Enhancement of Open-Circuit Voltage Using CF_4 Plasma Treatment on Nitric Acid Oxides

Je-Wei Lin, Chien-Hung Wu, Sheng-Wei Wu, Wei-Ping Hseih, Chen-Hsu Du, and Tien-Sheng Chao

***Abstract*—Surface passivation of solar cells is investigated using CF_4 plasma treatment on low-temperature oxides to enhance the open-circuit voltage of the solar cells. Low-temperature oxides grown by a nitric acid solution are treated with the CF_4 plasma. Solar cells undergoing this scheme show an improved performance, including low-saturation current density and good quantum efficiency at short wavelengths. Experimental results demonstrate that the CF_4 plasma pretreatment on low-temperature oxides can significantly improve the open-circuit voltage, short-circuit current, and fill factor for silicon wafer-based solar cells. This technique is very promising for in-line solar cell manufacturing.**

***Index Terms*—CF_4 plasma, low-temperature oxides, open-circuit voltage, surface passivation.**

I. INTRODUCTION

IN RECENT years, the passivation layer has been well known to attain a low surface recombination velocity (SRV). There has been much interest in the low-temperature passivating films, such as silicon dioxide (SiO_2), fixed-charge material (SiN_χ:H, Al_2O_3) [1], [2], and amorphous silicon (α-Si:H) [3]. Low-temperature passivating films offer a reduced thermal budget by comparison with thermal oxides. Ultrathin SiO_2 layers are a solution that has rapidly gained popularity in recent years as a thin-film passivation material for c-Si photovoltaic (PV) applications. They are easily grown using chemical solutions, simpler than the plasma-enhanced chemical vapor deposition (PECVD) and atomic layer deposition systems used to deposit SiN_x and Al_2O_3 films. A key focus of research is using the nitric acid oxidation of Si (NAOS) method. In 2008, Mihailetchi *et al.* [4] used an SiO_2 layer between the silicon emitter and the antireflection coating layer. The ultrathin SiO_2 is formed by the NAOS method at low temperature. A conversion efficiency enhancement of more than 2% higher than solar cells passivated without the SiO_2 layer was attained.

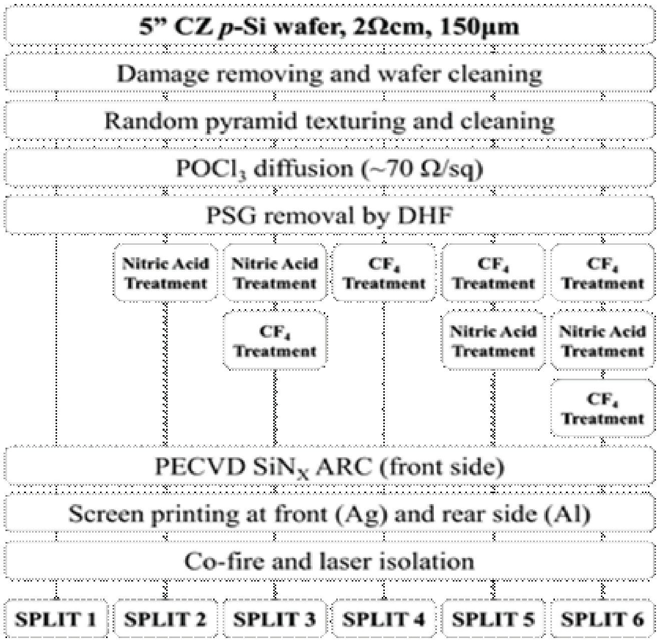

Fig. 1. Process flow diagram with CF_4 plasma and nitric acid treatment for *p*-Si solar cells fabricated in this letter.

In 2009, Grant *et al.* [5] used a two-step process to grow SiO_2 layers at low temperatures with concentrated nitric acid. After a 30-min nitrogen anneal at 1100 °C, an SRV of 107 cm/s (at $n = 1 \times 10^{15}$ cm^{-3}) was attained on 1 Ω-cm n-type silicon. The SRV was further decreased to 42 cm/s after a 30-min forming gas anneal at 400 °C. In 2010, Hu *et al.* [6] used various growth times and temperatures to grow an SiO_2 layer on the surface of a p-type silicon substrate under a nitric acid solution. After growing at 23 °C for 30 min, an efficiency improvement of absolute 2% was obtained.

Plasma treatment has been used recently as a simple way to improve device characteristics in the IC industry [7]–[9]. In this letter, the low-temperature oxides are treated with a carbon tetrafluoride (CF_4) plasma. The enhancements of the leakage current density and electrical properties have been previously investigated [10], [11]. In this letter, we use nitric acid oxides formed by the NAOS method with a CF_4 plasma treatment. The cell batch is split up into six batches, each of which receives a different CF_4 and nitric acid surface-passivation treatment. Characteristics of all samples, such as saturation current density, open-circuit voltage, short-circuit current, fill factor, external quantum efficiency, and conversion efficiency, will be discussed in this letter.

Manuscript received October 20, 2012; revised March 13, 2013; accepted March 14, 2013. Date of publication April 9, 2013; date of current version April 22, 2013. This work was supported in part by the National Science Council of Taiwan, under Contract NSC-100-2221-E-009-012-MY3, and by the Bureau of Energy. The review of this letter was arranged by Editor E. A. Gutiérrez-D.

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Digital Object Identifier 10.1109/LED.2013.2253757

II. EXPERIMENT

Fig. 1 shows the corresponding process flow diagram. As a starting material, we use (100)-oriented boron-doped Czochralski (CZ) c-Si wafers with a thickness of 200 μm and a resistivity of 1–2 Ω-cm. After etching of ~10 μm/side and cleaning of all samples using the standard RCA process the wafers are prepared by soaking them in DI water. The first step (called SC-1, where SC stands for Standard Clean) is performed with a 1:1:5 volume ratio solution of $NH_4OH + H_2O_2 + H_2O$ at 80 °C for 10 min. This is followed by transfer of the wafers into a DI water bath. The second step is a short immersion in a 1:100 volume ratio solution of HF + H_2O (called DHF, which stands for a dilute mixture of HF and DI H_2O) at 25 °C. The final step (called SC-2) is performed with a 1:1:5 volume ratio solution of HCl + H_2O_2 + H_2O at 80 °C for 10 min. A NAOS SiO_2 layer is grown on both wafer surfaces in a nitric acid solution at room temperature (RT) for cleaning. Subsequently, the silicon surface is textured with random pyramids in a 40 wt% KOH before mixing with IPA and DI water and volume ratio 1:3:46 solutions at 80 °C for 30 min. A single-step phosphorus emitter was diffused from a $POCl_3$ source, resulting in an n+-emitter with a sheet resistance of 70 Ω/square. The phosphorus silicate glass (PSG) was removed by a short HF dip. Except for the samples of splits 1 and 4, all samples were immersed in a nitric acid aqueous solution of 68% azeotropic concentration at RT for 15 min in this letter. The lifetime samples were subjected to the CF_4 plasma treatment performed in a direct PECVD, SAMCO PD220 system at 300 °C for 30 to 120 s, under a pressure of 67 pa, a power of 9 W, with CF_4 flow rate of 120 sccm. The fabrication of the structure of the lifetime samples is split 5. All the lifetime samples' structures were planar. At this point in the process, the cell batch was split up into six batches, each of which received a different CF_4 and nitric acid surface passivation treatment: 1) split 1 is the control cell with only SiNx surface passivation treatment; 2) split 2 is with NAOS; 3) split 3 is with NAOS and then CF_4 plasma posttreatment; 4) split 4 underwent CF_4 plasma pretreatment only; 5) split 5 underwent CF_4 plasma pretreatment first and then NAOS; and 6) split 6 underwent CF_4 preplasma treatment, then NAOS, and finally the CF_4 plasma posttreatment again. The remaining process steps are identical for all splits. The CF_4 plasma treatment time is 60 s in this letter. A surface passivating SiN_x antireflection coating was deposited on the front of the solar cell by PECVD at 450 °C. The electrode pattern was printed on the front and back surfaces of the cells using the screen printing by silver paste and aluminum paste methods and was co-fired at a peak temperature of 770 °C. Finally, all samples were isolated by laser. The cell samples were characterized using Quicksun IV measurement, $Suns - V_{oc}$ measurement, and Quantum efficiency measurement. The lifetime samples were characterized using the Quasi Steady-State PhotoConductivity (QSSPC) method. The aperture area of all solar cells fabricated in this letter is 7.14 cm^2, and the entire front metallization, including the busbar, is within the active cell area. The number of cells measured in each split is ten.

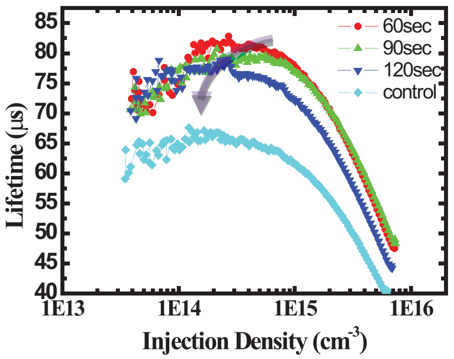

Fig. 2. Measured carrier lifetime of a 200-μm boron-doped 1–2 Ω-cm Cz Si wafer as a function of time of CF_4-treatment and the excess carrier concentration. The lifetime sample, split 5, has a flat structure fabricated by NaOH-etching and polishing.

III. RESULTS AND DISCUSSION

The dark current of p-n junctions can be described by the 2-diode model [12]. For an ideal solar cell, the V_{oc} depends on J_{sc} approximately according to [13]

$$V_{oc} \approx \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_{01}} + 1\right). \tag{1}$$

In (1) open-circuit voltage is significantly influenced by the saturation current density J_{01}. Therefore, in this experiment CF_4 plasma treatment on low-temperature oxides is used on the surface of the emitter. Fig. 2 shows the measured carrier lifetime of a 200-μm boron-doped 1–2 Ω-cm Cz Si wafer as a function of the excess carrier concentration. After emitter fabrication, we modify the pretreatment time of CF_4 plasma on the samples.

We verified that the average of bulk lifetime is above 600 μs and well below the Auger limit. Hence, our measured lifetimes are dominated by the emitter and surface recombination. We thus use effective lifetime instead of J_{0e} to discuss each of the samples in this letter. The results are shown in Fig. 2. It is found that the optimal time of CF_4 plasma pretreatment is 60 s. Previous work has found that CF_4 plasma pretreatment can improve low-temperature oxides by replacing dangling bonds with stronger Si–F or Si–O bonds [10], implying that the formation of Si–F bonds can reduce the number of interface traps between the Si and the oxide interface, and improve the reliability of the NAOS oxides. In this letter, lifetime is also influenced by the surface at the low injection level region. It is true that lifetime is better at a high injection level for samples treated for 90 s than for 60 s. However, when V_{oc} is around 620–630 mV, the maximum excess carrier concentration is about 5E14–1E15. Thus, the lifetime of the sample treated with 60-s plasma still has higher V_{oc} and the cells also work in this region. Therefore, we stated that under 1-sun illumination, 60 s is found to be optimal by using CF_4 plasma treatment. Fig. 3 shows the effect of different CF_4 pretreatment times on the saturation current density J_{01} and open-circuit voltage V_{oc} for p-Si solar cells. As the treatment time increases, the J_{01} improves, with the optimal value of V_{oc} obtained at 60 s. However, J_{01} increases slightly at 90 s because of damage to the emitter after a longer plasma

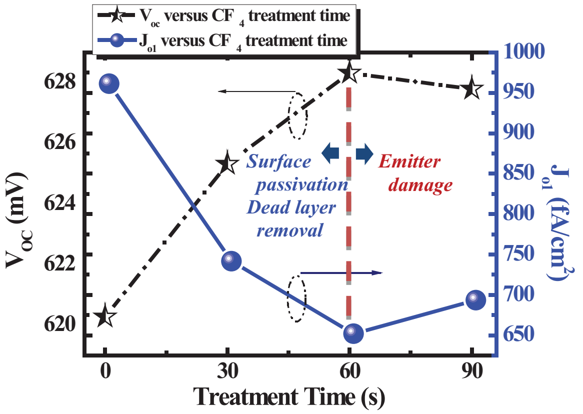

Fig. 3. Effect of different CF_4 pretreatment times on the diode saturation current density J_{01}, and open-circuit voltage V_{oc} for *p*-Si solar cells. The lifetime sample, split 5, has a flat structure fabricated by NaOH-etching and polishing.

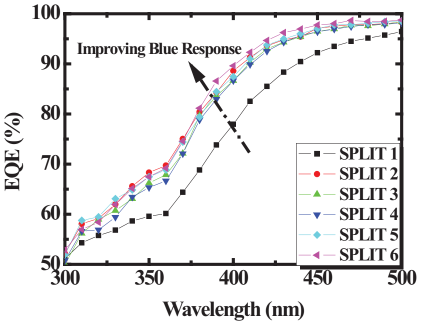

Fig. 4. Measured EQE as a function of wavelength λ for all splits with different CF_4 and nitric acid treatments.

TABLE I

OVERVIEW OF THE CELL CHARACTERIZATION RESULTS (AM1.5G) WITH DIFFERENT TREATMENT PROCESSES ON *p*-Si SOLAR CELLS. THESE ARE OPEN-AREA EFFICIENCIES. THE PROCESS SEQUENCES ARE GIVEN IN FIG. 1

Name	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)
Split 1	625.4	39.4	77.2	19.03
Split 2	628.9	39.4	77.7	19.24
Split 3	629.2	39.4	77.6	19.24
Split 4	630.3	39.5	77.8	19.36
Split 5	630.3	39.6	77.8	19.41
Split 6	632.2	39.6	77.8	19.48

pretreatment. We infer that CF_4 plasma not only passivates the surface but also removes the dead layer near the surface of the emitter [14].

Fig. 4 shows the measured external quantum efficiency (EQE) as a function of wavelength λ for all splits. It is obvious that EQE in the short wavelength region 300–500 nm is remarkably enhanced with good surface passivation by CF_4 plasma and nitric acid treatment. The NAOS oxides also remove some of the dead layer by consuming Si for its growth. The carrier recombination at this region is effectively suppressed, promoting a good blue response. Table I shows the characterization results for all splits (AM1.5G).

IV. CONCLUSION

In this letter, we successfully enhanced the open-circuit voltage on a *p*-Si solar cell using surface passivation by CF_4 plasma pretreatment and posttreatment by nitric acid oxides. It is found that the value of J_{01} is a very sensitive factor for V_{oc}. The carrier recombination at the surface can be effectively suppressed by our proposed scheme. By decreasing J_{01}, this scheme increases V_{oc}, J_{sc}, and the conversion efficiency. The CF_4 plasma pretreatment before SiN could be done in the same PECVD system. We also suggest that this process may be cheaper and better from an industrial standpoint.

ACKNOWLEDGMENT

The authors would like to thank the Nano Facility Center (NFC) of National Chiao Tung University, the National Nano Device Laboratory (NDL), and the Green Energy & Environment Research Laboratories (GEL), Industrial Technology Research Institute for providing process equipment.

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