Dependence of boron cluster dissolution on the annealing ambient

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Boron is introduced into silicon via implantation to form *p*-type layers. This process creates damage in the crystal that upon annealing causes enhanced diffusion and clustering of the boron layer. Reactivation of the boron is not a well-understood process. In this letter we experimentally investigate the effect of the annealing ambient on boron reactivation kinetics. An oxidizing ambient which injects silicon interstitials is compared to an inert ambient. Contrary to published theory, an excess of interstitials does not accelerate the reactivation process. © *2002 American Institute of Physics*. [DOI: 10.1063/1.1496505]

Ion implantation is the preferred method of introducing dopants due to the precision of the implanted dose, control and repeatability. Future technology nodes will require highly doped shallow junctions processed with a low thermal budget. Such conditions emphasize the role of point defects generated by the implantation process. Recombination of point defects and dopant activation take place during annealing after implantation. For nonamorphizing implants, the annealing step can form extended defects and dislocation loops, which can control enhanced diffusion.[1,2] Besides effects on dopant diffusion, high interstitial concentrations are also known to deactivate boron, through the formation of boron interstitial clusters (BICs).[3]

Ab initio studies provided information on the stability of some clusters used in several implementations of BIC models in Monte Carlo[4] and process simulators.[5,6] It is not clear if boron will cluster in an interstitial supersaturation lower than that found in ion implantation, and if measurement methods would be able to distinguish such a presumably low concentration of clustered boron from noise of the active boron profile. Specifically, characterization of low cluster densities is difficult, because low cluster densities are not detectable by secondary ion mass spectrometry (SIMS) profiles and could be below the detection limit of spreading resistance or Hall effect measurements. The behavior of BICs during dissolution, with respect to interstitial supersaturation, has not been verified experimentally. Pelaz *et al.*[7] have theorized that breakup of the clusters requires an interstitial to drive the process along an interstitial lean path. This theory suggests that the boron is driven to cluster in a large interstitial supersaturation, but a lower supersaturation might provide excess interstitials that will speed cluster dissolution. Notwithstanding, experimental evidence suggests that BICs can serve as a source of interstitials for transient enhanced diffusion (TED) in later stages of annealing, by dissolution of boron clusters.[8]

To test this hypothesis, implants of boron were performed to achieve peak boron concentrations on the order of 10^{19} cm^{-3}. Annealing is performed in two steps. Boron interstitial clusters form during the first anneal step and deactivate a significant part of the dose. The second anneal is used to determine the influence of annealing ambient on cluster formation or dissolution. Clustering effects are investigated via SIMS and Hall effect measurements.

Czochralski ⟨100⟩ *n*-type silicon wafers were implanted with boron. Three implant conditions with nominal boron peak concentrations of 10^{19} cm^{-3} were investigated. The implant doses and energies were 10^{14} cm^{-2} at 5 keV, 2×10^{14} cm^{-2} at 10 keV and 4×10^{14} cm^{-2} at 20 keV, respectively. The first anneal step was performed at 750 °C for 30 min in inert N_2 ambient. To investigate the influence of the ambient on B cluster dissolution, subsequent anneals were done in inert (N_2 flow) or oxidizing (dry O_2) ambient at 850 °C for 10, 20, 30, and 60 min. Oxidation of silicon is known to inject interstitials,[9] allowing investigation of BICs in a low supersaturated interstitial environment.

Samples were analyzed by SIMS, Hall effect and ellipsometry measurements. Boron depth profiles were measured by a Cameca IMS-3*f* SIMS instrument using an O_2^+ primary ion beam and a magnetic sector analyzer. The raster size and analyzed area were 200 and 60 μm in diameter, respectively. Samples were biased at 4.5 kV with effective impact energy of 5.5 keV. The Woollam EC110 ellipsometer was used for oxide thickness measurements, and showed no difference between the initial condition and inert annealed samples. Oxide thickness measurement of samples annealed in oxidizing ambient was used in aligning the SIMS profiles due to the con-

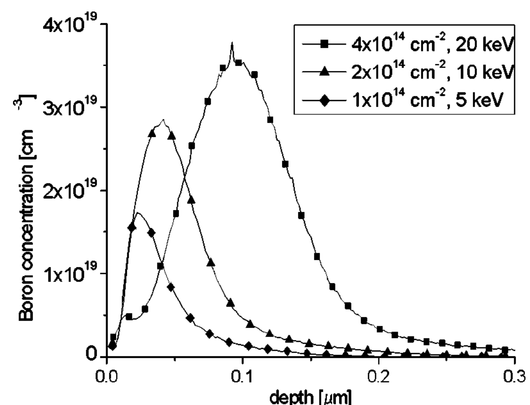

FIG. 1. SIMS measured boron profiles of investigated implant conditions after the first anneal step, 750 °C for 30 min in inert ambient.

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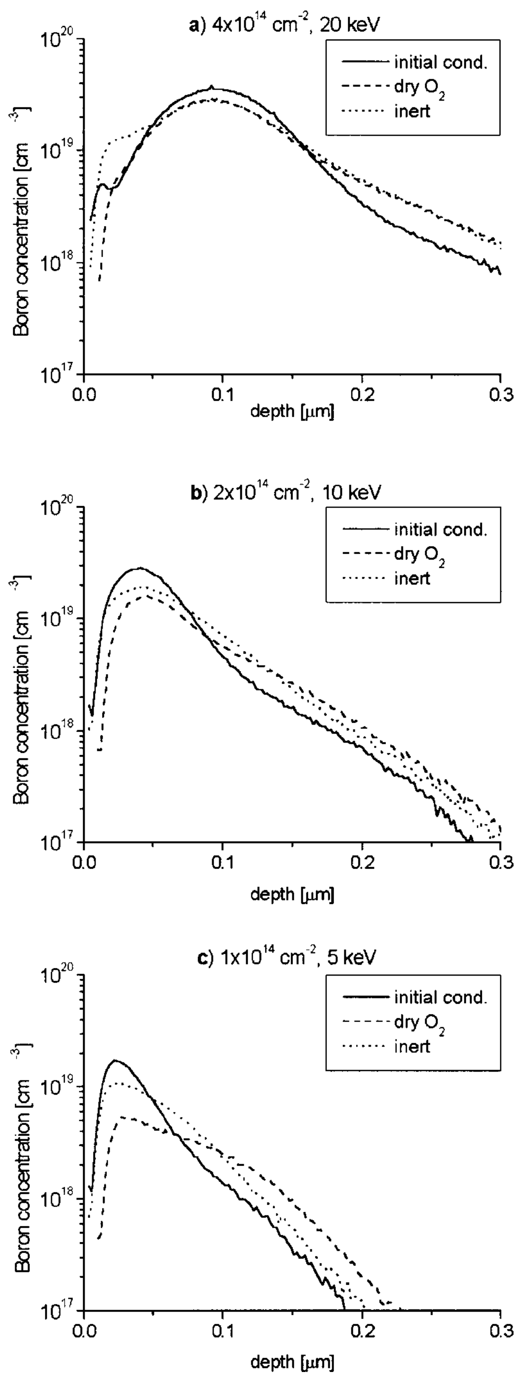

FIG. 2. SIMS measured boron profiles. The initial condition is after a 750 °C, 30 min inert anneal. Dry O_2 and inert are profiles after subsequent 850 °C, 60 min anneal in respective ambient. (a) Profile for 4×10^{14} cm^{-2}/20 keV, (b) profile for 2×10^{14} cm^{-2}/10 keV, and (c) profile for a 1×10^{14} cm^{-2}/5 keV B implants. These conditions are chosen because the peak concentrations and initial clustered concentrations are similar.

sumption of silicon. The measured oxide thickness agreed well with standard predictions at these temperatures. The active dose was measured using a MMR Technologies Inc. Hall–van der Pauw system. Measurements were performed using a magnetic field of 300 mT with the current ranging from 1 μA to 1 mA at room temperature. Square shaped samples with 14 mm sides had 1 mm diameter e-beam deposited Al contacts placed symmetrically near the corners. Factors contributing to the inaccuracy of the measurement include the nonuniform dopant distribution and heavy to light hole ratio. Assuming the measured profiles were steep

TABLE I. Boron dose retained [cm^{-2}] in different processing steps. The first anneal step is 750 °C, 30 min in inert ambient. The second anneal step is 850 °C, 60 min in inert and oxidizing ambient. Dose loss in the lowest implanted dose sample is comparable to the active dose measured by the Hall effect measurement.

Implanted dose [cm^{-2}]	First anneal step [cm^{-2}]	Second anneal step	
		Inert [cm^{-2}]	Oxidizing [cm^{-2}]
4×10^{14}	3.69×10^{14}	3.58×10^{14}	3.33×10^{14}
2×10^{14}	1.75×10^{14}	1.58×10^{14}	1.25×10^{14}
10^{14}	7.48×10^{13}	7.01×10^{13}	4.48×10^{13}

enough to neglect the influence of deeper layers with lower dopant concentration and higher mobility, we chose a value of 0.7 for the Hall mobility factor.[10]

The first annealing step provides the initial condition with BICs of similar peak concentrations for the implant conditions studied (Fig. 1). During this anneal excess interstitials from implant damage react with boron forming BICs. These clustered boron samples are further referred to as the initial condition. Figure 2 shows boron profiles at critical stages of thermal processing for each of the implant conditions studied. A comparison of oxidized and inert annealed profiles shows oxidation enhanced diffusion for the boron as expected for an interstitial diffusing species.[11] Direct comparison of the clustered fraction is difficult from the SIMS results because of the extra diffusion. Although the shallowest implant exhibits the highest diffusion enhancement, we do not believe the distance to the surface to be significant. Different diffusion enhancements may be a consequence of differences in the initial clustered dose, since oxidation is known to create uniformly deep enhancements in the bulk.[12] The surface influence in these samples is mostly through segregation and outdiffusion of boron, resulting in dose loss (Table I). Dose loss is most apparent in the lowest implant dose/energy sample, since it has the shallowest boron profile in sample set presented [Fig. 2(c)].

Hall effect measurements during various stages of annealing are shown in Fig. 3. The initial anneal deactivates a large fraction of the dose, creating the initial clustered concentration that establishes our initial condition. Subsequent annealing activates the boron by dissolving the clusters. Inert

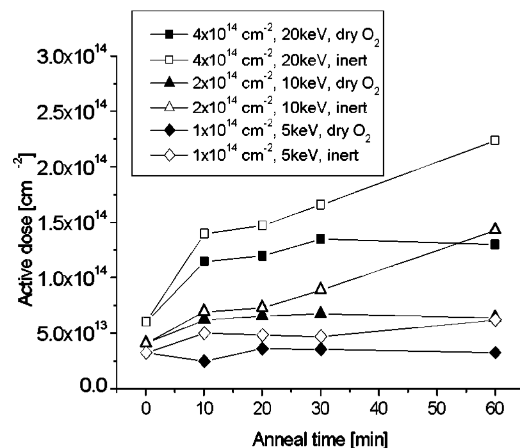

FIG. 3. Active dose measured by the Hall–van der Pauw method. The time zero measurement corresponds to the condition after a 750 °C, 30 min inert anneal.

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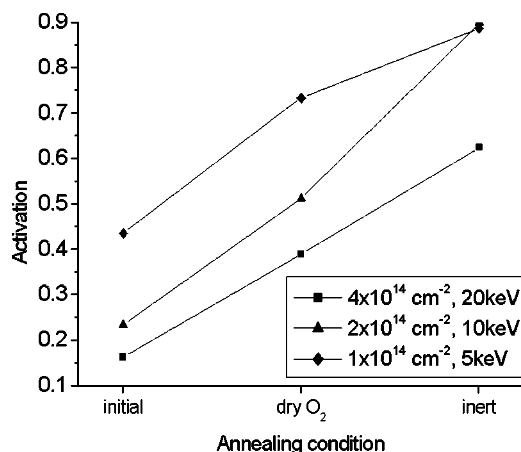

FIG. 4. Active fraction, the ratio of active to retained dose (integrated SIMS profile), compared for different annealing ambients at the end of the 850 °C, 60 min anneal. The initial condition is after a 750 °C, 30 min inert anneal.

anneals consistently have a higher active dose than oxidizing anneals. Considering dose loss and reactivation effects are mixed in the Hall effect measurement, defining activation as the ratio of active to retained dose (integrated SIMS profile) is used to distinguish them. Activation fractions for known boron profiles are presented in Fig. 4. An increase of activation by 15%–40% for inert annealed over oxidized annealed samples confirms the trends demonstrated by the Hall effect measurement. That leads to the conclusion that boron clusters dissolve slower in oxidizing ambient than in inert ambient. Extraction of an exponential decay rate of the BIC concentration shows time constants that vary with implant conditions. (One *caveat*: Time constants were extracted only for known activation fractions, those being for the initial condition and the second 60 min anneal.) Still, inert annealed samples have around half the time constant of oxidized samples for the same implant energy and dose.

Boron interstitial clusters were formed by a 750 °C anneal after implantation. A study of the activation rate was performed in two different ambient conditions. The oxidizing ambient shows consistently lower activation at a slower rate, which strongly demonstrates that the presence of excess interstitials slows cluster dissolution.

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