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Carrier collection characteristics of microcrystalline silicon–germanium p–i–n junction solar cells

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Abstract

We report on the carrier collection characteristics of hydrogenated microcrystalline silicon–germanium (μ c-Si_{1-x}Ge_x:H) p-i–n junction solar cells fabricated by low-temperature (\sim 200 °C) plasma-enhanced chemical vapor deposition. Spectral response measurements reveal that the Ge incorporation into absorber i-layer reduces the quantum efficiencies at short wavelengths. Furthermore, the illumination of the solar cells for $x \ge 0.35$, particularly in the wavelength range of <650 nm, induces a strong injection-level-dependent p–i interface recombination and a weak collection enhancement in the bulk. These results indicate that space charges near the p–i interface are largely negative, which gives rise to an electric field distortion in the i-layer. We attribute the negative space charges to the presence of the acceptor-like states that are responsible for the strong p-type conduction observed in undoped μ c-Si $_{1-x}$ Ge $_x$:H films for large Ge contents. 2008 Published by Elsevier B.V.

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μ c-Si:H) are currently combined into a tandem solar cell structure because of the better photovoltaic performance than their single junction devices. However, the achievable efficiency of the $a-Si:H/uc-Si:H$ tandem solar cells is still limited by the lack of infrared response in the μ c-Si:H bottom cell owing to its weak infrared absorption. To extend the spectral sensitivities of solar cells into longer infrared wavelengths, we have proposed the application of hydrogenated microcrystalline silicon– germanium alloys (μ c-Si_{1-x}Ge_x:H) as a bottom cell material in a triple-junction structure, i.e., $a-Si:H/\mu c-Si:H/\mu c$ - $\text{Si}_{1-x}\text{Ge}_x\text{:}H$. The μ c- $\text{Si}_{1-x}\text{Ge}_x\text{:}H$ films can be grown at low-temperature (\sim 200 °C) by plasma-enhanced chemical vapor deposition (PECVD), exhibiting the higher absorp-

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tion coefficients compared to μ c-Si:H over the entire solar spectrum [\[1–4\].](#page--1-0) Although this material is advantageous in terms of optical absorption, the photocarrier collection in μ c-Si_{1-x}Ge_x:H p-i-n solar cells has been shown to degrade severely as the Ge content increases in the i-layer particularly for $x > 0.2$ [\[3,4\].](#page--1-0) Recently, we found that the substantial Ge incorporation gives rise to an electrical change from weak n-type to strong p-type conduction with a monotonic decrease in photoconductivity [\[4\]](#page--1-0). In this work, we have studied the impact of these electrical changes due to Ge incorporation on the carrier collection characteristics of μ c-Si_{1-x}Ge_x:H p-i-n junction solar cells.

2. Experimental procedures

The μ c-Si_{1-x}Ge_x:H films were prepared by capacitivelycoupled 100-MHz PECVD using a $SiH_4-GeH_4-H_2$ gas mixture. Films were deposited on glass substrates at a temperature of 200 °C. For film characterization, Hall-effect measurements were performed at room temperature using

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the van der Pauw method. The electrical properties were also studied by the coplanar conductivity measurement under dark and AM1.5 (air mass 1.5, 100 mW/cm²) illumination. The dangling bond defect density of the μ c-Si_{1-x}- $Ge_x:H$ films was determined by ESR measurement. Solar cells fabricated in this study consist of glass/transparent conductive oxide $(TCO)/p$ (μ c-Si:H)–i (μ c-Si_{1-x}Ge_x:H)–n $(\mu c-Si:H)/ZnO/Ag$. For the front TCO layer, we employed the chemically-etched ZnO films with an antireflective $TiO₂–ZnO$ bilayer coating for efficient light trapping [\[5\].](#page--1-0) Solar cell performance was characterized by current–voltage measurement under standard AM1.5 (100 mW/cm^2) illumination using a dual-light source solar simulator. Carrier transport properties of the μ c-Si_{1-x}Ge_x:H p-i–n solar cells were characterized by spectral response measurement using a lock-in detection technique under modulated monochromatic light illumination (\sim 50 μ W/cm²) superimposed on a broadband bias light of much higher intensity $(AM1.5, 100 \text{ mW/cm}^2)$. Injection-level-dependent carrier transport was investigated by varying the bias light intensity and wavelength using various optical filters.

3. Results

3.1. Film properties

Fig. 1 shows the film properties of the μ c-Si_{1-x}Ge_x:H including (a) carrier concentration, (b) ESR defect density and (c) coplanar dark and photoconductivities as a function of Ge content. Hall-effect measurement reveals that films exhibit a weak n-type character with electron concentrations of 10^{12} –3 \times 10^{13} cm⁻³ when x < 0.75. With further increase in Ge content, a transition occurs from n- to p-type conduction, where the hole concentration increases by more than five orders of magnitude. In Fig. 1(b), the defect density of the μ c-Si_{1-x}Ge_x:H increases gradually with Ge content and takes a broad maximum of \sim 10¹⁷ cm⁻³ at $x \sim$ 0.5. However, we detected no ESR signal for the larger Ge content regime $(x > 0.75)$ where an electrical change occurs from weak n- to strong p-type conduction. In Fig. 1(c), we summarize the dark and photoconductivities of the μ c-Si_{1-x}Ge_x:H films prepared under different hydrogen dilutions and discharge powers. It is evident that the electrical conductivity is almost independent of these deposition parameters but strongly influenced by the alloy composition. The dark conductivity shows a small change between 10^{-7} and 10^{-6} S/cm for $x \le 0.7$, while the photoconductivity shows a monotonic decrease with Ge content and no photo-induced conductivity gain is obtained for $x > 0.7$ due to an increased dark conductivity. The decrease in photoconductivity can be attributed to the reduced carrier lifetime due to the increased Ge dangling bond density as shown in Fig. 1(b).

3.2. Carrier collection characteristics of $p-i-n$ solar cells

[Fig. 2](#page--1-0) shows the quantum efficiency (QE) spectra of the μ c-Si_{1-x}Ge_x:H p–i–n solar cells with different Ge contents

Fig. 1. Dependence of the film properties of μ c-Si_{1-x}Ge_x:H on Ge content. The data include (a) electron/hole concentration n/p, (b) ESR defect density N_s , and (c) coplanar conductivity σ measured at room temperature. In (c), closed and open symbols represent conductivities measured under dark and AM1.5 illumination, respectively. Conductivity data of samples prepared at different discharge powers, P and hydrogen dilutions, r: $[H_2]/[GeH_4]$ are plotted [circles: ($P = 30$ W, $r = 1800$), triangles: $(P = 15 \text{ W}, r = 1800)$, diamonds: $(P = 30 \text{ W}, r = 900)$, squares: $(P = 15 \text{ W}, r = 900)$].

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> in the *i*-layer $(x = 0.0, 0.20, 0.35, 0.42)$ measured under short-circuit and AM1.5 illumination conditions. The thickness variation of the i-layers is within a range of 0.9–1.0 µm. Note that the solar cell of $x = 0.42$ has an antireflective multilayer coating on the glass surface. In [Fig. 2,](#page--1-0) the μ c-Si_{0.8}Ge_{0.2}:H solar cell exhibits larger QEs than the μ c-Si:H solar cell for $\lambda > 600$ nm. As a result, we obtained an increase of short-circuit current density by \sim 4 mA/cm² and a conversion efficiency of 6.1% using a 1-µm-thick µc- $Si_{0.8}Ge_{0.2}$:H absorber [\[6\].](#page--1-0) The solar cells with larger Ge contents ($x \ge 0.35$) show a further enhancement of the infrared response (λ > 900 nm), whereas the QE peak at shorter wavelength deceases drastically. The decrease in short wavelength response can be attributed to the

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