Journal of The Electrochemical Society, **157** (7) H779-H782 (2010)
0013-4651/2010/157(7)/H779/4/$28.00 © The Electrochemical Society

Investigation of Surface Passivation on GaAs-Based Compound Solar Cell Using Photoelectrochemical Oxidation Method

Chun-Yen Tseng,[a] Chi-Sen Lee,[b] Hwa-Yuh Shin,[c] and Ching-Ting Lee[a,*,z]

[a] *Institute of Microelectronics, Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan*
[b] *Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan 48109–2122, USA*
[c] *Institute of Nuclear Energy Research Atomic Energy Council, Taoyuan 325, Taiwan*

A promising passivation method for the AlGaAs window layer of GaAs-based compound solar cells using photoelectrochemical (PEC) oxidation process was investigated. The advantage of this passivation method was attributed to the reduction of interface states between the window layer and oxide layer, and the decrease in original contaminants on the window layer surface by self-oxidation. The conversion efficiency of the solar cell could be improved by more than 3.68% due to the PEC treatment. The obtained results demonstrate that the PEC treatment is an effective low temperature technique for surface passivation, which enhances the performance of GaAs-based compound solar cells.

[DOI: 10.1149/1.3431542]

Manuscript submitted January 20, 2010; revised manuscript received April 21, 2010. Published May 27, 2010.

Recently, III–V compound solar cells have been extensively studied.[1-3] Owing to their high conversion efficiency and high radiation hardness, III–V compound solar cells were widely used in space and applied in the terrestrial concentrator photovoltaic systems.[4,5] GaAs-based compound solar cells exhibit high conversion efficiency under the global air mass (AM) 1.5 spectrum $(100\ \text{mW/cm}^2)$ due to its absorption matching well with the solar spectrum, and the use of GaAs-based semiconductors has been widely recognized for obtaining high conversion efficiency. However, to avoid the absorption of illuminating sunlight by the contact layer of compound solar cells, a selective etching procedure is usually performed in the fabrication process, which would induce a high surface state density and hence a high surface recombination rate. Consequently, the performances of the resulting compound solar cells are degraded.[6] Recently, various passivation methods, such as sulfidation surface treatment and chlorination surface treatment, have been investigated to improve the performances of semiconductor devices.[7-10] In this study, to passivate the window layer surface and to improve the conversion efficiency of GaAs-based compound solar cells, a photoelectrochemical (PEC) oxidation method was used to directly oxidize the AlGaAs window layer. By measuring the associated dark current density, the interface state density, and the conversion efficiency, the passivation function of the direct oxidation method was studied and analyzed. To focus the investigation of the function of PEC oxidation method, the relative conversion efficiency was emphasized by using the same single junction epitaxial structure of GaAs-based compound solar cells.

Experimental

The single junction epitaxial structure of the GaAs-based solar cells studied in this work was grown by a metallorganic chemical vapor deposition system and is shown in Fig. 1. A 350 nm thick p-GaAs $(4 \times 10^{17}\ \text{cm}^{-3})$ buffer layer was first grown on p-GaAs substrates, and then a 100 nm thick p-$\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ $(2 \times 10^{18}\ \text{cm}^{-3})$ back surface field layer, a 2000 nm thick p-GaAs $(3 \times 10^{17}\ \text{cm}^{-3})$ base layer, a 1000 nm thick undoped GaAs layer, a 500 nm thick n-GaAs $(2 \times 10^{18}\ \text{cm}^{-3})$ emitter layer, a 30 nm thick n-$\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ $(1 \times 10^{18}\ \text{cm}^{-3})$ window layer, and a 40 nm thick n^+-GaAs $(5 \times 10^{18}\ \text{cm}^{-3})$ contact layer were grown sequentially. The n-$\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ is referred to as n-AlGaAs hereafter. The bottom surface of the p-GaAs substrate was cleaned with chemical solutions of trichloroethylene, acetone, and methanol. The back electrode (Ag/Au, 25/150 nm) was immediately deposited on the cleaned p-GaAs surface using an electron-beam deposition system. To perform ohmic contact, the samples were then annealed in a H_2 ambient at 450°C for 3 min. The surface of the n^+-GaAs contact layer was also cleaned with chemical solutions of trichloroethylene, acetone, and methanol. A standard photolithography technique was used to define the area of metal electrode, as shown in Fig. 1. The top electrode (Au–Ge–Ni/Au, 200/100 nm) was immediately deposited on the n^+-GaAs contact layer using an electron-beam deposition system. After using the lift-off technique to remove the deposited metals outside of the defined electrode area, the samples were annealed in a H_2 ambient at 425°C for 3 min to perform ohmic contact. The n^+-GaAs contact layer beside the electrode area was etched down to the surface of the n-AlGaAs window layer using a selective etching solution of citric acid, H_2O_2, and H_2O (18 g:2.5 mL:10 mL). The as-etched samples were divided into two groups for fabricating solar cells without and with the PEC oxidation process, and the resultant devices were named as solar cell A and solar cell B, respectively, hereafter. For the fabrication of solar cell B, the as-etched surface of the samples was treated using the PEC oxidation system, as shown in Fig. 2. During the treatment, the samples were dipped in a hydrochloric acid (HCl) electrolytic solution, of which the pH value was adjusted to 3.5 measured using a Jenco 6007 digital pH meter. A He–Ne laser with a wavelength of 632.8 nm was used as the light source to create electrons and holes on the interface between the HCl electrolytic solution and the n-AlGaAs surface, and a voltage of 1.5 V was applied for 2 min. The reaction was expressed as

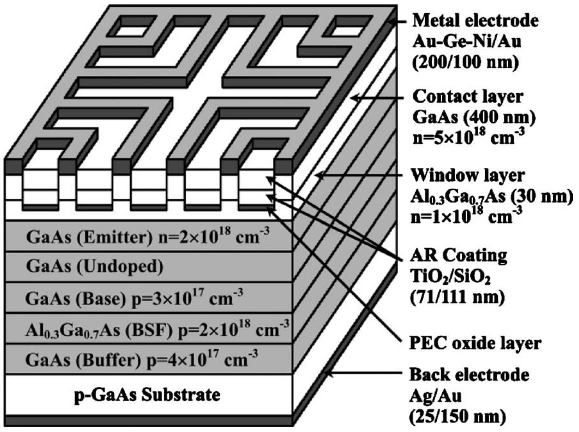

Figure 1. The schematic configuration of GaAs-based compound solar cells with PEC oxidation treatment.

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[*] Electrochemical Society Active Member.
[z] E-mail: ctlee@ee.ncku.edu.tw

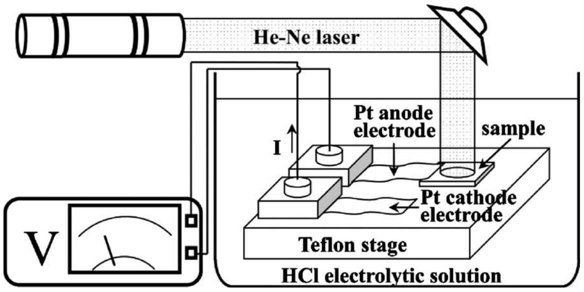

Figure 2. The schematic configuration of PEC oxidation system.

$$20Al_{0.3}Ga_{0.7}As + 60H_2O + 120h^+ \rightarrow 3Al_2O_3 + 7Ga_2O_3 + 10As_2O_3 + 120H^+ \quad [1]$$

where h^+ are holes. After using the PEC oxidation treatment, the samples were rinsed with deionized water and were blown dry with N_2 immediately. TiO_2/SiO_2 (71/111 nm) antireflection coating layers were instantly deposited using an electron-beam deposition system. A continuous solar simulator system under AM 1.5 global (100 mW/cm^2) was used as the light source for measuring the conversion efficiency. Moreover, to further investigate the passivation function of the PEC oxidation of the GaAs-based compound solar cells, Al/TiO_2/as-etched n-AlGaAs and Al/TiO_2/PEC oxidized n-AlGaAs metal-oxide-semiconductor (MOS) devices, as shown in Fig. 3a and b, were fabricated using standard photolithography technique and lift-off technique. The ring electrode of Au–Ge–Ni/Au (200/100 nm) with a radius of 150 μm was evaporated using an electron-beam deposition system. To obtain ohmic contact performance, the samples were annealed in a H_2 ambient at 425°C for 3 min. The n^+-GaAs contact layer beside the electrode area was etched down to the surface of the n-AlGaAs window layer using a selective etching solution of citric acid, H_2O_2, and H_2O (18 g:2.5 mL:10 mL). After the etching process, a PEC oxide layer on the window region of the n-AlGaAs was grown in a HCl electrolytic solution with a pH value of 3.5 under the illumination of a He–Ne laser and an applied voltage of 1.5 V for 2 min. A 50 nm thick TiO_2 film was evaporated using an electron-beam deposition system. A 200 nm thick Al circular pattern with a radius of 100 μm was defined at the center of the window region using the photolithography technique and lift-off technique. The associated interface state density was found from the capacitance–voltage (*C-V*) characteristics measured at 1 MHz using an HP 4280A.

Results and Discussion

The *C-V* characteristics of the Al/TiO_2/as-etched n-AlGaAs MOS devices and Al/TiO_2/PEC oxidized n-AlGaAs MOS devices are shown in Fig. 3a and b, respectively, when an applied voltage was swept from 2 to −8 V and then swept back to 2 V. The corresponding device structures are also shown in the insets of Fig. 3a and b, respectively. The threshold voltage shift ΔV_{th} is attributable to the different charging conditions of the interface states between the forward and reverse sweeps. The interface state density D_{it} could be estimated as[11,12]

$$D_{it} = \frac{(C_{ox}\Delta V_{th})}{(AqE_g)} \quad [2]$$

where C_{ox} is the accumulation capacitance, A ($=3.14 \times 10^{-4}$ cm^2) is the gate area of the MOS devices, ΔV_{th} is the threshold voltage shift, q is the electron charge, and E_g ($=1.8$ eV) is the bandgap of n-AlGaAs. On the basis of the *C-V* characteristics shown in Fig. 3a and b, the accumulation capacitance of 72.35 and 57.25 pF for the Al/TiO_2/as-etched n-AlGaAs and Al/TiO_2/PEC-oxidized n-AlGaAs MOS devices was measured, respectively. The smaller capacitance of the latter was caused by its thicker insulator layer composed of a TiO_2 layer and an oxidized n-AlGaAs layer. The associated voltage shifts of 1.02 and 0.50 V were obtained. Substituting those data in Eq. 2, the corresponding interface state density D_{it} of 8.2×10^{11} and 3.1×10^{11} cm^{-2} eV^{-1} was calculated for the Al/TiO_2/as-etched n-AlGaAs and Al/TiO_2/PEC-oxidized n-AlGaAs structures, respectively. The reduction of interface state density would result from the PEC oxidation passivation of the n-AlGaAs layer.

To investigate the effects of the PEC passivation on the GaAs-based solar cells, three kinds of devices with different surface treatments on the n-AlGaAs window layer were fabricated. As mentioned above, the GaAs-based compound solar cells fabricated without and with the PEC oxidation process were named as solar cell A and solar cell B, respectively. For the one named solar cell C, the n-AlGaAs window layer was first selectively etched and PEC oxidized, and then the oxidized layer was removed using dilute HCl. After the above-mentioned treatments on the n-AlGaAs window layer were performed, all the three kinds of solar cells were coated with a double antireflection layer composed of 71 nm thick TiO_2 and 111 nm thick SiO_2, as shown in Fig. 1. Figure 4 shows the reflectivity of the three kinds of GaAs-based compound solar cells in the wavelength region between 400 and 1000 nm, which was measured by a Hitachi U-4100 spectrophotometer system.

The typical dark current density–forward bias voltage (dark *J-V*) characteristics of the three GaAs-based compound solar cells measured by an HP 4156C semiconductor parameter analyzer are shown in Fig. 5. The dark *J-V* characteristics of solar cells A and C are very similar. The measured results of both optical reflectivity and electrical performance indicated that the electrical and optical properties were not obviously influenced by a slight thickness change in the window layer.[13] Compared with solar cells A and C, the dark current of solar cell B was obviously reduced and the dark *J-V* curve shifted to the larger forward bias voltage. This was due to the existence of the PEC-oxidized AlGaAs layer between TiO_2 and n-AlGaAs, which passivated the AlGaAs surface and hence reduced the carrier recombination rate through the interface states.[14,15] From the above

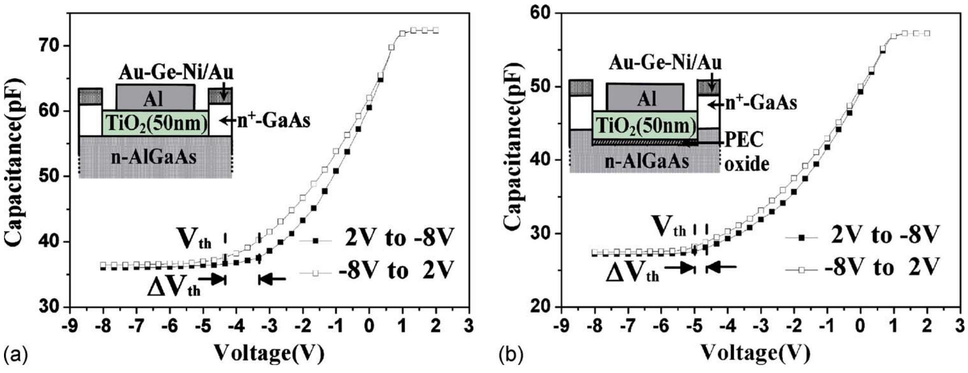

Figure 3. (Color online) The *C-V* characteristics of (a) Al/TiO_2/as-etched n^+-AlGaAs and (b) Al/TiO_2/PEC-oxidized n^+-AlGaAs MOS devices.

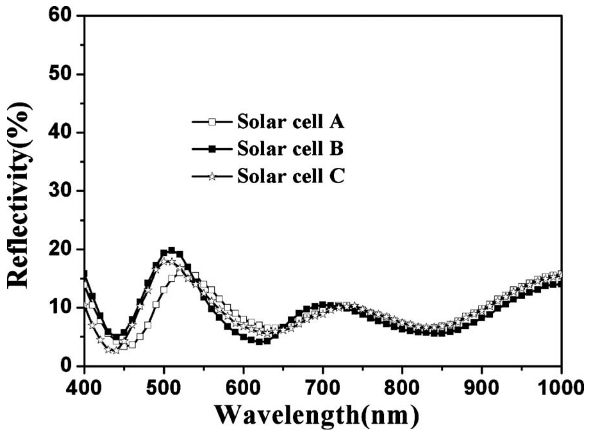

Figure 4. The reflectivity as a function of wavelength of GaAs-based compound solar cells with various treated AlGaAs window layers.

experimental results, it was reasonable to deduce that the major improvement in the dark current density was attributed to the passivation function of the PEC oxidation treatment.

Figure 6 shows the current density vs voltage (*J*-*V*) curves under the illumination of an AM 1.5 G spectrum for the above-mentioned three kinds of GaAs-based compound solar cells. Based on the experimental results, the fill factor (FF), conversion efficiency (η), short-circuit current density (J_{sc}), and open-circuit voltage (V_{oc}) were measured and are listed in Table I. The J_{sc} of 17.90, 21.88, and 18.21 mA/cm^2 were obtained for solar cells A, B, and C, respectively. The corresponding V_{oc} of 0.89, 0.93, and 0.89 V were obtained. The efficiency of 16.14% was obtained for solar cell B. The improvement in efficiency compared to the value of 12.46% for solar cell A could be ascribed to the passivation of the surface of the AlGaAs window layer by PEC treatment. To see the influence of the thickness of the window layer, solar cell C was fabricated to have the same thickness of the AlGaAs window layer as the solar cell B. The efficiency of solar cell C shows a slight increase compared to solar cell A, which is due to the different thicknesses of the AlGaAs window layer. However, the influence of the AlGaAs window layers with slightly different thicknesses on the antireflectivity performance was marginal, as shown in Fig. 4.

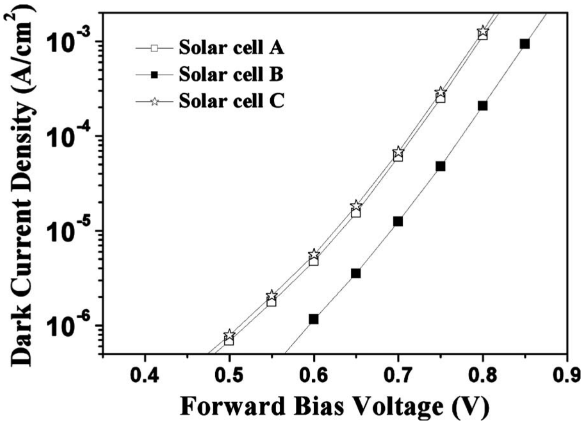

Figure 5. The *J*-*V* characteristics for the GaAs-based compound solar cells with various treated AlGaAs window layers.

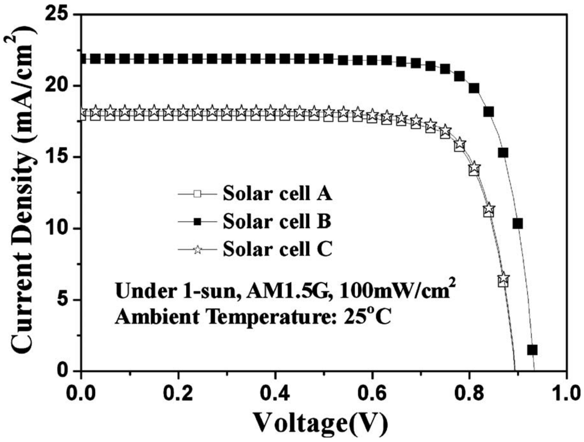

Figure 6. The illuminated *J*-*V* characteristics under AM 1.5 G spectrum for the GaAs-based compound solar cells with various treated AlGaAs window layers.

Table I. Performances of GaAs-based compound solar cells with various treated AlGaAs window layers.

Solar cell	J_{sc} (mA)	V_{oc} (V)	FF	η (%)
A	17.90	0.89	0.782	12.46
B	21.88	0.93	0.793	16.14
C	18.21	0.89	0.782	12.67

The spectral response of the GaAs-based compound solar cells, measured from 400 to 1000 nm, is presented in Fig. 7. The enhanced external quantum efficiency of solar cell B was attributed to the reduction of interface state density caused by the PEC oxidation treatment. The reduction of interface state density could decrease the loss of photogenerated carriers passing through the AlGaAs window layer. Because of the lower recombination rate of carriers, the carrier extraction capability of the external circuit was improved. This phenomenon verifies that the enhanced conversion efficiency can be attributed to the improvement of the electrical properties of the solar cells by using the PEC oxidation treatment.

Conclusions

In summary, the conversion efficiency improvement of a GaAs-based compound solar cell with PEC treatment was about 3.68% compared to the solar cells without PEC treatment. According to the *C*-*V* measurement results, this improvement was attributed to the passivation of dangling bonds and the reduction of the interface state density, which reduced the recombination rate of the photoinduced carriers. The PEC direct oxidation treatment is a promising simple method to improve the performances of GaAs-based compound so-

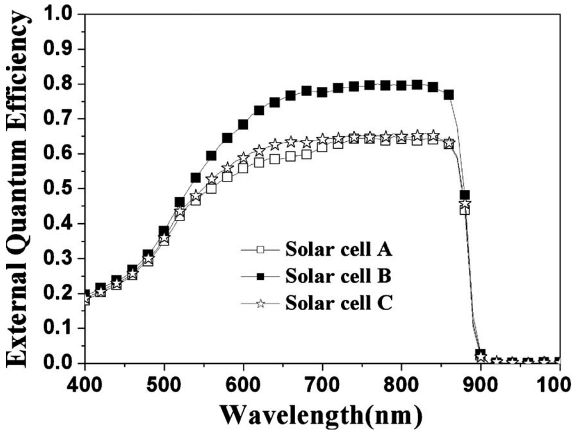

Figure 7. The spectral responses of the GaAs-based compound solar cells with various treated AlGaAs window layers.

lar cells. In this work, the conversion efficiency improvement of the PEC-treated solar cells was focused and demonstrated by using the same single junction epitaxial structure to fabricate solar cells with and without the PEC oxidation treatment.

Acknowledgment

The authors gratefully acknowledge the support from the Bureau of Energy, Ministry of Economic Affairs under contract no. 98-D0204-2 and the National Science Council of Taiwan under contract no. NSC-98-NU-E-006-018, no. NSC-98-2120-M-006-003, and no. NSC-98-3114-E-006-004-CC2.

National Cheng Kung University assisted in meeting the publication costs of this article.

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