Silicon Metal-Oxide-Semiconductor Solar Cells with Oxide Prepared by Room Temperature Anodization in Hydrofluosilicic Acid Solution

Chih-Hao Chen, Chao-Chi Hong, and Jenn-Gwo Hwu^z

Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan

It had been reported that liquid-phase deposition (LPD) using saturated hydrofluosilicic acid (H_2SiF_6) is useful for silicon metal-oxide-semiconductor (MOS) solar cells. However, the LPD preparation time is long. In this work, anodic oxidation in saturated H_2SiF_6 solution is proposed as an alternative method to grow the room temperature oxides for MOS solar cells. It was found that the oxide preparation time is reduced significantly without sacrificing the efficiency in comparison with that by the LPD method. The oxide prepared by anodization (ANO) in H_2SiF_6 was found to be deposition-like which is different from that by ANO in H_2O . The oxidation time is about 5 min for the ANO method, but it is up to 4 h for the LPD method to obtain about 50 Å thick oxide. After adding intercalathode semitransparent thin Al film between thick Al cathode lines, it is apparent that all performances of the solar cells are improved. The reliability and efficiency of solar cells can also be improved above the 200°C, 5 min postmetalization annealing treatment, and a conversion efficiency of 9.5% is shown.

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Since the first silicon solar cell was fabricated by using a diffused p-n junction at Bell Laboratories in the early 1950s, the reduction of cost has been a primary incentive in solar cell fabrication.¹ Cost reduction depends on the method of junction fabrication. It was reported that the simple deposited metal-semiconductor junction is very attractive.² However, intimate contact metal-semiconductor solar cells reveal a serious deficiency resulting from the thermionic emission dark current in Schottky barrier junctions. It is possible to surmount this disadvantage by using a very thin insulator to separate the metal and semiconductor that yields metal-oxide-semiconductor (MOS) solar cells.³ The MOS solar cell has received attention because its cost is low. Generally, the insulator of MOS solar cells should be very thin (2 nm) so that the tunneling current can be large enough for applications.⁴ However, there are several issues that must be considered in ultrathin oxides such as the control of oxide thickness uniformity and the quality of oxide.

It had been reported that liquid-phase deposition (LPD)^{5,6} using saturated hydrofluosilicic acid (H_2SiF_6) could be used in the preparation method of the oxide of silicon MOS solar cells.^{7,8} The LPD method has advantages such as no exact control of oxide thickness, room temperature process, and low cost. In particular, the trap-assisted tunneling^{9,10} property of the LPD oxide is useful for solar cell applications. However, the LPD preparation time is quite long.

In this work, anodization (ANO) in saturated H_2SiF_6 solution is proposed as a new method for preparing the room temperature oxides for silicon MOS solar cells. It is found that the oxide preparation time is reduced significantly without sacrificing the merits of the LPD method. Interestingly, it was found that ANO in H_2SiF_6 exhibits deposition-like oxide in current density-voltage (J - V) characteristics. This oxide is similar to that of LPD and is useful for solar cell applications. Also, it was found that the ANO in H_2O does not exhibit the above phenomenon.

It is known that the possible dark current mechanisms in a MOS solar cell can be described as¹¹

$$J_{\text{dark}} = J_{\text{pt}} + J_{\text{ps}} + J_{\text{Dn}} + J_{\text{rg}} \quad [1]$$

where J_{pt} is the hole tunneling currents, J_{ps} is the hole current through interface traps, J_{Dn} is the diffusion current, and J_{rg} is the recombination generation current in the depletion layer. The net current drawn from the MOS solar cell can be written as

$$J_{\text{t}} = J_{\text{light}} - J_{\text{dark}} \quad [2]$$

If the dark current J_{dark} decreases substantially, the efficiency of the MOS solar cell will increase. For lower interface trap density, the surface-state current component J_{ps} is reduced which means that the dark current J_{dark} becomes smaller.¹² In order to increase the efficiency of the solar cell, the reduction of interface traps by using postmetalization annealing (PMA) is efficient.¹³ In addition, the PMA treatment is useful in stabilizing the number of traps in the oxide. After the PMA treatment the performance and reliability of the solar cell are improved significantly. Thus, the PMA treatment was performed on MOS solar cells in this work.

Experimental

The flowchart for preparing the saturated H_2SiF_6 solution and oxide formation is shown in Fig. 1. For over 3 h at 30°C SiO_2 powder was added to the 3.09 M H_2SiF_6 solution to saturate this solution, and then the saturated solution was filtered to separate the undissolved SiO_2 powder. Deionized (DI) water was added to the filtered solution, and the ratio of the filtered H_2SiF_6 solution to DI water was 2:1. The H_2SiF_6 solution (saturated H_2SiF_6 : H_2O = 2:1) was used to deposit the LPD oxide or as the electrolyte for the ANO method.

Boron-doped silicon (100) wafers with a resistivity of 1-10 Ω cm were used as the substrate for MOS solar cells. We used platinum as the cathode plate and the H_2SiF_6 solution as the electrolyte. Anodizations were performed at various constant current densities. For comparison, the oxide prepared by the LPD method was also performed. The thickness of ANO and LPD oxides were measured by ellipsometry using a refractive index of 1.46. Then Al films with a thickness of about 200 nm were evaporated on oxides as the cathode. Al was selected to be the gate electrode because the process technology and theoretical derivations were well developed.^{7,11} Photolithography was carried out by using AZ1500 as the photoresist, ultraviolet light source, 300 K as the temperature of develop solution, and H_3PO_4 : HNO_3 : CH_3COOH : H_2O = 85:5:5:5 solution as the Al etchant. The back oxide was etched off by a buffered oxide etchant (BOE). 200 nm Al was evaporated on the back silicon surface as the anode contact electrode. The intercalathode semitransparent thin Al films with a thickness of 5 nm were then evaporated on the positive side of the wafer between cathode lines. The pattern and the cross section of solar cells is shown in Fig. 2a and b, respectively. Moreover, the solar cells without the intercalathode thin Al films and with the films only on the active area of cell but not the entire wafer were also fabricated for comparison. In addition to MOS solar cells, MOS capacitors of $150 \times 150 \mu\text{m}$ were also fabricated. In order to observe the effect of the PMA treatment on the

^z E-mail: hwu@cc.ntu.edu.tw

Figure 1. A flowchart showing the preparation of the saturated H_2SiF_6 solution and oxide formation.

performance of solar cells, different PMA temperatures and times were performed in N_2 ambient, and then the efficiencies of solar cells were measured at different times. The J - V characteristics of solar cells were measured under illumination using the Keithley measurement system, and the light source is a 100 W tungsten light bulb. For solar cell characterization a luminance intensity of 20 mW/cm^2 was employed.

Results and Discussion

Figure 3 shows the ANO oxide thickness vs. oxidation time with different constant current densities. The external electrical field can accelerate the rate of the oxide deposited on the Si substrate so that the oxidation time of the ANO method is much shorter than that of LPD method (see inset in Fig. 3). Besides, the ANO oxide thickness in pure water may be described as¹⁴

$$d(t) = 2.15(Jt)^{1/2} + b \quad [3]$$

where $d(t)$ is the time-dependent oxide thickness, J is the ANO current density in microamperes per centimeter squared, t is the growth time in minutes, and the constant b is approximately nine for an oxide above 4 nm and three for an oxide below 4 nm. From Fig. 3 it can be observed that under 0.01 A/cm^2 current density, it takes about 10 min to achieve 4 nm oxide thickness for ANO in H_2SiF_6 . But in pure water, it takes about 30 min, which can be evaluated from Eq. 3. An oxidation rate of ANO in H_2SiF_6 is much faster than that in pure water.

Figure 4a shows the J - V characteristics of MOS capacitors with about 3 nm oxide prepared by LPD, ANO in H_2O , and ANO in H_2SiF_6 for a positive forward bias. The saturation phenomenon of the current is observed for oxides prepared by LPD and ANO in H_2SiF_6 but not by ANO in H_2O . It is believed that a leaky oxide cannot hold enough minority electrons in silicon because of its large tunneling leakage current. When the applied voltage is increased, the depleted region in the silicon must increase to meet the quantity of electric charges and thus the oxide is not easy to break down. The saturation current level is determined by the properties of silicon, e.g., interface trap density, bulk defect density, etc.¹² It increases with increasing silicon surface damage due to more minority carriers being generated by defects. For an oxide prepared by ANO in H_2O , the bonds between Si and O are completely conjugated so that the penetrated oxygen seriously disturbs the silicon surface. This kind of oxide is used less for solar cell application in this work because its trap content is minimal. But for the deposited oxide, such as the LPD oxide, the silicon surfaces are less disturbed because of the

Figure 2. (a) Pattern and (b) cross section of silicon MOS solar cells.

weak Si-O bond and the nature of deposited oxide. Therefore, the saturated current of LPD oxide is lower than that of an oxide prepared by ANO in H_2O . It is noted that the current behavior of an oxide prepared by ANO in H_2SiF_6 is similar to that of the LPD oxide. That is, the oxide prepared by ANO in H_2SiF_6 is similar in deposition but not growth due to the oxygen atoms penetrating in

Figure 3. The ANO oxide thickness vs. oxidation time with different constant current densities. The inset shows oxide thickness vs. oxidation time for LPD.

Figure 4. The J - V characteristics of MOS capacitors with about 3 nm oxides prepared by LPD, ANO in H_2O , and ANO in H_2SiF_6 for (a) positive and (b) negative bias.

the silicon surface to form SiO_2 . The J - V curves under negative bias are depicted in Fig. 5b. Again, the properties of the oxide prepared by ANO in H_2SiF_6 are like those of the LPD oxide. ANO in pure water exhibits the direct tunneling phenomenon that belongs to a good oxide layer,¹⁵ but the tunneling current magnitude of ANO in H_2SiF_6 is much larger. It is supposed that the electrons tunneling through the ANO oxide do so also by way of trap-assisted tunneling, like the LPD oxide, which is useful for solar cell applications.

Figure 5a shows the J - V curves of solar cells under illumination (20 mW/cm^2) with and without intercatchode thin Al films for ANO. It was found that the solar cell performance is improved significantly in the appearance of increased open circuit voltage (V_{OC}), short-circuit current (J_{SC}) and fill factor after the intercatchode thin Al films deposition. For solar cells without the intercatchode thin Al films, many photogenerated electrons could be recombined before they are collected by the main electrode. The intercatchode thin Al films can accelerate the collection of photogenerated electrons through the oxide and thus the performance of the solar cell parameters can be improved.⁷

In order to show that the intercatchode thin Al films are thin enough so that even they are evaporated all over the entire wafer surface, the neighborhood cell effect due to parallel connections can be neglected, and the intercatchode thin Al films outside the active area of solar cell are removed. Figure 5b shows the J - V curves of a

Figure 5. (a) The J - V curves of a solar cell under illumination (20 mW/cm^2) with and without intercatchode semitransparent thin Al film for an oxide prepared by ANO. (b) The J - V curves of a solar cell before and after etching the thin Al film outside the active area of device.

solar cell before and after etching the intercatchode thin Al film outside the active area of the device. Their efficiencies are almost unchanged. Therefore, the neighborhood effect can be neglected in thin Al film deposition. The improvement of solar cell performance is mainly due to the direct collection of photogenerated electrons by the intercatchode thin Al films.

Figure 6a shows the efficiency of solar cells before and after PMA for various temperatures, while the change ratios were shown in Fig. 6b. The efficiency was calculated with a consideration of the total area. The PMA time is fixed at 5 min. The reduction of efficiency is observed for higher PMA temperatures ($>200^\circ\text{C}$). The values of efficiency even fall down to 0% when the PMA temperature is 400°C because the oxide is punched through by an Al spike. The cell J - V curves before and after 400°C PMA are illustrated in Fig. 7. Al spiking leads to zero V_{OC} , and thus zero efficiency is obtained. The efficiencies are improved at low PMA temperatures (100 – 200°C). It is known that the PMA treatment is useful in reducing interface trap density.^{9,16} For a lower interface trap density, the surface-state current component is lower which means that the dark current becomes lower. Therefore, the solar cells with PMA treatment reveal larger total currents and efficiencies.

Figure 6. (a) The efficiencies of solar cells vs. PMA temperature. Those before PMA are also indicated in this figure. (b) The efficiency change ratios of solar cells vs. PMA temperature.

Figure 7. The J - V curves of solar cells before and after 400°C, 5 min PMA.

Figure 8a shows the solar cell efficiency before and after PMA under various times while the change ratios are shown in Fig. 8b. The PMA temperature is fixed at 200°C. It was found that the efficiency decreases with increasing PMA time when the PMA time is

Figure 8. (a) The efficiencies of solar cells vs. PMA time for a PMA at 200°C. Those before PMA are also indicated in this figure. (b) The efficiency change ratios of solar cells vs. PMA time.

greater than 5 min. The efficiency increases apparently at the 5 min PMA time. It had been reported that the solar cells exhibit optimum performance under 7-8 nm deposition like oxide thickness and 5 nm intercalated thin Al film.^{7,17} In this work, the appropriate PMA conditions for improving efficiency were investigated, *i.e.*, 200°C and 5 min, as concluded from the above discussion. An efficiency of up to 9.5% is obtained. The J - V curves of one solar cell with an optimum performance before and after PMA are shown in Fig. 9. Both V_{OC} and J_{SC} increase after PMA treatment. This efficiency is quite attractive for real solar cell applications.

It had been mentioned above that the improvement of solar cell efficiency after PMA is mainly due to the reduction in interface density and thus the dark current. In order to provide more insight, conditions simulating the dependence between dark current and interface density were simulated. Figure 10 shows the theoretical J - V curves of MOS capacitors for different interface trap densities based on the equations in Ref. 12. The dark current indeed decreases with decreasing interface trap density. Some other studies also support this inference.^{18,19} It should be noticed that Fig. 10 only provides a qualitative description. The oxide thickness and minority carrier life time were held at 2 nm and 32.5 μ s, respectively. The experimental data in Fig. 5a were measured on 3.2 nm oxide, and the actual minority carrier life time was unknown. The saturation current density around 10^{-7} A/cm² in Fig. 5a does not give a direct indication that the interface densities of LPD and ANO in H₂SiF₆

Figure 9. The J - V curves of a solar cell before and after 200°C, 5 min PMA.

samples were about $3 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$, in comparison with Fig. 10. However, it is believed that the improvement of the performance of solar cells after PMA treatment is mainly due to the lower interface density.

Figure 11 shows the efficiency vs. room temperature anneal time for solar cells after 100 and 200°C PMA for 5 min. Samples were kept in a moisture proof box in the dark, except when measurements were carried out. It was found that the efficiency degradation phenomenon is still serious at 100°C PMA. It is supposed that this phenomenon is probably because the number of the traps existing in the oxide varies with time. These traps are suggested to be fluorine-related since ANO was carried out in H_2SiF_6 , and the resulting oxide is LPD-like. However, degradation is much suppressed for 200°C PMA because the proper PMA treatment can stabilize the traps in the oxide.

Figure 10. The theoretical J - V curves of MOS capacitors with 2 nm oxide for different interface trap density D_{it} .

Figure 11. Efficiency vs. room temperature anneal time for solar cells after 100 and 200°C PMA for 5 min.

Conclusions

Anodic oxidation in saturated H_2SiF_6 solution is proposed as an alternative method for growing room-temperature oxides for MOS solar cells. Oxide preparation time using the ANO method is significantly shorter than that using the LPD method. With the addition of inter cathode thin Al films, the performance of solar cells can be much improved. The PMA treatment can improve not only reliability but also the efficiency of MOS solar cell. Under 7-8 nm ANO oxide thickness and 5 nm inter cathode Al thickness, the suggested optimum condition of PMA is 5 min at 200°C. After the PMA treatment an efficiency of up to 9.5% can be obtained. Nevertheless, the proposed new method for preparing an oxide used in Si MOS solar cell in this work is simple and cost effective.

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References

1. A. Rohatgi, S. Narasimha, A. U. Ebong, and P. Doshi, *IEEE Trans. Electron Devices*, **46**, 1970 (1999).
2. D. L. Pulfrey, *IEEE Trans. Electron Devices*, **25**, 1308 (1978).
3. M. J. Keever and M. A. Green, *J. Appl. Phys.*, **75**, 4022 (1994).
4. J. Shewchun, R. Singh, and M. A. Green, *J. Appl. Phys.*, **48**, 765 (1977).
5. C. F. Yeh, C. L. Chen, and G. H. Lin, *J. Electrochem. Soc.*, **141**, 3177 (1994).
6. C. F. Yeh, S. S. Lin, and C. L. Fan, *IEEE Electron Device Lett.*, **16**, 473 (1995).
7. K. C. Lee and J. G. Hwu, *IEEE Electron Device Lett.*, **18**, 565 (1997).
8. K. C. Lee and J. G. Hwu, *J. Vac. Sci. Technol. A*, **16**, 2641 (1998).
9. M. Lenski, T. Endoh, and F. Masuoka, *J. Appl. Phys.*, **88**, 5238 (2000).
10. S. Takagi, N. Yasuda, and A. Toriumi, *IEEE Trans. Electron Devices*, **46**, 348 (1999).
11. M. Y. Doghish and F. D. Ho, *IEEE Trans. Electron Devices*, **40**, 1446 (1993).
12. M. Y. Doghish and F. D. Ho, *IEEE Trans. Electron Devices*, **39**, 2771 (1992).
13. J. Camp, Y. Shi, Y. Luo, F. Yan, and J. H. Zhao, *IEEE Trans. Electron Devices*, **46**, 511 (1999).
14. C. C. Hong, M. S. Thesis, National Taiwan University, Taipei, Taiwan (1998).
15. C. C. Ting, Y. H. Shih, and J. G. Hwu, *IEEE Trans. Electron Devices*, **49**, 179 (2002).
16. T. Hori, *Gate Dielectrics and MOS ULSIs: Principles, Technologies, and Applications*, Springer-Verlag, New York, (1997).
17. Y. P. Shen and J. G. Hwu, *IEEE Photonics Technol. Lett.*, **8**, 420 (1996).
18. C. Y. Chang and S. J. Wang, *Solid-State Electron.*, **29**, 339 (1986).
19. A. Ghetti, E. Sangiorgi, J. Bude, T. W. Sorsch, and G. Weber, *Tech. Dig. Int. Electron Devices Meet.*, **1999**, 731.