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Hall mobility reduction in single-crystalline silicon gradually compensated by thermal donors activation

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ABSTRACT

This letter focuses on the variation of the Hall majority carrier mobility with the dopant compensation level in purely Boron-doped Czochralski grown silicon single crystals. Compensation was varied continuously at the sample scale via a step by step activation of the oxygen-based thermal donors. At room temperature, we show a strong drop in mobility for high compensation levels in both *p*- and *n*-type Si. Mobility models taking into account carrier scattering on ionized impurities and phonons could not reproduce this drop. We conclude that a specific effect of compensation must be taken into account to explain the observed behaviour. We qualitatively discuss physical mechanisms susceptible to reduce mobility in highly compensated Si.

1. Introduction

This work was conducted as part of a broader study on the electrical properties of solar grade silicon (Si) purified at low-cost via the metallurgical route (SoG_M-Si) [1]. One major effect of the relatively high remaining impurity levels in SoG_M-Si is that this material is compensated, i.e. it contains both ionized acceptor and donor doping species at similar concentrations (resp. denoted N_A and N_D). In uncompensated Si at Room Temperature (RT), the majority carrier mobility (μ) is mainly limited by the interactions with lattice vibrations (phonons) and ionized impurities. In a compensated material having the same effective majority carrier concentration n (this notation will be invariably used for *n*- and *p*-Si), the weight of ionized impurity scattering is enhanced due to higher concentrations of ionized donors and acceptors. Consequently, μ is expected to be lower in compensated than in uncompensated Si.

This enhanced scattering of charge carriers is in principle well-covered in μ models [2–4]. However, recent measurements on compensated SoG_M-Si have reported significantly lower μ as compensation increases [5,6]. For instance, Libal et al. [5] carried out Hall mobility (μ_{Hall}) measurements on *p*-type boron (B)–phosphorus (P) compensated Czochralski Si (Cz-Si) crystallised from a 10% SoG_M-Si/90% EG-Si feedstock. They compared their results with numerical simulations taking into account a number of relevant scattering mechanisms (phonons, neutral and ionized impurities). For samples with a high dopant Compensation Level (C_l) defined as $C_l = (N_A + N_D)/(N_A - N_D)$, they measured deviations of as much as 40% (at $C_l = 23.5$) from the expected model value. Note that a similar observation was reported in our previous work on *p*-type B–P compensated multicrystalline SoG_M-Si (details in [6]). Nevertheless, the drop in μ in both studies could not be unambiguously attributed to a specific effect of C_l since the SoG_M-Si used also features high concentrations of many other species which are likely to reduce μ [5]. A few measurements of μ_{Hall} on much purer compensated Si have been reported [7,8]. However, they were made at low C_l – since high C_l are tricky to obtain – and at very low doping levels [7] or at cryogenic temperatures (T) [8].

The main objective of this study was to investigate the reduction in μ_{Hall} with gradually increasing C_l in one and the same sample, while avoiding the ambiguities related to SoG_M-Si. Using Electronic-Grade (EG) Cz-Si B-doped wafers, we progressively compensated the B-doping through the controlled activation of the so-called Thermal Donors (TD), up to very high C_l ($C_l = 140$) for which there is no previous report of μ. Extended activation led to a change from *p*- to *n*-type, thus allowing us to study the variation of μ_{Hall} in Si of both conductivity types in a wide range of C_l. We have approached Full Compensation (FC) ($C_l = \infty$) to a degree closer than one per hundred and measured more than 5-fold μ reduction. Comparison with regular μ models shows that these do not account for this behaviour, and that a compensation-specific mechanism should be added.

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2. Materials and methods

2.1. Compensation of boron by thermal donors

To simplify interpretation, EG⟨1 0 0⟩-oriented Cz-Si was chosen rather than SoG_M-Si. Starting with three initially *p*-type uncompensated wafers with $[B] = 7.2 \times 10^{14}\,cm^{-3}$ (wafer 01), $2.2 \times 10^{15}\,cm^{-3}$ (wafer 02) and $1.5 \times 10^{16}\,cm^{-3}$ (wafer 03) we managed to progressively achieve higher compensation by fine-tuning the formation of oxygen-related TD [9,10] at 450 °C, *T* at which their formation kinetics are well described [11]. On all wafers the interstitial oxygen concentration ($[O_i]$) was in the range $6–9 \times 10^{17}\,cm^{-3}$, as measured by Fourier Transform InfraRed (FTIR) spectroscopy. The main advantage of this method to adjust compensation is that C_I can be varied at will on the same sample, leaving the chemical composition unchanged other than TD formation. In studies of Si solar cells, previous use of C_I adjustment through TD activation has been made for various purposes, including the improvement of cell efficiency [12,13], and the reduction of Light-Induced Degradation (LID) [14], but not for study of μ at high C_I.

In lightly doped samples such as ours, it is now widely accepted that TD exhibit a double donor character [15]. The consequences of this are twofold. First, because one TD provides two free electrons, C_I has to be redefined as:

$$C_I = \frac{[B] + 2 \times [TD]}{[B] - 2 \times [TD]} \quad (1)$$

Also, because they are doubly ionized, their scattering power is enhanced by a factor of four compared to a singly-charged donor impurity such as P [16].

2.2. Mobility measurements

The wafers were first annealed at 650 °C for 30 min to remove potential pre-existing TD [10]. For reproducibility purposes, four $2 \times 2\,cm^2$ samples were cut from each wafer. The samples were then repeatedly annealed at 450 °C for different durations, in order to form TD. After each annealing step, μ_{Hall} and the Hall carrier concentration (n_{Hall}) were computed from the resistivity (ρ) and the Hall coefficient (R_H) measured with an Ecopia HMS3000 on a Van der Pauw configuration [17], according to:

$$n_{Hall} = \frac{1}{q \times R_H} \quad (2)$$

$$\mu_{Hall} = \frac{R_H}{\rho} \quad (3)$$

where *q* represents the electron charge. Because our Hall measurements were carried out under low magnetic field conditions ($\mu_B \ll 10^4\,T\,cm^2/V\,s$), μ_{Hall} and n_{Hall} differ from *n* and the true drift mobility (μ_{Drift}) by a factor close to unity, called the effective Hall factor (r_H) [18]:

$$n_{Hall} = \frac{n}{r_H} \quad (4)$$

$$\mu_{Hall} = r_H \times \mu_{Drift} \quad (5)$$

This set of relations shows that an accurate knowledge of r_H is needed to determine *n* and μ_{Drift} from Hall measurements. However, values of r_H in highly compensated Si as a function of *T*, doping and C_I are not reported in the literature. Nevertheless, as we will show in the light of our r_H measurements in Section 3, a fair assumption is to consider C_I-independent r_H values of 0.74 in *p*-type and 1.1 in *n*-type compensated Si. Under this condition, we were able to estimate the TD concentration ([TD]) after each annealing step from the following relation, the factor 2 arising from the double donor character of TD:

$$n_{Hall} = \frac{|[B] - 2 \times [TD]|}{r_H} \quad (6)$$

For each Hall measurement, ohmic contacts were formed by mechanically embedding liquid Indium–Gallium (InGa) at the corners of the sample. For *n*-Si, this method yielded fully coherent results even if InGa was not *a priori* suitable due to the acceptor character of In and Ga. Also, since high C_I correspond to high ρ, it appeared essential to check the validity of Hall measurements in the high ρ range. For this purpose, we estimated μ_{Hall} on an uncompensated *p*-type Cz-Si wafer with $\rho = 20\,k\Omega\,cm$. This gave a consistent result and ruled out measurements errors at high ρ. Nevertheless, in our experimental samples at very high C_I, μ_{Hall} data reached scattering levels of more than 20% and had to be discarded. We attribute this scattering to important spatial inhomogeneities in *n* within the sample close to FC arising from the strong dependence of the TD formation kinetics on the local $[O_i]$ [19].

From our set of μ_{Hall} data, we determined r_H for a number of C_I from Eq. (5), inserting μ_{Drift} as derived from 4-points-probe measurements by the relation $\mu_{Drift} = (q\rho n)^{-1}$, where *n* is derived from Capacity–Voltage (C–V) measurements at a frequency of 1 MHz on aluminum Schottky diodes. The main source of uncertainty on experimental μ_{Drift} was due to variations in *n* from diode to diode.

2.3. Mobility modelling

We also compared our experimental sets of μ_{Hall} and μ_{Drift} data to the predictions of μ_{Drift} from the semi-empirical model of Arora et al. [2]. This model is widely used in solar cell modelling programs such as PC1D [20]. It has been calibrated for uncompensated Si [2,21], but since it takes into account the scattering of majority carriers on ionized impurities, phonons and other charge carriers, it appears a reasonable extension to apply it to compensated Si as well.

3. Results and discussion

A first result of our study is that we were able to form TD at concentrations up to $1 \times 10^{16}\,cm^{-3}$. Therefore, FC can be achieved through TD activation on Cz-Si with initial [B] up to $1 \times 10^{16}\,cm^{-3}$, and possibly more on samples having higher $[O_i]$ [9]. The continuous tuning through the transition from *p*- to *n*-type is illustrated for wafer 01 on Fig. 1, which shows the evolution of $2 \times [TD]$ (i.e. the total number of electrons provided by TD), *n* and ρ versus annealing time for a typical sample. We have compared our experimental [TD] with the model of Wijaranakula [11], which was derived from experimental values fitted with a time dependent theoretical expression for [TD], with the initial $[O_i]$ as a parameter. The fit of our data led to $[O_i] = 7 \times 10^{17}\,cm^{-3}$, in excellent agreement with FTIR analyses. The good agreement between our results and the model supports the validity of our Hall measurements.

On wafer 01, the change in conductivity type occurred after almost 5 h at 450 °C. The condition closest to FC was $C_I = 1940$ on *p*-Si, where *n* was as low as $10^{12}\,cm^{-3}$. μ_{Hall} at this condition was extremely low, but as previously explained, it was subject to an unacceptably large uncertainty margin, and therefore we do not represent it in our further analysis. Fig. 2 then gives a plot of μ_{Hall} versus $1/C_I$, including points up to $C_I = 33$ (where $n = 6 \times 10^{13}\,cm^{-3}$ and $\rho = 650\,\Omega\,cm$). For both conductivity types, we observe a steep drop in μ_{Hall} close to FC, for C_I higher than around 5. On the *n*-type