LITHIUM-BORON ION PAIRING IN SILICON*

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The equilibrium constant of the ion-pairing reaction $\mathrm{Li}^+ + \mathrm{B}^- \leftrightarrow \mathrm{LiB}$ in silicon has been determined by Hall-effect measurements. The result can be expressed as $K = A \times \exp(E/kT)$ with $A = 21$ and $E = 0.39$ eV.

Lithium and boron ions, dissolved in silicon, interact via attractive Coulomb forces. The equilibrium reaction leading to formation of the neutral complex LiB is represented by $\mathrm{Li}^+ + \mathrm{B}^- \leftrightarrow \mathrm{LiB}$. The concentrations of the free ions and the associate are linked by the law of mass action: $K = [\mathrm{LiB}]/[\mathrm{Li}^+][\mathrm{B}^-]$. In this relation the concentrations are usually expressed as fractions of the number of silicon lattice sites $[\mathrm{Si}] = 5 \times 10^{22}\ \mathrm{cm}^{-3}$. The equilibrium constant K has a temperature dependence which is expected to be described by $K = A \exp(E/kT)$. In the past the reaction constant has been determined by two independent methods. Pell[1] measured the effective drift rate of lithium ions in a reverse-biased p-n junction. In his samples $[\mathrm{Li}^+] = [\mathrm{B}^-] = 1.4 \times 10^{17}\ \mathrm{cm}^{-3}$ or $1.5 \times 10^{16}\ \mathrm{cm}^{-3}$. Kröger[2] made an analysis of Pell's results and obtained $A = 19$ and $E = 0.39$ eV. In more recent experiments Spitzer and Waldner[3] measured the infrared absorption due to local vibrational modes associated with B^- and LiB. Their compensated samples contained a total boron and lithium concentration of $2.8 \times 10^{19}\ \mathrm{cm}^{-3}$. The parameters $A = 0.1$ and $E = 0.39$ eV give a best fit to the experimental data. Comparing the results of both methods it is clear that agreement reached for E, the binding energy between ions in a pair, is within experimental accuracy, whereas for the pre-exponential factor A there is a large discrepancy.

As a third essentially different method to determine K we measured the free-carrier concentration over a wide temperature range by the Hall effect. The basic material[4] was float-zoned single-crystalline silicon, p type from boron doping to the level of 1.54×10^{15} atoms/cm^3. The sample, a slice with a thickness of 0.272 mm, is immersed in a bath of liquid tin, containing 1.5 at.% lithium, for 3.5 h at 500°C. In this way a uniform counterdope by indiffusion of 6.22×10^{15} lithium atoms/cm^3 is achieved. To establish equilibrium of the ion-pairing reaction the sample is kept at the desired temperature for at least 7 time constants of the reaction. This is followed by rapid cooling in liquid nitrogen. A series of experiments consisted of Hall-effect measurements after equilibrium was established at (a) 20.2°C, (b) 48.9°C, (c) 0.1°C, (d) 72.8°C, (e) 96.4°C, and (f) 20.2°C, in this order. The final repeat run (f) was done to check reversibility and reproducibility, which turned out to be excellent as shown by the results. Measurements of the Hall effect were performed on the four-leaved clover-shaped sample in the temperature range 25-300 K in a magnetic field of 1.21 MA/m (15.2 kOe). Electron concentrations n were calculated from the Hall coefficient R_H by the relation $|R_\mathrm{H}| = r/ne$. Not doing justice to a tremendous amount of theoretical work,[5] an empirical procedure to determine the Hall factor r was adopted: The Hall factor was set equal to 1.25 at 300 K, given a temperature dependence such as to make n constant above 250 K, and made to approach 1 at the lowest temperatures where high-field conditions may be realized. In Fig. 1 the observed temperature dependence of the electron concentration is given. Our analysis of the variation of n with T is based on the Kohn-Luttinger model of n-type silicon.[6,7] In this model the statistical distribution of electrons between conduction-band, donor, and acceptor states is considered. We assumed the crystal-field splitting of the lithium ground state to be small compared with kT and that higher excited states may be ignored, which leads to

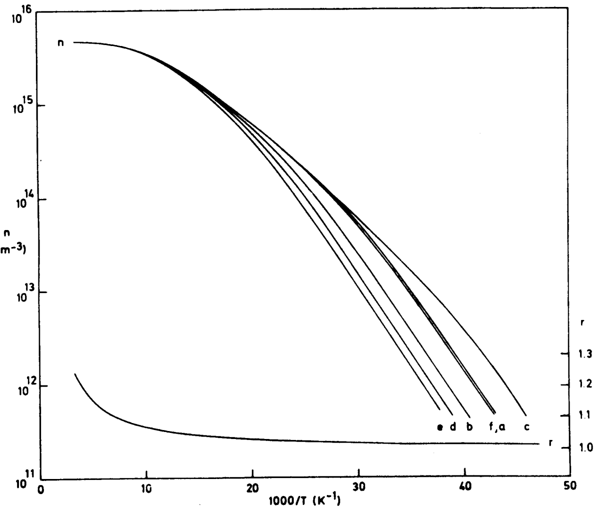

FIG. 1. Temperature dependence of free-electron concentration n after equilibrium was established at various temperatures between 0.1 and 96.4°C. Labeling of curves refers to the text. Our choice for the Hall factor r is also shown.

a degeneracy, including spin, $g=12$. Furthermore we assumed an effective electron mass of $0.33m_e$, a sixfold multiplicity of conduction-band minima, and a temperature-independent ionization energy E_{Li} of the lithium donor states. From the Kohn-Luttinger model one then derives the equality

$$n(n+[\text{B}])/([\text{Li}]-[\text{B}]-n)=4.6\times10^{14}T^{3/2}\times\exp(-E_{\text{Li}}/kT),$$

where [Li] and [B] represent total impurity concentrations, ionized or neutral, expressed in cm^{-3}. On choosing a value for E_{Li} the two concentrations [Li] and [B] are found by least-squares fitting of the theoretical expression to the experimental points. The equilibrium constant is then calculated from

$$K=[\text{Si}](1.54\times10^{15}-[\text{B}])/[\text{Li}][\text{B}].$$

Results for K corresponding to the six experiments (a) to (f) are least-squares adjusted to the relation $K=A\exp(E/kT)$. A best fit, obtained for $E_{\text{Li}}=30$ meV, yields $A=21$ and $E=0.39$ eV. This is illustrated by Fig. 2. Clearly the conclusions of Pell and Kröger are substantiated by our work.

The samples as used by Pell and in our experiments differ from those of Spitzer and Waldner in their much lower impurity concentration. In the heavily doped samples of Spitzer and Waldner the mean distance between boron ions, approximately 30×10^{-8} cm, is less than the range of the electrostatic forces, given by a Coulomb capture radius $R=e^2/4\pi\epsilon kT$, equal to about 50×10^{-8} cm at room temperature. The lithium ions are always in the potential well of the B^- matrix. In the supersaturated samples of Spitzer and Waldner some lithium may have been lost by precipitation. If in the resulting p-type silicon the Fermi level approaches the valence band within a few kT, not all boron will be ionized. The reaction scheme $\text{Li}^+ + \text{B}^- \rightarrow \text{LiB}$ then has to be supplemented with a second equilibrium: $\text{B}^- + h \rightarrow \text{B}$.

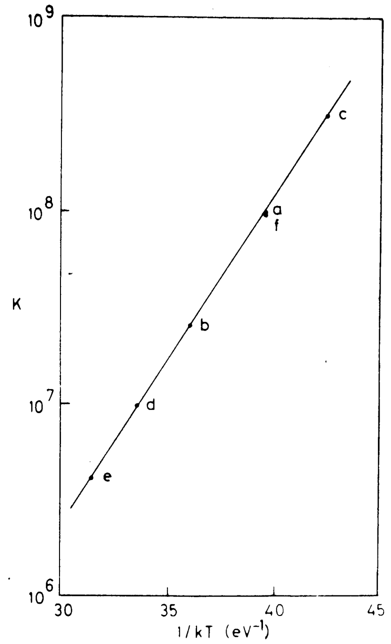

FIG. 2. K vs $1/kT$. Points are experimental results: straight line represents $K=A\exp(E/kT)$ with $A=20.8$ and $E=0.389$ eV.

In our silicon the oxygen content is probably below 10^{14} atoms/cm^3 ensuring that the competing reaction $\text{Li}^+ + \text{O} \rightarrow \text{LiO}^+$ does not need to be considered. Resistivity measurements were performed also and were combined with the Hall-effect data to calculate Hall mobilities. An analysis of the mobilities at low temperatures was made by means of the Brooks-Herring equations. Results obtained this way are less accurate than those derived directly from the Hall effect. Also consistent results were obtained from preliminary measurements made on a p-type sample. In literature the value $E_{\text{Li}}=33$ meV for the ionization energy of the lithium-donor level is generally cited.[8] Our result, $E_{\text{Li}}=30$ meV, is more in line with the value $E_{\text{Li}}=29$ meV based on calculations by the effective-mass theory.[6,9] This makes our assumption of negligibly small donor ground-state splitting more plausible.

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