectively interact with the ketene formed under the irradiation of orthonaphthoquinone diazide, which is a part of the FP-9120 positive photoresist [5]. This leads to the polymer hardening during irradiation and its high level of radiation resistance.

![Fig. 3. ESR spectrum of the photoresist film irradiated by phosphorous ions with energy of 100 keV at an implantation dose of 1.2 \times 10^{16} \text{ cm}^{-2}.

\[
g = 2.00264
\]

\[
\text{Reference line}
\]

\[
\begin{align*}
\text{Amplitude, rel. units} & \\
0 & \\
-700 & \\
700 & \\
2000 & 3000 & 4000
\end{align*}
\]

\[
H, G
\]

\[
\begin{align*}
\text{g} & = 2.00264 \\
& \text{Reference line}
\end{align*}
\]

\[
\begin{align*}
\text{Amplitude, rel. units} & \\
0 & \\
-700 & \\
700 & \\
2000 & 3000 & 4000
\end{align*}
\]

\[
\text{g} = 2.00264
\]

\[
\begin{align*}
\text{Reference line} & \\
\text{Amplitude, rel. units} & \\
0 & \\
-700 & \\
700 & \\
2000 & 3000 & 4000
\end{align*}
\]

![Diagram](https://via.placeholder.com/150)

\[
\begin{align*}
\text{g} & = 2.00264 \\
& \text{Reference line}
\end{align*}
\]
As the $P^+$ implantation dose increases above $6 \times 10^{15}$ cm$^{-2}$, stable radicals are formed in the phenol formaldehyde photoresist, which can be detected by the ESR. This indicates the formation of new types of free radicals in the polymer characterized by the extremely high thermodynamic stability, as well as stability against biradical reactions, in which paramagnetic particles in organic substances die.

Under the action of the electron deceleration of the bombarding ions and secondary charged particles, the phenol formaldehyde resin macromolecules are ionized and excited. In the subsequent reactions of the neutralization of oppositely charged ions and recombination of radicals, secondary excited macromolecules will be formed. The relatively high stability of the polymers containing aromatic rings against ionizing radiation is due to the fact that the excited states of their macromolecules are relatively stable, decay more rarely with the formation of radicals, and more frequently pass to the ground state by emitting an electromagnetic radiation quantum.

One type of reaction of the excited phenol formaldehyde resin macromolecules is decomposition with elimination of the hydrogen molecules (dehydrogenation), water (dehydration), or low molecular weight carbon compounds (decarbonization). Since irradiation with phosphorus ions occurs in a vacuum (under a residual pressure of $10^{-5}$ Torr), the entropy factor facilitates the molecular decay. As a result of the removal of the compounds with a low molecular weight from the phenol formaldehyde resin, the content of type-(IV) quinoid structures in it should significantly increase. The possibility of delocalization (distribution) of the excitation energy over the system of conjugated multiple bonds predetermines the stability of the quinoid structures under irradiation. In addition, it should be noted that the fragments similar to (IV) in the phenol formaldehyde resin can form not only during the molecular decay of the excited states but also during the disproportionation of the type-(II) and (III) radicals.

The type-(IV) quinoid structures differ from the initial polymer by the system of multiple conjugated bonds but retain some phenolic aromatic fragments. Therefore, when interacting with the carbon-centered radicals, e.g., methylene type (III), the phenolic fragments can be oxidized to the corresponding phenoxy radicals (V). A feature of such radicals is their very high degree of spin density delocalization in the quinoid system and, consequently, a significant increase in the lifetime of the paramagnetic centers.

![Diagram](image.png)

In our opinion, the narrow isotropic line with $g = 2.00654$ (Fig. 2) in the phenol formaldehyde resin observed in the ESR spectra can be caused by the phenol radicals with a high degree of delocalization, e.g., (V).

It can be seen that the unpaired electron in the phenoxy radical (V) is delocalized, in particular, on oxygen atoms. Therefore, at the photoresist—substrate interface, it can recombine with the formation of new Si–O–C bonds, which results in the additional inoculation of the photoresist onto the silicon surface. The possibility of such reactions is indirectly confirmed by our microhardness measurements [11]. For instance, when implanting the photoresist—silicon structures with $P^+$ ions, the polymer film was hardened at the photopolymer—silicon interface, as it was under implantation with $B^+$ ions.

The further increase in the $P^+$ ion implantation dose to $1.2 \times 10^{16}$ cm$^{-2}$ leads to an increase in the percentage of carbonization of the phenol formaldehyde photoresist by the elimination of the low molecular weight volatile substances and formation of new multiple bonds. In the irradiated polymer regions, the number of quinoid groups will be significantly larger than the number of phenolic fragments. In the region of thermalization of $P^+$ ions and, to a lesser extent, along the tracks, even amorphized carbon can be formed due to the highly intense destruction. This is indicated by the occurrence of a line with $g = 2.00264$ in the ESR spectrum at the dose mentioned above (Fig. 3).

A feature of all the quinoid structures is their electron-acceptor properties. The electrons generated by the ionization of the phenol formaldehyde photoresist macromolecules after thermalization will be captured with the formation of a semiquinone anion radical. If the quinoid structure has a high-power system of conjugated carbon—carbon bonds, the resulting semiquinone radical anion is delocalized to such an extent that it can be detected even weeks after the irradiation of the photo-
Thus, the formation of stable radicals detected by the ESR after the P⁺ implantation of the positive phenol formaldehyde photoresist, as well as the occurrence of the electronic conductivity in it, are mainly

resist. In addition, the charge transport through a system of conjugated multiple bonds determines the electronic type of the conductivity of the irradiated photoresist (Fig. 4).

Fig. 4. Probable mechanism of charge transfer through system of conjugated bonds of quinoid photoresist structures.
due to its carbonization and the formation of a powerful system of conjugated multiple bonds in the macromolecule.

In the boron-implanted photoresist samples, we could not detect stable radicals by the ESR at the implantation doses identical with phosphorus. The observed differences between the properties of the irradiated polymer are due to the fact that, during B⁺ implantation, the nuclear deceleration contribution is small (not more than 10–15% of the electronic deceleration). This is significantly lower than under the implantation of phosphorus, in which the nuclear (~40%) and electronic (~60%) deceleration loss are comparable. In addition, the linear energy transfer (the radiation energy loss per unit path length in the sample) under implantation with boron ions will be significantly lower. Therefore, under B⁺ implantation, the ionizing radiation energy will be distributed over a larger polymer volume and, consequently, the degree of radiolytic transformations of the phenol formaldehyde resin within the ion path range will be much lower. It can be expected that lines with a g factor of 2.00264 and a width of 3.96 G in the ESR spectrum, which are characteristic of a highly carbonized polymer, will arise with a significant increase in the dose of B⁺ ion implantation into a phenol formaldehyde resin.

CONCLUSIONS

The study of the electrical conductivity and paramagnetism of a 1.8-μm-thick FP-9120 positive photoresist films implanted with boron and phosphorus ions deposited on a KDB-10 single-crystal (111) silicon wafer surface by centrifugation showed that, as a result of the implantation of P⁺ ions, a layer with the controlled electronic conductivity satisfying the concept of the nanoconductivity of the dielectrics [2] can be formed. This effect can be used to drain electric charges during the induced excitation of the polymer film. At a phosphorus implantation dose of 6 × 10¹⁵ cm⁻², a narrow isotropic line with a g factor of 2.00654 and a width of 3.83 G is observed in the ESR spectrum, most likely due to the formation of phenoxy radicals. With an increase in the implantation dose to 1.2 × 10¹⁶ cm⁻², a line with a g factor of 2.00264 and a width of 3.96 G arises in the ESR spectrum due to the unpaired electrons delocalized according to the π-polyconjugated system.

REFERENCES
1. Rau, E.I., Evstaf'eva, E.N., Zaitsev, S.I., Knyazev, M.A., Svintsov, A.A., and Tatarintsev, A.A., Complex investigations of effects of charging a polymer resist (PMMA) during electron lithography, Russ. Microelectron., 2013, vol. 42, no. 2, pp. 89–98.
2. Abramshin, A.E., Development of the concept of nanoconductivity of dielectrics in domestic space technology, Tekhnol. Elektron. Sovremen., 2012, no. 3, pp. 29–30.
3. Doronin, A.N., Tyutnev, A.P., Saenko, V.S., and Pozhidaev, E.D., Conductivity of external dielectric coatings of spacecraft under the influence of cosmic ionizing radiation, Perspekt. Mater., 2001, no. 2, pp. 15–22.
4. Odzhaev, V.B., Kozlov, I.P., Popok, V.N., and Sviridov, D.V., Ionnya implantatsiya polimerov (Ion Implantation of Polymers), Minsk: Belgosuniversitet, 1998.
5. Brinkevich, D.I., Brinkevich, S.D., Vabishechevich, N.V., Odzhaev, V.B., and Prosolovich, V.S., Ion implantation of positive photoresists, Russ. Microelectron., 2014, vol. 43, no. 3, pp. 194–200.
6. Grassie, N. and Scott, G., Polymer Degradation and Stabilisation, Cambridge: Cambridge Univ. Press, 1985.
7. Veinger, A.I., Zabrodskii, A.G., Tisnek, T.V., and Mokhov, E.N., Peculiarities of the electron spin resonance in an n-type 4H-SiC:N in the insulator-metal transition region. II. The width and form line analysis, Semiconductor, 2004, vol. 38, no. 7, pp. 782–787.
8. von Bardeleba, H.J., Cantin, J.J., Zaellama, K., and Zb, A., Spin and microstructure of the amorphous carbon, Diamond Relat. Mater., 2003, vol. 12, pp. 124–129.
9. Eksperimental'nye metody khimii vysokikh energii (Experimental Methods of High Energy Chemistry), Mel'nikov, M.Ya., Ed., Moscow: Mosk. Gos. Univ., 2009.
10. Askadskii, A.A. and Kondrashenko, V.I., Komp'yuternoe materialovedenie polimerov. Tom 1. Atomnomolekul'nyi uroven' (Computer Materials Science of Polymers, Vol. 1: Atomic–Molecular Level), Moscow: Nauchnyi Mir, 1999.
11. Vabishechevich, S.A., Vabishechevich, N.V., Brinkevich, D.I., Prosolovich, V.S., Odzhaev, V.B., and Yankovskii, Yu.N., Strength properties of FP9120 photoresist-silicon structures, Vestn. Polotsk. Univ., Ser. C: Fundam. Nauki. Fiz., 2014, no. 2, pp. 69–73.

Translated by E. Bondareva