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Metastable acceptor centers in boron implanted silicon

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The evolution of the electrical activation with the annealing time in B^+ implanted (5.0×10^{14} cm^{-2}, 50 keV) Si was studied as a function of the annealing temperature. Electrical activation yields of 15%–30% were observed after annealing for 2 s at temperatures above 550 °C. Prolonging the annealing time from 2 to 900 s we observed that the electrical activation evolves differently according to the temperature: (i) at 550 °C$<T<$700 °C it decreases toward an equilibrium level, (ii) at 700 °C$<T<$800 °C it decreases during the first minutes and subsequently increases again, and (iii) at temperatures $<$550 °C or $T>$800 °C it increases continuously. In order to explain the carrier removal observed during annealing at 550–800 °C we proposed that metastable acceptor centers are formed during the B^+ implantation and/or the initial period of the annealing time. Interaction of Si self-interstitial atoms with these centers leads to their neutralization and/or dissociation with consequent decreasing of the carrier concentration. © *1995 American Institute of Physics.*

Boron is the preferred *p*-type dopant in Si IC technology. Besides the widespread use of B ion implantation, to our knowledge, a systematic investigation of the electrical activation kinetics has not yet been reported. In addition, there are features of the electrical activation of B, which are not fully understood at present. The reverse annealing phenomenon (i.e., the decreasing of the sheet carrier concentration with the increasing of the annealing temperature) has been reported[1–4,6] to occur in the temperature range of 500–650 °C after 15–30 min furnace annealing. It has been explained by different models, involving interaction between the implanted B atoms and dislocations,[2] formation of B–Si self-interstitial (Si_I) pairs,[3] or formation of substitutional B-interstitial B complexes.[4]

Van der Pauw devices[5] were fabricated using Czochralski *n*-type, 4–11 Ω cm resistivity (100) Si substrates. The central area of the devices was implanted with $^{11}B^+$ to the dose of 5.0×10^{14} cm^{-2} at 50 keV. The samples were annealed in a rapid thermal annealing (RTA) system, in nitrogen atmosphere. A heating rate of 100 °C/s was used during the ramp-up of the temperature in all the annealing cycles. The Van der Pauw devices were annealed in the temperature range of 450–900 °C for times from 2 to 900 s. From Hall effect measurements carried out in the Van der Pauw devices, the electrical activation yield (EAY) values were determined. The EAY is considered hereafter, as the ratio between the sheet carrier concentration, obtained from the Hall measurements, and the implanted dose.

Figure 1 shows the EAY of B after annealing for times of 2, 60, and 900 s. It is interesting to notice a transient activation (EAY values of 15%–30%) after annealing with the shortest time (2 s) at temperatures above 550 °C and the lack of the reverse annealing [see curve (a)].

Prolonging the annealing time up to 60 s a decreasing of EAY occurs in the temperature interval of 650–800 °C [curve (b)]. The reverse annealing phenomenon becomes apparent in the range of 600–700 °C. This range comprises temperatures somewhat higher than those commonly observed for reverse annealing after prolonged furnace annealing (550–650 °C). Comparing curves (a) and (b) one can conclude that the reverse annealing depicted in the latter curve results from removal of carriers which have been generated during the first 2 s of the annealing time. The maximum removed carrier concentration (30%) occurred at a temperature of ≈700 °C. Apparently, at 800 °C the carrier concentration was not affected by the additional 58 s of annealing. Very likely the removal of the carriers still proceeds at temperatures above 800 °C and below 600 °C, but at rates which are, respectively, too fast or too slow to be detected.

Curve (c) in Fig. 1 shows the EAY in samples annealed for 900 s. The data in curve (c) closely coincide with those of furnace annealed samples for 30 min.[6] The reverse annealing is clearly apparent in the temperature range of 550–650 °C. Comparing curves (c) and (b) one can notice that during the annealing from 60 to 900 s the carrier concentration decreased in the temperature range of 550–700 °C and increased at temperatures above 700 °C.

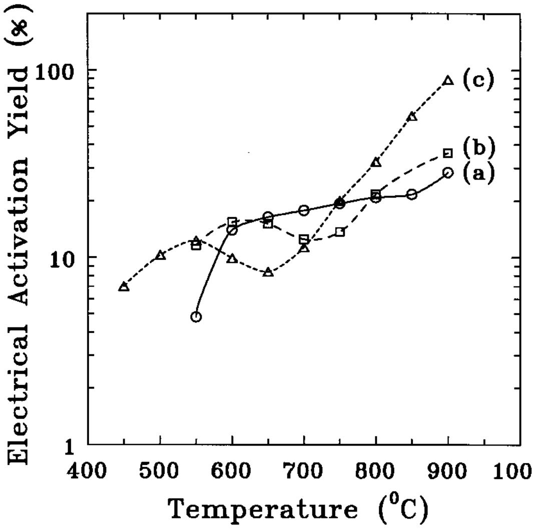

FIG. 1. Electrical activation yield in Si samples implanted with B^+ (5.0×10^{14} cm^{-2}/50 keV) after annealing for 2 s [curve (a)], 60 s [curve (b)], and 900 s [curve (c)].

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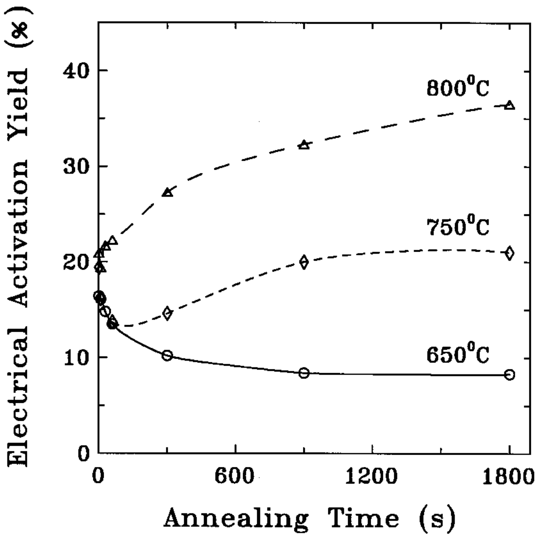

FIG. 2. Evolution of the electrical activation yield in Si samples implanted with $B^+(5.0\times10^{14}\ cm^{-2}/50\ keV)$ during annealing at temperatures of 650, 750, and 800 °C.

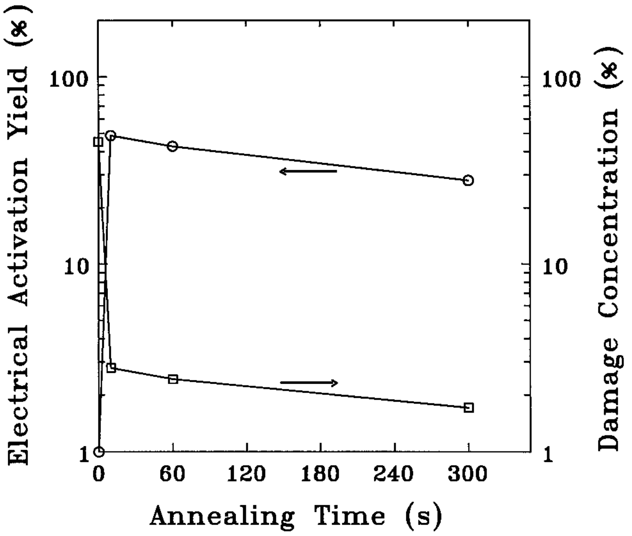

FIG. 3. Evolution of the electrical activation yield and defect concentration in B^+ implanted ($1.0\times10^{15}\ cm^{-2}$/50 keV at −40 °C) Si samples, during annealing at 650 °C.

Our data demonstrated that for 100% activation of the implanted B dose at 900 °C it is required a prolonged annealing (>15 min). This fact is in apparent contradiction with the previous data of Huang and Jaccodine.[7] These authors reported activation of the total B dose after RTA at temperatures above 550 °C. Furthermore, they reported the absence of reverse annealing phenomenon in the rapid thermally annealed samples. The cause for these discrepancies are presently unclear.

Further details of the evolution of the EAY with the annealing time are presented in Fig. 2. The temperatures of 650, 750, and 800 °C were chosen since different electrical activation kinetics are observed for each of these cases. It is apparent in the figure that the transient activation for the three considered temperatures reaches a value ≈15%–20%. However, in the case of samples annealed at 650 or 750 °C the transient activation is followed by a deactivation period. For the case of annealing performed at 650 °C the EAY reaches an equilibrium level after ≃10 min. At 750 °C the deactivation period lasts only for ≃1 min. Subsequently, an enhancement of the activation takes place. At 800 °C, the transient activation is followed by an additional activation period, however, at a much slower rate.

The analysis of the EAY curves in Figs. 1 and 2 permits the identification of three phenomena responsible for the electrical activation of B: (i) a transient activation of the implanted B taking place during the first few seconds, leading to a plateaulike curve for the EAY ($T>550$ °C). Process (i) is followed by two slower processes: (ii) deactivation of B and (iii) activation of B. Phenomena (ii) and (iii) proceed with rates which increase with the increasing of the annealing temperature. They are always operative and compete with each other. For a given annealing time longer than ≈60 s there is an interval of temperatures in the EAY curve, where process (ii) surpasses process (iii). The reverse annealing occurs in a segment of this interval, where process (iii) is negligible compared to process (ii). Hence, the EAY decreases with the increasing of the temperature due to the thermal dependence of the deactivation rate.

Two additional experiments were undertaken to obtain more insight on the deactivation process. In the first one B^+ was implanted to a dose of $1.0\times10^{15}\ cm^{-2}$ at an energy of 50 keV in a Si substrate cooled at −40 °C. These implantation parameters were chosen to result in an as-implant damage concentration of about 50% of that in amorphized Si. Pieces from this sample were annealed at 650 °C for times from 2 to 300 s. The damage in as-implanted and annealed samples were evaluated using aligned Rutherford backscattering analysis. The EAY and the damage concentration as a function of the annealing time at 650 °C are shown in Fig. 3.

It is clearly apparent in Fig. 3 that the decreasing of the EAY closely correlates with the annealing of the implantation damage. It seems to indicate that the point defects released during the annealing of the implantation damage clusters should play a role in the carrier removal. This reasoning is in agreement with our previous data[6] which suggest that the reverse annealing of B is influenced by the presence of Si_I atoms.

In the second additional experiment, samples previously implanted with B^+ ($5.0\times10^{14}\ cm^{-2}$ at 50 keV) were annealed at 900 °C for 30 min to obtain 100% electrical activation and negligible residual damage concentration. Subsequently, a damage concentration profile similar to the one produced by the previous B^+ implantation was created via additional implantation of an electrically neutral element ($^{20}Ne^+$ with a dose of $1.0\times10^{14}\ cm^{-2}$ at 90 keV). These samples were labeled as sample I. The damage concentration at the profile peak is of 7%.

Figure 4 compares the EAY values after annealing cycles at 650 °C in samples I [curve (a)] and in samples single implanted with B^+ (labeled as sample II) [curve (b)]. Besides the fact that the B atoms are surrounded by implantation damage in samples I and II, quite different activation

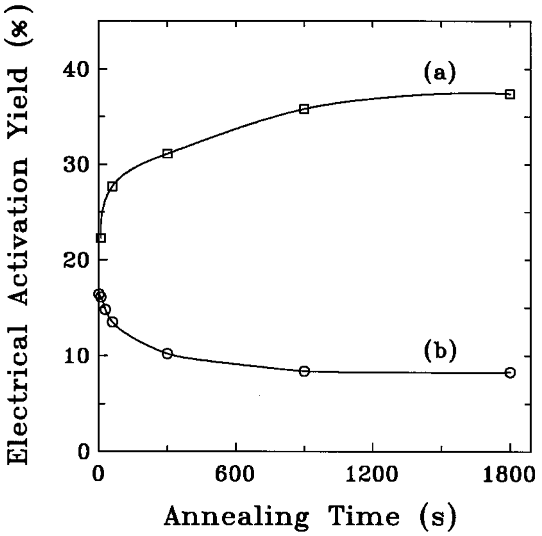

FIG. 4. Evolution of the electrical activation yield during annealing at 650 °C in samples (a) implanted with $B^+(5.0\times10^{14}\ cm^{-2}/50\ keV)$, annealed at 900 °C for 30 min and then implanted with Ne^+ $(1.0\times10^{14}\ cm^{-2}/90\ keV)$ and (b) implanted with $B^+(5.0\times10^{14}\ cm^{-2}/50\ keV)$.

kinetics are observed. The data in Fig. 4 show that while the EAY in sample II always decreases with the annealing time, that in sample I always increases. Contrary to what happens in sample II, the acceptor levels in sample I are stable against interactions with point defects released from the damage cluster during the annealing. The tetrahedral covalent bonds between the B atom and its four neighbors Si atoms, acquired during the annealing prior to the Ne^+ bombardment, probably were not significantly disturbed by the introduced damage. Since the B–Si tetrahedral structure is known to be stable in the presence of concentration of point defects, as usually occurs during high-temperature thermal treatments of B doped Si, it should be stable also during the damage annealing.

The carrier concentration in sample II, obtained during the transient annealing, should be provided by the ionization of metastable acceptor centers, probably formed by B atoms associated with point defects. The interaction of such a structure with Si_I released from the annealing of the implantation damage clusters leads to their neutralization and/or dissociation, with consequent carrier removal.

In summary, the activation of implanted B in Si was studied as a function of the annealing time and temperature. It was found that a significant fraction of the implanted B dose is activated during the first few seconds of the annealing period, forming a metastable carrier concentration. With prolongation of the annealing time, depending of the annealing temperature, the carrier concentration generated by the transient activation may: (i) decrease toward an equilibrium level (600–700 °C); (ii) decrease during the first minutes and then enhances again (700–800 °C); or be followed by a continuous increase ($T>800$ °C). The transient activation is considered as produced by the ionization of metastable acceptor centers formed during the B implantation and/or at the first seconds of annealing. The interaction of these centers with Si_I atoms, released by the annealing of the implantation damage clusters, leads to their dissociation and/or neutralization of the corresponding metastable acceptor levels. This neutralization during annealing at 550–800 °C causes the reverse annealing phenomenon. At temperatures above 700 °C, the slow activation process subsequent to the transient activation, is associated with the incorporation of B into substitutional lattice positions, forming stable acceptor centers.

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