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All-in-situ fabrication and characterization of silicon nanowires on TCO/glass substrates for photovoltaic application

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ABSTRACT

Silicon nanowires (SiNWs) provide new opportunities for developing a new generation of thin film Si solar cells with enhanced light trapping and increased overall performance. Here, we report on the fabrication of SiNW-based thin film solar cells directly on top of low cost TCO/glass substrates in an all-in-situ process. The SiNWs are obtained on ITO (or SnO_2) substrates via vapor–liquid–solid growth mechanism, with the nano-scaled In (or Sn) catalyst droplets prepared by using H_2 plasma superficial reduction of ITO (or SnO_2) in a plasma enhanced chemical vapor deposition system (PECVD). We demonstrate that the morphology and compositional properties of the SiNWs, as well as the catalyst remnant in the SiNWs, can be effectively controlled by tuning the growth temperature and plasma conditions. The enhanced light trapping and absorption effects have been achieved by growing SiNWs directly on top of the TCO substrates, with the absorption edge downshifting steadily to ~1.1 eV, indicating that the crystalline core of the SiNWs also participates in the light absorption. According to a real time monitoring using an in-situ MM-16 ellipsometer, the enhanced light trapping/absorbing effects can be attributed to the growth of long, sharp and straight SiNW. Prototype SiNWs-based thin film solar cells are successfully demonstrated.

1. Introduction

To date, the first generation solar cells, based on high quality and expensive mono and poly-crystalline Si wafers, still dominates the marketplace for photovoltaic modules [1]. In order to reduce the fabrication cost, the second generation thin film solar cell is realized using thin film materials, such as amorphous and microcrystalline silicon [2], which allows for a lower cost production process. However, efficiency of the thin film solar cell is limited by the quality of the amorphous materials. In order to improve further the performance of the thin film solar cell while preserving their low cost (associated also with a low temperature) fabrication process, several strategies have been proposed. In particular, the incorporation of silicon nanostructures, like Si nanodots and Si nanowires (SiNWs), through the established thin film technique is considered as a general and promising way to develop a new generation of high performance thin film solar cell.

Recently, the concept of SiNW-based solar cells has been proposed and tested.[3–6] SiNWs are usually produced via a vapor–liquid–solid (VLS) growth mechanism [7], which introduces high quality crystalline materials and extends the light absorption spectrum of the thin film structures [8,9]. Meanwhile, the incorporation of SiNW structure into the thin film solar cells helps to achieve strongly enhanced light trapping and absorption effects and thus provides a promising alternative to the conventional surface texturing process on the substrate surface. Since the growth of SiNWs in VLS mode is mediated/controlled by the catalyst drops, in order to incorporate the SiNWs into the thin film structure, a layer of nano-scale metal catalyst drops should be formed on top of the TCO layers (ITO or SnO_2, which are widely used in thin film solar cells). An all-in-situ and simplified formation of metal catalyst drops on TCO layers, with controllable uniformity and distribution, will provide a key basis for incorporating SiNW structures through the established thin film solar cell technology. Recently, we have demonstrated that nano-scale metal catalyst drops of tin (or indium) can be directly formed during a well-controllable in-situ H_2 plasma treatment on TCO layers in a plasma enhanced chemical vapor deposition (PECVD) system. [10,11] Meanwhile, the use of low melting point metals, like the tin (232 °C) and indium (156 °C), as catalysts for the growth of VLS SiNW, allows for a lower growth temperature for the SiNWs (down to ~240 °C in a plasma enhanced deposition process) [10,11]. This will enable a low temperature and low cost incorporation or fabrication process of the SiNWs structure into the thin film solar cells.

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Here, we propose and realize an all-in-situ fabrication of the SiNW-based thin film solar cells. Both the catalyst formation and the growth of SiNWs can be achieved in just one pump-down process in a PECVD system. We also explore a new real time technique to monitor the evolution of enhanced light trapping and absorption effects, arising from the growth of SiNWs on top of the TCO layers, using an in-situ ellipsometry module. Excellent conformal covering of the long and straight SiNWs has been realized and a prototype SiNW-based thin film solar cell has been demonstrated.

2. Experiments

As illustrated in Fig. 1(a)–(c), the all-in-situ fabrication process involves the following steps: (1) first, a H_2 plasma treatment (at 250–300 °C) of the TCO (SnO_2 or ITO)/corning glass substrate surface was performed to reduce superficially the TCO layers and to precipitate metallic tin or indium (from SnO_2 or ITO, respectively) for the following growth of SiNWs in VLS mode [12]; (2) then, the growth of SiNWs was initiated in a SiH_4 (or SiH_4 diluted in H_2) plasma at 300–600 °C and mediated by the catalyst drops. More experimental details for the catalyst formation and the growth conditions of SiNWs have been published elsewhere[10–12]; (3) finally, to make a prototype device, a thin intrinsic hydrogenated amorphous silicon (a-Si:H) layer (~260 nm) and a top n^+-type a-Si layer (20 nm) were conformally deposited on top of the SiNW structure. An in-situ ellipsometer (MM-16 module, Horiba) is used to monitor in real time the optical response of the sample surface during the growth of the SiNWs structure on top of the TCO layers. The morphologies of the SiNWs and the complete SiNW-based thin film structure were characterized by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Light trapping and absorption effects in SiNWs

The morphology, density and compositional properties of SiNWs directly grown on top of SnO_2 or ITO substrates can be well controlled by tuning the growth temperature and the H_2 dilution condition[10–12]. It is worth noting that, in contrast with the detrimental recombination centers introduced by gold (most widely used catalyst for obtaining SiNWs in VLS growth mode), tin and indium have a very low solubility in the crystalline SiNWs [13,14]. This has been directly confirmed using the electron dispersion spectrum (EDX) characterization of a single tin catalyzed SiNW. The concentration of tin in the bulk crystalline core of the SiNW is below the detection limit of the technique (~0.5%), while a much higher concentration of tin (5%) has been detected at the top of the SiNW, which could be the remnant of catalyst drop during VLS growth. This feature is important for utilizing the tin or indium catalyzed SiNWs as a high quality light trapping/absorption material.

Transmission spectra of the SiNWs on SnO_2 layers grown at T_{sub}=600 °C, with deposition times of 15, 60 and 120 min, are measured using a Perkin–Elmer Lambda 950 spectrophotometer with an integrating sphere and presented in Fig. 2(a). The SEM image of the as-grown SiNWs after 15 min deposition is shown in the top-right inset. Reference samples of SnO_2/Cg substrate before and after H_2 plasma treatment are also presented in the same plot. As pointed out in our previous study, the H_2 plasma treatment process can be precisely controlled by tuning the treatment time and substrate temperature [10,12]. Here, the H_2 treatment time is intentionally overdone at 300 °C for 15 min (as compared with our normal experimental conditions of 2–5 min at 250 °C for the growth of SiNWs), in order to accentuate the effect of the pre-deposition process. As we can see, after this overdone H_2 treatment and precipitation of tin drops on top of the SnO_2 layer, the overall transmission of SnO_2/Cg substrate decreases uniformly (almost independent of the photon wavelength/energy). In comparison, with the increase of deposition time of the SiNWs, the falling edge of the transmission curve shifts significantly to longer wavelength (that is to lower photon energy). This behavior is clearly different from the overall decrease of transmission due to precipitation of metal tin on SnO_2 surface. To give a clear view, the absorption spectrum of the same samples are also presented in Fig. 2(b), where we choose to focus on the transition edge of the absorption curves. It is clear that the absorption edge approaches the c-Si bandgap limit of ~1.1 eV with increase in length of the SiNWs. This observation indicates that the increased light trapping and absorption effects observed here are related to the growth of SiNWs on top of the SnO_2 layer. For the SiNWs grown on ITO/Cg substrates, similar results were also obtained. Actually, the samples with the long SiNWs grown on top usually look totally black, indicating a strongly enhanced light trapping and absorption effect.

3.2. Real time monitoring of the initial growth of SiNWs

In order to understand how the enhanced light trapping effect is gradually established during the initial growth of SiNWs structure on top of the TCO layers, we explore the utilization of an in-situ spectroscopic ellipsometer module, integrated in our PECVD system as shown in Fig. 3(d), to trace the optical response reflected from the sample surface during the growth of SiNW structure. This provides a convenient and all-in-situ diagnostic tool/strategy to monitor in real time the optical response evolution of the SiNW structure. Though a complete model dedicated to the complicated SiNW structure layer is still needed for a detailed and quantitative analysis of the ellipsometric results, as a first attempt, we here demonstrate that some straightforward measurements still provide valuable information about the optical response of the SiNWs especially during its initial growth. Meanwhile, according to angle-resolved reflection spectra measurements (not shown here), it is found that the detected spectra of the SiNWs structure collected at different angles show similar trends. This is because the arrangement of the SiNWs on the amorphous TCO layer (which gives no preferential

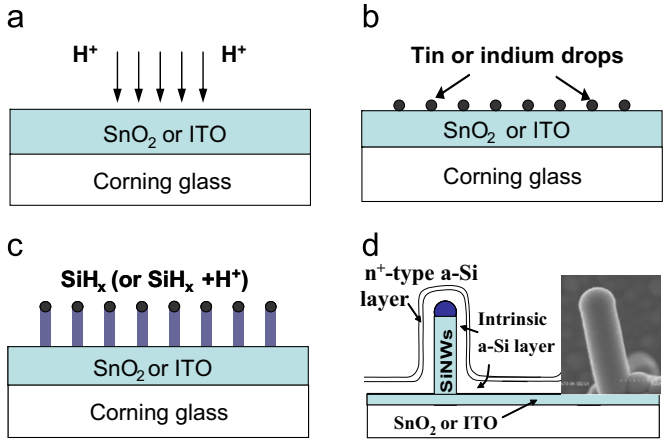

Fig. 1. (a)–(c) Fabrication steps for the growth of SiNWs on TCO layers and (d) schematic illustration for a SiNW-based thin film solar cell.