Hall-effect Characterization and Identification of Impurity Levels in Multi-crystalline Silicon Base Material for Solar Cells

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ABSTRACT

Samples of 1cm^2 sizes were made from the p-type multi-crystalline silicon boron doped 10^{16}cm^{-3}. Aluminium contacts were made in a vacuum of 10^{-6} Torr and post-annealed in Argon ambient at 400°C for 30 minutes for making the four contact electrodes. The activation energy based on low compensation was found to be 47 meV, 32 meV, and 18 meV, respectively. In order to obtain a more reliable solution, the differential evaluation on the temperature dependence of hole concentration was done. Four peaks were observed around 50, 56, 88, and 109 meV, which indicate several acceptor levels in multi-crystalline silicon (Mx-Si). Hall mobility at 300 K in this p-type sample was 189 (cm^2/Vs) and 3231 (cm^2/Vs) at 72 K. Based on acoustic phonon scattering the mobility decrease with temperature showed $T^{-1.96}$ dependence. This behavior indicates the inter-valley scattering as well as grain boundary effects.

KEYWORDS: Compensation, multi-crystalline silicon, activation energy, mobility, grain boundaries

1.0 INTRODUCTION

Multi-crystalline silicon (Mx-Si) is an alternative choice for a low-cost substrate developed for photo-voltaics, but lower material quality and hence lower efficiency than the single crystalline silicon fabricated by Czochralski method (Cz-Si) offset the economic benefit. Directional solidification (*DS*) ingots generally show a well-defined columnar structure along the growth direction; a nonperfect planar liquid-solid interface or nucleation normally causes deviations in morphology from crucible walls, which result in the variation of impurity doping. The grain boundaries and high defect and impurity concentrations lead to strong variations in the minority-carrier lifetime of Mx-Si material from the same ingot, even though the material is treated under the same growth and

processing conditions for cell fabrication. The aim of the study is to find out the correlation between the majority carrier concentration and their effect on minority-carrier mobility in Mx-Si solar cells. In single crystalline semiconductor materials the electrical properties of the majority carriers, (Hall mobility H and free carrier concentration p for p-type and n for n-type), might be directly obtained from the experimental results of Hall effect and direct-current (DC) electrical conductivity measurements, via the following equation (1) and (2).

$$p = \frac{r_H}{qR_H} \quad \text{.....1}$$

and

$$\mu_H = R_H \sigma = r_H \mu_D, \quad \text{.....2}$$

where q is the electronic charge, R_H the Hall coefficient, σ the electrical conductivity, r_H the Hall factor, p the hole concentration and μ_D the drift mobility. In multi-crystalline materials these equations could not be straightforwardly applied due to the presence of grain boundaries (GBs) and dislocations which introduce non-uniformity effects in the R_H and carrier concentration. As reported by Volger (1980) and then by Orton and Powell (1980), the problem can be studied using a geometrical model named "at two phases".

If we suppose that the mean free path of the electrons is less than the single grain size, we can consider the material as composed by single cubic crystals, having side l_1 and resistivity ρ_1 separated by GBs of length l_2 and resistivity ρ_2 (Fig.1.) Each single contribution to the Hall field can be added to the other, considering the equivalent circuit as composed by different elements connected in series and parallel.

In the case of large grain boundaries, $l_1 >> l_2$, and $\rho_1 << \rho_2$, we can write the Hall coefficient as in the next equation;

$$R_H = \frac{1}{p_1 e} \quad \text{.....3}$$

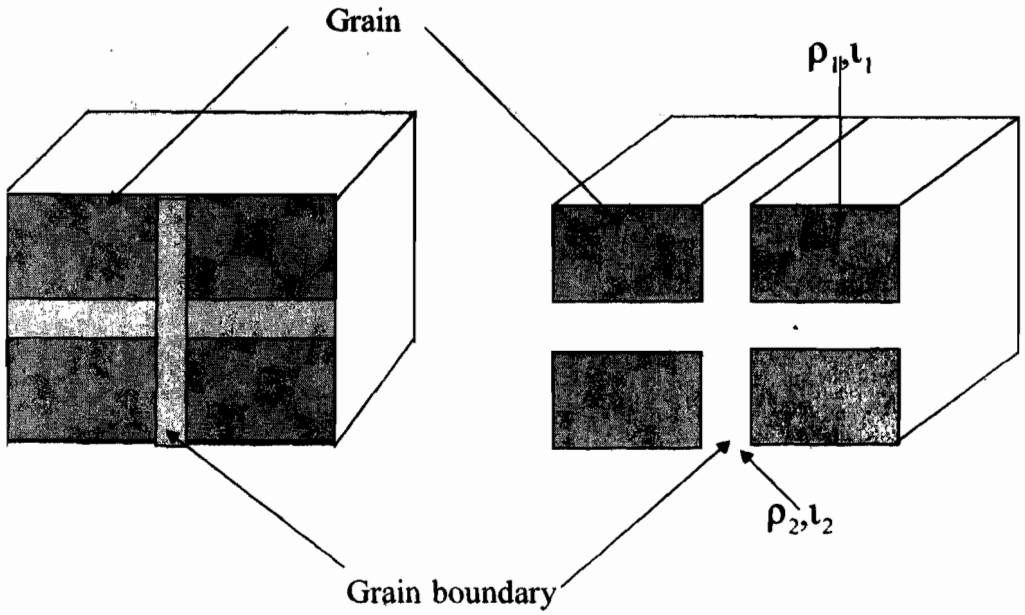


Figure 1. Schematic representation of grain boundaries in the model of "two phase" for carrier transport description in multi-crystalline materials

Where p_1, the carrier concentration in the grain, is directly obtained as the result of Hall-effect experiment. The mobility is then,

$$\mu_H = \frac{R_H}{\rho} \quad \text{.....4}$$

Where ρ is the measured resistivity of the material. It is, therefore, apparent that only the mobility is affected by the presence of GBs.

2.0 EXPERIMENTAL PROCEDURES

Hall effects were measured by the Van der Pauw method (1961). The schematic cross section of Hall-effect measurement by Resi-Test 8300 for a p-type sample from multi-crystalline silicon (Mx-Si) is shown in Fig. 2.

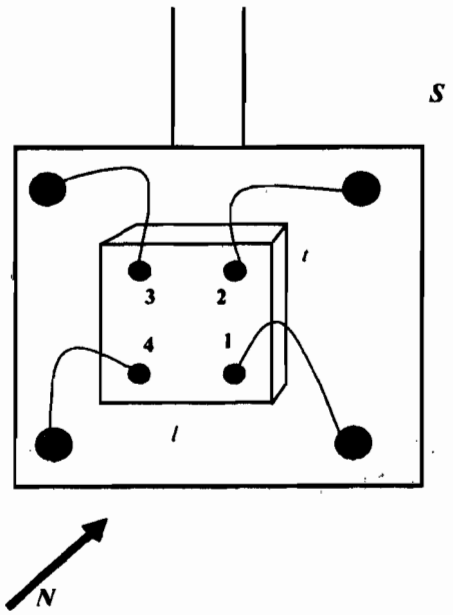


Figure 2. Hall effect set up.

The formation process of ohmic contacts was done by thermal evaporation of Al through a shadow mask in a vacuum of 3 x10^{-6} Torr, and subsequent annealing was carried out at 400 ^{0}C for 30 minutes in Ar gas ambience.

The measured parameters included:

(a) Resistivity:

$$\rho(\Omega cm) = \pi t / \{\ln 2\pi(R_a + R_b)\} f(r)$$

$$\text{and } R_a = \frac{1}{4\left\{V_{43}/I_{12} + V_{34}/I_{21} + V_{21}/I_{34} + V_{12}/I_{43}\right\}};$$

$$R_b = \frac{1}{4\left\{V_{14}/I_{23} + V_{41}/I_{32} + V_{32}/I_{41} + V_{23}/I_{14}\right\}}, \quad \ldots\ldots\ldots\ldots 5$$

where t = 300 μ m (sample thickness) and the balance factor (f(r) = 1).

(b) Hall coefficient R_H (cm^3 / C):

$$R_H = \frac{t}{B\left(\frac{R_c + R_d}{2}\right)} \times 10^8$$

$$\text{and } R_c = \frac{1}{4\left\{V_{42}/I_{N13} + V_{24}/I_{N31} + V_{24}/I_{R13} + V_{42}/I_{R31}\right\}};$$

$$R_d = \frac{1}{4\left\{V_{13}/I_{N24} + V_{31}/I_{N24} + V_{31}/I_{R24} + V_{13}/I_{R24}\right\}} \quad \ldots\ldots 6$$

where B is magnetic field in [Tesla], I_N forward bias, and I_R reverse bias current.

(c) Charge carrier concentration, n [cm^{-3}]:

$$n = 1/R_H q;$$

$$q = 1..6 \times 10^{-16}[C]$$

(d) Hall mobility, μ [cm^2/Vs]:

$$\mu = R_H/\rho$$

The carrier concentration density as in the case of single crystalline materials, when taken as a function of temperature gives information on different parameters (concentration of residual dopants, compensation ratio, and energy levels in the gap) Stillman and Wolfe (1976). We applied the same analysis to multi-crystalline materials. If we consider a Mx-Si sample doped with N_A cm-3 of boron (p-type) and having donor impurity N_D (typically phosphorous) ionized at all temperatures, the hole concentration can be given by

$$p = -\frac{1}{2}\left(N_D - N^*_V\right) + \frac{1}{2}\left[\left(N_D + N^*_V\right)^2 + 4N^*_V\left(N_D - N_A\right)\right]^{1/2},$$

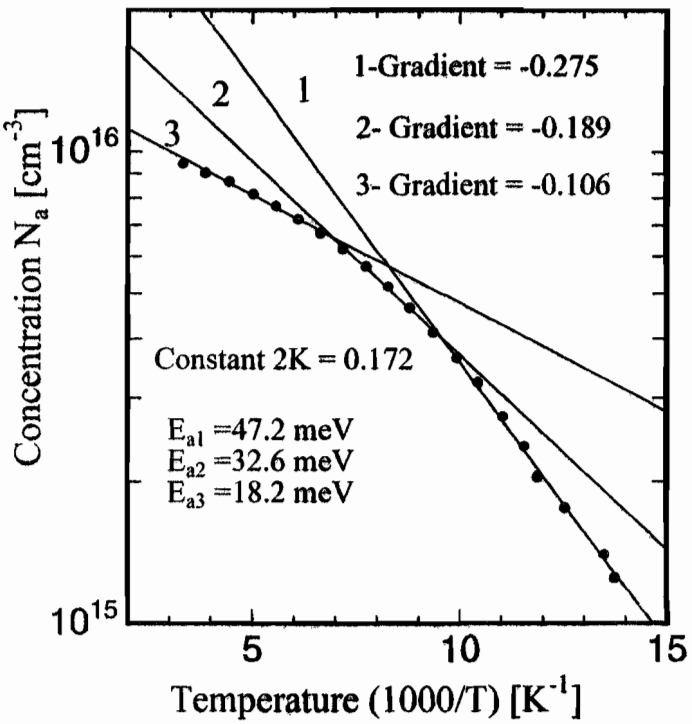
where

$$N^*_V = 1/2\, N_V \exp\left(\frac{-E_A}{k_B T}\right) \quad \ldots\ldots 7$$

Nv is the effective density of states in the valence band, E_A the ionization energy of boron levels. The density of state effective mass is take as $M = (m^{3/2}_{lh} + m^{3/2}_{hh})^{2/3}$ Sze (1981).

3.0 RESULTS AND DISCUSSION

Figure 3 is a plot of the hole concentration against inverse absolute temperature, for the base material, p-type Mx-Si. Taking the gradients along the curve, we determined the activation energy for this sample assuming low compensation, as 47, 32, and 18 meV, respectively.



Where 1 is the gradient of the curve at lower temperature, 2 is the gradient at mid-temperature and 3 is the gradient near room temperature. The dots are the measured values of impurity concentration.

Figure 3. A plot of concentration against absolute temperature for boron doped Mx-Si sample.

The hole concentration (p) is given by Orton and Powell (1986)

$$p = N_V \exp\{-(E_f - E_V)/k_B T\} \quad \ldots\ldots 8$$

where E_V is the valence-band energy. N_V is the effective density of states for holes in the valence band, and is given by Sze (1981).

$$N_V = 2.51 \times 10^{19} \left(\frac{m^*_p}{m_o} T/300 \right)^{3/2} [cm^{-3}] \quad \ldots\ldots 9$$

Here, m_p/m_o is the effective mass of hole in Mx-Si, and is (0.55). Since the concentration of free electrons in the conduction band is negligible, the electrical neutrality condition is given by Sze (1981).

$$p + N_d = N_a / \{1 + 1/g \exp[(E_a - E_f)/k_B T]\} \quad \cdots\cdots 10$$

where Ea is the acceptor level . The degeneracy factor is equal to 4 for the acceptors. From the above equations, the ionization energy of the acceptor Ea is written as

$$\Delta E_a = E_a - E_v = k_B T \ln\{4N_v(N_a - p - N_d)/p(p + N_d)\} \quad \cdots\cdots 4.11$$

In order to obtain unique and reliable solutions, the differential evaluation on the temperature dependence of hole concentration was carried out (Hoffman, 1979). This method has an advantage to yield each parameter uniquely. Figure 4 shows ($-k_B T\, dn/dE_F$) as a function of the Fermi energy $E_F - E_V$ (T). Four peaks can be observed around 50 meV, 56 meV, 88 meV, and 109 meV, which indicate several acceptor levels in Mx-Si. The first two values are within the expected range for single crystalline Si (45 meV) that is boron-doped.

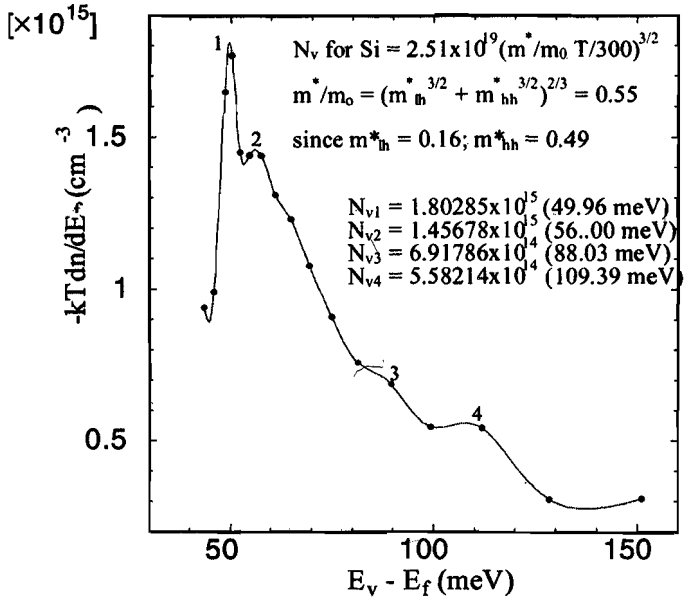


Figure 4. Showing the differential analysis to identify energy levels in a p-type Mx-Si (10^{16} cm^{-3})

As from the work of Orton and Powell (1986) in Mx-Si materials, it is possible to introduce the effect of GBs in the carrier mobility. This hypothesis was used by Singh

(1985) to obtain the equation for the effective mobility μ_{eff} with an assumption that the charge transport through the potential barrier might be well described by Thermionic Emission Diffusion theory developed by Crowell and Sze (1986). The results for the case of Mx-Si samples presenting large grains are described by the following equation:

$$\mu_{eff} = \frac{\mu_g}{1 + \frac{k_B T}{qLE_b} \exp\left(\frac{qV_B}{k_B T}\right)}, \quad \text{.....12}$$

where L is the grain length and E_b the maximum built-in electric field which is a function of the barrier height V_B, the acceptor density N_A, and the temperature T. From equation (4.12), it is possible to calculate the mobility of the material knowing the mobility in the grain g. This last quantity is calculated considering the single scattering mechanism independent from each other and the grain mobility g is obtained using Mathiessen rule Anderson and Apsley (1986). For the single crystalline silicon (Cz-Si) case, the most important scattering processes in the 72-300 K temperature range are 1-phonon scattering, 2- ionized impurity scattering, and 3-neutral impurity scattering (at high doping levels > 10^{17} cm^{-3}) [10-12].

For impurity scattering we can use the expression proposed by Arora *et al.* (1982).

$$\mu_H = \frac{5.6\times10^{17} T^{3/2}}{N_I \log\left[b(b+1) - \frac{b}{b+1}\right]}, \quad \text{.....13}$$

where N_I is the ionized impurity concentration, and

$$b = 2.5\times10^{15} T^2 \left[p\left(2 - \frac{p}{N_A}\right)\right]. \quad \text{.....14}$$

For phonon scattering, instead, we can use mobility temperature dependence as in equation (4.15) below

$$\mu_{po} = 1.58\times10^{8} T^{-2.23}. \quad \text{.....15}$$

The Hall mobility at room temperature in this p-type sample was 189 (cm2/Vs), while it was 3231 (cm2 / Vs) at 72 K (Fig. 5).

The increasing mobility at low temperatures reflects the low compensation in the p-type material (Mx-Si). When the acoustic phonon scattering is the dominant scattering mechanism, the mobility should decrease with temperature according to $T^{-1.5}$ dependence (Sze, 1981). However, the present result shows $T^{-1.96}$ dependence. This rapid decrease in

electron mobility at high temperatures is attributed to the inter-valley scattering as well as grain boundary effects (Long, 1986).

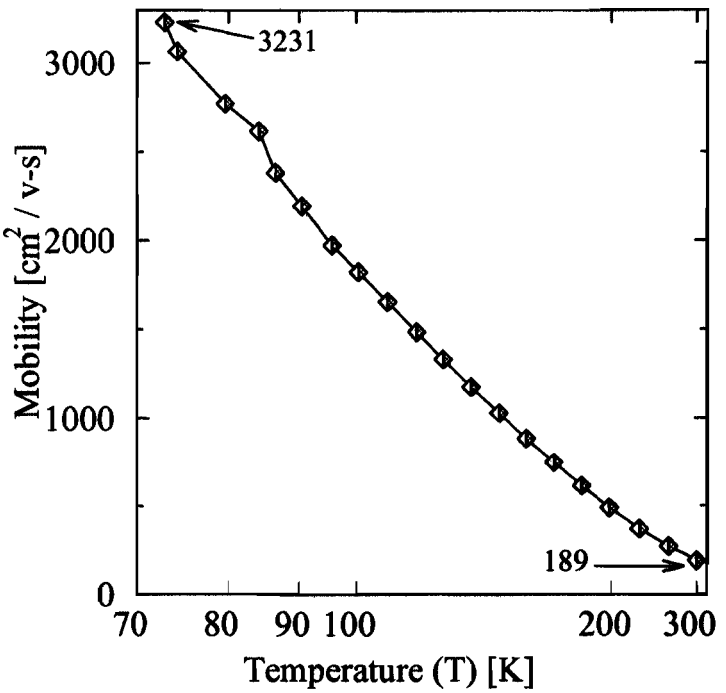


Figure 5. The temperature dependent on linear scale for p-type Mx-Si

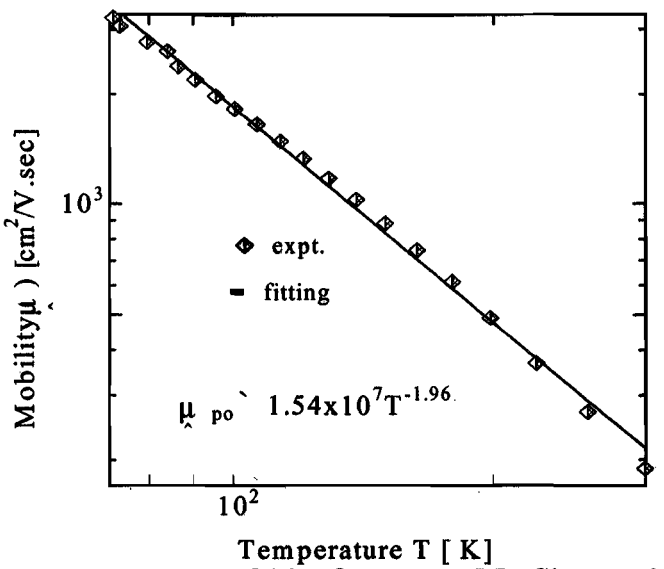


Figure 6. The temperature mobility for p-type Mx-Si material

This result shows that with a grain size of length 300 μm to 2000 μm as in Mx-Si of this study, the μ_{eff} is approximately equal to μ_g when considering the phonon scattering process. Therefore, bigger grain size Mx-Si material is good for high efficiency.

4.0 SUMMARY

In conclusion, we have demonstrated the possibility correlating Mx-Si and Cz-Si for solar cell application when taking the grain boundary as a thin region with high defect density, while the grains as those regions with properties like of single crystalline silicon. Four peaks can be observed around 50 meV, 56 meV, 88 meV, and 109 meV, which indicate several acceptor levels in Mx-Si. The present result shows $T^{-1.96}$ dependence. This rapid decrease in electron mobility at high temperatures is attributed to the inter-valley scattering as well as grain boundary effects.

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