

Determination of boron and phosphorus concentration in silicon by photoluminescence analysis

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A novel method to obtain boron and phosphorus concentration in silicon crystals by photoluminescence (PL) analysis at liquid-helium temperature is reported. The intensity ratio between intrinsic and extrinsic components in the PL spectra reflects the impurity concentration. The tentative calibration curves for boron and phosphorus for our method are obtained by comparison with the results of the resistivity measurement. The detection limit of this method is estimated to be as low as $1 \times 10^{11} \text{ cm}^{-3}$ for boron and $5 \times 10^{11} \text{ cm}^{-3}$ for phosphorus. The degree of compensation can be estimated also. The PL method makes it possible to determine nondestructively the concentration of small amount of impurities in a small region of a specimen.

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The recent technical advance in silicon devices, such as high-power devices, detectors and LSI, pushes forward the improvement of the crystalline quality and the purification of silicon crystals. Under these circumstances the characterization of silicon crystals, the impurity analysis in particular, is regarded as of major importance nowadays. However, there have been few methods for the analyses of a small amount of impurities and compensating impurities in silicon.

The net carrier concentration, $|N_D - N_A|$, (N_D : donor concentration, N_A : acceptor concentration), is usually determined from the conventional resistivity measurement with the aid of the Irvin curve.¹ However, we cannot determine the species of the impurities and a compensation ratio by this method. A compensation ratio can be calculated from the temperature dependence of the Hall coefficient,² although this method contains errors in some cases and has difficulty in making Ohmic contacts for high-resistivity specimens. The infrared spectroscopic method works satisfactorily to determine the total concentration of both B and P.³ This method can be applied to specimens with $\rho > 50 \text{ } \Omega \text{ cm}$, and the detection limit of this method is as low as $5 \times 10^{11} \text{ cm}^{-3}$. However, the light incident and exit surfaces of the specimen must be optically flat and parallel. Moreover, the thickness of the specimen must be increased for the detection of the low concentration of impurities (e.g., $t = 10 \text{ mm}$ for $\rho > 500 \text{ } \Omega \text{ cm}$).

The photoluminescence (PL) technique can be successfully applied to the characterization of silicon crystals as a powerful means for the analysis of shallow impurities.^{4,5} The PL method makes it possible to detect nondestructively a small amount of impurities in a small region of a specimen. Furthermore the size and shape of the specimen is not restricted (e.g., a small piece of a wafer of a few millimeters square is sufficient for the measurement).

In this paper, we show the relationship between the PL spectra and the resistivity. This relationship is useful for the determination of the impurity concentration. We have intentionally chosen weakly compensated specimens in this work. The degree of compensation has been checked from the PL intensity ratio between

compensating impurity and major impurity components.⁵

The specimens used for the experiment are silicon crystals commercially grown by the float-zone, Czochralski, or pedestal method, and ultrahigh pure silicon crystals specially grown by the float-zone method. The PL measurements were performed on the etched surface of the specimen which was immersed in liquid helium. The luminescence excited by the 514.5-nm line from an Ar ion laser was analyzed with a Spex 1701 grating monochromator and detected by a cooled RCA 7102 photomultiplier. The laser beam diameter was about 1 mm and the incident power was kept constant at 150 mW. In our experimental system, special precautions were taken to adjust precisely the optical path and to collect efficiently the luminescence light, which enabled us to obtain highly resolved spectra.

Figure 1 shows the PL spectra of P-doped silicon crystals at liquid-helium temperature as a function of a doping level. The resistivity of the specimen for Figs. 1(a), 1(b), and 1(c) are ~ 150 , ~ 100 , and $\sim 15 \text{ } \Omega \text{ cm}$, respectively. The $N_D - N_A$ values for these three specimens are estimated to be $\sim 3 \times 10^{13}$, $\sim 5 \times 10^{13}$, and $\sim 3 \times 10^{14} \text{ cm}^{-3}$, respectively, from the Irvin curve. The origin of each emission line was determined from the coincidence of the spectral positions of our results with those defined by Dean *et al.*,⁶ Kosai and Gershenson,⁷ and Hammond *et al.*⁸ Each line is labeled as follows: *I* denotes the intrinsic luminescence, *B* and *P* the extrinsic luminescence associated with boron and phosphorus, respectively; the subscript indicates the phonon emitted; and the notations in parentheses, FE, EHL, BE, b_n , and $2e$ denote the free exciton, electron-hole liquid,⁸ bound exciton, bound multiexciton complex,^{7,9} and two-electron transition,⁶ respectively.

The characteristic $P_{NF}(b_n)$ and $P_{TO}(b_n)$ series were clearly observed in the spectra. The *B* components, such as $B_{TO}(\text{BE})$, were always detected for all specimens, which suggests silicon crystals always contain base boron.⁴ Judging from the intensity of the *B* components, the degree of compensation of the specimens for Fig. 1 is relatively low. (As for the case of a highly compensated specimen, see Fig. 2 of Ref. 5.)

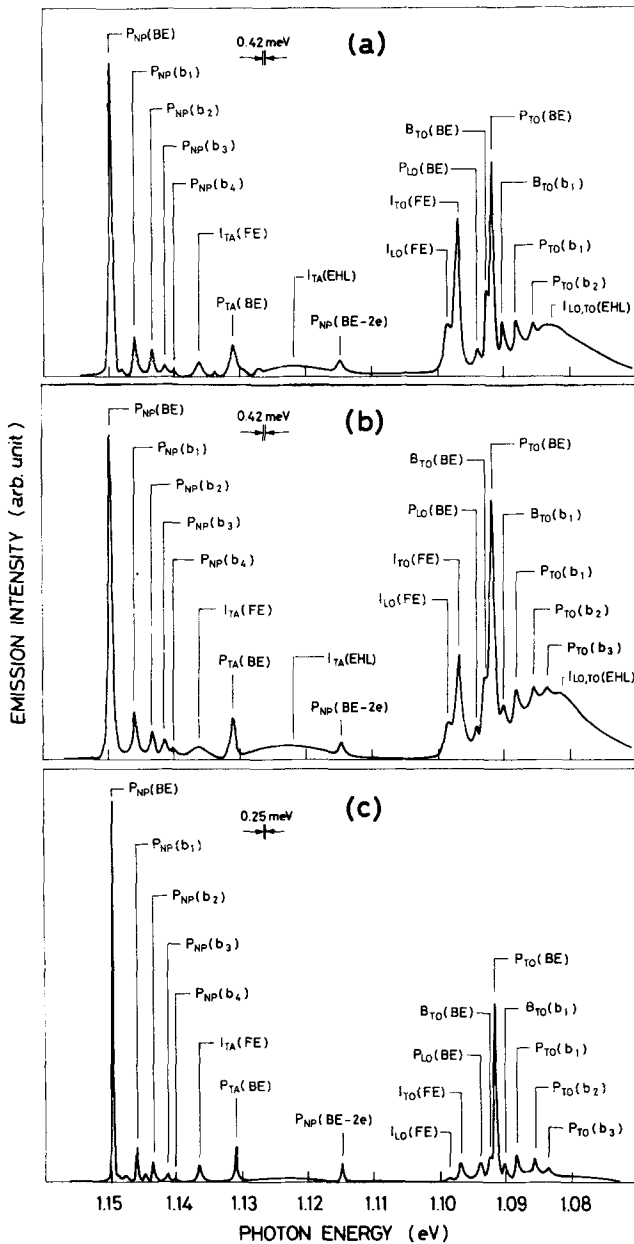


FIG. 1. PL spectra of P-doped Si at liquid-helium temperature as a function of a doping level. (a) $\sim 150 \Omega \text{ cm}$, $\sim 3 \times 10^{13} \text{ cm}^{-3}$; (b) $\sim 100 \Omega \text{ cm}$, $\sim 5 \times 10^{13} \text{ cm}^{-3}$; (c) $\sim 15 \Omega \text{ cm}$, $\sim 3 \times 10^{14} \text{ cm}^{-3}$. The photoresponse of the measurement system is not calibrated. The notation is explained in the text.

The intensity ratio of the P components to the intrinsic components increases with decreasing resistivity, namely, with increasing P concentration. In order to investigate the relationship between this ratio and the resistivity, we plotted $P_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ against ρ , or $N_D - N_A$, on a log-log scale as shown in Fig. 2. Dots and circles in Fig. 2 show the data for the weakly compensated specimens and those for highly compensated specimens, respectively. As for weakly compensated specimens, the data points give a straight line. In these specimens, $N_D - N_A$ is nearly equal to N_D (namely, the P concentration). Therefore, we can use this line as a calibration curve for determining the P concentration from the PL intensity ratio. The $P_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ value reflects the P concentration also for highly com-

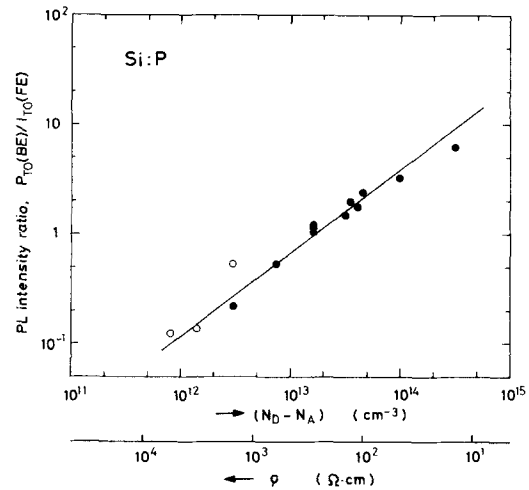


FIG. 2. Calibration curve for the PL method for P-doped Si. The PL intensity ratio between P and intrinsic components, $P_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ is plotted against ρ , or $N_D - N_A$. ●, weakly compensated specimen; ○, highly compensated specimen.

pensated specimens. Since N_A is no longer neglected in these specimens, the data points shift toward the left-hand side. The detection limit of this method is estimated to be as low as $5 \times 10^{11} \text{ cm}^{-3}$.

As for B in silicon, the similar relationship was obtained. In Fig. 3, $B_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ is plotted against ρ , or $N_D - N_A$, on a log-log scale. (As to the PL spectra of B-doped specimens, see Figs. 1 and 2 in Ref. 4.) Dots and circles in Fig. 3 show the data for weakly and highly compensated specimens, respectively. The detection limit for B is estimated to be as low as $1 \times 10^{11} \text{ cm}^{-3}$.

Since excitons responsible for the BE and b_n transitions are bound to neutral impurities, both P and B centers should be neutral under our experimental excitation condition (150 mW). In order to check whether the excitation intensity is sufficient for the neutralization

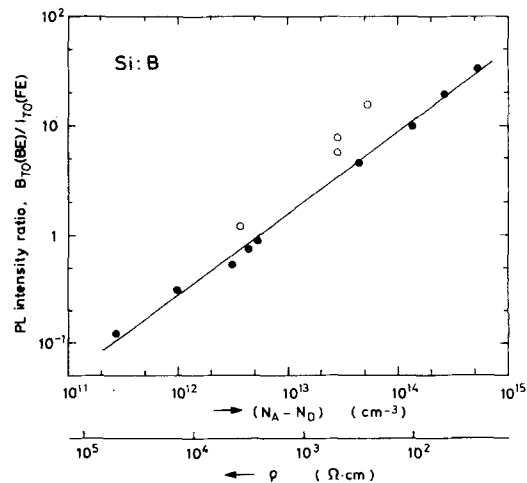


FIG. 3. Calibration curve for the PL method for B-doped Si. The PL intensity ratio of $B_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ is plotted against ρ , or $N_A - N_D$. ●, weakly compensated specimen; ○, highly compensated specimen.

or not, we performed the following experiments. (i) The PL analyses of the B-doped specimen ($\rho \sim 300 \Omega \text{ cm}$) were made under a wide variation of excitation intensity (2.3–300 mW). (ii) The PL analyses of three B-doped specimens ($\rho \sim 50000, 300, 50 \Omega \text{ cm}$) and three P-doped specimens ($\rho \sim 3500, 310, 12 \Omega \text{ cm}$) were made under 75- and 300-mW-excitation conditions. For all cases, no significant spectral changes due to the change of the excitation intensity were observed. The results of (i) showed that the *P* components were always detected besides the main *B* components. The results of (ii) showed that the deviations of the PL intensity ratio of $P_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ or $B_{\text{TO}}(\text{BE})/I_{\text{TO}}(\text{FE})$ due to the change of the excitation condition were within the experimental errors in most cases. The maximum deviation of the ratio was less than $\pm 30\%$ in comparison with the ratio under the 150-mW-excitation condition. These results indicate that both donor and acceptor levels are neutralized under the 150-mW-excitation condition.

In order to confirm the validity of the calibration curves, we have analyzed more than 100 specimens by the PL method. The data points for almost all those specimens lay just on, or very close to, the calibration curves. The relationship between the PL intensity ratio and the resistivity was also investigated under 75- and 300-mW-excitation conditions. No systematic deviations from Fig. 2 or 3 were recognized under those conditions. Even for the data points which deviated most from Fig. 2 or 3, the error in the impurity concentration was estimated to be less than a factor of 2. The error of a factor of 2 in the impurity concentration (10^{11} – 10^{15} cm^{-3}) is not so serious for practical purposes.

In this method we pay attention not to the intensity but to the intensity ratio of the PL spectral lines. This is a great advantage of this method because this intensity ratio does not depend very much on the differences in the vendors, the crystal growth method, and the surface condition of the crystals.

We can roughly estimate the compensation ratio by measuring both *P* and *B* concentrations from Figs. 2 and 3. However, the measured concentration of compensating impurities seems to contain some errors because the recombination processes associated with

B and those associated with *P* are not independent. The intensity ratio among the intrinsic, *P*, and *B* components [for example, $I_{\text{TO}}(\text{FE}) : P_{\text{TO}}(\text{BE}) : B_{\text{TO}}(\text{BE})$] may possibly reflect the degree of compensation more precisely. The proper relationship between this intensity ratio and the impurity concentrations may be acquired from the absolute measurement of the impurity concentrations by other analytical techniques, such as the activation analysis. Further discussions on this subject together with the physical background of our method will be described elsewhere.

In conclusion, we report a novel method to obtain *B* and *P* concentrations in silicon crystals from the PL analysis at liquid-helium temperature. The tentative calibration curves for *B* and *P* for the PL method have been obtained by comparison with the results of the resistivity measurement. The degree of compensation can be estimated by the method. This method is applicable to the investigation of specimens with $\rho > 10 \Omega \text{ cm}$. The detection limit is estimated to be as low as $1 \times 10^{11} \text{ cm}^{-3}$ for *B* and $5 \times 10^{11} \text{ cm}^{-3}$ for *P* at present.

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