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Determination of shallow minority-acceptor concentration in multiply doped silicon

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A method is presented, based on photothermal ionization spectroscopy (PTIS), for determining the shallow minority-acceptor concentration in multiply doped silicon, over the concentration range $10^{13}/\text{cm}^3$ – $10^{15}/\text{cm}^3$. The method is an extension of a model developed previously for the PTIS response in a multiply doped semiconductor, which accounts for the experimentally observed change in signature, from negative to positive, of the lower-energy lines of the deeper acceptor as the temperature is increased. It uses a calculated curve of the dependence on the shallow-acceptor concentration of the temperature at which the change in signature occurs, for a given line, and compares it to a determination of this temperature from actual spectra for the sample. The method is applied to the determination of boron concentration in the Si(Ga,B) system.

The doping of silicon with shallow acceptors, e.g., Ga, is frequently employed in the utilization of silicon-based materials as infrared detectors. In such applications the determination of dopant concentration is important and various techniques have been used, including those based on Hall-effect and photoabsorption measurements.^{1,2} Such techniques work reasonably well when only one acceptor is dominant but are more difficult to apply in determining the presence of a second acceptor, especially when it is close in energy to the first acceptor or present in low concentrations, e.g., B in Si(Ga). We present here a method for determining the minority-acceptor concentration based on photothermal ionization spectroscopy (PTIS), which may be useful over a range of concentrations from $10^{13}/\text{cm}^3$ to $10^{15}/\text{cm}^3$.

Our method is based on a model for the PTIS response in a multiply doped semiconductor which we developed previously.³ In that work the model was applied to Si(In,Al) and Si(Ga,B) to show that the presence of a shallower acceptor (Al or B) affects the signature of a given In or Ga excited state line. As observed experimentally, the lower-energy In or Ga lines go from negative to positive as the temperature is increased in multiply doped samples. This effect arises from the increase in the photothermal ionization probability with temperature and occurs for those lines which appear against the continuum background of the shallower acceptor (B or Al). For this work our PTIS model was extended to study how varying the boron concentration affects the temperature at which several gallium lines change signature. The results were used to determine the shallow

FIG. 1. Photothermal ionization spectrum of a doubly doped Si(Ga,B) sample, showing a gallium line 1 response which is negative at 15 K but has become positive by 25 K. $[\text{Ga}] = 6.5 \times 10^{16}/\text{cm}^3$, $[\text{B}] = 5.5 \times 10^{13}/\text{cm}^3$, donor concentration $1.7 \times 10^{13}/\text{cm}^3$.

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FIG. 2. Calculated boron concentration in Si(Ga,B) vs temperature at which the gallium photothermal ionization resonances change signature. The open circle indicates insufficient high-temperature data to determine the upper limit of uncertainty in T for this line. $[\text{Ga}] = 3.6 \times 10^{16}/\text{cm}^3$.

FIG. 3. "Universal" model curve of boron concentration in Si(Ga,B) vs the scaled temperature, $T' = kT/h\Delta\nu^{(i)}$, at which the gallium resonance changes signature. Data points represent calculations for line 1 (circles), line 3 (triangles), and line 6 (squares); open symbols refer to $[Ga] = 3.6 \times 10^{15}/\text{cm}^3$, closed symbols to $[Ga] = 3.6 \times 10^{16}/\text{cm}^3$.

acceptor concentration. Figure 1 shows the effect experimentally for the gallium line 1 in a Si(Ga,B) sample. Figure 2 shows the boron concentration in Si(Ga,B) calculated in our model versus the temperature at which the gallium excited state line changes signature, for three of the gallium lines. Curves such as those in Fig. 2 can be used to estimate the boron concentration by observing for real spectra the temperature at which a given line changes from negative to positive. For comparison, Fig. 2 includes experimental data

points, with estimated temperature uncertainties, obtained from spectra similar to Fig. 1 for several samples whose boron concentration had been determined by other techniques. The two samples with the lowest boron concentration had a concentration of shallow donors comparable to the boron; our calculated curves would give a lower bound to the boron content in such cases since the curves give the concentration of neutral boron.

The gallium concentration of the samples varied from $3.4 \times 10^{16}/\text{cm}^3$ to $6.5 \times 10^{16}/\text{cm}^3$, while the curves in Fig. 2 are for a single concentration of $3.6 \times 10^{16}/\text{cm}^3$. Additional calculations show, however, that the curves are virtually independent of gallium concentration, at least in the range $10^{15}/\text{cm}^3$ – $10^{17}/\text{cm}^3$. Furthermore, if the temperature is scaled by $h\Delta\nu^{(i)}/k$, i.e., if one used the dimensionless temperature,

$$T' \equiv kT/h\Delta\nu^{(i)}, \quad (1)$$

where $\Delta\nu^{(i)}$ is the frequency difference between the i th line and the photoionization threshold, then the three curves of Fig. 2 essentially coincide and a "universal" curve for the Si(Ga,B) system is obtained, independent of the specific line and of the Ga concentration. This is shown in Fig. 3 for lines 1, 3, and 6 and two Ga concentrations.

Although we have only considered the case of Si(Ga,B) here, we expect that similar results would be obtained for Si(In,Al) and related systems.

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