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Carrier lifetime limitation defects in polycrystalline silicon ribbons grown on substrate (RGS)

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ABSTRACT

Carrier lifetime limitation defects in polycrystalline silicon ribbons have been examined in samples with high oxygen and carbon content. Infrared spectroscopy showed that essentially all supersaturated oxygen impurities precipitated within 1 h annealing at over 800 °C. Preferential defect etching revealed that a much higher density of oxygen precipitates were generated in dislocation-free grains than in those highly dislocated (10^5–10^7 cm^{-2}) ones. Correlated with electron-beam-induced current imaging, we found that oxygen precipitates are the dominant carrier recombination defects in dislocation-free grains, while dislocations are the lifetime killer for highly dislocated grains. It is suggested that eliminating dislocations alone will not improve the carrier lifetime, considering that a higher density of oxygen precipitates formed in the absence of dislocation-related heterogeneous nucleation sites will significantly degrade the carrier lifetime.

1. Introduction

During the past several years, photovoltaic cell manufacturing grew at rates exceeding 30% per year. Crystalline silicon is by far the dominant photovoltaic material, and accounts for approximately 90% of the total cell production. The rapid growth has created a shortage in supply of polycrystalline silicon feedstock. The direct growth of thin silicon from molten Si is one of the several technology routes to alleviate the Si feedstock constrain. By decoupling the grain growth and the pulling directions, ribbon growth on substrate (RGS) silicon ribbons [1] can be pulled at a high speed of several meters per minute. The zero kerf loss and high productivity can significantly lower manufacture costs, making RGS ribbons highly suitable for low-cost terrestrial-based solar cells.

However, accompanying the cost-effective production advantages, RGS ribbons usually have a high density of grain boundaries, dislocations, twins, and other intragrain defects. The concentration of oxygen and carbon impurities is usually on the order of 10^{18} cm^{-3}, and transition metal content is also high due to the close proximity of the molten silicon and refractory materials used as dies or substrates [2,3]. The co-existence of a high density of structural defects, light element impurities and their precipitates, and transition metals can severely degrade the minority carrier recombination lifetime and cell efficiency. Thus, detailed knowledge on the distribution and evolution of defects and impurities is required in order to optimize ribbon growth/processing and to take advantage of this highly cost-effective growth process. In this paper, we first examined the dislocation profile, grain structures, and oxygen/carbon precipitation by preferential defect etching and Fourier transform infrared spectroscopy (FTIR). Minority carrier lifetime limitation defects were identified by correlation of electron-beam-induced current (EBIC) imaging and preferential defect etching.

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2. Experimental

RGS silicon ribbons of 200–300 μm thickness were grown at the Energy Research Center of the Netherlands. The ribbon wafers were boron doped and had a resistivity of approximately 1 Ω-cm. The specimens were annealed in a nitrogen atmosphere at temperatures between 800 and 1020 °C for various times. The precipitation of interstitial oxygen (O_i) and substitutional carbon (C_s) was examined by FTIR on a Digilab FTS-6000 spectrometer. A low oxygen containing float-zone silicon wafer was used as a reference to subtract the silicon lattice absorption. The concentrations of C_s and O_i were determined from the absorption peaks at 607 and 1107 cm^{-1} using conversion factors of 0.81×10^{17} and 3.14×10^{17} cm^{-2}, respectively, based on ASTM standards F1391 and F1188 [4].

Both as-grown and annealed samples were examined by EBIC and defect etching/Nomarski optical microscopy. Narrow strips cut from each sample were double-side polished to 300 μm in cross-section directions. Two millimeter diameter Schottky diodes were prepared on polished cross-sections by thermal evaporation of Al through a shadow mask. Ohmic contacts were produced by rubbing a eutectic Ga–In alloy on the opposite surface. EBIC measurements were performed on a scanning electron microscope at room temperature with an accelerating voltage of 20 KV and a probe current of ~0.1 nA. After EBIC measurements, the distribution of precipitates and associated extended defects was examined by Nomarski optical microscopy after stripping off the Al contacts in an HCl solution and preferentially etching the sample in Secco etchant for 30 s [5].

3. Results and discussion

3.1. Dislocations and light element impurities in as-grown sample

Fig. 1(a) is a plan-view Nomarski image after defect etching. Note that while some grains are almost dislocation-free, others contain a high density of dislocations, typically on the order of 10^5 or 10^6 cm^{-2}. Large thermal stresses are generated during rapid solidification and subsequent cooling processes. The inhomogeneous distribution of dislocations is in part due to the fact that the thermal stress exceeds the critical shear stress only in some particular orientated grains. Note that grains with none or low density of dislocations usually contain twin boundaries, while those highly dislocated grains usually do not have twins. This suggests that twin planes act as barriers for dislocation propagation and contribute to the inhomogeneous distribution of dislocations across various grains. Cross-sectional examination, see Fig. 1(b), shows that there are more dislocations near the wafer back surface than the top surface, suggesting a higher thermal stress exists there during solidification and subsequent cooling.

The concentration of C_s was generally in the range of 1.5×10^{18}–2.2×10^{18} cm^{-3}, and that of O_i in the range of 0.8×10^{17}–1.6×10^{18} cm^{-3}, respectively. Note that the carbon solubility in crystalline silicon is $\sim 3 \times 10^{17}$ cm^{-3} near the Si melting point [6]. The fact that the measured C_s concentration significantly exceeds the solubility suggests that the crystal growth rate is so high that a higher concentration of carbon was trapped in the crystal during solidification, in other words, the effective segregation factor of carbon impurities approaches unity. While the O_i and C_s contents can vary significantly from wafer to wafer by adjusting the growth thermal profiles and growth ambient, FTIR microspectroscopy showed no detectable oxygen and carbon variation across different grains within one sample. Fig. 2 is a representative FTIR spectrum of an as-grown sample. Note that absorption peaks due to nitrogen pairs [7] (766 and 963 cm^{-1}) and nitrogen–oxygen complexes [8] (801, 996 and 1026 cm^{-1}) are well resolved even though the sample thickness is only 300 μm. Using the calibration factor of 1.83×10^{17} cm^{-2} given in Ref. [7], the N_2 and N–O concentrations were determined to be 3×10^{16} and 1.5×10^{16} cm^{-3},

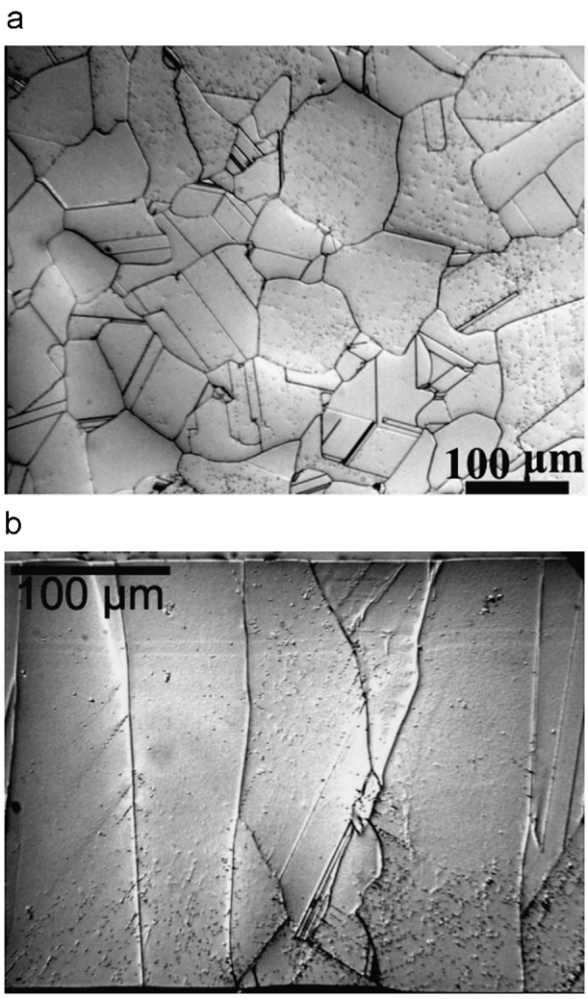

Fig. 1. (a) Plan-view and (b) cross-sectional Nomarski optical images of an as-grown sample after 30 s Secco defect etching.