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## **Hole Traps Produced by High-Temperature Heat Treatments of Silicon above 1300 °C**

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Heat treatments at high temperatures introduce various defects and impurities into silicon crystals. Most of them are electrically active, and affect the electrical properties of crystals. A number of investigations have been made for a long time on such quenched-in defects in silicon [1 to 9]. However, in most of those investigations, the heat treatment temperature was below 1200 °C, so that the effects of heat treatments above this temperature are not sufficiently studied yet. However, such high-temperature heat treatments may be important to homogenize the distribution of doping impurities and interstitial oxygen atoms and also to destroy any defect clusters and impurity precipitates formed during the crystal grow. This note presents experimental results of properties of deep-level defects produced into silicon by high-temperature heat treatments above 1300 °C. The origins of defects are discussed.

We have used a Czochralski-grown (CZ) silicon crystal doped with boron of  $1.2 \times 10^{15} \text{ cm}^{-3}$ . Its interstitial oxygen content was  $1.2 \times 10^{18} \text{ cm}^{-3}$ . Rod samples with dimensions of  $1 \times 2 \times 15 \text{ mm}^3$  were chemically etched and cleaned. They were heated at 1350 °C for 1 h in flowing argon or oxygen gas, and were quenched into water. Quenched samples were etched and titanium was evaporated to form Schottky junctions. Capacitance deep-level transient spectroscopy (DLTS) was applied to study the trap levels of quenched-in defects [10].

Fig. 1 shows the effects of isochronal annealing on DLTS spectra for a sample which was heated at 1350 °C in an argon atmosphere and quenched. In the as-quenched state (curve 1), two hole traps, H1(0.44) and H2(0.28), were observed. Their densities and hole capture cross sections were  $1 \times 10^{13} \text{ cm}^{-3}$  and  $5 \times 10^{-16} \text{ cm}^2$  for H1 trap, and  $3 \times 10^{13} \text{ cm}^{-3}$  and  $3 \times 10^{-17} \text{ cm}^2$  for H2 trap. The results of our experiments on Poole-Frenkel effect [11] indicated no peak shift occurring with increasing pulse voltage. If these trap levels have the acceptor character, their peak positions should be shifted toward low temperatures by increasing pulse voltage because of the lowering of ionization energies for the emission of a positive hole from a negatively charged acceptor [12]. Therefore, our results indicate the donor character of these two traps. Annealing at temperatures 50 to 100 °C caused

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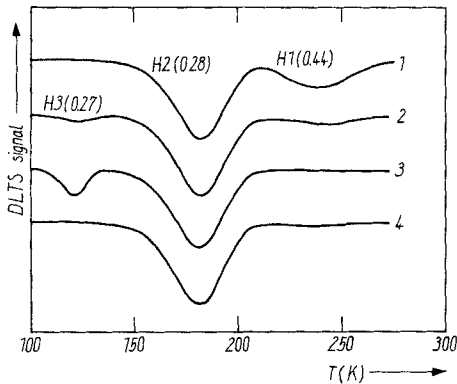


Fig. 1. Effects of isochronal annealing on DLTS spectra. The sample was heated for 1 h in the argon atmosphere at 1350 °C and quenched (curve 1) and then was annealed for 30 min at various temperatures, (2) 250, (3) 300, and (4) 350 °C. Figures in parentheses of H1-H3 traps represent their level ionization energies in eV with respect to the top of the valence band. Both of reverse bias and pulse voltages were 5 V. The emission rate window was set at  $57.1 \text{ s}^{-1}$ .

H1 trap to disappear once, and the subsequent annealing at 100 to 150 °C induced it to appear again, and the final annealing above 200 °C annihilated it completely. This behavior is characteristic of the interstitial iron,  $\text{Fe}_i$ , in silicon, and has been understood as the formation of iron-boron pairs at 50 to 100 °C, the dissociation of them at 100 to 150 °C and the precipitation of  $\text{Fe}_i$  above 200 °C [13 to 18]. Moreover, other characteristics of H1 trap such as energy level, hole capture cross section and donor character are also consistent with the properties of  $\text{Fe}_i$ . Therefore, we have come to the conclusion that H1 trap can be identified as  $\text{Fe}_i$  contaminating silicon crystals during heat treatments. On the other hand, H2 trap was not affected by annealing up to 400 °C, indicating that it is due to a rather stable defect.

Annealing above 200 °C not only annihilated  $\text{Fe}_i$  but induced a new trap, H3(0.27) (curves 2 and 3 in Fig. 1). Its hole capture cross section was large,  $6 \times 10^{-14} \text{ cm}^2$ , and it did exhibit the Poole-Frenkel peak shift, suggesting its acceptor character. Though its ionization energy was 0.25 eV under a reverse bias of 5 V, its zero-electric field value was 0.27 eV, so that it has been denoted as H3(0.27). This trap as well as the H2 trap was produced only by high-temperature heat treatments above 1300 °C. Its annealing behavior was studied in more detail. The results are shown in Fig. 2, where the density of H3 trap together with that of H1 trap are plotted versus the annealing temperature. The effects of the atmosphere ( $\text{Ar}$  or  $\text{O}_2$ ) during the high-temperature heat treatments are also shown. The density of H1, or  $\text{Fe}_i$ , produced by heat treatments in an argon atmosphere was much higher than that for an oxygen atmosphere. This may be ascribed to the  $\text{SiO}_2$  layer preventing the indiffusion of iron atoms from the outside of samples, or arise from the gettering of iron atoms due to their accumulation of the Si-SiO<sub>2</sub> interface [19]. The density of the H3 trap increases between 200 and 300 °C, attains the maximum around 300 °C, and finally decreases above this temperature. It is noticed that its maximum density and the

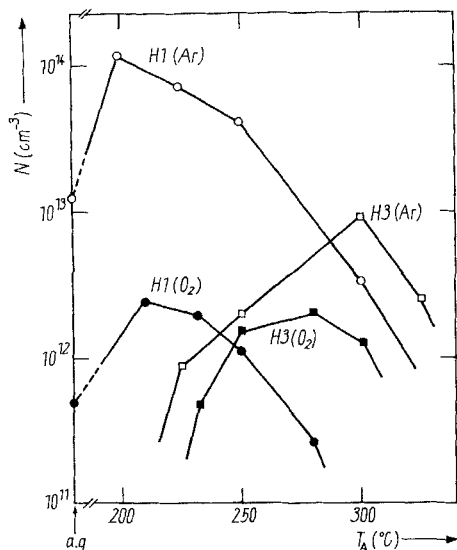


Fig. 2. Isochronal annealing behavior of H1 and H3 traps for samples heat-treated at 1350 °C in an argon or oxygen atmosphere. The trap density,  $N$ , is plotted against the annealing temperature,  $T_A$ , where samples were annealed for 10 min. Circles on the vertical axis represent as-quenched (a.q.) densities of H1 trap

temperature at which it is reached are higher for the argon atmosphere than for the oxygen one.

Chantre et al. /6/ found a hole trap having an acceptor level at  $E_v + 0.28$  eV, and attributed it to the chromium-boron pair. This pair was formed upon annealing at room temperature, and was

annihilated by its dissociation around 100 °C. The trap of Chantre et al., therefore, cannot be identical with the H3 trap, whose formation and dissociation temperatures are much higher. Fig. 2 shows that the density of H3 trap has some correlations with that of  $Fe_i$ ; that is, both densities are lower in samples heat-treated in the oxygen atmosphere, and the formation of H3 trap is associated with the annihilation of  $Fe_i$ . Therefore, we tentatively ascribe H3 trap to an iron-related metastable defect formed during the iron precipitation above 200 °C. Iron atoms may be trapped at some unknown defects or impurities introduced by high-temperature heat treatments to form H3 traps before reaching their precipitation sites. These complexes are not stable around 300 °C, so that they tend to dissociate and emit iron atoms, which are finally annihilated by the precipitation.

In summary, three traps, H1(0.44), H2(0.28), and H3(0.27), were found in boron-doped CZ silicon heat-treated at 1350 °C. H1 trap is identified as the interstitial iron acting as a donor. H2 trap is a donor defect stable up to 400 °C. H3 trap was formed around 250 °C, and was annihilated above 300 °C. This trap acts as an acceptor, and is tentatively ascribed to an iron-related metastable defect formed during the iron precipitation.

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#### References

- /1/ G. BEMSKI and C. A. DIAS, J. appl. Phys. **35**, 2983 (1964).
- /2/ L. ELSTNER and W. KAMPRATH, phys. stat. sol. **22**, 541 (1967).
- /3/ M.L. SWANSON, phys. stat. sol. **33**, 721 (1969).

- /4/ W. LESKOSCHEK, H. FEICHTINGER, and G. VIDRICH,  
phys. stat. sol. (a) 20, 601 (1973).
- /5/ H. FEICHTINGER, A. GSCHWANDTNER, and J. WATTL,  
phys. stat. sol. (a) 53, K71 (1979).
- /6/ A. CHANTRE, M. KECHOUANE, and D. BOIS, in:  
Defects in Semiconductors, Vol. II,  
Ed. S. MAHAJAN and J.W. CORBETT, North-Holland,  
New York 1983 (p. 547).
- /7/ K. NAKASHIMA, Japan. J. appl. Phys. 24, 1018 (1985).
- /8/ D.V. LANG, J. appl. Phys. 45, 3023 (1974).
- /9/ J. FRENKEL, Phys. Rev. 54, 647 (1938).
- /10/ L.C. KIMERLING and J.L. BENTON, Appl. Phys. Letters 39, 410 (1981).
- /11/ K. GRAFF and H. PIEPER, J. Electrochem. Soc. 128, 669 (1981).
- /12/ H. LEMKE, phys. stat. sol. (a) 64, 215 (1981).
- /13/ K. WUNSTEL and P. WAGNER, Solid State Commun. 40, 797 (1981).
- /14/ K. WUNSTEL and P. WAGNER, Appl. Phys. A 27, 207 (1982).
- /15/ L.C. KIMERLING and J.L. BENTON, Physica 116B, 297 (1983).
- /16/ S.D. BROTHERTON, P. BRADLEY, and A. GILL,  
J. appl. Phys. 57, 1941 (1985).
- /17/ K. HONDA, T. NAKANISHI, A. OHSAWA, and N. TOYOKURA,  
Proc. Conf. Microscopy of Semiconducting Materials 1987,  
Inst. Phys. Conf. Ser. No. 87, London 1987 (p. 463).
- /18/ Y. KAMIURA, F. HASHIMOTO, and M. IWAMI,  
Appl. Phys. Letters 53, 1711 (1988).
- /19/ Y. KAMIURA, F. HASHIMOTO, and M. IWAMI,  
Appl. Surf. Sci. 41/42, 447 (1989).

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