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Effects of Heat-Treatments on Electrical Properties of Boron-Doped Silicon Crystals

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ABSTRACT

The effects of heat-treatments around 1000°C and subsequent annealing on the electrical properties of boron-doped silicon have been studied by electrical conductivity, Hall effect, and deep-level transient spectroscopy measurements. The high-temperature heat-treatments always induced net densities of donors. Four recovery stages, stages I-IV, of heat-treatment-induced donors were observed on isochronal annealing up to 400°C. Conductivity changes in these stages can be explained as described below by the reactions of interstitial iron (Fe_i), its pair (Fe_iB_s) with substitutional boron (B_s), and two unknown donors (D₁, D₂). That is, stage I (25°-100°C): D₁ → sink and Fe_i + B_s → Fe_iB_s, stage II (100°-150°C): Fe_iB_s → Fe_i + B_s, stage III (200°-250°C): D₂ → sink, stage IV (250°-350°C): Fe_i → precipitation. Heat-treatments in an oxygen atmosphere greatly reduced the introduction of Fe_i and Fe_iB_s in comparison with an argon atmosphere and mainly introduced D₁ and D₂ donors. The density of D₂ was dependent on the heat-treatment temperature, while that of D₁ showed almost no dependence. In stage I, D₁ was annihilated by first-order kinetics with an activation energy of 0.8 eV. It was indicated that D₁ and D₂ have no relations to iron, copper, oxygen, nor carbon. Though their origins are still unidentified, there may be some interstitial impurities. In stage IV, Fe_i is suggested to precipitate at oxygen precipitates and dislocation loops formed by high-temperature heat-treatments. As to the application to iron gettering in the device fabrication process, it is proposed that annealing around 300°C is most suitable as the final heat-treatment step to remove iron and related defects from active regions of devices.

Silicon wafers receive complex heat-treatments at various temperatures in the fabrication process of electronic devices. Such heat-treatments introduce various contaminating impurities and point defects into the bulk of silicon crystals. In most cases, these impurities and defects affect the electrical properties of the crystals, and therefore have a significant effect on the performance of electronic devices. Although there have been a large number of experimental investigations (1-13) to study the energy levels arising from these impurities and defects and their carrier trapping and emitting properties by means of capacitance transient techniques such as deep-level transient spectroscopy (DLTS) (14), relatively little work has been accomplished so far on the effects of such electrically active centers on the electrical properties of silicon crystals (15-21). However, the results of such work would indeed be very helpful to design the optimum fabrication process of desirable devices.

It has been widely recognized that iron tends to contaminate silicon crystals on heat-treatments at high temperatures, and the characteristic properties of iron in silicon have been intensively studied (1-9, 12, 13, 22-24). Iron occupies the tetrahedral interstitial site in the silicon lattice (22-24), acting as a deep donor. Its single donor level is located at $E_V + 0.4$ eV (1-7, 25). This level traps a free hole in p-type silicon. Iron has high diffusivities and moves even at room temperature to form a complex with a doping acceptor such as boron (1-7). The iron-boron pair has a single donor level at $E_V + 0.1$ eV and acts also as a hole trap (1-7). Most of these characteristic features, however, have been

studied mainly by DLTS (2-7), while the effects of the interstitial iron and the iron-boron pair on electrical properties of heat-treated silicon crystals have not yet been sufficiently clarified and neither have the effects of other impurities and defects.

The aim of this paper is to present the results of electrical resistivity changes induced by high-temperature heat-treatments and subsequent annealing and to discuss these results in connection with roles of iron, iron-related defects, and also other defects. We have also investigated the effects of heat-treatment conditions such as temperature and atmosphere. A suggestion is made on the application of the present results to gettering of iron and iron-related defects.

Materials and Heat-Treatments

Two-kinds of boron-doped (111) silicon wafers were mainly used as the starting material. One is a Czochralski-grown (CZ) crystal with a room temperature resistivity of 10 Ωcm (CZ-B-10). The other one is a float-zoned (FZ) crystal of 30 Ωcm (FZ-B-30). The concentrations of interstitial oxygen dissolved in the crystals were 1.2×10^{18} atom/cm³ for CZ-B-10 and less than 1×10^{16} atom/cm³ for FZ-B-30 using a conversion factor of 3.1×10^{17} atom/cm² (26). The concentrations of substitutional carbon of both crystals were less than 1×10^{16} atom/cm³.

The crystals were cut into rod samples with typical dimensions of $0.5 \times 2 \times 15$ mm³. Samples were etched in acid (HNO₃:HF = 4:1) for a few minutes and rinsed with deionized water before heat-treatments. Samples were

then heated in flowing argon or oxygen gas on a quartz plate in a horizontal furnace for 1-20h at temperatures 700°-1100°C. Normally, no intentional impurity diffusion was performed during the heat-treatment, but some samples were first iron- or copper-coated by vacuum evaporation and then heated to let that impurity in-diffuse at high temperatures in an argon atmosphere. Quenching was done by pulling the quartz plate out of the furnace to let a sample fall into water. Quenched samples were annealed at temperatures 50°-450°C. Annealing was performed in silicone oil below 230°C and in molten salt (KNO₃:NaNO₃ = 1:1) above that temperature.

Measurement Procedures

Resistivity measurement.—Room-temperature resistivity was measured at 25°C by the four-point probe method before and after the high-temperature heat-treatment. After that, ohmic contacts were formed on samples at room temperature by welding aluminum wires by electrical discharge. Such contacts can be formed without raising the sample temperature and are stable against annealing up to 450°C. This enabled us to accurately measure resistivity changes induced by annealing. Resistivities were measured in CCl₄ at room temperature (RT, 25°C) and at liquid nitrogen temperature (LNT, 77 K).

Hall measurement.—Ohmic contacts were applied to quenched samples as described above. The Hall coefficient was measured as a function of temperature in the range 20-300 K in a magnetic field of 0.376T.

The hole density was calculated from the measured Hall coefficient using the Hall-mobility/conductivity-mobility ratio of Morin and Maita (27) in the temperature range above 100 K.

DLTS measurement.—Quenched samples of 1 × 2 × 3 mm³ were etched, and then titanium dots with a diameter of 1.5 mm were evaporated on them to form Schottky junctions. The sample temperature was kept well below 0°C during the evaporation to avoid the annealing of any of the quenched-in defects. Ohmic contacts were formed by welding aluminum wires to the opposite sides of the samples. Capacitance DLTS measurements were performed by scanning the temperature at a rate of 4 K/min from 40 to 300 K. The experimental equipment consists of Sanwa MI-401 (a capacitance meter and a pulse generator), NCC Mark-1 (an A/D converter), X-Y plotter, and personal computers, which control the pulse generator and the temperature scanning and also perform the data acquisition. Normally both the reverse bias and the pulse voltage were 5V. The sensitivity of our equipment was 2 × 10⁻⁴ as the concentration ratio of deep levels to shallow levels.

We have obtained an activation energy, *E*, for the hole emission from a particular trap using the familiar expression (28)

$$e/T^2 = A\gamma g \exp(-E/kT) \quad [1]$$

where *e* is the hole emission rate of the trap, *γ* is the cross section for capturing holes, *g* is the degeneracy factor of the trap level, and *A* = 3.52 × 10²¹ cm⁻² s⁻¹ K⁻². We have also estimated values of *γ* from the intersection of Arrhenius plots of *e/T*² using Eq. [1], assuming *g* = 1. The trap density, *N*, was calculated using the relation (14)

$$N = 2(\Delta C/C)(N_A - N_D) \quad [2]$$

where *C* is the capacitance of the diode under the quiescent reverse bias, *ΔC* is the capacitance change from *C* just after removing the applied bias pulse, and *N_A - N_D* is the net density of shallow acceptors ionized at the temperature concerned. *N_A - N_D* was determined from capacitance vs. voltage plots at a temperature near the pertinent DLTS peak position.

Experimental Results

Heat-treatments at high temperatures always induced electrical conductivities at RT and LNT to decrease, although the degree of decrease depended on heat-treatment conditions. This means that donor-type defects were mainly introduced by the heat-treatments and their den-

sity depended on heat-treatment conditions. Since iron-related defects have been known to be introduced by heat-treatments (8-13), we compared annealing behavior of thermally induced donors in normally heated and intentionally iron-diffused samples. Figure 1 shows the results of isochronal annealing for such comparison. The ordinate represents fraction not annealed, *f*, defined as

$$f = \frac{\sigma_0 - \sigma_A}{\sigma_0 - \sigma_Q} \quad [3]$$

where *σ₀* and *σ_Q* are conductivities before and after quenching from high temperatures, and *σ_A* is the conductivity after annealing. Since heat-treatments always yielded a net density of donors, the decrease in *f* means the annihilation of donors with levels above the Fermi levels at the conductivity-measuring temperatures, or the formation of acceptors with levels below the Fermi levels. In Fig. 1, we can see four recovery stages, stages I-IV. In stage I (25°-100°C), *f* at RT, *f_{RT}*, decreases, and *f* at LNT, *f_{LNT}*, also decreases for a normally heated sample, but it remains constant for an iron-diffused one. This apparent difference will be discussed in the next section. In stage II (100°-150°C), *f_{RT}* remains unchanged, while *f_{LNT}* decreases. In stage III, both *f_{RT}* and *f_{LNT}* decrease, though their amounts are relatively small. Finally, they both decrease to a large extent in stage IV, where thermally-induced donors completely disappear by annealing up to 400°C. In short, Fig. 1 indicates that the four recovery stages always appear, regardless of whether the iron diffusion was done or not, although the amount of recovery in each stage is slightly different for both cases. This may suggest that heat-treatments mainly introduced iron and related defects, which dominate the electrical properties of heat-treated samples. Since such defects have been studied intensively by the DLTS method (2-13), we have performed DLTS measurements to study the properties of defects responsible for the above recovery stages. Figure 2 shows DLTS spectra of heat-treated samples with and without iron diffusion. Two hole traps, H(0.10) and H(0.45), are seen in the spectra. Their energy levels and hole capture cross sections are *E_v* + 0.45 eV and 8 × 10⁻¹⁶ cm² for H(0.45) trap, and *E_v* + 0.10 eV and 4 × 10⁻¹⁵ cm² for H(0.10) trap. These properties are in good agreement with those of interstitial iron, Fe_i, and its pair, Fe_iB_s, with substitutional boron, B_s, respectively (2-7). Moreover, the results of our experiments on the Poole-Frenkel effect (29) for H(0.42) and H(0.10) traps indicated no peak shift occurring with increasing pulse voltage. If these traps have the acceptor character, the positions of their peaks should be shifted toward low temperatures by increasing pulse voltage, because of the

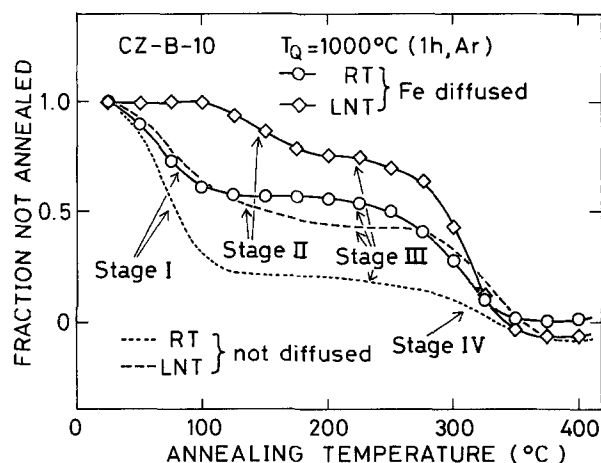


Fig. 1. Results of isochronal annealing of CZ-B-10 samples normally heated and iron-diffused at 1000°C. Samples were annealed for 10 min at each temperature. The ordinate represents the unannealed fraction of heat-treatment-induced donors and is defined by Eq. [3] using conductivities measured at 25°C (RT) and 77 K (LNT). Four recovery stages are indicated.

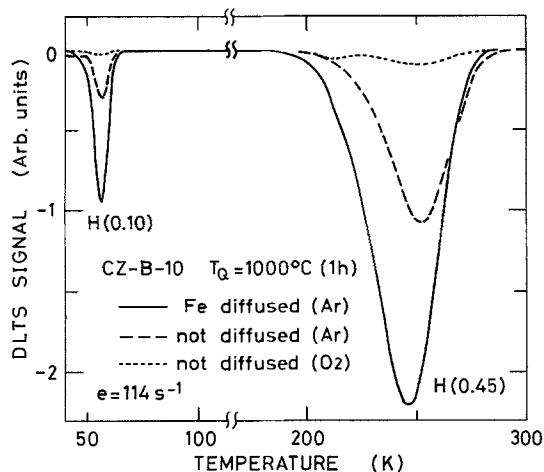


Fig. 2. DLTS spectra of CZ-B-10 samples heat-treated with and without iron diffusion in an argon or oxygen atmosphere. H(0.10) and H(0.45) represent hole traps whose levels are located at 0.10 and 0.45 eV from the top of the valence band, respectively.

lowering of ionization energies for the emission of a positive hole from a negatively charged acceptor (30). Therefore, the above results indicated that H(0.45) and H(0.10) peaks arise from the donor levels of Fe_i and Fe_iB_s . For the iron-diffused sample, the sum of Fe_i and Fe_iB_s densities is $2 \times 10^{14} \text{ cm}^{-3}$ and almost attains the solubility of Fe_i at 1000°C in silicon (1). In the undiffused samples, the densities of Fe_i and Fe_iB_s are much smaller for oxygen atmosphere than those for argon atmosphere. The reason will be discussed in the next section. The annealing behavior of Fe_i and Fe_iB_s is shown in Fig. 3, where their densities are plotted against the annealing temperature. Their behavior is completely consistent with the reported defect reactions of the Fe_i - Fe_iB_s system (2-7). Below 100°C, Fe_i disappears replacing the same density of Fe_iB_s , indicating the formation of Fe_iB_s . In the temperature range 100°-170°C, the reverse reaction, or the dissociation of Fe_iB_s , occurs. Above 170°C, both Fe_i and Fe_iB_s disappear, suggesting that Fe_i arising from the dissociation of Fe_iB_s is annihilated at sinks. Qualitatively the same results have been obtained for diffused not iron-samples.

Figure 4 shows the effects of successive annealing on the temperature dependence of hole density for iron-diffused samples. In the as-grown state (curve a), only the level of B_s is deionized below 100 K. The iron diffusion at 1000°C (curve b) induced a decrease in hole density in the whole temperature region but produced no new levels. Anneal-

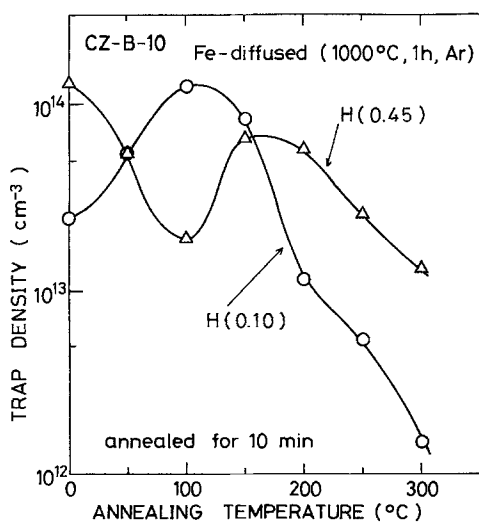


Fig. 3. Isochronal annealing behavior of H(0.10) and H(0.45) traps in a CZ-B-10 sample iron-diffused at 1000°C. Samples were annealed for 10 min at each temperature.

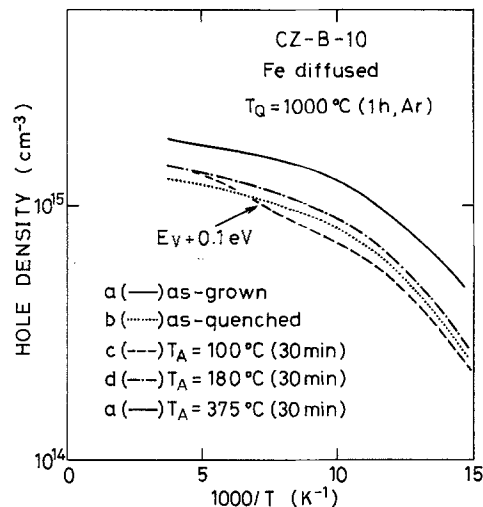


Fig. 4. The effects of successive annealing on temperature dependence of hole density of CZ-B-10 samples iron-diffused at 1000°C.

ing at 100°C for 30 min (curve c) induced a level at $E_v + 0.1 \text{ eV}$ and also caused the hole density around room temperature to increase. This level can be readily identified as the donor level of Fe_iB_s . If the reaction $Fe_i + B_s \rightarrow Fe_iB_s$ only occurs below 100°C (in stage I), the hole density at room temperature would not change, because the charge states of Fe_i , B_s , and Fe_iB_s are positive, negative, and neutral, respectively. Therefore, the present result strongly suggests that an unknown donor, to be named D_1 later, simultaneously disappears while the above defect reaction occurs. This is supported by the results of Fig. 1 where f_{RT} decreases in stage I. Annealing at 180°C (curve d) annihilated the $E_v + 0.1 \text{ eV}$ level leaving the room temperature hole density unchanged. This can be explained by the reaction $Fe_iB_s \rightarrow Fe_i + B_s$ only. The final annealing at 375°C (curve e) resulted in an increase in hole density in the whole temperature region, returning the sample conductivities to the as-grown values. This is consistent with the annihilation of donors in stage IV.

Our present results (Fig. 1 and 3) indicate that Fe_i precipitates above 250°C (stage IV). Many previous investigations have pointed out this behavior of Fe_i (1-7). However, no detailed information concerning the sites and mechanisms of the iron precipitation has been available. We emphasize that studies of this point are very important for developing effective iron gettering techniques. Figure 5 shows preliminary results of our experiments aimed at clarifying the sites of iron precipitation. In the experiments, several CZ and FZ samples were heated for various durations at 1000°C in an argon atmosphere and then were isochronally annealed up to 450°C. In CZ crystals, the temperature where stage IV occurred was shifted toward the low-temperature side as the preheating time at 1000°C was increased (Fig. 5a). In FZ crystals, no such shift was observed (Fig. 5b). Other annealing stages than stage IV were not affected by changing the preheating time. Increases in f observed in CZ crystals above 400°C are due to the formation of so-called thermal donors (31-35). It has been known that extended annealing of CZ silicon around 1000°C causes oxygen precipitation and the generation of dislocation loops from the precipitates (36-38). The results of Fig. 5 suggest that these oxygen precipitates and dislocation loops may provide the sites of iron precipitation in stage IV.

Figure 2 strongly suggests that iron contamination can be reduced by heating samples in an oxygen atmosphere. Figure 6 shows the results of isochronal annealing for a sample heated in O_2 at 1100°C. The prominent feature of this figure is that only stage I and III appear while stage II and IV do not. Since the latter two stages are concerned with the reactions of Fe_i and Fe_iB_s , the results of Fig. 6 support the idea that heating in the oxygen atmosphere suppresses the introduction of Fe_i and related defects. An-

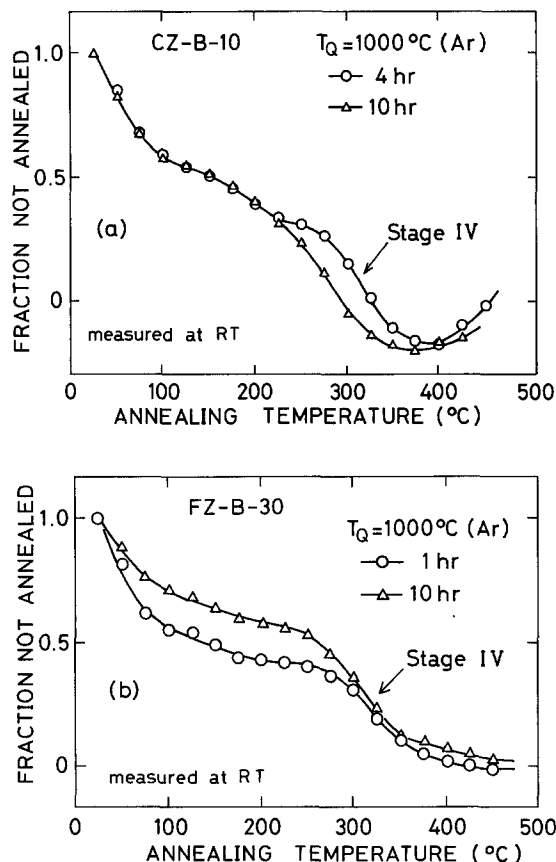


Fig. 5. The effects of heat-treatment time at 1000°C on isochronal annealing recovery of room temperature conductivity of (a) CZ-B-10, and (b) FZ-B-30 samples.

other important conclusion is that two unknown donors, D_1 and D_2 , which were annihilated in stage I and stage III, respectively, are not iron-related defects. Accordingly, in stage I for samples heat-treated in the argon atmosphere (Fig. 1 and 4), the annihilation of D_1 and the reaction $Fe_i + B_s \rightarrow Fe_iB_s$ occur simultaneously. When the heat-treatment temperature was lowered to 700°C, only stage I was observed. This means that the density of D_1 is hardly dependent on the heat-treatment temperature while that of D_2 depends on it. A typical density of D_1 was $2 \times 10^{14} \text{ cm}^{-3}$ for the heat-treatment at 700°C. This density is much higher than the solubility of Fe_i in Si at that temperature (1), clearly indicating that D_1 is not an iron-related defect.

We have studied the annealing behavior of D_1 in more detail. Figure 7 shows the kinetics of the annihilation process of D_1 . The sample conductivity was *in situ*-monitored

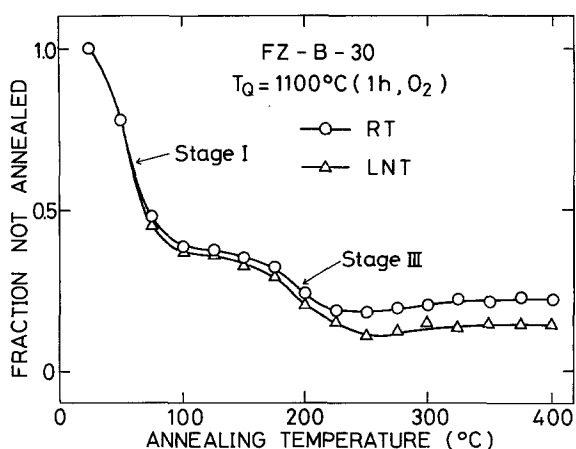


Fig. 6. The effects of an oxygen atmosphere of the heat-treatment at 1100° on the isochronal recovery of conductivities.

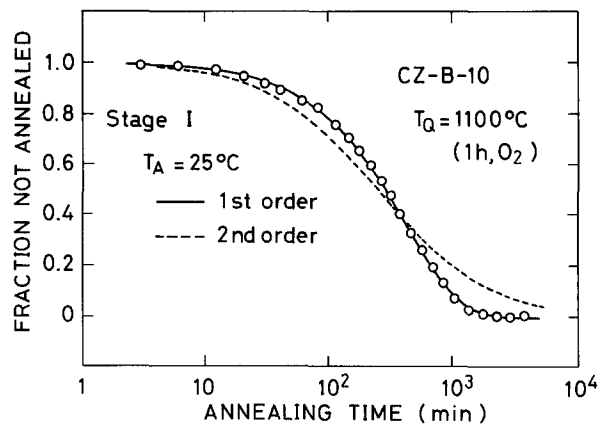


Fig. 7. Kinetics of the annihilation process of D_1 donor at 25°C (stage I).

during the annealing at 25°C. The ordinate represents f that is normalized so that f reaches zero when stage I completely finishes. The result of fitting shows first-order kinetics. The activation energy of annihilation of D_1 was determined by the method of changing slopes. Annealing was performed at 25° and 45°C, and conductivity measurements were done at 5°C. The results are shown in Fig. 8, which indicates that the activation energy is about 0.8 eV.

Discussion

Iron and related defects.—The present results clearly show that iron contaminates silicon crystals during heat-treatments around 1000°C, and iron itself and iron-related defects greatly affect electrical properties of heat-treated silicon. We first discuss the effects of Fe_i and Fe_iB_s levels and their reactions on conductivities at 25°C (RT) and 77 K (LNT). The levels of Fe_i , B_s , and Fe_iB_s are located in the bandgap as shown in Fig. 9, where the positions of the Fermi level, E_F , at RT and LNT under our experimental conditions are also indicated. This scheme gives the charge states of the above levels. Fe_i and B_s are always positively and negatively ionized, respectively, at RT and LNT, while Fe_iB_s is neutral at RT and positively ionized at LNT. Considering the charge states of these defects, we can expect that the reaction $Fe_i + B_s \rightarrow Fe_iB_s$ leaves f_{RT} unchanged and causes f_{LNT} to increase in stage I. However, our results (Fig. 1) shows that f_{RT} decreases, contrary to our expectation. Also, f_{LNT} does not change for the iron-diffused sample and it decreases for the undiffused sample, as opposed to the above reaction. We attribute these discrepancies to the simultaneous annihilation of an unknown donor, D_1 , occurring together with the above reaction. We will discuss the behavior of D_1 in the next subsection. In Fig. 1 it is barely noticeable that there is a small decrease in f_{LNT} around 50°C for the iron-diffused sample, followed by a small increase around 75°C. This

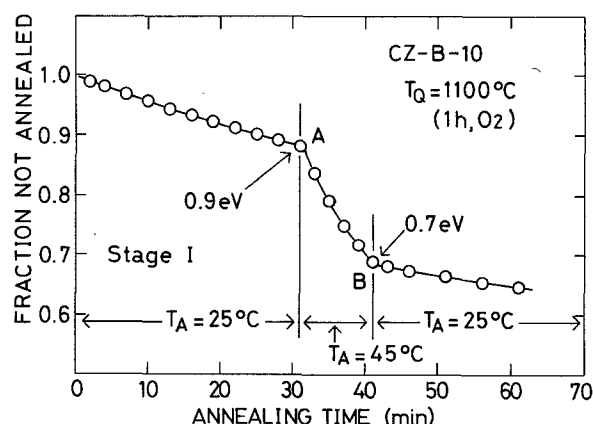


Fig. 8. Determination of the activation energy for the annihilation process of the D_1 donor in stage I by the method of changing slopes.

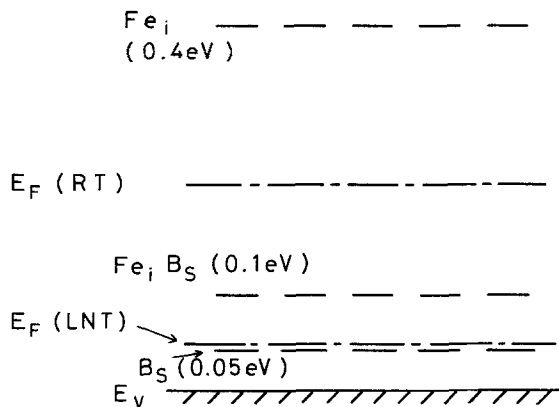


Fig. 9. Locations of the levels of Fe_i , B_S , and Fe_iB_S in the bandgap. All level energies are with respect to the top of the valence band, E_v . Positions of the Fermi level, E_F , at room temperature (RT) and liquid nitrogen temperature (LNT) are also shown.

may indicate that the annihilation of D_1 occurs first and subsequently the formation of Fe_iB_S follows it. Accidentally, this point was more clearly observed in a special sample which was heated for 20h in O_2 at 1100°C . The results are shown in Fig. 10 where the annihilation of D_1 occurs below 75°C , followed by the formation of Fe_iB_S in the region 75°C – 100°C . In stage II, the dissociation of Fe_iB_S into Fe_i and B_S can well explain the observed changes in f , no change in f_{RT} , and a decrease in f_{LNT} (Fig. 1 and 10). In the temperature region of stage II, the reaction between Fe_i and Fe_iB_S was found to be reversible by our resistivity, Hall effect, and DLTS measurements. This feature means that the dissociation and association reactions of Fe_iB_S maintain the equilibrium after sufficiently long annealing. We can therefore attribute stage II to the shift of the equilibrium with increasing temperature so that the dissociation of Fe_iB_S becomes more and more dominant. In stage IV, decreases in f_{RT} and f_{LNT} were observed. This is consistent with the precipitation of Fe_i .

Other defects than iron and related defects.—We have found that two kinds of unknown donors, D_1 and D_2 , are introduced by high-temperature heat-treatments and are annihilated below 100°C (stage I) and around 200°C (stage III), respectively. Figure 6 shows that in both stages f_{RT} and f_{LNT} change similarly, suggesting that the donor levels of D_1 and D_2 are located above the Fermi level at RT, $E_v + 0.2$ eV. Our DLTS measurements of CZ samples heated in O_2 around 1000°C to reduce iron contamination showed no DLTS peaks corresponding to neither D_1 nor D_2 (Fig. 2). This suggests that the both levels may exist in the upper half of the bandgap.

Defects corresponding to D_1 have often been observed by several investigators (19–21). Swanson (19) found that an unidentified donor with a level at $E_v + 0.4$ eV was produced by quenching from 800°C – 1100°C and was annihilated near 300 K by first-order kinetics with an activation energy of 0.8 eV. The annihilation of this donor caused recovery (increase) of conductivities at RT and LNT. The density of this donor was about $1 \times 10^{15} \text{ cm}^{-3}$, being almost independent of the quenching temperature. In light of the present results, the donor of Swanson, in fact, may not have been associated with the $E_v + 0.4$ eV level, but this level may be due to contaminating Fe_i , which may have been annihilated by the formation of Fe_iB_S by prolonged annealing at RT. Since this defect reaction does not affect the RT conductivity and causes the decrease of the LNT conductivity, the donor found by Swanson is not due to Fe_i but may be the same defect as our D_1 . This is supported by good agreements in kinetics and activation energy between both donors. It can therefore be concluded that in Swanson's experiments, too, an unknown donor and Fe_i may have been annihilated together around room temperature. Leskoschek and Feichtinger *et al.* (20, 21) observed that a shallow donor annealed-out around room temperature with an activation energy of 0.6–0.9 eV. They

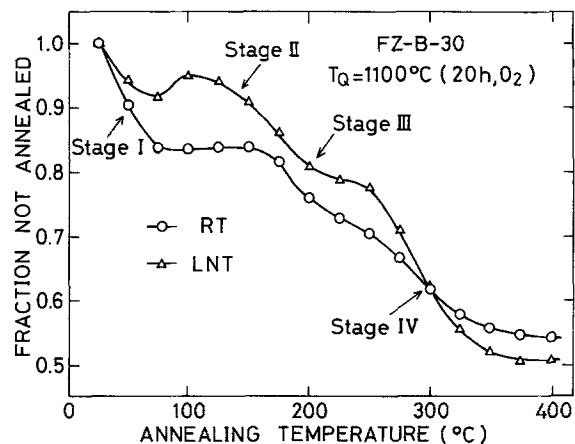


Fig. 10. Isochronal annealing recovery of conductivities of a FZ-B-30 sample heated for 20h at 1100°C in O_2 . It can be clearly demonstrated that in stage I the annihilation process of D_1 donor occurs first and then the formation process of Fe_iB_S follows it.

estimated the position of the donor level to be nearer than 0.07 eV to the bottom of the conduction band. This donor, therefore, affected RT and LNT conductivities of p-type material. These characteristics are in good agreement with those of our D_1 . They reported that the donor density hardly depends on the heat-treatment temperature below 1100°C , and above this temperature it decreases with increasing temperature. This feature is also consistent with our D_1 . Thus, the donor corresponding to D_1 has commonly been observed so far.

Little information has been available about the origin of D_1 . Swanson discussed it and concluded that D_1 has no connections to vacancies but is produced possibly by quenching strains. Feichtinger *et al.* made no such discussion. Our results presented above indicate that D_1 is not correlated with iron or oxygen. Moreover, our further experiments on copper diffusion during heat-treatments excluded the possibility that D_1 has any relations to this impurity. We have also found no increase in D_1 density in heat-treated, carbon-rich (9×10^{16} carbon atom/ cm^3) crystals, indicating no connections to carbon. The D_1 density had almost no temperature dependence below 1100°C and decreased with temperature above 1100°C in the previous work (21), and was also independent of the heat-treatment atmosphere in the present work. Moreover, no appreciable increase in D_1 density was caused by prolonged annealing in O_2 at 1100°C (Fig. 10). These results suggest that D_1 does not arise from any contaminating impurities from the outside of samples but is due to some unknown impurity already present in as-grown crystals. However, Feichtinger *et al.* (21) reported that the D_1 density was reduced from 10^{16} to 10^{15} cm^{-3} by etching samples before their heat-treatments. Their results suggest the possibility that D_1 can also indiffuse easily from the crystal surface. Quenching strain caused by nonetched surface might have assisted its indiffusion. Anyway, D_1 must be a fast-diffusing identity, probably an interstitial impurity.

Defects corresponding to D_2 have not been reported yet. The density of D_2 is relatively low so that its annihilation process (stage III) may have been hidden by the precipitation of iron (stage IV) in previous experiments. The present results indicate some similar features of D_2 as D_1 ; D_2 does not have any relations to iron, oxygen, carbon, and copper. Moreover, the heat-treatment time at high temperatures does not affect the D_2 density as well. However, contrary to D_1 , the density of D_2 depends upon the heat-treatment temperature. The origin of D_2 is still unknown.

Since D_1 can be annihilated by prolonged annealing at room temperature, it may not be so harmful to device characteristics. On the other hand, D_2 may be more harmful to the long-time reliability of electronic devices. This defect should be removed by proper annealing.

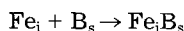
Application to iron gettering.—Iron has been known as a hard impurity to remove by gettering (39). Our results

(Fig. 2 and 6) show that iron contamination can be reduced by heating samples in an oxygen atmosphere. This effect may be explained by two mechanisms. First, the SiO₂ layer may act as a mask to prevent the indiffusion of iron atoms, if they hardly diffuse through the layer. Second, iron has been reported to accumulate at the Si-SiO₂ interface (40-42). This may also prevent iron from indiffusing into the bulk of silicon. However, these effects may not be favored by MOS devices because of possible degradation of characteristics of the SiO₂ layer and the interface. Figure 5 suggests that oxygen precipitates and dislocation loops provide precipitation sites for Fe_i. If this is the case, we can propose an effective gettering method by utilizing the so-called intrinsic gettering (IG) technique. This method consists of the annealing of IG wafers around 300°C, by which we can remove iron atoms from active regions of devices to precipitate them at oxygen precipitates formed inside the bulk of silicon by IG technique. This temperature is so low that so-called thermal donors are not generated and neither are device characteristics destroyed. Therefore, the above heat-treatment may be suitable as the final step in the device fabrication process.

Summary

The effects of heat-treatments around 1000°C and subsequent annealing on the electrical properties of boron-doped silicon have been studied by electrical conductivity, Hall effect, and DLTS measurements. The heat-treatments always induced conductivities at 25°C and 77 K to decrease, indicating the introduction of net densities of donor-type defects. Four recovery stages, stages I-IV, were observed on isochronal annealing up to 400°C, until which conductivities returned to their as-grown values. Conductivity changes in these stages can be explained as described below by the reactions of interstitial iron (Fe_i), its pair (Fe_iB_s) with substitutional boron (B_s), and two unknown donors (D₁, D₂).

stage I (25°-100°C): D₁ → sink,



stage II (100°-150°C): Fe_iB_s → Fe_i + B_s

stage III (200°-250°C): D₂ → sink

stage IV (250°-350°C): Fe_i → precipitation

Heat-treatments in an oxygen atmosphere greatly reduced the introduction of Fe_i and Fe_iB_s in comparison with an argon atmosphere, and mainly introduced D₁ and D₂ donors. They may have their energy levels in the upper half of the bandgap. The density of D₂ was dependent on the heat-treatment temperature, while that of D₁ showed almost no dependence. In stage I, D₁ was annihilated by first-order kinetics with activation energy of 0.8 eV. The present results indicate that D₁ and D₂ have no relations to iron, copper, oxygen, nor carbon. Although their origins are still unidentified, they may be some interstitial impurities. In stage IV, Fe_i is suggested to precipitate at oxygen precipitates and dislocation loops formed by high-temperature heat-treatments. As to the application to iron gettering in the device fabrication process, it is proposed that annealing around 300°C is most suitable as the final heat-treatment step to remove iron and related defects from active regions of devices.

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