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Silicon nanowire-based solar cells

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Abstract
The fabrication of silicon nanowire-based solar cells on silicon wafers and on multicrystalline silicon thin films on glass is described. The nanowires show a strong broadband optical absorption, which makes them an interesting candidate to serve as an absorber in solar cells. The operation of a solar cell is demonstrated with n-doped nanowires grown on a p-doped silicon wafer. From a partially illuminated area of 0.6 cm^2 open-circuit voltages in the range of 230–280 mV and a short-circuit current density of 2 mA cm^{-2} were obtained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Research on silicon nanowire-based solar cells is still in its infancy. The device physics of planar and radial p–n junction nanorod solar cells have, however, already been modelled and discussed [1] and Si wire arrays suitable for the corresponding photovoltaic devices have recently been grown [2]. Furthermore, a wet-chemical etching technique has been used to prepare silicon nanowire (SiNW) arrays showing very low reflectance. This low reflectance has been identified as being potentially interesting for photovoltaic applications when using the respective material as an antireflective coating [3]. Moreover, a strong broadband optical absorption has been measured and discussed for SiNWs fabricated on glass substrates by wet-chemical etching and chemical vapour deposition (CVD) [4], which makes these nanowires an interesting candidate to serve as an absorber in solar cells. In addition, SiNW-based solar cells have been demonstrated on stainless steel foil [5]. The effects of wire diameter, length and wire pitch on the optical absorption of periodic SiNW arrays have also been numerically analysed [6]. Finally, the study of individual core/shell SiNW photovoltaic elements demonstrated their potential for self-powered functional nanoelectronic systems [7].

In this paper, we investigated the fabrication of SiNW-based solar cells on silicon wafers and on multicrystalline diode laser crystallized silicon thin films (mc-Si) on borosilicate glass. The nanowires were grown by means of the vapour–liquid–solid (VLS) method [8] from a gold (Au) catalyst in the form of nanoscale Au droplets. VLS growth is based on a local liquid phase epitaxy that makes use of the low temperature eutectic of Si and Au at 363 °C when the Au in contact with Si turns liquid and can be supersaturated with additional Si, e.g. from the gas phase, so that an SiNW forms with the diameter of the Au droplet. The optical transmission and reflection characteristics of the SiNWs and the optoelectronic properties of the SiNW solar cells were measured to demonstrate their unique properties, which might be used in future thin film solar cells.

2. Experimental details

SiNWs were prepared by the VLS method using CVD from silane [9] on Si(111) substrates with different B-doping levels (5–10 Ω cm, <0.005 Ω cm) and on borosilicate glass substrates with a thin B-doped (0.01 Ω cm) mc-Si layer. For that purpose the substrates were etched in diluted HF to remove the native oxide and subsequently a 2 nm thick Au film was sputtered on the substrate and the sample was transferred into the CVD chamber. The Si substrates were annealed at ~580 °C and a pressure of $\sim 5 \times 10^{-7}$ mbar for 10 min. The temperature was then reduced to ~500 °C and a mixture of 10 sccm He and 5 sccm SiH_4 was introduced for the nanowire growth for 20 min at a pressure of 2 mbar. For the glass substrates we used the identical procedure. The applied thermal budget was close to the limit of what the glass could sustain, but still applicable.

The nanowires were doped during the growth process by adding 0.02–0.2 sccm PH_3 or B_2H_6 to the process gases. The mc-Si layer on glass results from an initially amorphous silicon (a-Si) layer deposition and subsequent crystallization

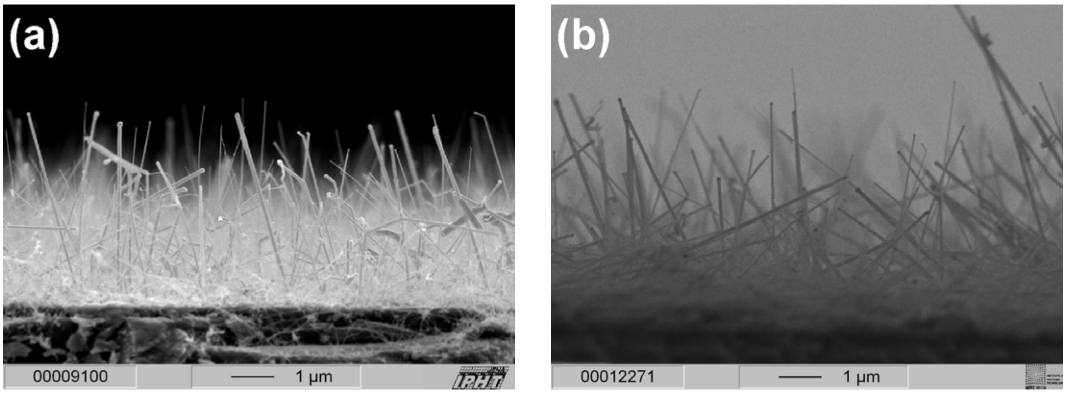

Figure 1. Cross-sectional SEM images of n-doped SiNWs grown on: (a) a p-doped silicon wafer and (b) a borofloat glass substrate (high temperature glass with large volume fraction of boron oxide) with a ∼500 nm thick mc-Si layer. Under the applied growth conditions the nanowires orient essentially along low index growth directions such as ⟨111⟩, ⟨110⟩, ⟨112⟩, and more rarely others, with an average wire length of about 5 μm.

by scanning a diode laser beam (300 μm × 800 μm) over the entire surface [10]. The energy intake of the a-Si is such that it is molten and recrystallizes. A typical a-Si thickness of ∼500 nm is crystallized at once and silicon grains of the order of a few 10 μm in width and several 100 μm in length result. Due to the melting process extensive doping of the mc-Si layer with B as diffused from the glass substrate has to be considered [11].

The morphology of the SiNWs was studied using field-emission scanning electron microscopy (FESEM) in a JEOL JSM6300F device. Transmission (T) and reflection (R) spectra were obtained using a UV–vis/NIR spectrometer (Perkin Elmer Lambda 900) equipped with a 150 mm integrating sphere. To measure the I–V curves the back side of the wafer was contacted by depositing a ∼130 nm aluminium layer by electron beam evaporation. The front side of the substrate with the SiNWs sticking out of the surface was contacted by pressing the nanowire film onto a transparent polymer foil covered with transparent conductive oxide (TCO). Acquiring an I–V curve of a p-doped wafer with a film of p-doped SiNWs showed ohmic behaviour. However, we cannot determine the resistivity of the SiNWs, since we do not know the dopant concentration in the wires and the number of contacted wires. The I–V curves under illumination were measured using a sun simulator (AM1.5, 1000 W m^{-2}, SS-80 PET).

3. Results and discussion

The nanowires grown under the applied conditions on silicon wafers and on mc-Si on glass have a length of about 3–6 μm and diameters typically in the range of 20–100 nm (figure 1). The addition of a dopant gas to silane is known to induce some variations of the growth rate of silicon (e.g. [12]) and for nanowire growth changes in morphology and structure have been observed [13, 14]. Our p-doped SiNWs have a uniform diameter (figure 1) and are single crystalline with a thin (∼2 nm) amorphous SiO_2 shell.

In figure 2 the optical absorption (A) of SiNWs on a glass substrate and on mc-Si on glass derived from transmission and reflection data ($A = 1 - T - R$) is compared to the

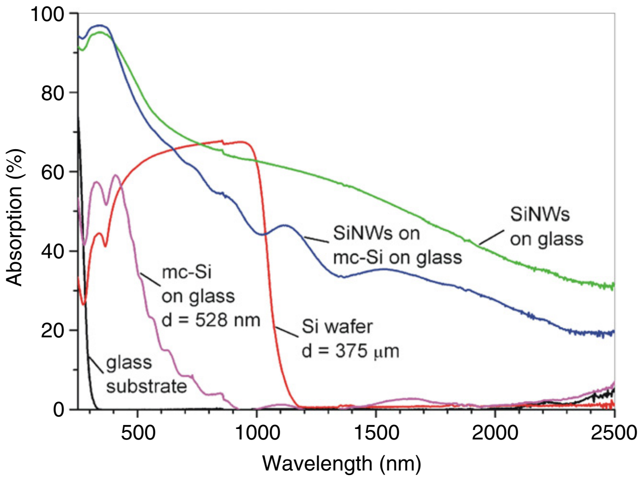

Figure 2. Optical absorption of SiNWs on a glass substrate and on mc-Si on glass compared to the absorption of a 375 μm thick Si wafer. The optical properties were measured without the transparent polymer foil on top of the nanowires.

absorption of a 375 μm thick Si wafer. A strong broadband optical absorption can be observed in the relatively thin SiNW films. This phenomenon has already been discussed in detail by Tsakalakos *et al* [4] and can be attributed to the significant reduction of the reflectance and the strong light trapping of the nanowires. The absorption of light with an energy below the bandgap energy has been discussed in terms of light trapping together with absorption by defect states, and plasmon coupling of light with the nanowires and an underlying nanocrystalline Au–Si film [4]. The increased absorption in SiNWs on glass as compared to SiNWs on mc-Si on glass (figure 2) could be due to the smaller diameter and the higher density of the nanowires grown directly on the glass substrate, and due to the presence of the aforementioned underlying nanocrystalline Au–Si film.

The operation of a SiNW-based solar cell has been demonstrated with n-doped nanowires grown on a p-doped silicon wafer (5–10 Ω cm). The current–voltage characteristics

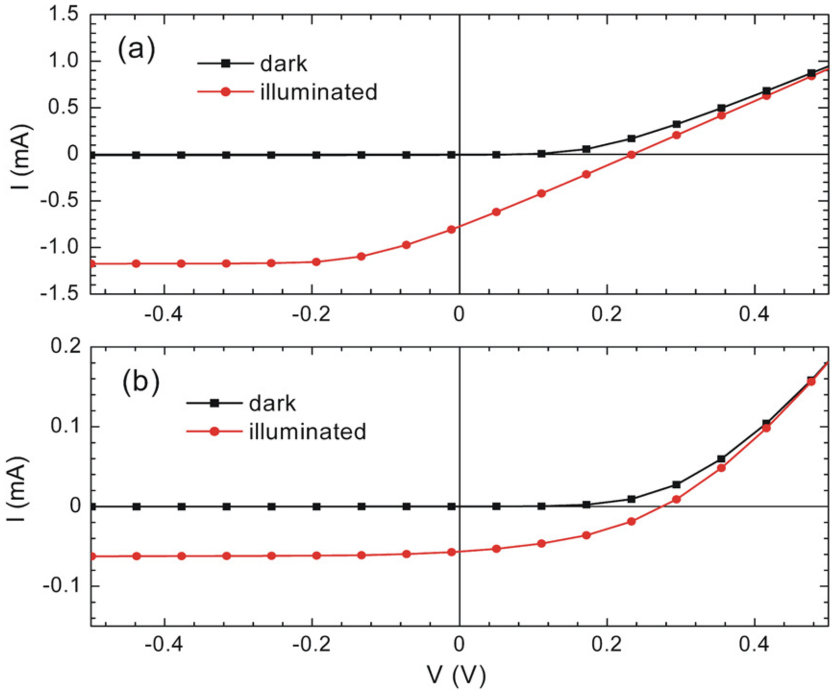

Figure 3. Measured I–V characteristics of a solar cell fabricated with n-doped SiNWs grown on a p-doped Si wafer: (a) with the gold caps on top of the nanowires; (b) after removing the Au by etching with aqua regia.

plotted in figure 3 show a diode-like characteristic in the dark, and solar cell behaviour under illumination. From an only partially illuminated area (0.6 cm^2) of the solar cell we obtained open-circuit voltages in the range of 230–280 mV and a short-circuit current density of 2 mA cm^{-2}. The fill factor is ∼0.2 and the conversion efficiency of the cell is 0.1%. However, these are the first qualitative results, since we do not know the dopant concentration in the wires and what fraction of these dopants is activated. Further open questions are, for example, the influence of surface charges from the silica shell of the wires on the concentration of free carriers in the wires, or the carrier recombination due to gold atoms incorporated into the nanowires. To exclude a possible influence of the gold caps on top of the nanowires on the I–V characteristics of the solar cell we removed the Au by etching with aqua regia. The diode-like as well as the solar cell behaviour can still be observed, however, at a lower short-circuit current density probably due to a higher contact resistance (figure 3).

In addition to the slightly p-doped silicon wafer (5–10 Ω cm; 2×10^{15} cm^{-3} dopant concentration) we used higher p-doped wafers (<0.005 Ω cm; 2×10^{19} cm^{-3} dopant concentration) for the identical experiments as well as the highly p-doped mc-Si on glass (0,01 Ω cm; 5×10^{18} cm^{-3} dopant concentration). We could not observe the same diode characteristics for the SiNWs (identical nominal n-doping during growth) on highly p-doped wafers or layers on glass. We speculate that intermixing of dopants between SiNWs and substrate during growth may be the reason. The exact reasons for that observation are currently being investigated.

Further work is now focused on the fabrication of SiNW-based solar cells on glass substrates and on the improvement of the front side contact of the device. For that, the nanowires will be embedded in a transparent isolating matrix and will be contacted by an electrode layer on top. Furthermore, we will try to use alternative catalysts that do not have such adverse effects on the minority carrier lifetime as Au.

In summary, we have shown that SiNWs grown with the VLS mechanism on Si wafers can behave as solar cells and that the nanowires possess unique optical properties. The extension of the fabrication process to glass substrates could make this system very promising for future thin film solar cells.

Acknowledgments

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