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ORIGINAL ARTICLE

Broadband optical absorption measurement of silicon nanowires for photovoltaic solar cell applications

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Abstract The broadband optical absorption properties of silicon nanowire films fabricated by electroless metal deposition technique followed by HF/$Fe(NO_3)_3$ solution-based chemical etching at room temperature on p-type silicon substrates have been measured and found absorption higher than that of the solid thin films of equivalent thickness. The observed behavior is effectively explained by light scattering and light trapping though some of the observed absorption is due to a high density of surface states in the nanowires films. Synthesized structures absorbed more than 82 % of incident radiation in case of Cu-deposited silicon nanowires, whereas for Ag it was maximum 83 %, which is much greater than that of the bulk silicon as they absorbed maximum 43 % of the radiation.

Keywords Silicon nanowires (SiNWs) · Electroless metal deposition (EMD) · Photovoltaic (PV) · Optical absorption

Abbreviations

SiNW	Silicon nanowire
EMD	Electroless metal deposition
PV	Photovoltaic
HF	Hydrogen fluride
SEM	Scanning electron micrograph
UV	Ultra violet

Introduction

To date, the catastrophic environmental pollution arising from burning fossil fuels has discriminating public concern, and thus the increasing dependence on renewable clean energy alternatively. Amongst the alternative energy sources, solar energy represents one of the most sustainable, environmentally acceptable and technologically promising renewable clean energy sources [1, 2]. Since the invention of solar cells in the 1950s [3], the solid-state junction photovoltaic solar cell devices have dominated photovoltaic solar energy converters. The most common material used in solar cells is silicon. Silicon accounts for more than 98 % of the solar cell market [4]. This is primarily because of silicon is earth abundant, highly efficient, and air stable. Crystalline silicon solar cells have achieved efficiencies approaching 25 % in the laboratory and 20 % commercially [5]. Much attention has been drawn on the investigation of solar cells for decades.

A potential candidate for the next generation of solar cells is silicon nanowires (SiNWs) and have already found application as antireflective layers [6] and as active

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elements in organic [7], dye-sensitized [8], quantum-dot sensitized [9], liquid-junction [10, 11], and inorganic solid-state devices [6]. SiNWs are 1D material and there has been interest to incorporate them into photovoltaic cell design due to the wide availability of the material and existing processing infrastructure and direct path for charge transport afforded by the geometry. In addition to that SiNWs have higher absorption capability, nearly 70 %, which is much greater than that of bulk silicon [12, 13]. SiNWs show higher absorption since when the SiNW arrays are placed in orthogonal direction to light absorption and charge separation by fabricating radial p–n junctions, it enables efficient carrier collection and light trapping in optically thick nanowire arrays, even when minority carrier diffusion lengths are shorter than the optical absorption length [14–16]. SiNWs arrays also show comparatively low reflection losses than planner semiconductor [14] which definitely leads to higher absorption also. The advantage of using nanowires is that, like quantum dots we can tune the band gap to a specific part of the solar spectrum by simply controlling the chemical composition and the coverage density of the wire surface. Significant shrinking of band gap occurs if halogens such as Cl, Br, and I are used instead of H as surface passivation elements without changing the characteristics of semiconductor nanowires [17, 18]. In this paper, we have measured the optical absorption of SiNWs of different dimensions synthesized by electroless metal deposition (EMD) over the range or 200–1,000 nm. Our finding shows that the absorption of SiNWs has greatly modified than that of the bulk silicon.

Methods

SiNWs array was grown by an aqueous electroless etching method by depositing noble metal nanoparticle like silver and copper. The fabrication process of SiNWs composed of three steps: (1) cleaning of the silicon wafers with ultrasonic bath, (2) electroplating the films of metal nanoparticles onto the cleaned silicon surface, and (3) immersion of the nanoparticle-deposited silicon wafers into HF-based aqueous chemical etching solutions. All the processes were conducted in Teflon lined autoclave.

For silver nanoparticle deposition, the concentration of $AgNO_3$ was 0.02 M with deposition time varied from 60 to 75 s. In case of copper nanoparticle deposition, concentration of $Cu(NO_3)_2$ was 0.02 and 0.05 M with deposition time varied from 60 to 120 s. In both the cases, concentration of HF was 5.0 M. After the electroless deposition of the silver and copper nanoparticle, the silver/copper metal covered Si substrate which was confirmed by scanning electron microscopy (SEM). Then, those metal (Ag/Cu) deposited Si samples were immersed in an aqueous HF/$Fe(NO_3)_3$ solution for etching. The concentration of HF and $Fe(NO_3)_3$ was 5 and 0.02 M, respectively. Etching was performed at room temperature for 30–75 min in case of Ag-treated Si samples and 60–120 min for Cu-deposited Si samples. Then after the preparation process, the obtained samples were rinsed copiously in deionized water and dried at room temperature.

Figure 1 shows a schematic picture of top view of SEM image and Fig. 2 shows a schematic picture of side view of SEM image of SiNWs array fabricated on p-type Si substrate. From the SEM micrograph, it has been seen that SiNWs have formed with excellent vertical alignment, uniformity, and packing density, with about 50 % area density. The typical wire diameter from the SEM ranges from 45 to 300 nm having length from 2 to 4 µm long.

Optical absorption spectra were obtained on a UV-1700 spectrophotometer employing halogen lamps, and equipped to measure wavelength range from 200 to 1,000 nm.

The effective absorption (A) in the films was defined as $A = 1 - (T + R)$ without any correction for thin film effects or other possible losses, since comparisons of samples on the same types of transparent substrate were made.

Results and discussion

The absorption measurement was carried out over a range of wavelengths 200 to 1,000 nm, which covers most of the spectrum that is useful for SiNWs-based solar cells. Figure 3 shows typical total optical absorption spectra of Cu-treated samples: type-A sample (sample-b, sample-c and sample-d) along with absorption of bulk silicon (sample-a). The absorbance of the solid silicon film shows typical behavior as expected for silicon shown by Run et al. [19]. Here, we have noted that Si film’s absorption begin to increase at 400 nm and remain almost steady up to 1,000 nm and might be decreased somewhere around 1,100 nm because of back-reflected loss for long wavelength from top surface [20]. Si absorbs maximum of 47 % of incident radiation, whereas absorption of SiNWs for Cu-treated samples (sample-b, sample-c and sample-d of Fig. 3) was maximum of 78 %. For sample-b, etching time was 1 h and concentration of $Cu(NO_3)_2$ was 0.05 M. Whereas for sample-c and sample-d, treating time was 2 h with 0.02 and 0.05 M $Cu(NO_3)_2$.

From the above, we have observed that, absorption of bulk Si film is much smaller than that of SiNWs array over the same wavelength range. This is because by precisely controlling the orientation (vertical vs. slanted), size (nano vs. micro-scale), density and length of SiNWs reflectivity can be reduced. It is also well known that, porous SiNWs

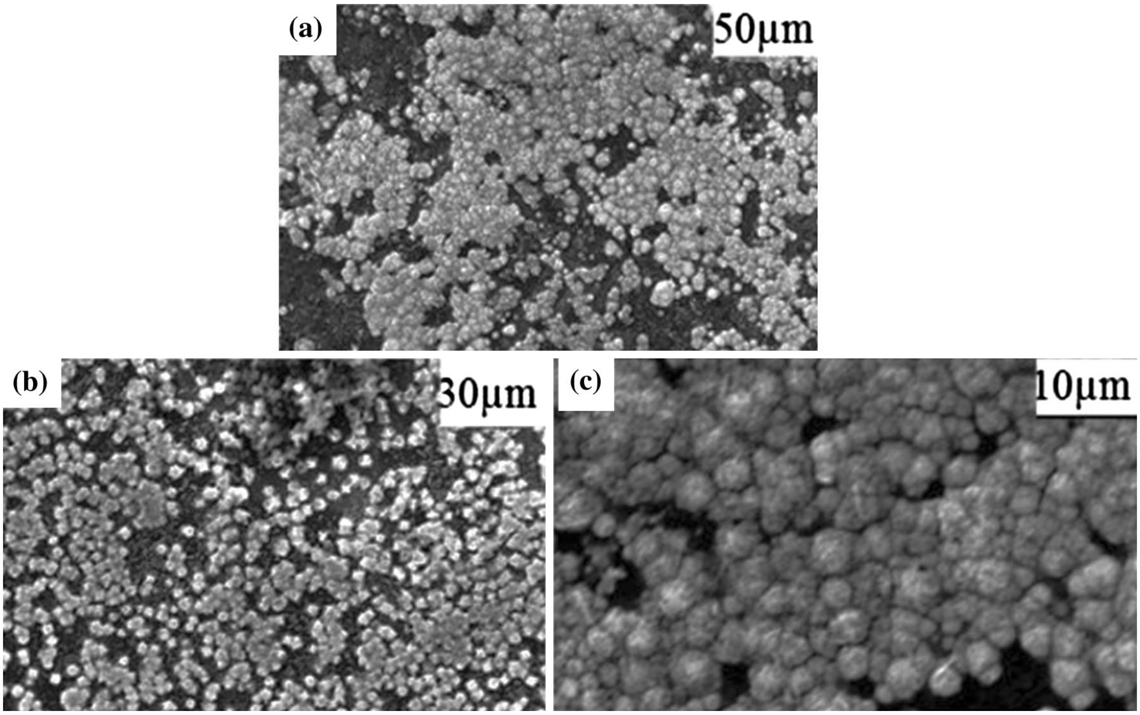

Fig. 1 *Top view* of SEM image of SiNWs array fabricated on Si substrate

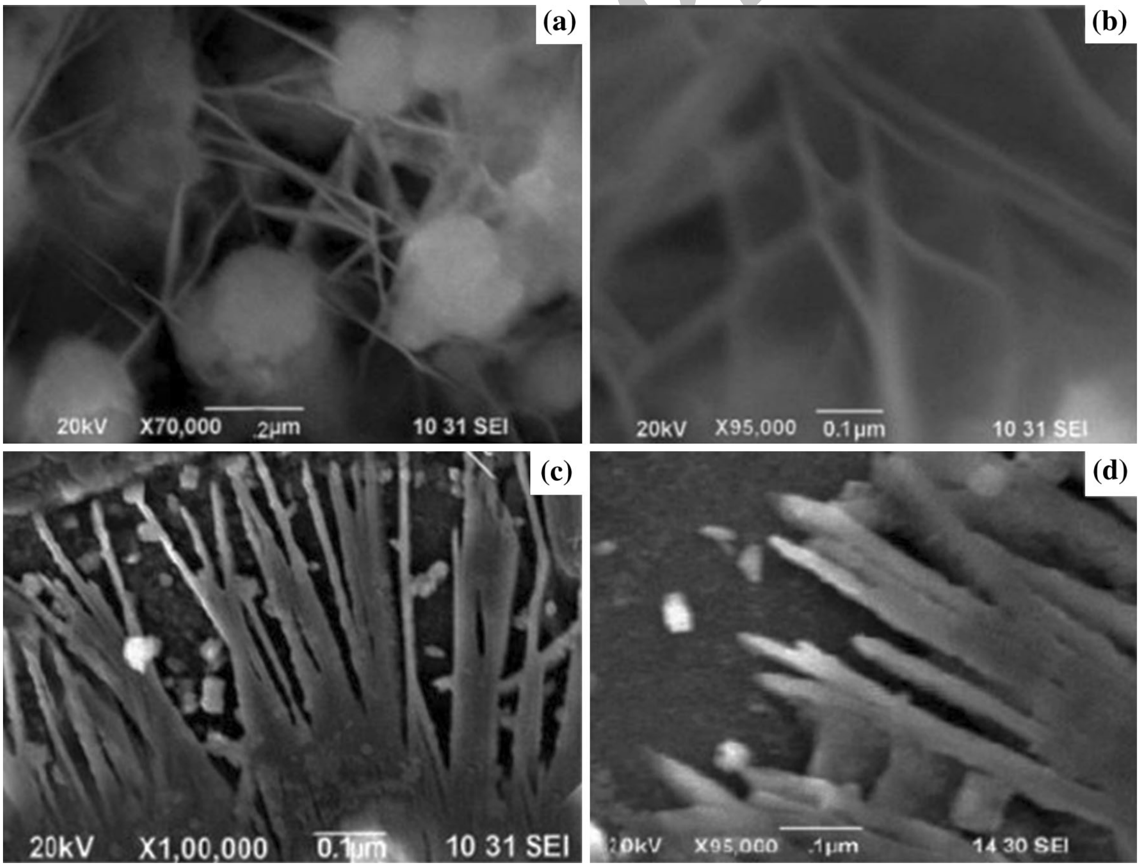

Fig. 2 **a**, **b** *Side view* of Cu synthesized SiNW array and, **c**, **d** *Side view* of Ag-synthesized SiNW array fabricated on Si substrate

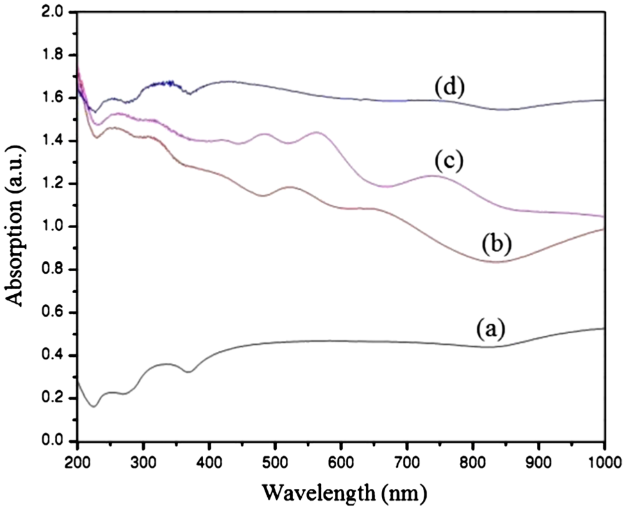

Fig. 3 *a* Optical absorption spectrum of p-type Si (111) wafer, *b* Absorption spectrum of nanowires arrays prepared in 5.0 M HF containing 0.02 M $Fe(NO_3)_3$ and 0.05 M $Cu(NO_3)_2$ with etching time 1 h, *c* Absorption image of Cu-treated nanowires film using 0.02 M $Cu(NO_3)_2$ with etching time 2 h and, *d* Absorbance of nanowires film with etching time 2 h with 0.05 M $Cu(NO_3)_2$

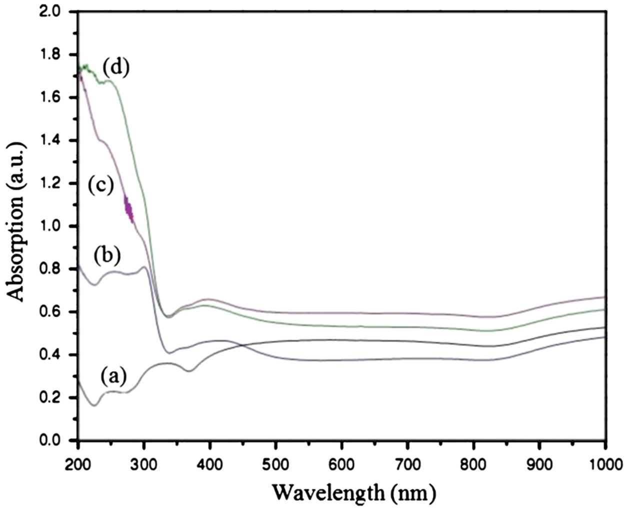

Fig. 4 *a* Optical absorption spectrum of solid Si film. *b* Absorption of Ag-deposited nanowires film on Si substrate with etching time 45 min. *c* Absorption data for Ag-deposited nanowires film on Si substrate with etching time 45 min with 0.02 M $AgNO_3$ and, *d* absorption measurement for Ag-treated Si substrate with etching time 75 min by means of 0.02 M $AgNO_3$

can reduce the back reflection up to 5.8 % in the wavelength range of 400–1,000 nm [6] which leads to higher absorption and therefore can replace other surface-textured microstructure and anti-reflection coatings. At the same time, high aspect ratio nanowires and micropillars enhance absorption through superior light-trapping mechanism, allowing significantly thinner structures and thus reduced material cost. This is especially important for Si because of the low absorption cross-section inherent to its indirect bandgap, which requires tens to hundreds of times thicker materials for complete absorption compared to direct bandgap material solar cells. The thicker structure also adversely affects carrier extraction due to bulk recombination, especially for less pure low-cost materials. Additionally, high aspect ratio structures allow core–shell radial p–n junctions, which effectively lessen the minority carrier collection path to be on the same order of the wire or pillar diameter.

From Fig. 3, it has also been observed that the absorbance of the Cu-deposited SiNWs films increases continually with increasing etching time. The length of the SiNWs films with 2 h etching was greater than that of the SiNWs synthesized by 1 h etching time and the diameter decreases with etching time elapse. It has also looked into that with increasing treating time and concentration, higher absorption can be accomplished, may be due to better light-trapping capability. Therefore, greater quantum confinement of photon occurs and for this reason high absorption achieved. Consequently, we can say that at optimum condition of etching time and density of catalytic metal better findings might be possible.

Absorption measurement was also carried out for Ag-synthesized samples: type-B sample (sample-b, sample-c, and sample-d) with different etching time for same wavelength range of 200–1,000 nm as shown in Fig. 4. It has been found that, the absorption of sample-b was slightly low for wavelength range of 350–1,000 nm but absorbance increased to 80 % in the range of 200–350 nm. For sample-c and sample-d, absorption of light energy was greater than the silicon wafer in 350–1,000 nm but it was increased tremendously up to 83 % in 200–350 nm.

Conclusion

In conclusion, we have demonstrated that SiNW films possess unique macroscopic optical properties. The nanowires yield significantly increased optical absorption over the full spectrum above the bandgap, as well as reduced transmission and reflectance for wavelengths in case of Cu-deposited SiNWs, whereas for Ag-deposited SiNWs, absorbance was maximum 83 % which is much greater than that of the bulk silicon as they absorbed maximum 43 % of the radiation. This inspection facilitates that the synthesized nanostructure could be a potential contender for efficient PV solar cell.

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Conflict of interest The authors declare that they have no competing interests.

Author's contributions The authors clearly proclaim that all the authors have equal contribution on this paper

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