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Fabrication of TiO_x thin film on Si using solution-based process and its passivation performance

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Abstract

Silicon solar cells featuring carrier selective contacts have been demonstrated to reach ultra-high conversion efficiency. Particularly, titanium oxide (TiO_x) is expected as an electron selective contact material. In this work, TiO_x layer via solution synthesis way was deposited on Si to reduce electrical losses. This method is not only simple but also low-cost. In order to further improve its passivation performance, we also tried a new solution-based post treatment method. The effective carrier lifetime (τ_{eff}) after post-treatment increased from 95 µs to 316 µs checked by microwave photoconductive decay.

1. Introduction

At present, the highest conversion efficiency of crystalline Si (c-Si) solar cells have reached 26.7 % (Kaneka company). Heterojunction solar cells have been actively researched to improve the conversion efficiency of c-Si solar cells. In particular, titanium oxide (TiO_x) has received a great deal of attention as a material for the electron selective layer. TiO_x, which has high passivation performance, has many ways to form such as atomic layer deposition (ALD) [1], sputtering [2] and plasma enhanced chemical vapor deposition [3-5]. However, all of these methods are consumed a lot of material and complicated since they need a vacuum condition. In order to reduce production costs, study on a low-cost solution-based synthesis of TiO_x film has been intensively conducted. In fact, Liu *et al.* reported that power conversion efficiency of 14.3% was achieved for textured Si/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) solar cell by incorporating TiO_x layer between Si and aluminium electrode. However, the heterostruture has a low effective carrier lifetime (τ_{eff}) of 65µs [6]. Other film-forming methods such as ALD can achieve a τ_{eff} up to 407.2 µs [7]. In order to improve the passivation performance, it is necessary to increase the τ_{eff} by reducing carrier recombination velocity at the TiO_x/Si interface. Although there are many ways to enhance the performance of passivation such as hydrogen plasma treatment [7] and laser treatment [8], more simple method is preferable.

In this study, we report on the preparation of TiO_x thin film and improvement of passivation performance by simple and low cost chemical solution processes.

2. Experimental method

Cleaned (100)-oriented Si substrates (280 µm, n-type, 2.0-5.0 Ω·cm, double side mirror-polished) were cut into 1.7×1.7 cm^2. Then the substrates were immersed into acetone and methanol for 5 min sequentially with additional with deionized (DI) water rinsing to get rid of residual organic solution. Finally, the substrates were dipped into HF solution to remove Si oxide. The precursor solution used in the experiment consisted of different amounts of $TiCl_4$ dissolved in 1000 ml of ethanol ($TiCl_4$ was the source of titanium, and ethanol was the solvent). Then, precursor was spin-coated on the substrate at a velocity of 3000 rpm for 1 min, followed by thermal annealing at 90-110 °C for 10 min to remove the residual solvent. After that, dipping was performed in various oxidizing solutions for 2-10 min with the intention of reducing the oxygen vacancies in the TiO_x thin film that act as the carrier recombination centers. The passivation performance was evaluated using τ_{eff} measured by the microwave photoconductive decay method (incident pulse laser wavelength of 904 nm and photon density of 1×10^{14} photons/cm^2, microwave frequency of 10 GHz).

3. Results and discussion

Figure 1 shows the relationship between τ_{eff} and the amount of $TiCl_4$ in precursor solution. From this figure, we can see that τ_{eff} increases with the increase of the amount of $TiCl_4$, and when the addition amount of $TiCl_4$ is 100 ml, τ_{eff} reaches the maximum value of 95 µsec. Therefore, the amount of $TiCl_4$ added is set at 100ml for subsequent experiments.

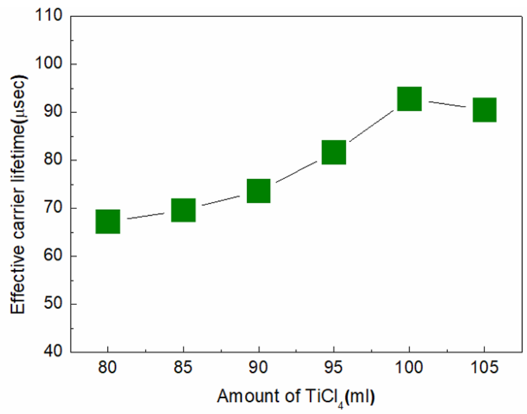

Fig.1. Effective carrier lifetime as a function of amount of $TiCl_4$ in precursor solution.

Table 1 shows the effect on τ_{eff} of annealed samples (110°C) after post treatment (2 min) with different oxidizing solutions. The oxidizing solution consists of acid, H_2O_2 and DI-water (400 ml). It can be seen from the table that after post treatment, τ_{eff} is increased significantly, and the sample which dipped into H_3PO_4 mixture solution has a highest improvement on τ_{eff}, so follow-up experiments are carried out with H_3PO_4.

Table 1 The effect on τ_{eff} after post treatment with different oxidizing solutions.

Kinds of acid (100ml)	Amount of H_2O_2 (ml)	Effective carrier lifetime (μs)
HCl	100	272
HNO_3	100	308
H_3PO_4	100	316
No post treatment		95

Figure 2 shows the change on τ_{eff} of the annealed samples (110°C) after post-treatment (2 min) with/without H_2O_2 added and the effect of different amounts of H_3PO_4 is also shown. From this figure, it can be seen that the presence of H_2O_2 can improve the passivation performance, τ_{eff} is greatly increased by the post treatment in the H_3PO_4 solution, and τ_{eff} increased with increasing amount of H_3PO_4.

It can be seen that the content of H_3PO_4 and H_2O_2 in the oxidizing solution plays an important role in improving the passivation performance, which will become a key to controlling the passivation performance. Does this mean that a higher concentration of acid solution improves the passivation effect more significantly? In fact, we are also trying to find the relationship between multiple variables and τ_{eff} in the study through machine learning. By constructing a regression model of variables and τ_{eff}, we should be able to find which variables are more important to the experimental results to assist our research. Of course, in order to fit the model better, more experimental data is needed.

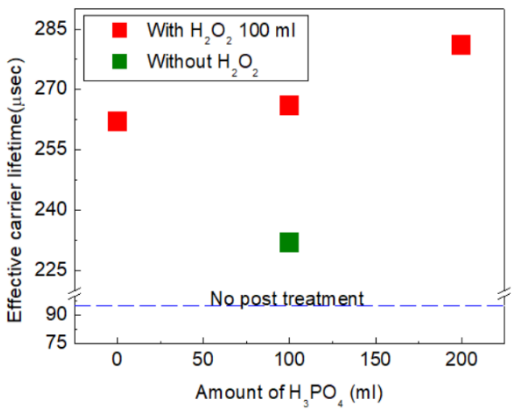

Fig.2. Effective carrier lifetime as a function of oxidizing solution composition (amount of H_3PO_4 and H_2O_2) in chemical treatment

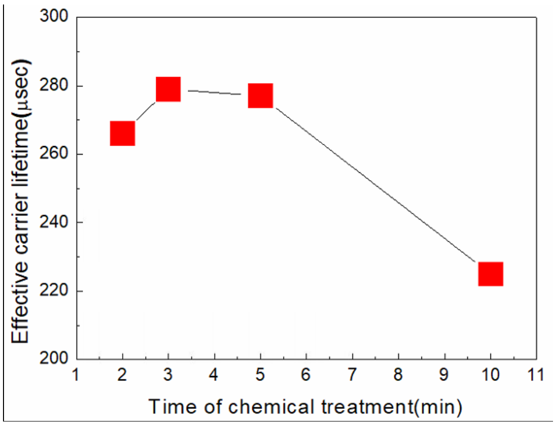

Fig.3. Effective carrier lifetime as a function of time of post- treatment (HCl mixture solution used).

Figure 3 shows the effect of post-treatment time on τ_{eff}. It can be seen from the figure that when the treatment time is 3 minutes, the increase of passivation effect reaches its peak. If the treatment time is extended, the life expectancy will show a downward trend and a significant drop can be observed at 10 minutes. We think this is because as the processing time increases, the oxygen vacancies in TiO_x layer continue to decrease, and makes TiO_x tends to TiO_2, which improves the passivation effect. However, when the treatment time is too long, the oxidizing solution begins to penetrate into the surface of the silicon substrate and react with it to form silicon dioxide, and τ_{eff} begins to decrease.

4. Conclusions

We have shown that the TiO_x passivation film was successfully synthesized by solution-based method, and the passivation performance of the film prepared by this method was confirmed. In addition, the passivation performance is also improved by a simple post-processing method, and by controlling a variety of experimental parameters, the experimental operation is optimized to a certain extent We. believe that with the aid of machine learning, more suitable experimental parameters can be obtained, and the passivation effect will be further improved

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