A quenched-in defect in boron-doped silicon[a)]

J. D. Gerson, L. J. Cheng, and J. W. Corbett

The Institute for the Study of Defects in Solids, Department of Physics, State University of New York at Albany, Albany, New York 12222

(Received 6 June 1977; accepted for publication 23 June 1977)

We observed a majority-carrier trapping level at $E_v + 0.45$ eV in boron-doped silicon with a wide range of resistivities after being quenched from 900 to 1200°C. The carrier capture cross section was measured to be 4×10^{-18} cm^2. The activation energy for migration and defect formation energy were found to be 0.76 ± 0.05 and 2.8 ± 04 eV, respectively, consistent with that of the interstitial iron in silicon. However, we found a marked boron dependence, indicating that the nature of the defect processes may be complex.

PACS numbers: 71.55.Fr, 72.20.Jv, 81.40.Rs, 61.70.−r

Thermal processes such as fast cooling or quenching create defects in silicon crystals. However, the nature of these defects is rarely understood, even though manufacturers have adopted suitable processes, such as slow cooling, to avoid the influence of these defects on devices. Silicon crystals currently available contain many impurities, as demonstrated by chemical and physical analysis.[1] Most of them are electrically inactive by nature or in precipitates in the crystal. Impurities of the latter type are known to be active when individually dispersed in the crystal and, presumably, are in the form of precipitates because of extremely low solubilities at room temperature and relatively high mobilities at low temperatures. In principle, these impurities can become active if the sample is heated to an elevated temperature, allowing them to be dispersed into the crystal, and then quenched to room temperature, preventing the precipitation. This has been demonstrated by a recent experiment of Lee *et al.*[2] who identified an EPR spectrum in quenched silicon to be the interstitial iron (Fe°). The iron is present in as-grown silicon and moves to the T_d interstitial site upon heat treatment. In this paper, we discuss the observation of a majority-carrier trapping level in p-type silicon, by deep-level transient spectroscopy (DLTS),[3] which correlates with the interstitial iron. In addition, the formation and annealing characteristics are found to be of a complex nature involving boron.

We used commercially available boron-doped polished wafers of floating zone (FZ) crystals of 1-, 4-, 10-, and 100-Ω cm resistivities and Czochralski (CZ) crystals of 2- and 10-Ω cm resistivities. They were heated in an atmosphere of nitrogen at a temperature in the range 900—1200 °C for a period of 1 h and then cooled to room temperature at a cooling rate of $\sim10^3$ °C/min. The material of the samples within 10 to 20 μm from the surface was etched off in 3 : 1 HNO_3-HF solution to avoid surface defects. These were the same procedures used in the EPR observations.[2] In order to study the samples using DLTS, Al or Ti dots of 1 mm diameter 5000 Å thick, were vacuum evaporated onto the polished surface of the samples to form Schottky diodes. The samples were investigated immediately after the formation of the Schottky barrier or were stored at ~ − 20 °C for later measurements.

Figure 1 shows a typical spectrum from a sample of 10-Ω cm (FZ) silicon quenched from 1100 °C. Two defect energy levels located at $E_v + 0.45$ and $E_v + 0.48$ eV were found. The $E_v + 0.45$-eV level is the major defect consistently appearing in all the samples (except those of 1 Ω cm) and is the subject of this paper. No defect energy levels were observed in any untreated samples or samples which had been treated at high temperature for 1 h and then cooled down slowly to room temperature overnight. The lack of detectable defects in slowly cooled samples indicates that our samples were not "contaminated" during the thermal processing.

Majority-carrier capture cross sections for the $E_v + 0.45$-eV and $E_v + 0.48$-eV levels were measured to be 4×10^{-18} and 2×10^{-16} cm^2, respectively, indicating that both levels are neutral charge states when the Fermi level is above them. The nonsequential ordering of the appearance of the two levels with temperature could be explained by the difference in their respective capture cross section.

From the measurements of relative defect production rate as a function of heat-treatment temperature in 10-Ω cm samples, we found the activation energy for the formation of the $E_v + 0.45$-eV level to be 2.8 ± 0.04 eV which is comparable with the value obtained by Lee *et al.*[2] and Swanson[4] from his quenching experiments.

Isothermal annealing experiments at 160, 180, and

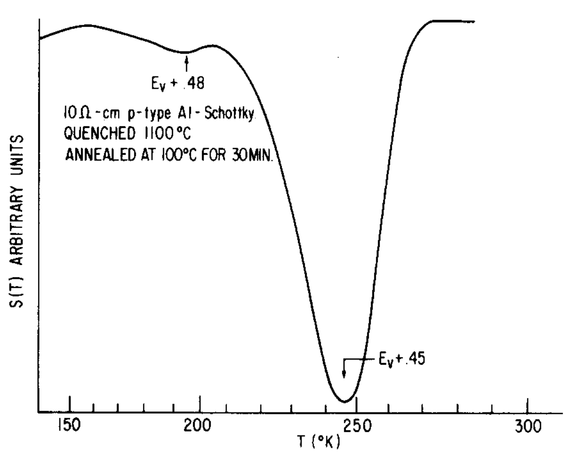

FIG. 1. Typical DLTS spectrum of 10-Ω cm p-type B-doped silicon after quenched from 1100°C and then annealed at 100°C for 30 min.

a)Supported in part by the Office of Naval Research under Contract No. N00014-75-C-0919.

205 °C done on 10-Ω cm (FZ) samples revealed the activation energy for the disappearance of the $E_v + 0.45$-eV level to be $E_m = 0.76 \pm 0.05$ eV with a frequency factor of ~10^5 sec^{-1} which is consistent with the results of Lee *et al.*[2] and Swanson.[4]

The $E_v + 0.45$-eV level must arise from a characteristic defect produced during the thermal treatment, since the level has not been observed in irradiated *p*-type silicon.[5,6] The location of the level is in reasonable agreement with that of a level reported by Collins and Carlson[7] who observed an $E_v + 0.40$-eV level in quenched iron-doped silicon using electrical and photoconductivity measurements. Based on the experimental data available, the correlation of our result on the $E_v + 0.45$-eV level to the interstitial iron reported by Lee *et al.*[2] is reasonably good.

Isochronal annealing studies show that the $E_v + 0.45$-eV level annealing temperature varies as a function of boron. The annealing temperature for 100 Ω cm (FZ) and 10 Ω cm (FZ) was seen to be 350 and 275 °C, respectively. Assuming the dependence of the disappearance of the level with respect to boron concentration to be first order (such as a simple pairing mechanism suggested by Collins and Carlson[7]), the predicted value for 2 Ω cm should be ~150 °C. However, for 2 Ω cm (CZ), the annealing temperature was observed to be 80 °C. This indicates that the boron effect is complex. The failure to observe the $E_v + 0.45$-eV level in 1 Ω cm (FZ) is consistent with the rest of our data, because the defect is expected to anneal out around room temperature. In addition, the intensity of the level in 10-Ω cm (FZ) samples increased markedly upon annealing around 50–100 °C. Furthermore, the $E_v + 0.45$-eV level was not observed in aluminum-doped samples [1–4 Ω cm (FZ)] quenched from high temperatures (1000–1200 °C). Either iron was not present at the time of manufacture or aluminum also affects the appearance of the electrical activity of iron. Obviously, the behavior of iron as well as of other impurities is very complex. Consequently, more intensive studies are needed before a complete and clear picture can appear.

[1] A. Mayer, Solid State Technol. **15**, 1138 (1972).
[2] Y. H. Lee, R. L. Kleinhenz, and J. W. Corbett, Appl. Phys. Lett. **31**, 142 (1977).
[3] D. V. Lang, J. Appl. Phys. **45**, 7 (1974).
[4] M. L. Swanson, Phys. Status Solidi **33**, 721 (1969).
[5] Y. H. Lee, L. J. Cheng, J. D. Gerson, P. M. Mooney, and J. W. Corbett, Solid State Commun. **21**, 109 (1977).
[6] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett, Phys. Rev. B **15**, 3836 (1977).
[7] C. B. Collins and R. O. Carlson, Phys. Rev. **108**, 6 (1957).