INFLUENCE OF NITROGEN ON THERMAL WARPAGE IN CZOCHRALSKI SILICON WAFERS①

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ABSTRACT The effect of nitrogen on thermal warpage in nitrogen-doped Czochralski (CZ) silicon wafers after heat treatment was studied. After preannealing at 1 000 ℃ for 6 h, the warpage of the silicon wafers was suppressed during subsequent thermal warping test due to the formation of nitrogen-oxygen clusters with smaller size. After preannealing at 1 000 ℃ for 16 h, the silicon wafers show a large increase during thermal warping test due to the large amount of oxygen precipitation. The results indicate that the nitrogen is very effective to increasing the mechanical strength of silicon wafers of CZ silicon at high temperature.

Key words nitrogen thermal warpage mechanical strength silicon wafers

1 INTRODUCTION

For many years, warpage of silicon wafers has been concerned in very large-scale integrated circuit (VLSI) manufacturing[1-4]. Usually, the initial warpage of freshly cut and polished wafers is rather small, but it can increase drastically by thermal stresses due to quickly cooling or heating in semiconductor device processing. Warpage reduces the transfer accuracy of circuit patterns from a mask to a wafer in photolithographic processing. Also it is known that dislocations introduced by plastic deformation exert negative effects upon electrical properties of devices[5]. All these considerations show that warpage and its accompanying features are highly undesirable in silicon device manufacturing and should be avoided.

It is well known that the mechanical strength of Czochralski (CZ) silicon wafers is significantly affected by oxygen in silicon[6]. The interstitial oxygen provides dislocation pinning, which improves the yield stress and the mechanical strength. In recent years, it has been found that nitrogen in silicon has the same effect as oxygen on the mechanical strength of silicon. It has been reported that nitrogen has a strengthening effect on float-zone silicon wafers in low oxygen concentration[7]. However, there is a little work about the effect of nitrogen on the mechanical properties of CZ silicon wafers[8,9]. The present work is to investigate the effect of nitrogen on the suppression of thermal warpage.

2 EXPERIMENTAL

The n-type ⟨111⟩ nitrogen-doped CZ silicon (NCZ) was grown in a nitrogen protective atmosphere under reduced pressure[10]. Samples with the resistivity of 20 ~ 50 Ω•cm were 0.43 mm in thickness, 76.00 mm in diameter and were polished in single side. The initial oxygen and nitrogen concentrations of samples were about 7.8×10^{17}, 3.6×10^{15} cm^{-3}, respectively. For comparison, n-type ⟨111⟩ CZ silicon wafers grown under an argon ambient (ACZ) with the same oxygen concentration were also prepared. Sample wafers were preannealed in a nitrogen ambient at 1 000 ℃ for 0, 6, and 16 h, respectively. They were inserted into and pulled out of a furnace very slowly to prevent them from slip produced by thermal stresses.

Thermal warping test introducing thermal stress was carried out after preannealing. The

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test temperature was also 1 000 ℃. Wafers were stacked vertically in a quartz boat, and the span-space between neighboring silicon wafers was 2.5 mm or 5.0 mm for two test groups of samples, respectively. The wafers on the boat were brought into a furnace slowly, held for 20 min to reach the operating temperature uniformly. And then the wafers were pulled out rapidly to be induced thermal stresses for testing thermal warpage (Fig. 1). The warpage values were measured by an ADE 6034 contactless gauge (consistent with ASTM F657 - 80) before and after thermal warping tests.

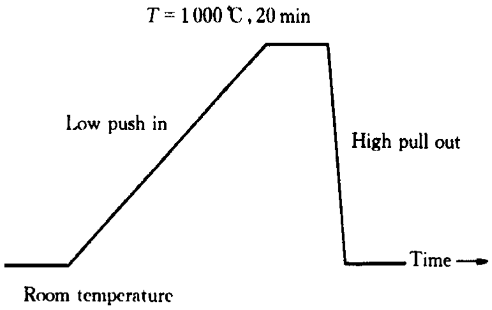

Fig.1 Heat treatment procedure of wafters

3 RESULTS AND DISCUSSION

In the first group, the spacing between neighboring silicon wafers is 5.0 mm. After thermal warping test at 1 000 ℃, the thermal warpage of silicon wafers versus preannealing time is shown in Fig.2. It is found that no warpage is observed for unpreannealing in both NCZ and ACZ silicon wafer. The warpage of the ACZ silicon wafer preannealed for 6 h is about 100 μm, while no warpage appeared in the NCZ silicon wafer. For the wafers preannealed for 16 h, the warpage of the NCZ silicon wafer is as same as that of the ACZ silicon wafer. It means that to some extent nitrogen can suppress the thermal warpage of silicon wafers.

In the second group, the sample span-space is only 2.5 mm. Fig. 3 shows the thermal warpage of silicon wafers as a function of the preannealing time after thermal warping test. It is obvious that the thermal warpage of both the NCZ and ACZ wafers is larger than that of the first group. The warpage of two kinds of wafers without preannealing is still larger than 100 μm. It indicates that the distance between wafers plays an important role in the thermal warpage of silicon wafers because thermal stress increased drastically when span-space decreased. However, the warpage of the NCZ silicon wafer preannealed for 6 h is still lower than that of the ACZ wafer, and even lower than that of unpreannealing silicon wafer. It means that for the samples preannealed at 1 000 ℃ for 6 h, nitrogen in silicon can suppress thermal warpage and increase mechanical strength.

Fig.2 Variation of warpage with preanealing time

Fig.3 Variation of warpage with preanealing time

When regularly spaced wafers are quickly pulled out of a high temperature furnace as in semiconductor device processing, every wafer is cooled nonuniformly, resulting in a drastic radial temperature gradient between the rim and the center. This inhomogenous temperature field generates thermal stresses. Mokuya and Matsuba[11] pointed out that thermal stresses were reduced to about a half as the wafer span-space was increased by a factor of two or three. They also described the yield strength of silicon by the following equation:

$$\sigma_s = C\dot{\varepsilon}^{1/n}\exp(E/nkT) \qquad (1)$$

where E is activation energy of glide movement, T is wafers' temperature, k is the Boltzmann constant, $\dot{\varepsilon}$ is strain rate, and n and C are constants depending on the material. The yield strength is influenced not only by temperatures and strain rates, but also by interstitial oxygen contents, amount of oxygen precipitates, and other impurity contents, especially the nitrogen.

When the thermal stress is small in the first warping test group, no warpage in unpreannealing wafers appears (Fig.2). The results indicate that the unpreannealed wafers can stand some thermal stress because of the locking dislocations of disperse interstitial oxygen atoms and nitrogen atoms. Furthermore, the interstitial oxygen concentration in the NCZ silicon is two orders of magnitude higher than nitrogen concentration. The role of nitrogen to lock dislocations in the unpreannealed NCZ silicon can be ignored in comparison with oxygen.

After preannealing for 6 h, in the first group the NCZ silicon wafer shows no warpage, while the ACZ silicon wafer shows the warpage of about 100 μm (Fig.2). In the second group, the warpage of the NCZ silicon wafer is smaller than that of the ACZ silicon wafer (Fig.3). It has been reported that nitrogen could interact with oxygen to form nitrogen-oxygen (N-O) complexes, and then N-O clusters during annealing at high temperatures for a short time[12,13]. In our experiments, the N-O clusters might be formed after preannealing at 1 000 ℃ for 6 h. The sizes of the N-O clusters in the NCZ silicon might be smaller than that of oxygen precipitates in the ACZ silicon. The capability of pinning dislocations of the N-O clusters with smaller sizes is stronger. The high density of small N-O clusters is responsible for improving upper stress and increasing resistance to warpage. Thus, the warpage of the NCZ silicon wafers preannealed for a shorter time is suppressed.

During the thermal warping test after preannealing for 16 h, the warpage of all of the samples exhibits a significant increase. However, the warpage of the NCZ silicon wafer is the same as that of the ACZ silicon wafers. It is because the N-O clusters can attract more oxygen to generate oxygen precipitates after annealing at high temperatures for a longer time[12]. In this case the amount and size of oxygen precipitates depend on initial oxygen concentration, annealing time and temperatures, rather than nitrogen concentration. In the experiments, the initial oxygen concentrations in NCZ and ACZ silicon are the same. Thus, the warpage of the NCZ silicon wafer is the same as that of the ACZ silicon wafer (Figs.2 and 3).

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