DOI 10.1007/s10812-020-01049-4
Journal of Applied Spectroscopy, Vol. 87, No. 4, September, 2020 (Russian Original Vol. 87, No. 4, July–August, 2020)

MECHANISM OF THE ADHESIVE INTERACTION OF DIAZOQUINONE-NOVOLAC PHOTORESIST FILMS WITH MONOCRYSTALLINE SILICON

S. D. Brinkevich,[a*] E. V. Grinyuk,[a] D. I. Brinkevich,[a] R. L. Sverdlov,[a] V. S. Prosolovich,[a] and A. N. Pyatlitski[b]

UDC 535.3;548.0

Fourier-transform infra-red spectroscopy with frustrated total internal reflection was used to study radiation-induced processes upon the implantation of boron and phosphorus ions into positive FP9120 diazoquinone-novolac photoresist films on silicon. Strengthening of the photoresist adhesion to monocrystalline silicon was found to be caused by the formation of ester linkages between hydroxyl groups on the surface of the silicon wafer oxide layer and carboxyl groups of 1-H-indene-3-carboxylic acid.

Keywords: *frustrated total internal reflection spectrum, diazoquinone-novolac photoresist, implantation, adhesion, silicon.*

Introduction. One of the most promising methods for controlling the electrophysical, strength, and biological properties of polymer surface layers is ion implantation [1, 2]. In recent years, interest has arisen in the study of processes in polymer materials induced by ion irradiation due to the urgent need to develop new materials for use in areas such as space technology and medicine [1, 3]. Ion implantation is also commonly used in modern electronics, permitting precise control of trace alloying elements. This is a general and versatile method. Silicon serves as the major material for the preparation of semiconductor devices. Diazoquinone-novolac (DQN) resists are composites of light-sensitive O-naphthoquinone diazide and phenolformaldehyde resin, which play an important role in submicron and nanolithography processes in the construction of various instruments [4]. The interaction of DQN resists with UV, x-ray, and visible radiation has been studied in rather considerable detail, while processes induced by ion radiation have not been sufficiently investigated although they can have a significant effect on the quality of the manufactured devices [4–7].

In previous works [8–10], we have shown that upon the ion implantation of polymers, radiation-induced processes occur not only in the region of the ion path length but also beyond it. In particular, we found that the implantation of B^+ and P^+ ions leads to strengthening of the adhesion interaction of the DQN-resist film with silicon [10]. However, the mechanism of the radiation-induced processes responsible for change in the adhesion properties of DQN resists to silicon has not been established.

Fourier-transform IR (FT-IR) spectroscopy with frustrated total internal reflection is commonly used to study thin films and permits us to obtain quantitative information on the composition and structure of complex organic molecules and their mixtures in the solid aggregate state [11]. There have not yet been any FT-IR studies of DQN-photoresist films on the surface of ion-irradiated monocrystalline silicon. In the present work, we studied the mechanism of the adhesive interaction of DQN-resist films with monocrystalline silicon.

Experimental. Films of positive FP9120 photoresist, which is a composite of light-sensitive O-naphthoquinone diazide and phenolformaldehyde resin, with thickness 1.0, 1.8, and 2.5 μm were deposited on a silicon surface by centrifugation [9]. The thickness h of the photoresist is a function of the rotational rate of the centrifuge rotor: 1.0 μm when ν = 8300 rpm, 1.8 μm when ν = 2900 rpm, and 2.5 μm when ν = 1200 rpm. Wafers of KDB10 monocrystalline silicon with diameter 100 μm and orientation (111) were used as the bases. Prior to formation of the photoresist film, the silicon wafers were subjected to

[*]To whom correspondence should be addressed.

[a]Belarusian State University, 220030, Minsk, Belarus; email: brinkevichsd@bsu.by; [b]JSC "INTEGRAL"Holding Management Company, 220600, Minsk, Belarus; email: petan@tut.by. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 87, No. 4, pp. 589–594, July–August, 2020. Original article submitted May 11, 2020.

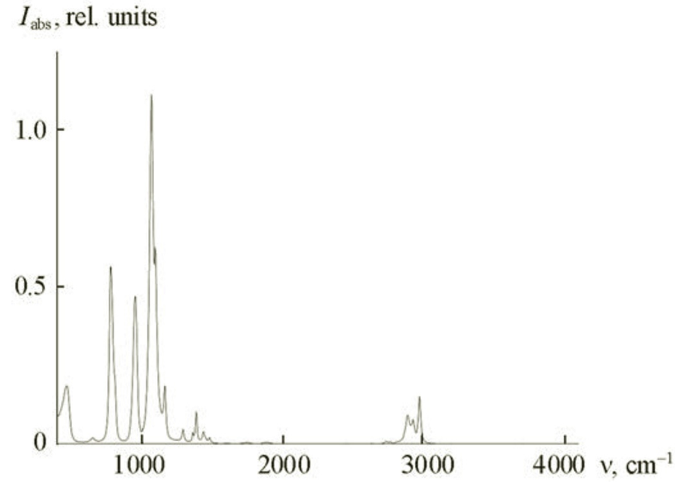


Fig. 1. FT-IR spectra of tetraethoxysilane.

a standard cycle of surface cleaning using organic and inorganic solvents. The centrifuge rotor rotation time was 40 s. After deposition of the photoresist on the working side, the wafers were dried for 50–55 min at 88°C. The photoresist film thickness was monitored with an MII4 microinterferometer using five fixed points located on two mutually perpendicular diameters on each wafer.

The implantation of P^+ phosphorus ions (energy 100 keV) and B^+ boron ions (energy 60 keV) with a dose of $1.2 \cdot 10^{16}$ cm^{-2} and ion current density $j = 4$ μA/cm^2 was carried out at residual vacuum not worse than 10^{-5} Pa in a Vesuvius-6 ion beam accelerator. The FT-IR spectra of the photoresist/silicon structures were recorded in the 400–4000 cm^{-1} range at room temperature using a Bruker ALPHA Fourier-transform spectrometer. The resolution was 2 cm^{-1} using 24 scans. Background correction was carried out prior to each measurement.

Results and Discussion. In previous work [10], we studied the adhesive properties of photoresist/silicon structures with implanted P^+ and B^+ ions and proposed that the major reason for the enhanced adhesion between silicon and the DQN photoresist is the formation of new C–O–Si bonds on the photoresist/silicon separation boundary. In order to check this hypothesis, we studied the FT-IR infra-red spectra of tetraethoxysilane (Fig. 1) containing the Si–C–Si bond and compared them with the spectra of the starting and implanted photoresist/silicon structures. We note that the implantation of light (B^+ and P^+) and heavy (Sb^+) ions has different effects on the adhesive properties of FP9120 photoresist to silicon. The adhesion is enhanced upon the insertion of B^+ and P^+ ions [10], while the adhesion deteriorates after the implantation of Sb^+ ions [12].

The strongest FT-IR lines in the spectrum of tetraethoxysilane due to vibrations of the Si–O–C group are seen at ~1070 and ~780 cm^{-1} (Fig. 1). These bands are also present in the spectra of FP9120 photoresist films shown in Fig. 2; their intensity depends significantly on the type of implanted ions and correlates with the adhesive properties of the resist. Thus, a rather strong band appears at ~780 cm^{-1} in the FT-IR spectrum of the photoresist/silicon structures after ion implantation with B^+ ions (Fig. 2a, curve 2). This band is hardly evident on the noise background for the starting unimplanted films (curve 1).

The intensity of the band at 780 cm^{-1} upon the implantation of P^+ ions is greater than for samples implanted with B^+ ions with identical ion dose $1.2 \cdot 10^{16}$ cm^{-2} (Fig. 3). This result correlates well with the finding that the adhesion of samples with implanted P^+ ions is higher than upon the implantation of B^+ ions [10]. In previous work [12], we found that the adhesion of the photoresist to silicon is lower by an order of magnitude in the spectra of FP9120/silicon implanted with large doses of Sb^+ ions [12]. The spectra of these structures do not show bands with maxima at ~780 and ~1070 cm^{-1} attributed to C–O–Si bond vibrations. These experimental data indicate that the adhesion between silicon and the DQN photoresist results from the formation of C–O–Si bonds on the photoresist/silicon separation boundary.

Analysis of the behavior of the band at ~1070 cm^{-1} is difficult due partial overlap of a band with maximum at ~1100 cm^{-1} attributed to the vibration of C–O bonds in the R–O–CO–Ar fragment [13, 14]. Thus, in the starting unimplanted photoresist/silicon structures, the band at ~1070 cm^{-1} appears as a hardly visible maximum on the low-energy wing of a broad band with maximum at ~1100 cm^{-1} (Fig. 2b, curve 1). After B^+ ion implantation, the intensity of the maximum at 1070 cm^{-1} is enhanced and becomes comparable to the intensity of the band at ~1100 cm^{-1} (curve *2*). These results support the above conclusion concerning the formation of adhesive Si–O–C bonds at the result of ion implantation.

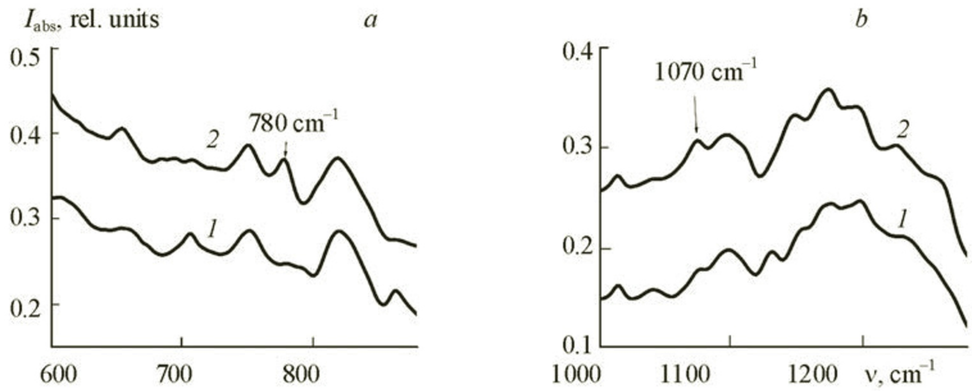


Fig. 2. FT-IR spectra of starting FP9120 films (1) and films implanted with B^+ ions (dose $1.2 \cdot 10^{16}$ cm^{-2} (2) on silicon (film thickness 2.5 μm) at 600–860 cm^{-1} (a) and 1000–1250 cm^{-1} (b).

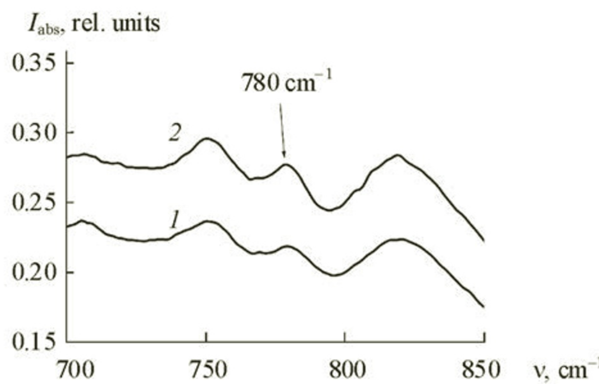
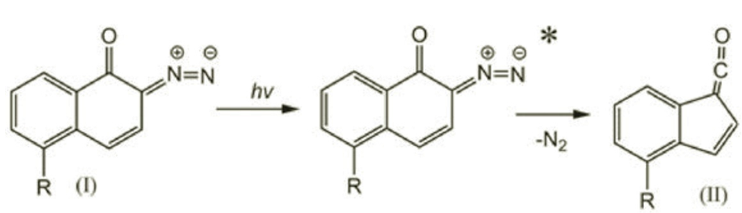


Fig. 3. FT-IR spectra of FP9120-photoresist films implanted with B^+ (1) and P^+ ions (2). The dose was $1.2 \cdot 10^{16}$ cm^{-2} and the film thickness was 1.8 μm.

The bands at ~780 and ~1070 cm^{-1}are observed only in the spectra of photoresist films with thickness ≤2.5 μm. When the film thickness is increased to 5 μm, these bands are hardly noticeable on the noise background, perhaps because the thickness of the adhesion layer on the polymer/silicon separation boundary is ~100 nm [13]. Thus, the contribution of the adhesion layer to the FT-IR spectra decreases with increasing film thickness.

The thirdmost intense FT-IR band of tetraethoxysilane with maximum at ~970 cm^{-1} (Fig. 1) is observed only for photoresist film samples with thickness 1 μm. In this case, the intensity of this band is very low (hardly noticeable on the noise background) and not suitable for analysis.

The major reason for the increase in the adhesion of the FP9120 phenolformaldehyde photoresist to silicon after the implantation of B^+ and P^+ ions proposed in our previous work [10] is attributed to radiation-induced processes involving the photosensitive component, namely, orthonaphthoquinone diazide (I). This compound is chemically linked to the phenol-formaldehyde resin and can undergo diazotization upon the action of photons with energy 2.8–4.0 eV (UV radiation) to give highly reactive ketene (II) [3, 12]:



(1)

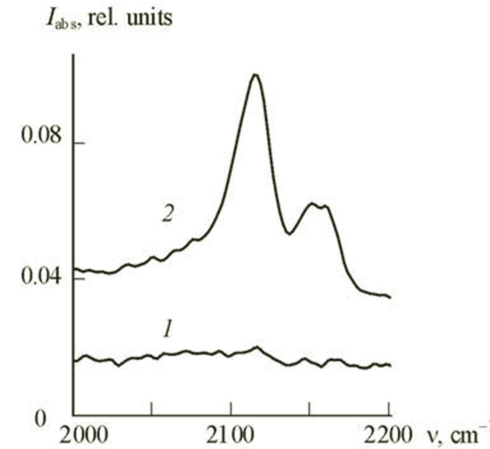
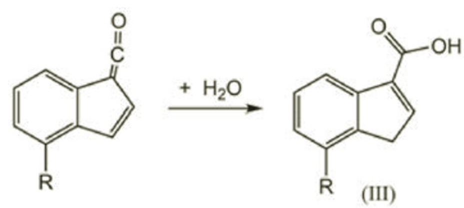


Fig. 4. FT-IR spectra of starting FP9120 films (1) and films implanted with B^+ ions (2) on silicon in the region of the stretching vibrations of C=C=O cumulative double bonds; the dose was $1.2 \cdot 10^{16}$ cm^{-2} and the film thickness was 2.5 μm.

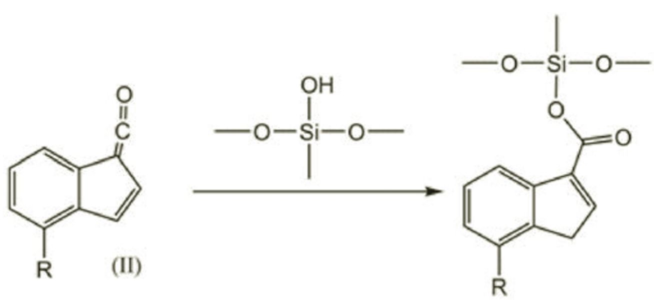
Under conditions of the photolithographic process, ketene II rapidly reacts with water present in amounts of ~1% in the film:



(2)

leading to the formation of 1-H-indene-3-carboxylic acid (III), which accounts for the enhanced solubility of the "over-exposed regions" of the resist in 0.1–0.3 M aqueous NaOH and other alkaline etchants [4, 5, 12].

The increase in the adhesion of the photoresist to the silicon base upon the implantation of B^+ and P^+ ions, as proposed in our previous work [10], can be related to the following reaction:



(3)

since water is virtually entirely removed from the film upon carrying out this operation at high vacuum of 10^{-5} Pa.

The presence of a ketene necessary for reaction (3) in the implanted photoresist/silicon structures is indicated by the FT-IR band at 2100–2170 cm^{-1} (Fig. 4, curve 2) due to stretching vibrations of the C=C=O cumulative double bonds [14, 15]. We note that this band is absent from the spectra of nonirradiated photoresist/silicon structures (curve 1).

The formation of new Si–O–C ester bonds occurs at depths 5–15 times greater than the projected ion path length in the polymer films studied. Thus, diazotization of the light-sensitive component of the photoresist occurs due to the transfer of low-energy excitation (<4 eV) from the ion thermalization region where there is active neutralization of oppositely charged ions and radical recombination over macromolecular chains to the polymer/silicon phase separation boundary.

Other mechanisms for the adhesive interaction of the polymer with monocrystalline silicon are also possible. Thus, Lu and Mi [16] noted the formation of hydrogen bonds on the polyacrylamide/silicon separation boundary, which appeared in the spectrum as an increase in intensity and shift in the maximum of the Si–O bond stretching vibrations at 1107 cm^{-1}. In our experiments, in contrast, we found a decrease in intensity of the band with maximum at ~1100 cm^{-1} upon the implantation of B^+ ions. We also did not find a significant transformation of the FT-IR spectrum in the region of the stretching vibrations of hydrogenbonded OH groups [17]. Hanisch et al. [18] also described the formation of Si–C bonds on the polymer/silicon separation boundary. However, this requires special treatment of the silicon surface.

Conclusions. Fourier transform IR spectroscopy with frustrated total internal reflection was used to obtain evidence of the formation of Si–O–C ester crosslinks between the hydroxyl groups on the surface of the oxide layer of the silicon wafer and the carboxyl groups of 1-H-indene-3-carboxylic acid, which can account for the increase in the adhesion of FP9120 diazoquinone novolac resist to monocrystalline silicon upon the implantation of B^+ and P^+ ions.

REFERENCES

1. A. Kondyurin and M. Bilek, *Ion Beam Treatment of Polymers: Application Aspects from Medicine to Space*, Elsevier (2015).
2. R. J. Composto, R. M. Walters, and J. Genze, *Mater. Sci. Eng.: R: Rep.*, **38**, Nos. 3–4, 107–180 (2002).
3. A. N. Doronin, A. P. Tyutnev, V. S. Saenko, and E. D. Pozhidaev, *Perspekt. Materialy*, No. 2, 15–22 (2001).
4. W. M. Moreau, *Semiconductor Lithography. Principles, Practices and Materials*, New York–London, Plenum Press (1988).
5. Roy Debmalya, P. K. Basu, P. Raghunathan, and S. V. Eswaran, *Magn. Res. Chem.*, **41**, 84–90 (2003).
6. V. I. Lebedev, V. E. Kotomina, S. V. Zelentsov, E. S. Leonov, and K. V. Sidorenko, *Vestn. Nizhegorod. Univ.*, No. 1, 178–182 (2014).
7. J. S. Martins, D. G. A. L. Borges, R. C. Machado, A. G. Carpanez, R. M. Grazul, F. Zappa, W. S. Melo, M. L. M. Rocco, R. R. Pinho, and C. R. A. Lima, *Eur. Polym. J.*, **59**, 1–7 (2014).
8. D. I. Brinkevich, A. A. Kharchenko, S. D. Brinkevich, M. G. Lukashevich, V. B. Odzhaev, V. F. Valeev, V. I. Nuzhdin, and R. I. Khaibullin, *Poverkhnost' Rentgen., Sinkhrotr. I Neutron. Issled.*, No. 8, 25–30 (2017).
9. D. I. Brinkevich, A. A. Kharchenko, V. S. Prosolovich, V. B. Odzhaev, S. D. Brinkevich, and Yu. N. Yankovskii, *Mikroélektronika*, **48**, No. 3, 235–239 (2019).
10. S. A. Babishchev, S. D. Brinkevich, D. I. Brinkevich, and V. S. Prosolovich, *Khim. Vysokikh Énergii*, **54**, No. 1, 54–59 (2020).
11. J. Bocker*, Spektroskopie*, Vogel Industrie Medien Gmbh & Co KG, Wurzburg (1997).
12. D. I. Brinkevich, S. D. Brinkevich, N. V. Babishchev, B. V. Odzhaev, and V. S. Prosolovich, *Mikroélektronika*, **43**, No. 3, 193–199 (2014).
13. R. D. Priestly, C. J. Ellison, L. J. Broadbelt, and J. M. Torkelson, *Science*, **309**, No. 5733, 456–459 (2005).
14. B. N. Tarasevich, *IR Spectra of the Major Classes of Organic Compounds. Handbook Materials* [in Russian], Moskovsk. Gos. Univ., Moscow (2012).
15. E. Pretsch, P. Bühlmann, and C. Affolter, *Determination of Organic Compounds. Tables of Spectral Data*, Springer (2000).
16. Xiaolin Lu and Yongli Mi, *Macromolecules*, **38**, No. 3, 839–843 (2005).
17. V. S. Prosolovich, D. I. Brinkevich, S. D. Brinkevich, E. V. Grinyuk, and Yu. N. Yankovskii, *Materials of the Thirteenth International Conference on the Interaction of Radiation with Solids,* Minsk, September 30–October 2, 2019 [in Russian], Izd. Tsentr Belarus. Gos. Univ. Minsk (2019), pp. 169–171.
18. J. Hanisch, K. Hinrichs, and J. Rappich, *ACS Appl. Mater. Interfaces*, **11**, No. 34, 31434–31440 (2019).