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RADIATION CHEMISTRY

Radiation-Induced Processes in Diazoquinone–Novolac Resist Films under Irradiation with ^{60}Co γ-Rays

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Abstract—The processes occurring under the irradiation of FP9120 diazoquinone–novolac resist films on silicon with ^{60}Co γ-rays have been studied by attenuated total reflectance (ATR) FTIR spectroscopy. It has been found that a significant modification of the ATR spectra of the photoresist films was noticeable only at absorbed doses above 200 kGy, and it occurred due to the radiation-induced transformations of methyl, methylene, hydroxymethyl, and phenoxyl groups of phenol–formaldehyde resin and *o*-naphthoquinone diazide (a photosensitive component). At the same time, the ATR spectra exhibited no signs of the destruction of aromatic fragments in the resist at doses to 300 kGy. In the region of the stretching vibrations of C=O bonds, a decrease in the maximum intensity of a band at ~1700 cm^{-1} was observed upon irradiation with its simultaneous broadening and shift to the high-energy region by ~30 cm^{-1} due to a change in the nearest environment of the C=O group. An increase in the absorption band intensity at 1650 cm^{-1} indicated the accumulation of formaldehyde upon the γ-irradiation of the resist as a result of the fragmentation of hydroxymethyl residues in the phenol–formaldehyde resin.

Keywords: IR spectrometry, ATR, diazoquinone–novolac photoresist, γ-irradiation, silicon

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INTRODUCTION

The studies of radiation-induced processes in polymers are of interest due to the widespread use of such materials in space technology and medicine [1, 2]. In addition, ionizing radiation is an effective tool for modifying polymer materials because even relatively small doses can cause significant changes in polymer properties due to the high molecular weight of the polymer [3]. Radiation significantly changes the surface characteristics of polymers, in particular, the surface wettability and adhesion to semiconducting materials [4, 5].

Polymer composites are widely used as resists in the production of semiconductor devices and integrated circuits [6–8]. Diazoquinone–novolac (DQN) resists, which are composites of photosensitive *o*-naphthoquinone diazide and phenol–formaldehyde resin usually taken in a ratio of 1 : 5, are the main type of positive resists [6]. The mixtures of acetates, alcohols, and glycols are most commonly used as solvents.

The aim of this work was to study the modification of the ATR spectra of FP9120 positive diazoquinone–novolac resist films under irradiation with ^{60}Co γ-rays.

EXPERIMENTAL

The FP9120 positive diazoquinone–novolac photoresist films of 2.5 and 5.0 μm in thickness were deposited onto the surface of Si by centrifugation [9]. The KDB-10 single-crystal (111) silicon wafers (100 mm in diameter) were used as substrates. Before the formation of a photoresist film, the silicon wafers were subjected to a standard cycle of surface cleaning in organic and inorganic solvents. After applying the photoresist to the working side of a wafer, drying was carried out for 50–55 min at a temperature of 88°C. The photoresist film thickness was monitored at five fixed points using an MII-4 microinterferometer.

The γ-irradiation of photoresist films at a dose to 300 kGy was carried out on an MRKh-γ-25M unit with a ^{60}Co source at room temperature and atmospheric pressure. The dose rate was 0.12 ± 0.003 Gy/s. The ATR spectra of photoresist–silicon structures in the range ν = 400–4000 cm^{-1} were recorded at room temperature using an ALPHA Fourier transform IR spectrophotometer (Bruker Optik GmbH). The resolution was 2 cm^{-1}, and the number of scans was 24. The background was corrected before each measurement.