EFFECTS OF HEAT TREATMENTS ON THE MICROSTRUCTURE OF POLYCRYSTALLINE SILICON: A REVIEW

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ABSTRACT

This paper presents a systematic review of heat treatments on polycrystalline silicon wafers. Its goal is to analyze the microstructural changes caused by annealing heat treatments carried out by different authors over the last decade. The search covered papers published in Web of Science, Scopus, Science Direct and IEEE Xplore from 2014 to May 2023. A total of 11 articles were selected and analyzed in terms of the annealing profile adopted and the behavior of crystalline defects such as dislocations, grain boundaries and impurities after annealing. The results showed that high temperature annealing were mainly used to reduce the dislocation density, while lower temperatures were used to reduce the impact of impurities. Some studies have evaluated the lifetime of the charge carriers, which improved with the microstructural changes caused by the heat treatments.

Keywords: *Polycrystalline silicon, annealing, microstructure, crystalline defects.*

INTRODUCTION

Most solar photovoltaic panels use crystalline silicon cells, which accounted for 95% of all global production in 2020 [1]. The silicon used in solar cells can be either monocrystalline (mono-Si) or polycrystalline (poly-Si). These cells are still the most widely used due to the abundance of silicon and its excellent electronic, chemical and mechanical properties [2]. Mono-Si cells are manufactured from single crystal silicon ingots produced by complex and energy-intensive manufacturing processes, such as the Czochralski (CZ) process, while poly-Si cells are obtained from polycrystalline ingots manufactured by melting silicon in crucibles, usually by the directional solidification method [3]. Because of this, poly-Si cells are cheaper and the period required for the PV system to generate the same amount of energy that was used to produce it is also shorter [4].

Although they are a lower cost alternative to mono-Si, poly-Si cells are less efficient because they have more defects in their microstructure, such as grain boundaries, dislocations and impurities, which limit the lifetime of charge carriers [5]. Moreover, impurity precipitates tend to accumulate at grain boundaries and both also serve as a site for dislocation clustering, which are considered the most harmful defects to the electrical properties of poly-Si [6].

Annealing heat treatments can be employed to alter the microstructure and improve the performance of polycrystalline silicon in photovoltaic applications. Although several studies have been carried out in the last two decades, few reviews regarding the subject have been published. Among them are the papers of Sabatino e Stokkan [7], Hofstetter et al. [8] and Woo et al. [9].

Therefore, the motivation for conducting this review is the absence of recent reviews on the state of the art of the effects of annealing heat treatments on the microstructure of polycrystalline silicon wafers. Thus, the aim of this review is to analyze the results of different studies on the heat treatment of polycrystalline silicon and identify correlations between the various annealing profiles adopted, the microstructural changes caused and their impact on the material's electrical properties.

MATERIALS AND METHODS

The search was carried out in Web of Science, Scopus, Science Direct and IEEE Xplore databases with the following logical expression: ("poly-crystalline silicon"OR "polycrystalline silicon"OR "multicrystalline silicon"OR "multi-crystalline silicon") AND ("heat treatment"OR "annealing"OR "thermal treatment") AND ("defects"OR "microstructure"). The searches were carried out in the title, abstract and keywords fields of the databases for works published between January 2014 and May 2023.

Figure 1 shows the flowchart of the filtering process used for the selection of papers. A total of 184 articles were obtained, 42 in Web of Science, 96 in Scopus, 38 in Science Direct and 8 in IEEE Xplore. 76 repeated works were removed, leaving 108 articles for initial analysis with the application of the inclusion criteria: works that analyze microstructural changes caused by heat treatments in polycrystalline silicon, with a focus on crystalline defects that affect the efficiency of poly-Si used in photovoltaic cells. The first analysis consisted of evaluating the title, keywords and reading the abstract, 66 articles were eliminated at this stage because they were not in accordance with the research objective.

After dynamic reading of the remaining 42 papers, 8 were selected for the systematic review. The snowballing technique was used, both in the references and in the works that cited these articles, and another 3 articles were added, totaling 11 works for evaluation of the results obtained regarding the microstructural changes caused by the treatments and their impacts on the electrical properties of the material.

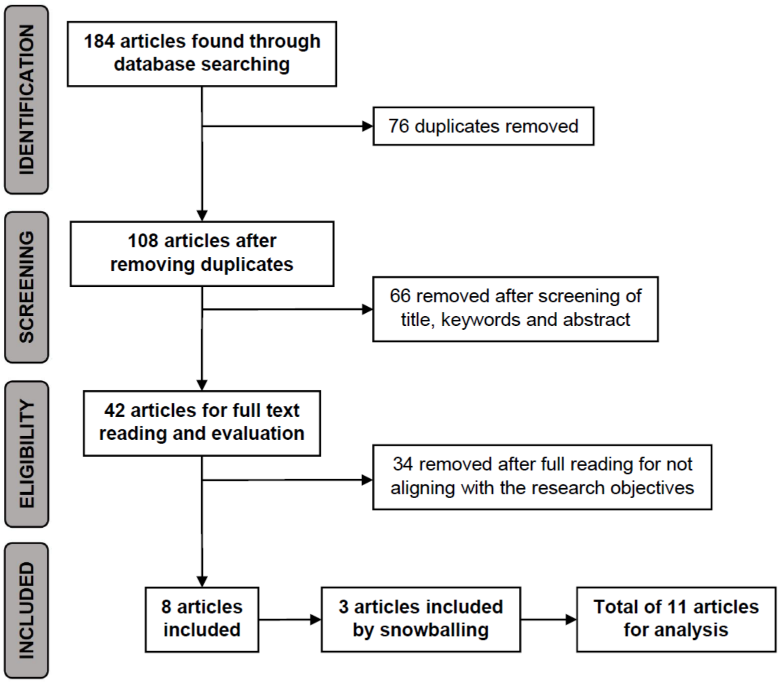

Fig. 1 - Filtering process applied in this systematic review.

RESULTS AND DISCUSSION

A summary comparison of the heat treatment conditions used and the main results of each work is shown in Table 1.

Table 1: Comparison between the different heat treatments applied and their main results.

Authors	Year	Heat treatment profile	Key results
Shen et al. [10]	2020	- 1300 °C for 2 and 10 h - Argon atmosphere	- Dislocation reduction - Grain growth - Impurity diffusion at grain boundaries - Increased lifetime
Shen et al. [11]	2019	- 800-1200 °C for 120 s - Argon atmosphere	- Dislocation reduction - Grain boundaries reduction - Grain size - Lifetime increase
Wu et al. [12]	2019	- 1400 °C for 30 min - Deformation from 10% to 1150 °C - 1400 °C for 15 min after deformation - Argon atmosphere	- 90% initial recrystallization - Reduction of dislocation density - Grain growth (>100 μm)
Vahanissi et al. [13]	2017	- 900-1150 °C for 10 min to 16 h - Nitrogen atmosphere	- Dislocation density increase in wafers of the middle region - Reduction of Fe concentration - Lifetime increase in red zone samples - Red zone do not reappear after oxidation
Al-Amin and Murphy [14]	2016	- 300, 400 and 500 °C for several time intervals (15 min - 15 h) - Nitrogen atmosphere	- Reduction of Fe concentration - Improvement in lifetime of low quality wafers
Choi et al. [15]	2015	- Isothermal at 1300 °C for 6-24 h - Cyclic between 1260 and 1340 °C for 6-24 h - Isothermal + cyclic for 24 h - No controlled atmosphere	- Dislocation reduction - Largest reduction: 12 h cyclic + 12 h isothermal
Castellanos and Buonassisi [16]	2015	- 1390 °C for 24 h - Nitrogen atmosphere	- Dislocation density reduction - Inclusions reduce effectiveness
Reimann et al. [17]	2015	- 1200 and 1365 °C for 1, 3 and 5 h with load - 1300 °C for 6-96 h without load - Argon atmosphere	- No dislocation reduction - The chemical etch solution can interfere in the results
Liu and Macdonald [18]	2014	- Surface passivation at 1000 °C for 45 min in dry oxigen - 400-700 °C for time intervals ranging from minutes to hours - Argon atmosphere	- Reduction of interstitial Fe concentration - Precipitation of Fe increases with density of dislocations
Kojima et al. [19]	2014	- 650 °C for 120 min - 1000 °C for 90 min - Nitrogen atmosphere	- Ni is not the dominant factor of recombination at grain boundaries
Takahashi et al. [20]	2014	- 700 °C for 35 min - 700 °C in 7 cycles of 5 min - No controlled atmosphere	- Suppression of defects generation - Removal of intra-granular interstitial Fe - Lifetime improvements

Most of the analyzed works address the effect of heat treatments on dislocations in polycrystalline silicon. These defects affect the electrical properties of silicon and it is possible to reduce their density with heat treatments. Most of the papers with this objective used high temperatures (1000-1400 °C) which increases the possibility of dislocation annihilation because their movement within the grains is not restricted to specific crystallographic glide planes at these temperatures [11]. Of the works analyzed, the only one in which the treatments did not cause significant changes in dislocation density was that of Reimann et al. [17], and increases were observed by Vähänissi et al. [13] in treatments before phosphorus diffusion gettering.

Dislocations are commonly analyzed indirectly with the observation of etch-pits, regions with high density of dislocations, being optical microscopy the most used technique. The quantification of these defects is performed by analyzing the images obtained with the aid of an algorithm, as mentioned in the methodology of Shen et al. [11], Vähänissi et al. [13], Choi et al. [15] and Reimann et al. [17]. In Wu et al. [12], the images were obtained by a developed high-resolution EBSD method. Other papers quoted dislocation density reduction values, but did not mention how they obtained the figures presented.

Heat treatments at low temperatures (400-700 °C) were carried out in Al-Amin and Murphy [14], Takahashi et al. [20], Liu and Macdonald [18] and Kojima et al. [19] with the aim of reducing the impact of impurities on the properties of poly-Si. Iron was studied in three of these papers and is a very common impurity that is deleterious to the performance of silicon. According to Vähänissi et al. [13], treatments at low temperatures help to reduce the density of iron precipitates, but do not contribute notably to reduce the total concentration, which the authors achieved with treatments at higher temperatures (900-1150 °C). The work of Kojima et al. [19] was the only one to study nickel as an impurity in silicon, focusing on its interaction with grain boundaries. One of the mechanisms involved in the annealing process at low temperatures is the diffusion of impurities distributed in the silicon matrix, which can be segregated in specific regions of the material, such as grain boundaries, reducing their concentration within the grains. Regions with impurity precipitation also act as sites for dislocations clustering and can hinder the effectiveness of heat treatments, as was also observed by Castellanos and Buonassisi [16] in high temperature annealing.

Constant temperature annealing is more common and was applied in all the selected works, but cyclic treatments were also performed by Takahashi et al. [20] and Choi et al. [15]. In the former with a focus on interstitial Fe removal and in the latter with a focus on dislocation reduction. In both papers, the cyclic treatments showed better results than the isothermal ones, and even better ones in combinations of isothermal and cyclic as observed by Choi et al. [15], since only cyclic treatments with multiple heating and cooling cycles can also contribute to defect multiplication. Furthermore, these two works were also the only ones that did not use controlled atmosphere in the annealing furnaces, but obtained satisfactory results despite this.

The crystallographic orientation maps obtained with EBSD were used to understand the grain boundary migration phenomena in polycrystalline silicon in Shen et al. [10] and Shen et al. [11] after annealing, and recrystallization after hot deformation and annealing in Wu et al. [12]. These works point out that the effects of annealing at elevated temperatures on grains and grain boundaries orientations are little addressed in the literature (unlike dislocations, which were also studied in these three works), but are also relevant microstructural features since they influence grain growth and boundary migration. Grain growth may improve the electrical properties by increasing the diffusion length of charge carriers, and the migration of the boundaries contributes to the diffusion of impurities and annihilation of dislocations. Kojima et al. [19] also used EBSD to obtain crystallographic information of the grain boundaries, concluding that the recombinative activity in these regions of the material is not restricted to the presence of Ni impurities.

Takahashi et al. [20], Al-Amin and Murphy [14], Vähänissi et al. [13], Shen et al. [10] and Shen et al. [11] used photoconductance tests to measure the lifetimes of charge carriers in samples before and after annealing, also using microscopy or photoluminescence techniques to identify correlations between changes in electrical properties and microstructure after heat treatment. The anneals applied in these five works resulted in increases in lifetime both in samples considered good and in samples that already have low lifetimes due to the material (e.g., metallurgical grade poly-Si, red zone samples). These improvements were attributed to changes in microstructural defects, reiterating that annealing has the potential to improve polycrystalline silicon used in photovoltaic cells, as has been reported in the literature in previous reviews.

CONCLUSIONS

This paper presented a systematic review on the effects of heat treatments on the microstructure of polycrystalline silicon wafers. Articles published between January 2014 and May 2023 were searched in Web of Science, Scopus, Science Direct and IEEE Xplore. A total of 11 articles were selected for analysis based on the inclusion criteria, with the most recent being from 2020.

The treatments used in the selected works caused different effects, such as diffusion of impurities with lower temperatures and reduction of dislocation density and migration of grain boundaries with high temperature heat treatments. The works that evaluated changes on the lifetime of the charge carriers obtained positive results, showing the feasibility of annealing to improve the efficiency of photovoltaic cells.

It was possible to notice that from 2014 until then, many efforts were dedicated to reducing dislocation density and their interactions with other defects, especially in the articles published in 2014 and 2015. This review also showed a lack of recent research on the subject, as the most recent article on the topic was published in 2020.

Considering the results and discussions of the works analyzed, this review is useful for researchers working with poly-Si wafers, who can use what has been presented to determine different heat treatment profiles according to the microstructural changes sought in each study.

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