Applied Energy 87 (2010) 3425–3430

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Application of phosphorus diffusion gettering process on upgraded metallurgical grade Si wafers and solar cells

H.B. Xu, R.J. Hong, B. Ai, L. Zhuang, H. Shen *

Institute for Solar Energy Systems, State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou 510006, China

ARTICLE INFO

Article history:
Received 31 January 2010
Received in revised form 14 March 2010
Accepted 27 March 2010
Available online 6 July 2010

Keywords:
Phosphorus diffusion gettering
Upgraded metallurgical grade Si
Minority carrier lifetime
Impurity content
Conversion efficiency

ABSTRACT

Although phosphorus (P) diffusion gettering process has been wildly used to improve the performance of Si solar cells in photovoltaic technology, it is a new attempt to apply P diffusion gettering process to upgraded metallurgical grade silicon (UMG-Si) wafers with the purity of 99.999%. In this paper, improvements on the electrical properties of UMG-Si wafers and solar cells were investigated with the application of P diffusion gettering process. To enhance the improvements, the gettering parameters were optimized on the aspects of gettering temperature, gettering duration and $POCl_3$ flow rate, respectively. As we expected, the electrical properties of both multicrystalline Si (multi-Si) and monocrystalline Si (mono-Si) wafers were significantly improved. The average minority carrier lifetime increased from 0.35 μs to nearly about 2.7 μs for multi-Si wafers and from 4.21 μs to 5.75 μs for mono-Si wafers, respectively. Accordingly, the average conversion efficiency of the UMG-Si solar cells increased from 5.69% to 7.03% for multi-Si solar cells (without surface texturization) and from 13.55% to 14.55% for mono-Si solar cells, respectively. The impurity concentrations of as-grown and P-gettered UMG-Si wafers were determined quantitively so that the mechanism of P diffusion gettering process on UMG-Si wafers and solar cells could be further understood. The results show that application of P diffusion gettering process has a great potential to improve the electrical properties of UMG-Si wafers and thus the conversion efficiencies of UMG-Si solar cells.

1. Introduction

Since 2000, photovoltaic (PV) industry has achieved a rapid development at an annual average rate of 40% as one of the fastest sector among all sorts of renewable energy. This growth is not only led by progress in materials and the technology of manufacturing but mainly by the market introduction [1]. However, the worldwide PV market is so limited and shares less than 1% in the whole power market because of the high manufacturing costs and relatively low conversion efficiencies of PV cells. As the main raw materials of traditional PV cells, the production cost of high purity Si is relatively high and accounts for more than 30% in PV modules at present. In order to find more cost-effective method of production of Si materials, upgraded metallurgical grade Si (UMG-Si) with the purity of 99.999% (5 N) has been successfully purified from high purity Si oxide with physical and metallurgical method and the UMG-Si solar cells with an average conversion efficiency of more than 13.3% have been put into commercial production on a scale of several hundred megawatts. Since the UMG-Si material can be used to prepare relatively high performance Si solar cells with low cost, it is recognized as the most promising substitute for the traditional chemically purified high purity Si to realize large-scale industrial production of crystalline Si solar cells [2–4]. How to improve the performance of UMG-Si materials and thus the conversion efficiency of UMG-Si solar cells has become an urgent problem.

As we know, the UMG-Si with 5 N purity has a relatively high concentration of impurities, especially transition metal impurities, such as Fe, Al, Ca, Ni, Cu and Cr. [5]. Due to the generally high charge carrier recombination activity of especially transition metals and their precipitates, the presence of such contamination may limit the electrical performance of UMG-Si wafers and solar cells [6]. It is well known that phosphorus (P) diffusion gettering process has been wildly used to improve the performance of conventional high purity Si wafers and solar cells in PV industry. Because P diffusion gettering process can effectively reduce the transition metal contaminants in the bulk of silicon wafers and enhance the minority carrier recombination lifetime of the wafers [7–9]. The efficiency of P diffusion gettering process is of crucial importance during the processing of crystalline silicon solar cells due to the detrimental effects on the solar cell performance of even relatively small amounts of electrically active transition metals [10–12]. However, few studies reported the application of P diffusion get-

---

* Corresponding author. Tel.: +86 020 39332861; fax: +86 020 39332866.
E-mail address: shenhui1956@163.com (H. Shen).

0306-2619/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.apenergy.2010.03.026

tering process on UMG-Si wafers and solar cells. So it is a new attempt to apply P diffusion gettering process to UMG-Si wafers so that the detrimental effects of transition metal impurities can be reduced and the performance of UMG-Si solar cells can be improved effectively.

This paper investigates the improvements of P diffusion gettering process on the electrical properties of UMG-Si wafers and ultimately on the performance of screen-printed UMG-Si solar cells fabricated on the wafers, with particular focus on the response of transition metal impurity content to P gettering process and the influence of the different diffusion parameters on the gettering behavior of the wafers. Through the application of P diffusion gettering process on UMG-Si wafers and solar cells, the necessity and great potential to apply P gettering in the UMG-Si solar cell fabrication process will be presented and discussed in the following sections.

2. Experimental

All samples investigated in this study were processed on 1.0–1.5 Ω cm boron (B) doped UMG monocrystalline Si (mono-Si) and multicrystalline Si (multi-Si) wafers, acquired from commercial production by Czochralski (Cz) method in Cz single crystal furnace and consequent wire sawing. For comparison, neighboring wafers with almost the same physical properties were selected to compare the variations on electrical properties of the wafers and performance of the solar cells after different gettering processes. P diffusion gettering processes were performed in a diffusion furnace tube using liquid $POCl_3$ (P source) as the dopant source carried by nitrogen (N_2). More details on P diffusion gettering process mentioned above are given in Section 3 upon discussion of the results.

Mapping of the minority carrier lifetime was performed by microwave photoconductance decay (μW-PCD) measurements on SEMILAB WT2000 tester. Prior to the recombination lifetime measurements, the samples were prepared by chemical polish in a mixture of HF, HNO_3, and CH_3COOH in order to remove any traces on the surface of the previous processing. The content of the main transition metal impurities were tested by inductively coupled plasma optical emission spectrometer (ICP-OES). Screen-printed solar cells were fabricated on P-gettered and as-grown UMG-Si wafers (monocrystalline and multicrystalline) with the same processing respectively. And no surface texturization was performed on the multi-Si solar cells because the solar cell fabrication in this study was just in the purpose of investigating the efficiency of P diffusion gettering process on UMG-Si wafers and solar cells. The conversion efficiency of the solar cells were tested by TDC-156AZ *I–V* characteristic curve tester which was made in Kunming Photovoltaic Technology Limited Company.

3. Results and discussion

3.1. Fundamentals of diffusion gettering process

As mentioned above in Section 1, high concentration of transition metal impurities and their precipitates exist in the UMG-Si bulk. These transition metal contaminants may be present in different states, for example, interstitially dissolved, as metal-silicide precipitates, or as larger micron-sized particles [13,14]. And the different forms of contaminants may cause formation of dislocation networks or structural defects in certain regions of the material during Si crystal growth, especially during solidification of UMG multi-Si block, known to increase the minority carrier recombination activities in such regions and ultimately limit the electrical performance of UMG-Si solar cells [15,16].

As mentioned above, P diffusion gettering process is widely used to decrease the impurity content in photovoltaic or microelectronic devices and thus the detrimental effects of the impurity contamination. Several methods for achieving such impurity gettering are employed in Si device processing, which are usually based on exploiting naturally occurring or deliberately introduced sinks for diffusing impurities within the bulk (internal gettering) or at the surface (external gettering) of the Si wafer and thus capturing the impurities in regions of the material where the detrimental effects are minimized [17]. According to a review study by Myers et al. [18], impurities gettering can be classified into following five different categories based on the mechanisms involved: (i) precipitation of metal silicides at energetically favorable nucleation sites, such as at the surface, at grain boundaries or dislocations within the Si material; (ii) atomic trapping at lattice defects without formation of a second phase; (iii) segregation into a second phase due to the impurity solubility difference in different phases; (iv) interaction with electronic dopants due to electrostatic attraction between ionized dopant atoms and oppositely charged metals; (v) P diffusion gettering which combines all or some of the above mechanisms. Due to the significant effect on improving the electrical performance of Si devices, P diffusion gettering process is usually treated separately in spite of the incomplete understanding of this phenomenon. By analysis of the individual mechanisms contributing to the P diffusion, the intrinsic diffusivities of the impurity atoms or impurity-induced defects can be expressed as [19]:

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \tag{1}$$

where D denotes the intrinsic diffusivity of the impurities or defects, D_0 is diffusion constant, E_a corresponds to the activation energy needed to activate the impurities or defects to diffuse away, k_B is Boltzmann constant, and T is the diffusion gettering temperature.

3.2. P diffusion gettering on UMG-Si wafers

As we know, P diffusion gettering can be treated separately to improve the electrical performance of photovoltaic devices, such as Si wafers and solar cells [20–22]. It is also necessary to decrease the detrimental effects of transition metal impurities incorporated in the UMG-Si wafers and thus improving the performance of UMG-Si solar cells. This is a new attempt to apply P diffusion gettering process to UMG-Si wafers before solar cells were fabricated. The P diffusion gettering was treated in a commercial $POCl_3$ tube furnace with $POCl_3$ carried by N_2. To evaluate the effects of P diffusion gettering process on the electrical properties of UMG-Si wafers, the parameters such as P diffusion gettering temperature, gettering duration and P source flow should play important roles that directly determine the gettering efficiency of Si wafers. The minority carrier recombination lifetime was measured before and after P gettering process. Prior to the measurement of minority carrier lifetime, P gettering layer with a thickness of about 10 μm on the sample surface was removed by chemical polish.

A tentative experiment of P gettering was performed on UMG mono-Si and multi-Si wafers before investigating the dependence of P gettering efficiency on different gettering parameters. $125 \times 125\ \text{mm}^2$ square UMG-Si wafers with radius angles and a thickness of 200 μm are used in the experiment. The digital photographs of as-grown UMG-Si wafers and their minority carrier lifetime maps are shown in Fig. 1. The gettering temperature, gettering duration and P source flow rate were 930 °C(2100 s) + 980 °C(600 s) and 1800 ml/min respectively. In comparison, the average lifetime results of UMG mono-Si and multi-Si wafers are shown in Fig. 2. It can be seen that the average life-