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# Phosphorus doping of silicon at substrate temperatures above 600 °C

P.E. Thompson [a,*], G.G. Jernigan [a], D. Simons [b], P. Chi [b], B.T. Jonker [a], O.M.J. van 't Erve [a]

[a] Naval Research Laboratory, Washington, DC 20375, United States
[b] National Institute of Standards and Technology, Gaithersburg, MD 20899, United States

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ABSTRACT

Phosphorus doping of silicon during growth by molecular beam epitaxy (MBE) has been investigated in the temperature regime 700 °C to 870 °C. By designing a growth sequence that fully accounts for the P deposited in a delta-doped layer, and then tracks the P as it segregates into the undoped Si and traps the surface P in a low temperature Si cap, it was determined that the onset of significant P evaporation during growth occurred at a substrate temperature of 663 °C ± 10 °C. The P sublimation process had an activation energy of 199 kJ/mol ± 22 kJ/mol.

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## 1. Introduction

Among the n-type dopants of Si, P has only been recently used in solid-source epitaxy growth systems [1,2]. P doping is of interest for several reasons. The solid solubility of P in Si is approximately 10 times higher than that of Sb in Si, permitting the higher doping concentrations required in sub-micron devices and in tunneling devices. In addition, it has been suggested that in a silicon-based quantum computer, accurately positioned P donors would function as quantum bits (qubits) [3]. However, the high vapor pressure of P prevents its use as an elemental dopant in a molecular beam epitaxy (MBE) growth system. There have been previous investigations of co-evaporation of highly P-doped Si, [1] and reports of the use of GaP in a Knudsen cell [2]. However, a comprehensive study of P doping of Si using GaP is lacking. We report here P segregation, surface evaporation, and electrical activation during growth using a GaP source, focusing on growth temperatures greater than 600 °C, which are necessary to minimize the Si point defect density.

## 2. Experimental

All samples were grown using solid-source MBE employing elemental Si in an e-beam source. The base and growth pressures were $5\times10^{-9}$ Pa and $3\times10^{-7}$ Pa, respectively. The GaP Knudsen dopant cell was specially designed to exploit the differential evaporation of Ga and P. Secondary ion mass spectrometry (SIMS) was used to determine the atomic P profiles in Si. Previously it was established using SIMS that for a doped Si layer having a P concentration of $2\times10^{19}/cm^3$, the concentration of Ga was at least three orders of magnitude less [4]. Carrier concentrations were measured using spreading resistance profiles.

In a previous study [4], we measured the segregation of P during the growth of Si in the temperature interval 380 °C to 650 °C. In that experiment, after the growth of a smooth Si buffer layer at 700 °C, the substrate temperature was reduced to less than 380 °C for the deposition of a P delta-doped layer, having a concentration of $1.2\times10^{14}cm^{-2}$. Then the substrate temperature was increased to temperature, *T*, and an undoped Si cap was deposited at a growth-rate of 0.1 nm/s. The GaP cell temperature was reduced during the Si growth to minimize background P. SIMS was used to measure the penetration of the P into the undoped Si, as a function of growth temperature. An overlay of the SIMS profiles is presented in Fig. 1. It should be noted that in the figure, the P deposition in all samples occurs at "0" and then Si is deposited at the specified temperature. The growth direction is toward the right. If we can assume that an insignificant amount of P had evaporated from the surface during the growth of the "undoped" Si, the surface segregation ratio of the P can be determined by comparing the amount of P on the surface (normalized to the Si(100) surface site density) to the P bulk concentration (normalized to the Si atomic concentration) [4]. In the present work, since we are interested in growth temperatures above 600 °C, we cannot make the assumption that the P is not evaporating during growth. We have modified the design of the experiment to include a 100 nm Si cap deposited at a substrate temperature <300 °C that will trap any P that has segregated to the surface. Once again the P atomic concentration profiles were measured with SIMS. An overlay of the SIMS profiles of the high temperature growths is presented in Fig. 2. As noted before, in the figure the P deposition in each sample occurs at "0" and the growth direction is toward the right. The P concentration peaks observed at the end of each profile are evidence of the segregating P trapped by the low temperature Si growth.

* Corresponding author.
*E-mail address:* phillip.thompson@nrl.navy.mil (P.E. Thompson).

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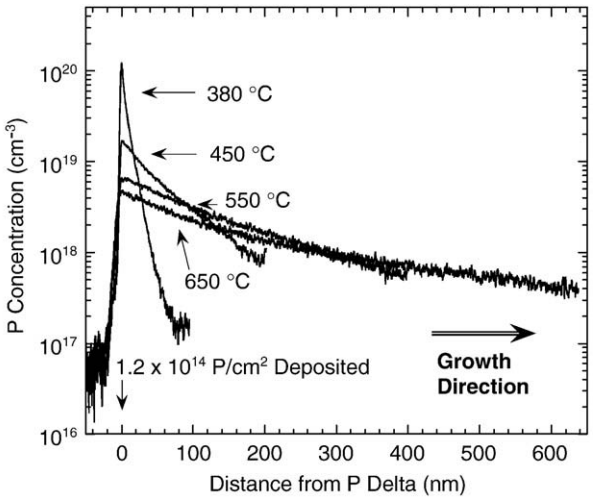


**Fig. 1.** SIMS atomic concentration profiles of P resulting from a delta layer deposited at "0" followed by undoped Si deposited at temperatures between 380 °C and 650 °C.

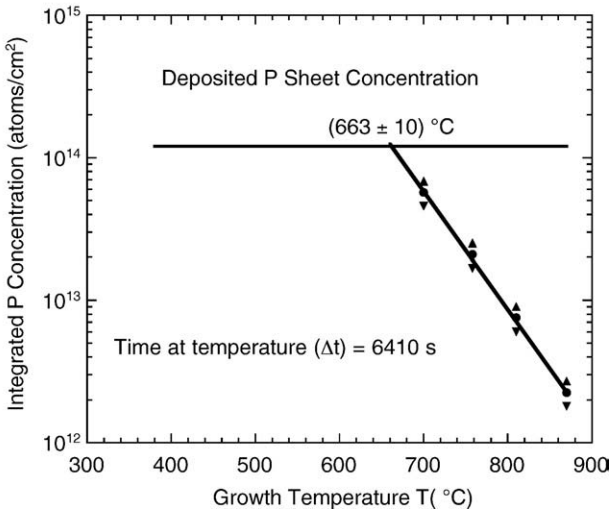


**Fig. 3.** Total P in the sample including the P trapped at the surface. $\Delta t$ is the total time at the growth temperature. There is clear evidence of P evaporating from the surface during growth. Error bars (triangles) represent ±20% estimated relative uncertainty in atomic concentration measured by SIMS.

## 3. Results and discussion

Besides the temperature-dependent segregation of the P into the Si, seen in Figs. 1 and 2, we observed that the P was evaporating from the Si surface during growth. The stability of P on the Si surface during growth at a specific temperature has been established by the integration of the total P in the sample, including P in the delta doped region, the P segregated into the Si, and the P remaining on the surface, which was trapped by the growth of a Si cap at low temperature. The total time at growth temperature, *T*, for each sample shown in Fig. 2 was 6410s. The integrated P concentration versus growth temperature is presented in Fig. 3. The "no evaporation" line was verified by the numerical integration of the P atomic concentration of the sample grown at 380 °C. The error bars represent the ±20% estimated relative uncertainty in the atomic concentration measured by SIMS. It is clear that since the logarithm of P has a linear dependence on the growth temperature, the evaporation process is exponential with temperature. We can determine two key parameters. By extrapolating the P concentration back to its original concentration, it is observed that the P does not evaporate from the Si surface at growth temperatures below 663 °C with an estimated uncertainty of ±10 °C. Thus, the assumption that the P evaporation was negligible in the calculation of the P surface segregation ratio [4] in the temperature interval 380 °C to 650 °C is valid. The activation energy for the P evaporation can be determined by plotting the logarithm of remaining P versus 1/*T*, Fig. 4. Once again, the error bars represent the ±20% relative standard uncertainty in the atomic concentration measured by SIMS. This plot is only valid since the time at temperature for each sample is the same, 6410s in this case. The activation energy for P evaporation has been determined to be 2.07 eV ± 0.23 eV or 199 kJ/mol ± 22 kJ/mol, Fig. 4, from the data in Fig. 3. This corresponds very well to prior determinations for the sublimation of P, by the reaction

$$2P(s) \rightarrow P_2(g) \quad (1)$$

by L'vov and Novichikhin [5] of 184 kJ/mol and that of Kane [6] of 218 kJ/mol.

Results of this investigation were successfully applied to the growth of an $n^+$ Si layer at 750 °C. This structure was requested for the

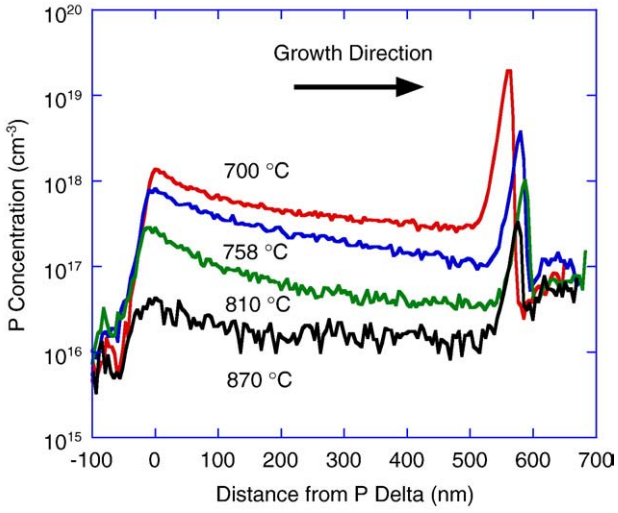


**Fig. 2.** SIMS atomic concentration profiles of P resulting from a delta layer deposited at "0" and undoped Si deposited at temperatures between 700 °C and 870 °C. Room temperature Si was deposited to trap the surface P at the end of growth.

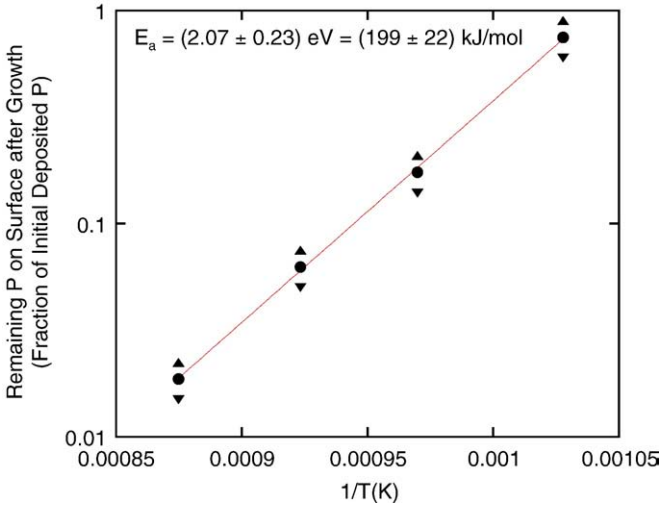


**Fig. 4.** Determination of the activation energy for P evaporation from the Si surface. Error bars (triangles) represent ±20% estimated relative uncertainty in atomic concentration measured by SIMS.

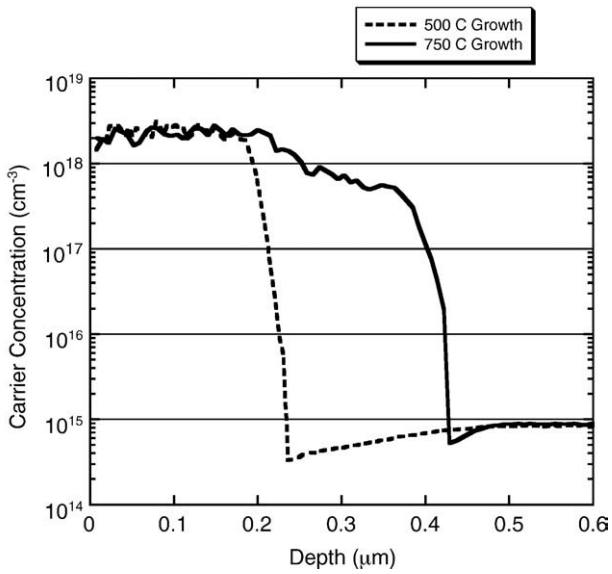


**Fig. 5.** Uniform P doping at 750 °C was obtained by using a P delta layer pre-deposition and high P flux to compensate for both surface evaporation and surface segregation. Uniform P doping at 500 °C is shown for comparison.

electrical injection and detection of spin-polarized carriers in a lateral transport geometry. While this effect has already been reported for an $n^+$ Si layer grown at 500 °C, [7] it is anticipated that longer spin lifetimes due to decreased interaction with point defects will be observed in the sample grown at 750 °C. The carrier concentration profiles of both samples are presented in Fig. 5. The 500 °C growth had a 210 nm undoped buffer layer grown with the substrate at 650 °C and a 210 nm $n^+$ layer grown with the substrate at 500 °C. The Si growth-rate was 0.1 nm/s and the P flux was maintained at $2\times10^{10}/(cm^2\cdot s)$. The 750 °C sample had the same buffer layer structure. To compensate for the P evaporation and P segregation during the 750 °C growth, a P delta layer ($5\times10^{13}/cm^2$) was deposited while the substrate temperature was increased from the buffer growth temperature, 650 °C. During the growth of the $n^+$ layer at 750 °C, the P flux was maintained at $5\times10^{11}/(cm^2\cdot s)$ with a Si growth-rate of 0.1 nm/s. An unfortunate by-product of having the GaP cell at a higher temperature during the buffer layer growth is that a P background doping of about $7\times10^{17}/cm^3$ is measured in the buffer layer. It should be noted that during the 500 °C growth approximately 80% of the P incident upon the surface becomes electrically active. In the 750 °C growth only approximately 3% of the incident P becomes incorporated into the sample and is electrically active.

## 4. Conclusions

We have investigated the n-type doping of Si during growth by MBE using a GaP effusion cell. The substrate temperature during growth was maintained between 700 °C and 870 °C in order to complement a previous study during which the substrate temperature during growth was kept between 380 °C and 650 °C. In the high temperature growth regime we have observed both P segregation and P evaporation. We have determined that P surface evaporation becomes significant for substrate temperatures greater than 663 °C ± 10 °C. The P surface evaporation is an exponential function of the surface temperature and has an activation energy of 199 kJ/mol ± 22 kJ/mol, which is comparable with prior determinations for the sublimation of P.

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