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Diffusion and Segregation of Nitrogen in Polycrystalline Silicon and at the Poly-Si/SiO_2 Interface

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The diffusion of in-situ doped or implanted nitrogen in polysilicon and the pile-up of nitrogen at poly-Si/SiO_2 interfaces during annealing at 700-1000°C were investigated using secondary ion mass spectroscopy. Nitrogen in polysilicon film diffused and piled up at the poly-Si/SiO_2 interface during heat treatment above 800°C. The amounts of segregated nitrogen were independent of the initial amount of nitrogen in polysilicon film. A fraction of nitrogen in polysilicon film above a certain threshold concentration was immobile. This threshold concentration and the nitrogen diffusion were dependent on the polysilicon structure.

Introduction

We recently reported a new p+ polysilicon gate with a nitrogen-doped silicon layer for surface channel PMOSFETs(1) and a nitrogen in-situ doped poly buffer LOCOS technology for deep submicrometer silicon devices(2). Kuroi et al also proposed a nitrogen implanted polysilicon gate for quarter micron dual gate CMOS(3) devices. A key material for these new techniques is nitrogen doped polysilicon film. This makes it essential to correctly understand the diffusion behavior of nitrogen in polysilicon.

Many investigations of the behavior of nitrogen in bulk silicon have been carried out. However, very few studies have reported on the behavior of nitrogen in polysilicon film during annealing. In this paper, we report the diffusion of in-situ doped or implanted nitrogen in polysilicon films and the segregation of nitrogen at the poly-Si/SiO_2 interfaces during annealing at 700-1000°C.

Experimental Procedure

Polysilicon films were deposited on thermal oxide films in a conventional low pressure CVD reactor using Si_2H_6 or Si_2H_6-NH_3 at about 500°C, and using SiH_4 gas at about 620°C. The films deposited at 500°C using Si_2H_6 gas were amorphous. These films crystallized during heat treatment above 700°C. The films deposited at 620°C using SiH_4 gas were polysilicon. Implantation into undoped amorphous, poly or crystal silicon was carried out using N_2^+ ions with $1x10^{15}$ or $1x10^{16}$ ions/cm^2 at 140-KeV. After implantation, wafers were diced into 1cm squares. They were then heat treated in N_2 ambient in a conventional electric furnace at 700-1000°C.

Nitrogen concentration distributions were measured by secondary ion mass spectroscopy (SIMS). Primary ions were Cs^+ and the secondary ions were Si^- and SiN^-. Nitrogen concentrations in polysilicon films were calibrated using a N_2 implanted amorphous silicon film.

Results and Discussion

Figure 1 shows the nitrogen distribution in polysilicon films before and after heat treatment at 1000°C. As shown in Fig. 1(a) , undoped amorphous silicon film was deposited on silicon dioxide, followed by subsequent nitrogen in-situ doped silicon film deposition without a processing break. The thickness of the nitrogen-doped polysilicon and the undoped polysilicon layers are 100 nm. Figure 1(b), and Fig. 1(c) plots the relationships when undoped amorphous silicon films were implanted with N_2^+ ions of $1x10^{15}$ and $1x10^{16}$ ions/cm^2. Pile-ups at the poly-Si/SiO_2 interfaces and at the surface of polysilicon films were observed after heat treatment regardless of the nitrogen doping method and initial nitrogen amounts in the polysilicon films. These pile-ups were not observed in the as-deposit and as-implantation samples. The pile-up at the surface disappeared after etching of surface oxide, which was covered with thin silicon oxide grown during annealing, using hydrogen fluoride solution. This indicates that the nitrogen atoms pile up on the oxide side of the poly-Si/SiO_2 interface. Ion count peaks at the interface of SiO_2/bulk silicon were also observed in all samples. These nitogen atoms were incorporated into the interface of SiO_2/bulk silicon during oxidation of the bulk silicon, and these peaks were constant during heat treatment of the polysilicon films.

Corresponding to the pile-up at the poly-Si/SiO_2 interfaces and at the surfaces, we found that the nitrogen amounts in the polysilicon films decreased. In our experiment, TDS analysis showed the out diffusion of nitrogen from polysilicon films was below $1x10^{12}$ atoms/cm^2/sec. Thus, we can ignore the out diffusion of nitrogen from polysilicon films during heat treatment. This suggests that the decreasing amount of nitrogen in

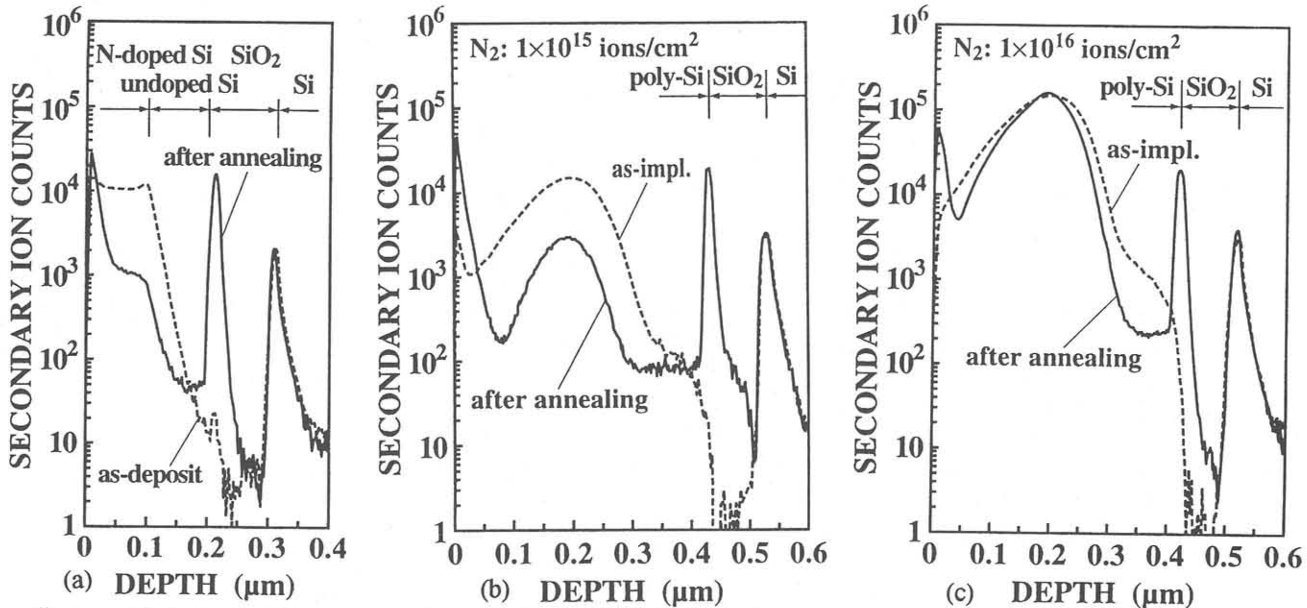

Figure 1. Nitrogen distributions in the polysilicon films on SiO_2 before and after 30 min heat treatment at 1000°C. Figure (a) is the nitrogen in-situ doped polysilicon film. Figures (b) and (c) are nitrogen implanted polysilicon films with N_2^+ ions of $1x10^{15}$ and $1x10^{16}$ ions/cm^2.

the polysilicon films compensate for the segregated nitrogen amount.

Although the amount of nitrogen in the polysilicon films decreased after heat treatment, the nitrogen concentration in the region close to SiO_2 did not decrease below a threshold value. It should also be noted that the nitrogen profiles in the polysilicon films did not spread after heat treatment. This indicates that a fraction of the nitrogen atoms in the polysilicon film were immobile at higher concentrations than the threshold value.

It is difficult to quantitatively estimate the amount at the surface and interface with SIMS analysis. Almost all of the nitrogen in the polysilicon film segregated at the surface and the poly-Si/SiO_2 interface after 8-hour heat treatment at 1000°C. Then, assuming that the amount of segregated nitrogen at the surface and poly-Si/SiO_2 interface were equal, we evaluated the relative sensitive factor (RSF) at the interface using the sample annealed at 1000°C for 8 hours and estimated the segregation nitrogen amounts.

Figure 2 shows the anneal time dependence of the segregated nitrogen and nitrogen amount in polysilicon films. The amount of segregated nitrogen increased and the amount of nitrogen in the polysilicon films decreased

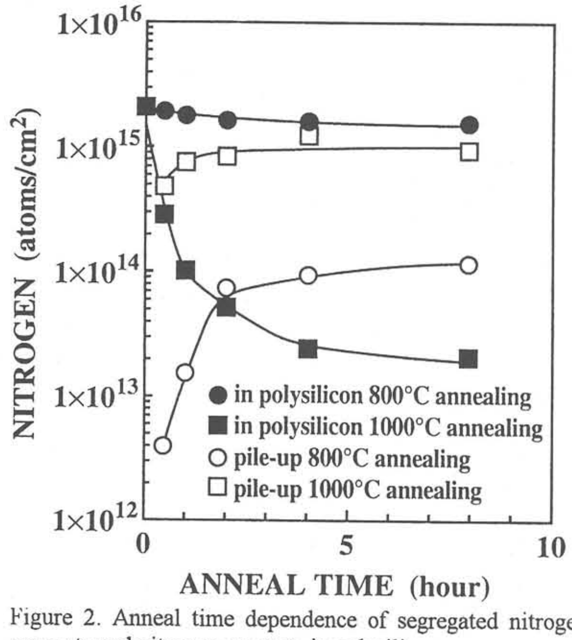

Figure 2. Anneal time dependence of segregated nitrogen amounts and nitrogen amounts in polysilicon.

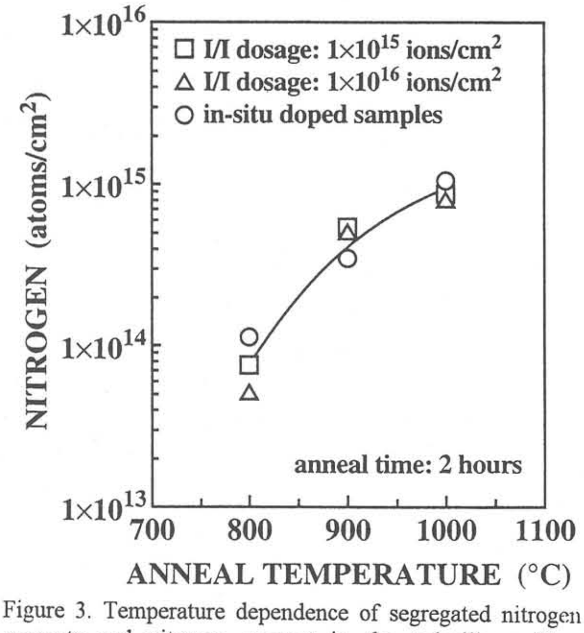

Figure 3. Temperature dependence of segregated nitrogen amounts and nitrogen amount in the polysilicon films.

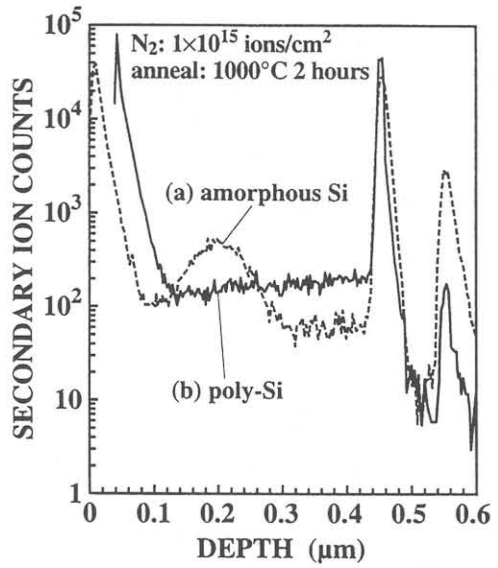

Figure 4. Nitrogen profile in polysilicon films deposited under different conditions. Sample (a) was amorphous silicon and sample (b) was polysilicon before nitrogen implantation.

with increasing anneal time up to 4 hours, beyond which they level off. For the 1000°C annealing, 99% of the nitrogen in polysilicon segregated at the poly-Si/SiO_2 interface, while only 5% of the nitrogen in polysilicon film piled up at the interface. This result suggests that the amount of pile-up at the interface is limited to a certain value which depends on temperature.

Figure 3 shows the anneal temperature dependence of the segregated nitrogen for in-situ doped samples and for nitrogen implanted samples whose initial nitrogen dosage into polysilicon films were 1×10^{15} ions/cm^2 or 1×10^{16}ions/cm^2. The segregation amounts of nitrogen increased with higher anneal temperature and were almost the same regardless of the initial nitrogen amounts in the polysilicon films and the doping methods.

The nitrogen profiles of the polysilicon films deposited under different conditions after heat treatment at 1000°C are shown in Figure 4. Sample (a) was amorphous silicon film and sample (b) was polysilicon film before annealing. After annealing, sample (a) became crystallized. These samples had different polysilicon structures as shown in Fig. 5. These TEM micrographs show that sample (a) had large grains over several hundred nanometers and sample (b) had small grains below one hundred nanometers. In Fig. 4, the nitrogen concentration peak in the polysilicon film was observed in sample (a), while the nitrogen profile in sample (b) has a uniform distribution whose concentration was higher than the threshold value close to the poly-Si/SiO_2 interface of sample (a). These data indicate that the diffusion of nitrogen in polysilicon films and the threshold concentration for nitrogen diffusion depends on the polysilicon structure.

Conclusion

Nitrogen in polysilicon film diffuses and piles up at the poly-Si/SiO_2 interface during heat treatment above 800°C. The decrease in the amount of nitrogen in the polysilicon films compensates for the segregated nitrogen amounts. The amounts of segregated nitrogen and nitrogen in polysilicon films after heat treatment are not dependent on the initial amounts of nitrogen in the polysilicon film. They are, however, dependent on annealing conditions. A fraction of nitrogen above a threshold concentration was immobile. This threshold concentration for nitrogen diffusion depends on the polysilicon structure.

Acknowledgment

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References

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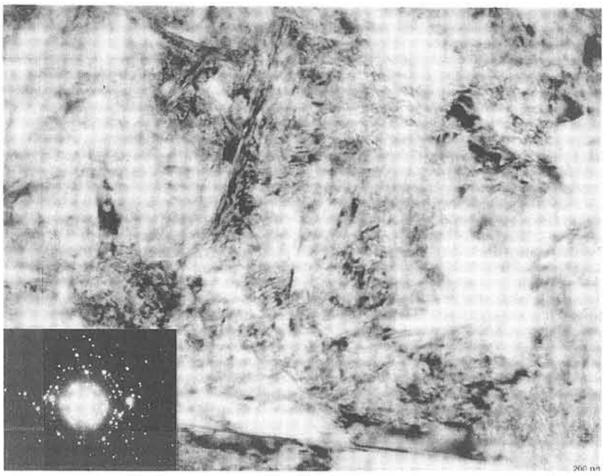
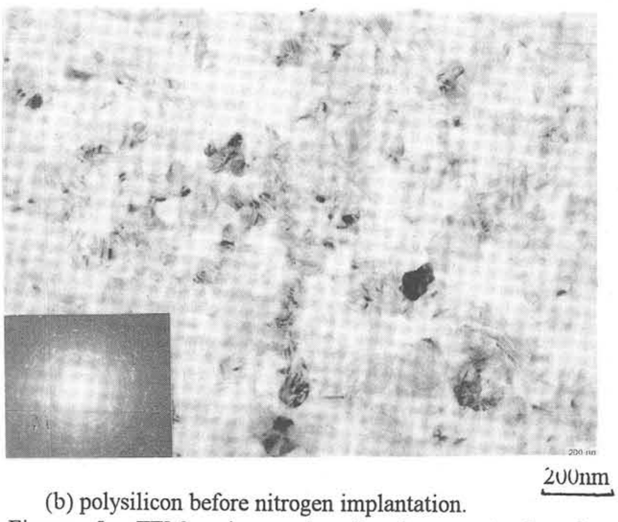


(a) amorphous silicon before nitrogen implantation



(b) polysilicon before nitrogen implantation.

Figure 5. TEM micrograph of nitrogen implanted polysilicon films after 1000°C annealing.