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# The majority carrier electrical properties of selected thin film polycrystalline solar cell window and absorber layers are determined by the method of four coefficients.

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## Abstract

Recently the need to utilise more abundant and less toxic materials in thin film solar cells has driven investigation of TCO window layers such as those based on ZnO, (ZnO:Al, ZnO:Al:Mg) and new absorber layers including Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> (CZTS) and Cu<sub>3</sub>SbS<sub>3</sub>.

We report measurement of Resistivity, Hall Seebeck and Nernst coefficients on each sample in one measurement system.

Measurements of Hall mobility verses temperature were used to determine how the majority carrier electrical properties are related to the process and film morphology

In some TCO cases by using the method of four coefficients (4C), we could also determine the carrier effective mass, a parameter related to the fundamental properties, which determine the upper limit of the TCO performance.

## Majority carrier electrical properties of thin film semiconductors.

The method of the Van der Pauw is typically used to determine resistivity and the Hall measurement to determine carrier concentration [1], [2]. The carrier hall mobility is then simply determined by the relation:

$$\mu_h = 1/n.e.p \quad (1)$$

Where: n is the carrier concentration, e the electron charge and p the resistivity.

Inorganic semiconductor thin films on insulating substrates may be formed as one (or a mixture) of the following crystal structures: (a) as an amorphous layer or (b) as polycrystalline layer (often with a columnar texture and preferential grain orientation) or (c) an epitaxial layer on a single crystal substrate.

In the case of an amorphous semiconductor the carrier transport is generally dominated by "carrier hopping" from one site to another. The resulting mobilities are generally very low and may not be measurable using the DC hall method described in this paper.

In the case of polycrystalline thin films boundaries between the grains may present energy barriers, impeding carrier transport and usually dominating the carrier transport across the thin film. Several models have been developed to describe such transport. According to Seto's [4], and Zhang's [5] model for non-degenerate semiconductors;

$$\mu_{eff} = L.e\{1/2\pi m^*kT\}^{1/2}.\exp\{-E_B/kT\} \quad (2)$$

Where: L is the mean grain size, e the electron charge, E<sub>B</sub> the grain barrier height and m\* the effective mass.

Whereas in the case of an n-type degenerate semiconductor;

$$\mu_{eff} = B.T^{-1}.\exp\{-E_a/kT\} \quad (3)$$

$$\text{and: } E_a = E_B - (E_F - E_C) \quad (4)$$

Where E<sub>a</sub> is the activation energy needed for the electron to traverse the grain boundary and B is a constant.

In the case of epitaxial thin films then the lateral transport is dominated by scattering of the carriers by collision events between other charge carriers or defect imperfections within the crystal. In such cases it is possible to use the method of four coefficients to determine fundamental electrical properties. In very thin films (nm range) corrections must be made for surface scattering and depletion effects, which reduce observed mobilities.



Conditions similar to the epitaxial case may also be observed in polycrystalline thin films provided the barriers at the grain boundaries  $E_a$  are low enough to not significantly impede the majority carrier transport. This is in fact the case for several transparent conducting oxides. In these cases Drude's free electron theory can be applicable [6].

The Drude relaxation time approximation assumes a mean time between elastic collisions  $\tau$ , as carriers are decay from an excited state to an equilibrium distribution.

In this case from Drude's theory the carrier mobility can be given by:

$$\mu = e \tau / m^* \quad (5)$$

Where  $e$  is the electron charge,  $m^*$  is the density of states effective mass.

#### The method of four coefficients.

If the relaxation time approximation is applicable then analytical solutions of the Boltzmann equation for the coefficients resistivity and hall coefficient in terms of carrier concentration, effective mass and mean scattering time can be derived. However, in order to determine these additional unknown variables two more "simultaneous equations" are required.

Zhitinska et al first proved that the Seebeck and Nernst Coefficients could be utilized for such a solution methodology, applying the method to PbTe single crystals [7]. Later Kaidenov has promoted the potential applicability of "the method of four coefficients" to other materials systems [8].

Young et al have utilized this method to measure properties of transparent conducting oxides [9].

This relaxation time between collisions is not a function of direction of the carrier motion, but is a function of energy and possibly temperature. The frequency of elastic collisions,  $\tau^{-1}(E)$ , depends on the density-of-states function. The Nernst voltage is very sensitive to the type of scattering, ionized or neutral impurities, or acoustic phonon.

The 4C method allows calculation of the effective mass and mean scattering time at a specific temperature and doping concentration. Young et al have shown that by careful analysis of these parameters as a function of carrier concentration details of the energy band structure can be elucidated for certain transparent conducting oxide (TCO) thin films on insulating substrates [9] and more generally for epitaxial thin films on insulating substrates [10].

#### New 4C System implementation

Other groups have described built laboratory set-ups to measure the four coefficients and they all emphasized the need to accomplish all of the measurements on the same sample in one measurement system [7], [9] to avoid errors associated with measurement of the coefficients in different systems.

Our four-coefficient (4C) instrument has been designed specifically for the measurement of conducting thin films on insulating substrates.

Thin film test samples are deposited on electrically insulating substrates through a specially designed shadow mask to define the cross pattern shown in Figure 1. Where necessary the sample was given further treatment in selenisation or sulphurisation in a reaction chambers.

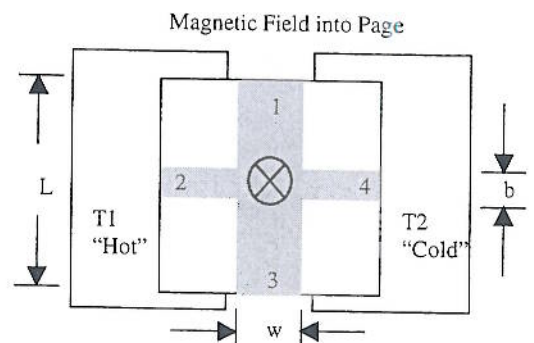


Fig 1 Schematic of sample arrangement

Following formation of the test sample cross, four ohmic metal contacts were deposited through a shadow mask. The contacts extend out to large contact pads.



The sample is held down, film side up, on two heating/cooling blocks by spring clips, which also provide electrical contact to the contact pads and allow fast sample exchange.

The gap between the heating/cooling blocks is nominally 4mm both of which can be controlled independently to 0.1 Kelvin over the temperature range 80 - 500Kelvin

The high aspect ratio of  $W \ll L$  and the small size of the ohmic contacts conforms to the specimen shape dictated by the ASTM designation F76-8616 for Van der Pauw resistivity and Hall measurements.

The cross shape also creates a large temperature gradient between the contacts 2-4 for the Seebeck voltage and maximizes the Nernst voltage between contacts 1-3, whilst minimizing any temperature gradient between the latter contacts.

In all our samples  $w=3\text{mm}$ ,  $b=1\text{mm}$ , and  $L=16\text{mm}$ . The samples are on glass substrates 25mm square with three samples on one 75mm x 25mm glass slide.

The measurements require switching and measurement algorithms to minimise and correct for measurement errors. Keithley Instruments nanovoltmeter, current source and nanovolt switching unit perform electrical measurements and switching. The measurements are time consuming therefore it is essential that the system be fully automated.

The following data collection sequence is used to measure the four coefficients:

- 1) Resistivity (Coefficient): is measured by biasing contacts 3-4 while measuring the voltage across contacts 1-2. Measurement as per ASTM designation F 76-86.
- 2) Hall Coefficient: is measured by biasing contacts 1-3 while a magnetic field is applied in the z direction and then measuring the resulting voltage across the contacts 2-4.
- 3) Nernst coefficient: is measured by maintaining the temperature gradient between contacts 2-4 while applying a magnetic field in the z direction. A Nernst voltage is thus established between contacts 1-3.

- 4) Seebeck Coefficient: is measured by creating a temperature gradient between contacts 2-4 and measuring the voltage developed between the same two contacts.

The Seebeck measurement requires a calibration with a material of known absolute Seebeck coefficient because the test sample and the sample holder itself form a thermoelectric couple. A Lead (Pb) thin film verified using a NIST SIRM [11] was used to calibrate our instrument. We first find the Seebeck coefficient for the probe/contact arrangement used.

$$\alpha_{\text{cont}} = \alpha_{\text{stan}} - \alpha_{\text{cal}} \quad (6)$$

Where:  $\alpha_{\text{cont}}$  is the contact Seebeck coefficient,  $\alpha_{\text{stan}}$  the known standard Seebeck coefficient and  $\alpha_{\text{cal}}$  the Seebeck coefficient measured value.

$$\alpha_s = \alpha_{\text{cont}} + \alpha_{\text{meas}} \quad (7)$$

Where:  $\alpha_s$  is the sample absolute Seebeck coefficient and  $\alpha_{\text{meas}}$  is the measured Seebeck coefficient.

## Results & Conclusions

The data were taken at slightly different ambient temperature, however the correlation is very reasonable. The measurements were made in Northumbria University many months after the measurements in NREL.

The measurements and analysis is still ongoing at the time of writing this paper. The final results and conclusions will be presented at the meeting.

On those sample measured by the time of writing this paper we found that for degenerate TCOs, the grain boundaries did indeed play a minor role in majority carrier transport and we could thus readily separate defect scattering mechanisms from the material structure.

However in lightly doped absorber layers the grain boundaries did limit the transverse transport and the inter-grain boundary scattering could not easily be separated from the intra-grain electrical properties. It was possible to fit to an electrical grain boundary model of the polycrystalline thin film.

### Experimental Correlation Results

Sample ID	Temp (K)	Thickness (nm)	Resistivity (Ohm.cm)	Hall Coeff (m <sup>3</sup> /C)	Seebeck Coeff (uV/K)	Nernst Coeff (uV/K)
H3522 UNN A	308	1.50E+03	2.81E-03	7.60E-08	-1.12E+02	-9.16E-03
H3522 NREL	295	1.50E+03	2.81E-03	7.14E-08	-1.34E+02	-3.70E-02

System= 22(uV/K)

Sample ID	Temp (K)	Thickness (nm)	Doping (cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> /Vs)	DOS mass (m*/me)	Scattering Time (s)
H3522 UNN A	308	1.50E+03	-8.22E+19	2.71E+01	7.02E-01	1.08E-14
H3522 NREL	295	1.50E+03	-8.74E+19	2.51E+01	9.76E-01	1.41E-14

Table 1b (Lower Table) compares values calculated from four coefficients the 4C data Table 1a and for the same sample from NREL (Dr. David Young).

Table 1a (Upper Table) compares four coefficients measured using our 4C system and same sample measured in NREL (by Dr. David Young).

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