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Parlevliet, D. and Jennings, P. (2011) Thin film silicon nanowire photovoltaic devices produced with gold and tin catalysts. Journal of Nanoparticle Research, 13 (10). pp. 4431-4436.

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Thin Film Silicon Nanowire Photovoltaic Devices Produced With Gold and Tin Catalysts

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Abstract

Silicon nanowires produced using pulsed plasma enhanced chemical vapor deposition have been used as part of a thin film photovoltaic device. Nanowires of differing morphologies were produced by using both gold and tin thin films as a catalyst for growth. A prototype silicon nanowire based thin-film photovoltaic device was produced by using doped silicon nanowires as the p-layer. Amorphous silicon was used as the intrinsic and n-layers of the device. The nanowires used in the photovoltaic devices had an average diameter of 420nm after the deposition and coating of amorphous silicon intrinsic and n-layers. The nanowires were deposited in bulk as films of 3 μ m to 42 μ m in thickness. The resulting device, although of low efficiency, had a demonstrable photocurrent. Tin-catalyzed nanowires were found to produce a thin-film device with a measurable photocurrent whereas gold-catalyzed silicon nanowires did not. This was attributed to the length of the nanowires and thickness of the p-layer produced when using gold-catalyzed nanowires.

silicon nanowire; photovoltaic; amorphous silicon; Pulsed PECVD

INTRODUCTION

Silicon nanowires are a semiconductor nanostructure that has been the focus of much recent interest as a potential material for photovoltaics (Tian et al. 2007; Tsakalakos et al. 2007). Silicon nanowires are of interest as their properties, such as the band-gap (Ma et al. 2003), vary greatly with the diameter of the structure, allowing the tuning of the band-gap for different applications. A method commonly used for the growth of silicon nanowires is Chemical Vapor Deposition (CVD) (Westwater et al. 1997). However, there is a variant of CVD known as Plasma Enhanced CVD (PECVD) which can be used to produce silicon nanowires at an improved deposition rate (Hofmann et al. 2003), when a catalyst such as gold is used. PECVD uses radio frequency plasma to crack or decompose the feed gas. This technique is widely used in the production of amorphous and nanocrystalline silicon thin films. It has previously been shown that a modification of PECVD with a 1kHz square wave (Pulsed PECVD) aids the growth of gold-catalyzed silicon nanowires (Parlevliet and Cornish 2006). As Pulsed PECVD (PPECVD) improves the growth of silicon nanowires at comparatively low substrate temperatures it was used to produce the silicon nanowires in this work.

Gold is widely used to produce crystalline silicon nanowires due to the low Au-Si eutectic point (363°C) (Wagner and Ellis 1964). Tin has only recently been used as a catalyst in the fabrication of silicon nanowires by either a thermal method (Chen et al. 2007; Shao et al. 2007), hydrogen-radical assisted method (Jeon et al. 2009) or PPECVD (Parlevliet and Cornish 2007) although it had earlier been mentioned as a catalyst that may be suitable for low-temperature Vapor Liquid Solid (VLS) growth (Iacopi et al. 2007; Sunkara et al. 2001). Tin is a suitable catalyst when used with PPECVD as it was shown to produce high areal density nanowires. These tin-catalyzed nanowires produced by PPECVD were described as curving rather than having abrupt changes in

direction (Parlevliet and Cornish 2007), which was attributed to the nanowires comprising of amorphous silicon rather than crystalline silicon. The density at which they grew makes them a suitable for use as a thin film photovoltaic material. Tin is also a promising candidate for the production of semiconductor nanowire devices as it does not form intermediate compounds with silicon, it is electrically neutral in silicon and has limited silicon solubility (Iacopi et al. 2007). In comparison, gold is known to act as a recombination centre in silicon, adversely affecting the minority carrier lifetime (Sze and Ng 1981) and hence device performance of a photovoltaic device produced using silicon with gold impurities. Gold and tin were both used in this work to investigate the influence of morphology and presence of traps on the characteristics of silicon nanowire photovoltaic devices.

Silicon nanowires have been used to produce addressable photodetectors using photolithography techniques for locating where the nanowires grow (Servati et al. 2007). These photodiodes consisted of essentially intrinsic silicon nanowires grown on p-type crystalline silicon substrates via the VLS mechanism. The devices showed a promising photoresponse to incident illumination (Servati et al. 2007). This bodes well for the use of silicon nanowires as solar cells.

As components in a Grätzel solar cell the electron transport properties of silicon nanowires could remove the transport bottleneck that is present within a conventional Grätzel solar cell (Wu et al. 2002).

Large area p-n junction arrays have been produced from doped crystalline silicon using an HF and AgNO₃ etching technique (Peng et al. 2004). The p-n junction created showed a nonlinear and rectifying behavior with a turn-on voltage of ~1 V (Peng et al. 2004). Peng, Huang and co-workers (2004) also measured the IV characteristics of silicon nanowire arrays made of n-type silicon. They showed a rectifying behavior likely due to the formation of a Schottky diode. Later work by this group has shown that the silicon nanowire arrays created by the etching method are suitable for photovoltaic applications (Peng et al. 2005). The nanowires were used as part of an anti-reflection coating to improve the absorption of light by the solar cell. Unfortunately the efficiency of the device was less than a similar one produced without the nanowires, due to low current collection efficiencies at the front contact (Peng et al. 2005).

Tian, Zheng and co-workers (2007) have recently reported the fabrication of a single silicon nanowire based photovoltaic device. This device consists of a p-type nanowire encased in intrinsic polycrystalline silicon with a further layer of n-type polycrystalline silicon resulting in a coaxial wire type morphology (Tian et al. 2007). The nanowire was then etched to reveal the core and contacts were made to the core and outer n-layer some distance along the wire. Current Voltage (IV) characteristics of this silicon nanowire solar cell showed an open circuit voltage VOC of 0.26V, a short circuit current ISC of 0.503nA and a fill factor of 55% under AM 1.5G illumination (Tian et al. 2007). The short circuit current was found to be scalable with nanowire length while the open circuit voltage was maintained.

Amorphous silicon may be an alternative and advantageous material for the encasing intrinsic and n-layers as it has a much higher optical absorption coefficient in the visible portion of the spectrum than crystalline silicon (Shah et al. 1999). This work details several devices created using a hybrid of thin-film amorphous silicon and highly textured silicon nanowire layers. The nanowires were used as a weakly doped p-layer. The electrical characteristics of the created devices were measured using IV characterization techniques. Samples were also imaged using an FESEM to observe surface morphology changes from the pristine nanowires and to verify that silicon nanowires had grown on the sample.

Experimental Details

ITO coated Corning glass substrates were cleaned in an ultrasonic bath using decon-90, ultra-pure water and propanol. The substrates were dried using high purity nitrogen before being transferred into a vacuum system for deposition of a catalyst layer.

Gold and tin catalysts were used for the growth of silicon nanowires via the VLS mechanism. Catalyst films were kept at a constant 100nm in thickness for all samples.

Silicon nanowires were grown at high density using Pulsed PECVD (PPECVD) at a temperature of approximately 345°C. Silane was used as a source of silicon for VLS growth of the silicon nanowires. A square wave produced by a pulse generator (SRS Model DG535) was used to modulate the 13.56MHz signal used to produce a 35W plasma. A modulation frequency of 1000Hz was used and the mark space ratio was held at a constant ratio of 1:1. The RF power was supplied to an insulated circular plate electrode of 100mm in diameter that is 15mm beneath the upper electrode. The sample was allowed to heat up under 3.0 torr of argon for 35 minutes and for a further 35 minutes under the mixture of reactant gasses. The silicon nanowires were produced using silane mixed with diborane (1% in argon) with 70% silane and a plasma duration of 40 seconds. After the period of PPECVD, the plasma was switched off but gas flow and temperature were maintained allowing a further period of CVD of 10 minutes to aid the nanowire growth. The growth conditions used to produce the silicon nanowires in this work were selected and optimized for the high density growth of silicon nanowires.

Several different layers were used in creating the devices in this work. All of the layers were deposited within the one chamber. The amorphous silicon layers (intrinsic and n-type) were deposited at a temperature of 225°C and a chamber pressure of 0.7 torr. PECVD was used to deposit the amorphous silicon layers at a typical plasma power of 4W. Undiluted silane was used to create the intrinsic amorphous silicon layer and a deposition time of 25 minutes was used to produce a 470nm layer. The n-layer was produced over 3 minutes using a gas mixture of phosphine (1% in argon) and silane (100%) which deposited a 22nm layer.

After the deposition the system was purged with argon and cooled to near room temperature, the samples were then removed for further treatment. Back-contacts, or a series of Al contacts, were placed on the sample using the thermal evaporation system so that the electrical characteristics could be measured.

Once the contacts were in place the IV characteristics of the samples under dark and illuminated conditions were measured. Some of the samples were then mounted on SEM stubs for measurement using a ZEISS 1555 VP FESEM and Philips XL20 to verify the presence of silicon nanowires.

RESULTS

Silicon nanowires have been used, along with amorphous silicon, as a test bed for silicon nanowire based photovoltaics. A series of substrate-p-i-n devices were produced using gold and tin-catalyzed p-type nanowires which were coated with an intrinsic amorphous silicon layer and an n-type amorphous silicon layer. Under the growth conditions used, nanowires nucleated and grew before being coated in amorphous silicon layers.

Both gold and tin were found to produce high density growths of silicon nanowires under the growth conditions used, however the morphology of the nanowires were distinctly different for each catalyst. This difference in morphology can be seen in Figure 1. The average diameter of both the gold catalyzed nanowires and tin catalyzed silicon nanowires after the amorphous silicon layers had been deposited was 420nm. However, it should be noted that the tin catalyzed silicon nanowire samples had a much more uniform distribution of nanowires diameters than the gold catalyzed silicon nanowire samples as can be clearly seen in Figure 1. The extent and location of the gold and tin within the nanowire structure, and whether trace amounts are distributed along the nanowire itself is not clear from these micrographs. However, no steps were taken to remove the catalyst after the sample was produced so the original catalyst content is still within the finished photovoltaic device which could influence the electrical characteristics. The gold catalyzed silicon nanowires display growth defects such as kinking, which is common to crystalline nanowires. The nanowires in the tin catalyzed sample had a 'knotted' morphology, shown in the right panel in Figure 1, as previously described for tin-catalyzed nanowires produced by PPECVD with the same method (Parlevliet and Cornish 2007) which indicates an amorphous structure.

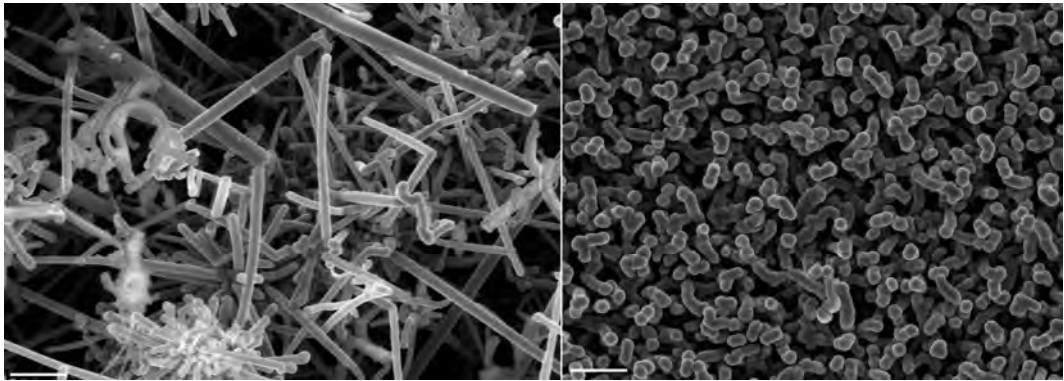


Fig 1 SEM micrograph of a gold catalyzed silicon nanowire photovoltaic device (left) and a tin catalyzed silicon nanowire photovoltaic device (right). The scale bar for both is 2 μ m

The gold catalyzed nanowires grown in this work were confirmed to be crystalline through x-ray diffraction measurements of the samples. Figure 2 shows XRD spectra from gold and tin catalyzed silicon nanowire photovoltaic devices. In the sample of silicon nanowires produced using a gold catalyst the silicon (111) and (220) peaks are clearly visible indicating the presence of crystalline silicon. Where a tin catalyst was used these peaks were not apparent which indicates the sample does not contain crystalline silicon and is entirely amorphous.

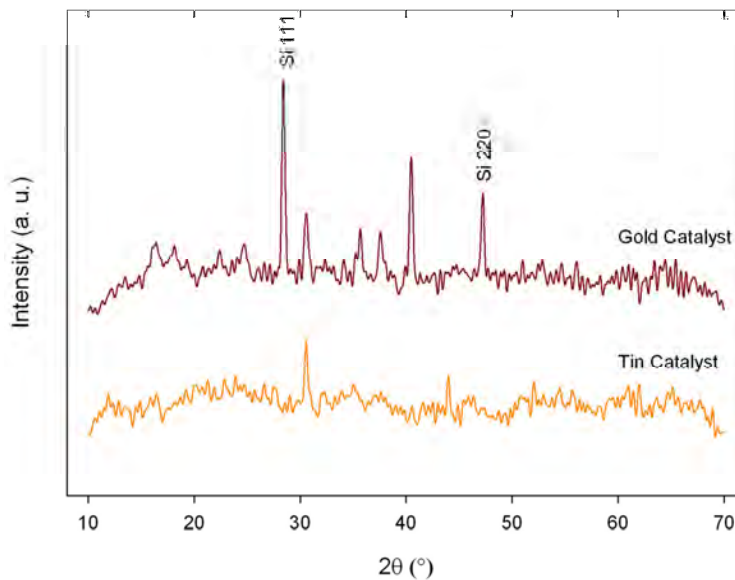


Fig 2 XRD spectra of silicon nanowire photovoltaic devices produced with gold and tin catalysts

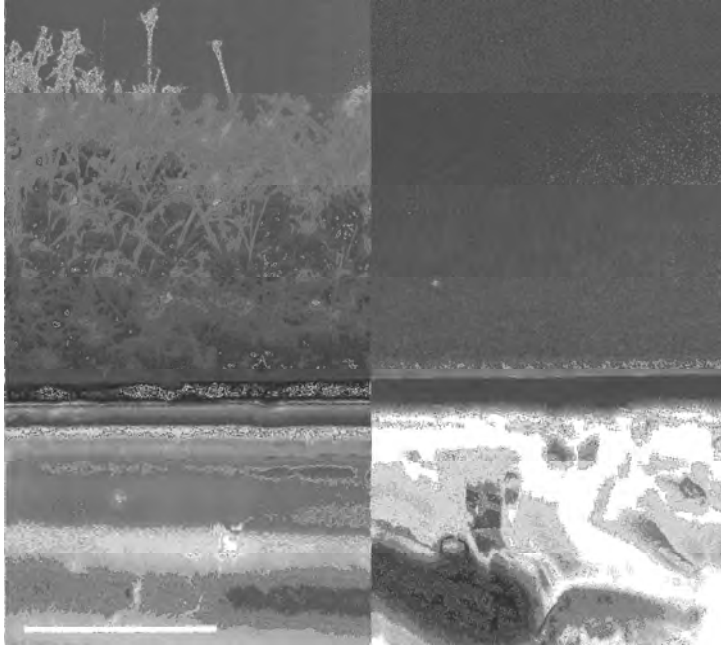


Fig 3 Cross-sectional SEM micrograph of a gold catalyzed silicon nanowire photovoltaic device (left) and tin catalyzed silicon nanowire photovoltaic device (right). The scale bar for both is 20 μm)

The silicon nanowire films produced using different catalysts had distinctly different thicknesses as is shown in Figure 3. In this figure the silicon nanowire photovoltaic device can be seen in cross-section. The lower portion of the image is the glass substrate. The gold-catalyzed nanowires films were much thicker in appearance when compared to the tin catalyzed silicon nanowire film. The average thickness of the gold catalyzed silicon nanowire film was measured to be 42 μm although there were many localized variations due to the loosely packed nature, high aspect ratio and random orientation of the gold catalyzed silicon nanowires. In comparison the tin catalyzed silicon nanowire films were much more compact and uniform in appearance with an average thickness of 3 μm .

The device produced using gold-catalyzed silicon nanowires, although being photoconductive and having a diode characteristic, did not generate any measurable photocurrent. The IV characteristic for this device is shown in Figure 4. The conceptual schematic in Figure 4 shows how the device was structured, although it should be noted that due to the wide spacing of the silicon nanowires the amorphous silicon will tend to encase the silicon nanowires rather than forming an even film. The lack of photocurrent is likely to arise from the thickness and weak doping of the p-layer in comparison to standard amorphous silicon devices, thickness of the device and shorts within the device. The detrimental influence of the gold contaminant within the nanowire on the minority carrier lifetime may also reduce the photocurrent.

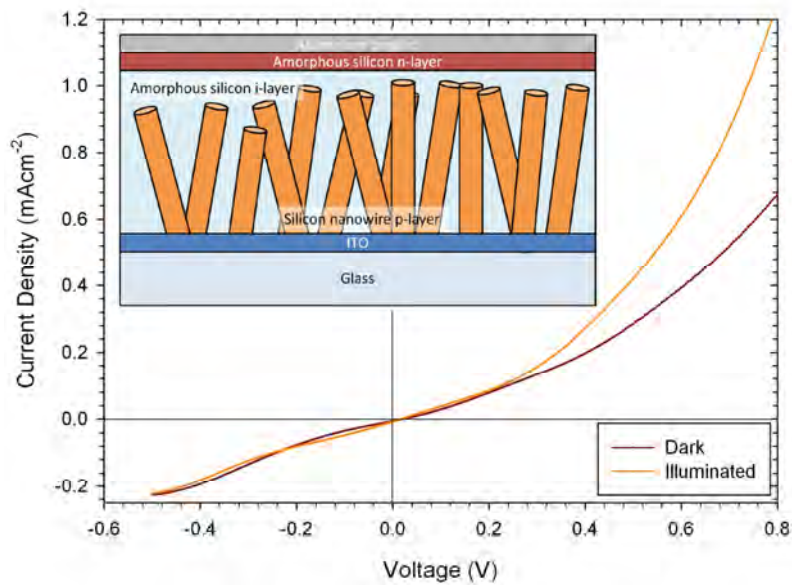


Fig 4 IV characteristics of a device using gold-catalyzed p-type nanowires with an amorphous intrinsic and n-layer. Inset: A conceptual schematic of the silicon nanowire device

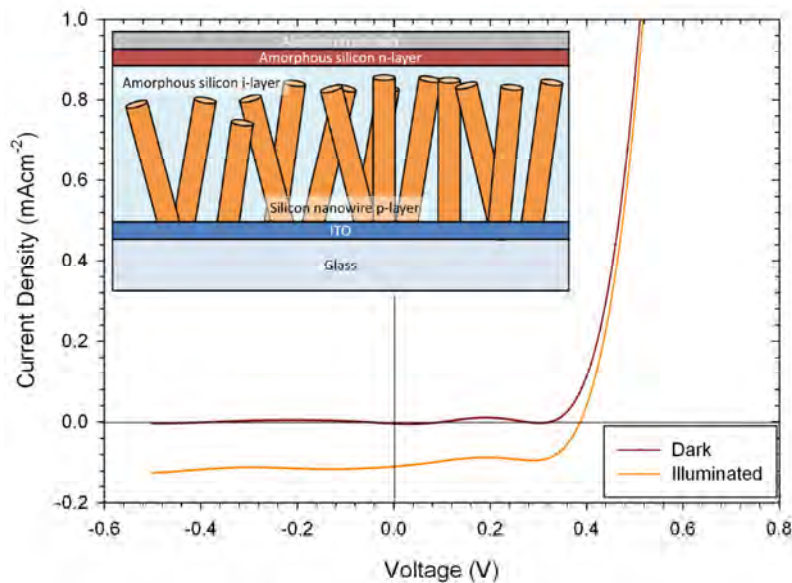


Fig 5 IV characteristics of a device using tin-catalyzed p-type nanowires with an amorphous intrinsic and n-layer. Inset: A conceptual schematic of the silicon nanowire device

A functioning solar cell was produced by lightly doping tin-catalyzed nanowires and using them as a p-layer in an amorphous silicon device in the same structure as the device shown in Figure 4. This device displayed a measurable photocurrent when illuminated. An IV characteristic of this device is shown in Figure 5. The efficiency of this device was found to be 0.031% with a VOC of 0.39V and a JSC of 0.11mAcm⁻². This efficiency is substantially lower than that of standard amorphous silicon devices and other silicon nanowire devices (Tian et al. 2007). However, when compared with the device using gold-catalyzed nanowires, the use of tin-catalyzed nanowires

produces thinner layers, in the order of $3\mu\text{m}$, and takes advantage of the fewer traps in tin-catalyzed silicon nanowires creating a device with a measurable photocurrent and efficiency. This low efficiency in this device is partly due to the lightly doped p-layer. A low ratio of dopant gas to silane was used in order to produce a high density growth of silicon nanowires as the dopant gasses were present 1% in argon. It was found that for lower partial pressures of silane the growth density of the silicon nanowires tended to decrease under these growth conditions. So to maintain a sufficiently high nanowire growth density the amount of dopant had to be kept fairly low, which results in a slightly p-type material. For more heavily doped nanowires the device should become more efficient.

A second reason for this low efficiency is the thickness of the p-type nanowire layer. This layer is very thick in comparison with the p-type amorphous silicon layer of $\sim 40\text{nm}$ which is normally used to produce thin film amorphous silicon p-i-n solar cells in this PECVD chamber. The much thicker p-layer with only slightly p-type nanowires would result in poor minority carrier transport out of the device. The VOC produced by the tin-catalyzed silicon nanowire device was also significantly lower ($\sim 0.4\text{V}$) than that for an amorphous silicon device ($\sim 0.8\text{V}$). This could be due to both the dopant profile and structure of the nanowires.

The morphology of the gold and tin catalyzed silicon nanowires were distinctly different and are likely to contribute to the different electrical properties of the devices produced using them. The gold-catalyzed silicon nanowires had an average film thickness an order of magnitude larger than that of the tin-catalyzed nanowires. This longer conduction path through an only slightly doped p-layer results in an increased series resistance within the device and a lower photocurrent. The demonstrated efficiency is substantially lower than that of other silicon nanowire devices (Tian et al. 2007). However, the VOC of the thin film silicon nanowire device was larger than that of the single nanowire photovoltaic device of Tian and co-workers (2007) due to the materials used. The use of amorphous silicon rather than microcrystalline silicon contributed to the higher VOC. Amorphous silicon sheaths would also have an advantage over polycrystalline materials as amorphous silicon can be deposited at temperatures far below the nanowire growth temperature ($\sim 345^\circ\text{C}$) thus ensuring the cessation of silicon nanowire growth

Conclusions

A prototype silicon nanowire based photovoltaic device was produced by using doped tin-catalyzed silicon nanowires as the p-layer. This device, although of low efficiency, had a demonstrable photocurrent. The photocurrent shown by the devices using tin-catalyzed doped silicon nanowires as a p-layer is encouraging and demonstrates the use of silicon nanowires, without the deep-level traps present in gold-catalyzed nanowires, as semiconductor nanostructures for photovoltaic applications. With optimization, by increasing the doping of the nanowire p-layer or by producing shorter silicon nanowires, the device would be expected to have higher efficiency and demonstrate the advantages of using silicon nanowires. These advantages include a high absorbance of light and the ease and low cost of manufacture of thin film devices. The thin film

devices could also show an improved resistance to photodegradation if crystalline nanowires, such as much finer gold-catalyzed silicon nanowires, were used, due to the crystalline content.

Acknowledgements

The authors acknowledge the facilities, scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterization & Analysis, The University of Western Australia (UWA), a facility funded by UWA, Western Australian and Commonwealth Governments.

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