

Dominant Factor for the Concentration of Phosphorus Introduced by Vapor Phase Doping

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1. Abstract

The possibility of high concentration doping by vapor phase doping technique was investigated. It was found that the surface concentration of phosphorus could be controlled dominantly by the temperature and the PH_3 partial pressure. In addition, it was confirmed that a mono-layer of phosphorus was adsorbed on the silicon surface during the doping process. A new diffusion model via this adsorption layer at the surface is proposed to explain the surface concentration behavior. Surface phosphorus concentration of as high as 8×10^{19} atoms/cm³ with electrically activated phosphorus was obtained successfully.

2. Introduction

The development for the fabrication of shallow junction with a high surface concentration has been attempted for n-type and p-type doping. For p-type doping, ion implantation has a disadvantage of the channeling effect of ions. To overcome this problem, several different processing techniques have been investigated such as molecular layer doping(MLD)[1] and rapid vapor-phase doping(RVD)[2]. On the other hand, for n-type doping, very-low-energy ion implantation is effective. But this technique has the problem of wafer damage by energetic ions that induce leakage current in devices. Hence other processing techniques are required to fabricate shallow junctions with a high surface concentration for the future. However, in previous experiments[3] a high concentration at the surface can't be obtained on the contrary for boron[2]. In this paper, the possibility of high concentration doping by vapor phase doping using phosphine is reported. And the mechanism of dominating the surface concentration will be explained by the new model of the diffusion via a mono-layer of phosphorus adsorbed at the surface.

3. Experimentals

P-type (100) silicon wafers were used. Just before phosphorus doping, wafers were annealed in hydrogen ambient to remove a native oxide. Then phosphorus doping using phosphine was carried out sequentially. Typical doping conditions are listed in Table I. Pure hydrogen and 1% phosphine in hydrogen were used as the carrier gas and doping gas, respectively.

The sheet resistance was measured by the four point probe method. The phosphorus profile and carrier concentration were measured by secondary ion mass spectroscopy(SIMS) and differential hall effect measurement, respectively. The chemical state of P on Si surface was analyzed using X-ray photoelectron spectroscopy(XPS).

4. Native oxide as a diffusion barrier and its removal

In vapor phase doping, doping characteristics are strongly affected by the surface condition of the wafer. Especially a native oxide works as a diffusion barrier and have to be removed completely. Native oxide removal condition was investigated for wafers with 1nm thick chemical oxide. Hydrogen annealing temperature was varied from 800°C to 1000°C. Subsequent doping was

performed at lower temperature, 800°C, to minimize the oxide removal effect of doping step. Sheet resistance for various anneal temperature is plotted in Fig.1. Lower than 900°C, sheet resistance was unchanged from as received wafer because of doping suppression by the remaining oxide. On the other hand, in the case of 1000°C, sheet resistance increased, which indicates the removal of a chemical oxide and the phosphorus diffusion into silicon. Thus, hydrogen anneal temperature was fixed at 1000°C in our experiment.

5. The concentration of phosphorus induced by VPD

A typical SIMS profiles of the phosphorus doped layer are shown in Fig.2. Both samples were diffused at the identical condition. One sample was additionally capped with poly silicon film after doping. The phosphorus depth profile is same between the two samples except at the silicon surface. A high concentration of phosphorus exists only at the poly/silicon interface of the capped sample.

The areal concentration of phosphorus at the interface was 5×10^{14} atoms/cm² and the same order of atom density of silicon crystal surface. This layer exists regardless of the conditions such as temperature, the flow rate of PH_3 or H_2 . Even if the surface was exposed to the atmosphere once. It was also confirmed that this phosphorus wasn't affected by re-evaporation from the chamber wall during depositing the poly silicon. Therefore, it is obvious that a mono-layer of phosphorus adsorbs at the surface throughout the doping process.

To investigate this surface adsorption layer, XPS analysis was performed. The P2p peaks are shown in Fig.3. The peak position of diffused sample indicates that the phosphorus isn't oxidized and exists in the form of ⁰P. It is indicated that the phosphorus adsorbs without any tight bindings. By the fact that the phosphorus on the surface of uncapped sample can easily desorb from the surface at the initial stage of SIMS measurements.

As for the diffused phosphorus into the wafer, the activation of all diffused phosphorus was confirmed by Hall measurements. The depth profile of the electrical active phosphorus and of the chemical phosphorus are shown in Fig.4. At PH_3 partial pressure of 800mTorr, surface concentration of 8×10^{19} atoms/cm³ was obtained.

SIMS profiles for various doping time at 1000, 1100°C are shown in Fig.5. The surface concentration maintains constantly in same level and the junction depth increases linearly with the square root of the doping time at each temperature. The diffusivity of phosphorus is identical to that in the conventional diffusion method.

The PH_3 partial pressure dependence of surface concentration is shown in Fig.6. In this figure, the PH_3 partial pressure was varied by changing the flow rate of PH_3 , H_2 and total pressure. From these results, the surface concentration increases as the partial pressure increases and is independent of the flow rate of H_2 and the total pressure. Thus, the phosphorus concentration at the surface can be controlled by the PH_3 partial pressure.

The phosphorus depth profiles for various temperature are shown in Fig.7. In the region below 1000°C, the surface concentration increased as the doping temperature increased. Above 1000°C, the surface concentration was constant. However, these phosphorus concentration are lower than the solid solubility limit of phosphorus in silicon at each temperature.

To explain these data, a new model of vapor phase doping of phosphorus is proposed as shown in Fig.8. The reaction between vapor phase and the adsorption layer and that between the adsorption layer and the silicon substrate are both under the equilibrium condition. Thus, in order to obtain the higher phosphorus concentration on the surface the phosphine partial pressure should be higher. The limiting factor of the surface concentration at higher temperature than 1000°C might be some other effects, such as the suppression of phosphine decomposition by hydrogen.

6. Conclusion

It was found that the phosphorus concentration on the surface was independent of doping time and could be controlled by the PH₃ partial pressure and the temperature. All the diffused atoms were electrically activated. Adsorbed mono-layer of phosphorus was formed on the silicon surface during the doping step. And it was confirmed that the phosphorus diffuses from vapor phase into silicon substrates via this adsorbed layer.

References

- 1) J. Nishizawa et al., IEEE Electron Device Lett. **11** (1990) 105.
- 2) Y. Kiyota et al., J. Electrochem. Soc. **140** (1993) 1117.
- 3) Y. Kiyota et al., J. Electrochem. Soc. **141** (1994) 2241.

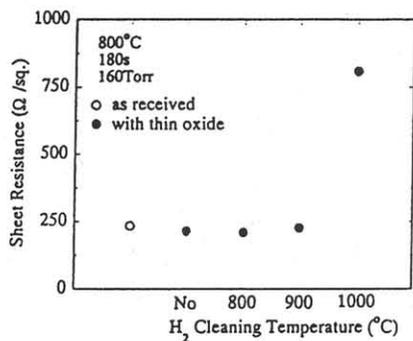


Fig.1 Temperature dependence of hydrogen annealing for native oxide removal.

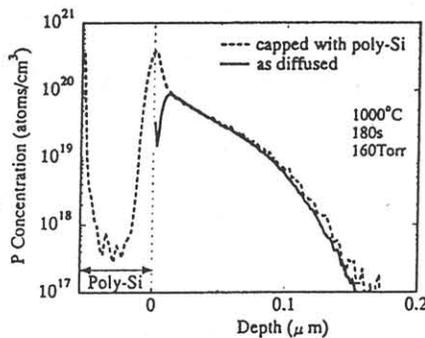


Fig.2 Depth profiles of phosphorus. One sample was capped with poly silicon and the other wasn't.

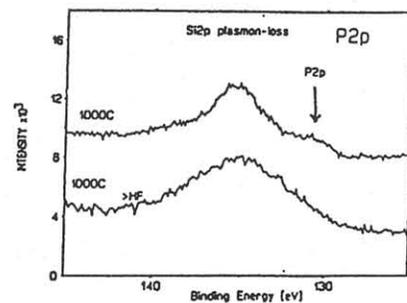


Fig.3 XPS spectra for diffused samples. P peak was observed only on the sample without HF treatment.

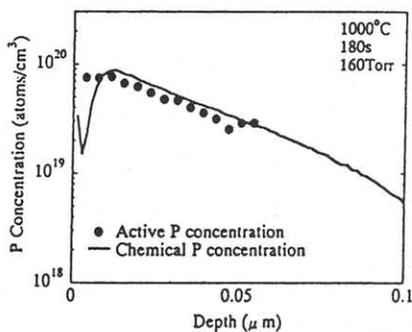


Fig.4 Carrier concentration profiles measured by Hall measurement.

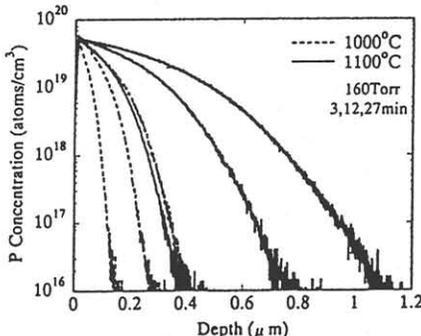


Fig.5 Depth profiles of phosphorus. Doping time were 3, 12 and 27min.

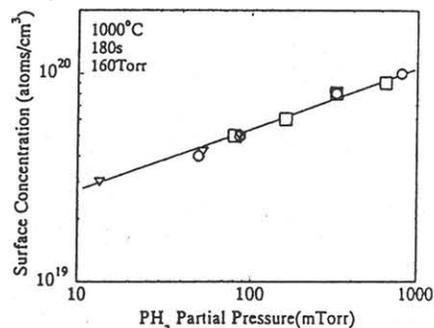


Fig.6 PH₃ partial pressure dependence of the surface concentration. (○) PH₃ flow rate dependence, (▽) H₂ flow rate dependence, (□) total pressure dependence

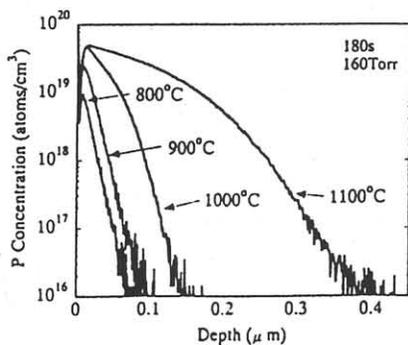


Fig.7 Depth profiles of phosphorus. Doping temperature were 800, 900, 1000 and 1100°C.

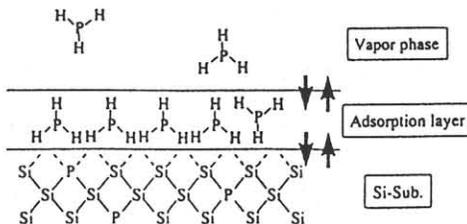


Fig.8 The model of phosphorus vapor phase doping via the adsorption layer at the surface.

Table. I Doping conditions.

Temperature	800~1100°C
Pressure	40~320Torr
Time	3~27min
PH ₃ flow rate	100~500sccm
H ₂ flow rate	0.5~15.5slm