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Study on Optical Properties and Structure of Silicon Nanowires

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Abstract

Silicon wafers were etched in $HF/AgNO_3$ solution with temperature varying from 35°C to 50°C for 40 minutes followed by wet etching in HNO_3 using Ag nanoparticles to synthesize the nanowires. Optical and structural characterizations performed on the synthesized nanowires using techniques like UV/VIS spectroscopy, SEM and XRD are reported. Over majority of the spectrum, the reflectance of all the nanowire films are less than 3%. The absorptions of the nanowire films are found to be over 95% for the total silicon band edge. The sizes of nanowires are found to be within ~5nm to ~32nm.

Key words: Nanowires, chemical etching, optical absorprion, optical reflection

1. Introduction

The potential of Silicon nanowires (SiNWs) in photovoltaic application is very high and it has been studied in the present paper. The importance of electrochemistry in Si microelectronic technology has given rise to intense research activity [1]. In particular, silicon shows novel electrochemical properties in solutions containing hydrofluoric acid: the complex electrochemical etching behaviour has raised considerable research interest.

Electroless metal deposition (EMD) and electroless etching have been widely investigated and now the EMD technique has been extended to the fabrication of various nanostructures.

The high aspect ratio of the nanowires (typically on the order of 100 to 1000) and sharp dielectric contrast with surroundings leads to optical anisotropy as observed in individual silicon nanowires[2]. Moreover, sub- wavelength diameters and proximity, combined with micron scale length may lead to interesting optical properties such as, low reflectance and high absorption, as we have shown in this paper.

The remarkably reduced reflective property of SiNWs suggests the nanostructures as a candidate for anti-reflective surface structures. The strong broadband absorption indicating the interaction of light of varying wavelength with SiNWs which implies its potentialities to enhance the PV efficiency of silicon based solar cell[3].

The high performance light trapping shemes have the potential to enhance short-circuit photocurrent, and therefore efficiency in various solar cells by as much as 25%[4].

2. Synthesis Mechanism of Silicon Nanowires

The method we have used to synthesize the silicon nanowires is based on the galvanic displacement reaction. This implies that there is a cathodic process where reduction of metal ions take place and an anodic process where the oxidation of Si atoms occur. Both the process occur simultaneously at the Si surface, while the charge is exchanged through the Si substrate. Ag salt has highly positive equilibrium reduction potentials. Therefore, the galvanic displacement reaction on Si with Ag salts is expected to occur by the injection of holes into the valence band (VB). The electrons used to reduce the metal salt are the silicon–silicon bonds on the Si surface. This leads to the subsequent dissolution of the Si substrate in presence of HF solution.

The energy levels of the Ag^+/Ag system lie well below the Si VB edge in $HF/AgNO_3$ solution. Thus as a consequence of the presence of bonding electrons, the reduction of Ag^+ ions is not limited by the minority carrier concentration.

Simultaneous electrochemical processes including cathodic and anodic reactions occur on the Si surface exposed to the fluoride solution containing Ag^+ ions. Surface Si atoms are oxidized (anodic reaction) and supply the electrons for the Ag^+ reduction (cathodic reaction). The corresponding reaction can be outlined by the two half-cell reactions: Equation (1) (cathodic reaction) and Equation (2) and Equation (3) (anodic reaction), which occur underneath Ag nanoparticles.

Cathodic Reaction :

$$Ag^+ + e_{VB} \rightarrow Ag^0(s) \qquad (1)$$

Anodic Reaction:

$$Si(s) + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^-_V \qquad (2)$$

$$SiO_2(s) + 6HF \rightarrow H_2SiF_6 + 2H_2O \qquad (3)$$

Ag particles on the Si surface oxidize the Si underneath it and produce SiO_2. Simultaneousely the dissolution of SiO_2 form underneath the Ag particles occurs in the presence of HF acid. Thus the Ag particles gradually sink into the bulk silicon and the silicon nanowire arrays gradually emerge with the elapse of treatment time.

3. Experimental Details

The ultrasonic bath solvent cleaning sequence was followed in our experiment. In the etching solution, the concentration of $AgNO_3$ and HF was 0.02mol/L and 5.3mol/L, respectively. The formation of SiNWs has been done using a simple indigenously developed Teflon cell for EMD.

The samples were treated differently with each sample etched in different temperature. Three samples have been treated in temperatures 35°, 40°, 45°C and three samples were treated in 50°C. Each sample was dipped in the solution for 40 minutes.

After etching in $HF/AgNO_3$, solution the samples with 35°, 40° and 45°C treatment temperature were further etched with HNO_3. The samples treated in 50°C temperature were kept unetched.

The obtained samples were contained of residual Ag layer and other contaminations which were removed by copiously cleaning with DIW as long as the residual layer has not come off.

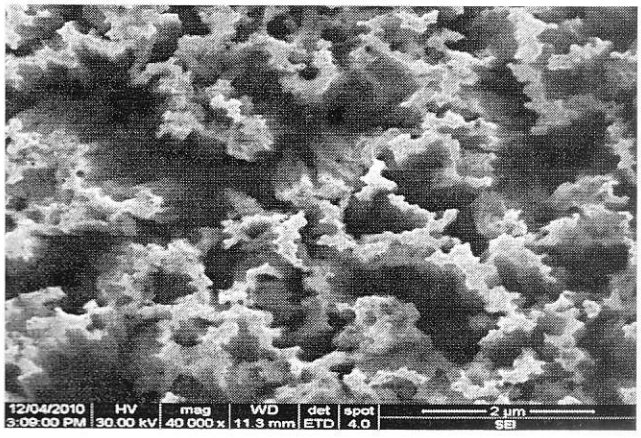
4. Characterization of the Nanowires

Three characterization techniques have been performed for synthesized nanowires namely **1)** Scanning Electron Microscopy (JEOL JSM- 6490 LA) **2)** X-ray diffraction (PW 3040 X'Pert PRO) **3)** UV-spectroscopy (UV 1201V) to study the morphology, to find the nanosizes and the spectral behaviour of the as synthesized samples, respectively.

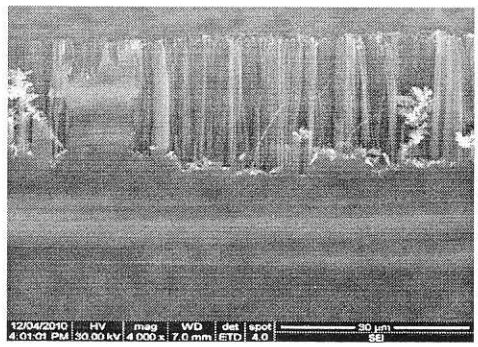
5. Results and Discussion

5.1 Scanning Electron Microscopy (SEM)

Figure 1 shows SEM images of the as synthesized samples treated in 50°C temperature which shows traces of nanoswires.



(a)



(b)

Fig. 1:(a) Top view image of the as synthesized samples; (b) Cross- sectional image of the as- synthesized sample

An abundant amount of Ag particles can be seen as further etching has not been done after etching with HF- based aqueous solution containing silver nitrate.

Our experimental results indicate that the oxidation and dissolution of the Si substrate do not occur alongside the Ag deposits, but beneath them. Peng et al.[5] also proposed in his report that oxidation and dissolution of the Si substrate occur underneath the deposited silver particles in the presence of aqueous ferric nitrate.

Moreover, Morinaga et al.[6] and Kim et al.[7] have reported that electrochemical Cu deposition simultaneously accompanies the localized oxidation and dissolution of silicon, which take place underneath the deposited Cu and induces pits in the same position as a result of etching with dilute HF solution. Recently, Mitsugi et al.[8] reported pit formation induced by Cu contamination in dilute HF solution. They proposed that the local redox couple between Cu and the nearby Si surface is essential to the formation of localized pits, which were formed at the same position as the Cu islands.

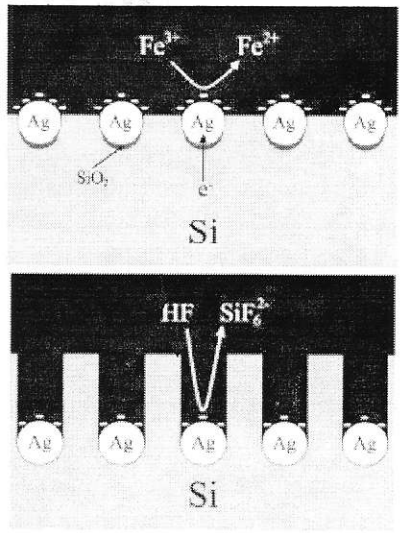


Fig. 2: Mechanism of silicon nanowire array formation.

In the initial stage of silver deposition, Ag^+ ions in the vicinity of the silicon surface capture electrons from the VB of Si, and are deposited in the form of metallic Ag nuclei on a nanoscopic scale[5] (*Figure 2*).

Shallow pits would immediately form underneath the Ag nanoparticles, due to the etching of SiO_2 by the HF solution; then the Ag particles enter the forming pits (*Figure 2*). Therefore, the Ag particles trapped in these pits do not move horizontally. This illustration is consistent with our SEM observations, which confirmed that the oxidation and dissolution of the Si substrate occurred from beneath the Ag particles that are trapped in the formed pits. As Ag nanoparticles are pinned by the pits and cannot move horizontally on the silicon surface, local etching in the close vicinity of Ag nanoparticles occurs, and deeper pits form owing to the continuous etching away of the SiO_2 underneath the Ag particles and the sinking of the Ag nanoparticles with prolonged immersion in the solution.

Simultaneously, large quantities of nanoscale Si needles protruded outward from the interspaces between the Ag particles on the Si surface. These phenomena imply that the appearance of Si needles may be ascribed to the sinking of Ag particles into bulk silicon, because the "growth" of Si needles is impossible in this case.

5.2 UV Spectroscopy

The study of the spectral behaviour showed excellent antireflection properties. *Figure 3* shows the reflection curves for the samples treated in 35°and 45°C which were further etched with HNO_3 and reflection curve for sample treated in 50°C which was kept unetched.

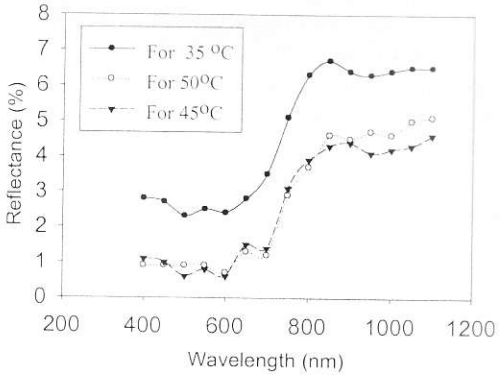
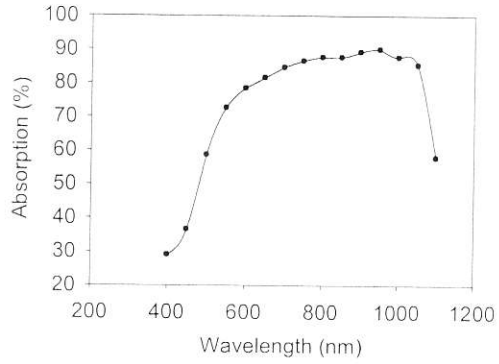


Fig. 3: Total reflectance curves for the sample treated at 35°C, 45°C and 50°C temperature.

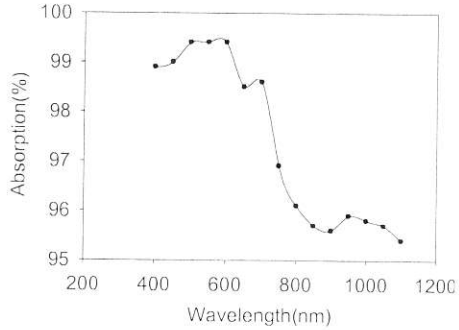
It is evident from the above figures that the samples treated at different temperatures, both etched and unetched shows similar behaviour. The reflectance of all the nanowire films were less than 3% over majority of the spectrum from UV to mid-visible region and begin to increase ~ 700nm to values of ~ 6% at the silicon band edge (1100nm).

It is also noteworthy that the spectral dependence and the magnitude of the total reflectance for our samples are much improved compared to those found in the literature. In the wavelength range of 400-650 nm, our samples have typically showed a constant total reflectance of ≤ 2%. By comparison, Rappich et al.[9] obtained reflectance values for nanoporous silicon ranging from ~2-30 % and ~2- 20% in anodized nanowire-like structures in the 300-850 nm wavelength range. An ultrahigh surface area due to a high density of SiNWs; the subwavelength-structured (SWS) surface of the SiNWs, which could suppress the reflection over a wide spectral bandwidth[10] and a possible porosity gradient throughout the SiNWs, could be attributed to this remarkably low reflectance of the as synthesized samples[11].

The absorption characteristics measured by UV-spectrometer shown in *Figure 4(a)* and *Figure 4(b)* clearly shows that the absorption peak shifted from wavelength range 800nm-1000nm for Si substrate to 400nm-650nm for Si nanowires.



(a)



(b)

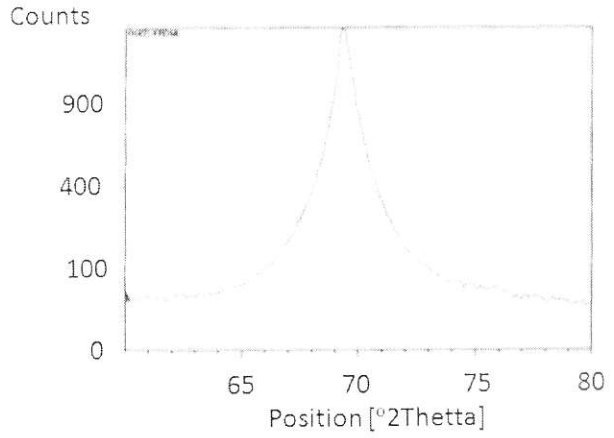
Fig. 4: (a) Absorption characteristics of Silicon substrate; (b) Absorption characteristics for Silicon nanowire

This indicates the bandgap modification of Silicon due to quantum confinement effect[12]. This strong broadband

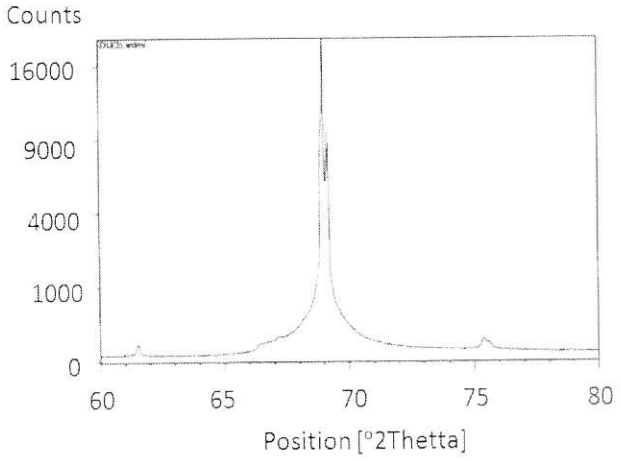
optical absorption can be attributed to the significant reduction of the reflectance and the strong light trapping of the nanowires[13].

5.3 X-Ray Diffraction (XRD)

The structural properties of the two unetched samples both treated at 50°C temperature were investigated by X-Ray diffraction photometry.



(a)



(b)

Fig. 5: (a) X-ray diffraction spectra for sample treated in 50°C temperature (b) X-ray diffraction spectra for another sample treated in 50°C temperature.

Figure 5 shows the X-ray diffraction spectra for the two samples.

The size of synthesized nanowires determined by these XRD spectrum is in the range of **~5nm** to **~32nm.**

The formula used to calculate the sizes of the nanowires is as follows:

$$D_g = \frac{79.4A^0}{\Delta \cos\theta}$$

6. Conclusion

The direction of the silicon peaks obtained from x- ray diffraction spectrum was very strong showing good crystalline conditions of the silicon nanowires. The reflectances of the as synthesized samples were found to be as low as 2%; therefore, the behavior of the SiNWs more closely resembles a multi-antireflection coating. The reduction of wavelength of absorptivity peak implies the increase in bandgap of Si nanostructures compared to bulk which enhances the possibility of increasing efficiency of solar cell based on theses nanostructures.

References

1. V. Lehmann, "*Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications*" (Wiley-VCH, Weinheim, Germany, 2002).
2. J. Qi, A. M. Belcher, J. M. White, "Spectroscopy of individual silicon nanowire," Appl. Phys. Lett. 82 (16), 2616-2618 (2003)
3. A. V. Shah, M. Vanecek, J. Meier, F. Meillaud, J. Guillet, D. Fischer, C. Droz, X. Niquille, S. Fay, E. Vallat-Sauvain, V. Terrazzoni-Daudrix, J. Bailat, "Basic efficiency limits, recent experimental results and novel light-trapping schemes in a-Si:H, lc-Si:H and 'micromorph tandem' solar cells," J. Non-Cryst. Sol.338-340(1), 639-645(2004).
4. Tsakalakos, L. Balch, J. Fronheiser, J. Shih, M. "Strong broadband optical absorption in silicon nanowire films", Journal of Nanophotonics, Vol. 1, 013552 (2007).
5. K. Q. Peng, J. Hu, Y. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee, J. Zhu, "Fabrication of Single-Crystalline Silicon Nanowires by Scratching a Silicon Surface with Catalytic Metal Particles", Adv. Funct. Mater., 16, 387–394 (2006).
6. H. Morinaga, M. Suyama, T. Ohmi, "Mechanism of Metallic Particle Growth and Metal Induced Pitting (MIP) on Si Wafer Surface in Wet Chemical Process", J. Electrochem. Soc. 1994, 141, 2834 (1994).
7. J. S. Kim, H. Morita, J. D. Joo, T. Ohmi, "The Role of Metal Induced Oxidation for Copper Deposition on Silicon Surface " J. Electrochem. Soc. 1997, 144, 3275 (1997).
8. N. Mitsugi, K. Nagai, "Pit Formation Induced by Copper Contamination on Silicon Surface Immersed in Dilute Hydrofluoric Acid Solution" J. Electrochem. Soc. 2004, 151, G302 (2004).
9. J. Rappich, S. Lust, I. Sieber, W. Henrion, J. K. Dohrmann, W. Fuhs, "Light trapping by formation of nanometer diameter wire-like structures on μc-Si thin films," J. Non- Cryst. Sol. 266-269(1), 284-289 (2000).
10. Y. Kanamori, M. Sasaki, K. Hane, "Broadband antireflection gratings fabricated upon silicon substrates," Opt. Lett. 1999, 24, 1422 (1999).
11. C. C. Striemera, P. M. Fauchet, "Dynamic etching of silicon for broadband antireflection applications" Appl. Phys. Lett. 2002, 81, 2980. (2002).
12. Nolan, M. O'Callaghan, S. Fagas, G. Greer, J.C. "Silicon Nanowire Band Gap Modification", Nano Letters, Vol 7, 34-38 (2007)
13. Erik Garnett and Peidong Yang. "Light Trapping in Silicon Nanowire Solar Cells" *Nano* Letters, *2010; 100202130154041(201*