Stress Elimination of LPCVD Silicon Nitride Films by Low-Dose Ion Implantation

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1. Introduction

The large tensile stress of low-pressure chemical vapor deposition (LPCVD) Si_3N_4 films causes bending and shrinkage of silicon wafers, resulting in defects in substrates and misalignment in the photolithography process. Although the stress in Si_3N_4 films can be reduced by implanting ions to the Si_3N_4 /substrate interface[1], interface implantation is undesirable because it can introduce defects into the substrate and thus degrade device performance. We have investigated the effect of ion-implantation into Si_3N_4 films on the film stress, and found that the film stress is eliminated by low-dose implantation to the middle of the film without damaging substrates. The elimination around the broken Si-N bonds due to the tensile stress in the films.

2. Experimental

LPCVD Si₃N₄ films, 120 or 200 nm thick, were grown with SiH₂Cl₂ and NH₃ on 6-inch silicon substrates in a hotwall vertical reactor. After removing the backside films, the stress of the surface Si₃N₄ films was determined from the wafer curvature. Then, P, Ar or As ions were implanted at 50-350 keV with a dose of 1×10^{13} to 1×10^{15} cm⁻², and the stress change due to the implantation was estimated. Wet etching of implanted Si₃N₄ films by hot phosphoric acid, and the measurement of the film thickness and the wafer curvature were repeated to determine the distributions of the etching rate and stress.

3. Stress Reduction by Ion Implantation

Energy dependence

Figure 1 shows the relationship between the Si₃N₄ film stress and the implantation energy of P, Ar, and As ions with a dose of 2×10^{14} cm⁻². Regardless of the implanted ion species, the film stress decreased with an increase in the energy; it finally disappeared at over a certain critical energy. The critical energy is smaller for lighter ion species and for smaller Si₃N₄ film thicknesses when the implantation energy is the same. Figure 2 shows the Si₃N₄ film stress as a function of ion projected range R_p normalized by Si₃N₄ film thickness t_{Si3N4} for a dose of 2×10^{14} cm⁻². The relationship between the stress and the projected range can be expressed as a common curve for all ion species and film thicknesses tested. The stress became almost zero when $R_p \ge t_{Si3N4}/2$. *Dose dependence*

As the ion dose increased, the Si₃N₄ film stress decreased and finally disappeared as shown in Fig. 3. Table I shows the dose necessary to reduce the stress to 10% of the asdeposited value. It is only about $3 \times 10^{13} \text{ cm}^{-2}$ for As ions. A dose of $6 \times 10^{14} \text{ cm}^{-2}$ is sufficient to eliminate the Si₃N₄ film stress for even light B ions. Because these values are considerably smaller than the critical dose necessary to form a continuous amorphous layer in single crystalline silicon[2], most of the Si-N bonds in these implanted films were considered not to be broken.

4. Stress Distribution in Si₃N₄ Films

The integrated stress, the integral of stress over the film thickness, of an as-deposited film was proportional to the remaining film thickness when the film was being etched (Fig. 4), meaning a constant stress distribution over the film thickness. For P-implanted films, however, the integrated stress was smaller and almost constant until a certain thickness was removed. Below this thickness, it behaved the same as for the as-deposited film. This means that while the stress below the certain thickness was not affected by implantation at all, it was eliminated above the thickness. The thickness of the stress-free region is larger for higher implantation energy.

Figure 5 shows the wet-etching characteristics of initially 200-nm-thick Si_3N_4 films implanted with P at 50 and 100 keV. The etching rate in the surface-side region of the implanted films was increased to about 2.5 times that in asdeposited film, while the etching rate in the substrate-side region remained unchanged. However, the etching rate recovered after annealing at $950^{\circ}C(\bullet)$. The thicknesses of the region where the etching rate becomes large coincides with those of the stress-free region in Fig. 4. Because the etching rate of an Si_3N_4 film is thought to be dependent on its defect density, the observed stress elimination in the film must also be closely related to the density of defects introduced by the implantation.

5. Discussion

As stated above, the stress reduction takes place at a considerably lower dose than that needed to break the majority of Si-N bonds in the film. This is probably because the tensile stress increases the atomic distance of the bonds broken by implantation, and this increase in the broken bond distance, in turn, reduces the stress and strain of the network. Because the strain in an as-deposited film calculated from its stress and biaxial modulus 3.7×10^{11} Pa is as small as 3.2×10^{-3} , breaking only a part of Si-N bonds in the network can effectively reduce the stress in the films.

When ions are implanted to the middle of the film with the minimum dose to eliminate the film stress shown in Table I, the amount of ions reaching the substrate through the film is of the order of 10^{10} cm⁻², one order less than the dose for channel doping of MOSFETs. Therefore, the effect of implantation to Si₃N₄ films on device characteristics is negligibly small.

In an additional experiment, LOCOS isolations were formed using the Si_3N_4 film of 200-nm-thick implanted with 2×10^{14} cm⁻² As ions at 300keV as an oxidation mask (Fig.6). No difference in the shape of LOCOS oxide was observed between the samples using implanted and unimplanted Si_3N_4 films. This, together with the etching-rate recovery shown in Fig.5, is probably because the implantation damage was eliminated during thermal oxidation.

6. Conclusion

Stress reduction effect in LPCVD Si₃N₄ films by lowdose ion implantation of P, Ar and As is investigated. Tensile stress of Si₃N₄ films can be eliminated by implanting to the middle of the film with the dose as low as 3×10^{13} to 1.2×10^{14} cm⁻². Under this condition, the influence of the implantation to the LOCOS formation and device characteristics is negligibly small.

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References

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Fig.1 Si₃N₄ film stress as a function of implantation energy with dose of 2×10^{14} cm⁻².



Fig.2 Si₃N₄ film stress as a function of the projected range R_p of implanted ions normalized by the film thickness t_{Si3N4} .



Fig.6 LOCOS of 64Mbit DRAM using Si₃N₄ films (a) unimplanted, and (b) implanted with $2 \times 10^{14} \text{cm}^{-2}$ As ions at 300keV. Profile is delineated by buffered hydrofluoric acid etching.



Fig.3 Si_3N_4 film stress as a function of the dose of implanted ions. Implantation energies are selected so that the projected range almost coincides with the middle of the film.

Table I critical dose to reduce the Si_3N_4 film stress to 10% of as-deposited film.

As	Ar	P	В
3×10 ¹³	7×10 ¹³	1.2×10 ¹⁴	7×10 ¹⁴



Fig.4 Thickness dependence of the integrated stress in Si₃N₄ films normalized by that of as-deposited film.



