Kinetics of boron reactivation in doped silicon from Hall effect and spreading resistance techniques

Aaron D. Lilak,[a] Mark E. Law, and Ljubo Radic
Department of Electrical Engineering, University of Florida, Gainesville, Florida 32611

Kevin S. Jones and Mark Clark
Department of Materials Science, University of Florida, Gainesville, Florida 32611

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In this work, a series of 13 boron implants were performed into Czochralski silicon substrates with doses of 2×10^{14}–1.6×10^{15} cm^{-2} at energies of 10–80 keV. The boron was deliberately clustered with a 750 °C anneal of 10 or 30 min and the electrical activation of the boron implants was determined following a second anneal at 750 or 850 °C with a Hall effect system with certain samples also being analyzed with a spreading resistance technique. Analysis of the reactivation rates allows for the determination of the net energy to boron reactivation to be approximately 3.0 eV assuming the reactivation process is mediated by release of a boron interstitial with a migrational energy of 0.3 eV. This results in a critical binding energy of approximately 2.7 eV from the process limiting the dissolution of the most stable boron-interstitial cluster. © *2002 American Institute of Physics*. [DOI: 10.1063/1.1508438]

It is known that thermal treatment of ion-implanted boron leads to the formation of boron-interstitial clusters.[1–5] The boron contained in these clusters is not fully activated and the clusters themselves may serve to degrade the carrier mobility; both of which will lead to higher sheet resistances and limit metal–oxide–semiconductor device performance. In addition to this, the boron contained in the clusters is immobile, which presents an interesting phenomena which must be considered for accurate process modeling. For these reasons, it is imperative to gain a thorough physical understanding of the energetics controlling the clustering/declustering of interstitials by boron in silicon.

Prior studies of boron clustering/reactivation processes have largely focused upon the diffusion behavior exhibited following the thermal treatment of ion-implanted boron as measured by secondary ion mass spectrometry (SIMS) or capacitance–voltage measurements. These experiments are usually conducted from the as-implanted state, which will produce data that blurs the clustering and reactivation kinetics into a single data point. Such studies are also highly sensitive to the implant conditions; a slight variation in implant recipe can produce a different damage profile and potentially an entirely different clustered boron signature. To avoid these complexities, a multistep anneal sequence was used in this study along with Hall and a spreading resistance technique. Utilizing electrical measurement techniques in this manner allows for the determination of the differential transient activation from a known reference condition (the first step of the anneal) to the measurement condition (the second step of the anneal) and avoids many of the complexities associated with process variations.

A series of 13 (100) oriented, Czochralski silicon wafers were implanted with boron at energies of 10 keV to doses of 2×10^{14}, 4×10^{14}, 8×10^{14}, and 1.6×10^{15} cm^{-2} and at 20, 40, and 80 keV to doses of 4×10^{14}, 8×10^{14}, and 1.6×10^{15} cm^{-2}. The implanted dose was verified for all cases through the use of SIMS. The wafers were then diced to approximately 14.4 mm$\times$14.4 mm and backside scribed for later identification. One sample from each wafer was subjected to a 750 °C 10 min anneal while the others are subjected to 750 °C 30 min anneals. These anneals were chosen knowing they induce strong deactivation in similarly processed material.[6] Samples which were subjected to the 750 °C 30 min clustering anneal were then subjected to a secondary "bounce" anneal at 750 °C for times of 30, 90, or 330 min or 850 °C for times of 10, 20, or 60 min. All furnace anneals were conducted in flowing N_2 ambient with negligible push/pull times and temperatures were monitored throughout the anneal.

Following this processing, a silicon alloy (3.5% silicon, 96.5% aluminum) was sputtered through a patterned contact mask in a VanDerPaaw structure and used to electrically contact the silicon samples.[7] Following a 450 °C 30 min inert anneal, used to scinter the deposited contact, the ohmicity of the contacts was verified and the material was analyzed with a Hall effect system. Certain samples were then sent for analysis with spreading resistance profilometry (SRP) by a commercial vendor to verify the accuracy of the Hall effect measurement.

Excellent agreement was obtained between the sheet number from the Hall effect analysis and the integrated carrier concentration obtained from the SRP analysis for the pooled data set of 104 experimental splits in this study. This confirms both the accuracy of the Hall effect system in the region of this study and also provides carrier profiles, which were useful in verifying the depth uniformity of the reactivation process.

While it is impossible to present the entire data set here due to the need for brevity in this publication, certain trends

[a]Author to whom correspondence should be addressed; electronic mail: aaron.d.lilak@intel.com

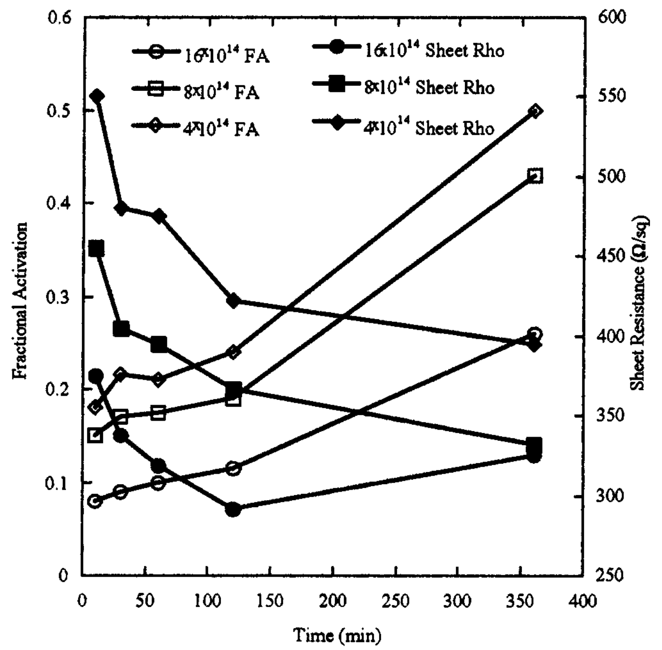

FIG. 1. Fractional activation (taken as the ratio of sheet number to as-implanted dose from SIMS) and sheet resistance measurements for the 80 keV boron implants of varying dose annealed at 750 °C from Hall effect measurement.

in the data are evident. The fractional activation was found to generally increase with increases in the implant energy or decreases in implanted dose. Conversely, the sheet resistance would generally monotonically decrease with either decreasing implant dose or increasing implant energy. In other words, it was much easier to activate boron at lower concentrations. An example of this can be seen in Fig. 1 for the 80 keV implants subjected to 750 °C anneals and in Fig. 2, which shows the reactivation of the 4×10^{14} cm^{-2} implants

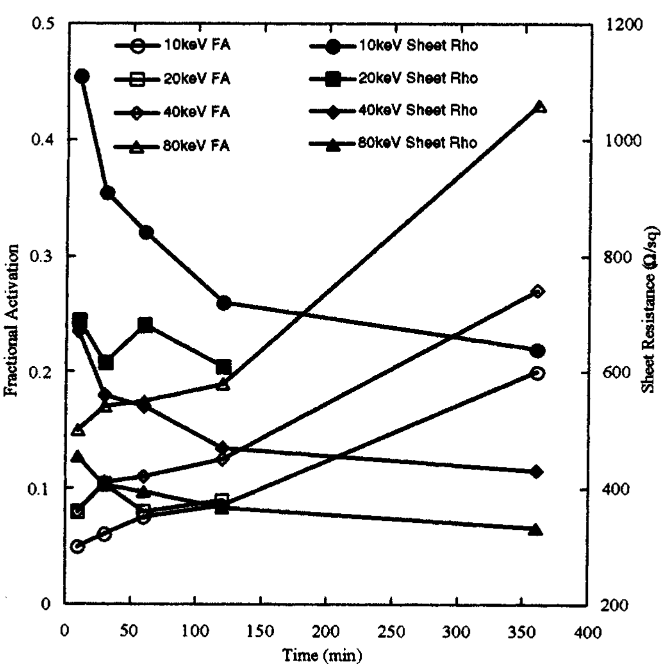

FIG. 2. Fractional activation (taken as the ratio of sheet number to as-implanted dose from SIMS) and sheet resistance measurements for the 4×10^{14} cm^{-2} boron implants at varying energy annealed at 750 °C from Hall effect measurement.

TABLE I. Extractions from the anneal data at 750 °C for the 13 wafer implant matrix.

Boron implant energy/dose	C_{BIC} (time=0) (cm^{-2})	1/tau (1/min)	R (error to fit)	Binding energy (eV)
10 keV 2×10^{14} cm^{-2}	2.32×10^{14}	0.00071	0.9738	2.63
10 keV 4×10^{14} cm^{-2}	5.00×10^{14}	0.00040	0.9612	2.68
10 keV 8×10^{14} cm^{-2}	9.85×10^{14}	0.00048	0.9924	2.66
10 keV 16×10^{14} cm^{-2}	2.24×10^{15}	0.00033	0.9807	2.70
20 keV 4×10^{14} cm^{-2}	4.70×10^{14}	0.00057	0.9334	2.65
20 keV 8×10^{14} cm^{-2}	9.88×10^{14}	0.00060	0.6451	2.65
20 keV 16×10^{14} cm^{-2}	2.02×10^{15}	0.00006	0.7028	2.85
40 keV 4×10^{14} cm^{-2}	4.07×10^{14}	0.00070	0.6927	2.63
40 keV 8×10^{14} cm^{-2}	9.56×10^{14}	0.00064	0.9894	2.64
40 keV 16×10^{14} cm^{-2}	2.06×10^{15}	0.00022	0.9851	2.74
80 keV 4×10^{14} cm^{-2}	4.43×10^{14}	0.00134	0.9729	2.58
80 keV 8×10^{14} cm^{-2}	7.48×10^{14}	0.00111	0.9728	2.59
80 keV 16×10^{14} cm^{-2}	1.95×10^{15}	0.00063	0.9882	2.64

at 750 °C. Lilak[5] presents a more complete picture of the data.

If one assumes that the reactivation of boron from a boron-interstitial cluster is dominated by the release of a boron interstitialcy from a wholly-inactive dominant cluster configuration it is possible to apply kinetic rate theory to extract the energy to mediate boron reactivation and gain insight into the energetics of the cluster configuration. Such analysis also relies upon the assumption that, during the reactivation time period, the recombination rate of the boron-interstitial cluster far exceeds the formation rate which minimizes the recycling of released interstitials into the formation of new boron clusters.

Kinetic rate theory will yield an expression for the reactivation rate, which incorporates a binding energy of the boron-interstitial cluster

$$\frac{dC_{\mathrm{BIC}}}{dt}=-K_{\mathrm{rate}}{}^{*}C_{\mathrm{BIC}}{}^{*}\exp\left(-\frac{E_b}{KT}\right), \tag{1}$$

$$K_{\mathrm{rate}}=4^{*}pi^{*}a_{\mathrm{silicon}}{}^{*}C_{\mathrm{silicon}}{}^{*}D_{\mathrm{Bi}}, \tag{2}$$

where a_{silicon} is the lattice spacing of the silicon crystal, t is time in arbitrary units, C_{BIC} is the concentration of clustered/deactive boron, E_b is the binding energy of the cluster, and D_{Bi} is the diffusivity of the boron interstitialcy. This has a solution of form

$$C_{\mathrm{BIC}}=C_{\mathrm{BIC}}(t=0)^{*}\exp\left(-\frac{t}{\mathrm{tau}}\right), \tag{3}$$

$$\frac{dC_{\mathrm{BIC}}}{dt}=-\frac{1}{\mathrm{tau}}{}^{*}C_{\mathrm{BIC}}(t). \tag{4}$$

The reactivation data from Hall effect measurements were fit to an exponential function of the form of Eq. (3) for each of the 13 wafers at temperatures of 750 and 850 °C and binding energies of boron interstitialcy cluster were extracted by equating Eq. (1) to Eq. (4) and assuming a migrational energy of 0.3 eV for the boron interstitialcy. These results are shown in Tables I and II for 750 and 850 °C anneals, respectively. For the 750 °C anneals the binding energies ranged from 2.58 to 2.85 eV with a standard deviation of 0.069 eV, while the 850 °C anneals had binding energies ranging from

TABLE II. Extractions from the anneal data at 850 °C for the 13 wafer implant matrix.

Boron implant energy/dose	C_{BIC} (time=0) (cm^{-2})	1/tau (1/min)	R (error to fit)	Binding energy (eV)
10 keV 2×10^{14} cm^{-2}	2.21×10^{14}	0.01010	0.9911	2.63
10 keV 4×10^{14} cm^{-2}	4.73×10^{14}	0.00510	0.8942	2.70
10 keV 8×10^{14} cm^{-2}	9.49×10^{14}	0.01020	0.9976	2.63
10 keV 16×10^{14} cm^{-2}	2.11×10^{15}	0.00330	0.9086	2.74
20 keV 4×10^{14} cm^{-2}	4.87×10^{14}	0.04180	0.9153	2.49
20 keV 8×10^{14} cm^{-2}	9.17×10^{14}	0.00466	0.8916	2.70
20 keV 16×10^{14} cm^{-2}	1.86×10^{15}	0.00545	0.9103	2.69
40 keV 4×10^{14} cm^{-2}	4.2×10^{14}	0.01950	0.9831	2.57
40 keV 8×10^{14} cm^{-2}	8.90×10^{14}	0.01630	0.9316	2.58
40 keV 16×10^{14} cm^{-2}	1.80×10^{15}	0.00409	0.7101	2.72
80 keV 4×10^{14} cm^{-2}	4.65×10^{14}	0.18600	0.9976	2.35
80 keV 8×10^{14} cm^{-2}	6.85×10^{14}	0.03170	0.9813	2.52
80 keV 16×10^{14} cm^{-2}	1.85×10^{15}	0.01670	0.9705	2.58

2.35 to 2.74 eV with a standard deviation of 0.110 eV. The standard deviation of the binding energy for the pooled data set was 0.095 eV.

The reactivation kinetics of clustered boron are shown through a large matrix of SRP and Hall effect data to be governed by a process mediated by a net energy of approximately 2.8–3.0 eV (binding plus migrational). The reactivation process is assumed to be mediated by the release of a boron interstitialcy with migrational energy of 0.3 eV. The binding energy of the most stable boron-interstitial cluster would then be approximately 2.5–2.7 eV across the matrix of 104 different implant/anneal conditions utilized in this study. The excellent agreement in the binding energies between 750 and 850 °C across the entire implant matrix, are consistent with a similar boron-interstitial cluster dissolution process for the wide range of processing conditions studied. These experimental results are also in rough agreement with results obtained from theoretical studies of boron diffusion and activation processes.[8,9]

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