

Preparation and Performance Analysis for Thin-Film Materials of Crystalline Silicon Solar Cell Based on Chemical Method

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With the deepening of the sustainable development concept, solar cells as a clean energy has become the most promising material to replace fossil energy. The production cost of crystalline silicon thin film materials accounts for more than over 90% of solar cell raw materials, so it is the focus of research on solar cells to prepare the crystalline silicon thin film materials. In this paper, crystalline silicon solar cell films were prepared by rapid photothermal annealing (RPA) and rapid thermal chemical vapor deposition (RTCVD). Then, the properties of the films were investigated. The results show that RPA and RTCVD are important methods for preparing large crystalline silicon films; annealing conditions, annealing time and deposition temperature all affect the deposition of crystalline silicon. The most critical process to ensure solar cell quality is the junction process. In order to obtain a greater probability of carrier collection, the p-n junction should be as close as possible to the surface and form a shallow junction. This study provides experimental and theoretical basis for the preparation of crystalline silicon solar cell film materials at high temperature and low temperature.

1. Introduction

As an engine of national economy and national science and technology development, energy has been an indispensable substance in people's lives, and human demand for energy has been increasing (Yan et al., 2018). Solar energy is the most widely distributed, convenient, clean and pollution-free energy on the planet. It seeks to use solar energy for photothermal and photoelectric conversion, and the development of solar cells has become an important way to solve the worldwide energy crisis and environmental pollution (Borisuyuk et al., 2016; Han et al., 2016). Due to its high reliability, long life and ability to withstand various environmental changes, solar photovoltaic technology has become an important "green" energy in civil, military and high-tech fields (Wu and Lin, 2011). The solar cell is a physical device that utilizes the photovoltaic effect of the P-N junction. When the P-type region and the N-type region receive light, the electrons in the P-type region move to the N-type region to form a potential difference, thereby forming a power source (Fischer et al., 2013; Gnanamuthu et al., 2012).

Silicon materials are commonly used solar cell film materials, including single crystal silicon, cast polycrystalline silicon, thin film amorphous silicon, ribbon polycrystalline silicon, and thin film polycrystalline silicon (Hwang and Park, 2010). Compared with monocrystalline silicon solar cell film materials, polycrystalline silicon solar cell film materials have lower cost and can directly produce large-sized square silicon ingots suitable for large-scale production, making crystalline silicon solar cells more efficient and stable (Huang et al., 2016). Amorphous silicon cells have a larger absorption coefficient than crystalline silicon cells, and integrated technology can be used to complete the components at a time in the battery preparation process, eliminating the need for separate fabrication of materials, devices, and components (Boldyrev et al., 2013). The crystalline silicon thin film materials include low temperature preparation, medium temperature preparation and high temperature preparation (Pan et al., 2017). In this paper, crystalline silicon solar cell films were prepared by RPA and RTCVD, and the properties of the films were then studied. Besides, it proposes a new cost-cutting layer transfer technology for the preparation of crystalline silicon solar cells.

2. Crystalline silicon solar cell film material prepared by rapid photothermal annealing

2.1 Effect of annealing conditions and deposition temperature on crystallization of thin films

The crystallization rate of thin film materials prepared by plasma enhanced chemical vapor deposition is very slow, while that of crystalline silicon solar cell film materials can be greatly increased by the RPA (Mortazzavi et al., 2017). The heat source for RPA is a tungsten halogen lamp. The new technology is short in use, low in heat consumption, and large in yield. Thus, the crystal silicon film obtained by crystallization has few defects and low internal stress (Sun et al., 2013). Light irradiation is generated through the tungsten halogen lamp in a concentrating cavity, irradiated onto the sample through a quartz cell, and most of the light is absorbed by the silicon wafer, so that the temperature rises rapidly (Yan et al., 2014). Annealing conditions and deposition temperature etc. can affect the crystallization effect. Table 1 shows the relationship between grain size, dark conductivity and annealing temperature of crystalline silicon film. It can be seen that at the annealing temperature of 900 °C, the grain size is the largest and the dark conductivity is the biggest. Table 2 lists the relationship between grain size, dark conductivity and annealing time of crystalline silicon film; the grain size and dark conductivity show the same change rule. With the increase of annealing time, the grain size and dark conductivity increase.

Table 1: Relationship between grain size, dark conductivity and annealing temperature of crystalline silicon thin films

Annealing time/min	Annealing temperature/°C	Grain size/nm	Dark conductivity/ $\Omega^{-1}\text{cm}^{-1}$
3	800	18.3	6.22×10^{-7}
3	900	24.7	6.56×10^{-6}
3	1000	18.8	8.71×10^{-7}
3	1100	15.5	7.09×10^{-7}
6	800	31.4	7.14×10^{-5}
6	900	35.7	1.35×10^{-4}
6	1000	18.1	7.76×10^{-7}

Table 2: Relationship between grain size, dark conductivity and annealing time of crystalline silicon thin films

Annealing temperature/°C	Annealing time/min	Grain size/nm	Dark conductivity/ $\Omega^{-1}\text{cm}^{-1}$
900	2	22.2	7.61×10^{-7}
900	3	24.7	5.56×10^{-6}
900	6	35.7	1.35×10^{-4}
1000	2	16.2	9.71×10^{-8}
1000	6	18.1	7.76×10^{-7}
1000	11	13.2	1.63×10^{-7}

2.2 Rapid preparation of crystalline silicon film by improved rapid photothermal annealing method at low temperature

The light wavelength and intensity are the main factors affecting the crystallization rate. The thermal photothermal annealing process has thermal effects and quantum effects. Short-wavelength photons play an important role in RPA. The improved RPA equipment still has abundant short-wavelength light when the annealing temperature is low. Under such circumstances, we adopt low-temperature rapid preparation of crystalline silicon solar film. Figure 1 shows the relationship between the annealing temperature and the conductivity of the rapid photothermal treatment in two control mods. Compared with the second annealing mode, at the annealing time of 2.5h in the first mode, the annealing temperature is increased and the conductivity is not as good as that in the second mode at the annealing time of 70 minutes. Changing the power supply voltage of the tungsten halogen lamp can change the luminescence spectrum. Figure 2 shows the change of conductivity under different irradiation light intensity, indicating that the higher the light intensity, the faster the crystallization rate, but with the increase of annealing time, the effect of light intensity is not significant.

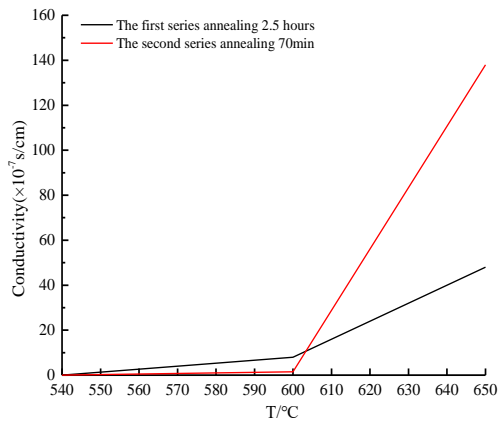


Figure 1: Relationship between annealing temperature and conductivity of rapid photothermal treatment in two control modes

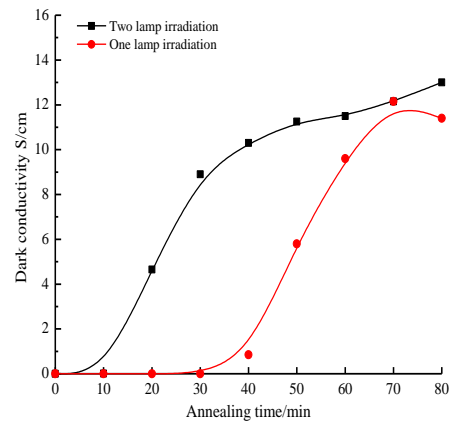


Figure 2: Conductivity change under different irradiation light intensity

3. Crystalline silicon solar cell film materials prepared by rapid thermal chemical vapor deposition

3.1 Process and characteristics of silicon film prepared by RTCVD

The RTCVD method means utilizing light heating or radio frequency induction to heat the substrate and the substrate support and achieve the energy required for the deposition reaction. It has simple equipment, high deposition rate, and high heating rate. RTCVD requires stable, suitable vapor pressure, epitaxial distortion of the crystal layer and minimal distortion of the crystal structure. Table 3 lists the experimental conditions and data sheets of the RTCVD silicon film. It can be seen that when the flow rate of SiH_2Cl_2 is 880, the deposition rate and thickness value increase; when it continues to increase, the saturation point of the mixed gas decreases, which can promote the formation of particulates in the gaseous state, and reduce the effective reactants. Figure 3 shows the time versus thickness at different temperatures. As the film formation time increases, the film thickness value increases, and the film thickness value (slope) of the high temperature deposition becomes larger. Figure 4 shows temperature versus deposition rate. It can be seen that when the temperature is below 1000 °C, the deposition rate is approximately positively linear with temperature; when the temperature is over 1000 °C, the deposition rate is not sensitive to temperature.

Table 3: Experimental conditions and experimental data sheets for rapid thermal chemical vapor deposition of silicon films

SiH_2Cl_2 flow	Thickness/ μm	Time/min	Speed $\mu\text{m}/\text{min}$
50	8	25	0.36
100	9	15	0.81
150	19	25	0.96
200	15	15	1.16
250	16	15	1.51
400	26	15	2.51
600	43	15	4.19
900	52	15	5.09
1600	40	15	3.91
2000	39	15	3.82

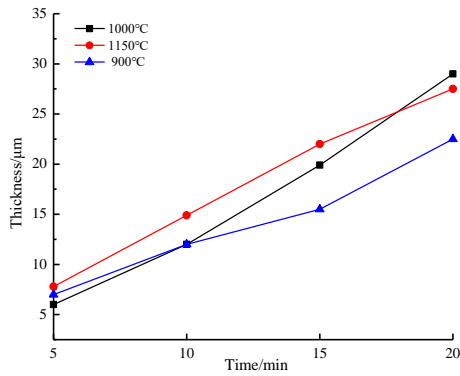


Figure 3: Time-thickness diagram at different Temperatures

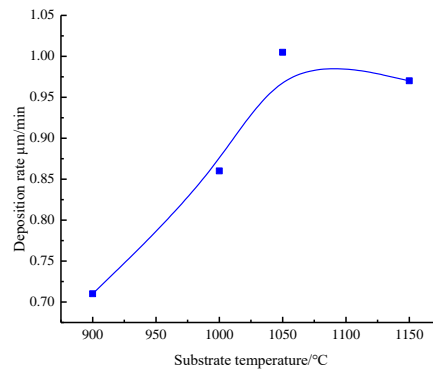


Figure 4: Relationship between temperature and deposition rate

3.2 Hall mobility measurement

The Hall test is to determine the resistivity, carrier concentration and mobility of the prepared solar cell film material. Figure 5 shows the schematic diagram of the Hall measurement system. The essence of the Hall effect is that the charged particles q is laterally deflected by the Lorentz force in the magnetic field B at a velocity v , and the charged particles are concentrated on the lateral sides of the semiconductor wafer to form an electromotive force and also a Hall electric field inside the semiconductor wafer. Table 4 shows the Hall mobility of the film. It can be seen that the mobility of the film largely depends on the size of the crystalline silicon grains, and the grain boundaries play a major role in the scattering of the film carriers.

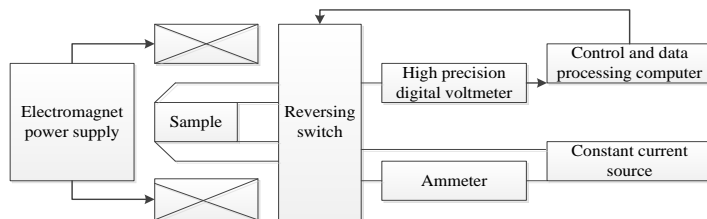


Figure 5: Hall measurement system schematic

Table 4: Hall mobility of thin films

Substrate	N-type single crystal silicon	Polysilicon	Granular silicon ribbon	SiO ₂	Al ₂ O ₃	SiSiC
Film resistivity	0.06	0.06	0.06	0.06	0.06	0.06
Grain size	Single crystal	100μm	40-100μm	20μm	2-6μm	1-5μm
Hall mobility	255	110	65	45	40	20

4. Crystalline silicon solar cell film material prepared by layer transfer technology

4.1 Crystalline silicon thin film solar cells on the foreign substrate

The pre-curing temperature gradient has an important influence on the quality of the crystalline silicon film. The preheating lamp and the heating lamp intensity are the most important parameters. Figure 6 shows the lateral temperature distribution of the substrate under different preheating lamp and heating lamp intensity ratios. The temperature of the heating field exhibits a symmetric distribution characteristic. The larger the proportion of the heating lamp, the higher the temperature in the field and the smaller the temperature gradient, which is beneficial to the zone melting and recrystallization process of the silicon region. In addition to the surface silicon crystal layer, the film material also needs to have a substrate and a diffusion barrier layer which can block impurities and transition elements, thereby improving the efficiency and lifetime of the solar cell. In this paper, the thin film structure of SiO₂/SiN_x/SiO₂ (ONO) was used as the diffusion barrier layer. Table 5 lists the plasma enhanced chemical vapor deposition parameters of the ONO barrier layer. With good

density in the film of ONO barrier film, it can be seen from the deposition rate that the deposition of the ONO barrier layer is fast. The most critical process for solar cell quality is the junction process. In this paper, p-type silicon or n-type silicon was prepared by thermal diffusion p-n junction method. The junction depth and doping problem of the junction are represented by carriers and collection probability. Figure 7 shows the probability and generation rate of carrier collection, in which the probability of carrier collection is zero on the surface of the battery, and the carrier generation rate is the largest on the surface of the battery. As the distance from the battery increases, the probability of carrier collection shows the trend of increasing-invariant-reducing, and the increasing rate is obviously higher than the decreasing rate. In order to obtain a larger probability of carrier collection, the p-n junction should form a shallow junction as close as possible to the surface.

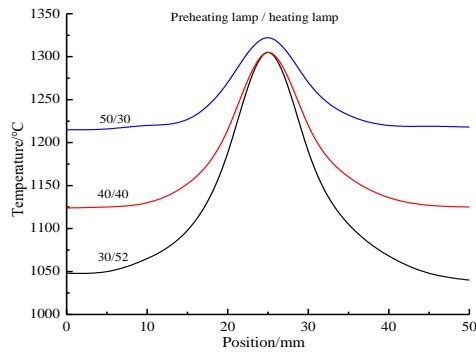


Figure 6: Lateral temperature distribution of the substrate under different preheating lamp and heating lamp intensity ratio

Table 5: Plasma enhanced chemical vapor deposition parameters of ONO barrier layer

	SiO ₂	SiN _x
Power/W	120	75
SiH ₄ flow sccm/min	180	70
N ₂ O/NH ₃ flow sccm/min	1500	65
Deposition rate nm/min	60	20

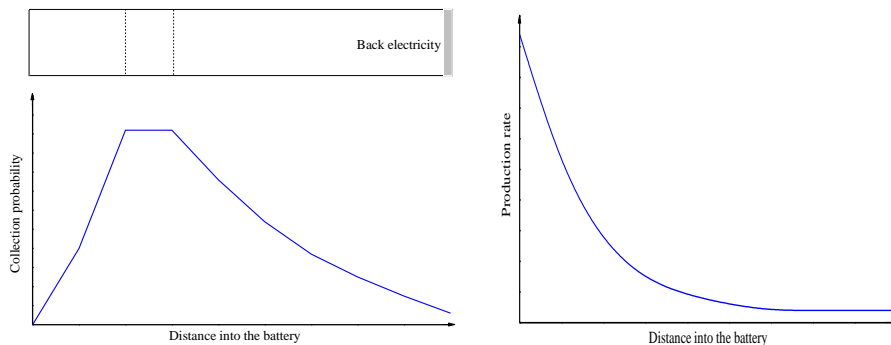


Figure 7 Carrier collection probability and generation rate

4.2 New layer transfer technology for preparing crystalline solar cell thin film materials

The cost of solar thin film materials prepared by crystalline silicon is 90% of solar cell raw materials. It is the key to reducing the cost of solar cells by finding new technologies for preparing crystalline silicon thin film materials. In the layer transfer technology, a meltable intermediate layer together with a coating layer is applied to separate the silicon film material from the substrate, which can reduce the film stress of the crystalline silicon chemical deposition, improve the film quality, and reduce the manufacturing cost of the crystalline silicon film. This technology can also reduce the problem of the decline in the quality of the silicon film due to the mismatch of the thermal expansion coefficients.

5. Conclusions

In this paper, crystalline silicon solar cell films were prepared by RPA and RTCVD. The properties of the thin films were also studied. The specific conclusions are as follows:

- (1) During the precipitation process of crystalline silicon film, the grain size and dark conductivity increase with the increase of annealing time. The higher the light intensity, the faster the crystallization rate, but with the increase of annealing time, the effect of light intensity is not significant.
- (2) With the increase of film formation time, the film thickness value increases, and the film thickness value of high temperature deposition is larger. When the temperature is below 1000 °C, the deposition rate is approximately positively linear with temperature; when it is over 1000 °C, the deposition rate is not sensitive to temperature.
- (3) The probability of carrier collection is zero on the surface of the battery, and the carrier generation rate is the largest on the surface of the battery. As the distance to the battery increases, the probability of collection of carriers shows an increasing-invariant-decreasing tendency, and the increase rate is significantly greater than the rate of decrease.

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