

SILICON NANOWIRE BASED HETEROJUNCTION SOLAR CELLS

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ABSTRACT: Silicon nanowire solar cells with heterojunctions were prepared on single crystalline silicon wafers. The nanowire arrays were generated by silver catalyzed etching of n-type wafers. After careful removal of the metallic silver particles a p-doped amorphous silicon shell was deposited around the nanowires by PECVD, which served as a heteroemitter. Then a transparent conductive oxide (aluminum doped zinc oxide) layer was deposited by atomic layer deposition which filled the space between the nanowires. The cells were characterized by SEM, TEM, and EBIC. Under AM1.5 illumination an open circuit voltage of 476 mV and an efficiency of 7.3% was observed on a cell of 7 mm² area.

Keywords: Silicon, Nanowires, Heterojunction, Solar Cell

1 INTRODUCTION

Silicon nanowire solar cells received growing interest in the last few years [1-9]. Compared to classical wafer cells they could be produced at much lower cost, whereas compared to amorphous silicon thin film cells they have the potential for much higher efficiencies. The main point with the nanowire cells is the perfect light trapping which leads to high absorption even in 1 μm thick crystalline silicon nanowire arrays [10]. There are two concepts for these cells [1]. In the concept used here the p-n junction is in a radial configuration. The doped core of the nanowire is surrounded by a shell of opposite doping. In this case the light generated charge carriers have to diffuse only by the radius of the nanowire to arrive at the p-n junction where they are separated. Therefore, the diffusion length in the nanowire needs not to be larger than about 100 nm. In another concept the p-n junction is axial, i.e. the doping changes along the nanowire length. In this case the diffusion length has to be in the order of the nanowire length, i.e. about 1 μm .

For preparing silicon nanowires two methods are well known. In a bottom up method the nanowires are grown by CVD catalyzed by metal nanotemplates [11]. Usually gold droplets are used with the drawback that gold is dissolved into the silicon nanowires to reduce the carrier life time. In a top down approach used here, the nanowire arrays are generated by silver catalyzed etching [12,13]. During this process silver nanoparticles form which afterwards have to be carefully removed.

The nanowires were covered by a shell of hydrogenated amorphous silicon deposited by classical PECVD. This shell acts as a heteroemitter. As a front contact AZO (aluminum doped zinc oxide) was deposited as TCO (transparent conductive oxide) by ALD (atomic layer deposition). The AZO layer filled the space between the nanowires completely.

For cost reduction the nanowires finally should be prepared on multicrystalline silicon thin films on glass instead of wafers. Both preparation methods, bottom up as well as top down, work on thin films as well. Moreover, all involved preparation steps are compatible with glass substrates.

2 EXPERIMENTAL

The nanowires were prepared by wet chemical

etching [12,13]. As substrates we used n-doped silicon wafers ($1 \times 10^{15} \text{ cm}^{-3}$ phosphorus).

The wafers first were cleaned by acetone and 2-propanol, and then at 80 °C for about 10 minutes by a solution of H₂SO₄ (97%) and H₂O₂ (30%) (1:1 by volume) to remove any organic and inorganic contaminants from the surface. The cleaned substrate was mounted in an etching cell which allows only the upper side to get in contact with the etching solution. For nanowire etching a mixture of 10 ml AgNO₃ (0.02 M) and 10 ml HF (5 M) at room temperature was applied for 30 minutes. Then the sample was rinsed thoroughly with deionized water. In the etchant nanoparticles of silver form which catalyze the self-organized etching of channels into the silicon substrate so that silicon nanowires remain. After etching there are silver dendrites at the outer surface and silver nanoparticles in the holes between the nanowires. Before further solar cell preparation the silver particles have to be removed carefully to avoid shunting of the cells. The cleaning procedure begins with a 3 min. dip in concentrated HNO₃ (65%) to remove the large amount of silver dendrites on the sample surface. The sample then is rinsed in deionized water for several times. After that 10 ml NH₄OH (4.6%) together with 5 ml 2-propanol is added to the etching cell. Air is bubbled through the mixture for 25 minutes. In a further silver removal step the sample was treated by a neutral Na₂S₂O₃ (0.1 M):2-propanol solution for 20 min. After the cleaning, the sample was dipped into a HF (2%):2-propanol solution for 8 minutes to remove the oxide layer on the nanowire surface. In all these procedures 2-propanol serves as a surfactant so that the etchants can penetrate into the nanowire array.

After rinsing in deionized water, the sample was immediately placed into a PECVD chamber to deposit an about 5 nm thick a-Si layer at 225 °C. Thin intrinsic a-Si (20 seconds at a silane flow rate of 2 sccm, chamber pressure of 0.5 mbar) was deposited prior to highly p-doped a-Si (2 min at a silane flow rate of 2 sccm and diborane of 1 sccm (2% diluted in He), chamber pressure 0.5 mbar). Intrinsic a-Si is very effective in reducing the surface recombination at the interface of a-Si/c-Si [14-16]. The layer sequence i/p is similar as in HIT wafer cells [17-20]. As TCO about 200 nm AZO was deposited on top of the a-Si layer at a substrate temperature of 225 °C by ALD.

The samples were mesa-etched and the contact areas of the solar cells were determined by a microscope. Finally, the ohmic back contact was made by rubbing

InGa alloy on the rear side of the wafer.

For structural characterization in different preparation stages the samples were investigated by a JEOL field emission scanning electron microscope (SEM) and by transmission electron microscopy (TEM, not shown here). Optical characterization of nanowires etched into a silicon thin film was performed in an UV-Vis spectrometer using an integrating sphere. In this way, reflection R and transmission T were measured and absorption A was determined according to $A=1-T-R$. An integrating sphere is necessary since even by the naked eye one immediately observes that there is nearly no specular but only small omnidirectional reflection. I-V-curves were measured in the dark and under AM1.5 illumination by a cw sun simulator. To make sure that most of the photocurrent really does come from the nanowires and not from the silicon substrate, EBIC (electron beam induced current) measurements were performed on the surface of the sample as well as on a cross section.

3 RESULTS

In Figs. 1 and 2 SEM images of a nanowire carpet after etching and the final solar cell after AZO deposition are shown.

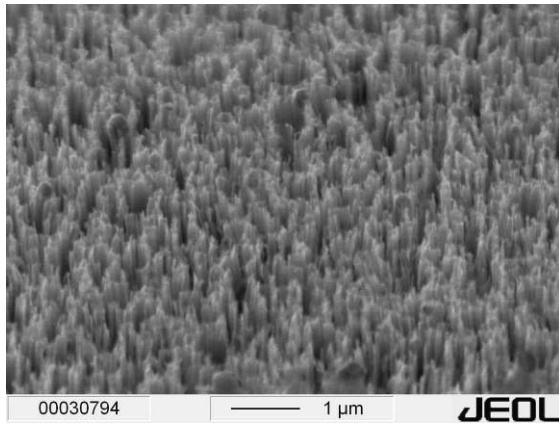


Figure 1: SEM image of an etched silicon nanowire array.

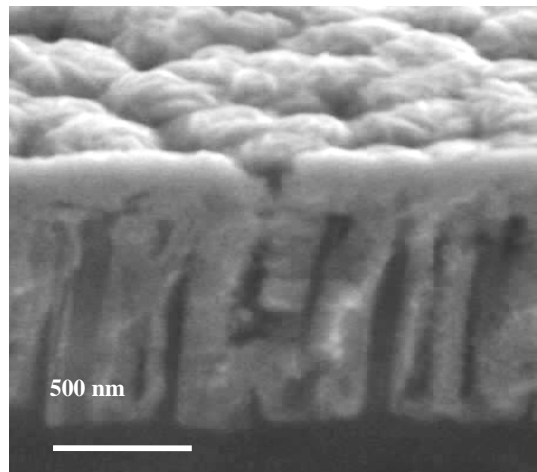


Figure 2: SEM image of a nanowire solar cell with AZO.

Fig. 3 shows the reflection, transmission, and absorption of a 1.5 μm thick crystalline silicon thin film on glass prior and after etching of the nanowires. Obviously, the reflection of the nanowire sample in the visible wavelength range is much lower than that of the original silicon thin film. This demonstrates the light trapping effect of the nanowire array.

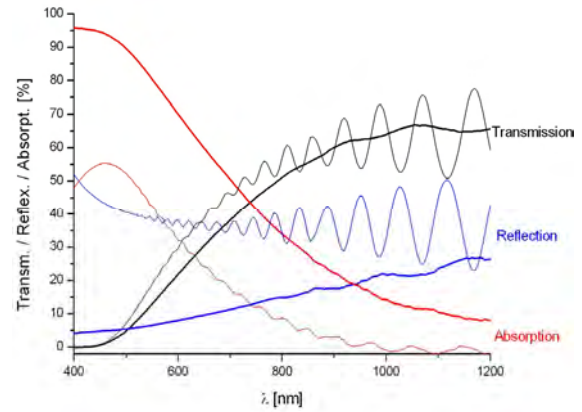


Figure 3: Reflection, transmission, and absorption of a 1.5 μm thick crystalline silicon thin film in the virgin state (thin lines) and after nanowire etching (bold lines).

I-V curves in the dark and under AM1.5 illuminations of a silicon nanowire solar cell 7 mm^2 in area are shown in Fig. 4. The dark curve under reverse bias demonstrates that no shunts are present. This indicates that the metal particles originating from the etching procedure were effectively removed. The solar cells show an efficiency of 7.3%, an open circuit voltage of 476 mV, and a short circuit current of 27 mA/cm^2 .

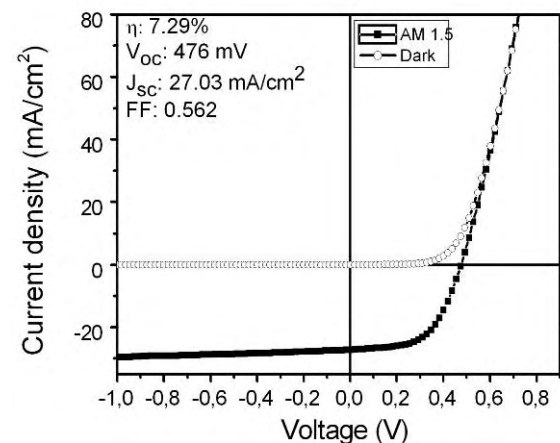


Figure 4: I-V curves of a nanowire solar cell 7 mm^2 in size in the dark and under AM1.5 illumination.

In case of nanowire solar cells prepared on a wafer there can arise doubts if the photovoltaic activity really stems from the nanowires and not from the wafer substrate. To clarify this we prepared EBIC measurements (30 kV, 280 pA excitation) on the cells, particularly from an edge of the cells as shown in Fig. 5. There one can observe that the EBIC current in the substrate region (right) is about just the incoming electron current. On the side of the nanowires (left) the current is a bit higher. However, there the exciting electrons are stopped mostly in the

AZO layer covering the nanowire solar cell. Therefore the EBIC current there does mostly not come from the nanowires. In the central region the exciting electron beam hits the side of the nanowire solar cell. There the EBIC current shows a strong peak demonstrating the photovoltaic activity of the nanowires.

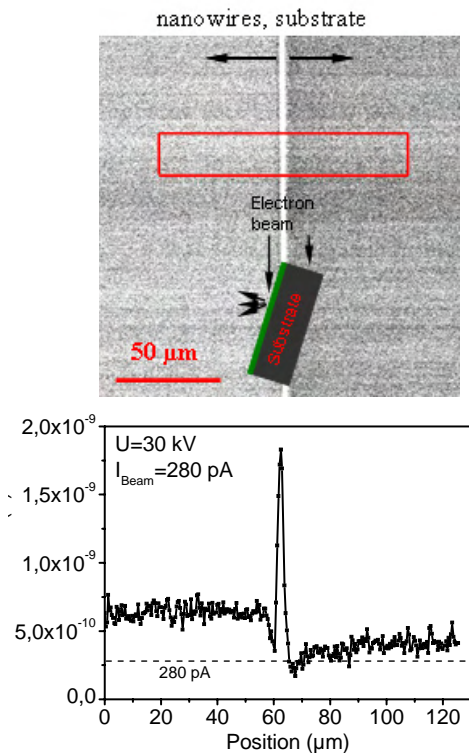


Figure 5: EBIC image (upper) taken at 30 kV and beam current of 280 pA at a tilt angle of 70° (to left side, see the inset) and the average current profile (lower) in the area marked by red rectangle.

4 SUMMARY

Highly efficient core-shell TCO/a-Si/Si nanowire heterojunction solar cells have been prepared on silicon nanowire arrays cost-effectively by metal assisted wet chemical etching of silicon wafers followed by deposition of an a-Si heteroemitter and an AZO layer. It was demonstrated that the nanowire carpet acts as a perfect light trapping structure. Great improvement concerning the optoelectronic properties and of the energy conversion efficiency was obtained in comparison with previous solar cells [3,7,9] based on SiNW arrays produced in a similar way. The improvement is attributed to a thorough three-step cleaning procedure removing silver particles even from the holes between nanowires.

Work is in progress to prepare similar nanowire solar cells on multicrystalline silicon thin films on glass.

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