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Defect Evaluation of Heavily Phosphorus-Doped Si Epitaxial Films Grown by Plasma Chemical Vapor Deposition

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Investigation of vacancy-related defects in heavily phosphorus-doped Si:P grown by plasma chemical vapor deposition (CVD) has been carried out using variable-energy positrons. Modeling and fitting of S parameters indicate that a high concentration of vacancy-related defect ($> 10^{-3}$ /atom) exists in both as-deposited and annealed specimens. The 600°C annealed one has a lowest carrier concentration, highest sheet resistivity and highest concentration of vacancies. The vacancy-related defects were assigned for the electrical deactivation. At higher annealing temperature (900°C), the precipitation of phosphorous may also play an important role in the electrical deactivation.

1. INTRODUCTION

Conventional Si epitaxy with chemical vapor deposition (CVD)[1] technique uses processing temperatures exceeding 1000°C and causes impurity redistribution and thermal stress. To minimize autodoping and solid state diffusion effects for an abrupt impurity profile, several low temperature approaches including molecular-beam epitaxy (MBE)[2] and CVD techniques[3, 4] have been proposed. Among these techniques, plasma-CVD appear to be one of the most suitable process due to its high throughput and low cost. In this paper, we demonstrate the investigation of vacancy-related defects in heavily doped Si films with doping level of 10^{21} cm^{-3} deposited by plasma-CVD at low temperature of 250°C.

2. EXPERIMENTAL

The substrate used was a (100)-oriented Si wafer which has a resistance over 1000 Ω·cm. The reactant gases SiH_4 , SiF_4 , H_2 and PH_3 are introduced into the plasma-CVD reactor with a base pressure of 10^{-7} Torr. The substrate temperature was 250°C during the growth and the annealing was performed at 600°C and 900°C in N_2 ambient for 1 hr. Two series of specimens with different epilayer thickness (200 nm and 340 nm) were obtained. The dopant concentration ($\sim 10^{21}$ cm^{-3}) was verified by SIMS measurement. Hall effect measurements were made on van der Pauw specimens at room temperature following a standard procedure.

The Doppler broadened spectra of annihilation radiations were measured using a slow positron beam line. The Doppler broadened spectra were characterized by the line shape parameter S. All the measurements were performed at room temperature. Table 1 shows the measured electrical properties.

3. RESULTS AND DISCUSSION

3.1. Positron Annihilation

Figure 1 shows the S parameters as a function of incident positron energy for as-deposited, 600°C annealed and 900°C annealed Si (340 nm)/Si specimens. The solid lines indicate the best fitting of positron trapping model. The remeasured S parameters after the removal of oxide on the surface of Si epitaxial layer are show in Fig. 2. The correspondent plot for Si (200 nm)/Si is not included here because of its similarity with Si (340 nm)/Si. The S parameters in Fig. 1 for as-deposited Si (340 nm)/Si differs significantly from that of defect-free Si wafer. The high S parameter in the epitaxial layer indicates the vacancy-type defects were introduced during the growth of epitaxial Si layer. From Figs. 1 and 2, one can find that the S parameter for the 600°C annealed specimen increased in comparison with that of as-deposited one, indicating the increase

Table 1
Electrical properties for Si:P

Samples	Thickness (nm)	Carrier concentration (cm^{-3})	Mobility ($cm^2/V\cdot sec$)	Resistivity ($\Omega\cdot cm$)
As-deposited Si/Si	200	1.11×10^{21}	14.76	3.82×10^{-4}
	340	1.10×10^{21}	13.02	5.52×10^{-4}
600°C annealed	200	5.76×10^{19}	60.16	1.08×10^{-3}
	340	2.75×10^{19}	57.43	3.94×10^{-3}
900°C annealed	200	3.50×10^{20}	89.30	2.01×10^{-4}
	340	3.21×10^{20}	57.09	3.40×10^{-4}

of vacancy-type defects after annealing at 600°C. Furthermore, the S parameter for 600°C annealed specimen holds highest value in the interfacial region between epitaxial layer and the Si substrate. However, by annealing at 900°C, the drastic decreasing of S parameter was observed, indicating the recovery of vacancy-type defects. The

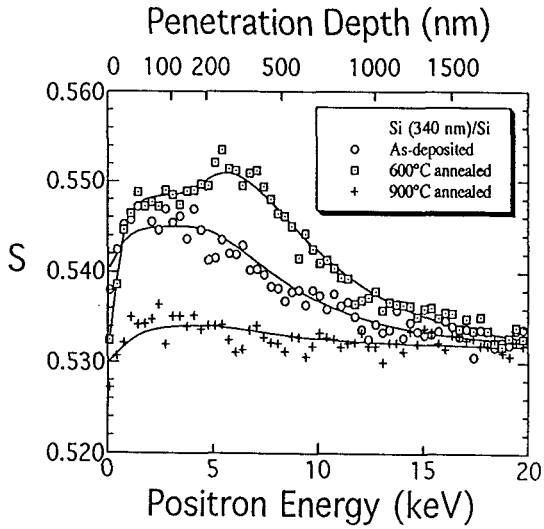

Figure 1. S parameter versus positron energy for as-deposited, 600°C annealed and 900°C annealed Si (340 nm)/Si. Solid lines denote the fits to the experimental data.

data have been modeled using a variation of an analysis successfully used in the previous investigation of Si and GaAs.[5–7] The implantation profile P(x, E) of positrons may be described by

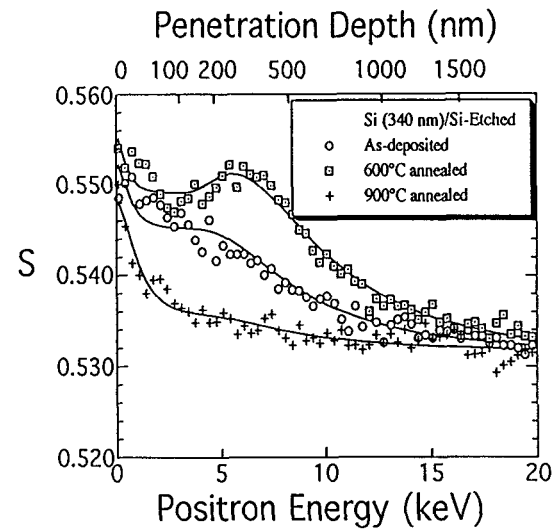

Figure 2. S parameter versus positron energy for as-deposited, 600°C annealed and 900°C annealed Si (340 nm)/Si after removal of oxide on the surface of specimens.

a Makhovian profile[8]

$$P(x,E) = -\frac{d}{dx}[\exp(-\frac{x}{x_0})^m], \quad (1)$$

$$x_0 = \bar{x}/\Gamma(1+1/m), \quad (2)$$

where m is selected as 1.9 and $\bar{x}$ is the mean penetration depth of positrons, which is expressed as $\bar{x} = (40/\rho)E^{1.6}$. The S parameter can be expressed by summing the integral of P(x, E) and weighting by the characteristic S value for different depth of specimen.

The area analyzed in the case of the Si:P was divided into three regions: (i) the surface; (ii)

the epitaxial layer with a considerable amount of defects; and (iii) the defect-free region. For the 600°C annealed specimen the interfacial state was also taken into account. Therefore, the energy-dependent S parameter, S(E), can be defined as

$$S(E) = S_s F_s(E) + S_{epi} F_{epi}(E) + S_i F_i(E) + S_b F_b(E) \quad (3)$$

where S_s, S_{epi}, S_i and S_b indicate the characteristic values of S parameter for the annihilation at surface, in the epitaxial layer, at the interface and in the defect-free substrate, respectively.

The obtained parameters by fitting procedures are summarized in Table 2. From Table 2, one can find that the ratio of S parameter for epitaxial layer, S_{epi}, to that for a annihilation in Si substrate are 1.026, 1.032(4) and nearly 1 for as-deposited, 600°C annealed and 900°C annealed specimens, respectively. The value of 1.032(4) is close to the characteristic value of positron annihilation in divacancy, implying the production of divacancy-like defects in the epitaxial layer during annealing at 600°C. Furthermore, the Si is more higher than the saturated value of annihilation in divacancy. Therefore, the agglomeration of vacancies at the interface should be considered. By annealing at 900°C, the S parameter drastically decreased, however, the diffusion length of positrons remains significantly short as listed in Table 2. The precipitation, which may be responsible for the shortening of diffusion length of positrons, is expected to occur after annealing at 900°C, since the dopant concentration extended the solid solubility of phosphorous in Si prior to the annealing treatment.[9] We roughly estimated the concentration of vacancies by taking $\lambda_f = 4.55 \times 10^9$ s^{-1} [10], $L_{free} = 180$ nm and $\mu = 3 \times 10^{-14}$ s^{-1} [11], as listed in Table 2.

3.2. Vacancy Complex Model

Pandey *et al.*[12] showed by *ab initio* total-energy calculations that a new defect complex (V-As$_4$), a vacancy surrounded by four arsenic atoms, is responsible for explaining electrical deactivation when heavily As-doped Si was annealed. The chemical property of phosphorus is similar to arsenic, so we supposed that a defect complex (V-P$_4$), a vacancy surrounded by four phosphorus atoms, is also formed by annealing the heavily P-doped Si films. Furthermore, calculations for the total number of complex have been carried out from the thermodynamical point of view. The calculation can be illustrated as follows:

The multiplicity W of distinguishable distribution of V-P$_4$ complex is given by the formation of

$$W = {}_{N_t+N_c}C_{N_c} \times {}_{N_t-4N_c}C_{N_p-N_c}, \quad (4)$$

where N_t , N_p and N_c are the total number of lattice site, the phosphorus atoms and the total number of V-P$_4$ complex, respectively. The free energy must be minimized subject to the equilibrium constraint. Therefore the electron concentration at various temperature can be determined by $N_e = N_p - 4N_c$. Other analogous vacancy-complex, such as V$_2$-P$_6$ and V-P$_2$, may calculated by the similar way.

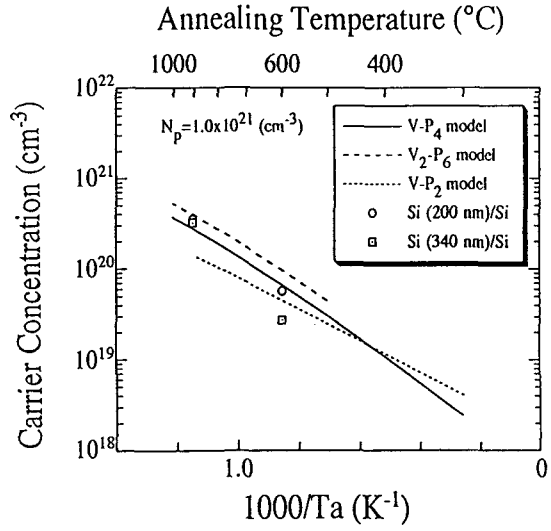

Figure 3. Carrier concentration as a function of annealing temperature. Open circles (o) and dotted squares (□) are experimental data obtained from the Hall measurement.

Figure 3 shows the carrier concentration as a function of annealing temperature. The good agreement between the calculation using V-P$_4$

Table 2
Summary of obtained parameters by fitting the positron diffusion equation to the experimental data.

Samples	S_{epi}/S_b	S_i/S_b	L (nm)	C_v(/atom)
As-deposited Si (200 nm)/Si	1.026	—	8	7.6×10^{-3}
As-deposited Si (340 nm)/Si	1.026	—	10	4.8×10^{-3}
600°C annealed Si (200 nm)/Si	1.032	1.075	12	1.7×10^{-3}
600°C annealed Si (340 nm)/Si	1.034	1.074	7	5.0×10^{-3}
900°C annealed Si (200 nm)/Si	1.007	—	39	3.0×10^{-3} a)
900°C annealed Si (340 nm)/Si	1.006	—	21	1.3×10^{-3} a)

a) For divacancy.

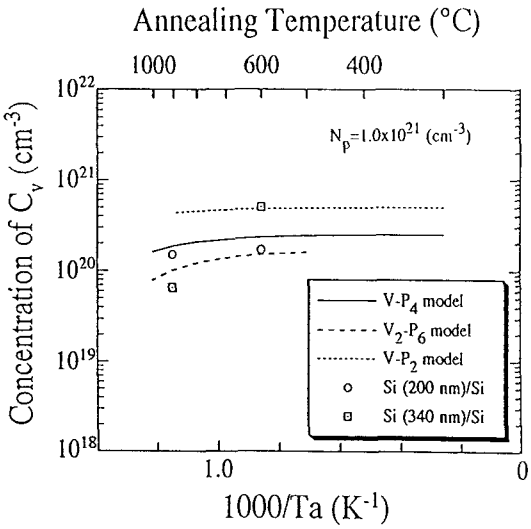

Figure 4. Concentration of vacancies as a function of annealing temperature. Open circles (○) and dotted squares (□) are data obtained from the positron annihilation.

complex model and the electrical measurement was obtained. The defect concentration obtained from the calculation coincides with the results of positron annihilation in the same order as shown in Fig. 4. However, the specification of defects by positron annihilation is discrepant with the calculation of the complex model. The configuration of vacancy complex may be more complicated. Nevertheless, it is acceptable, from the present experiment, that the vacancy complex results in the electric deactivation in Si:P after heat treatment. The precipitation may also play an important role in the electric deactivation when annealing at high temperature.

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