Comparative studies of EFG poly-Si grown by different procedures

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Abstract

The impurity content in EFG polycrystalline silicon materials grown by different procedures from graphite and quartz crucible has been extensively studied using Fourier transform IR technique. It is shown that the oxygen content in the material is much more dependent on the growth atmosphere at meniscus than on the type of crucible. In all samples the carbon content remains supersaturated up to very high temperatures of annealing, not affected by the oxygen presence. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A polycrystalline silicon material grown with the edge-defined film-fed growth (EFG), as a useful material for low-cost solar cells production, has been investigated since the early 1970s [1]. The main advantage of EFG Si over Czochralski (CZ) Si, as a material for solar cell production, is a low wafer cost by using the capillary action shaping growth technique. The use of this technique eliminates needs for subsequent expensive wafering where ≈50% of the material is lost. EFG crystals are grown in a form of a hollow tube (typically octagon with 10 cm wide one side) several meters long, and about 200 μm thick. Due to low-cost processing and its polycrystallinity,
EFG material contains various crystallographic defects such as: grain boundaries, dislocations, intersecting twins stacking faults, etc., and high concentration of impurities such as carbon (C), oxygen (O) and metal impurities. The problem with metal impurities, though it presents a serious problem for the solar cell operation, is related to gettering action and/or control of the feed stock quality and will not be further discussed here. On the other hand, non-doping impurities often present in silicon, and particularly in this kind of material, affect significantly its electronic parameters [2]. Here we shall focalize on C and O as impurities intentionally or unintentionally introduced into the bulk during the course of production.

The graphite die, used for the shaping of crystal tubes, and graphite crucibles are an unavoidable source of the C found in EFG-Si material. Partition of C among substitutional sites, SiC and other C containing complexes in EFG sheets have been well documented [3] but not completely understood even on the qualitative level. C in silicon lattice is electrically neutral and appears to play no significant role other than to form pair defects with interstitial oxygen (O\text{I}) atoms. Nevertheless, when present in concentration higher than \(10^{16}\) atoms/cm\(^3\) it affects strongly the crystal perfection and the behavior of the Si wafers during device fabrication. Moreover, the C atom may be pushed from its regular position into the interstitial position, where it diffuses rapidly even at 300 K and it is trapped by the other impurity or structural defect. Such a newly formed complex structure may dominate lifetime in many polycrystalline materials used for photovoltaic applications.

O presence is found in all types of Si materials that have been processed in contact with quartz containers. The process of O incorporation has been recently reviewed by Borghesi et al. [4]. O presence in the bulk of the material affects significantly its mechanical and electronic properties. It has been shown that solar cells fabricated on O lean float zone (FZ) single crystal Si show a few percent higher efficiency than on CZ Si. Moreover, it is generally known that the formation of SiO\text{x} precipitates within the bulk of CZ Si affects both the recombination and generation lifetimes. In a polycrystalline material like EFG, O present up to the certain level (\(5 \times 10^{17}\) atoms/cm\(^3\)) is found to be very beneficial to solar cells properties [5]. Nevertheless, in spite of significant experimental and modeling efforts covering all interesting parameters of solar cells, a substantial singular mechanism for the improvements caused by O was not found. It was concluded that the action of O appears to reduce recombination on a wide variety of defects in all parts of the cell, thus leading to the general improvement in all parameters.

O introduction into the bulk of the growing polycrystalline sheet is possible either through the quartz container (than the process of O dissolving and incorporating into the bulk is expected to be similar as in the case of single crystals, as described in Ref. [4]), or by addition of O carrying gases like CO and CO\text{2} to the inert atmosphere close to the meniscus of the growing crystal. Here we shall examine both cases and try to understand the differences in O and C content due to different growth procedures.
2. Experimental

Two different types of EFG Si sheets for the present study were grown at Mobil Solar Energy Corp. (now ASE Americas Inc.) and at Foteks Ltd. (Moscow). The details of growth conditions of these two different types of EFG crystals were described in Refs. [3,6], respectively. All of the samples were boron-doped, with resistivity 2–4 $\Omega$cm and their thickness were about 200 $\mu$m. ASE Americas’s EFG samples were grown in argon atmosphere with or without addition of various amounts of CO$_2$ gas using a graphite die-crucible. FOTEKS’s EFG samples were grown in vacuum using a quartz crucible and a graphite die. Crystalline structure of the latter crystals was demonstrated to be very similar to ASE Americas’s EFG samples [7–9]. However, O and C content in these two different kinds of EFG crystals was expected to differ and was of particular interest under the present study.

IR measurements were performed with Fourier transform IR spectrometer Bruker IFS 113v. Spectra were collected from 5000 to 400 cm$^{-1}$, 4 cm$^{-1}$ resolution, and 512 scans were averaged to improve signal-to-noise ratio. FZ single crystal silicon wafer was used as a reference to remove multiphonon absorption.

3. Results and discussion

Fig. 1 shows typical differential IR spectrum of an ASE America’s EFG grown in the inert atmosphere using a graphite crucible versus O and C-free FZ Si wafer. Besides well pronounced peak at 605 cm$^{-1}$ due to $C_S$ in the bulk of silicon in concentration of $8 \times 10^{17}$ atoms/cm$^3$, Fig. 1 shows a broad peak from about 950–1100 cm$^{-1}$. The deconvolution showed two contributions, one due to $O_I$ (centered at 1107 cm$^{-1}$ and about 30 cm$^{-1}$ in FWHM) and the other at lower wave numbers, indicating the presence of O agglomerated in the suboxide-like form SiO$_x$. Such O is very likely agglomerated close to structural defects [10]. Moreover, very high $C_S$ concentration present in material would further promote such O agglomeration.

![Fig. 1. Differential IR spectrum of EFG-Si grown from the graphite crucible in inert atmosphere versus FZ Si sample.](image)
ASE America’s EFG samples grown in inert and in oxidizing atmospheres contain O\textsubscript{1} in concentration of about 2–6 \times 10^{16} and 6–12 \times 10^{16} atoms/cm\textsuperscript{3}, respectively. It is interesting to note, however, that in FOTEKS’s EFG samples grown from quartz crucible in vacuum (Fig. 2), we found only 1–2 \times 10^{16} atoms/cm\textsuperscript{3} of O\textsubscript{1}. This result suggests that in contrary to the expectation, material grown from quartz crucible contained less O\textsubscript{1}, i.e. is almost O\textsubscript{1} free. Moreover, as shown in Fig. 2, there was no indication for the significant presence of the larger SiO\textsubscript{x} clusters. However, annealing of such samples even at intermediate temperatures (650°C in vacuum for 24 h) evidenced a significant increase in SiO\textsubscript{x}-related bands in IR spectrum, as shown in Fig. 3. Fig. 3 shows a differential spectrum of the same sample, as shown in Fig. 2, but annealed at 650°C, versus the annealing step at 550°C. A strong increase in bands at about 1030 and 1090 cm\textsuperscript{-1} evidenced the formation of oxide precipitates in the bulk of the sample.

The mechanism responsible for the observed results is not quite clear yet and requires further study. One possible explanation of our results assumes that when EFG crystals are grown using a quartz crucible, incorporation of O into their bulk is significantly reduced in comparison to CZ process. This might occur due to the fact that crucible is fixed and hence convection in the melt is significantly reduced, so that major part of dissolved O evaporated in SiO form. Moreover, a die may additionally suppress the convection. The other possible explanation assumes that, since the meniscus of liquid silicon in EFG process and the growing tube are very thin, O out diffusion and evaporation from the meniscus also may substantially reduce O content, even for crystals grown from a quartz crucible. Nevertheless, certain portion of O gets incorporated but not in interstitial positions or in the form of larger, IR visible, SiO\textsubscript{x} precipitates. Thermal treatment already at 650°C drives this O to precipitate and therefore it becomes IR visible.
These EFG types of polycrystalline silicon contain C in a high supersaturation due to the specific design of the puller (graphite die and perhaps graphite crucible). The observed C content in the material grown from the graphite crucible (ASE America’s sample) was typically about $8 - 10 \times 10^{17}$ atoms/cm$^3$, while material grown from the quartz crucible (FOTEKS’s samples) was found to contain about $2 \times 10^{17}$ atoms/cm$^3$ of CS.

The CS content in various EFG samples and CZ silicon after different steps of thermal annealing is shown in Fig. 4. The C-doped single crystal CZ sample exhibits a strong reduction in the CS concentration after annealing in the temperature range 600–800°C, as it was already reported [11]. At the same time, the CS behavior in the EFG poly-Si material is completely different. The CS content in the EFG material grown from the graphite crucible seems not to be significantly affected by long term annealing up to about 1000°C. This occurs despite the fact that C concentration in

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**Fig. 3.** Differential IR spectrum of EFG-Si grown from the quartz crucible and annealed at 650°C versus the same sample annealed at 550°C for 24 h.

**Fig. 4.** Effect of isochronal annealing on substitutional C concentration in different EFG samples.
these samples was much higher than the solubility limit for given temperatures. The observed stable supersaturation of C remains in the material irrespectively of the O addition to the growing atmosphere [12]. A significant decrease in the Cs concentration is observed only upon annealing at the highest temperatures (of about 1150°C), as shown in Fig. 4, and in this particular case O presence enhances this process.

In material grown from the quartz crucible, as shown in Fig. 4, annealing at 450°C produces some very small change in the Cs content. Further annealing up to very high temperatures did not change Cs content significantly. Although many candidates (incoherent twin boundaries, dislocations, grain boundaries, etc.) for the nucleation center for C precipitation were already present in as-grown material, a prolonged annealing in the intermediate temperature range did not cause any significant variation in Cs concentration like in single crystals. Moreover, even O presence in the bulk did not affect C content in that temperature range.

Presented results are explained with the model of Si I lean lattice described in details in Ref. [12]. Comparing to the CZ single crystal Si, EFG polycrystalline Si was found to be a completely different environment for C, because this material is extremely poor in Si I. A gold diffusion study [13] confirmed this finding. This means that extended lattice defects in the bulk had an effective absorption coefficient for Si I about a factor of 10 higher than in CZ Si. This specific Si I-poor lattice in EFG material helped in maintaining high C supersaturation.

On the other hand, O is known for playing an important role in enhancing Si I concentration in CZ Si during the annealing, due to the known effect of Si I emission during O precipitation [4]. Therefore, for O-poor EFG, the initial shortage of Si I might cause a different C behavior in comparison to CZ material. On the other hand, even for O-rich type of EFG material, in spite of the significant portion of O present in the bulk, overall Cs behavior was the same and the significant difference appeared only at highest temperatures of annealing. It means that for such type of material even with substantial O present in the bulk, thermal treatments that usually produce O precipitation, and therefore Si I generation, were inefficient. The lack of Si I impact on the C content was due to the fact that sinks for Si I are more effective than the generation centers.

4. Conclusion

A comparative study of the impurity content in EFG Si grown from graphite and quartz crucibles has been performed. It has been shown that samples grown from graphite crucible contain negligible amount of O I, and in this case O may be intentionally added during the growth process through an oxidizing atmosphere. On the other hand, samples grown from quartz crucible, contain apparently negligible amount of O I, too. However, the certain amount of O is dispersed in small clusters and therefore it is IR invisible in as-received samples. Annealing of such samples at intermediate temperatures produces O redistribution, i.e. O precipitation. Nevertheless, influence of thermal treatment on C content in both types of EFG-Si is
almost negligible up to very high temperatures. This is explained with Si$_1$ deficiency in the Si lattice.

References