

Ion Implantation in Diazoquinone–Novolac Photoresist

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Abstract—The processes of modifying the structural and optical properties of FP9120 and S1813 diazoquinone–novolac photoresist films on single-crystal silicon wafers beyond the range of ions by implantation of light B⁺, P⁺ and heavy Sb⁺ ions have been studied using the techniques of attenuated total reflection Fourier-transform IR spectroscopy, indentation, and measurement of reflection spectra. It has been shown that during the implantation of light B⁺ and P⁺ ions, the processes involving the photosensitive photoresist component, naphthoquinone diazide, are dominant, which lead to the formation of ketene and its subsequent reactions. In the case of implantation of heavy Sb⁺ ions, radiation-induced reactions behind the implantation layer proceed predominantly with the participation of macromolecules of the main photoresist component phenol–formaldehyde resin. The established differences are due to the prevalence of the electronic stopping mechanism for light ions and nuclear stopping for heavy ions.

Keywords: diazoquinone–novolac photoresist, silicon, implantation, B⁺, P⁺, Sb⁺

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INTRODUCTION

Lithography is one of the main technological processes in the micro- and nanoelectronics industry [1], which is multiply repeated at various stages of the production of micro- and optoelectronic devices. Thus, when forming the element base according to the BiCMOS technology, up to 22 photolithography operations are used [2]. It is the technical parameters of lithography that largely determine the production efficiency and quality of electronics production. Composites of phenol–formaldehyde resins and naphthoquinone diazide are widely used as a protective photosensitive material (photoresist (PR)) in lithographic processes for the manufacture of semiconductor devices, integrated circuits, metallized templates, scales, grids, and printed circuit boards [1].

Currently, there is an increase in the role of ion implantation (II) in the production processes of modern electronics [3]. An increase in the degree of integration imposes high requirements on the set of operations that provide ion beam masking, and this circumstance causes an increased interest in the processes of modifying the properties of a photoresist film on single-crystal silicon wafers during II. When polymeric materials are irradiated with fast ions, their structure is rearranged. Vibrations of most molecular groups of polymers lie in the mid-IR range; therefore, the study of absorption spectra in this range provides

valuable information on the modification of the photoresist structure upon II.

Modification of the structure of a diazoquinone–novolac (DQN) resist of the AZ-1350 J brand in the range R_p of ions with different masses and, consequently, with different types of stopping, is considered in [4]. However, the range of charged particles in the cited study is comparable to or exceeds the film thickness. At the same time, for the energies used in microelectronics, the range of ions is much less than the photoresist film thickness, which is usually 1.0–2.5 μm . Thus, the projected ion range R_p in the case of implantation of 100-keV B⁺ ions is $\sim 0.4 \mu\text{m}$, whereas $R_p = 0.06 \mu\text{m}$ for 60-keV Sb⁺ ions [2, 5]. On the other hand, it is known [5–7] that the transformation of the structure of polymeric materials during II can be observed far beyond the range of ions, at a distance of 1–5 μm or greater. With the thickness of photoresist films used in modern lithographic processes (less than 3 μm), this can lead to a modification of the physical and mechanical properties throughout the entire thickness of the film and, more importantly, change the adhesion of the PR to the silicon wafer [8]. However, the mechanism of ion implantation-induced transformation of the structure of DQN resists beyond the range of ions and, accordingly, changes in the mechanical and adhesive properties of photoresist films on Si has not yet been finally established. We note that the long-range effect, i.e., the change in the

structure and properties of films at depths significantly exceeding the range of implanted ions, was previously observed by various authors in solids and polymers [2, 5–9].

Previously, it was established in [10] that the main contribution to the attenuated total reflectance (ATR) IR spectra of PR films on silicon in the wavenumber range of 400–4000 cm^{-1} is made by the photoresist layer behind the ion range, which makes it possible to obtain objective information about the modification of the PR structure in this area.

The aim of this work was to study the features of the modification of the structural and optical properties of DQN resist films of the FP9120 and S1813 brands on single-crystal silicon wafers beyond the range of ions during implantation with light and heavy ions.

EXPERIMENTAL

Films of FP9120 and S1813 positive photoresists of a 1.0–5.0 μm thickness were deposited by centrifugation on the surface of single-crystal silicon wafers with (100) and (111) orientations [11]. Prior to the formation of the PR film, silicon wafers were subjected to a standard surface treatment cycle in organic and inorganic solvents in order to remove various types of surface contaminants. After applying the photoresist to the working side of the wafer, drying was carried out for 50–55 min at a temperature of 88°C.

Implantation with B^+ , P^+ , and Sb^+ ions (energy 30–100 keV) in the fluence range of 5×10^{14} – $6 \times 10^{17} \text{ cm}^{-2}$ in the constant ion current mode (ion current density $j = 4 \mu\text{A}/\text{cm}^2$) was carried out at room temperature in a residual vacuum of not worse than 10^{-5} Pa using a Vesuvius-6 ion implanter. The employed ion implantation modes are widely used in the manufacture of integrated circuits.

The attenuated total reflectance (ATR) spectra of the photoresist–silicon structures in the range of $\nu = 400$ – 4000 cm^{-1} were recorded at room temperature with an ALPHA Fourier-transform IR spectrophotometer (Bruker Optik). The resolution was 2 cm^{-1} , and the number of scans was 24. Background correction was performed before each measurement.

The strength properties were studied by microindentation at room temperature using a PMT-3 instrument. The load on the indenter in the form of a tetrahedral diamond pyramid with a square base in an NPM-type frame and an apex angle $\alpha = 136^\circ$ varied within 1–100 g. The loading duration was 2 s; exposure under load 5 s. At each measurement, at least 50 prints were made on the surface of the sample, and the measurement results were processed using mathematical statistics methods. To quantify the adhesion properties, we determined the interfacial fracture energy (G) of the films, which is widely used to study various

polymer films on glass substrates [8] and is calculated by equation (1):

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

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.

RESULTS AND DISCUSSION

It has been established that being placed in an aqueous 3 M KOH solution, an unirradiated photoresist film swells and peels off without external influences, with the film peeling off completely within 30–50 s. The photoresist film implanted at fluences of 5×10^{14} – $6 \times 10^{17} \text{ cm}^{-2}$ for all types of ions is much more resistant to the action of an alkaline solution, and it dissolves inhomogeneously. Light lines appear on the surface of the structure after a few minutes of holding in the 3 M KOH solution, due to the local dissolution of the photoresist film up to exposure of the silicon substrate. Their number and size (length and width) increase with time. A slight delamination of the film from silicon is observed along the edges of these lines. The etching process lasts up to 90 min and ends with the formation of a grid on the surface of the silicon substrate, which peels off from Si and decomposes into individual carbon “filaments” that are barely visible to the naked eye and are insoluble in 3 M KOH [2].

This behavior of the films is due to the fact that at the aforementioned fluences, the PR film is carbonized in the range of ions, and this layer becomes insoluble in an aqueous 3 M KOH solution. The photoresist beyond the range of ions retains the properties of the phenol–formaldehyde resin and dissolves in 3 M KOH, although its etching rate is much lower than that of the initial PR films. A decrease in the etching rate indicates structural and conformational changes in the PR behind the ion inclusion layer. The penetration of the etchant to the PR layer beyond the range of ions and, accordingly, its dissolution occur along microcracks in the implanted layer formed during bombardment. With an increase in the etching time, the cracks increase both in width and in length, forming lacy nets that propagate over the surface and turn PR residues into islands that decrease in size with time. The remains of the implanted layer form carbon fibers (“threads”) insoluble in 3 M KOH. This behavior was observed for implantation of different types of ions into both FP9120 and S1813 diazoquinone–novolac photoresists.

A study of the attenuated total reflectance spectra of PR films on silicon has shown [10, 12] that in the case of implantation with both light (B^+ and P^+) and