A novel structure, high conversion efficiency \textit{p}-SiC/graded \textit{p}-SiC/\textit{i}-Si/\textit{n}-Si/metal substrate-type amorphous silicon solar cell

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A novel structure, high conversion efficiency amorphous silicon (a-Si)/metal substrate-type solar cell has been developed. The new structure, deduced from the conventional \textit{pin} junction by the use of a gradual compositional grading \textit{p}-type a-SiC:H layer between an ultrathin ($\sim 20\ \text{Å}$) wide optical band gap ($\sim 2.4\ \text{eV}$) \textit{p}-type a-SiC:H layer and the \textit{i} layer, exhibits markedly enhanced open-circuit voltage ($V_{oc}$) and short-circuit current density ($I_{sc}$) over the conventional \textit{a-Si pin}/substrate-type solar cell. Especially, the collection efficiency in the newly developed structure was found to be remarkably increased at short wavelengths. The experimentally observed improvement in the blue response is due to the reduction in effective interface recombination combined with the enhanced window effect. An energy conversion efficiency of 8.40\% under air mass (AM) 1 (100 mW/cm$^2$) illumination has been obtained in the first trial of a cell fabricated by the rf glow discharge decomposition of pure silane (SiH$_4$).

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I. INTRODUCTION

Since the first announcement of the invention of hydrogenated amorphous silicon (a-Si:H) solar cells by Carlson and Wronski, amorphous silicon produced by the glow discharge decomposition of silane (SiH$_4$) became attractive as a potential and low cost photovoltaic material. As a result of the tremendous and intensive efforts to enhance the efficiency in recent years, a-Si:H solar cells have been developed to the point where AM1 (100 mA/cm$^2$) conversion efficiencies in excess of 10\% can be achieved. The structure of the cell with the highest conversion efficiency reported is a glass/TC/\textit{p}-a-SiC:H/\textit{i}-a-Si:H/\textit{n}-metal, where TC is a transparent conducting layer and the \textit{p} a-SiC:H is a \textit{p}-type amorphous silicon carbide film.\textsuperscript{1} High conversion efficiencies of over 9\% have also been achieved by employing the structure of a TC/\textit{n}p-a-Si:H/SS, where the SS is a stainless-steel substrate.\textsuperscript{2} Another important a-Si:H solar cell structure is a TC/\textit{p}-a-SiC:H/\textit{i}-a-Si:H/\textit{n}-metal substrate. With this structure, the highest conversion efficiency reported so far is only 7.5\%.\textsuperscript{3} This poor photovoltaic performance is caused by a high recombination velocity of carriers at the \textit{p}/\textit{i} interface\textsuperscript{4} and by undesirable residual impurity (phosphorus) doping of the \textit{i} layer, resulting in a lower open-circuit voltage as compared with a cell fabricated in the order of \textit{n}, \textit{i}, and \textit{p} layers\textsuperscript{5,6} (the first and second structures mentioned above).

In this paper, we propose a novel structure of a solar cell to enhance the photovoltaic performance of the conventional TC/\textit{p}-a-SiC:H/\textit{i}-a-Si:H/\textit{n}-metal substrate-type solar cell. We introduced a gradual compositional grading \textit{p}-a-SiC:H layer in the \textit{p}/\textit{i} interface in order to reduce the effective interface recombination losses and use an ultrathin, wide optical band gap, \textit{p}-type a-SiC:H layer on the graded \textit{p} layer as a window material.

II. SAMPLE PREPARATION

All the samples were prepared by the rf glow discharge decomposition of silane in a rotary separated reaction chamber system,\textsuperscript{7} in which the \textit{p}, \textit{i}, and \textit{n} layers were deposited separately in different reaction chambers in order to effectively minimize the undesirable impurity doping.\textsuperscript{8} Figure 1 shows a schematic structure of the low cost Al substrate used in this study. This substrate, produced by Mitsubishi Chemical Industries Ltd., is widely used as a mirror material, called A-Lock. The principal feature of this substrate is that a mirror surface is obtained by electroplating Cr/Ni without polishing. The photovoltaic device configuration used in this study is depicted in Fig. 2. Figure 2(a) shows a conventional \textit{pin}/substrate-type solar cell, in which the deposition of a low resistivity microcrystalline (\textmu c) \textit{n} layer on the Al substrate by the rf glow discharge decomposition of silane, hydrogen, and phosphine gas mixture, was followed by a slightly boron doped \textit{i}-layer deposition. During the \textit{i}-layer deposition, operations were made to dope boron gradually into the \textit{i} layer by increasing diborane (B$_2$H$_6$) concentration toward the end of this layer. The effect of gradually boron doping the \textit{i} layer on the photovoltaic performance has already been reported by the authors.\textsuperscript{7} Then, a \textit{p}-type a-SiC:H film with optical band gap of 2.0 eV was deposited on the \textit{i} layer as a window material. Finally, indium-tin-oxide (ITO) was evaporated by an electron beam onto the amorphous silicon surface as the top contact and also as an antireflective coating layer. The thicknesses of the \textit{n}, \textit{i}, and \textit{p} layers were $\sim$ 80 Å, $\sim$ 0.5 \textmu m, and $\sim$ 100 Å, respectively.

Figure 2(b) shows the novel structure, deduced from structure (a) by introducing a gradual compositional grading.
p a-SiC:H layer as thick as 100 Å in the p/i interface. The graded p layer, obtained by gradually increasing the methane (CH₄) mole fraction to silane from 0 to a predetermined value, was prepared in the p chamber. During deposition, the gas mixture (CH₄ + SiH₄) did not contain diborane (B₂H₆), but we consider that the obtained layer is of slightly p type due to the residual boron doping effect from the chamber. Then an ultrathin (~20 Å), wide optical band gap (~2.4 eV) p a-SiC:H film was deposited. The other deposition processes were as described above.

III. EXPERIMENTAL RESULTS

A. Effects of the p-layer band gap and thickness on the solar cell performance

Figure 3 shows the collection efficiency of two types of solar cells; ITO/p/a-Si:H/n μc-Si:H/substrate and ITO/p/a-SiC:H/i a-Si:H/n μc-Si:H/substrate. The heterojunction cell exhibits substantial enhancement in the response at short wavelength region as compared with the ITO/pin/substrate cell. The peak response is larger in magnitude and shifted to a shorter wavelength due to the window effect of the wide optical band gap (~2.0 eV) p a-SiC:H layer. However, the peak response is limited to 0.7 even in the heterojunction cell, and we observed a steep falloff in the collection efficiencies for wavelengths shorter than 530 nm.

It is well known that the p-layer thickness in an a-Si pin-type solar cell has a strong effect on the cell performance. Figure 4 shows the effect of the p-type a-SiC:H layer thickness (~125 Å) having an optical band gap of ~2.0 eV on the photovoltaic performance of the conventional type cell shown in Fig. 2(a). Here the p-layer deposition rate was about 5 Å/sec and the measurements were carried out under AM1 (100 mA/cm²) simulated illumination. As shown in this figure, the ITO/in/substrate cell without p layer exhibits lower values of Voc and FF as compared to cells with p layers. Voc and FF increase gradually with the p-layer thickness. But increasing the p-layer thickness over 25 Å reduces the fill factor (FF) due to the series resistance effect of a thick p layer. However, with a p layer of 25~100 Å thick, the maximum conversion efficiency can be obtained. Figure 4 also shows that the maximum Voc achievable in the conventional p(a-SiC)/in/substrate solar cell is only 0.775 V. This value is about 0.1 V lower than that for metal/nip(a-SiC)/SnO₂ glass-type solar cell. As discussed in Sec. IV, we think here that the open-circuit voltage is limited by the large interface.
recombination velocity due to abrupt compositional change in the p/i interface.

B. Photovoltaic performance of the novel structure, p-a-SiC:H/graded p-a-SiC:H/i-a-Si:H/n-m-Si:H/substrate solar cell

We designed a novel structure of p(a-SiC) in/substrate-type solar cell which has a compositional grading p layer in the p/i interface. The photovoltaic performance of this new type of solar cell structure exhibits markedly enhanced $V_{oc}$ and $I_{sc}$ compared with the conventional p(a-SiC)in/substrate-type solar cells. A typical performance of the new structure cell is $V_{oc} = 0.850 \text{V}$, $I_{sc} = 14.8 \text{ mA/cm}^2$, FF = 0.568, and a conversion efficiency of 7.18% under AM1 illumination for a cell area of 4 mm$^2$. In this case the graded p-a-SiC:H layer thickness was about 100 Å. The thickness and optical band gap of the p-a-SiC:H layer were $\sim 80$ Å and $\sim 2.0$ eV, respectively. The collection efficiency spectra of this cell and the conventional heterojunction solar cell without graded p layer are shown in Fig. 5. As shown in this figure, although the collection efficiency of the new type solar cell is markedly improved, especially near the peak of solar energy spectra, the falloff in short wavelength region is still steep. This is caused mainly by the surface reflection of incident light and the photon absorption in the relatively thick p layer.

Figure 6 shows the effect of the graded p-layer thickness on the cell photovoltaic parameters. Here, in order to minimize the ineffective absorption losses of the p layer, we used a very thin ($\sim 20$ Å), wide optical band-gap ($\sim 2.4$ eV) p-type a-Si:C:H film as the window material. Although the fill factor remained almost constant with increasing graded p-layer thickness up to 100 Å (20 sec), $V_{oc}$ and $I_{sc}$ increased gradually up to 0.830 V and 15.4 mA/cm$^2$, respectively. $I_{sc}$ began to decrease for graded p layers thicker than 100 Å. Consequently, the photovoltaic performance could be enhanced drastically with increasing the graded p-layer thickness, and for 100 Å, the maximum conversion efficiency obtained was 7.88%. The improvement of the cell performance is mainly due to the enhancement of the short wavelength response as shown in Fig. 5. The short wavelength response of the cell with a thin ($\sim 20$ Å), wide band-gap ($\sim 2.4$ eV) p layer is remarkably improved as compared with the cell having a relatively thick ($\sim 80$ Å), narrow band-gap ($\sim 2.0$ eV) p layer. Figure 7 shows a typical $I$-$V$ characteristic of the novel structure, $p$/graded $p$/in/substrate-type solar cell having an ultrathin ($\sim 20$ Å), wider optical band-gap ($\sim 2.4$ eV) p layer and a graded p layer as thick as about 100 Å. Under AM-1 (100 mA/cm$^2$) simulated illumination, an energy conversion efficiency of 8.40% has been obtained. The cell area, $V_{oc}$, $I_{sc}$, and FF were 4 mm$^2$, 0.834 V, 16.4 mA/cm$^2$, and 0.613, respectively.

![Graph of Collection Efficiency vs. Wavelength (nm)](image)

**FIG. 5.** Improvement of the spectral response of an ITO/p(a-SiC)in/substrate heterojunction-type solar cell (a), by the use of a graded p layer in the p/i interface (b), and an ultrathin ($\sim 20$ Å), wider optical band-gap p layer ($\sim 2.4$ eV), i.e., the spectral response of the novel structure solar cell (c).

![Graph of Current vs. Voltage (V)](image)

**FIG. 7.** Typical current-voltage characteristic of the novel structure, $p$/graded $p$/in/substrate-type solar cell.
IV. DISCUSSIONS

It is well known that the collection efficiency of hydrogenated amorphous silicon solar cells falls off at the high incident photon energy side. This decrease in spectral response at short wavelengths has been attributed to various effects, i.e., interface recombination losses, carrier collection losses in the p layer, and surface reflection losses, etc.⁸-¹² An essential requirement for improving short wavelength response must be to reduce the absorption losses of the window layer and to minimize the effective interface recombination losses due to carrier and/or hot carrier diffusion. A marked improvement of the short wavelength response has recently been achieved by Tawada et al.¹³ Using amorphous silicon carbide alloy (a-SiC:H) film as a wide band-gap (1.8-2.2 eV) window material, they succeeded in realizing a high conversion efficiency (8.04%) solar cell with the glass/p(a-SiC)in/metal heterojunction structure. Although the blocking barrier effect for electrons of the wide band-gap p-a-SiC layer caused the marked increase of collection efficiency at the short wavelength region, the effective interface recombination at p/i interface rather increased.⁴ We have also achieved the high efficiency of 9.45% with the same cell structure.⁷ However, as shown in Fig. 3, the ITO/p(a-SiC)in/substrate-type solar cell shows quite a low spectral response at the short wavelengths, resulting in a low conversion efficiency (6.07%).

The ineffective absorption loss in the p (a-SiC) layer is not significant at the short wavelength region, i.e., the absorption in the p(a-SiC) layer with the thickness of 100 Å is about 18%-25% for an absorption coefficient of 2-3 × 10⁶/cm at a wavelength of 400 nm. We consider here that ITO/p(a-SiC)in/substrate-type solar cells have larger effective interface recombination velocities as compared with the corresponding glass/p(a-SiC)in/metal-type solar cells. A large interface recombination velocity reduces heavily the short wavelength response. The structural difference between the two types of solar cells is that as the i layers of the glass/p(a-SiC)in/metal-type solar cells are deposited on the p-a-SiC layers, a compositional grading (especially carbon) may unintentionally occur at the interface due to the residual impurity effects as reported by Kuwano et al.,¹⁴ while for the ITO/p(a-SiC)in/substrate-type cells, whose p-a-SiC layers are deposited on the undoped layers, the compositional grading effect may be minimized. The lattice structure of p-type a-Si:H is quite different from that of an undoped i-a-Si:H, and an abrupt change of composition may induce a large amount of defects at the interface as usually observed in the single-crystal lattice mismatching heterojunctions [see Fig. 8(a)]. Therefore, we propose, in this work, to introduce intentionally a graded band-gap layer at the p/i interface, to minimize the interface recombination velocity [Fig. 8(b)]. As shown in Fig. 5, the collection efficiency of the new type solar cell with a graded p layer at p/i interface is markedly improved. Moreover, it is worth noticing that the $V_{oc}$ is largely enhanced by introducing the graded p layer [Fig. 6]. The enhancement of $V_{oc}$ indicates that the dark current flowing through the defects of the p/i interface could be minimized.

In a second step, we tried to minimize the ineffective absorption in the p-a-SiC layer by using a very thin p-a-SiC layer with the optical band gap of 2.4 eV for the window material on the graded p-a-SiC layer. The absorption in a p layer as thin as 20 Å is only ~1% at a wavelength of 400 nm. As shown in Fig. 5 the short wavelength response of the cell is remarkably increased by the use of this ultrathin, wide optical band-gap p layer. In this case, only a 20 Å-thick p-a-SiC layer, combined with a 100 Å-thick graded p layer, is sufficient to obtain $V_{oc}$ of over 0.8 V.

As mentioned in a previous section, the compositional grading p layer was deposited on the i layer in the p chamber in such a way that the methane mole fraction to silane is gradually increased from zero to a predetermined value towards the end of the graded p layer. Considering the methane mole fraction to silane of about 0.8 at the end of the graded p-layer deposition, the optical band gap at the end of the graded p layer is about 1.8-1.85 eV.

In view of better methane gas controllability we also made several cells by employing a constant compositional p-a-SiC buffer layer at p/i interface instead of graded p layers as shown in Fig. 8(c). Such cells also showed marked increase in both $V_{oc}$ and $I_{sc}$, but are likely to peel off with larger methane fraction. This is caused by strains induced by lattice mismatch and difference in thermal expansion coefficient between the buffer p and the i layers and also between the p-a-SiC window and the buffer p layers.

V. CONCLUSIONS

A novel structure, high conversion efficiency p-a-SiC/graded p-a-SiC/i-a-Si/n µc-Si/metal substrate-type solar cell has been developed by introducing a gradual compositional grading p-a-SiC:H layer in the p/i interface and using an ultrathin (~20 Å), wide optical band-gap (~2.4 eV) p-a-SiC:H layer as the window material on the graded p layer. The cell prepared in accordance with compositional grading technique and the use of an ultrathin p-a-SiC:H layer exhibits marked enhancement in both $V_{oc}$ and $I_{sc}$ over the conventional a-Si pin/substrate-type solar cells. Especially, the collection efficiency in the newly developed structure was found to be remarkably increased at short wavelength region. The experimentally observed improvement in the blue response is due to reduction in effective interface recombination by the use of the graded p layer, combined with the enhanced window effect. The energy conversion efficiency of 8.40% under AM1 simulated illumination has been ob-
tained in the first trial of a cell fabricated by the rf glow discharge decomposition of pure silane.

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