Improvement on the Si/PEDOT:PSS hybrid solar cells by rear-sided passivation with SiN_x:H layers

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Abstract. A patterned silicon nitride (SiN_x:H) passivation layer was employed to improve the performance of silicon/poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (Si/PEDOT:PSS) hybrid solar cells, achieving of an enhancement in the power conversion efficiency (PCE) of 0.6%. The insertion of patterned SiN_x:H layer with a 80% SiN_x:H-to-substrate ratio boosted the open circuit voltage (V_{oc}) from 523.1 mV to 573.4 mV, suggesting the well-passivation property of the patterned SiN_x:H thin layer that was created by plasma enhanced chemical vapor deposition and lithography processes.

Introduction

Si/Organic hybrid solar devices which combine the advantages of both organic and inorganic have attracted intensive interest. Among numerous materials, poly(3,4-ethylenedioxythiophene):poly(style
-nesulfonate) (PEDOT:PSS) is an ideal candidate polymer due to its outstanding properties of conductivity and transmission. Up to now, the power conversion efficiency (PCE) of Si/PEDOT:PSS hybrid solar cells has been improved to above 13% by a range of research activities.

SiN_x:H is widely used in photovoltaic industry. One of its advantage is the ability to provide good passivation for the n-type Si substrate because of this dielectric layer containing considerable amount of hydrogen bond and positive charge (typically several 10^{12} cm^{-2})[1], offering good chemical and field-effect passivation on H-terminated n-type emitter[2].

Here, for the purpose of passivating n-type Si substrate, we applied patterned SiN_x:H passivation layer onto the rear side of substrate. In order to make a good contact, we left a considerable substrate region to be contacted with the rear electrode. Moreover, we also compared the performance of cells with different contact coverage. The test results showed that the improvement of the PCE is largely the result of suppressed recombination on the rear side. Compared with common cells, the V_{oc} of the cell with a SiN_x:H-to-substrate ratio of 60% improved by 523.1 mV to reach 558.0 mV, and the J_{sc} improved by 24.1 mA/cm^2 to reach 24.8 mA/cm^2. Finally we got the cell with a PCE of 9.03% under the simulated solar illumination (AM 1.5G, 100 mW/cm^2).

Experimental

Device fabrication. The n-type (100) Si substrate (single side polished, float zone, 20×20 mm, thickness 300±15 μm, resistance 1-5 Ωcm) was cleaned using RCA, and 8% (volume ratio) HF cleaning procedures before putting into the plasma enhanced chemical vapor deposition (PECVD) chamber. SiN_x:H films (100 nm) were deposited onto the unpolished side of silicon substrates at 350 °C using a NH_3(5 sccm)/SiH_4(40 sccm)/Ar(40 sccm) gas mixture and a processing pressure of 70 Pa for 10 minutes. In order to make the uniform layer of hexagonal SiN_x:H, normalized lithography process was employed. After spin-coating, baking, UV-exposing and photoresist development process, the photoresist patterns were formed on the SiN_x:H films. 0.25% HF(volume ratio) solution etching step was underwent for 30s after lithography process. After removing the portion of the SiN_x:H layer without the protection of photoresist and washing away the photoresist remaining, a Si substrate partially covered by patterned SiN_x:H film was obtained. Next, PEDOT:PSS layer was spin coated on the polished side of substrate at a speed of 3000 rpm for 1min, then heated on a hotplate at 125°C for 15 min to remove the solvents. Finally, a top Ag grid electrode and 200nm-thick Al rear electrode were deposited by thermal evaporation.

Material and device characterization. The surface topography and thickness of the patterned SiN_x:H passivation layer were observed by SEM(Hitachi S-4800 SEM). The chemical bonding characteristics of SiN_x:H layers were obtained by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Harrick). Using microwave photoconductance decay (μ-PCD) technique (WT2000PVN, Semilab), the minority carrier lifetimes of SiN_x:H layers were characterized. After calibrating irradiation intensity of standard silicon photovoltaic device (Oriel, model 91150V), the density-voltage (J-V) characteristics of the hybrid solar cells were tested with a Keithley 2400 digital source meter (Keithley) under simulated sunlight (100 mW/cm^2) illumination provided by a xenon lamp (Oriel) with an AM 1.5 filter. The open area of the cells was 0.7 cm×0.8 cm, and the shading grid of Ag was 0.11cm2, so the active area of the device was 0.45 cm^2. Newport silicon detector and 300 W xenon light source with a spot size of 1 mm×3 mm were used to measure the external quantum efficiency (EQE).

Discussion.

SiN_x:H Surface topography. The pattern consists of same-size of hexagons. From the SEM picture (Fig. 1), it was found the unpolished Si surface was covered by a uniform layer of 100nm hexagonal SiN_x:H with steep edge. Through this design, we obtained a passivation layer with a passivation-to-substrate coverage ratio of 60% and 80%. It was observed that during the HF etching process, excessively high concentration of HF or long etching time could result in pores on the SiN_x:H (Fig. 1c insert), which could also bring negative impact on or even neutralize passivation.

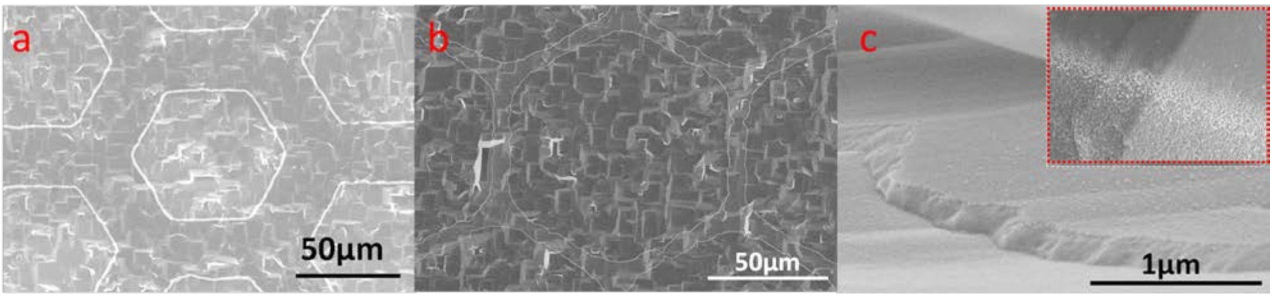

Fig. 1 SEM images of the patterned SiN_x:H layer. The SiN_x:H hexagons are of uniform sizes with a SiN_x:H-to-substrate ratio of 60% (a) and 80% (b). Fig 1(c) represents SiN_x:H film with good etching result and uniform coverage, without residual photoresist and symptom of overetching. The insert in (c) shows the pores as a result of HF overetching.

Passivation of SiN_x:H film. The average minority carrier lifetime of Si wafers with different surface treatments were shown in Fig. 3a. Compared with the lifetime of reference Si substrate (8μs), the average carrier lifetime increased to 470μs after the deposition of 100 nm SiN_x:H layer on both sides in full area. While, the value decreased to 47μs and 63μs for 60% and 80% SiN_x:H ratio after HF etching. It is only 10% ~13% of that of the unetched sample, but still about 7~8 times of that of the reference sample. After coating PEDOT:PSS film, the average lifetime of minority carrier was 23μs of reference sample where as the lifetime became 85μs and 98μs after 60% and 80% ratio of the passivation layer were added which were roughly 3~4 times longer. The test results suggest that although HF etching will cause a dramatic reduction in the lifetime of the minority carriers, the patterned SiN_x:H layer still bring enhanced passivation ability before or after PEDOT:PSS coating.

Chemical bond structure of SiN_x:H layer. In order to confirm the chemical bond characteristics of the SiN_x:H film, ATR-FTIR test was carried out (Fig. 2b). The dominating absorption peak around 878 cm^{-1} can be ascribed to the Si-N bending stretching vibration[3]. The peak located at 1173 cm^{-1} and 3340 cm^{-1} are typically ascribed to N-H absorption feature[4, 5]. According to earlier ATR-FTIR analyses reported by Patil et al., the peak around 2349 cm^{-1} occurring in the ATR-FTIR spectrum is resulted from the vibration of Si-H bond[6]. Besides, H_2O molecules absorption peaks are obtained in the region from 3580 cm^{-1} to 3670 cm^{-1} and around 1650 cm^{-1}[7]. The ATR-FTIR curve indicates Si-N bond structure is the dominant bond type in the SiN_x:H film which will contribute mainly to the field-effect passivation. In addition, hydrogen related bonds such as N-H and Si-H were observed in ATR-FTIR spectrum, which may offer good chemical passivation on H-terminated n-type Si.

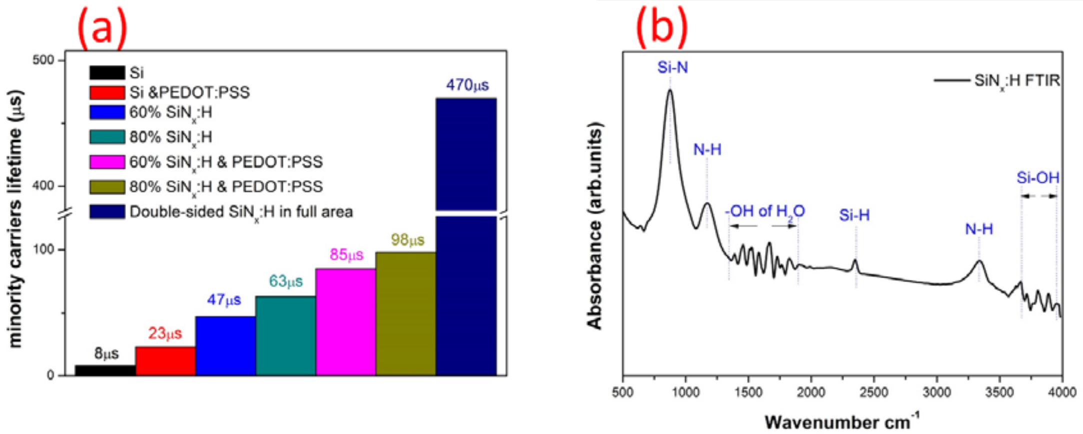

Fig.2 (a) Minority carriers lifetime of Si substrate with different surface treatments. (b)ATR-FTIR Curve of SiN_x:H film.

Photovoltaic Characteristics of the Solar Cells. Figure 5 depicts the light current density-voltage (*J-V*) curves of three types of cells, namely the reference samples, the samples with SiN_x:H-to-substrate ratio of 60% and 80%, measured under 100 mW/cm^2 illumination. Table1 lists the average values of open circuit voltage (V_{oc}), circuit current density (J_{sc}), fill factor (FF), PCE and series resistance (R_s) of the fabricated devices as a function of SiN_x:H passivated layer.

Table 1 Performance indicators of Si/PEDOT:PSS heterojunction solar cells

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s (Ω cm^2)
Reference	523.1	24.1	66.8	8.40	8.0
60% SiN_x:H	558.0	24.8	65.2	9.03	10.4
80% SiN_x:H	573.4	25.0	63.0	9.01	17.3

Compared with reference devices, the introduction of patterned SiN_x:H passivation layer on the rear surface of the Si substrate that effectively suppresses the recombination rate. As a result, the V_{oc} of SiN_x:H deposited samples increased to 558.0 mV and 573.4mV for 60% and 80% SiN_x:H ratio devices respectively. The J_{sc} of the sample with SiN_x:H layers reached a maximum value of 25.0 mA/cm^2 compared with the value of 24.1 mA/cm^2 observed in reference/PEDOT:PSS cells, possibly because the decreasing of recombination enhanced charge carrier density at longer wavelength range. With the coating of the SiN_x:H layer, it reduce the contact area between the Si and the rear electrodes resulting in the increasing of R_s and degradation of FF. For the above reasons, the addition of SiN_x:H layer brought enhanced PCE of the SiN_x:H-coated solar cells, with a PCE of 9.03% and 9.01% for 60% and 80% SiN_x:H-to-substrate ratio respectively. In general, the insertion of patterned SiN_x:H passivation layers perform higher PCE value, and the 60% SiN_x:H-to-substrate ratio devices display maximum PCE of 9.03% which is 0.6% higher than the reference sample.

To further verify the effect of the patterned rear passivation layer, the external quantum efficiency (EQE) was measured, as shown in Fig. 3b. Benefiting from recombination suppression occurring on the rear surface, both 60% and 80% SiN_x:H ratio devices displayed higher EQE value in the visible and near infrared region. With the better passivation, 80% SiN_x:H ratio exhibited better EQE within the wavelength range of 900-1100 nm than 60% one which is consistent with the higher J_{sc}.

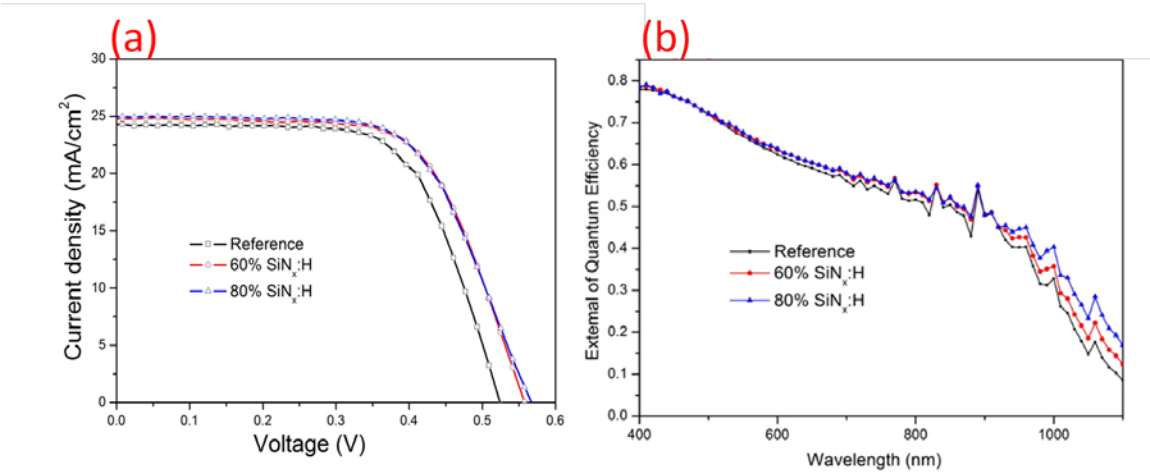

Fig. 3 (a) Current density versus voltage characteristic of the hybrid solar cells from reference, SiN_x:H-to-substrate ratio of 60% and 80% under 100 mW/cm2 illumination (AM 1.5). (b) EQE curve of Si/PEDOT:PSS cells with reference, SiN_x:H-to-substrate ratio of 60% and 80%.

Summary

We have demonstrated that the performance of Si/PEDOT:PSS hybrid solar cells could be improved by adding a patterned passivation layer of SiN_x:H onto the rear surface of the Si substrate. The main reason was the SiN_x:H layer suppress recombinations occurring on the rear side. Compared with 80% SiN_x:H-to-substrate ratio devices, cells with 60% ratio exhibited higher PCE(9.03%), which is 0.6% higher than reference cells.

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