Participation of $EL2$ in the donor activation of silicon implanted into GaAs

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A simple model describing the electrical activation of moderate doses of silicon implanted into GaAs is presented. It involves only the defects Si_i^+, Si_{Ga}^+, Si_{As}^-, and $EL2$. Besides fitting available activation data (carrier concentration versus silicon concentration), it also fits existing data describing the variation of carrier concentration with substrate $EL2$ concentration.

I. INTRODUCTION

It is well established that the donor activation efficiency of Si implanted into semi-insulating (SI) GaAs substrates has a positive correlation with both the substrate concentration (N_{E0}) of the native defect $EL2$ and with the arsenic-atom fraction in the melt (f_{As}) used to grow the crystal. Experimental evidence comes directly from measurements of the room-temperature carrier concentration (n) versus N_{E0} (Refs. 1–5) and versus f_{As},[6–8] and indirectly from measurements of the threshold voltage of field-effect transistors versus N_{E0} (Refs. 9–11) and versus f_{As}.[12] The most extensive data bearing on this behavior are those obtained by Brierley, Anderson, and Grabinski.[1] These data, showing how n varies with N_{E0} for an estimated total silicon concentration N_S of 2.33×10^{17} cm^{-3}, are reproduced in Fig. 1. Data from the other references[2–12] we have cited are less definitive when interpreted on an n versus N_{E0} plot, but all support a positive correlation and are not in conflict with Fig. 1.

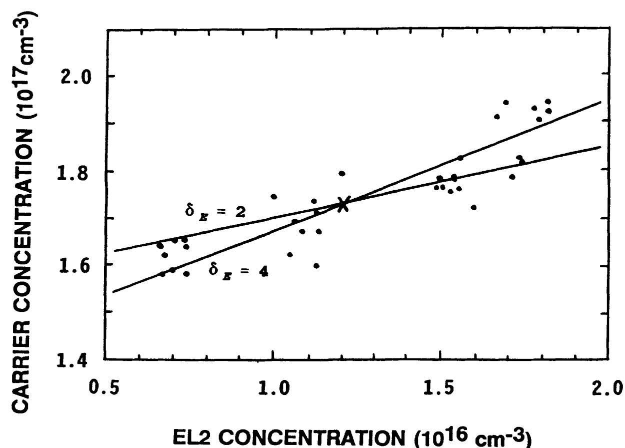

FIG. 1. Dependence of carrier concentration on $EL2$ concentration in semi-insulating GaAs substrates for an estimated implanted silicon concentration of 2.33×10^{17} cm^{-3}. Data are from Ref. 1; the lines are from a model where δ_E measures the off stoichiometry of $EL2$. In judging the quality of the fits, attention should be focused on the slopes of the lines and not on their intercepts. The point (×) corresponds to a similarly labeled point in Fig. 2.

Since the activation process of implanted Si involves defect reactions occurring during the activation anneal, it seems reasonable that one or more of the participating defects is native and that its concentration depends on f_{As}. The primary native defect so involved has not yet been identified, but obvious candidates are $EL2$ and V_{Ga}, the concentrations of which are either known[1,13] (in the case of $EL2$) or conjectured[14,15] (in the case of V_{Ga}) to increase with increasing f_{As}. We adhere to the view that $EL2$ is the relevant defect, in part because it is the dominant native defect in SI GaAs, and in part because its concentration has been observed to be reduced in the implant region.[16] (We suggest that this reduction may be due to the interaction of silicon with $EL2$ rather than to the "out diffusion" of $EL2$.)

Several years ago one of us outlined an activation model[17] that incorporates the active participation of $EL2$. To our knowledge no other model has been presented that attempts to account for the striking $EL2$ effect exhibited by the data of Fig. 1. In the present paper we refine that earlier model and use it to fit these data. In the Appendix we consider the consequences of adopting V_{Ga} as the defect responsible for these data, treating $EL2$ as benign during the activation anneal while still serving as a measure of f_{As}. We find that this model requires a physically unacceptable off stoichiometry for $EL2$.

II. MODEL

To successfully account for the data of Fig. 1, we require a comprehensive implant activation model that dictates (1) the site selection of implanted silicon atoms and (2) the influence of $EL2$ on this site selection. The latter behavior is a small perturbation on the former, as Fig. 1 shows. Thus, some understanding of the overall activation curve of n versus N_S is needed before the $EL2$ effect can be addressed successfully. Activation models have already been studied by one of us,[17,18] and we draw on ideas put forward there in developing the present model.

Experimental data on silicon activation, extracted[18] from several sources, is displayed in Fig. 2. They show a great deal of scatter due both to different substrate properties and to different processing treatments. In spite of

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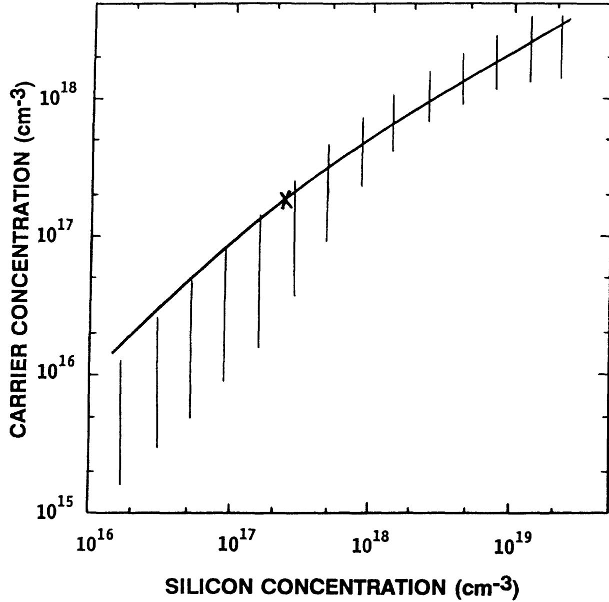
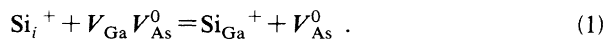


FIG. 2. Activation curve of silicon-implanted GaAs. The hatched area depicts the range over which the data are spread (Ref. 18). The curve is a model fit constrained to pass through the point (×), which corresponds to a similarly labeled point in Fig. 1.

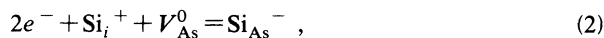
this scatter, the data do serve to restrict the possible models as we will show below.

In building an activation model, we are primarily interested in the equilibrium concentration of defects attained during the activation anneal (and our final mass-action equations deal with this situation). Nevertheless it is informative to conjecture reactions that can affect the relatively immobile $EL2$ and implanted silicon during the anneal. Such defect reactions almost certainly involve mobile native defects such as vacancies. One possible kinetic scheme is as follows. The implanted silicon atoms, imagined to initially occupy interstitial sites, react with divacancies that are thought to diffuse rapidly,[19,20] to form $\mathrm{Si_{Ga}}$ donors and arsenic vacancies



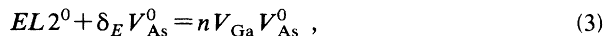
$$\mathrm{Si}_i{}^{+} + V_{\mathrm{Ga}} V_{\mathrm{As}}^0 = \mathrm{Si_{Ga}}{}^{+} + V_{\mathrm{As}}^0 \ . \tag{1}$$

Since the supply of divacancies is inexhaustible (they readily diffuse in from the surface), their concentration need not be large to support this reaction. The generated arsenic vacancies then diffuse and undergo reactions leading either to the production of $\mathrm{Si_{As}}$ acceptors



$$2e^- + \mathrm{Si}_i{}^{+} + V_{\mathrm{As}}^0 = \mathrm{Si_{As}}{}^{-} \ , \tag{2}$$

or to the conversion of $EL2$ to divacancies



$$EL2^0 + \delta_E V_{\mathrm{As}}^0 = n V_{\mathrm{Ga}} V_{\mathrm{As}}^0 \ , \tag{3}$$

where the number n of divacancies produced is unimportant for our purpose [see the paragraph following Eq. (5) below].

The integer parameter δ_E measuring the off stoichiometry[17,21] of $EL2$, equals the number of arsenic atoms minus the number of gallium atoms in an integral number of primitive bases encompassing $EL2$ ($\delta_E = 2$ for $\mathrm{As_{Ga}}$, $\delta_E = 3$ for $\mathrm{As_{Ga}}\ V_{\mathrm{Ga}}$ and $\mathrm{As_{Ga}\ As}_i$, etc.). Since the microscopic structure of $EL2$ is not known, we must leave δ_E unspecified.

In writing Eq. (3), we are assuming that all native point defects that constitute $EL2$ are completely destroyed when $EL2$ is destroyed with no remnant of $EL2$ remaining. This maximizes the effect of $EL2$ on the carrier concentration. Experimentally it has been observed[22,23] that the concentration of $EL2$ near the surface of GaAs samples decreases during unprotected anneals, the interpretation being that $EL2$ reacts with arsenic vacancies diffusing in from the surface. It is unclear if the annihilation of $EL2$ is as complete as we are postulating.

Although arsenic vacancies are important in treating reaction kinetics in our model, they are not needed in fitting the data of Figs. 1 and 2. Indeed, it turns out that as the arsenic vacancy concentration is allowed to increase, the carrier concentration at large values of N_S decreases, ultimately to a value that is too small. This is true independent of which charge states[24,25] $(+,0,-)$ of V_{As} are included. Adequate fits in Figs. 1 and 2 can be obtained by neglecting the arsenic vacancy. This we can do simply by eliminating V_{As}^0 from Eqs. (1)–(3) to obtain

$$2e^- + 2\ \mathrm{Si}_i{}^{+} = \mathrm{Si_{Ga}}{}^{+} + \mathrm{Si_{As}}{}^{-} \ , \tag{4}$$

and

$$EL2^0 + \delta_E \mathrm{Si}_i{}^{+} = \delta_E \mathrm{Si_{Ga}}{}^{+} \ . \tag{5}$$

We have also dropped the neutral divacancy from Eqs. (4) and (5) since its concentration is dependent only on temperature and can be absorbed into the equilibrium constants. We now assume that the defects remaining in these two reactions occur in the charge states $\mathrm{Si}_i{}^{+}$ $[N_{\mathrm{SI}}]$, $\mathrm{Si_{Ga}}{}^{+}$ $[N_{\mathrm{SG}}]$, $\mathrm{Si_{As}}{}^{-}$ $[N_{\mathrm{SA}}]$, and $EL2^0$ $[N_E]$ where the concentration symbols are noted in square parentheses. All other charged defects that might conceivably be present are assumed to have negligible concentrations, i.e., less than that of $EL2$. This of course means that our model is not reliable for small silicon concentrations but is certainly adequate for silicon concentrations in excess of $10^{17}\ \mathrm{cm}^{-3}$, our region of focus in this paper.

One questionable defect we have included in our model is the silicon interstitial as a completely ionized donor. Theoretical calculations[15,21] indicate that Ga_i and possibly As_i should appear as donors so it seems reasonable that Si_i should also. Since Si_i and $\mathrm{Si_{Ga}}\ V_{\mathrm{As}}$ are stoichiometrically equivalent, we could instead of Si_i have included the latter. In any event, we find that some completely ionized silicon-related donor, in addition to $\mathrm{Si_{Ga}}$, is needed in order to yield an acceptable activation curve.

Under equilibrium conditions at the annealing temperature, the mass-action equations for the reactions of Eqs. (4) and (5) are

$$K_1 N_{\mathrm{SI}}^2 n^2 = N_{SG} N_{SA} \ , \tag{6}$$

and

$$K_2N_EN_{SI}^{\delta_E}=N_{SG}^{\delta_E} . \quad (7)$$

Several constraint equations are also applicable. Charge neutrality demands

$$n-n_i^2/n=N_{SI}+N_{SG}-N_{SA} , \quad (8)$$

where n_i is the intrinsic carrier concentration.

Conservation of implanted silicon requires

$$N_S=N_{SI}+N_{SG}+N_{SA} . \quad (9)$$

Finally, the constraint that the deviation from stoichiometry of the crystal is unaffected by the implant-anneal process means that[17,18]

$$\delta_EN_{E0}=\delta_EN_E+N_{SG}-N_{SA} . \quad (10)$$

Our model then consists of Eqs. (6)–(10) at the annealing temperature of ~900 °C and Eq. (8) at room temperature. These equations are solved numerically to yield the room-temperature carrier concentration as a function of N_S and N_{E0}. We choose K_2 large enough so that $N_E \ll N_{E0}$ for $N_S=2.33\times10^{17}$ cm^{-3}, this being the silicon concentration used for the data of Fig. 1. This choice for K_2 maximizes the impact of $EL2$ on n, i.e., all $EL2$ is annihilated. Then for each selected integer value of δ_E, we choose K_1 so that the activation curve passes through the point ($\times$) in Figs. 1 and 2, characterized by $N_S=2.33\times10^{17}$ cm^{-3}, $N_{E0}=1.20\times10^{16}$ cm^{-3}, and $n=1.73\times10^{17}$ cm^{-3}. Having so chosen δ_E, K_1, and K_2, there are no free parameters and the model can then be used to predict the dependence of n on N_{E0} and N_S as shown in Figs. 1 and 2, respectively. We find that changing the value of δ_E by ±1 has a negligible effect on the Fig. 2 curve.

It is worth noting that since our focus is on the activation process for silicon concentrations in excess of 10^{17} cm^{-3}, we have neglected shallow C_{As} acceptors and various other defects. Their inclusion in the model would affect the activation curve for small silicon concentrations. The value of K_2 also impacts the curve in this region.

III. DISCUSSION

The slopes of the curves in Fig. 1 increase with increasing values of δ_E, so it is apparent that the data discriminate against large values of δ_E. Thus, since $\delta_E=2$, 3, or 4 are considered to be reasonable values for $EL2$, our contention that $EL2$ participates directly in the activation process is supported. Otherwise, there is no reason to except *small integer* values of δ_E to yield the best fits. That is, if $EL2$ is not involved in the activation process then the reactions of Eqs. (3) and (5) must be replaced by other reactions and a completely unphysical value of δ_E may be needed to fit the data of Fig. 1. An example of such a model is treated in the Appendix, where we regard $EL2$ as a benign defect that remains intact during the activation anneal, while V_{Ga} is the active defect in the substrate responsible for the increase of donor activation with increasing f_{As}. We find that $\delta_E\approx\frac{1}{5}$ is needed to fit the data of Fig. 1, a value that is unphysical.

Unfortunately, the data of Fig. 1 do not discriminate strongly among $\delta_E=2$, 3, and 4. Therefore, we are unable to unequivocally endorse as correct the currently popular model[26,27] of $EL2$ as As_{Ga}. Clearly it would be valuable to have more data of the type exhibited in Fig. 1 in order to further restrict the acceptable range of δ_E, an important parameter whose value has not been determined through other measurements.

ACKNOWLEDGMENT

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APPENDIX

In this Appendix we suppose that the concentration of $EL2$ remains at its substrate value of N_{E0} during the activation anneal and that V_{Ga}^- with concentration N_{VG} undergoes reactions with V_{As} and Si_i. (Our specification of V_{Ga} as a singly charged rather than multiply charged acceptor is not a critical restriction.)

In place of Eqs. (3), (5), (7), and (10) we have, respectively,

$$V_{Ga}^-+V_{As}^0=e^-+V_{Ga}V_{As}^0 , \quad (A1)$$

$$V_{Ga}^-+Si_i^{\,+}=Si_{Ga}^{\,+}+e^- , \quad (A2)$$

$$K_2N_{VG}N_{SI}=N_{SG}n , \quad (A3)$$

and

$$N_{VG0}=N_{VG}+N_{SG}-N_{SA} , \quad (A4)$$

where Eq. (A3) is the mass-action equation for the reaction of Eq. (A2) and where Eq. (A4) expresses the deviation from stoichiometry constraint.

The substrate concentration N_{VG0} is related to N_{E0} through

$$K_3N_{E0}n^{\delta_E}=N_{VG0}^{\delta_E} , \quad (A5)$$

which is the mass-action equation for the reaction

$$EL2^0+\delta_Ee^-=\delta_EV_{Ga}^- \quad (A6)$$

that we suppose equilibrates during crystal growth.

To establish K_3, we take $N_{VG0}=5\times10^{15}$ cm^{-3} as a representative value[14,15] when $N_{E0}=10^{16}$ cm^{-3}. We then use Eq. (A5) to relate changes in N_{E0}, the abscissa in Fig. 1, to changes in N_{VG0}.

Our new set of model equations is solved much as the others were, K_2 being chosen so that $N_{VG} \ll N_{VG0}$ for $N_S=2.33\times10^{17}$ cm^{-3}. The activation curve in Fig. 2 is essentially unchanged except for small values of N_S. However, to fit the Fig. 1 data we need $\delta_E\approx\frac{1}{5}$. This result can be understood by the following rough argument. Suppose N_{E0} is increased from 10^{16} cm^{-3} by $\Delta N_{E0}=10^{15}$ cm^{-3}. From Eq. (A5), N_{VG0} increases from 5×10^{15} cm^{-3}

by $\Delta N_{VG0}=(0.5/\delta_E)\times 10^{15}$ cm^{-3}. These additional $V_{\mathrm{Ga}}{}^{-}$ in the substrate can convert $\mathrm{Si}_i{}^{+}$ to $\mathrm{Si}_{\mathrm{Ga}}{}^{+}$ via the reaction of Eq. (A2) resulting in an increase in the carrier concentration by ΔN_{VG0}. In order for this increase in carrier concentration to equal 2.5×10^{15} cm^{-3}, as required from Fig. 1 for the specified change in N_{E0}, we must have $\delta_E \approx \frac{1}{5}$. Since this is a physically unacceptable value, the model presented in this appendix must be rejected.

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