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Effect of Thermal Annealing on Characteristics of Polycrystalline Silicon

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Abstract: Oxygen and carbon behaviors and minority-carrier lifetimes in multi-crystalline silicon (mc-Si) used for solar cells are investigated by FTIR and QSSPCD before and after annealing at 750~1150 ℃ in N_2 and O_2 ambient. For comparison, the annealing of CZ silicon with nearly the same oxygen and carbon concentrations is also carried out under the same conditions. The results reveal that the oxygen and carbon concentrations of mc-Si and CZ-Si have a lesser decrease, which means oxygen precipitates are not generated, and grain boundaries in mc-Si do not affect carbon behavior. Bulk lifetime of mc-Si increases in N_2 and O_2 ambient at 850, 950, and 1150 ℃, and the lifetime of mc-Si wafers annealed in O_2 are higher than those annealed in N_2, which shows that a lot of impurities in mc-Si at high temperature annealing diffuse to grain boundaries, greatly reducing recombination centers. Interstitial Si atoms filling vacancies or recombination centers increases lifetime.

Key words: polycrystalline silicon; oxygen; lifetime
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1 Introduction

Polycrystalline Si wafers have become prevalent in the recent photovoltaic market. However, they need further quality improvement for highly efficient, low-cost solar cells. First we must understand the behaviors of impurities and defects in the polycrystalline Si wafers in more detail. Because there are grain boundaries and more impurities and defects, mc-Si material has more complicated physical behavior in high temperature annealing than mono-crystalline silicon. Oxygen in mc-Si is a very important impurity that affects the electrical and mechanical properties of silicon material during heat treatments[1]. However, the formation of oxygen precipitates, the variety of minor carrier lifetimes, and the influence of the annealing ambient are less investigated for polycrystalline silicon solar cells. In this paper, the effects of thermal annealing on oxygen behavior and carrier lifetimes for polycrystalline Si wafers are investigated.

2 Experiment

The polycrystalline Si wafers provided by Bayer Solar Corporation in this experiment were p-type, 0.9Ω·cm, and 285μm thick. The interstitial oxygen and substitute carbon concentrations of the samples were 8.3×10^{17} and $2\times10^{17}cm^{-3}$, respectively. For comparison, p-type CZ-Si samples with 〈100〉 orientation, 1~3Ω·cm, a thickness of 330μm, and almost the same oxygen concentration were also studied. The samples were cleaned with chemical solution, and Si oxide was removed in an HF(10%) solution. Then they were subjected to heat treatment at 1260 ℃ for 1h in N_2 ambient so as to eliminate the influence of thermal history before

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annealing[2]. A single step heat treatment was then carried out in the temperature range of 750～1150 ℃for 4h in N_2 and O_2 ambient. Interstitial oxygen concentrations and minority-carrier lifetimes before and after annealing were determined by FT-IR (Fourier transmission infrared spectroscopy) and QSSPCD (quasi-steady state photoconductance decay). Finally, the samples were etched by Sirtl or Wright solution and were examined with an optical microscope and SEM.

3 Results

3.1 Change of the interstitial oxygen concentrations

Figures 1 and 2 show the profiles of the interstitial oxygen concentration of CZ-Si and mc-Si during single step annealing in the temperature range of 750～1150 ℃in N_2 and O_2 ambient. It can be seen that the oxygen concentration in CZ-Si and mc-Si slightly decreases (except for the light increase in mc-Si at 950 ℃). The change of oxygen concentration is almost uniform in N_2 and O_2 annealing. This indicates that there is almost no generation of oxygen precipitates in CZ-Si and mc-Si wafers in N_2 or O_2 ambient. This has less influence on oxygen concentration during single step annealing.

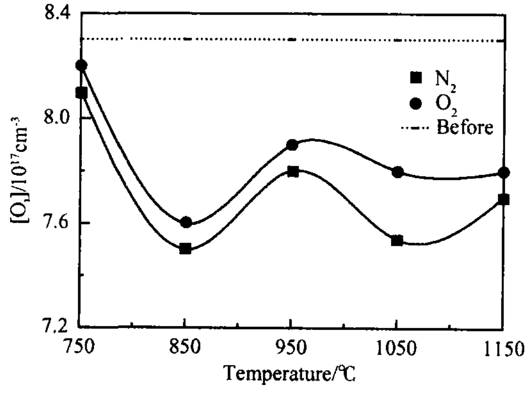

Fig. 1 Interstitial oxygen changes with annealing temperature under N_2 and O_2 surrounding in CZ-Si wafers

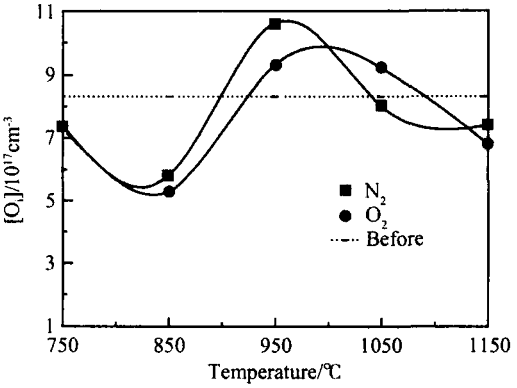

Fig. 2 Interstitial oxygen changes with annealing temperature under N_2 and O_2 surrounding in mc-Si wafers

3.2 Change of substitute carbon concentration

Carbon in CZ silicon has been reported to have a significant influence on oxygen precipitation during heat treatments. In addition, there is a much higher carbon concentration in mc-Si than in CZ silicon. Carbon can enhance the nucleation of oxygen precipitates at low temperatures (< 850 ℃) and does not affect the amount of oxygen precipitates at higher temperatures (> 950 ℃)[2]. Carbon concentration after annealing was determined by FT-IR. As shown in Table 1, the carbon concentration does not affect the amount of oxygen precipitate at higher temperatures in single annealing, and grain boundaries in mc-Si do not affect carbon behavior.

Table 1 Change of substitute carbon concentration of mc-Si

T/ ℃	750	850	950	1050	1150
$[C_s]/10^{17}cm^{-3}$ N_2 ambient	2.05	1.9	2.15	2.2	1.6
$[C_s]/10^{17}cm^{-3}$ O_2 ambient	2.4	2.6	2.5	1.8	2.6

3.3 Change of carrier lifetime

Figures 3 and 4 show change of carrier lifetime of silicon wafers during single step annealing in the temperature range of 750～1150 ℃in N_2 and O_2 ambient. The lifetime of CZ-Si wafers after annealing decreases drastically with increasing annealing temperature but has a recovery at 950 ℃, which probably generates many defects and new recombination centers ,and some interstitial Si atoms filling vacancies or recombination centers result in lifetime recovery at 950 ℃ Also ,the lifetime of CZ-Si wafers annealed in O_2 ambient is lower than those annealed in N_2. This phenomenon is probably due to the fact that during annealing in O_2 ambient ,interstitial Si atoms are supplied from a growing SiO_2/ Si interface so that excess interstitial Si atoms might recreate new recombination centers[3].

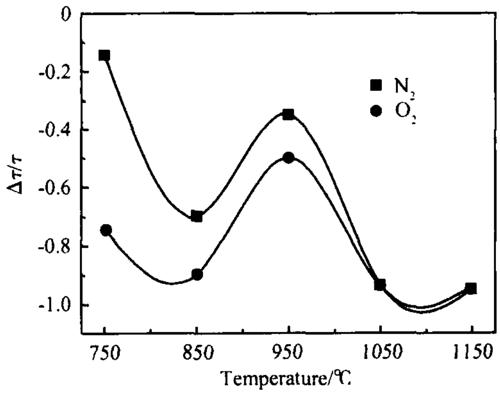

Fig. 3 Ratio of minority carrier lifetime changes with annealing temperature under N_2 and O_2 surrounding in CZ-Si wafers

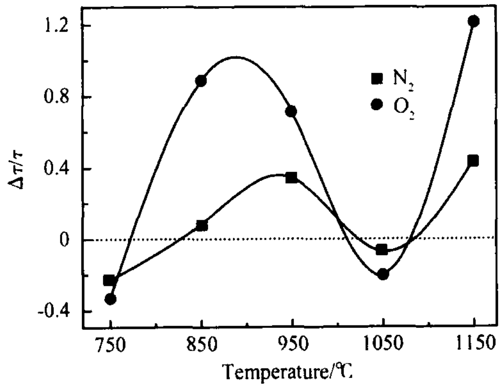

Fig. 4 Ratio of minority carrier lifetime changes with annealing temperature under N_2 and O_2 surrounding in mc-Si wafers

As shown in Fig. 4 ,the lifetime of minority carriers in mc-Si wafers has great increases at 850 , 950 ,and 1150 ℃,respectively. The changes of lifetime in N_2 and O_2 ambient are almost the same. The lifetime of mc-Si wafers annealing at 1150 ℃ increases 120 % in O_2 ambient and the lifetime of mc-Si wafers annealed in O_2 ambient is higher than those annealed in N_2. The reason for the increase is probably due to the fact that a lot of impurities in mc-Si at high temperature annealing diffuse to grain boundaries , greatly reducing recombination centers. On the other hand , interstitial Si atoms filling vacancies or recombination centers results in a lifetime increase.

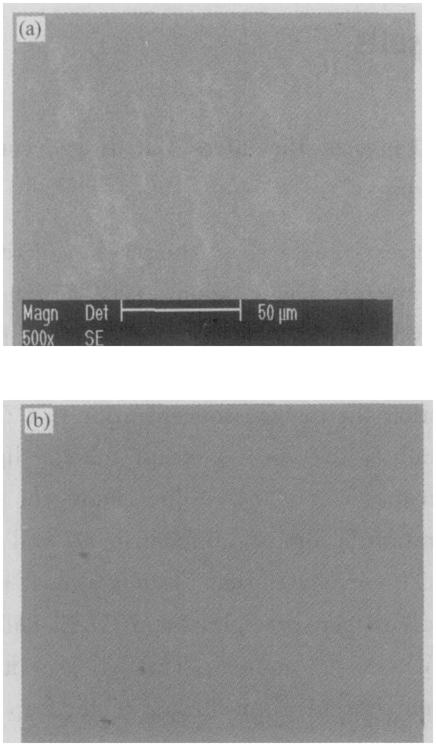

Fig. 5 SEM(500 ×) (a) and optical micrographs (200 ×) (b) of defects in the cleavage plane of mc-Si after annealing at 1050 ℃

4 Conclusion

We conclude that the oxygen concentration of mc-Si and CZ-Si had a slight decrease (except for a light increase in mc-Si at 950 ℃) in N_2 and O_2 ambient during single-step annealing , which means oxygen precipitates were generated. Lower carbon concentration did not affect the amount of oxygen precipitates at higher temperatures , and grain boundaries in mc-Si did not affect carbon behavior.

Bulk lifetime of mc-Si increased with temperature in N_2 ambient at 850, 950, 1150 ℃, and annealing in O_2 showed better results than in N_2. On the contrary, the lifetime of CZ-Si annealed in N_2 or O_2 decreased rapidly. The changes of lifetime and oxygen concentration in N_2 and O_2 annealing were almost the same. The reason for the lifetime increase is probably due to the fact that a lot of impurities in mc-Si at high temperature annealing diffuse to grain boundaries, greatly reducing recombination centers. On the other hand, interstitial Si atoms filling vacancies or recombination centers results in a lifetime increase.

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热退火对多晶硅特性的影响

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摘要: 为研究热退火对太阳电池用多晶硅的影响,在 750～1150 ℃,N_2 和 O_2 环境下分别对硅片进行热处理. 用傅里叶红外光谱仪和准稳态光电导衰减法测量退火前后的氧碳含量和少子寿命的变化. 为了比较,对有相同氧碳含量的直拉硅片进行同样处理. 结果发现:在多晶和单晶片中氧碳含量下降很小,意味着没有氧沉淀产生,晶界对碳行为影响不大. 多晶硅片在 N_2 和 O_2 环境下,850、950 和 1150 ℃下退火,少子寿命都有很大提高,并且在 O_2 中退火比 N_2 中退火少子寿命上升得更多,可能由于在高温退火时大量杂质扩散到晶界处,减少了复合中心. 另外,间隙硅原子填充了空位或复合中心从而导致寿命提高.

关键词: 多晶硅; 氧; 寿命

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