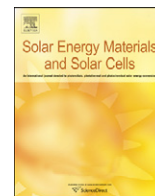




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## Effects of acid-treated silicon nanowires on hybrid solar cells performance

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## ABSTRACT

We demonstrate the efficiency improvement of hybrid solar cells based on silicon nanowires (SiNWs) and organic materials. This progress is readily achieved by acid treatments of SiNWs. Tin (Sn) catalyzed SiNWs contain residual Sn and Sn oxide drops on their top which are deleterious for a solar cell performance. Removal of this Sn and Sn oxide contamination is performed with hydrochloric acid. X-ray photoelectron spectroscopy measurement verified that the amount of Sn and Sn oxide on SiNWs array is decreased according to the immersing time. This brings open-circuit voltage and shunt resistance increase thus the hybrid solar cell performance is improved. Light intensity dependent open-circuit voltage clearly reveals that this efficiency improvement results from a reduced trap-assisted recombination through Sn and Sn oxide. In addition to the residual catalysts removal, native oxide removal by hydrofluoric acid also considerably contributes to further improvement in terms of short-circuit current and fill factor. Clearly, the improvement of SiNWs quality is essential for an optimization of hybrid solar cell performance.

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## 1. Introduction

Researches on hybrid solar cells based on inorganic and organic materials draw great attention for next generation of solar cells. Silicon nanowires (SiNWs) have been proposed as attractive inorganic material for efficient hybrid solar cells even though there are various other options of materials such as ZnO, CdSe, TiO<sub>2</sub> and GaAs. The interests for SiNWs are related to their accumulated merits: abundance of natural resources, widely available synthesis methods, knowledge of electronics and photonics of silicon and advantages of nanowire morphology [1].

Recently, a number of demonstrations using SiNWs and organic materials have been reported with power conversion efficiency of 5–10% [2–5]. The main advantage is due to the lower reflectivity (higher absorption) and large surface area of nanostructured silicon which leads to further improvement of solar cells performance compared to planar structures. In such devices, the organic material is used as a hole transport layer thanks to their high coverage capability of extremely rough surfaces. Most research groups fabricated nanostructured silicon with the top-down approach by lithography or etching of bulk silicon wafer [6]. However, nanostructured silicon from bulk wafer has disadvantages when it is applied for solar cells in terms of fabrication cost and processing issues such as SiNWs

aggregation. Therefore, bottom-up approaches such as chemical vapor deposition (CVD), plasma enhanced CVD (PECVD), molecular beam epitaxy are more appropriate for SiNWs growth for solar cell applications [7].

Here, we focus on PECVD to promote silicon nanowire growth. The plasma is used to partially crack the silicon precursor (silane in most cases) at relatively low temperature. Thus, it facilitates and enhances the supply of silicon to the catalyst droplets. The SiNWs growth by CVD methods requires metal catalyst to initiate the SiNWs growth from the cracked precursor gas by vapor-liquid-solid (VLS) mechanism [8]. Note the fact that SiNWs grown by PECVD could contain residual catalysts after all the growth procedures. Residual catalysts raise problems affecting hybrid solar cell performances, for example, a parasitic absorption of incident light from metal, low shunt resistance ( $R_{sh}$ ), recombination etc. because they are considered as defects in the devices [9,10]. For these reasons, the removal of these residual catalysts is one of important factors to improve hybrid solar cell efficiency. There are few reports discussing the catalyst thickness effects on solar cells performance by employing SiNWs based inorganic core-shell solar cells and also hybrid solar cells [11,12]. However, the thickness variation of catalysts for SiNWs growth accompanies the changes of nanowire morphology and residual catalyst quantities at the same time. Thus, the analysis on the catalyst effects could be carried out with limited scope. To observe the effect of catalyst removal, the analyses of hybrid solar cell performance have to be conducted with SiNWs grown by same thickness of catalyst.

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In this study, we fabricated hybrid solar cells based on SiNWs and organic materials on indium tin oxide (ITO)/glass substrates. Simple chemical treatments were performed to optimize the surface of SiNWs array and also to improve the hybrid solar cell performance. Those treatments remove residual catalysts and native oxide from SiNWs array. The effects were analyzed by characterizing the solar cell performance. The open-circuit voltage ( $V_{oc}$ ) dependence on the light intensity is analyzed to verify relative trap-assisted recombination strength. The results suggest that the better efficiency could be achieved by optimizing the surface state of SiNWs array.

## 2. Experimental

The hybrid solar cells with structures ITO/SiNWs/PEDOT:PSS/P3HT:PCBM/LiF/Al are fabricated. Sn catalyzed SiNWs are synthesized by PECVD and VLS mechanism [8]. Several nanometers of Sn are evaporated on ITO surface to serve as catalyst for SiNWs growth using thermal evaporation technique. The Sn/ITO/Glass substrates are loaded into PECVD system. A hydrogen plasma are used to make catalyst droplets at 300 °C during 2 min with flow rate, chamber pressure and radio-frequency (RF) power of 100 sccm, 380 mTorr and 5 W respectively. The catalyst drops are made by superficial reduction mechanism of Sn oxide [13] because metal Sn is easy to be oxidized. Then, 10 sccm of silane ( $\text{SiH}_4$ ) and 1.5 sccm of tri-methyl boron ( $\text{B}(\text{CH}_3)_3$ ) are additionally introduced for p-type Sn-catalyzed SiNWs growth at 600 °C during 2 min.

The scanning electron microscope (SEM) image of SiNWs is shown in Fig. 1 inset which clearly illustrates the existence of residual catalyst drops on their top. A 5% hydrochloric acid (HCl) is employed to remove residual catalysts at room temperature. SiNWs are dipped during from 0 to 20 min. Transmittance of SiNWs/ITO is measured to see the optical changes. The decrease in Sn concentration was characterized by X-ray photoemission spectroscopy (XPS) measurement using Sn-catalyzed SiNWs on silicon wafer.

The native oxide on the surface of SiNWs is of great importance for solar cell applications [14–16]. Here, we removed the native oxide by immersing SiNWs into 5% hydrofluoric acid (HF) at room temperature during few seconds after HCl dipping. The effects of HF are investigated regarding solar cells performance.

Organic layers are prepared by spin-coating method on acid treated SiNWs surface under nitrogen atmosphere. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is first spin-coated on SiNWs with thickness around 50 nm and annealed

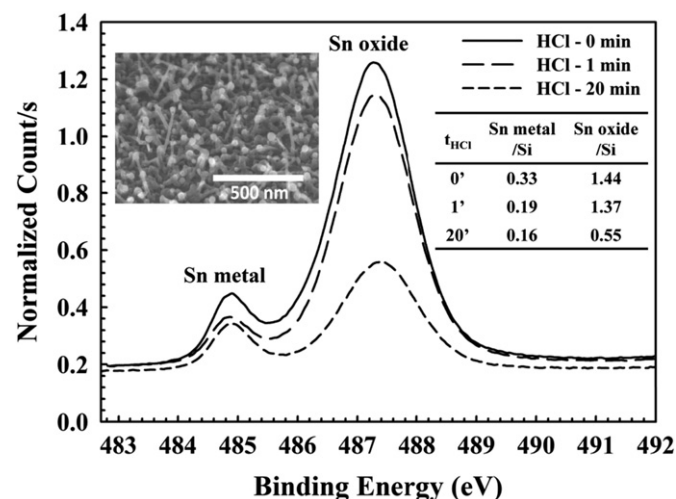


Fig. 1. XPS results as a function of HCl dipping time (minute). Inset figure: SEM image before HCl dipping which indicates residual catalyst drops of as grown SiNWs. Inset table: Sn metal and Sn oxide peak area ratio to silicon peak.

at 110 °C during 2 min. PEDOT:PSS is used to improve an anode selectivity [17] and to reduce the roughness of needle-like SiNWs surface that is harmful for organic layers. Then, poly(3-hexylthiophene)(P3HT):phenyl C61 butyric acid methyl ester (PCBM) (1:1, 2 wt % in 1,2-dichlorobenzene) blend is spin-coated as an active layer with thickness around 250 nm and annealed at 110 °C during 1 min. Lastly, lithium fluoride/aluminum (1.2 nm/100 nm) are deposited via thermal evaporation as a cathode.

X-ray photoemission spectroscopy (XPS) analyses were performed with a Kratos Axis Ultra DLD using a high-resolution monochromatic Al-K $\alpha$  line X-ray source at 1486.6 eV. Fixed analyzer pass energy of 20 eV was used for core level scans. The photoelectron take-off angle was always normal to the surface. The absorbance of SiNWs and/or P3HT:PCBM films is measured with a JENWAY 6800 double-beam UV/vis spectrophotometer. The current–voltage characteristics are measured with a Keithley 2635 system Source Meter under nitrogen atmosphere. Solar cell performances are characterized under various light intensity of AM 1.5 illumination with an Atlas Solar Constant 575PV simulator. The sample is illuminated through glass substrate.

## 3. Results and discussion

### 3.1. Residual catalyst removal by HCl

A considerable amount of residual catalyst drops is effectively removed by HCl dipping process. XPS measurements are carried out for quantitative analysis of HCl effects on residual catalysts removal. SiNWs grown on p-type silicon wafer under identical growth conditions with SiNWs on ITO are used for XPS measurement because ITO contains a lot of Sn. The SiNWs/Si substrates are dipped into 5% HCl during 1 and 20 min. Fig. 1 shows the XPS results according to the HCl dipping time. Interestingly, both Sn metal and Sn oxide are detected at 484.9 and 487.2 eV of binding energy respectively. Note that Sn is easily oxidized even at room temperature [18]. Thus, Sn oxide has higher counts than Sn. As HCl dipping time increases, Sn and Sn oxide counts are decreased. The peak area ratio of Sn and Sn oxide to silicon is summarized in inset table of Fig. 1. HCl removes almost 50% of Sn during initial 1 min. Then, there is no significant reaction between HCl and Sn. While the amount of Sn oxides is decreased about 5% compared with the HCl untreated sample during 1 min. The continuing reaction between HCl and Sn oxide results in further decrease of Sn oxide till 62% of the initial amount in 20 min. It is supposed that the diffused Sn into silicon wafer and/or SiNWs during the growth could not be etched by HCl [19]. Moreover, catalyst droplets covered by amorphous silicon during the SiNWs growth could be protected from HCl. The HCl preferentially attacks Sn at the beginning of reaction and then it continues to attack Sn oxide. The HCl treatment is a simple way to significantly reduce the amount of residual Sn and Sn oxide.

The effects of residual catalysts removal on the optical properties of SiNWs/ITO/glass substrates have to be considered for solar cell applications. Fig. 2(a) shows transmittance of ITO and SiNWs/ITO for various the HCl dipping times. The transmittance of SiNWs/ITO is greatly increased in the wavelength region (from 300 to 800 nm) by 1 min of HCl dipping. HCl dipping longer times than 1 min brings just a slight increase in the transmittance. On the other hand, the ITO shows negligible changes in the transmittance with different HCl dipping times. Note that 1 min HCl dipping removes 50% of Sn in inset table of Fig. 1. It means that Sn removal is responsible for the strong increase in the transmittance of SiNWs/ITO. Sn works like a parasitic absorber in the solar cell. It reduces the number of photons entering P3HT:PCBM layer which will result in short-circuit current density ( $J_{sc}$ ) decrease.

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