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Thin-film amorphous silicon germanium solar cells with p- and n-type hydrogenated silicon oxide layers



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ABSTRACT

Keywords: Hydrogenated amorphous silicon germanium Hydrogenated silicon oxide Light management Parasitic losses Mixed-phase hydrogenated silicon oxide $(SiO_x:H)$ is applied to thin-film hydrogenated amorphous silicon germanium (a-SiGe:H) solar cells serving as both p-doped and n-doped layers. The bandgap of p-SiO_x:H is adjusted to achieve a highly-transparent window layer while also providing a strong electric field. Bandgap grading of n-SiO_x:H is designed to obtain a smooth transition of the energy band edge from the intrinsic to n-doped layer, without the need of an amorphous buffer layer. With the optimized optical and electrical structure, a high conversion efficiency of 9.41% has been achieved. Having eliminated other doped materials without sacrificing performance, the sole use of SiO_x:H in the doped layers of a-SiGe:H cells opens up great flexibility in the design of high-efficiency multi-junction thin-film silicon-based solar cells.

1. Introduction

Hydrogenated amorphous silicon germanium (a-SiGe:H) is a meaningful building block in multi-junction thin-film silicon-based solar cells. Its electronic bandgap decreases as the Ge content increases in the matrix [1–3]. As an absorber material, a-SiGe:H offers an adjustable, intermediate bandgap between those given by the widely used hydrogenated amorphous silicon (a-Si:H, 1.7 eV) and hydrogenated nanocrystalline silicon (nc-Si:H, 1.1 eV). A combination of these absorbers can lead to better spectral utilization in triple- and quadruple-junction solar cells [4–7].

To form a p-i-n junction, p-type hydrogenated amorphous silicon carbide (a-SiC:H), a-Si:H, nc-Si:H, hydrogenated silicon oxide $(SiO_x:H)$, and n-type a-Si:H, nc-Si:H, $SiO_x:H$ have been used in the p- and n-layer, respectively, of a-SiGe:H solar cells. Among these materials, SiOx: H is worth extra attention because of its multifunctionality and adaptability demonstrated in the application of thin-film silicon-based solar cells. SiOx:H is a mixed-phase material comprising nanocrystalline silicon filaments embedded in an amorphous silicon oxide matrix [8-14]. The anisotropic growth of the material results in good transverse and poor lateral conductivity, thus improving the electrical performance of the solar cell. Optically, its relatively wide bandgap and low absorption coefficient suppress own parasitic absorption, while providing a high built-in voltage as a p-layer. The tunable refractive index offers a means to reduce the reflection at the window layer, or to enhance the intermediate reflection when used after an absorber layer [5,15-17]. Given that well-performing tunnel recombination junctions (TRJs) can be formed between p-type and n-type $SiO_x:H$ [17], $SiO_x:H$ opens a great versatility for the light management in multi-junction solar cells. Lastly, n-type $SiO_x:H/Ag$ was also used to replace the typical ZnO:Al/Ag back reflector, as the low refractive index of $SiO_x:H$ can limit the plasmonic absorption in Ag [18–20], just like in ZnO:Al/Ag stack. Fig. 1 shows the optical properties of the p- and n-type $SiO_x:H$, in comparison to other typical materials used in a-SiGe:H cells.

So far, the use of SiOx:H in a-SiGe:H solar cells is not as popular as it is in a-Si:H or nc-Si:H cells. N-type SiOx:H has been used as the nlayer of a-SiGe:H cells behind either intrinsic a-Si:H [6] or a-Si:H/nc-Si:H [21] buffer layer(s). On the p-side, Schüttauf et al. tested several p-layer configurations and reported a significant drop in $V_{\rm OC}$ when the p-layer was solely constituted of p-type SiO_x:H, compared to those which also include a a-SiC:H or a-Si:H laver between the oxide laver and the absorber [6]. Nevertheless, taking into account the adaptability of SiO_x:H materials and its successful applications in a-Si:H and nc-Si:H solar cells, it is natural to think of making a a-SiGe:H cell using only SiOx:H for the doped layers, without compromising the performance. From the optical perspective, it can reduce the parasitic absorption caused by the other more absorptive supporting materials, and at the same time provide the most flexibility in light management for both single- and multi-junction devices. Electrically, the doped SiO_x:H materials can be tuned such that they give favorable band offset at the interfaces, or form efficient TRJs with minimized losses. In this paper, we explore the possibility of using both p- and n-type SiO_x :H in thin-film a-SiGe:H solar cells without extra buffer layers adjacent to the

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Fig. 1. Optical properties of typical materials used in a-SiGe:H solar cells: (Left) Absorbance $A = \alpha \cdot d$, where α is the absorption coefficient and d is the typical thickness of the material used in a device; (Right) Refractive index at wavelength λ =550 nm. The shaded areas in blue and red color represent the adjustable properties of p and n-type SiO_x:H, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

absorber layer. Additionally, we evaluate the performance of $n-SiO_x:H/Ag$ back reflectors and optimize the light management of such device.

2. Experimental

The thin-film silicon alloy materials, including intrinsic a-SiGe:H, p- and n-type SiO_x :H and n-type a-Si:H, were deposited in a cluster tool using plasma-enhanced chemical vapor deposition (PECVD) at radio frequency (RF) of 13.56 MHz. The maximum substrate area and electrode area are 100 cm² and 144 cm² in square, respectively. Silane, germane and carbon dioxide were used as the source of silicon, germanium and oxygen, respectively. Diborane and phosphane (phosphine) were used as the doping gas for the p- and n-type materials, respectively. The deposition conditions of the PECVD materials are summarized in Table 1.

Thin-film a-SiGe:H solar cells were deposited on glass coated with nanotextured SnO₂:F (Asahi VU-type, Asahi Glass Co., Ltd. [22]) in superstrate p-i-n configuration. The typical device structure is glass/SnO₂:F/ZnO:Al/p-layer/i-a-SiGe:H/n-layer/Ag/Cr/Al. A thin layer of 20-nm-thick ZnO:Al was deposited using RF magnetron sputtering to protect the SnO₂:F against hydrogen plasma in the PECVD process [23]. The p-layer consists of a 4-nm-thick p-nc-Si:H on top of the front transparent conductive oxide (TCO) forming a good ohmic contact [14], and a 12-nm-thick p-SiO_x:H as the main p-type material for providing the electric field. The total thickness of the intrinsic a-SiGe:H is 200 nm. To mitigate the transportation barrier caused by the misalignment of energy bands between the intrinsic and doped materials [24–27], U-shape bandgap grading was applied by linearly reducing the GeH₄ flow in the a-SiGe:H deposition near the p-i and i-n interfaces. The thickness of the graded layers is 70 nm and 50 nm at

the p- and n-side, respectively. It leaves the middle part of the intrinsic layer, which has the lowest bandgap, 80 nm in thickness. The n-layer is made of either n-a-Si:H, n-SiO_x:H, or a combination of the two. The Ag/Cr/Al metal stack with thicknesses of 300/30/800 nm serves as the back reflector as well as back electrode. It was deposited by thermal (Ag) or e-beam (Cr/Al) evaporation with a shadow mask so that the patterned metallic pad also defines the cell area. There are 30 cells on each sample and each cell has a squared area of 16 mm². Cell isolation was completed by etching away the materials outside the metal pads using anisotropic reactive ion etching (RIE). In occasions that ZnO:Al is used after the deposition of n-layer, the samples were dipped in diluted hydrochloric acid to remove the ZnO:Al prior to RIE.

The optical properties of the thin-film materials were characterized by spectroscopic ellipsometry (SE). The measurements were conducted at multiple incident angles using an M – 2000DI[®] Spectroscopic Ellipsometer (J.A. Woollam Co.), which is equipped with a dual-lamp light source covering the wavelength range of 193–1690 nm. To determine the optical bandgap of a-SiGe:H, the Tauc-Lorentz model [28,29] was fitted to the SE data measured from samples of single thin films deposited on glass substrates, and the result gave the optical bandgap E_{Tauc} . In addition, optical bandgap E_{04} was found as the energy with which a photon has an absorption coefficient of 1×10^4 cm⁻¹ in the material.

The performance of the solar cells was examined by the illuminated current-voltage (I-V) measurement and external quantum efficiency (EQE) measurement. The I-V measurement was conducted at a controlled cell temperature of 25 °C, with a dual-lamp continuous solar simulator (WACOM WXS-90S-L2, class AAA). The two filtered lamps in the solar simulator were adjusted with two monocrystalline silicon reference cells manufactured by and traceable to the Fraunhofer Institute for Solar Energy Systems (ISE), to provide an incident irradiance of 1000 W m⁻² with optimum spectral matching with AM1.5G solar spectrum. The EOE measurement was performed using an in-house system, in which the electrical signal is detected by a lockin amplifier, and the chopped monochromatic light is provided by a xenon light source, a 3-grating monochromator and a chopper. A silicon photodiode, which was regularly calibrated by Fraunhofer ISE, was used to calibrate the light source in the EQE measurement. As for the external parameters of the solar cells, the open-circuit voltage $(V_{\rm OC})$ and fill-factor (FF) are determined by the I-V measurement, while the short-circuit current density (J_{SC}) is calculated by weighting the measured EQE with the AM1.5G solar spectrum. The cell performance reported in this work is the average taken from the 12 better performing cells (40%) out of the 30 cells on each sample. While the EQE measurement was conducted on the best performing cell in each sample, the reported deviation in $J_{\rm SC}$ was obtained from the *I-V* measurement.

3. Results and discussion

3.1. Use of SiO_x:H in p-layer

In this section, p-SiO_x:H is applied in a-SiGe:H cells as the main player, and the cell performance is examined. To compare the effect of different p-SiO_x:H, the device structure except the p-layer was kept the

Table 1

Deposition conditions of the PECVD materials used in this work. The constitution of gaseous precursors is shown by their flow rates in standard cubic centimeter per minute (sccm).

Material	<i>T</i> (°C)	p (mbar)	$P \text{ (mW cm}^{-2})$	SiH_4	${\rm GeH}_4$	H_2	B_2H_6	PH_3	CO_2
p-nc-Si:H p-SiO _x :H i-a-SiGe:H n-a-Si:H n-SiO _x :H	180	2.2 2.2 3.6 0.6 1.5	243.1 90.3 20.8 27.8 69.4	0.8 0.8 30.0 40.0 1.0	- - 3.65 - -	190 190 200 10.8 101	0.004 0.004 - - -	- - 0.22 0.024	- 0.8-2.2 - - 0.5-2.6

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