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Stabilizing Treatment of Negative Photoresist Films of the AZ nLOF20XX Series on Silicon

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Abstract—Films of negative photoresists (PR) AZ nLOF2020 and AZ nLOF2070 about 6.0 μm thick, deposited on the surface of monocrystalline silicon wafers by centrifugation, are studied using FTIR spectroscopy and microindentation methods. It is shown that after exposure to light with $\lambda = 404$ nm for 106 s and subsequent baking at 115°C for 60 s, a shift of the interference band maxima toward the high-energy region is observed in the reflection–absorption spectra of the photoresist films. It is caused by a decrease in the thickness of the PR film due to the evaporation of the solvent during baking. These processes occur more intensively in AZ nLOF2020 films, in which the shift of interference bands is ~9%, while in AZ nLOF2070 films it did not exceed 1%. It is shown that absorption bands with maxima at 1070 and 1100 cm^{-1}, caused by asymmetric and symmetric stretching vibrations of C–O–C bonds in aliphatic ethers, and at 2940 cm^{-1}, caused by asymmetric stretching vibrations of CH_3 bonds, are associated with the solvent. It is established that the microhardness of AZ nLOF20XX series films increases after stabilizing baking, which is due to the cross-linking of phenol–formaldehyde resin molecules, the base of the photoresist. The obtained experimental data are explained by the ordering of the photoresist film structure near the PR/silicon interface due to the orientation of the molecules and the higher concentration of residual solvent in AZ nLOF2020.

Keywords: negative photoresist, silicon, FTIR spectroscopy, microhardness, solvent evaporation, baking

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1. INTRODUCTION

Lithography is one of the most important technological stages in the production of semiconductor devices and integrated circuits. It is a combination of photo- and physicochemical processes used for the layer-by-layer formation of the topological pattern of integrated circuits, as well as elements of nanostructures. The main material for forming a topological pattern are resists, which are liquid polymer compositions applied to a substrate. The accuracy of the pattern transfer onto the material of an integrated circuit largely depends on the quality of the resistive layer formed during the lithography process.

The defining stage of the formation of photoresist (PR) films on silicon is baking, whose quality significantly affects all subsequent lithographic operations. During baking, the solvent is removed from the PR film and a complex relaxation process of dense molecular packing occurs, reducing internal stresses and changing the adhesion of the film to the substrate. In addition, additional thermal polymerization of the photoresist occurs during baking. The solvent must be completely removed, since it shields the photosensitive parts of the molecules during exposure [1].

Negative photoresists of the AZ nLOF20XX series (manufactured by MicroChemicals Gmbh, Germany) are designed for use in lift-off lithography processes and are thermally stable [2]. They are designed for the *i*-line ($\lambda = 365$ nm) of an arc lamp and are insensitive to its *g*- and *h*-lines with wavelengths of 435 and 404 nm, respectively. The main component of these PRs is phenol formaldehyde resin and propylene glycol monomethyl ether acetate (PGMEA) is used as the solvent [2, 3]. Photoresists AZ nLOF2020 and AZ nLOF2070 have different viscosities and are used to form photoresist films of different thicknesses. At a spin-coating speed of 3000 rpm, the film thickness for AZ nLOF2070 is ~7.0 μm, while for AZ nLOF2020, it is ~2.0 μm. The specified PRs have the same base and differ only in the concentration of the solvent.

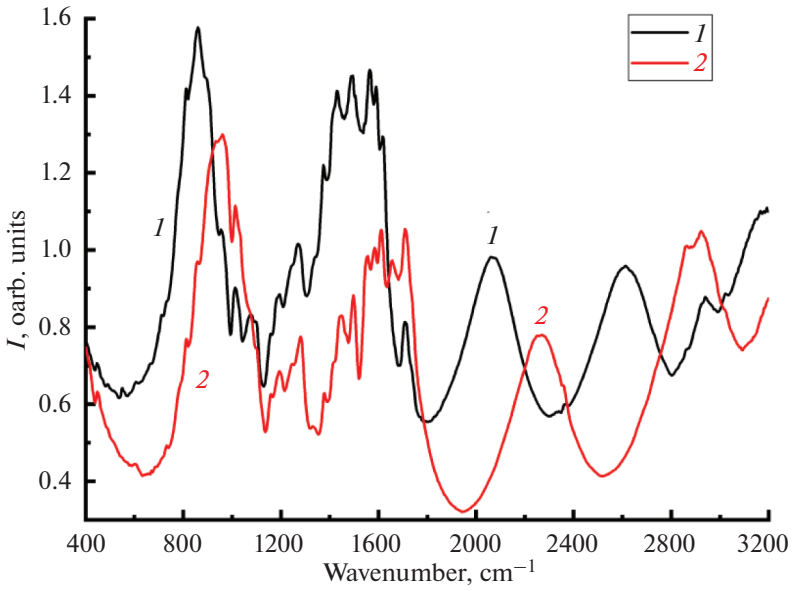

Fig. 1. Reflection–absorption spectra of AZ nLOF2020 PR films (d = 6.0 μm): initial (*1*) and after ST (*2*).

The measurement of reflection–absorption FTIR spectra of photoresistive films using a diffuse reflectance attachment, which does not require special sample preparation and is an express, noncontact study [4], is a promising method for obtaining information on the composition and structure of complex organic compounds and their mixtures in solid and liquid states. The features of this noncontact method include ease of sample preparation, fast measurement speed, and reproducibility of results [5]. It should be noted that the prospects for using a diffuse reflection attachment in the study of photoresist films deposited on monocrystalline silicon wafers were previously considered in [6].

The aim of this paper is to study the physicochemical processes occurring during the baking of films of negative photoresists of the AZ nLOF20XX series on a silicon substrate.

2. EXPERIMENTAL

Films of negative photoresists AZ nLOF2020 and AZ nLOF2070 ~6.0 μm thick (d) were deposited onto the surface of monocrystalline silicon wafers with (100) orientation by spin coating [7]. Before PR application, the wafers were subjected to a standard cycle of mechanical treatment and physicochemical surface cleaning in organic and inorganic solvents. After the formation of the PR film, it was baked at T = 110°C for t = 60 s. Some of the samples were subsequently subjected to stabilizing treatment (ST) to further strengthen the photoresist film; this consisted of exposure to light with λ = 404 nm for t = 106 s, followed by thermal treatment at T = 115°C for t = 60 s. The geometric thickness of the photoresist films was measured using a HITACHI S-4800 scanning electron microscope.

The FTIR spectra of photoresist/Si structures were recorded in the range of 400–4000 cm^{-1} at room temperature using an ALPHA spectrophotometer (Bruker Optik GmbH) with a DRIFT attachment for measuring diffuse reflectance. The number of scans was 24, the resolution was 2 cm^{-1}, and background correction was performed before each measurement.

Microindentation was carried out using a PMT-3 instrument at room temperature. Measurements of the recovered microhardness (H) were performed according to the standard method [8]. The load P on the indenter varied from 1 to 20 g. The loading time was 2 s and the holding time under load was 5 s. During the measurement, at least 50 indents were made on the sample surface for each experimental point. Moreover, the measurement error of microhardness did not exceed 2.5% at a confidence probability of 0.95.

3. RESULTS AND DISCUSSION

In reflection–absorption FTIR spectra of photoresist/silicon structures, absorption bands are observed against a background of broad interference fringes (Figs. 1, 2). Since the energy position of the maxima of the interference fringes is determined by the expression

$$m\lambda = 2nd,$$

where m is the interference order; λ is the wavelength corresponding to the maximum; n is the refractive index of the film; and d is the geometric thickness of the film—with a known refractive index n—it becomes possible to determine the geometric thickness of the photoresist film.

After the stabilizing treatment, a shift of the interference band maxima to the high-energy region is

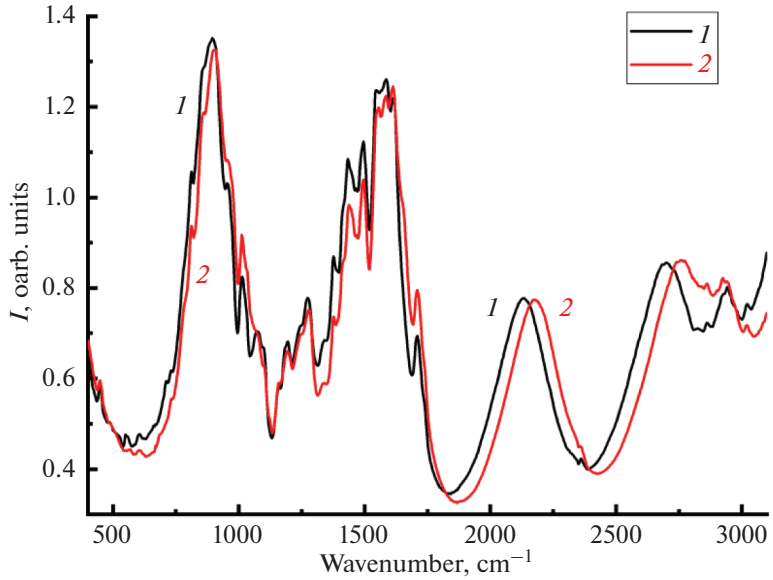

Fig. 2. Reflection–absorption spectra of AZ nLOF2070 PR films (d = 6.0 μm): initial (*1*) and after ST (*2*).

observed (Figs. 1, 2). The magnitude of the shift of the interference fringe maxima in photoresist films differed by almost an order of magnitude. Thus, during baking of the AZ nLOF2070 series, the interference maxima shifted by ≤1% (Fig. 2), whereas for AZ nLOF2020 they shifted by ~9% (Fig. 1). As noted above, photoresists of the AZ nLOF20XX series are not sensitive to light irradiation at λ = 404 nm; therefore, the observed effects are due to the removal of the solvent during the stabilizing thermal treatment. Significant changes in the refractive index n of the photoresists are not expected under these conditions; therefore, the observed shift of the interference fringes can be associated with a decrease in the geometric thickness of the PR films. This conclusion is confirmed by direct measurements of the geometric thickness of the PR films using a scanning electron microscope (Table 1).

After stabilization of the PR films, no significant change in the energy position or intensity of the strongest absorption bands was observed (Figs. 1, 2). This indicates that neither light exposure nor additional heat treatment affected the structure of the main component of these PRs. The absence of a significant effect of irradiation with light of wavelength λ = 404 nm on the structure of photoresists is understandable since, as noted above, they are designed for the *i*-line of an arc lamp (λ = 365 nm) and are not sensitive to longer wavelength radiation.

Significant changes in the absorption spectra of PR films after ST were observed only in the ranges of wave numbers ν = 1050–1150 cm^{-1} and 2900–3000 cm^{-1} (Figs. 3–5). The most pronounced decrease in intensity in both films occurred for the absorption band with a maximum at 1070 cm^{-1}. It is caused by the stretching vibrations of C–O–C groups in aliphatic

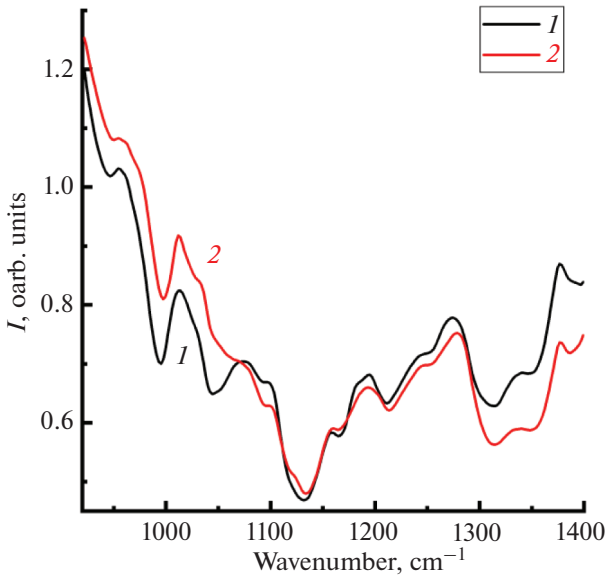

Fig. 3. Reflection–absorption spectra in the C–C and C–O stretching region for AZ nLOF2070 PR films (d = 6.0 μm): initial (*1*) and after ST (*2*).

ethers [9, 10]. Two such bonds are present in the solvent of the studied PRs: propylene glycol monomethyl ether acetate (PGMEA). After additional baking, this band was transformed into shoulders on the high-

Table 1. Geometric thickness of photoresist films

Photoresist	Original film, μm	Film after ST, μm
AZ nLOF2070	5.91	5.80
AZ nLOF2020	5.83	5.50

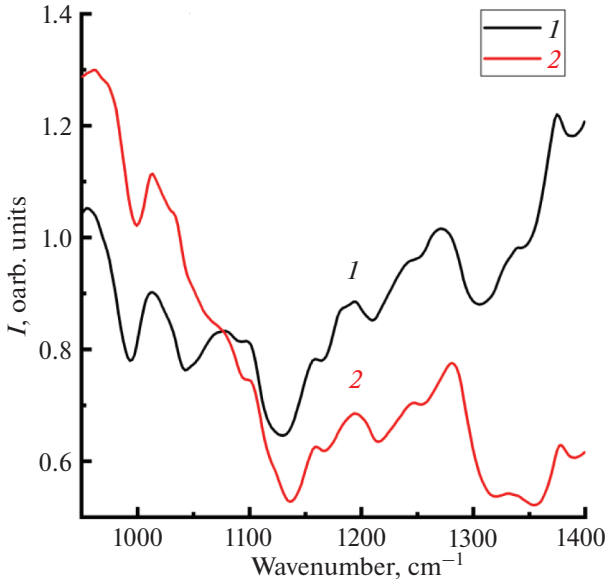

Fig. 4. Reflection–absorption spectra in the C–C and C–O stretching region for AZ nLOF2020 PR films ($d = 6.0$ μm): initial (*1*) and after ST (*2*).

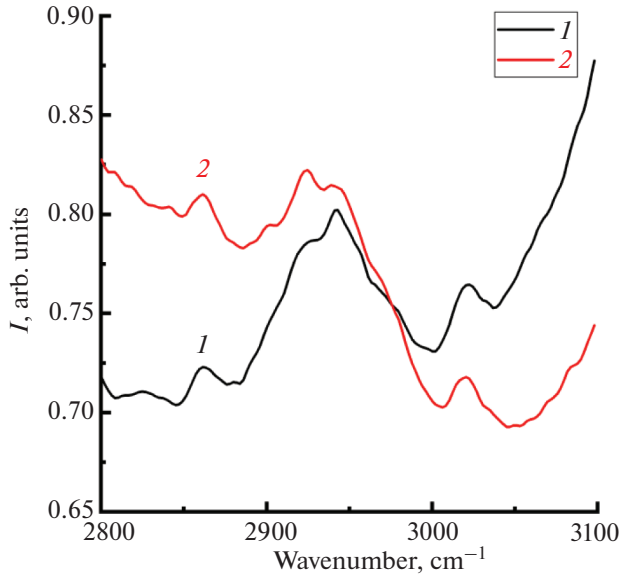

Fig. 5. Reflection–absorption spectra in the C–H stretching region for AZ nLOF2070 PR films ($d = 6.0$ μm): initial (*1*) and after ST (*2*).

energy wing of the first interference fringe, with a maximum at ~880 cm^{-1} (Figs. 3, 4). We also note that the intensity of these bands in the original AZ nLOF2020 films was higher than in similar AZ nLOF2070 films, which indicates a higher solvent content in the AZ nLOF2020 PR.

Noticeable transformations of the absorption spectrum during additional baking were also observed in the region of C–H bond vibrations. After additional stabilizing baking, absorption in the wavenumber range of 2900–2980^{-1} cm decreased significantly (Fig. 4). Here two closely spaced absorption bands are observed, caused by asymmetric stretching vibrations of CH_2 (maximum at ~2925 cm^{-1}) and CH_3 (maximum at ~2940 cm^{-1}) groups. Moreover, in the initial films, the band with a maximum at ~2940 cm^{-1}, caused by CH_3 bonds, dominates; however, after additional baking its intensity noticeably decreases and the band with a maximum at ~2925 cm^{-1} becomes dominant, associated with the CH_2 bonds inherent in phenol–formaldehyde resin [11–13]. Note that in the structure of PGMEA—the solvent used in AZ nLOF20XX photoresists—there are three CH_3 bonds and one CH_2 bond. This circumstance allows us to attribute the transformation of the spectrum in the C–H stretching region observed during additional baking to the evaporation of the solvent.

The obtained experimental results can be explained by taking into account the following circumstances. As noted above, the AZ nLOF2070 and AZ nLOF2020 photoresists differ in solvent concentration. The AZ nLOF2070 photoresist, designed for a film thickness of 7.0 μm, has a higher viscosity and, accordingly, a lower solvent content compared to AZ nLOF2020. Standard baking (110°C, 60 s) after film deposition almost completely removes the solvent from the AZ nLOF2070 film. The residual solvent concentration is low and shrinkage of the AZ nLOF2070 film during additional baking (115°C, 60 s) is insignificant, about 0.5–0.9% of its original geometric thickness. The AZ nLOF2020 photoresist is designed to form films with a thickness of 2.0 μm, and the solvent content in it is higher than in AZ nLOF2070. Standard baking at $T = 110$°C for $t = 60$ s after film deposition only partially removes the solvent from the AZ nLOF2020 films of $d \sim 6$ μm. Therefore, the additional ST of these films significantly affects the optical properties and geometric dimensions of PR films of this type.

The microhardness of the AZ nLOF20XX series photoresist films increased with increasing load (Fig. 6). This effect was most pronounced in AZ nLO*F*2020 films at loads of 1–5 g (Fig. 6b). Note that at a load of 1–2 g, the microhardness of the original AZ nLOF2020 films was almost 50% lower than that of AZ nLOF2070 films (curves *1* in Figs. 6a, 6b) due to the higher solvent concentration in AZ nLOF2020 films. The stabilization treatment increased the microhardness of both photoresist films with the most pronounced effect observed in AZ nLOF2020 films, which is due to the removal of the residual solvent.

The increase in microhardness of PR films during baking is due to the formation of covalent crosslinks between polymer chains [14]. The lower microhardness values at loads of 1–2 g in AZ nLOF2020 films compared to AZ nLOF2070 and their subsequent equalization under ST are related to the presence and evaporation of the residual solvent in the AZ nLOF2020

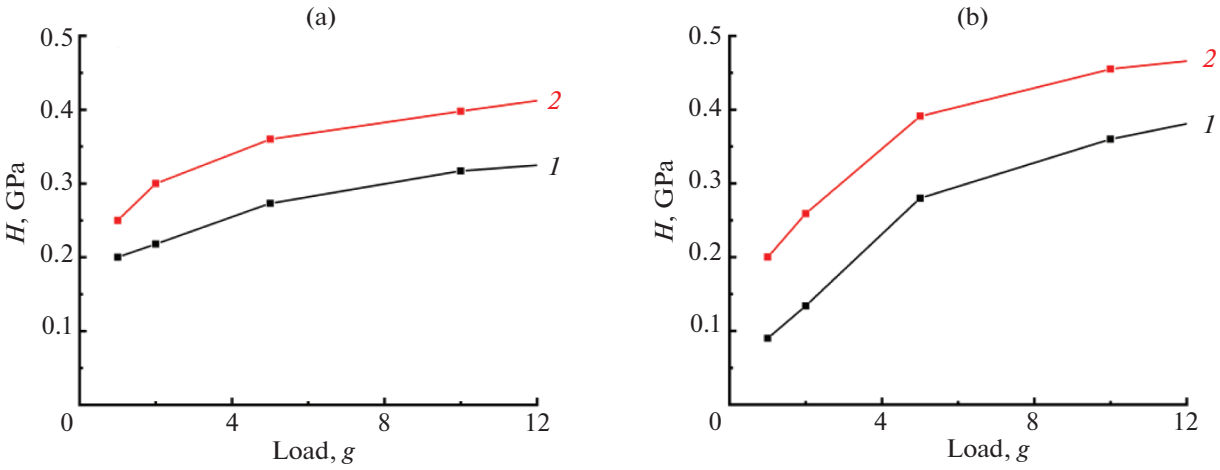

Fig. 6. Dependence of microhardness on load for AZ nLOF2070 (a) and AZ nLOF2020 (b) PR films: initial (*1*) and after ST (*2*).

films. As follows from the experimental data, the solvent content is higher in the surface layers of the AZ nLOF2020 film. This is due to the specific drying regime, in which heating was carried out from the substrate side. At the same time, the lower PR layers (adjacent to the substrate) are heated more strongly. A temperature gradient develops across the thickness of the photoresist, with the surface being the coldest part of the coating and the lower layers at the PR/silicon interface the hottest. Consequently, the drying front moves from the substrate to the surface of the photoresist film, so that the residual solvent content near the PR surface remains higher than near the photoresist/silicon interface.

When analyzing the experimental results, the following circumstances should also be taken into account. At loads ≤10 g, the penetration depth of the indenter in the photoresistive film does not exceed two-thirds of its thickness. As is known [15], in the case of a soft film on a hard substrate, plastic deformation is localized in the film. In this case, the influence of the substrate is not dominant. However, as reported in [16], polymer films can become oriented due to changes in the conformation of macromolecules near the photoresist/silicon interface. As is known [17], the interaction of phenol–formaldehyde photoresists with substrate atoms occurs through the formation of Si–O–C bonds between hydroxyl groups on the surface of the oxide layer of the silicon wafer with carbon atoms, predominantly of the phenol group. The native oxide on the silicon surface has an ordered structure that reproduces the silicon lattice [18, 19]. Because photoresist molecules are predominantly bonded via the carbon atoms of phenolic groups, they become oriented with the structure of the oxide layer on the silicon wafer. This stable order must be maintained even after the solvent is removed. The ordering of the photoresistive film structure near the PR/silicon interface due to the molecular orientation promotes the strengthening of the polymer film along the orientation direction, which was manifested in our experiments as an increase in the microhardness of photoresistive films with increasing load (i.e., increasing indentation depth into the PR film).

CONCLUSIONS

Irradiation of AZ nLOF20XX photoresist films ~6.0 μm thick with light of wavelength $\lambda = 404$ nm for 10^6 s, followed by baking at $T = 115$°C for 60 s, resulted in a shift of the interference maxima in the diffuse-reflectance spectra toward the high-energy region. It is caused by solvent evaporation during baking and the accompanying decrease in film thickness. The effect was about an order of magnitude stronger in AZ nLOF2020 films (~9%) than in AZ nLOF2070 films (<1%). It was found that the bands with maxima at 1070 and 1100 cm^{-1}, caused by asymmetric and symmetric stretching vibrations of C–O–C bonds in aliphatic ethers, and the band at 2940 cm^{-1}, corresponding to asymmetric stretching vibrations of CH_3 groups, were identified as solvent-related. The microhardness of AZ nLOF20XX films increased after stabilizing treatment due to cross-linking of the photoresist molecules. Removal of the solvent from the photoresistive film during baking not only enhanced the microhardness but also probably improved adhesion of the PR film to the monocrystalline silicon substrate. These findings were explained by ordering of the photoresist film structure near the PR/silicon interface due to the molecular orientation and the presence of the residual solvent in AZ nLOF2020 films.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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