Vacancy generation resulting from electrical deactivation of arsenic

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Electrical deactivation of arsenic in highly doped silicon has been studied using the positron-beam technique. Direct experimental evidence linking the formation of arsenic-vacancy complexes (i.e., As_n-v) to the deactivation process is reported. The average number of arsenic atoms per complex, $\bar{n}>2$, was determined by comparing the observed complex concentrations with those of the deactivated arsenic inferred from Hall-effect measurements. © *1995 American Institute of Physics.*

Nonequilibrium processing[1–4] consisting of ion implantation followed by annealing (typically rapid thermal annealing although laser melt annealing has proven to be an effective research tool) is employed for producing highly doped silicon used in a variety of integrated circuit applications. However, the success of such techniques is undermined by partial electrical deactivation of the dopant atoms during subsequent heating.[5] In the case of arsenic, it has been proposed[6] that the deactivation results from the production of arsenic-vacancy clusters, As_nSi_{4-n}-v (i.e., a monovacancy with tetrahedral coordination of arsenic and silicon atoms), via silicon interstitial Si_i, generation ($As_nSi_{4-n}-Si \rightarrow As_nSi_{4-n}$-$v + Si_i$). *Ab initio* total energy calculations[7] indicate that the As_4-v complex is energetically favored over both isolated substitutional As and substitutional As_4-Si configurations. For the fully relaxed As_4-v complex, the maximum in the density of states associated with the lone-pair orbitals lies well below the top of the valence band. Thus the neutral As_4-v complexes are electrically inactive.

Experimental evidence for Si_i generation in association with the arsenic-deactivation process has recently been reported.[6] Electrical deactivation of a near-surface arsenic-doped layer was observed to induce enhanced boron diffusion within a buried layer in epitaxially grown silicon. The enhanced diffusion resulted from the interaction between the generated Si_i and the substitutional boron.[8] On the other hand, generation of the corresponding high concentration of vacancies has yet to be confirmed, raising doubts about the validity of the proposed deactivation process. In this letter, generation of the As_nSi_{4-n}-v complexes is verified using the positron-beam technique.[9]

The samples investigated correspond to those used in the previous enhanced boron-diffusion study.[6] Epitaxial silicon was grown onto *p*-type Cz⟨100⟩-Si wafers to a thickness of 0.8 μm. The first 0.2 μm was boron doped *in situ* to a concentration of 1×10^{18} cm^{-3}. Arsenic ions were then implanted at 35 keV with a 7° sample tilt. Surface melting with an excimer laser ensured that: (1) the arsenic was electrically activated (8×10^{20} cm^{-3}); (2) the concentration profile was constant with a sharp fall-off at a depth of 0.2 μm; and (3) the implant damage was removed. Arsenic deactivation was subsequently induced by annealing at 750 °C either for 15 s in a rapid thermal annealer or for 2 h in a conventional oven. A summary of the arsenic doping and anneal processing of the samples is given in Table I. Further details regarding the sample preparation and characterization can be found elsewhere.[6]

The University of Western Ontario positron-beam apparatus[9] was used to collect annihilation γ-ray energy spectra as a function of the mean positron-implantation depth,[10]

$$z[\text{Å}] = 172E[\text{keV}]^{1.6}, \neg \quad (1)$$

where E is the positron-implantation energy. The spectra were characterized using the sharpness parameter S defined as the number of counts in the central region of the annihilation photopeak (510.3–511.7 keV) divided by the total number of counts in the peak region (504.5–517.5 keV). These energy windows are typical of those used to maximize the statistical quality of the calculated S parameter values.

A change in S represents a change in the electronic environment in which the positrons annihilate. For example, the S parameter value resulting from positrons which annihi-

TABLE I. Sample descriptions and measurement results. C_d is the defect concentration determined by fitting the S-z data in the near-surface ($z<0.2$ μm) region: defect 1 accounts for divacancies ($S_{\text{trap}}=1.03$) present in the as-grown epitaxial silicon; defect 2 accounts for As_nSi_{4-n}-v complexes ($S_{\text{trap}}=1.00$) resulting in arsenic deactivation in the highly doped silicon layer. L_+ is the calculated effective positron diffusion length [see Eq. (2)]. C^{deact} is the electrically deactivated arsenic concentration determined from Hall-effect measurements and $\bar{n}=C^{\text{deact}}/C_d$ is the average number of arsenic atoms per vacancy cluster. Uncertainties in the parameter values are given in parentheses.

Sample	1	2	3	4	5
Arsenic implanted	⋯	⋯	*Y*	*Y*	*Y*
Laser melted	⋯	*Y*	*Y*	*Y*	*Y*
Annealed at 750 °C	⋯	⋯	⋯	15 s	2 h
C_d[a] defect 1 (10^{17} cm^{-3})	3.5(1.0)	7.5(1.0)	⋯	⋯	⋯
defect 2 (10^{19} cm^{-3})	⋯	⋯	3.5(1.0)	20(5)	20(5)
L_+ (nm)	181(5)	154(5)	31(3)	14(4)	14(4)
C^{deact} (10^{20} cm^{-3})	⋯	⋯	0(0.5)	5.0(0.5)	6.5(0.5)
$\bar{n}\neg$	⋯	⋯	⋯	2.5(0.7)	3.2(0.8)

[a]For 0.2 μm$<z<$0.8 μm, $C_d=3.5(1.0)\times10^{17}$ cm^{-3}.

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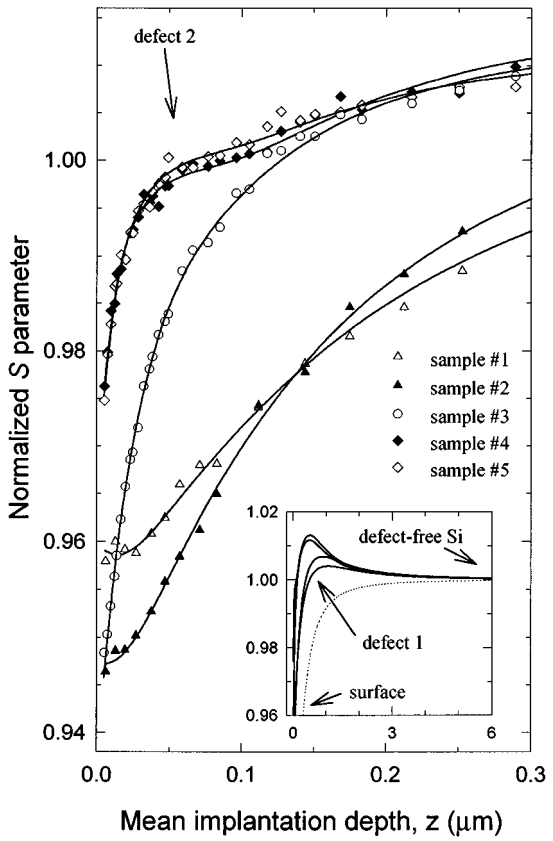

FIG. 1. Positron S-z data. The S parameter values are normalized to that of bulk defect-free Cz-Si. The S-z curves were obtained by solving for the diffused positron distribution and least-squares fitting to the S-z data. The inset shows the S-z curves extending to the maximum z measured. The S-z curve for defect-free Cz-Si (dotted line) is also shown.

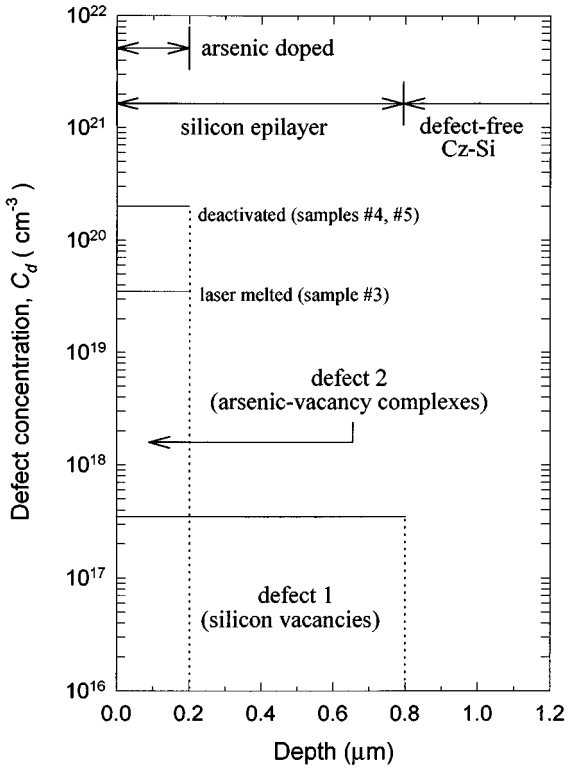

FIG. 2. Defect model used to fit the S-z data. Defect 1 ($S_{\text{trap}}=1.03$) accounts for vacancies within the silicon epilayer. Defect 2 ($S_{\text{trap}}=1.00$) accounts for arsenic-vacancy complexes corresponding to electrical deactivation of arsenic within the highly doped region. Within the defect-free Cz-Si, $S=1.00$.

late within vacancies is generally higher than that from positrons in a defect-free region. In such cases, the wave function of the trapped positron localizes within the vacancy, reducing its overlap, and thus its annihilation probability, with high-momentum core electrons. This reduces the overall Doppler broadening of the annihilation spectrum resulting in a higher S parameter value.

The S-z data and fitted curves are presented in Fig. 1. The positron implantation distribution and subsequent diffusion were deconvolved using the program POSTRAP5, followed by least-squares fitting of the defect models to the S-z data with the program SPOSFIT5.[11] Regions of constant field were used in the fitting procedure to approximate the electric fields derived from SIMS and Hall-effect measurements.

For the control unimplanted epitaxial sample (No. 1), a single defect type ("defect 1," $S_{\text{trap}}=1.03$ normalized to defect-free Cz-Si) corresponding to the epitaxial layer is required to successfully fit the data. Except for the introduction of electric fields, no distinction is required between the undoped and boron-doped epitaxial regions. Laser melt annealing of this sample (No. 2) did not result in any change in the defect type. For the arsenic implanted samples (Nos. 3, 4, and 5) a second defect type ("defect 2," $S_{\text{trap}}\sim1.00$) is required to fit the arsenic-doped region of the S-z data. The defect model is illustrated in Fig. 2.

The low surface S parameter values in Fig. 1 correspond to positron annihilation with the high-momentum electrons bound to the oxygen atoms in a surface-oxide layer. For shallow positron-implantation depths, the S values are weighted averages of those from the near-surface bulk region and the surface oxide. The surface oxide contribution results primarily from positron diffusion back toward the surface prior to annihilation. Thus the increase in S with z in the near-surface region of the S-z curves is related to the effective positron-diffusion length,

$$L_+=\sqrt{D_+/(\lambda+\nu C_d/\rho)}, \tag{2}$$

where C_d is the concentration of vacancy-type defects which trap the positrons and ρ ($=5\times10^{22}$ cm^{-3} for silicon) is the atomic density. The positron diffusion coefficient D_+, defect-free annihilation rate λ, and defect trapping rate ν in silicon have been experimentally determined to be ~2.1 cm^2/s,[12] 4.5×10^9 s^{-1}, and $\sim3\times10^{14}$ s^{-1},[13,14] respectively. A steep slope (i.e., rapid increase in S with z) corresponds to a large C_d and a short L_+. The fitted C_d and calculated L_+ values are listed in Table I. For defect-free Cz-Si, we obtain $L_+=220\pm6$ nm.

Consider first the control samples with no arsenic. The combination of a high S parameter and low effective positron diffusion length L_+ for the epitaxially grown layer results

from positron trapping in a measurable concentration [$C_d=(3.5\pm1.0)\times10^{17}$ cm^{-3}] of vacancies. It is believed that divacancies are the principal defect-type since monovacancies are migrant at room temperature. Hence isolated monovacancies tend to annihilate at surfaces or aggregate into (principally) divacancies. In fact, the S-z data for sample No. 1 are well fit assuming divacancy trap sites (i.e., $S_{\text{trap}}\sim1.03$).[15] Laser melting of the epitaxial Si (sample No. 2) decreased L_+ (i.e., increased C_d) but did not result in a change in the principal defect-type (i.e., no change in S_{trap}).

Arsenic doping resulted in a considerable reduction in L_+ (see Table I) due to an increase in the vacancy concentration. Furthermore, S_{trap} decreased to ~1.00, indicating a change in the principal defect-type associated with the presence of the arsenic. For the highly activated, laser-melt annealed sample (No. 3), we find $C_d=(3.5\pm1.0)\times10^{19}$ cm^{-3}. Hall-effect measurements indicate the arsenic to be fully activated. However, the uncertainty in such measurements renders the technique insensitive to deactivation levels of up to several percent. In fact, x-ray standing wave data suggest $\sim$7% of the arsenic atoms remain electrically inactive. It therefore appears that the residual vacancy concentration and change in the S_{trap} value result from the formation of arsenic-vacancy complexes.

The deactivation anneals resulted in the shortest L_+ ($=14\pm4$ nm). For such a low value of L_+ the positrons can no longer be considered to be freely diffusing since the mean-free path length would be comparable to the spatial extent of the positron wave function. The motion of the positrons is thus limited to transitions between adjacent trap states. Although the details of these states are unclear, for both the anneal at 15 s (sample No. 4) and 2 h (sample No. 5), the results indicate $C_d=(2.0\pm0.5)\times10^{20}$ cm^{-3} and $S_{\text{trap}}\sim1.00$.[16] Furthermore, this increase in C_d is correlated with an increase in the deactivated arsenic concentration, C^{deact} (see Table I). Comparison of the deactivated arsenic [e.g., $(6.5\pm0.5)\times10^{20}$ cm^{-3} for sample No. 5] and vacancy complex [$(2.0\pm0.5)\times10^{20}$ cm^{-3}] concentrations indicates that the average number of arsenic atoms involved in the tetrahedral coordination about the vacancies, $\overline{n}>2$.

Further evidence that the short positron diffusion length in the deactivated arsenic layer is associated with the arsenic atoms has been obtained by analyzing the core-electron contributions to the Doppler-broadened annihilation spectra.[17] A coincidence technique, which was used to reduce the background will be described in a subsequent publication (see also Ref. 18). The deactivated samples (Nos. 4 and 5) show a significant contribution to the annihilation spectra from arsenic core electrons, and cannot be decomposed as a sum of annihilations from defect-free silicon, silicon divacancies, and surface oxide.

In summary, positron-annihilation measurements confirm the generation of $\text{As}_n\text{Si}_{4-n}$-$v$ complexes in conjunction with electrical deactivation of arsenic atoms in highly doped silicon. The deactivation process has been correlated with a reduction in the positron diffusion length (vacancy formation) and the emergence of arsenic nearest-neighbors (''decoration'' of the vacancies) to the annihilation sites. Although experimental uncertainties preclude the distinction between clusters involving $n=2$, 3, and 4, the average number of arsenic atoms per vacancy, $\overline{n}>2$. Additional investigation is required to verify whether or not n is a function of the arsenic concentration. Calculations are planned in an effort to better understand the nature of the positron localization.

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[1] A. Lietola, J. F. Gibbons, and T. W. Sigmon, Appl. Phys. Lett. **36**, 675 (1980).
[2] A. Lietola, R. B. Gold, J. F. Gibbons, T. W. Sigmon, P. D. Scovell, and J. M. Young, J. Appl. Phys. **52**, 230 (1981).
[3] J. Goetzlich, in *Ion Beam Processes in Advanced Electronic Material and Device Technology*, edited by B. R. Appleton, F. H. Eisen, and T. W. Sigmon (Materials Research Society, Pittsburgh, PA, 1985), p. 349.
[4] S. Luning, P. M. Rousseau, P. B. Griffin, P. G. Carey, and J. D. Plummer, IEDM Tech. Dig. **1992**, 349.
[5] W. K. Chu, S. R. Mader, and E. Rimini, in *Laser and Electron Beam Processing of Materials*, edited by C. W. White and P. S. Peercy (Academic, New York, 1980), p. 253.
[6] P. M. Rousseau, P. B. Griffin, and J. D. Plummer, Appl. Phys. Lett. **65**, 578 (1994).
[7] K. C. Pandey, A. Erbil, G. S. Cargill, III, R. F. Boehme, and D. Vanderbilt, Phys. Rev. Lett. **61**, 1282 (1988).
[8] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).
[9] P. J. Schultz, Nucl. Instrum. Methods B **30**, 94 (1988).
[10] P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).
[11] G. C. Aers, in *Positron Beams for Solids and Surfaces*, edited by P. J. Schultz, G. R. Massoumi, and P. J. Simpson (AIP, New York, 1991), p. 162.
[12] T. E. Jackman, G. C. Aers, M. W. Denhoff, and P. J. Schultz, Appl. Phys. A **49**, 335 (1989).
[13] G. Dlubek, Phys. Status Solidi A **102**, 443 (1987).
[14] S. Dannefaer, Phys. Status Solidi A **102**, 481 (1987).
[15] R. D. Goldberg, P. J. Schultz, and P. J. Simpson, Appl. Surf. Sci. **85**, 287 (1995).
[16] Annealing the unimplanted sample (No. 2) at 750 °C (not shown) did not result in a change in either S_{trap} ($=1.03$) or L_+ ($=154\pm5$ nm).
[17] P. J. Simpson, U. Myler, D. W. Lawther, and G. C. Aers (unpublished).
[18] K. G. Lynn, J. E. Dickman, W. L. Brown, M. F. Robbins, and E. Bonderup, Phys. Rev. B **20**, 3566 (1979); M. Alatalo, H. Kauppinen, K. Saarinen, M. J. Puska, J. Mäkinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **51**, 4176 (1995).