Determination of the Electrical Properties of Doped Germanium Using The Hall Effect

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ABSTRACT
The Hall effect is demonstrated to determine the electrical properties in a doped germanium sample with an unknown dopant. Measurements of voltage, current and magnetic flux density are used to identify a p-type semiconductor, with a Hall coefficient of $R_H = 7.89 \pm 0.04 \times 10^3$ $\mathrm{cm^3 A^{-1} s^{-1}}$, a Hall mobility of $\mu_H = 2810 \pm 20$ $\mathrm{cm^2 V^{-1} s^{-1}}$, and a carrier density of $n = 7.91 \pm 0.04 \times 10^{14}$ $\mathrm{cm^{-3}}$. Susceptibility to magnetoresistance is shown and the quadratic dependence of magnetic flux density on resistance is verified. Hall voltage is shown to decrease linearly with increasing temperature due to the activation of intrinsic charge carriers, and the polarity is shown to change when the intrinsic concentration exceeds that of extrinsic charge carriers. The band gap energy of undoped germanium is determined to be $E_g = 0.72 \pm 0.01$ eV, where discrepancy with the literature value is thought to be caused by the anisothermal measurement technique used in this experiment.

1 INTRODUCTION

Germanium is a widely used semiconductor in electronics applications. This investigation seeks to characterise the electrical properties of a germanium sample, using the Hall effect.

Semiconductors are conductors characterised by having a full valence band of electrons and an empty conduction band, separated by a band gap [1]. For conduction to occur, electrons in the valence band must first be thermally excited to an energy which is greater than or equal to the band gap energy E_g. In the temperature range at which thermal excitation is possible, the semiconductor is said to be intrinsic, because it is assumed that all of the charge carriers belong to the semiconductor material.

In the intrinsic range, the temperature dependence of electrical conductivity, σ, is dominated by an exponential [1],

$$\sigma = \sigma_0 \exp(-\frac{E_g}{2k_B T}), \tag{1}$$

where k_B is the Boltzmann constant, σ_0 is a constant and T is temperature in Kelvin. More generally, conductivity is defined as the reciprocal of resistivity [2], which gives the geometrical relation

$$\sigma = \frac{lI}{AV_S} \tag{2}$$

where I is current, V_S is the sample voltage, l is the sample length and A is the cross-sectional area. By combining these definitions of conductivity and taking the natural logarithm of Eq. (1),

$$\ln(\sigma) = \ln(\sigma_0) - \frac{E_g}{2k_B T}, \tag{3}$$

an experimental means of determining the band gap energy for a semiconductor is obtained; by measuring voltage as a function of temperature for a fixed current, the gradient, $E_g/k_B T$, can be solved for E_g.

At lower temperatures where thermal excitation is not possible, known as the extrinsic region, conductivity is dependent on impurities within the semiconductor. Impurities are the presence of atoms from other elements and occur naturally in crystals such as silicon and germanium [3]. Deliberately introducing impurities to a crystal is known as doping, and this provides additional donor or acceptor states, depending on the dopant [1]. Donor atoms contribute an electron to the conduction band whereas, acceptor atoms accept an electron from the valence band, freeing up a positively charged hole. This allows for a distinction to be made between semiconductors with either electrons or holes as the majority charge carrier in the extrinsic region, and are called n- or p-type semiconductors, respectively.

The majority charge carrier type and concentration has implications on the electrical properties of the semiconductor. This can be demonstrated in the Hall effect, which is a phenomenon that occurs when an external magnetic field is applied to a current-carrying sample such that, the magnetic flux density, $\vec{B}$, is perpendicular to the drift velocity, $\vec{v}$, of the charge carriers in the sample. Under these conditions, the Lorentz force [2] acts on the charge carriers – perpendicularly to both $\vec{B}$ and $\vec{v}$ – according to the equation

$$\vec{F} = e(\vec{v} \times \vec{B}), \tag{4}$$

where e is the elementary charge. As a result, charge carriers build up on one side of the sample, which creates an electric field and therefore, a measurable potential difference across the sample, known as the Hall voltage V_H. Here the distinction between V_S and V_H should be made clear: the sample voltage is measured along the direction of conventional current whereas, the Hall voltage is measured perpendicular to conventional current (see figure 1). The polarity of V_H for a given positive current depends on the majority charge carrier, which enables the semiconductor type to be determined. For a sample of thickness d, the Hall voltage is given by [3]

$$V_H = \frac{IR_H B}{d} \tag{5}$$

where I is the current through the sample, R_H is the Hall coefficient and B is the magnitude of the magnetic flux density. The Hall coefficient is defined as

$$R_H = \frac{1}{en}, \tag{6}$$

where e is the elementary charge and n is the carrier density: the number of charge carriers per unit volume. Semiconductors typically have lower carrier densities than other conductors [1] and therefore, produce a larger Hall voltage for a given magnetic flux density.

The Hall coefficient is related to the rate at which charge carriers travel through the sample due to the Hall effect, known as the

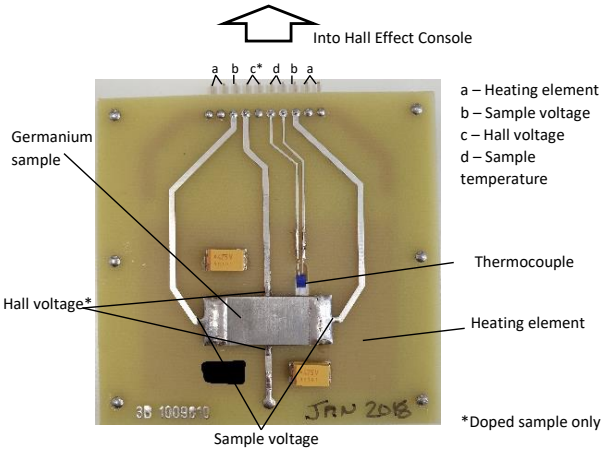

Figure 1. A doped germanium sample fitted to a circuit board with pin connections compatible with a 3B Scientific Hall Effect Console. Components marked with an asterisk are specific to the doped sample only.

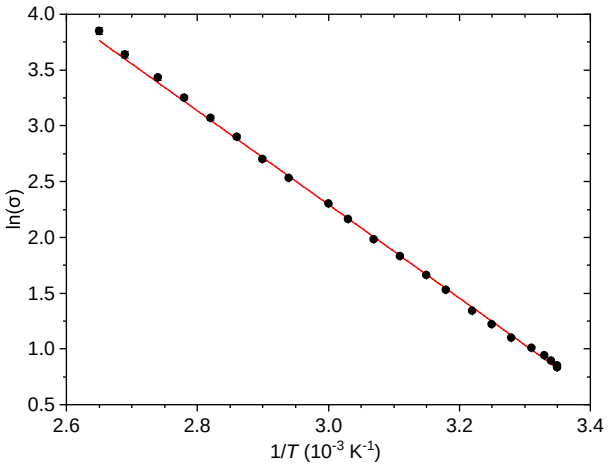

Figure 2. The natural logarithm of conductivity as a function of the reciprocal of temperature, with a linear fit. The data was taken at a fixed current of 4 mA using an undoped germanium sample.

Hall mobility, and is given by the equation

$$\mu_H = R_H \sigma_0. \tag{7}$$

Here σ_0 is the conductivity of the sample in the absence of a magnetic field, and may be written out explicitly using Eq. (2) and Ohm's law to give

$$\sigma_0 = \frac{l}{R_0 A}, \tag{8}$$

where R_0 is the resistance of the sample at room temperature. Therefore, by making measurements of Hall and sample voltage, current, and magnetic flux density, a number of electrical properties can be determined for a semiconductor.

In this paper, the band gap of germanium is determined using an undoped sample, and the Hall effect is observed in a doped germanium sample, from which, the Hall coefficient, carrier density, and Hall mobility are determined. The behaviour of sample voltage under the presence of a magnetic field is investigated, as is the effect of temperature on Hall voltage. Finally, consideration is made to the relevance of the methodologies and results presented, in electrical waste recycling.

2 METHOD

The two germanium samples – one of which had been doped by an unknown impurity – were 20 mm long, 10 mm wide and 1 mm thick, and pre-fitted to circuit boards, as shown in figure 1. The circuit board pin connections were compatible with a 3B Scientific Hall Effect Console, from which measurements of sample current and temperature could be made directly from the in-built display to a precision of 0.1 mA and 0.1 °C. The heating element of each board and the current polarity were also controlled by the console. The console had four output sockets that were used to connect a Thandar TM356 digital multimeter in order to measure sample voltage with a precision of 0.001 V or, in the case of the doped sample, Hall voltage with a precision of 0.1 mV. Measurements of the magnetic flux density were taken from a PHYWE teslameter to a precision of 0.1 mT, which was connected to a Hall probe, inserted into the Hall Effect Console directly on the sample. The apparatus was powered by a 12 V AC power supply with an additional set of DC connections used to power the teslameter and adjust the strength of the magnetic field using the DC voltage and current controls. Measurements not related to temperature dependence were conducted at room temperature although, the sample temperature may have varied due to its high resistivity [2].

A single set of measurements was taken for the following tests that are to be described. Therefore, the main contribution to measurement error was assumed to be instrumental, and was taken as half the instrument precisions stated above. Measurements requiring a varying magnetic flux density were prone to small voltage fluctuations, in which case the error associated with voltage was increased to represent the size of the fluctuation.

The undoped sample was used to determine the band gap energy of germanium and was carried out by measuring sample voltage as a function of temperature, as the sample cooled from 104°C to 25°C, with a fixed current of 4.0 mA.

The doped germanium sample was used in the following four tests. Hall voltage was measured as a function of current from −35.1 mA to 34.2 mA, with a constant magnetic flux density of 250 mT. Sample voltage was measured as a function of magnetic flux density from 0 mT to 300 mT, with a constant current of 25.0 mA. Similarly, Hall voltage was measured as a function of magnetic flux density, but the range was extended to include negative B values up to −300 mT, and the current was set to 30.0 mA. Finally the dependence of temperature on Hall voltage was investigated by heating the sample and taking measurements of Hall voltage as it cooled from 113.6 °C to 29.9 °C, with constant current and magnetic flux density values of 30.0 mA and 300 mT, respectively.

3 RESULTS & DISCUSSION

Figure 2 shows the natural logarithm of conductivity plotted as a function of the reciprocal of temperature, for the undoped germanium sample at a fixed current of 4.0 ± 0.05 mA. A linear fitting model was applied resulting in a correlation coefficient [4] of $r = 1$, indicating a good fit of Eq. (3). Instrumental errors of temperature (±0.05 °C) and voltage (±0.005 V) were propagated to errors in $\ln(\sigma)$ and $1/T$ using the general formula for error propagation [4], and were approximately ± 1% and ± 0.01%, respectively. A gradient of -4200 ± 90 K was also obtained giving a band gap energy of $E_g = 0.72 \pm 0.01$ eV, using a reference value of the Boltzmann constant [5]. The band gap of germanium has previously been determined as 0.67 eV [5], which gives does not agree

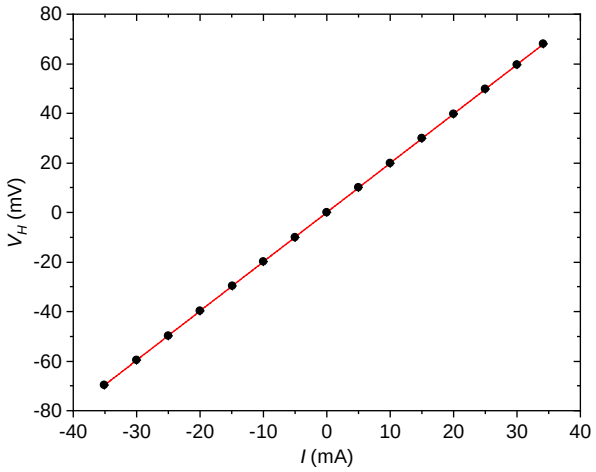

Figure 3. Hall voltage as a function of sample current for a doped germanium sample, under a constant magnetic flux density of 250 mT, with a linear fit.

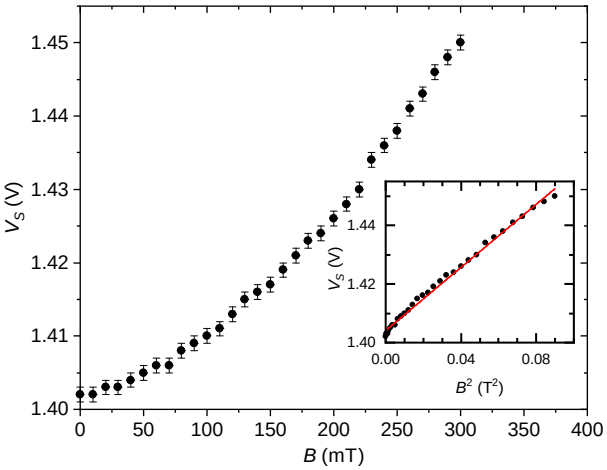

Figure 4. Sample voltage as a function of magnetic flux density for a doped germanium sample at a constant current of 25.0 mA. The quadratic dependence of magnetic flux density on sample voltage for the same data set is shown in the inset, with a linear fit.

with this experiments result to within 3 standard deviations, instead giving a value of 5. This discrepancy may be due to the assumption that the conductivity is dominated by the exponential dependence on $1/T$ whereas, theoretically, conductivity depends on the product of $T^{1.5}$ with the exponential dependence [1]. However, more concern is given to the fact that the reference value of the band gap energy is stated at a temperature of 300 K, but this experiment cannot claim to have measured the band gap energy at any one particular temperature. E_g is implicitly dependent temperature and can be seen to decrease significantly in silicon approaching 300 K [6]. This leaves some ambiguity since this test was conducted anisothermally.

Figure (3) shows Hall voltage as a function of current for the doped germanium sample, using a constant magnetic flux density of 250 ± 0.5 mT. By using a linear fitting model, it was found that Hall voltage was linearly dependent on current, with a correlation coefficient of $r = 1$ so, the relation may be written as

$$V_H = \alpha I + \beta, \tag{9}$$

where the gradient is $\alpha = 1.988 \pm 0.001$ VA^{-1}, and the intercept is $\beta = 0.01 \pm 0.02$ mV. Comparison to Eq. (5) implies that $\alpha = R_H B/d$, and gives the Hall coefficient as $7.95 \pm 0.02 \times 10^3$ cm^{3}A^{-1}s^{-1}. The non-zero value of the intercept is thought to be due to instrument noise.

Moreover, figure (3) shows that Hall voltage is positive for positive values of current. This implies that the build up of positive charge (due to the Lorentz force) is greater than the build up of negative charge, and therefore, that the majority of charge carriers in the extrinsic range are positively charged holes. So, the doped germanium sample is a p-type semiconductor. Although the specific dopant(s) is not resolved here, it is thought to likely belong to group 13 of the periodic table because these elements are commonly used as acceptors for group 14 semiconductors [3].

Figure 4 shows how sample voltage varies with magnetic flux density, under a constant current of 25.0 ± 0.05 mA. In this test the error associated with the sample voltage was increased from an instrumental error to ± 0.001 V to account for observed fluctuations of an equivalent size. The increase in V_S with B should be expected because the Lorentz force increases with B, which deflects charge carriers more strongly, increasing the effective resistance of the sample. More precisely, the functional form may be explained by the effect of magnetoresistance, which occurs when the resistance of a material changes due to the presence of a magnetic field;

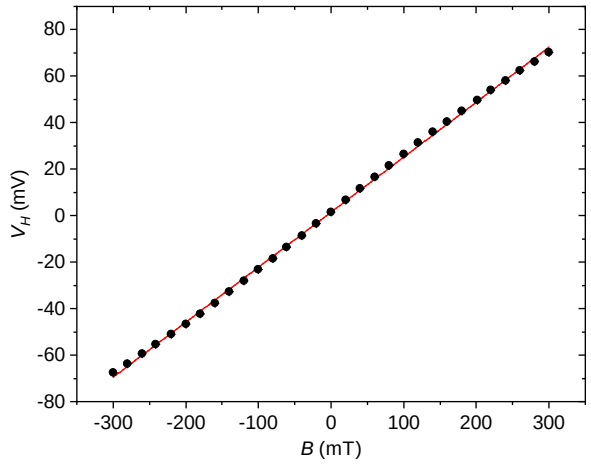

Figure 5. Hall voltage as a function of magnetic flux density for a doped germanium sample at a fixed current of 30.0 mA, with a linear fit.

the increase in resistance is known to be proportional to B^2 at low fields [7]. The inset of figure 4 shows sample voltage for the same set of data but as a function of B^2. A linear fit was applied resulting in a correlation coefficient of $r = 0.997$. There is good agreement for most data points but V_S deviates from the fit somewhat at (relatively) high and low values of B^2. A more rigorous fit may resolve these issues as, generally, the fit strongly indicates the relation between V_S and B^2.

When $B = 0$ mT, resistance no longer depends on the magnetic flux density so, Ohm's law can be used to give the resistance of the sample as $R_0 = 56.1 \pm 0.1\ \Omega$, where the relative errors of $V_s(B = 0)$ and I were summed in quadrature and multiplied by the value of R_0, to give the error. This will be required to determine the Hall mobility.

Figure 5 shows Hall voltage as a function of magnetic flux density for a constant current of 30.0 ± 0.05 mA. The plot is based on Eq. (5) and is linear, with a correlation coefficient $r = 1$, however, $|V_H|$ is slightly larger than expected around magnetic flux densities of ± 150 mT. Errors in voltage were increased to ± 0.1 mV to account for observed fluctuations. The gradient,

Table 1. A summary of the results obtained by measurement of the Hall effect in a doped germanium sample compared to representative data of n-type, antimony doped germanium from Gaidar *et al* [8].

Property	This Experiment p-type doped Ge	Representative Data n-type Sb doped Ge
Sample resistance, R_0 (Ω)	56.1 ± 0.1	–
Hall coefficient, R_H ($\mathrm{cm^3 A^{-1} s^{-1}}$)	$7.89 \pm 0.04 \times 10^3$	9.04×10^4
Hall mobility, μ_H ($\mathrm{cm^2 V^{-1} s^{-1}}$)	2810 ± 20	3070
Carrier density, n ($\mathrm{cm^{-3}}$)	$7.91 \pm 0.04 \times 10^{14}$	8.05×10^{13}

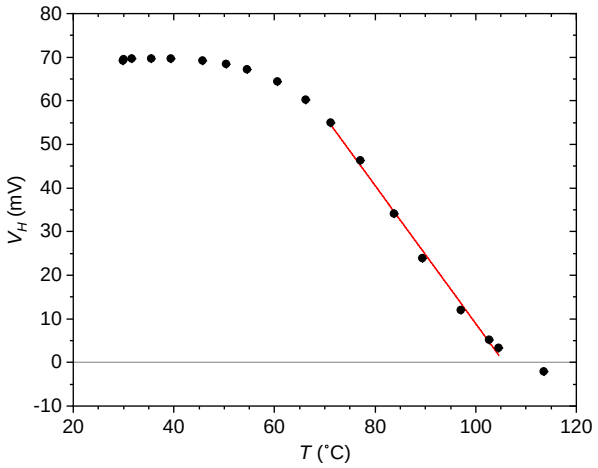

Figure 6. Hall voltage as a function of temperature for a doped germanium sample at a fixed current of 30.0 mA and magnetic flux density of 300 mT. The solid red line is a "guide to the eye".

$0.237 \pm 0.001\ \mathrm{VT^{-1}}$, can be used to calculate the Hall coefficient, similarly to how it was determined using figure 3. Using this value of the Hall coefficient, and the sample resistance from figure 4, the Hall mobility and carrier concentration may also be obtained using Eqs. (6 - 8), the results of which are summarised in table 1. The error associated with each value was propagated using the general formula for error propagation.

Gaidar *et al.* [8] previously determined the Hall coefficients, carrier concentrations and charge mobilities for n-type germanium samples doped with antimony, using a magnetic flux density of 234 mT, and an example of their results is given in table 1. The results agree with this experiments p-type sample to within an order of magnitude. A closer comparison shows that the n-type samples tend to have larger Hall coefficients and consequently, larger mobilities: characteristic of electrons, which tend to move faster than holes [3].

The quantities given in table 1 depend on the sample purity (excluding dopants) [8], the dopant(s) and the doping concentration, as well as, numerous other conditions, including temperature [9]. Therefore, it should not necessarily be expected to obtain identically reproducible results with differing samples and setups. However, this does indicate the potential in fine-tuning the electrical properties of a semiconductor.

The dependence of temperature on Hall voltage is shown in figure (6), which was measured with a constant current and magnetic flux density of 30.0 ± 0.05 mA and 300 ± 0.5 mT, respectively. V_H is linearly dependent on temperature between approximately 70 °C to 110 °C, and saturates at a value of around 70 mV, below temperatures of 60 °C. This behaviour is thought to come from the activation of intrinsic electrons at higher temperatures. Evidence of this can be seen at temperatures above 110 °C, where V_H changes polarity, indicating that the majority charge carrier has swapped to the negatively charged electron. Saturation occurs at lower temperatures when the intrinsic electrons do not have enough thermal so, a peak Hall voltage due to holes is observed.

The results obtained demonstrate how the Hall effect can be used to characterise and control the electrical properties of a semiconductor. With further study into the identification of specific impurities from Hall measurements under standardised conditions, the methods described above could be of use in the process of recycling germanium from electronic waste [10]. Being able to quickly identify the electrical properties and impurities of a sample could help to sort and specialise the recycling procedure, in order to recover a greater yield, and even allow waste to be directly reused, where appropriate.

4 CONCLUSIONS

The Hall effect has been used to determine the electrical properties of a doped germanium sample with an unknown dopant. Measurements of voltage, current and magnetic flux density have led to the result that the semiconductor was p-type, with a Hall coefficient of $R_H = 7.89 \pm 0.04 \times 10^3\ \mathrm{cm^3 A^{-1} s^{-1}}$, a Hall mobility of $\mu_H = 2810 \pm 20\ \mathrm{cm^2 V^{-1} s^{-1}}$, and a carrier density of $n = 7.91 \pm 0.04 \times 10^{14}\ \mathrm{cm^{-3}}$. Susceptibility to magnetoresistance was also observed and the quadratic dependence of magnetic flux density on resistance was verified. Hall voltage was found to decrease linearly with increasing temperature due to the activation of intrinsic charge carriers, and to change polarity when the intrinsic concentration exceeded that of extrinsic charge carriers. The band gap energy of undoped germanium was determined to be $E_g = 0.72 \pm 0.01$ eV, where discrepancy with the literature value was thought to be caused by the anisothermal measurement technique used in this experiment.

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