Dr Jeff Lindemuth, Lake Shore Cryotronics, USA

Hall mobility measurement of solar cell material

What new processes can be used to determine carrier concentration, carrier type, and the mobility of materials?

Free electrical charge, when placed in an electrical field, is accelerated by the electric field. If the charge is in a material, it will quickly begin to scatter off atoms and imperfections in the material. The scattering will keep the charge moving at a constant velocity rather than accelerating. Mobility is the ratio of the velocity to the electric field. High mobility means that the velocity of the charge is high. Mobility is an important parameter of semiconductor materials used in solar cells.

The simplest model of a solar cell is that light is absorbed in the cell, creating charged carriers. The carriers need to move to the electrodes of the cell to produce usable energy. The higher the mobility of the material, the more quickly the carriers will reach the electrodes and the less likely they will be lost before they can reach the electrode. Owing to technology needs and manufacturing methods, semiconductors used in solar cells have inherently low mobilities. For example, the mobility of microcrystalline silicon is 1,000 to 10,000 times lower than the mobility of high-purity silicon used in device manufacturing.

The Hall effect is the most common method to measure the mobility of carriers in semiconducting materials. It is used to determine the carrier concentration, carrier type, and when coupled with a resistant measurement, the mobility of materials. The traditional method used in Hall measurement uses a DC magnetic field. This method has a long history of successful measurements on a wide range of materials including semiconductors. However, materials with low mobility, such as those important in solar cell technology, thermoelectric technology, and organic electronics, are very difficult to measure using DC Hall effect methods.

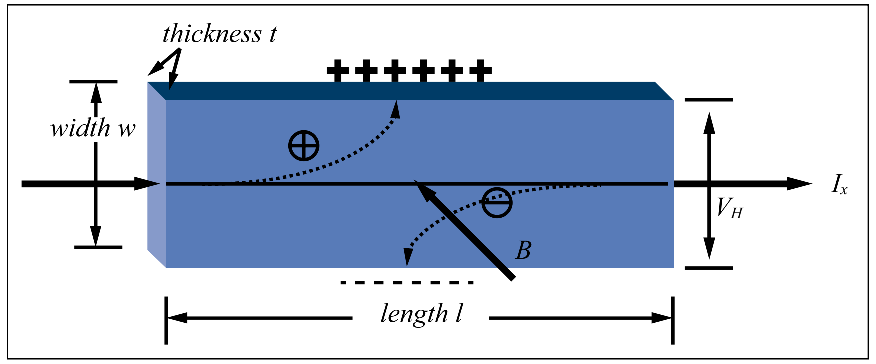

Figure 1 **Outlining the overall geometry of the Hall effect**

Review of Hall effect measurements

The Hall effect is created when a magnetic field is applied perpendicular to a current flowing in a semiconducting device. The combination of the current and magnetic field produces a force – called the Lorentz force – on the carriers. This force pushes the carriers into circular paths around the magnetic field lines. Some of the charges will strike the sides of the sample. This build-up of charge creates an electric field perpendicular to both the current and the magnetic field. The voltage produced by this electric field is called the Hall voltage. When the force from the Hall voltage exactly cancels the Lorentz force, a steady state condition is reached. The balance between the Lorentz force and Hall voltage means the Hall voltage (V_H) is proportional to the magnetic field (B), current (I), and Hall coefficient (R_H) and depends inversely on the thickness (t).

w/L	α	μ (cm²/(Vs) = α/B=1/(1T))
1	0	
0.99	0.014	140
0.9	0.14	1,400
0.5	1.11	11,100

Table 1: **Misalignment factor α values for point contacts on the corner of the rectangle**

	Field	Current	Voltage	V/I	Hall resistance with current reversal	Hall resistance with field reversal	Hall coefficient
	T	amps	volts	ohms	ohms	ohms	m²/C
Positive field	0.6	9.93E-08	1.91E+00	1.92E+07	N/A	-1.07E+05	-1.78E+05
Positive field and current reversal	0.6	-9.92E-08	-1.77E+00	1.78E+07	1.85E+07		
Negative field	-0.6	9.93E-08	1.92E+00	1.93E+07	N/A		
Negative field and current reversal	-0.6	-9.92E-08	-1.80E+00	1.81E+07	1.87E+07		

Table 2: **DC measurement of a high-resistance micro-crystalline silicon sample of n type**

$$V_H = \frac{R_H\, I\, B}{t}$$

The Hall coefficient and resistivity (ρ) of the material can be related to material properties, carrier density (n) and mobility (μ) by the following relations (e is the charge of the carrier):

$$n = \frac{1}{R_H\, e}$$

$$\mu = \frac{R_H}{\rho}$$

The sign of the Hall voltage is the same as the sign of the charge of the carriers. Hence, the Hall effect provides a determination of carrier type (holes or electrons).

In an ideal geometry, the measured Hall voltage is zero, with zero applied field. However, the voltage measured (V_m) in a practical experiment also includes a misalignment voltage (V_o) and a thermoelectric voltage (V_{TE}). The misalignment voltage is proportional to the resistivity of the material (n), the current and a factor (μ) that depends on the geometry. This factor converts resistivity to resistance between the two Hall voltage probes. The thermoelectric voltage arises from contacts between two different materials. It is independent of the current, but it does depend on the thermal gradients present.

"THE SAMPLES EXPLORED FOR THIS PAPER WERE CHOSEN SPECIFICALLY TO PROVIDE TRANSPARENCY CONCERNING THE VALIDITY OF THE AC HALL EFFECT"

$$V_m = \frac{R_H iB}{t} + V_O + V_{TE}$$

$$V_m = \frac{R_H iB}{t} + \alpha\frac{\rho}{t}i + V_{TE}$$

The mobility (μ) is the Hall coefficient divided by the resistivity.

$$V_m = \frac{\rho i}{t}(\mu B + \alpha) + V_{TE}$$

The factor α, called the misalignment factor can be as small as zero (for no offset), but typically it is about 1. A well-defined protocol using DC magnetic fields has been developed to remove the effects of the misalignment voltage and thermoelectric voltage. A common method to remove the thermoelectric voltage is to measure the voltage at both positive and negative voltages. The difference of the voltages will remove the offset thermoelectric voltage. Field reversal can be used to remove the unwanted effects of the misalignment voltage. The Hall voltage depends on the magnetic field, but the misalignment voltage does not. Assuming that the thermoelectric voltages have been removed by

Semiconducting materials

Field	Current	Voltage	V/I	Hall resistance	Hall coefficient
T	amps	volts	ohms	ohms	m^2/C
In phase signal					
0.339	1.00E-07	1.212E-04	1.21E+03	-9.70E+02	-2.86E+03
	-1.00E-07	2.219E-04	2.22E+03		
Quadrature signal					
0.339	1.00E-07	1.212E-04	1.21E+03		
	-1.00E-07	-6.080E-05	1.051E-04		

Table 3 **AC measurement of a high resistance micro-crystalline silicon sample of n type**

current reversal, the measured voltage at a field B1 can be calculated as $V_m(B_1) = \rho I\mu B_1/t + \rho I\alpha/t$ and the measured voltage at a second field B2 can be calculated as $V_m(B_2) = \rho I\mu B2/t + \rho I\alpha/t$. Normally $B_2 = -B_1$. Then the quantity $\rho I\mu/t$ is calculated as $\rho I\mu/t = (V_m(B_1) - V_m(B_2))/(B_1 - B_2)$. Since I and t are known quantities, the Hall coefficient ($R_H = \rho\mu$) can be obtained.

Disadvantages of the DC method

For low mobility materials, the quantity μB can be very small compared to α. When the expression $(V_m(B_1) - V_m(B_2))$ is calculated, the subtraction between the two large numbers gives a small result. Any noise in the measurement can easily dominate the actual quantity, and consequently, produce imprecise results. This is often the reason that Hall measurements on low mobility materials identify incorrect carrier types and yield imprecise mobility values.

AC Field Hall Measurements

A second method to remove the effect of the misalignment voltage is to use an AC magnetic field. If the magnetic field is made a sinusoidal signal ($B(t) = B\sin(\omega t)$), then in the quasi-static approximation, the Hall voltage will become time dependent as well, $V_H(t) = i\,\rho\mu/t\,B\sin(\omega t)$. The misalignment voltage is independent of the magnetic field, and consequently remains a DC voltage. The measured voltage is now

$$V_m = \frac{\rho i}{t}(\mu B\sin(\omega t) + \alpha)$$

The measurement electronics using a lock-in amplifier can separate the desired AC signal from the undesired DC signal with a high degree of precision. However, there is a new term in the measured voltage. This is proportional to the time derivative of the magnetic field, and it is proportional to the inductance of the sample and the leads used in the measurement. If the proportionality constant is β, the measured voltage should be written as

$$V_m = \frac{\rho i}{t}(\mu B\sin(\omega t) + \alpha) + \beta\frac{dB}{dt}$$

Since this is an AC signal, the lock-in will measure this term as well as the Hall voltage term. Since this term is independent of the current, just like the thermoelectric voltage, one method is to use current reversal to remove this term. This term is also 90° out of phase from the signal. Phase resolution on the lock-in amplifier can eliminate this term using a combination of current reversal and phase measurement.

The AC advantage in Hall measurements

As stated above, the major disadvantage of using the DC field technique is that the misalignment voltage can be much larger than the Hall voltage. The use of field reversal to remove the misalignment voltage is consequently limited by the dynamic range of the DC voltage measurement. The true advantage of the AC method when measuring Hall voltage is that the misalignment and thermoelectric voltage remain DC voltages, while the Hall voltage becomes an AC voltage. This separation in frequency space is key to measuring the small Hall voltage present in low mobility materials. If the misalignment voltage is extremely small, which is very difficult to obtain in practice, the DC field method can be extended to lower mobility materials.

It is useful to look at some typical measurement scenarios to understand how quickly the misalignment voltage can increase. A common method to measure resistivity and Hall effect in materials is the van der Pauw method. In this method a square or rectangular sample is used. Four contacts to the sample are used to measure the resistivity and Hall voltage. Typically the contacts are made to the corners of the sample.

The ideal configuration is mathematical point contacts exactly on the corners of a perfectly uniform square sample. For this configuration, the misalignment factor α, would be exactly zero and there would be no misalignment voltage.

There are many distortions from this ideal case that can cause α to be different from zero. For instance, in a real sample the contacts are never mathematical points and are not all the same size or symmetrically placed, see Figure 2 opposite. For example, in a real sample the contacts are never mathematical points, and are not all the same size or symmetrically placed. However, for this example, the contacts will still be considered to be point contacts at the corner of the sample, but the sample is no longer a perfect square, but is a rectangle. Using a finite elements calculation, it is possible to calculate α for any ratio of the rectangle width to length. The results are summarized in Table 1. If the ratio of the width to length is 0.99, that is a 1% deviation from perfect square, α is 0.014. To understand the significance of this number, suppose the Hall voltage is measured using a magnetic field of 1 tesla. Then the quantity μB is equal to α when μ is $0.014m^2/(Vs)$ or $140cm^2/(Vs)$. This means that for a material with mobility of 140, the Hall voltage, when measured at 1 tesla, would be equal to the misalignment voltage. If we assume that the measurement system can measure a Hall voltage that is 1% of the misalignment voltage, the smallest mobility that can be measured would be $1.4cm^2/(Vs)$. If the width-to-length ratio of the rectangle is 0.9, instead of 0.99, under the same assumptions, the smallest mobility that can be measured is $14cm^2/(Vs)$. This calculation supports the statement that the lowest mobility that can be reliably measured using DC field Hall effect is about $10cm^2/(Vs)$.

An example measurement

Measurements were made on a high-resistance, 247MΩ/sqr microcrystalline silicon sample of n type, with an expected mobility of $<1cm^2/Vs$. This measurement was conducted with a 0.6 T field for the DC measurement, and a 0.339 T field for the AC measurement. To extract low mobility carriers using DC techniques, very large fields have to be applied to measure the small Hall voltages, whereas in the AC technique this is not necessary since all the unwanted voltages that contribute to the total measured voltage are easily negated.

The details of the DC measurements on this sample are summarized in Table 2. This table shows both the current reversal measurement and the field reversal measurement. The voltage measured at plus current is different from the voltage measured at negative current. The thermoelectric voltages are not small compared to the approximate measured voltage of 1.8V (~70mV). The current reversed Hall resistance for positive field is 18.5MΩ and for negative field 18.7MΩ. The Hall resistance calculated using field reversal is 107kΩ, about 0.5% of the measured value. The measurement of the Hall coefficient and resistivity give a mobility of $7cm^2/(Vs)$, which is much larger than the expected value.

The AC measurement is summarized in Table 3. In this case, the measured voltage is only the Hall voltage, since the misalignment voltage is removed before the measurement. However, the current reversed voltages differ from each other. This means that the phase errors for the high resistance sample are large. Using the quadrature signal as well as the in phase signal, the Hall resistance is corrected for the phase error to 970Ω. It's important to note the Hall resistance measured with the AC method is 1% of the DC Hall resistance. The mobility for this measurement is $0.1cm^2/(Vs)$ – more in line with the expected results.

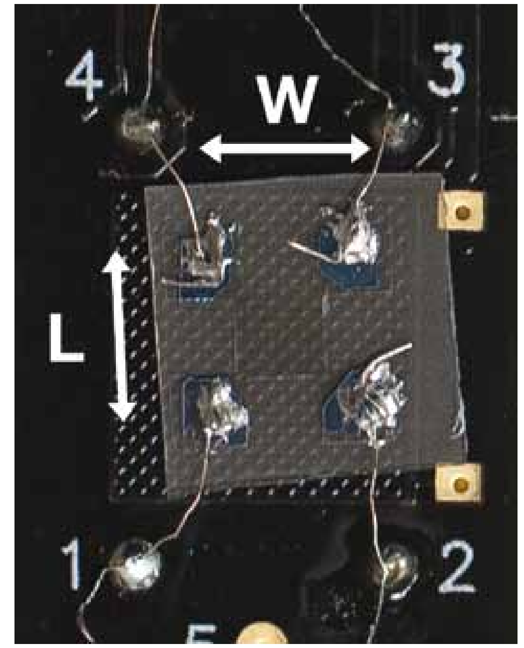

Figure 2 **Van der Pauw sample with four wires attached. The width and length are marked with arrows. This sample does not have point contacts on the edge of the sample, the contacts are different size, the contacts are not symmetrically placed and the width (W) and length (L) are not the same. These distortions increase the misalignment voltage and make measurement of small Hall voltages very difficult using the DC field method. The AC field method minimizes the impact of these misalignment errors**

Conclusion

Semiconducting materials required for use in solar cells are inherently low mobility materials. Measuring the mobility of the materials using DC field Hall methods is limited in practical measurements. The AC field method, with the inherent ability to separate unwanted DC voltages from the AC signal of interest, provides a better solution to the measurement needs of solar cell materials.

The samples explored for this paper were chosen specifically to provide transparency concerning the validity of the AC Hall effect. A comparison between AC and DC methods, for which it is known that the DC method is not adequate, was measured. While the sample's mobility was expected to be $<1cm^2/Vs$, the DC method provided a result much higher than that ($7cm^2/(Vs)$). However, the AC method measured the Hall resistance at 1% of that measured with the DC method. This resulted in obtaining the low mobility for this sample of $0.1cm^2/(Vs)$.

With its capability of measuring low mobility materials, the AC Hall effect method provides solutions to those exploring key materials used in solar cell, thermoelectric, and organic materials. ■