Silicon Nitride Passivation of Silicon Nanowires Solar Cell

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Abstract. Vertical aligned silicon nanowires were synthesized using chemical etching of silicon wafer. Influence of a silicon nitride layer on the top of the silicon nanowires solar cell has been investigated. The optical properties of a Si NWs array with and without silicon nitride passivation layer are examined in terms of optical reflection property. In the presence of silicon nitride layer, 1% reflection ratio in the spectral range (250-1000nm) is achieved. In addition, the solar cell characteristics have been significantly improved, which exhibits high short circuit current as well high efficiency. Based on the current –voltage measurements and morphology results, we show that the silicon nitride layer can passivate the defects generated by wet etching processes.

1. Introduction
Silicon nanowires (SiNWs) attract significant attention because of their potential applications in many fields like sensors, transistors, lithium batteries, diodes and photovoltaics’ [1-5]. Particularly it can be applied on silicon solar cells as an antireflection coating, due to low average reflectance values [6-7]. Several synthesise methods have been used to fabricate SiNWs including chemical vapour deposition [8], laser ablation [9], thermal evaporation, and solution methods [10-12]. Among these synthesis methods, wet chemical etching has been frequently used to prepare SiNWs. The electrochemical wet etching is advantageous for achieving SiNWs with controlled diameter, length, spacing and density, avoiding high –cost and low throughput conventional lithographic processes [13]. Recently, it was found that the silicon nanowires antireflection coating (ARC) prepared by electrochemical etching has achieved nearly perfect antireflection coating [14]. The superior antireflection property of the nanowires surface attributed to three reasons: huge surface area of SiNWs, rough surface morphology which leads to strong light scattering as well absorption, and graded refractive index profile between air and SiNWs that closely implies a multilayer antireflection coating [6,14-15]. Some other properties of SiNWs, as for example crystal ordination, good doping level, and excellent uniformity, imply utilization of SiNWs in silicon solar cells.

Despite all these features maximum obtained efficiency of planar solar cells used SiNWs ARC does not exceed 10%. This low efficiency can be attributed by many factors. One of factors is that the surface recombination velocity strongly increases when using SiNWs ARC, due to the large surface area [16-17]. Therefore it is necessary to develop a passivation way of the SiNWs surface and minimizing the surface states [18]. The most common and practical method of passivation is to grow high quality of nanowires silicon nitride as it is commonly done in standard solar cell processing [19]. This will also be beneficial for the development of the antireflection property of the SiNWs. In this
work, we study the effect of SiNx layer on the surface passivation of the SiNWs ARC. Measurement of the open circuit voltage, $V_{oc}$ and short circuit current $I_{sc}$ gave brief information on the surface passivation quality.

2. Experimental details

Growth of aligned SiNW arrays was carried out on p-type (100) silicon (0-1 $\Omega$cm) wafers with 6 inch diameter. The etching of 3×3 cm $^2$ cutted samples were carried out in a Teflon beaker containing 5 M HF /0.02 M AgNO3 solution, at room temperature for different etching time. Prior to the etching, the samples were sequentially cleaned with acetone, ethanol and de-ionized water for 5 minutes each. Followed by cleaning with boiling piranha solution (H2SO4:H2O2 = 3:1 by volume, for 60 min) to remove any organic containments. The samples were then rinsed thoroughly with de-ionized water followed by dipping in 10% HF solution to remove any surface oxides. After that the cleaned silicon wafers were immersed in the etching solution .Hence, the tree like silver pattern wrapping the silicon samples were detached by NH3OH /H2O2 (3:1) solution. Finally, samples were rinsed with deionized water and blown dry in air.

After synthesis of SiNWs on p-type c-Si wafer, phosphorous diffusion was performed on the front surface using liquid POCl3 diffusion source at 900C. The samples were then dipped in 5% HF solution to remove the parasitic layer. Plasma –assisted nitride was deposited on SiNWs samples for 1,2,3,4 and 5 minutes. All plasma assisted nitridization was performed at a power of 100W and a temperature of 150°C, a pressure of 1 Torr and NH3/SiH4 gas flow ratio equals to 3. The back and front sides were deposited then using E-gun, followed by baking individual sides of the wafers. Finally, dried samples were co-fired in belt furnace to achieve an Ohmic contact at both ends. The optical and morphological characteristics of the SiNWs synthesized on c-Si wafer were estimated by spectrophotometer and field emission scanning electron microscopy (FE-SEM). The current–voltage (I–V) properties of the fabricated SiNWs solar cell were investigated using solar simulator (AM 1.5, 100 mA/cm$^2$)

![Figure 1. The schematic of the SiNx/ SiNWs-array solar cell](image-url)
3. Results and discussion

3.1. Optical properties of Silicon nanowires layer

Etching time is the most essential parameter used to optimize the antireflection properties of silicon nanowires. In our case, silicon nanowires were etched for different duration time from 20 to 80 min. With the increase of etching time, the length of nanowires increased from few nanometres to micrometers. Referring to figure 2, it has been found that the length of SiNWs increases linearly with etching time for duration (0-80 min). The estimated average etching rate is 40 nm min\(^{-1}\) for HF and AgNO\(_3\) concentration of 5.25 and 0.02 M, respectively at room temperature. The best reflectance is obtained when the etching time is 80 min, presents an effective reflectivity of 2.5 % (between 250 and 1000 nm). R value of our nanowires at different times ranging from 2.5 % to 3.85 % in the 250–1000 nm wavelength range. Referring to previous work [20] it was confirmed that the recombination effect is strongly dependent, increases with an increase in the etching time due to large SiNWs density as well larger surface area. For this reason our solar cell used SiNWs etched for 25 min with 3.5 % reflectivity. Figure 3 represents the spectral reflectivity of the used SiNWs along with polished silicon wafer.

Figure 2. (a) Silicon nanowires length as a function of etching time

Figure 2. (b) Reflectance spectra of SiNW arrays and polished Si wafer.
3.2 Morphology of SiNWs/SiNx
The surface and cross-sectional views of the SiNWs with SiNx passivation layer were analyzed using field-emission scanning electron microscopy (FESEM), as shown Figure 3. The length of the NWs was found to be ca. 700 nm and the diameter is in the range of 50-100nm. By increasing the deposition time of SiNx, it can be seen that SiNWs diameters start to increase from 50- 100nm to 100- 130 nm. This increase in SiNWs diameters indicates radial SiNx coating of the nanowires which could be considered as a uniform passivation way. Following the FESEM photos of SiNx deposition from 1 to 5 min, it is clear that the SiNx passivation starts from bottom to up, fills the cavity between Nanowires and then start to be deposited on the surface. This can be approved by the SiNx thickness data achieved by ellipsometer measurement shown in figure 4. By comparing ellipsometer results for two samples; SiNWs and polished silicon coated with SiNx for 5 minutes, the thickness of SiNx decreases from 70 nm for polished silicon to 32 nm of SiNx for SiNWs. The decreasing in thickness confirmed the whole passivation of the SiNWs. After SiNx deposition we try to examine the reflectivity for different time durations Figure 4 , we found out that best reflectivity when we deposit SiN for 3 minutes, as we got 1% in the range 250-100nm. This result can be understood in conjunction with shallow passivation effect. Using the SiNx thickness measurements and have optimized deposition duration for SiNx (3min) with approximate thicknesses of 27 nm and spectral reflectivity of 1% in the range 250-1000nm.

![Figure 3. Plane- and cross-sectional SEM images of SiNx deposited on SiNWs for different durations (a,f) 1min, (b,g) 2min, (c,h) 3min, (d,i) 4 min, (e,j) 5 min.](image-url)
3.3 Surface passivation results

Figure 5 shows that a low reflectivity can be obtained using by optimization of SiNWs/SiNx structure and length leading to an increase in the short circuit current by 15%. The values show that the silicon nitride partly improves the surface passivation, leading to an increase of Voc, from 450 mV to 490 mV around 8% enhancement. This passivation enhancement is related to the high content of hydrogen in the SiNx:H layers: H diffuses within the thin SiNWs layer and passivates the recombination centre elimination of the recombination centre results in better collection of electron hole pairs leads to large Voc which reflects relatively low surface recombination velocity of the Si/electrode junction and good bulk properties of NWs. However, low enhancement fraction of Voc reflects that the recombination rate and surface state density is not decreased well due to the high surface-to-volume ratio.

The calculated FF of SiNx passivated SiNWs solar cell improved by 6%, reaching 65.7%. This improvement can be attributed to decreasing contact area between electrode and SiNWs. However the original FF of SiNWs non passivated solar cell still low. This low magnitude is more related to the main problem facing SiNWs solar cell that is the the electrode contact (2). Hopefully by solving metal contact problem the fill factor can reach better results. Our SiNx passivated SiNWs solar cell exhibits an improved efficiency by 23%, an open circuit voltage by 7%, a short-circuit current by 15% and a fill factor by 6%, as compared Control planar solar cells without SiNx, respectively. However, the recombination rate and surface state density is not decreased well due to the high surface-to-volume ratio which needs more optimization of passivation techniques as well passivation materials. Thus, solar cells with SiNx passivated SiNWs are better than the control samples without any SiNx, which verify the importance of passivation.
4. Conclusion

In order to reduce recombination effect in the SiNWs ARC solar cells, a SiNx film has been deposited to passivate the SiNWs array. The reflectivity can be effectively reduced up to 1% in 250-1000 nm range, leading to an increase in the short-circuit current density in the SiNWs ARC solar cells. The combination of SiNWs ARC with dielectrics layers allows increasing the surface passivation quality (Sun-Voc increase of ~8%). We obtain thus better reflectivity results than with a SiNx layer, with a minimisation of the surface degradation. However, obtaining high efficiency of SiNWs ARC solar cell needs optimizing the surface passivation and improving the electrode-contact property.

Acknowledgments

The authors thank Malaysian Government for funding this project.

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