ISSN 0018-1439, High Energy Chemistry, 2020, Vol. 54, No. 2, pp. 115–122. © Pleiades Publishing, Ltd., 2020.
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RADIATION CHEMISTRY

EPR Spectroscopy of Diazoquinone–Novolac Resist Films Implanted with P^+ and B^+ Ions

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Received August 28, 2019; revised August 28, 2019; accepted October 21, 2019

Abstract—The nature of stable radicals in FP9120 positive photoresist films implanted with boron and phosphorus ions and deposited on the surface of single-crystal silicon wafers has been determined using the EPR technique. At an implantation fluence of 6×10^{15} cm^{-2}, a narrow singlet isotropic line with a *g*-factor of 2.0064 is observed in the EPR spectrum. As the fluence increased to 1.2×10^{16} cm^{-2}, the *g*-factor decreased to values close to the *g*-factor of the free electron. The concentration of paramagnetic centers was higher during implantation of phosphorus ions than in the samples implanted with boron ions. This difference is due to a smaller contribution of nuclear stopping during B^+ implantation, which does not exceed 10–15% of electronic stopping. The formation of long-lived paramagnetic centers recorded by EPR a week after implantation of positive phenol–formaldehyde photoresist is due to the presence of a powerful system of conjugated >C=O and –C=C– multiple bonds in the structure of the radicals.

Keywords: photoresist, implantation, phosphorus, boron, EPR, semiquinonoid radical anions

DOI: 10.1134/S0018143920020046

INTRODUCTION

One of the most promising methods for controlling the electrophysical, strength, and biological properties of the surface layers of polymers is ion implantation [1, 2]. Thus, ion bombardment leads to a monotonic increase in the electrical conductivity of the implanted layer, the value of which can vary by 10–18 orders of magnitude [3]. The advantage of magnetic resonance methods (in particular, EPR) is high sensitivity, which is especially important in the study of thin films. Electron paramagnetic resonance spectroscopy has been widely used in physics, chemistry, biology, and medicine since the middle of the last century. It is the main, and often the only possible, method for studying free radical processes [4].

The aim of this study was to investigate radiation-induced processes in films of the diazoquinone–novolac photoresist FP9120 during implantation of boron and phosphorus ions and irradiation with γ-rays.

EXPERIMENTAL

Films of positive photoresist FP9120, which is a composite of photosensitive *o*-naphthoquinone diazide and phenol–formaldehyde resin, with a thickness of 1.0, 1.8, and 2.5 μm were deposited on a Si surface by spin coating [5]. The thickness *h* of the photoresist film was determined by the spinning speed to be 1.0, 1.8, or 2.5 μm at a speed of v = 8300, 2900, or 1200 rpm, respectively. As substrates, wafers (100 mm in diameter) of KDB-10 single crystal silicon with the (111) orientation were used. Before forming the photoresist film, the silicon wafers were subjected to a standard surface cleaning cycle in organic and inorganic solvents. After applying the photoresist to the working side of the wafer, drying at a temperature of 88°C was carried out for 50–55 min. The thickness of the photoresist films was monitored using a MII-4 microinterferometer.

The EPR spectra of the photoresist films were recorded at room temperature on an X-band RadioPan SE/X-2543 spectrometer with an H_{102} cavity. The maximum microwave power in the cavity was 200 mW. The magnetic field modulation frequency was 100 kHz with an amplitude of 0.1 mT. To control the quality factor of the measuring cavity, adjust the magnetic field modulation phase, and calibrate the magnetic component of microwave radiation, a ruby crystal mounted on the cavity wall was used. The sensitivity of the spectrometer was 3×10^{12} spin/mT.

Implantation with phosphorus P^+ (energy 100 keV) and boron B^+ (energy 60 keV) ions in the fluence range of 6×10^{14}–1.2×10^{16} cm^{-2} at an ion current density of j = 4 μA/cm^2 was carried out in a residual vacuum of not higher than 10^{-5} mmHg on the Vesuvius-6 ion beam accelerator. Irradiation of polymer films with γ-rays at a dose of up to 270 kGy was carried out on an