Sensors & Transducers, Vol. 27, Special Issue, May 2014, pp. 142-146

Sensors & Transducers

Hybrid Solar Cells Based on Silicon Nanowire Arrays for Remote Chemical Sensing

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Received: 31 December 2012 /Accepted: 10 August 2013 /Published: 26 May 2014

Abstract: Disordered arrays of silicon nanowires have been produced by the OAG technique. The UV-visible absorption spectrum of the SiNWs shows a main increase of the absorption extending in the near infrared and similar absorption than bulk crystalline silicon below 400 nm. T EMT simulation of the UV absorption of silicon nanowires predicts a main optical absorption for a nanowire orientation parallel to the electric field vector of the incident light, as expected for SiNW lying with a dominant orientation parallel to the substrate. The enhanced optical absorption tail extending above 400 nm has been attributed to the combination of band gap opening shown by the PL emission and high densities of silicon surface states at high surface/volume ratio. Hybrid solar cells have been fabricated through the dispersion of silicon nanowires in a poly(3-hexylthiophene) thin film leading to a 1.14 % conversion yield, which was increased to 3.04 % upon SiNW surface functionalization, opening new perspectives for self sufficient power supplies applicable to remote sensing.

Keywords: Silicon nanowires, P3HT, Photoluminescence, Quantum confinement, Hybrid solar cells

1. Introduction

The unique electronic properties of silicon at the nanoscale have stimulated extended work in the past decades after the discovery of the photoluminescence of porous silicon at room temperature [1]. A new interest for silicon nanostructures is presently growing with the development of techniques enabling the mass production of silicon nanowires (SiNWs) offering attracting opportunities for the development of low cost, light and large scale solar cells.

The vapour-liquid-solid (VLS) technique has been extensively studied for the production of ordered arrays of vertical silicon nanowires for photovoltaic applications [2]. The silicon nanowire growth is initiated in that case from nanosized droplets of gold, deposited on an appropriate substrate. The use of a metallic catalyst however is a main drawback for developing high-efficiency solar cells since gold is known to be at the origin of deep electronic levels acting as recombination centres [3]. However SiNW lattices, where the distance between

Article number P_SI_490

individual nanowires can be monitored by the elaboration conditions, are interesting for the production of an antireflection top layer [2] or for the nanostructuration of the photovoltaic layer itself to form an extended heterojunction [4].

The Oxide Assisted Growth (OAG) enables a high yield production of silicon nanowires [5] with no metallic catalyser need. SiNWs are collected as a foam which can be dispersed in usual solvents to get a SiNW ink for deposition on glass or ITO substrates. A disordered network of silicon nanowires is observed by scanning electron microscopy (SEM) [6], whereas high resolution transmission electron microscopy (HRTEM) shows that the nanowires have a crystalline silicon core (of ~10 nm diameter) surrounded by a SiO_2 sheath (~3 nm thickness). The Fano resonance appearing on the low wavenumber side of the Raman spectrum is the signature of the n type of the silicon nanowires [7].

The integration of a network of n type silicon nanowires in a p type semiconducting polymer layer provides an easy way for the production of hybrid solar cells combining the unique electronic properties of silicon with the good film forming properties of polymers. The intimate mixing of n and p type domains at the nanoscale level leads to the production of an extended interface, known as bulk heterojunction (BHJ), providing a mean to efficiently dissociate the charge pairs generated under sunlight [8] which can be collected at the electrodes of a diode structure.

The purpose of this paper is a study of the optical properties of a disordered array of silicon nanowires deposited on a glass substrate to check the specific effects induced at diameters lower than 10 nm and for a dominating SiNW orientation parallel to the substrate. The main differences with the optical properties reported for vertical arrays of silicon nanowires [4, 9] will be discussed and perspectives for the development of low cost thin film solar cell will be proposed.

2. Experimental

The silicon nanowires have been produced by the Vapor-Solid technique without using any metal catalyst. The oxide assisted growth (OAG) mechanism is based on a dismutation reaction of the silicon monoxide formed from the mixture of Si and SiO_2 at 1200 °C under gas flow, leading to the deposition of SiNWs on a graphite collector. The nature of the gas carrier has a limited effect on the SiNWs properties but a larger influence on their production yield. Argon and phosphine have given the best results for these optical investigations. However we will focus the discussion on SiWNs produced under argon, due to the large concentrations of defects (kinks) observed by TEM for SiNWs fabricated under phosphine inducing degraded electrical properties. The influence of the elaboration parameters on the morphology of the SiNWs network has been presented in a previous paper [10].

The as-produced SiNWS have been immersed for 10' in a 5 % fluorhydric acid solution in distilled water to remove the oxide overlayer and dried under vacuum. The time between surface preparation and optical characterizations was reduced to the minimum to avoid a new oxidation in ambiant air. The photoluminescence (PL) studies have been performed at room temperature using the 364 nm excitation wavelength of an argon laser. The optical absorption spectra of the silicon nanowires have performed in the 250-800 nm range with a "Lambda 35 spectrophotometer" from Perkin Elmer.

3. Infrared and PL Characterization

The treatment by a fluorhydric acid solution (5 %) is a common way to remove the surface oxide of silicon wafers. Infrared spectroscopy has been used to monitor the etching of the SiO_2 sheath using the evolution of the IR peak intensities [11] resulting from HF treatment. A weakening of the Si-O-Si peak at 800-820 nm (symmetric stretching) and main decrease of the 1100-1220 cm^{-1} one (asymmetric stretching) is observed in the IR spectra (Fig. 1) of the as-produced SiNWs showing that the SiO_2 sheath has almost been removed. New peaks have emerged at 910 and 2100 cm^{-1} in the IR spectrum of the HF etched SiNWs, which can be attributed to Si-H_x vibrations (respectively deformation and asymmetric stretching). The IR spectra changes show the formation of hydrides species upon HF etching of the SiNWs leading to the passivation of the silicon surface.

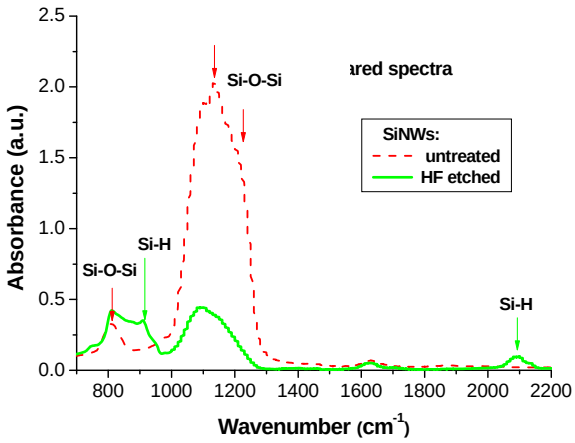

Fig. 1. Infrared spectra of as-produced and HF treated SiNWs showing the weakening of the Si-O-Si vibration modes and appearance of Si-H_x modes upon SiO_2 sheath removal.

Excitation in the absorption edge of the silicon nanowires (at 364 nm) led to drastically different PL responses (Fig. 2) in relation with the different

chemical states shown by the SiNW IR spectra. The photoluminescence spectrum of the as-produced nanowires exhibits a broad emission band in the green centered at 2.38 eV (520 nm) which disappears upon SiO_2 surface layer removal. A PL emission band, which has probably the same origin, appearing at 500 nm in silicon nanostructures covered by a SiO_2 layer has been attributed in literature [12, 13] to silicon defect states at the SiNWs/SiO_2 interface or in the SiO_2 sheath thickness. Simultaneously a strong PL emission at room temperature of SiNWs at 1.44 eV (860 nm) appears after HF etching. This intense photoluminescence can be attributed to the electronic confinement effect described by Canham et al. in porous silicon [1, 14] and corresponds to the opening of the band gap for nanostructure sizes below 10 nm. According to the theoretical calculation of Delarue et al. [15] the nanowire diameter can be estimated to 7 nm.

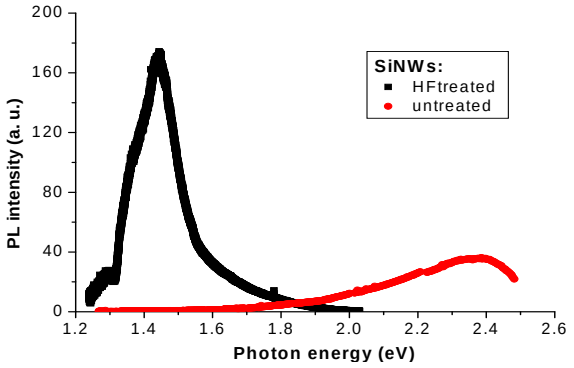

Fig. 2. PL spectra showing the disappearance of the peak at 2.38 eV attributed to SiO_2 centers and appearance of the silicon photoluminescence at 1.44 eV upon SiNW HF etching.

The strong photoluminescence exhibited by HF treated SiNWs at room temperature has shown that the nanowire diameter is about 7 nm. Considering that the optimum thickness of the polymer in which the SiNWs will be dispersed is 90 nm [6] to fabricate a thin film solar cell (active area ~ 24 mm^2), we observe that the nanowires will have a dominant orientation parallel to the substrate. It implies a very different morphology than for ordered arrays of vertical silicon nanowires [4, 9] where the electrical field vector is perpendicular to the nanowires for a normal incident light. The influence of these different architectures on the resulting optical absorption will be discussed in the following step.

4. Optical Absorption Properties

The UV-visible spectrum of silicon nanowires has been plotted in Fig. 3 with a spectrum calculated using the optical constants of bulk silicon [16] for reference. The two spectra show almost the same features for the direct transitions below 380 nm but the sharp resonances associated to the Van Hove singularities [17] are considerably damped for SiNWs. Main differences appear for wavelengths above 380 nm where a broad absorption tail extending towards the near infrared is observed for SiNWs, in the region corresponding to indirect transitions where the density of states of bulk silicon is low [17]. This enhanced absorption is an indication of a high density of electronic surface states resulting from the large surface/volume ratio.

Investigations of the electronic properties of silicon nanowires have been reported in literature using ab-initio calculations. Bruneval et al [18] argue that the local field effects can be more easily taken into account in a classical approach providing comparable results for SiNW diameters > 2 nm. The result of a calculation of the SiNWs optical absorption based on the effective medium theory (EMT), using the optical constants of bulk silicon, is presented in Fig. 4. Main polarisation effects are observed considering the electric field vector parallel or perpendicular to the axis of oriented nanowires. A strong optical absorption is predicted for a dominant nanowire orientation parallel to the substrate (depolarisation factor L=0) and vertical incident photons whereas a weak polarisation resonance is expected for vertical nanowire arrays (depolarisation factor L=0.5), in accordance with the optical absorption results we obtained for SiNWs lying with a dominant orientation parallel to the substrate.

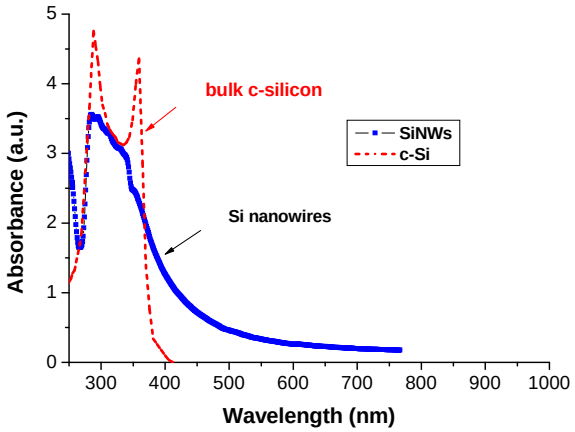

Fig. 3. Experimental UV-visible and EMT calculated SiNW absorption spectra.

However large polarisation effects are expected for the transverse E polarisation according to the SiNWs surrounding medium, surface defects in particular silicon dangling bonds or functional chemical groups at the surface. The modelisation will require in that case an additional polarisation term in the dielectric constant to take into account the electronic surface effects.

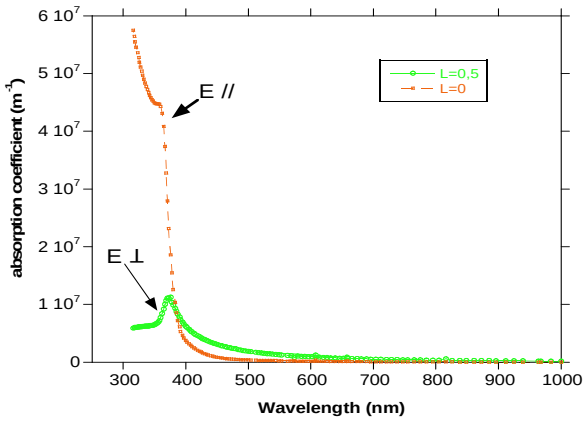

Fig. 4. EMT calculated absorption spectra of ordered SiNWs for longitudinal or transverse E polarizations. SiNWs fill factor = 0.8, in vacuum.

The dominant parallel polarisation in the case of SINWs lying on the substrate in a thin layer leads in our case to an enhanced optical absorption compared to a vertical array of nanowires, which is less favourable, explaining the much longer length (several µm) of the nanowires used in literature [4, 9] for such a configuration. Taking into account the more sophisticated technology needed to produce such ordered arrays, the route of thin hybrid films appears attracting for the fabrication of low cost solar cells for the electric supply of devices such as sensors requiring only a limited power.

The following Table 1 summarizes the improvement of the photovoltaic parameters obtained upon incorporation of silicon nanowires exhibiting different surface states in a poly (3-hexylthiophene) thin film. The last results obtained for short poly (styrene) chains grafted at the SiNW surface [19] shows that new progresses are still possible upon silicon surface functionalization.

Table 1. Performances of hybrid solar cells for different SiNW surface treatments.

P3HT/SiNW hybrids	Voc (V)	Isc (mA/cm^2)	FF	η (%)
P3HT	0.35	0.01	0.33	0.006
as-produced SiNWs	0.4	0.88	0.31	0.57
HF treated SiNWs	0.45	1.42	0.34	1.14
PS grafted SiNWs	0.5	3.3	0.35	3.04

5. Conclusions

The study of the optical properties of silicon nanowires has shown the crucial role of the silicon surface for wire diameters below 10 nm. A main interplay between the surface chemistry of the nanowires and the photoluminescence emission at the frontier of the red was shown by infrared spectroscopy. An emission at 520 nm associated to localized states of the SiO_2 sheath was observed for as-produced SiNWs and was eliminated upon removal of the oxide coating. Simultaneously a strong PL emission appears at 860 nm after HF solution etching at room temperature which was attributed to a confinement effect leading to the broadening of the bad gap of the silicon nanostructures. The optical absorption spectrum of silicon nanowires has shown an absorption enhancement in the domain of the indirect transitions above 380 nm. According to an EMT calculation of the absorption spectrum of silicon nanowires a weak polarisation resonance is expected at 380 nm for a transversal light polarisation in respect to the SiNWs orientation whereas an absorption component similar to the bulk silicon one is found for a parallel polarisation. A high absorption level is then expected for SiNWs exhibiting a dominant orientation perpendicular to the incident photons as it was observed in our configuration for SiNWs deposited on a substrate below 380 nm. The enhanced absorption tail extending towards the near infraredis not predicted by the EMT modelisation and can be attributed to high concentrations of silicon surface states. The combination of the surface polarisation effects and of the surface dangling bonds acting as electron traps appears of main importance for the control of the interfacial charge transfers. The role of the interfacial electronic processes is emphasized by the photocurrent enhancement induced by the silicon surface functionalization opening perspectives for the development of low cost solar cells which could be used as electrical supplies in remote sensors.

Acknowledgements

We address our thanks to the ANR (French Research National Agency) for the support of this work in the framework of the Photovoltaic Programme (Physipo Project).

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