Pulsed PECVD for the Growth of Silicon Nanowires

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Silicon nanowires of high density and high aspect ratio similar to those shown in the literature [1, 2] have been grown using a variation of Plasma Enhanced Chemical Vapour Deposition (PECVD) known as Pulsed Plasma Enhanced Chemical Vapour Deposition (PPECVD) using a range of different modulation frequencies. For the range of frequencies used it was found that the presence of a modulated silane plasma increases the average density and sample coverage of silicon nanowires. Both of these effects are proposed as being due to the increase in the number of times the plasma is struck and turned off during the deposition process. For low temperature growth of silicon nanowires the presence of a pulsed silane plasma improves the density and sample coverage of silicon nanowires.

INTRODUCTION

Recently there has been a great deal of interest in the fabrication of semiconductor nanomaterials and nanostructures. Silicon nanowires are one such variety of nanostructure. Silicon based nanostructures are attracting interest as the growth techniques are largely compatible with existing semiconductor fabrication processes.

There are several techniques used to grow silicon nanowires. These include the laser ablation of a silicon containing target [3], reactive ion etching [4] and magnetron sputtering of silicon [5]. The most common method of fabrication involves the Chemical Vapour Deposition (CVD) of a gas containing silicon and the subsequent metal catalyst moderated growth of silicon nanowires. This involves the Vapour Liquid Solid (VLS) mechanism as first proposed by Wagner and Ellis [6]. In the VLS mechanism, a thin layer of metal catalyst, usually Au, is deposited onto a substrate which is subsequently heated so as to melt the metal catalyst. Upon melting the catalyst tends to form islands or droplets. A gas containing silicon such as SiH_4 is then introduced into the system and is thermally decomposed and absorbed by the liquid metal catalyst. When the droplet becomes supersaturated with silicon, crystalline silicon is deposited underneath the catalyst droplet which rides on top of the developing nanowire. The presence of a catalyst droplet on one end of a nanowire is indicative of the VLS mechanism [6].

There is a variant of chemical vapour deposition known as Plasma Enhanced Chemical Vapour Deposition (PECVD) which uses a 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. With the addition of a metal catalyst, PECVD has been used to produce silicon nanowires and is known to improve the deposition rate of silicon nanowires [2]. A further modification of this deposition technique is known as Pulsed Plasma Enhanced Chemical Vapour Deposition (PPECVD).

PPECVD involves the modulation of the 13.56MHz RF signal used to generate the plasma [7]. Use of suitable apparatus allows the modification of the modulation frequency as well as the ratio of plasma on time to off time (mark space ratio). For the deposition of microcrystalline silicon thin films a modulation frequency of between 1kHz and 100kHz and a mark space ratio of 10% to 50% is used [8].This technique increases the deposition rate of a-Si, nc-Si and μc-Si while suppressing the dust formation that tends to occur when the deposition rate is increased simply by increasing the plasma power [9].

This work aims to determine the effect on growth rate and morphology of silicon nanowires grown using PPECVD via the VLS mechanism for a range of modulation frequencies. The addition of a pulsed plasma could lead to higher deposition rates or a denser and more uniform growth of silicon nanowires due to the suppression of dust formation and higher deposition rate generated by PPECVD.

EXPERIMENTAL DETAILS

Polished n-type Si(100) substrates were cleaned by an ultrasonic bath using decon-90, ultra-pure water and propanol. After a final ultra-pure water rinse the substrates were dried using high purity nitrogen before being transferred into a vacuum system for deposition of the catalyst layer.

Gold catalyst layers of 100nm in thickness were deposited onto the substrates by thermal evaporation of Au metal (99.99%) from a tungsten wire under vacuum. The thickness of the catalyst layer was measured in-situ using a quartz crystal microbalance. Gold was used as it is a catalyst often used to grow silicon nanowires since the eutectic temperature of gold and silicon is 363°C.

The catalyst coated samples were loaded into a parallel plate PECVD chamber and mounted on a heater block. The samples were heated to 335°C for 35 minutes in the presence of 3 Torr of argon. The argon was then removed and silane at 3 Torr was introduced in to the chamber, the system was allowed to stabilise for a further 15 minutes before the deposition commenced.

A square wave generated by a pulse generator (SRS Model DG535) was used to modulate the 13.56MHz signal used to generate the plasma. A range of modulation frequencies between 125Hz and 1000Hz were used and the mark space ratio was held at a constant ratio of 1:1. The deposition time for each of the modulation frequencies and catalyst thicknesses used was maintained at 5s or 10s with plasma followed by a 10 minute interval without the presence of the plasma. Following this, the system was evacuated.

Once the chamber was cooled to room temperature the samples were removed and mounted on Scanning Electron Microscope (SEM) stubs for measurement. The samples were analysed using a Phillips XL20 SEM.

RESULTS

The presence of a pulsed plasma during deposition, at any of the frequencies used, created a sample with a greater overall coverage of nanowires. That is, nanowires were found to grow all over the substrate rather than in limited areas of the substrate. This coverage also tended to increase with the frequency used.

Under the growth conditions used, the temperature of the substrate can vary across its surface. The substrate is held in a stainless steel substrate holder which is bolted directly to the heater block so as to hold the substrate snugly to the heater. However, the centre of the substrate can often be cooler than the portions in direct contact with the substrate holder. This leads to nanowire growth in limited areas of the substrate towards the edges as shown by the different coloured bands in figure 1b and the density of growth regions in figure 1a. Using the pulsed plasma it was found that the nanowires tended to grow in regions that covered larger portions of the substrate. In most samples this resulted in an even growth across the portion of the substrate coated in gold.

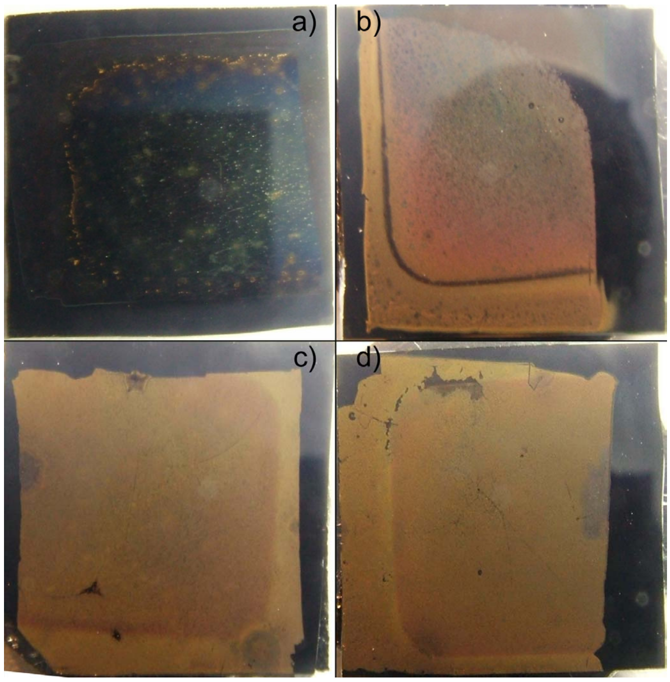

Figure 1. Silicon nanowire films on silicon substrates under different pulse frequencies, a) no pulse, b) 125Hz, c) 500Hz and d) 1000Hz.

The increase in coverage can be seen in figure 1 a series of photographs of the substrate, the substrates pictured are $1cm^2$ pieces of crystalline silicon. Figure 1a shows the patchy growth of silicon nanowires grown at 335°C with a plasma time of 5s with no pulsing on a 100nm Au coated substrate. The nanowire growth is evidenced by the gold-orange coloured spots scattered across the substrate with a higher density towards the edge of the gold film on the top and left of the image where the contact with the substrate holder was greatest. Figure 1b used the same growth condition with the addition of a pulsed plasma at 125Hz. It can be seen that the nanowire film covers a large portion of the substrate as demonstrated by the colouration of the film. Figures 1c and 1d show the samples produced using 500Hz and 1000Hz respectively. A more uniform growth across the gold coated portion of the substrate can be evidenced by the even colouration of the film.

A series of SEM micrographs were taken of each sample and the morphology and density of nanowire growth was measured. There was some variation in the density of silicon nanowires in differing regions of a single sample, so an average across several images of various locations on the sample was taken. It was found that the number of nanowires (NW) per μm^2 increased with the increase in plasma modulation frequency.

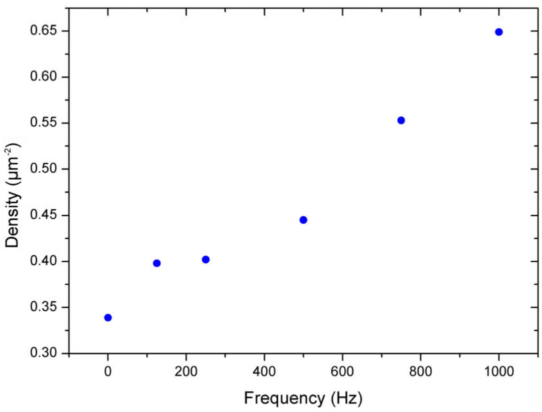

Figure 2. The increase in nanowire density for increasing plasma modulation frequency.

Figure 2 shows the increase in average nanowire density with increasing plasma modulation frequency. The density ranged from 0.34 µm^{-2} for the sample produced using no modulation frequency to 0.65 µm^{-2} for the samples produced with a modulation frequency of 1000Hz.

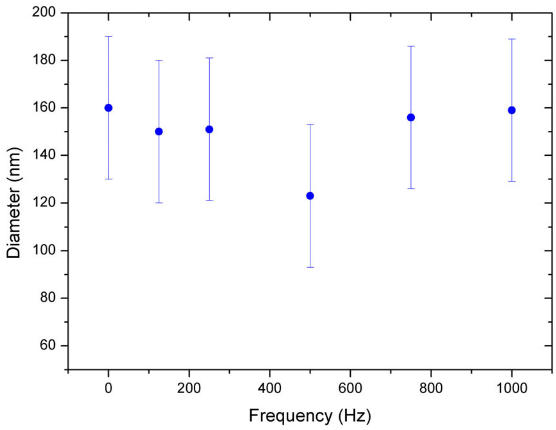

Figure 3. The average diameter of silicon nanowires grown by PPECVD

The average diameter of the nanowires was measured for each of the frequencies used. It was found that there was no notable change in nanowire diameter (figure 3) with an increase in plasma modulation frequency. The average nanowire diameter for nanowires grown using a 100nm thick Au catalyst layer was 150nm. The upper image (secondary electron) in Figure 4 shows typical nanowire growth of moderate density. The lower image (back scattered electrons) clearly shows that gold is present on the tips of the silicon nanowires, indicated by the bright dots on the end of the nanowires. This indicates that the growth mechanism used to produce the silicon nanowires was the Vapour-Liquid-Solid (VLS) mechanism.

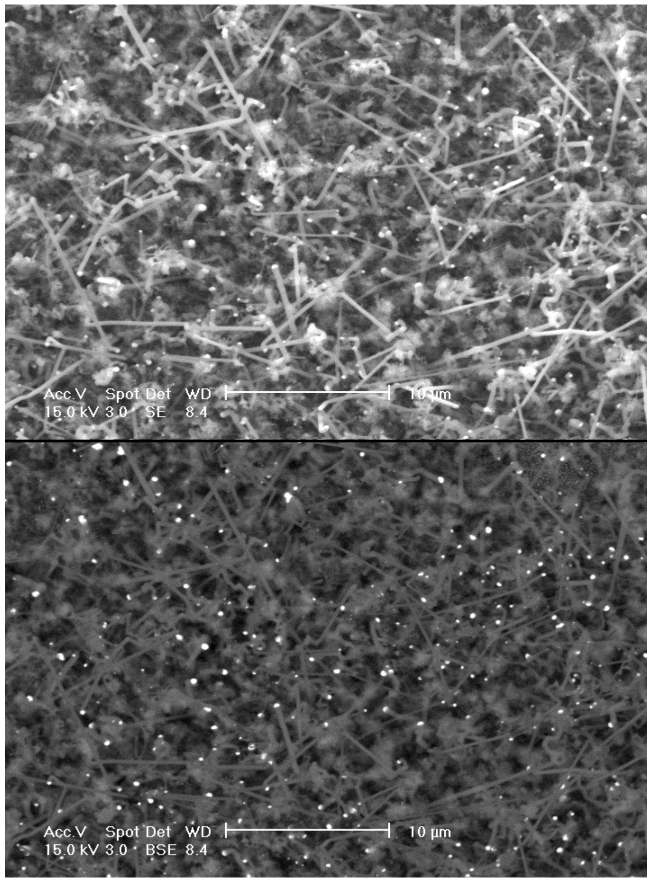

Figure 4. Typical growth of silicon nanowires images with a) secondary electron and b) back scattered electron detectors.

DISCUSSION

It was found that the average density of the nanowire growth increased with increased plasma modulation frequencies at the growth conditions used. This increase is quite distinct as seen in figure 2. The coverage of the sample by the nanowire film was also found to improve with the presence of a pulsed plasma and tended to improve with an increase in plasma modulation frequency. This trend can be seen in the photos in figure 1. Figure 1 also shows the colours that a silicon nanowire film of high density tends to produce, these mainly being a dull gold-orange colour. The density of nanowires grown in this work is greater than the densities of nanowires grown by other groups, who obtained nanowire densities of 3×10^{7} cm^{-2} [10], although under vastly different growth conditions. The nanowire density for the unmodulated plasma in this work was 3.4×10^{7} cm^{-2} which increased to 6.5×10^{7} cm^{-2} for the plasma modulated at 1000Hz.

Both the increase in sample coverage and nanowire density are proposed as being due to the increase in the number of times the plasma is struck and turned off during the deposition process. Previous work [11] has shown that differing plasma durations yield similar nanowire growth. This previous work was conducted using similar growth conditions to the current work, with the exception that the silane plasma was turned on and off manually. This work indicated that under the growth conditions used, the nanowire growth occurred primarily when the plasma was first struck or turned off. Hence an increase in the number of times the plasma is struck or turned off improves the growth of silicon nanowires under these conditions. The improvement in growth could be due to heating of the substrate by a current induced by the repeated striking of the plasma. It has been shown that the growth rate of silicon nanowires improves with increasing temperature [12]. The slight heating of the substrate by a repeatedly induced current would increase the temperature of the centre of the substrate to conditions more favourable to nanowire growth.

Another possibility is that the conditions in the steady state RF plasma are not optimal for the growth of Si nanowires. A better set of conditions occurs during the start-up or extinguishing phase of the plasma. These conditions may only be transitory but by repeatedly cycling through them improved nanowire growth is achieved.

PPECVD is known to increase the deposition rate of a-Si, nc-Si and μc-Si while suppressing the dust formation that tends to occur when the deposition rate is increased simply by increasing the plasma power [9]. It has also been previously shown that the use of a silane plasma increases the growth rate of silicon nanowires [2]. From this it follows that the use of PPECVD should yield an improved crop of silicon nanowires.

The diameter of the silicon nanowires grown using PPECVD did not exhibit any notable changes with an increase in plasma modulation frequency as seen in figure 3. The role of a plasma in silicon nanowire deposition is to increase the growth rate of silicon nanowire. However, it also improves the uncatalysed deposition of silicon across the substrate [2]. It was expected that with an increase in the uncatalysed deposition of silicon due to the introduction of a pulsed plasma the diameter of the silicon nanowires would increase due to the deposition of amorphous silicon on the wire during growth. The wires would also be expected to taper due to the build up of amorphous silicon around the base of the wire. However, this was not observed, which indicates that with the growth times and conditions used the uncatalysed deposition of amorphous silicon is very slight, not significantly adding to the nanowire diameter. The system used for this work deposits amorphous silicon thin films at an approximate rate of 0.3nm/s. For the deposition times used this would increase the average diameter of the nanowires by less than 6nm which is not readily detectable on the SEM used.

The VLS mechanism can be invoked to explain the growth of the silicon nanowires in this work. One of the characteristics of the VLS mechanism is a gold tip on the end of the nanowires. Figure 4 showing both the SE and BSE images of the same nanowires clearly shows the bright tip expected for nanowires grown by the VLS mechanism. Thus, the introduction of a modulated plasma has not affected the growth mechanism used to produce these silicon nanowires.

Conclusion

The use of PPECVD with a silane plasma modulated at frequencies between 125Hz and 1000Hz improved the yield of silicon nanowires produced at low deposition temperatures. The average density of silicon nanowires increased with an increased plasma modulation frequency due to the repeated striking of the plasma. The average diameter of the silicon nanowires grown was found to be unchanged with increased plasma modulation frequency. Although the use of PPECVD tends to increase the deposition rate of amorphous silicon, for the deposition times used the increase in amorphous silicon deposition rate did not affect the nanowire diameter. For low temperature growth of silicon nanowires the presence of a pulsed silane plasma improves the density and sample coverage of silicon nanowires.

References

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