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# Germanium-doped Czochralski silicon for photovoltaic applications

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ABSTRACT

Germanium (Ge)-doped Czochralski (GCZ) silicon has been grown for photovoltaic (PV) applications. It is found that Ge doping improves the mechanical strength of CZ silicon, resulting in the reduction of breakage during wafer cutting, cell fabrication and module assembly. Boron–oxygen (B–O) defects that lead to the light-induced degradation (LID) of carrier lifetime are effectively suppressed by Ge doping. The decrease in the maximum concentration of B–O defects increases with an increase of Ge concentration. The efficiency of GCZ silicon solar cells and the power output of corresponding PV modules both exhibit smaller loss under sunlight illumination. The current work suggests that GCZ silicon should be potentially a novel substrate for thin solar cells with low LID effect.

## 1. Introduction

About 35% of solar cells are currently fabricated using Czochralski (CZ) silicon in the world. The further widespread application of CZ silicon solar cells is limited by their high cost [1]. The adoption of thin silicon wafers for the fabrication of solar cells is effective in the cost reduction of CZ silicon solar cells [2,3]. In the past few years, the thickness of silicon wafers used for solar cells has decreased from 400 to 180 μm. It is predicted that the wafer thickness will be around 120 μm by 2020. This will definitely cause higher breakage during wafer cutting [4]. Meanwhile, the warpage will be a more serious problem during the cell fabrication [5]. Therefore, it is important to find a way to increase the mechanical strength of silicon wafers and assure a reasonable production yield for thin solar cells. The cost of CZ silicon solar cells may also be reduced by improving the cell conversion efficiency [6]. It is known that the boron-doped CZ silicon solar cells widely used in the photovoltaic (PV) industry unavoidably suffer efficiency degradation up to 10% under sunlight illumination [7,8]. The light-induced degradation (LID) effect is attributed to the formation of a metastable recombination center in silicon, which is composed of boron and oxygen [9]. This suggests that the LID effect of CZ silicon solar cells can be suppressed by reducing the concentration of either boron or oxygen [9,10]. Growth of CZ silicon crystal in a magnetic environment [11] or replacement of boron with gallium [12] may be employed to reduce or avoid the formation of boron–oxygen (B–O) defects in the practical production. However, the application of a magnetic field causes the cost of silicon crystal to increase. There exists a significant variation of resistivity along the axial direction in gallium-doped silicon crystal due to the small segregation coefficient of gallium in silicon.

In this work we demonstrate a novel silicon substrate doped with germanium (Ge) for photovoltaic applications. It is found that Ge doping improves the fracture strength of CZ silicon at room temperature, reducing breakage during cell and module fabrications. The performance of Ge-doped CZ (GCZ) silicon solar cells and their PV modules has lower degradation under sunlight illumination. These results suggest that GCZ silicon can be used for the fabrication of thin solar cells with low LID effect in the PV industry.

## 2. Experimental procedure

Several p-type boron-doped CZ silicon crystals with a resistivity of 1–3 Ω cm were grown under the same conditions. One is conventional CZ silicon, and the others are GCZ silicon with different Ge doping levels. After sampling the wafers from the seed-ends of these crystals, the interstitial oxygen concentrations were determined to be $\sim 1.0 \times 10^{18}/\mathrm{cm}^3$ by a Fourier transform infrared spectroscope (FTIR, Bruker, IFS 66 V/S) with a calibrated coefficient of $3.14 \times 10^{17}/\mathrm{cm}^2$. Ge concentrations in the GCZ samples were in the range of $10^{18}-10^{21}/\mathrm{cm}^3$, which were measured by a secondary ion mass spectrometer (SIMS, Cameca, IMS-4F).

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The influence of Ge on the mechanical strength of CZ silicon was investigated by two methods. One was to compare the fracture strength of the conventional CZ and GCZ samples. The 10mm × 20 mm rectangular samples with a thickness of 200 μm were prepared. After chemical etching in an acid solution ($HNO_3$:HF=3:1) for 1 min at room temperature to remove the surface damaged layers, the fracture strength of samples was measured by a universal testing machine (Zwick/Roell Z2.5) using three-point bending method. Note that the load span was $L=12$ mm, and the testing was carried out with a loading speed of 0.5 mm/min. The other method was to compare the statistics of breakage for several thousand wafers, comparing the conventional CZ and GCZ silicon during standard wafer cutting, cell fabrication and module assembly at the Trina Solar Company.

For samples cut from the similar positions of the conventional CZ and GCZ silicon ingots, both surfaces were passivated using plasma-enhanced chemical-vapor deposited silicon nitride films after the damaged layers were removed. A microwave photoconductance decay system (MW-PCD, Semilab, WT-2000) was used to measure the carrier lifetimes of these samples at 25 °C. In order to investigate the behaviors of B–O defects in the conventional CZ and GCZ silicon samples, the effective carrier lifetime ($\tau_{eff}$) was initially measured after annealing at 200 °C for 30 min and then inspected after one sun (100 mW/cm$^2$) illumination for 72 h.

Solar cells were fabricated from the 125mm × 125 mm quasi-square CZ and GCZ silicon wafers with a thickness of 200 μm on the same production line at the Trina Solar Company, and subsequently made into PV modules. Internal quantum efficiencies (IQE) of the CZ and GCZ cells were obtained from the cell spectral responses and the spectral reflectances. The illuminated current–voltage characteristics of the cells and modules were measured under one sun with AM 1.5 Global spectrum at 25 ± 1 °C, using Berger Flasher PSS 10 and Spire Spi-Sun Simulator 4600 solar simulators, respectively. The illumination intensity was calibrated using a reference cell obtained from FISE, Germany. After exposure to outdoor sunlight illumination for 2 weeks, the cell efficiencies and the module power output were both investigated again.

## 3. Results and discussion

### 3.1. Ge segregation during the CZ silicon crystal growth

Fig. 1(a) shows the Ge concentrations at the seed-ends of different GCZ silicon crystals and the designed Ge concentrations in the melt. It is known that the effective segregation coefficient ($k_{eff}$) of Ge during silicon crystal growth can be directly obtained by the Ge concentration at the seed-end of crystal divided by that in the melt. So, it can be deduced that the value of $k_{eff}$ is 0.56 from our experiments in which the rate of crystal growth ($v$) is 1.2 mm/min. Based on the theory of segregation, the Ge concentration in a silicon crystal, $C_s$, can be calculated using

$$C_s = C_0 k_{eff}(1-g)^{(keff-1)} \tag{1}$$

where $C_0$ is the initial Ge concentration in the silicon melt and $g$ the solidified fraction. Fig. 1(b) shows the measured and theoretically calculated concentrations of Ge at different positions of a GCZ silicon crystal. It can be seen that the simulation based on the segregation coefficient of 0.56 fits the experimental data well.

According to the classical Burton–Prim–Slichter (BPS) theory [13], the $k_{eff}$ can be expressed as

$$k_{eff} = \frac{k_0}{k_0 + (1-k_0)\exp(-(v\delta/D))} \tag{2}$$

where $\delta$ and $D$ are the impurity boundary thickness and diffusion coefficient, respectively. Using $\delta/D=120$ s/cm for the crystal rotation ($\omega$) of 20 rpm from Kodera [14] and Tiller [15], we obtain that the steady state segregation coefficient ($k_0$) of Ge is 0.5. This

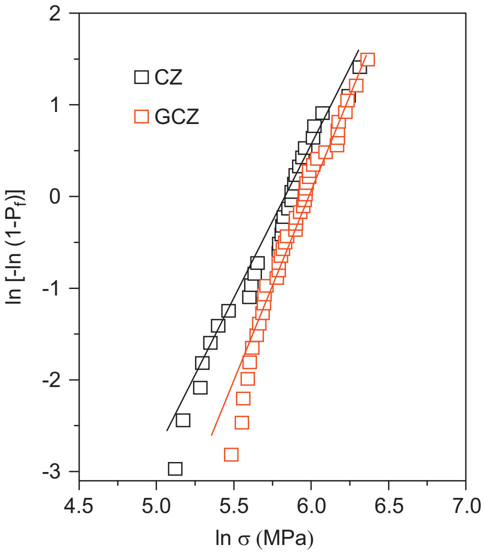

**Fig. 2.** Weibull plots of the variation of fracture strength with the applied stress for the conventional CZ and GCZ silicon.

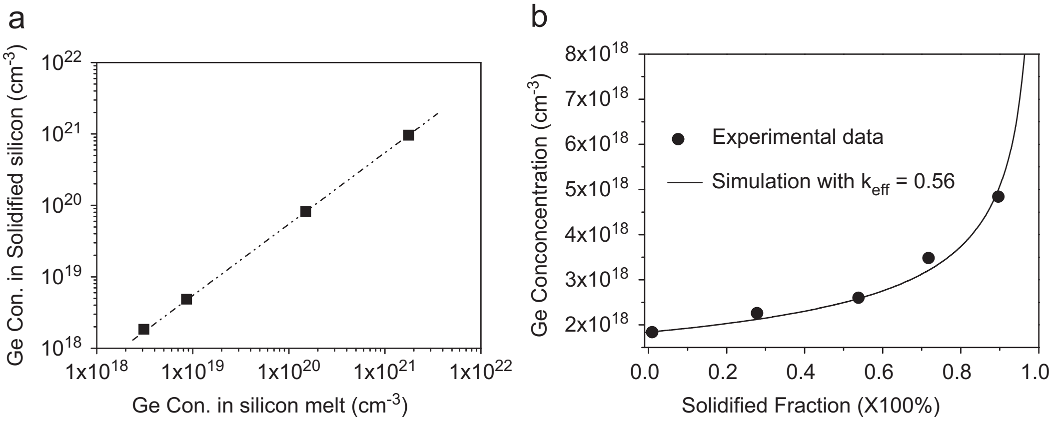

**Fig. 1.** (a) Measured Ge concentrations at the seed-ends of GCZ silicon crystals and the designed Ge concentrations in the silicon melt and (b) Ge concentration as a function of solidified fraction during the growth of a GCZ silicon crystal.