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Fabrication and Characterization of Solar Cells Based on Silicon Nanowire Homojunctions

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Abstract

Silicon nanowire homojunction p-n solar cells were fabricated using Zn and Au metals as catalysts for growing the NWs. This design consisted of SiNWs, doped as p and n-types, catalyzed with Zn and Au catalysts to fabricate p-n homojunctions within each wire. The surface morphology, structure, and photovoltaic properties were investigated. The morphology for each of the catalyzed SiNWs was significantly different; the Zn catalyst produced short and thick NWs with diameters ranging from 190nm to 260nm, whereas the Au catalyst produced long SiNWs with diameters ranging from 140nm to 210nm. The Zn-catalyzed SiNW p-n solar cell showed a higher efficiency of 1.01% compared with the Au-catalyzed SiNW p-n solar cell with an efficiency of 0.67%.

Keywords: Silicon nanowires, Solar cells, PECVD.

1. Introduction

One-dimensional (1D) semiconductors are one of the most important nanostructured materials because they have several unique properties, including high crystallinity, self-assembly, high surface-to-volume ratio, quantum confinement effects as well as slow electron-hole recombination that allow them to be used in novel miniaturized electronic, optoelectronic as well as energy conversion and storage devices [1,2]. Silicon is the most important semiconducting material in microelectronics, and silicon-based (single crystal, polycrystalline and amorphous) solar cells have played a dominant role in the photovoltaic market for a long time [3]. The silicon nanowire (SiNW) is one of the most attractive one-dimensional (1D) nanostructure semiconductors because of its unique electrical and optical properties, which are often remarkably different from other semiconductors in the bulk phase [4]. SiNWs have received much attention, as shown by the increasing number of publications investigating SiNWs since 1993.

Various synthetic methods have been established for developing SiNWs after the initial discovery of high aspect ratio Si micro- and nanostructures in the 1960s by Wagner's group [5]. SiNWs with unique properties are significantly different from bulk Si, and these properties vary according to the NW morphology. The morphology, crystalline structure, as well as the optical properties of SiNWs depend on the deposition methods, growth conditions, and growth mechanisms, which affect the SiNWs properties and applications.

Vapor-Liquid-Solid (VLS) is a typical growth mechanism that is widely used to synthesize SiNWs. In this method, the morphology and other properties of the grown SiNWs can be controlled through the parameters of the process, especially the catalyst type and thickness that controls the wires diameter. Therefore, fabrication of solar cells based on SiNWs grown by the VLS mechanism have attracted the attention of many researchers nowadays [6]. The choice of

Choosing a suitable catalyst for NW growth depends on the

eutectic temperature of the metal–semiconductor system. The properties of the grown SiNWs using the VLS mechanism, such as morphology and crystallinity are affected by the catalyst type and thickness [1,7-9]. Increasing thickness of catalyst led to an increase the catalyst droplet diameter and in turn an increase in the diameter of the grown SiNWs.

The conversion efficiency of solar cells is affected by many factors, such as optical absorption and band gap. By using silicon nanostructures, the absorption of sunlight can be improved from typically 60% to over 90% in the wavelength range between 400 and 1100 nm [10-12]. Nanowires are one of the best structures that can be used in order to increase absorption of sunlight, and in turn increase the conversion efficiency, of a solar cell. The nanowires act as light trapping devices due to their strong scattering capacities [13] and for the same reason as antireflective coatings [14]. In the present work, homojunction solar cells based on SiNWs synthesized by the PPCVD method were fabricated and the properties of the grown wires and solar cells were investigated.

2. Experimental Details

The PPCVD method was used to fabricate SiNW homo-junction solar cells. ITO-coated glass was used as the substrate for the solar cells. Zn and Au metal thin films were used to catalyze the SiNWs with thicknesses of 80 and 100nm, respectively, and were deposited by thermal evaporation. To prepare p-type SiNWs, the temperature was fixed at 400°C for 35min, and then SiH₄ and B₂H₆ gases were introduced with a flow rate of 280 sccm for 25min (as silicon and boron sources, respectively). After this phase of the deposition was completed, B₂H₆ gas flow was stopped and PH₃ gas was inserted at a flow rate of 0.7 sccm for 20min to produce the n-type SiNWs. After the fabrication process of the SiNW p-n junction, the system was purged with argon and cooled to room temperature. Figure1 shows the schematic of the homojunction p-n structure of SiNW solar cells fabricated using p and n type SiNWs catalyzed with Zn and Au.

The scanning electron microscope (SEM; Philips XL20 SEM) was used to study the surface morphology of the prepared devices and the structural properties were also investigated by X-ray diffraction (XRD) on a PANalytical X'Pert PRO MRD PW3040 instrument with CuK α radiation. The optical reflection of the fabricated device was carried out at room temperature using a Shimadzu UV-vis 1800 spectrophotometer at wavelengths ranging from 400 to 1000nm. The electrical characteristics (IV) under dark and illumination conditions of the fabricated devices were measured by depositing aluminium (Al) metal thin films by thermal evaporation onto the solar cell surface to serve as the back contact. The schematic of the fabricated solar cells is presented in Figure 1.

3. Results and discussion

3.1 Surface morphology

The surface morphologies of the SiNWs synthesized using 80nm-thick Zn and 100nm-thick Au catalysts are shown in Figure 2. Both Zn and Au produced a high density of SiNWs under these growth conditions. However, the morphology of the NWs was significantly different for each catalyst. The SiNWs grown using the Zn catalyst appeared on the substrate as short curved NWs, whereas the Au catalyst produced long and homogeneous SiNWs, as shown in Figure 2.

The cross-sectional FESEM images of the Zn- and Au-catalyzed SiNW photovoltaic devices are shown in Figure 3. The wires were randomly oriented on the substrate with a straight structure. The lengths ranged from 5.6 μ m to 11 μ m for the SiNWs grown using the Au catalyst and from 0.16 μ m to 0.38 μ m using the Zn catalyst.

Figure 4 shows the analysis of the diameter distribution of the fabricated devices using Zn and Au catalysts. The wire diameter of the SiNWs grown using the Zn catalyst ranged

from 190nm to 260nm (mode=210nm), whereas the SiNWs prepared with the Au catalyst had a wire diameter range from 140nm to 210nm (mode=190nm). Moreover, the density of the SiNWs was calculated, to be 8 and 5NWs/ μm^2 for the wires grown using Au and Zn catalysts, respectively.

The SiNWs catalyzed by Zn were thicker and shorter compared with those catalyzed by Au. According to the phase diagram, the eutectic points of the Au–Si and Zn–Si systems were 363 and 420°C, respectively, and the melting point of Zn was 420°C, whereas that of Au was 1064°C [15]. The substrate was annealed at 400°C for 35min before the SiH₄ gas was inserted into the preparation chamber. Thus, the Zn particles aggregated and were larger in diameter than the Au, which in turn led to an increase in the grown wire diameters. For this reason, the density of the grown SiNWs pber unit area is decreased when the diameter of wires increasred [7].

Parlevliet et al.[16] grew SiNWs by PPECVD using a 100nm thin film thickness of Au as a catalyst, and found that the average diameter of the deposited SiNWs was 420nm. Also Kelzenberg et al [17] prepared SiNWs using a 100nm thin film thickness of Au catalyst and obtained diameters of prepared wires ranging from 200nm to 1.5 μm . Yu et al. [18] and Chung et al. [19] used Zn as a catalyst to grow SiNWs by the CVD method. The Zn catalyst was formed using SiH₄ and ZnCl₄/ethanol solution at 450°C. They obtained SiNWs with diameters ranging between 15 and 35nm. Clearly the deposition conditions have a significant effect on the SiNW morphology.

3.2 Crystalline structure

Figure 5 shows the XRD patterns of the Zn- and Au-catalyzed SiNW-based solar cells. The SiNWs, produced using Au as catalyst, showed diffraction peaks at 28.6, 47.6, and 56.3°,

corresponding to the (111), (220) and (311) planes, respectively, of the Si diamond structure. The XRD pattern of the Zn catalyzed sample shows a high diffraction peak at 28.4° corresponding to the (111) plane of the Si crystalline structure. Moreover, the diffraction peaks corresponding to the Zn and Au catalysts are also apparent in Figure 5.

These results are in accordance with other researchers [16,3] who synthesized SiNWs by PPECVD and CVD methods, respectively, using Au as catalyst and obtained highly crystallized SiNWs. Moreover, the diffraction peaks of the sample prepared using the Au catalyst were sharper than those for the sample that was synthesized using a Zn catalyst, which means the crystallinity of the Au-sample is better.

The peaks due to the metal catalysts were detected because the metals were located on top of the SiNWs. Also, other authors have used Sn and Al catalysts to grow SiNWs by PPECVD and PECVD methods [16, 20]. They found that these grown SiNWs exhibited amorphous structure.

3.3 Optical reflectance

The optical reflectance of SiNWs solar cells prepared using Au and Zn catalysts is measured in the wavelength range of 400-1000nm as shown in Fig.6. The samples show very low reflection ($\sim 0.6\%$) over their whole spectral range compared with Si solid films [21]

However, low reflectance of light means increasing light absorption by the solar cell that could lead to an increase in the conversion efficiency of the device. Huang et al. notes that the reflectivity value of SiNWs prepared by wet electroless etching is decreased from 25.6% to 3.1% when the wire length increased from 60nm to 2934nm [22].

3.4 J–V characteristics

The efficiency of a solar cell is measured by the ratio of the electrical output power and the incident optical power, and is usually expressed in terms of short circuit current, open circuit voltage, and fill factor [23].

$$\eta = \frac{J_m V_m}{P_{in}} \times 100\% \quad , \quad (1)$$

where J_m is the maximum power point current density, V_m is the maximum power point voltage, and P_{in} is the power of the incident light. The Fill Factor FF is the ratio between the power at the maximum operation point and the product of the short circuit current and open circuit voltage [23].

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (2)$$

The Fill Factor is reduced by series resistance, leakage current over the edges of the solar cell, or leakage current caused by recombination.

The J–V characteristics of the p-n junction SiNW solar cells fabricated using the Zn and Au catalysts are shown in Figure 6. These devices exhibited clear photovoltaic behavior with an efficiency of 1.01 % for the p-n Zn solar cell, while the p-n Au solar cell produced an efficiency of 0.67%. In addition, J_{sc} and V_{oc} were derived from Figure 7. The V_{oc} of the solar cell produced by the Au-catalyzed SiNWs was significantly less than the V_{oc} of the solar cell fabricated using Zn as the catalyst. This difference may be attributed to the fact that the Au in Si acts as a recombination centre that reduces the charge carrier lifetime, which consequently reduces the open-circuit voltage [24].

The η of the p-n junction fabricated solar cells catalyzed by Zn and Au metals were measured at several different sites on the cells' surfaces. The cell parameters are summarized

in Tables 1 and 2. The calculated η showed a variation in values that could be due to the difference in metal-Si contact quality. The as-grown SiNWs had various morphological differences such as diameter, shape and NW density that could have led to significant effects on the metal-Si contact quality. The fabricated p-n junction solar cells catalyzed with Zn exhibited a range of efficiencies from (1.01%-0.29%), while the efficiencies of the p-n junction cells catalyzed with Au ranged between (0.67%- 0.25%). The best η value of the p-n junction solar cell fabricated using Zn was 1.01%, whereas the best result for the one that was fabricated using the Au catalyst was 0.67%. The surface morphology of the grown SiNWs like the length, diameter, and density can affect the efficiency of the solar cells due to the long NWs having a low minority carrier lifetime as a result of the high recombination rate; thus, all of the key cell parameters are low for long NWs[25].

The morphology of the as-grown SiNWs catalyzed by Zn was significantly different from those prepared using a Au catalyst (Figure 2). The former exhibited a greater diameter with shorter NW length (around $0.38\mu\text{m}$) compared with those fabricated using a Au catalyst and which produced a maximum length of $11\mu\text{m}$. Thus, increasing the wire length led to a reduction in the minority carrier lifetime. Junshai et al [26] noted that the efficiency of their fabricated SiNW/organic hybrid solar cells increased from 3.76% to 5.59% when the length of the as-grown NWs decreased from $5.59\mu\text{m}$ to $0.37\mu\text{m}$ [26]. Furthermore, increasing the wire diameter minimized the area between the SiNWs and reduced the reflection of the incident light.

Other researchers have also studied the optical properties of SiNW arrays, and found that η increases as the NW diameter increases. Junshuai et al. [27] and Tsakalacos et al. [28] prepared p-type SiNWs catalyzed by Au and covered with n-type a-Si to fabricate the p-n

junction of a SiNW- based solar cell on a metal foil substrate by the CVD method. These authors achieved an efficiency of <0.1%.

SiNW solar cells with radial p-n junction structures were fabricated by the CVD method using Au as a catalyst on a crystalline Si substrate at 550°C [29]. The authors observed that the efficiency enhancement, due to the presence of the NWs, increased light trapping within the device, and the fabricated cells showed a maximum efficiency of 0.9%, with $V_{oc} = 300\text{mV}$, and $J_{sc} = 11\text{mA/cm}^2$. The spectral efficiency showed that the surface recombination effect increased on the large surface area of the NW cells when Au was used as catalyst.

Stelzner et al. [30] fabricated SiNW solar cells on Si wafers and multicrystalline Si thin films on glass, and obtained a V_{oc} of 230mV to 280mV, J_{sc} of 2mA/cm^2 , and η of 0.1%. Thomas et al. [31] prepared a solar cell based on single crystal SiNWs grown by the VLS method with a Au catalyst, and these devices exhibited $V_{oc} = 0.29\text{V}$, $J_{sc} = 3.5\text{mA/cm}^2$, and a maximum efficiency of 0.5% [31].

The best FF of our Au-catalyzed SiNW solar cells was 59%, which was about twice that of the best Zn-catalyzed SiNW solar cell. This value of the FF was significantly higher than that reported for other SiNW solar cell devices with FFs of 20% and 40% [32,20]. The series resistance (R_s) is another parameter that can affect cell performance. High R_s reduces the output voltage under load, thereby decreasing the FF. Thus R_s should be low because increasing the R_s of a solar cell increases the voltage drop within the cell. [33]. The R_s of the Zn-catalyzed SiNW solar cell was 833.3Ω , which was much higher than that of the Au-catalyzed SiNW solar cell with 120.4Ω . This disparity may be attributed to the difference in the morphology of the wires such as (diameter, shape, length and density). These results

demonstrate the feasibility and promise of this concept. Clearly, better results may be obtainable by systematically optimizing the doping and morphology of the SiNWs.

4. Conclusions

Silicon nanowire p-n homojunction solar cells were successfully fabricated by the PPECVD method at 400°C on an ITO-coated glass substrate. These structures were fabricated with both Zn and Au catalysts and doped as p and n types to produce SiNW p-n homojunction solar cells for the first time. The SiNWs grown with Zn and Au catalysts produced two very different NW morphologies. The NWs grown using Zn as catalyst exhibited larger diameters and shorter lengths than those grown using Au as the catalyst. Crystalline structure analysis showed that both prepared SiNWs using Au and Zn catalyst are crystalline with preferred orientation toward (111) direction. The conversion efficiency of the fabricated SiNW p-n junction solar cells catalyzed by Zn and Au were calculated for different areas of the surface. The best fabricated p-n solar cell, based on the Zn-catalyzed SiNWs, showed a higher efficiency of 1.01% compared with the best Au-catalyzed SiNW p-n solar cell with an efficiency of 0.67%. The difference in the efficiencies of the two fabricated solar cells was due to the difference in the morphology and crystalline structure of the prepared SiNWs, which in turn was due to the different properties of the catalysts and the deposition conditions.

References

- [1] H.F. Al-Taay, M.A. Mahdi , D. Parlevliet, Z. Hassan, P. Jennings, *Superlattice. Microst.* 61(3013)134-145.
- [2] M.A. Mahdi, J.J. Hassan, S.S. Ng, Z.Hassan, N.M. Ahmed, *Physica E* 44 (2012) 1716–1721
- [3] C.Y. Kuo , C. Gau, B.T. Dai, *Sol. Energy Mater. Sol Cells* 95(2011)154-157
- [4] J. David, *Device Applications of Silicon Nanocrystals and Nanostructures*, Ottawa, Ontario, Canada, 2009
- [5] R.S. Wagner, W.C. Ellis, K.A. Jackson,S.M. Arnold, *Journal of Applied Physics*, 35(1964) 2993-3000.
- [6] L. Yu, L. Rigutti, M. Tchernycheva, S. Misra, M. Foldyna, G. Picardi, P.R. Cabarrocas, *Nanotechnology* 24 (2013) 275401-275407.
- [7] H.F. Al-Taay , M.A.Mahdi , D.Parlevliet , P.Jennings, *Materials Science in Semiconductor Processing* 16 (2013) 15–22
- [8] H.F. Al-Taay, M.A.Mahdi, D.Parlevliet, Z.Hassan, P.Jennings, *Physica E* 48 (2013) 21–28
- [9] H.F. Al-Taay a,b,†, M.A. Mahdi c, D. Parlevliet a, Z. Hassan d, P. Jennings, *Superlattices and Microstructures* 68 (2014) 90–100
- [10] S.K. Srivastava, D. Kumar, P.K. Singh, M. Kar, V. Kumar, M. Husain, *Sol. Energy Mater. Sol. Cells.*, 94(2010)1506–1511
- [11] S.K. Srivastava, D. Kumar, P.K. Singh, M. Kar, V Kumar, M. Husain, *Sol. Energy Mater. Sol. Cells.*, 95(2011) 215–218
- [12] V. Sivakov, G. Andr, A. Gawlik, A. Berger, J. Plentz, F. Falk, *Nano Lett.*, 9(2009)1549–1554
- [13] G. Brnstrup, F. Garwe, A. Cski, W. Fritzsche, A. Steinbrück, S. Christiansen, *Phys. Rev.*, B 84(2012) 1–10
- [14] W.Q. Xie, J.I. Oh, W.Z Shen, *Nanotechnology*, 22(2011) 065704
- [15] V. Schemidt, J.V. Wittemann, S. Senz, U. Gosele, *Adv. Mater.*, 21(2009)2681–2702.
- [16] D. Parlevliet, P. Jennings, *J. Nanopart. Res.* 13(2011)4431 - 4436.
- [17] D. Kelzenberg, B. Daniel, A.H. Atwater, *Nano Lett.* 8(2008)710-714.
- [18] L. Yu, P.J. Alet, G. Picardi, I. Maurin, P.R. Cabarrocas, *Nanotechnology*, 19(2008) 485605–485610.

- [19] S.W. Chung, Y. Yu, J.R. Heath, Appl. Phys. Lett. 76(2000)2068-2070.
- [20] F. Iacopi, P.M. Vereecken, M. Schaekers, M. Caymax, N. Moelans, B. Blanpain, O. Richard, C. Detavernier, H. Griffiths, Nanotechnology, 18(2007)505307–505313.
- [21] M. Hasan, M.F. Huq, Z. H. Mahmood, SpringerPlus 2(2013)151-158.
- [22] B.R. Huang, Y.K. Yang, T.C. Lin, W.L. Yang, Sol. Energy Mater. Sol Cells 98(2012)357-362
- [23] S.J. Fonash, Solar cell Device Physics, academic press in an important of Elsevier, oxford, UK (2010).
- [24] S.M. Sze, Physics of Semiconductor Devices, Third Edition, WILEY Interscience, A John Wiley and Sons, INC, USA (2007).
- [25] S.C. Shiu, S.B. Lin, S.C. Hung, C.F. Lin, Appl. Surf. Sci. 257(2011)1829-1834.
- [26] H.J. Syu, S.C. Shiu, C.F. Lin, Sol. Energy Mater. Sol. Cells 98 (2012) 267-272.
- [27] L. Junshuai, L.Y. Hong, Appl. Phys. Lett. 95 (2009)243113-243115
- [28] L. Tsakalacos, J. Balch, J. Fronheiser, B.A. Korevaar, Appl. Phys. Lett., 91(2007) 233117-233119.
- [29] O. Gunawan, S. Guha, Sol. Energy Mater. Sol Cells 93(2009)1388-1393.
- [30] T. Stelzner, M. Pietsch, S. Christiansen, Nanotechnology 19(2008)295203-295206.
- [31] J. Thomas, T. Bozhi, C.M. Lieber, Nano Lett. 8(2008)3456-3460.
- [32] D. Kelzenberg, B. Daniel, A.H. Atwater, Nano Lett. 8(2008)710-714.
- [33] Solanki, C.S. (2011) Solar Photovoltaic's Fundamentals, Technologies and Applications, Second Edition, PHI Learning Private limited, New Delhi,.