Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

Wide bandgap p-type nanocrystalline silicon oxide as window layer for high performance thin-film silicon multi-junction solar cells

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ABSTRACT

High efficiency thin-film silicon multi-junction solar cells require both high open-circuit voltage (V_{oc}) and high blue spectral response in the top amorphous silicon (a-Si:H) cell. Here we investigated the mixed-phase p-type nanocrystalline silicon oxide (p-SiO$_x$) films and used this material as window layer in high V_{oc} a-Si:H p–i–n solar cells. The introduction of oxygen suppresses the nucleation of Si nanocrystallites. Therefore, p-SiO$_x$ film with low oxygen content should be used for the contact layer, to guarantee growth of highly conductive Si nanocrystallites in the initial few nanometers. With p-SiO$_x$ as p-layer, the optimal p-SiO$_x$ film has high oxygen content and thus high bandgap, resulting higher V_{oc} and better spectral response than the standard p-type amorphous silicon carbide alloys (p-SiC) based window layer. Although the optimal p-SiO$_x$ film has very low planar conductivity (in the order of 10^{-12} S/cm), the filament-like Si nanocrystallites which grow perpendicular to the substrate enable the adequate transverse conduction for the solar cells. Consequently, a-Si:H solar cells with $V_{oc} > 1$ V and $FF > 70\%$ have been obtained. Finally, the p-SiO$_x$ window layers were successfully applied to thin-film silicon multi-junction solar cells. A high initial efficiency of 14.4% has been achieved in a-Si:H/nc-Si:H tandem solar cells.

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1. Introduction

Thin-film silicon (TF-Si) solar cells have received much attention due to the abundance of the raw materials and the potential for large-area low-cost manufacturing. However, the efficiency should be further increased to be competitive with other thin-film PV technologies. Multi-junction solar cells based on hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) can offer both high efficiency and good stability [1–7]. As top cell, the a-Si:H sub-cells with high V_{oc} and high blue spectral response are highly desirable for high-efficiency devices. The p-type window layer and its interface with the intrinsic absorber layer play an important role to achieve high performance a-Si:H solar cells. There are several critical requirements for a promising p-doped material as window layer: (1) good ohmic contact with front TCO layer; (2) high bandgap to achieve high build-in voltage (V_{bi}) and thus high open-circuit voltage (V_{oc}); (3) good conductivity to obtain high fill factor (FF); and (4) low absorption loss over the short wavelengths range (300–600 nm). Especially for triple- or quadruple-junction solar cells, good transparency of the window layer are crucial to enable thinner a-Si:H absorber layers and thus higher stabilized efficiency.

The p-type protocrystalline silicon (p-pc-Si:H, also called microcrystalline silicon) deposited under very high hydrogen dilution is commonly used for high V_{oc} n–i–p substrate-type a-Si:H solar cells [8,9]. For p–i–n superstrate-type a-Si:H solar cells, p-type amorphous silicon carbide (p-SiC) or p-SiC with embedded nanocrystalline silicon phase is traditionally used as the p-layer [1–3,10,11]. The optimized p-SiC films have higher optical bandgap (∼2.0 eV) and lower absorption loss than p-pc-Si:H, resulting in higher V_{oc} and better blue spectral response. It is interesting to note that V_{oc} higher than 1 V can be achieved with oxygen- or carbon-free p-pc-Si:H in substrate-type a-Si:H solar cells [8,12,13]. A pure protocrystalline character is observed at the i/p interface, which results in low recombination at the i/p interface and high V_{oc} [9]. However, similar high V_{oc} has not yet been reported in p–i–n superstrate-type a-Si:H solar cells with p-pc-Si:H doped layers. This phenomenon indicates that both high bandgap in p-layer and low defects density at the p/i interface are crucial to achieve high V_{bi} and thus high V_{oc}.

In this study, we aim at reaching p–i–n a-Si:H cells with high V_{oc} and high blue spectral response by using p-type nanocrystalline silicon oxide (p-SiO$_x$) as window layer. This material presents

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even higher bandgap and lower absorption loss than p-SiC, which makes p-SiO$_x$ an promising material for the window layer [14,15]. Doped nanocrystalline silicon oxide is a key material as functional layers in TF-Si solar cells and modules because of its low absorption and low refractive index after incorporation of oxygen. It is a mixed phase material comprising oxygen-rich amorphous SiO$_x$ matrix with embedded nc-Si:H phase [16,17]. The n-doped silicon oxide (n-SiO$_x$) layers with low refractive index are widely used as intermediate reflector and back reflector in multi-junction solar cells [18–25]. The p-doped silicon oxide (p-SiO$_x$) with relatively high crystalline fraction is also widely used as p-layer for nc-Si:H solar cells, leading to reduced optical loss and improved electrical performance compared to p-nc-Si:H [25–29]. However, the use of p-SiO$_x$ as window layer has been seldom investigated in a-Si:H solar cells [14,15,30–32]. Biron et al. studied the p-SiO$_x$ as window layer for high V_{oc} n–i–p a-Si:H solar cells and increased the V_{oc} up to 940 mV [14]. However, the increased V_{oc} is commonly accompanied with relatively low FF, which is also observed in other studies [14,15,30–32]. Therefore, developing p-type window layer with high transparency and good conduction is crucial to simultaneously achieve high V_{oc}, high FF and high blue spectral response in a-Si:H solar cells. Here, we demonstrate that the p-SiO$_x$ window layer can result in high V_{oc} a-Si:H solar cells with high FF and excellent blue spectral response. The p-SiO$_x$ window layers were also successfully applied to high performance multi-junction solar cells.

2. Experimental details

To study the microstructure and opto-electrical properties, the p-SiO$_x$ films with a thickness of 40 nm were deposited on the Corning Eagle XG glass using a RF-PECVD cluster tool at the frequency of 13.56 MHz. The typical deposition condition used for the p-SiO$_x$ films is presented in Table 1. Both planar conductivity (σ) and activation energy (E_{act}) were determined by the dark conductivity measurements after evaporating aluminum contacts on the layers. The refractive index and optical bandgap were determined from the spectroscopic ellipsometry (SE). The optical band gap E_{04} is determined at the absorption coefficient of 10^4 cm^{-1}. The SE measurements were fitted with an effective-medium model with three materials: a-Si:H, SiO$_2$, and poly-Si. The combination of a-Si:H and SiO$_2$ resembles the a-SiO$_x$ matrix, and the poly-Si corresponds to the nanocrystalline Si phase in the film, similar to the fitting method used in Ref. [17] but with minor modification. Advantage of the method here is that we can indirectly obtain the oxygen content and crystallinity (X_c, volume fraction of the crystalline phase) besides the optical properties. The films were also measured by Raman spectroscopy with a 514 nm laser. The X_c is defined by $X_c = (I_{520}+I_{510})/(I_{520}+I_{510}+0.8 \times I_{480})$, where I_i denotes the integration area under Gaussian fitting peak centered at i cm^{-1}. We have found that the X_c determined from Raman measurements and the oxygen content deduced from X-ray photoelectron spectroscopy (XPS) are consistent
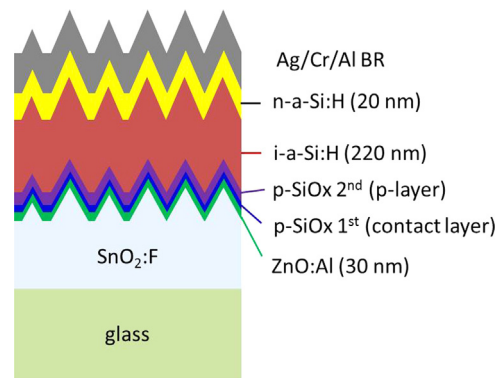
Table 1
Typical deposition condition used for the deposition of p-SiO$_x$ films.

CO$_2$/SiH$_4$	0–4.0
H$_2$/SiH$_4$	210
B$_2$H$_6$/SiH$_4$	0.4%
Substrate temperature	180 °C
Pressure	2.2 mbar
RF power density	35 mW/cm^2
Deposition rate	2 nm/min

Fig. 1. The schematic structure of a single junction a-Si:H solar cell with p-SiO$_x$ window layer. The window layer consists of two layers of p-SiO$_x$, namely contact layer and p-layer.

with the results from SE measurements (Fig. 3b). However, it is difficult to use Raman measurements to determine X_c value when it is lower than 20%. The transmission electron microscopy (TEM) was used to study the microstructure and growth behavior of p-SiO$_x$ using a FEI-Tecnai F30 setup with incident electron energy of 200 kV. The plasmon imaging was acquired by a Tridiem Gatan energy filter with a slit width corresponding to 4 eV. Samples for TEM characterization have a thickness of around 100 nm.

Unless otherwise stated, the p–i–n solar cells were deposited on the nanotextured Asahi-VU (SnO$_2$:F) substrates. A thin layer of ZnO:Al (30 nm) was sputtered on the substrates before the deposition of the p-SiO$_x$ layers to protect the SnO$_2$:F under H-rich plasma. The single junction a-Si:H cells have a device structure shown in Fig. 1. Note that the window layer consists of two layers, namely contact layer (the first p-SiO$_x$ layer) which makes good ohmic contact with front TCO (SnO$_2$:F/ZnO:Al here) and p-layer (the second p-SiO$_x$ layer) which enables high build-in voltage and good interface with the i-a-Si:H absorber layer. After the deposition of p-SiO$_x$ layers, H-plasma treatment for 2 min was deployed before the deposition of i-a-Si:H. The i-a-Si:H layers were deposited using mixture gases of H$_2$ and SiH$_4$ at a pressure of 10 mbar and power density of 10 mW/cm^2. The bandgap of a-Si:H can be tuned by changing the H$_2$/SiH$_4$ dilution ratio and deposition temperature [33–36]. For the nc-Si:H subcell in the tandem and triple-junction solar cells, the nc-Si:H layers were deposited at high-pressure and high-power regime at 40.68 MHz. The deposition rate of the i-layer is ~40 nm/min, and neither profiling techniques nor buffer layers were deployed [25]. The area of single junction a-Si:H cells is 4×4 mm^2, and the area of the tandem and triple-junction cells is 1.05×1.05 cm^2, as defined by the back metal contacts. Silicon layers without metal contacts were removed by plasma dry etching to reduce lateral collection of current. The current–voltage (J–V) measurements of solar cells were performed in their initial state under an AM 1.5 G solar simulator (100 mW/cm^2) at 25 °C. The short-circuit current density (J_{sc}) values were calculated from the external quantum efficiency (EQE) measurements by weighting with the AM 1.5 G spectrum. The statistical analysis on solar cell performance was deduced from the J–V measurements over 30 dots for single junction solar cells or 6 dots for multi-junction solar cells on one substrate (10×2.5 cm^2). The series resistance was extracted from the J–V curves near open circuit conditions. The scanning electron microscopy (SEM) cross-section images of solar cells were taken with a high resolution Hitachi S4800 setup using back scattering mode to resolve the fine cross-sectional structures of the devices.