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# Comparison of characterization techniques for measurements of doping concentrations in compensated n-type silicon

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**Abstract**

Nowadays, compensated silicon (Si) is used in photovoltaic (PV) processes, whether it is through intentional co-doping of resistivity-adjusted Czochralski ingots for high efficiency n-type Si solar cells, as a result of alternative Si purification processes for the production of low-cost Si feedstock, or as a result of recycling end-of-life materials. Whatever the origin of the compensated Si, the doping concentrations need to be accurately and quickly characterized in order to control such processes. In this work, a rapid and highly sensitive characterization technique based on low temperature Hall Effect measurements is described in scientific details and compared to three well-established chemical methods: Glow Discharge Mass Spectrometry (GDMS), Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), and Secondary Ion Mass Spectrometry (SIMS). The characterized samples were extracted from the n-type top part of a casted solar grade Si ingot. A very good agreement is observed between the dopants densities extracted from the electrical method and from the standard methods. With the advantage of a very low detection limit combined with a short measurement time, the advanced Hall Effect technique is promising for the rapid and accurate characterization of dopant concentrations in compensated Si.


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*Keywords:* Compensated; silicon; solar grade; characterization; Hall effect; GDMS; SIMS; ICP-MS; metallurgic; purification; recycling; co-doping

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## 1. Introduction

New ingot manufacturing techniques are being developed to improve solar cell efficiencies and lower production costs. Particularly for high efficiency n-type Si solar cells, Phosphorus (P) - Gallium (Ga) co-doping of Si ingots [1] is for example considered in order to flatten resistivity (ρ) profiles and enhance the fraction of the ingot compatible with the PV requirements. Moreover, alternative materials such as Upgraded-Metallurgical-Grade Si (UMG-Si), or recycled Si have raised interest to lower the overall costs and the environmental impacts. Those alternative materials involve the cohabitation between donor and acceptor doping impurities in similar amounts (compensated Si). Single ρ measurements used to characterize the dopant density in uncompensated Si can no longer be used in this specific type of Si, as both components of ρ, respectively the majority charge carrier density ($n_0$) and the majority carrier mobility (μ) are influenced by the compensation of the dopants. $n_0$ (free electron density in this paper as n-type Si is studied), is indeed governed by both minority and majority dopant densities (Equ. 1), and μ is strongly affected by the compensation-induced reduction of the electrostatic screening of ionized charges by free carriers [2].

$$n_0 = N_D^+ - N_A^- = N_D^+ - N_A \tag{1}$$

With $N_A$ (respectively $N_D$) the acceptor (respectively donor) dopant density. As all minority dopants are ionized by the majority dopants, the ionized minority dopant density ($N_A^-$) is equals to the minority dopant density [3]. This paper first describes an alternative technique to well established-techniques to measure dopant concentrations in compensated Si, based on advanced Hall Effect measurements as a function of temperature (T), including the models developed hereafter. An experimental study is then carried out on n-type compensated Si to compare the advanced Hall Effect procedure with classical physical or chemical methods such as SIMS, GDMS and ICP-MS. Table 1 sums up different characteristics of each characterization technique.

Table 1. Comparison of some characteristic elements of each technique.

| | GDMS | ICP-MS | SIMS | HALL EFFECT |
|---|---|---|---|---|
| Estimated or provided uncertainty | *20%* | *10%* | *10-15%* | *10%* |
| Lower detection limit | *~$10^{15}$cm$^{-3}$(*)* | *~$10^{14}$cm$^{-3}$(*)* | *~$10^{12}$cm$^{-3}$(*)* | *<$10^{11}$cm$^{-3}$* |
| | *(*:given for B and P. May be lower for other elements)* | | | |
| States of the element detected | *All* | *All* | *All* | *Only the electronically active ones* |
| Limits | High uncertainty | *Very clean environment required* | *Need for a reference sample* | *Concentrations above $10^{18}$cm$^{-3}$ not detectable* |

## 2. Theoretical considerations and experimental issues

### *2.1. Principle of the electrical characterization technique*

The carrier freeze-out associated with a decrease in T in compensated n-type Si (with one majority doping impurity) can be described by Fermi-Dirac statistics and reads [3]:

$$n_0(T) = -\left(\frac{N_A}{2} + \frac{N_C}{2g}\exp\left(-\frac{E_d}{kT}\right)\right) + \frac{1}{2}\left(\left(N_A + \frac{N_C}{g}\exp\left(-\frac{E_d}{kT}\right)\right)^2 + \frac{4N_C}{g}\exp\left(-\frac{E_d}{kT}\right)(N_D - N_A)\right)^{\frac{1}{2}} \tag{2}$$

With $E_d$ the energy level with the higher occupancy probability introduced by the majority dopant in the band gap, and g the degeneracy factor associated (other terms have their usual meanings). Adjusting equation (2), which depends on dopants densities, to experimental measurements of $n_0(T)$ allows to access $N_A$ and $N_D$ [4], as long as the other components (g and $E_d$) can be assumed constant with doping densities and T. In this respect, $E_d$ was known to be independent of T [5] and its variation with dopant density is constant until dopant concentrations up to