SELECTIVE VAPOR-LIQUID-SOLID GROWTH OF NEEDLE ARRAYS BY HOTWIRE CHEMICAL VAPOR DEPOSITION WITH LOW SUBSTRATE TEMPERATURE

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ABSTRACT

We present the technology for low substrate temperature (~400°C) growth of high-density, defect-free (without kinks and branches), unidirectional arrays of Si needles with positive profiles and sub-µm tips using selective vapor-liquid-solid (VLS) mechanism. The low substrate temperature allows possible integration with on-chip CMOS circuitry or biomaterials with minimal thermal damage. The effect of processing parameters on needle growth modes is analyzed. Needles with similar characteristics have been successfully grown under the optimized conditions on Si<111>, Si<100> and polysilicon on insulator substrates. We envision these needle arrays (6-8µm tall, sub-µm tips) as high density electrodes of an integrated retinal implant.

KEYWORDS

Needles, HWCVD, VLS, low substrate temperature.

INTRODUCTION

Vapor-liquid-solid growth (VLS) is a common process for semiconductor nanowire synthesis [1]. VLS growth of doped silicon microprobe arrays at 700°C substrate temperature is discussed in [2] with successful integration of on-chip circuitry. Recently, in [3] the group extends its work to show a needle array of graded lengths. In [4] an array of silicon needles has been grown at 950°C. In [5], 10nm wide Si nanowires were grown at 320ºC, however, significant growth defects (bending and kinking) and lack of directional control were reported at these low temperatures. In this work the technology for low substrate temperature (~400°C) growth of high-density, defect-free, unidirectional arrays of needles with positive profiles and sub-µm tips using selective vapor-liquid-solid (VLS) mechanism is presented. The low substrate temperature allows possible integration of the needle arrays with on-chip CMOS circuitry or biomaterials with minimal thermal damage. In the VLS process gold (Au) is used to catalyze the decomposition of a Si containing source gas. Au and Si then form a liquid phase alloy at a eutectic temperature of 363ºC. Finally Si nanowires crystallize and grow from the supersaturated alloy [1]. The low substrate temperature (~400°C) growth was performed in a hot-wire CVD (HWCVD) chamber that offers the unique advantage of high filament temperature (1500 - 2200ºC) to decompose the SiH_4 (rate limiting step in the VLS mechanism), while maintaining a low substrate temperature (limited only by the Au-Si eutectic temperature ~363°C).

Low substrate temperature Si needle array growth in the HWCVD involved optimization of several parameters. An overview of the parameters varied in this work, their effect on needle growth modes and their optimum values for desired needle characteristics (high yield of needles from an array, controlled predictable, defect-free and unidirectional growth with sub-µm tips) is summarized in Table 1.

Table 1. *Parameter optimization for low substrate temperature needle array growth in the HWCVD by VLS mechanism.*

Parameter	**Range**	**Optimum Value**
Substrate temperature (°C) (critical for substrate degradation and growth initiation)	350 - 700	400
Filament temperature (°C) (controls SiH_4 decomposition efficiency)	1800 - 2100	2000
Substrate filament distance (cm) (critical for high yield of unidirectional needles in an array, but affects nucleation location)	2 - 6	3
SiH_4 flow rate (critical for direction control) Optimum SiH_4 partial pressure is about 5.2e-2mbar	5 - 13.5	8
Au thickness (nm) (affects nucleation)	~50 - ~ 372	~160nm for 2 µm diameter arrays
Growth time (min) (critical to avoid blanket powdery a-Si film deposition on needles)	15 - 120	30mins Growth saturation
Hydrogen dilution (sccm)	SiH_4 : H_2 8:120	No needle growth

EXPERIMENTAL RESULTS

Fabrication was started with a 2 inch, single side polished, p doped (resistivity of 4-6 Ω cm), Si<111> wafer. A representative set of arrays (2, 4 and 10µm dot arrays with 8, 10, 20 and 50µm end-end spacing between the dots, the smallest pattern being 2µm diameter dots with 8µm spacing) was patterned and repeated throughout the wafer using a laser writer (model LW405 from MICROTECH: 405nm gallium nitride diode writing laser). Au-Si seed dots were then patterned using evaporation

(without Cr adhesive layer) and liftoff. Needle growth was done in a HWCVD chamber.

Figure 1 portrays the optimization of the filament temperature during HWCVD needle growth. The substrate filament distance was kept at 6cm. Needles grew only where the Au-Si eutectic alloy had formed. Substrate annealing (600°C for 5min) followed by growth lead to substrate degradation, scattered metal mass and peeling. Low yield, singly nucleated, unidirectional needle growth was seen at a filament temperature of 2000°C and substrate temperature of 350°C. High filament temperature (2100°C) lead to substrate degradation.

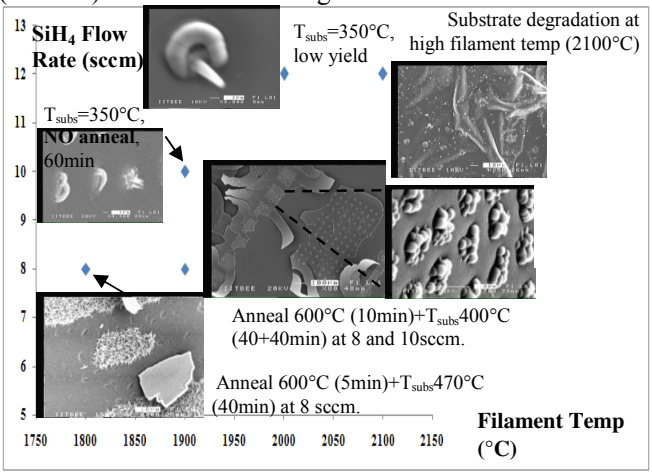


Figure 1. *Elimination of high substrate temperature (>600°C). Variation of filament temperature and SiH_4 flow rate during HWCVD needle growth.*

Substrate filament distance proved to be an important factor to get high yield unidirectional needle growth in the HWCVD (Fig. 2). Reducing the substrate filament distance reduces the time of flight (TOF) of Si atoms from the hotwire to the Au-Si eutectic alloy. Reduced TOF of Si atoms enables more efficient diffusion of Si into the Si-Au eutectic alloy. It also reduces the probability of the decomposed Si combining with other products of the decomposition. This in general minimizes unwanted powdery film deposition on the substrate that is commonly found in the HWCVD. Au thickness was a critical factor affecting the nucleation at a given substrate filament distance. The needle heights could be controlled by varying the SiH_4 partial pressures with the same SiH_4 flow rate by throttling the gate valve. From these experimental results it seemed that excellent control over unidirectional growth was possible as the substrate filament distance was reduced and the SiH_4 flow rate was correspondingly lowered (to reduce the oversupply of SiH_4). However when the substrate was too close to the filament (2cm), multiple nucleation dominated, with much shorter needles. The needles in this condition grew between the Au-Si dots within the array boundary.

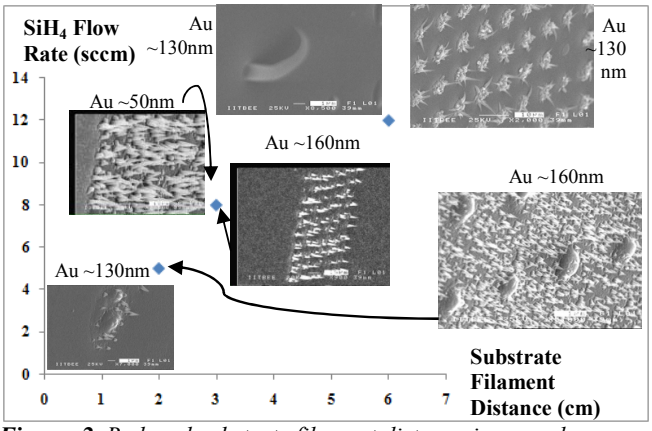


Figure 2. *Reduced substrate filament distance improved directionality but affected nucleation location (best results at 3cm).*

The trend in needle growth by VLS mechanism in the HWCVD during parameter optimization is shown in Fig. 3. With the optimized growth conditions given in Table 1 it is possible to get good control over the shape (positive profiles, sub-µm tips, 6-8µm height) and directionality of the needles.

Figure 4 finetunes the growth parameters. Nullification of needle growth at substrate temperatures ≥700°C in the HWCVD and a reduction in the needle height with an increase in substrate temperature were observed. The 10sccm flow rate was the boundary for directional control at the optimized substrate temperature of 400°C (max needle height of 6-8µm).

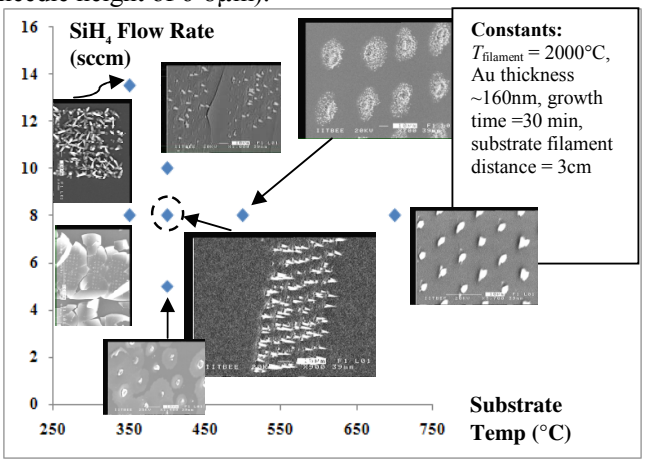
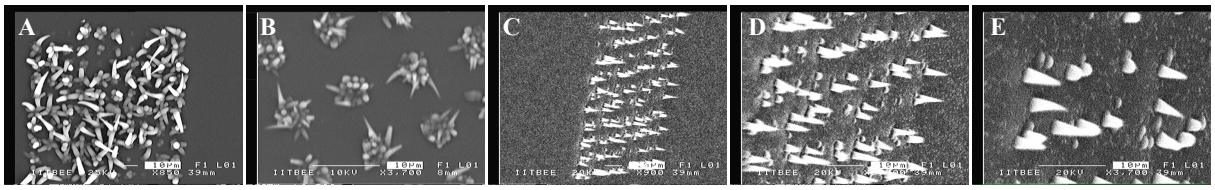


Figure 4. *Finetuning of SiH_4 flow rate and substrate temperature to achieve high growth yield and directional control (best results at 8sccm /400°C).*

Si<111> wafer orientation is traditionally used for VLS growth of silicon nanowires [1-5]. Substrate orientation independence of HWCVD grown needles by VLS method is shown in Fig. 5 (HWCVD growth is not epitaxial by nature but diffusion-based). The excellent, defect-free directional control of growth, especially on deposited



A: *SiH_4 13.5sccm, Au ~50nm at 3cm substrate filament distance*

B: *SiH_4 12.5sccm, Au ~50nm at 6cm substrate filament distance*

C,D,E: *SiH_4 8sccm, Au~160nm at 3cm substrate filament distance (different arrays, closeup views)* ***(A-E)****: Low substrate temperature = 350-400°C, filament temperature 2000°C, scale bar = 10µm, starting seed arrays for VLS growth (A-E): 2µm diameter Au-Si dots with 8µm end-end spacing*

Figure 3. *Optimizing parameters in the HWCVD for low substrate temperature unidirectional needle array growth.*

polysilicon on insulator substrates opens integration possibilities of the needle arrays with an integrated biocompatible retinal implant device.

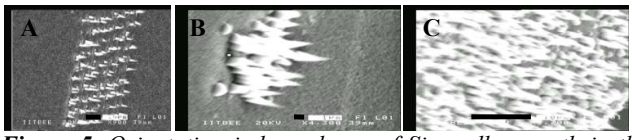


Figure 5. *Orientation independence of Si needle growth in the HWCVD. (**A.** Growth from Si<111> 2µm diameter array. **B.** 4µm dot closeup- Si<100>. **C.** Growth from Au strip on a PolySi on insulator array). Scale bars: A and C = 10µm, B = 1µm.*

Figure 6 shows that longer growth times did not result in taller needles. Needles 6-8µm tall were seen after 30min of growth. Unidirectional defect free growth was observed for all growth times.

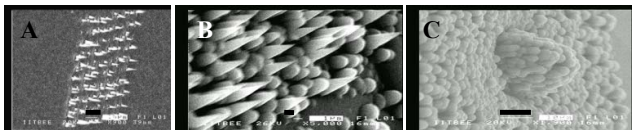


Figure 6. *Longer growth times did not result in taller needles Needles grown with optimized conditions in Table 1.*
A. *Needle growth for 30min (2µm diameter array).* ***B.*** *Needle growth from Au strip for 60 min.* ***C.*** *Needle growth for 120min from Au strip. Scale bars: A and C = 10µm, B = 1µm.*

HWCVD NEEDLE GROWTH ANALYSIS

The needle arrays developed here are simply large nanowires and therefore the analysis of nanowires by VLS mechanism in [6] is adapted for this work. Following the notation in [6] we assume that the needle to be grown is $X_pY_qZ_r$ needle (X, Y, and Z are needle elements, and p, q, and r are mole fractions, p, q, and r may be an integer and one or two of them may be zero). $X_pY_qZ_r$ together with X, Y, and Z are referred to as R_S species and the droplet including the foreign element catalytic agent (FECA)/X is the R_L species where X=Si and FECA=Au.

Several instances of needle overgrowth in the HWCVD were observed. These growths were often grass-like and multi directional, but almost always defect free. This is possibly due to the continuous oversupply of the R_S species or improper choice of the SiH_4 flow rate. In the HWCVD, since gas molecules are decomposed by two-dimensional collision between the hot filament surface and the gas molecules instead of three dimensional collisions between electrons and gas molecules (e.g., in PECVD), the decomposition efficiency in the HWCVD becomes very high. Thus it is reasonable to assume that there is likely to have been a very high concentration of the R_S species in particular Si, in the HWCVD (compared to other VLS growth chambers) leading to an "oversupply." Oversupply of R_S species, and interplay of surface energies of the needle and/or liquid droplet, could result in droplet oscillation and multiple nucleation. There have also been instances where the Au dot arrays were not visible on the substrate after the VLS growth in the HWCVD. It is possible that the abundance of atomic hydrogen (SiH_4 decomposition product) resulted in physical etching of the Au dot arrays. Needle growth in the HWCVD by VLS mechanism is likely to suffer from competition with parasitic deposition of a blanket film of amorphous Si (a-Si) especially at low substrate temperatures, high filament temperatures, and oversupply of R_s species if the incubation time for VLS growth initiation is high. Dilution of the incoming SiH_4 gas with hydrogen (to decrease the deposition rate of a-Si), was not conducive to needle growth. Reasons for droplet overgrowth, decay, disintegration and instability during VLS growth is discussed in detail in [6].

Needle Shaped Unidirectional Defect Free Growth

The needles grown in the HWCVD were free of growth defects like kinks and branches, which are often undesired artifacts of VLS growth especially in non-isothermal conditions. Absence of growth defects suggests a relatively isothermal environment in the HWCVD at a SiH_4 partial pressure of 0.02mbar. This environment is particularly useful for integration with CMOS circuitry or biomaterials. However at the 2cm substrate filament distance the needle growth from a 2µm diameter Au-Si dot exhibited a U-shape (Fig. 2) indicating a possibility of bending defect under this condition. The SiH_4 flow rate was a crucial factor affecting the directionality of growth.

Needle-shaped VLS growth in the HWCVD can happen under one of the following conditions (adapted from [6] to fit the experimental conditions in the HWCVD). First: The droplet is not sufficiently stable at the growth temperature and pressure to resist decay or disintegration by hydrodynamic stress or the impulse of charge particles. So, the droplet becomes gradually smaller as the needle grows. Second: One or more of the R_S species react with FECA gradually, altering the very composition of the droplet alloy. This is usually observed at higher temperatures [6]. In this work, substrate temperature is deliberately maintained low, but it is possible that one or more of the R_s species could react with the FECA alloy at lower substrate temperatures due to the proximity of the filament at 2000°C, reduced TOF of the R_s species to the FECA/X alloy and the high decomposition rate of the SiH_4 in the HWCVD. The second condition explains the nullification of needle growth at temperatures ≥700°C in the HWCVD. Scattered metal particles at substrate temperatures > 600°C, lying on the substrate surface corroborate the suggestion that the loss of metal mass due to disintegration by hydrodynamic stress does indeed take place.

Growth Saturation

The needles grown by VLS mechanism in the HWCVD under the optimized growth conditions were about 6-8 µm tall with submicron tips and positive profiles. Longer growth times did not result in increasing the height of the needle. Unidirectionality of growth and absence of defects (i.e. no kinks or bends) was observed for longer growth times (upto 120min). Increasing the SiH_4 flow rates, partial pressures or substrate temperatures in an attempt to increase the growth rate lead to grass-like growth in multiple directions or substrate degradation, possibly due to oversupply of Si. It appears as though the needle growth in the HWCVD saturates at a height of 6-8µm. Adapted from [6], under Si-rich conditions (especially for HWCVD), growth was limited by saturation possibly due to a reduction in the difference of electronegativities between the Au-Si eutectic alloy droplet and the Si that lands on the droplet. At one point, the difference is too small for Si to land on the droplet surface leading to saturation in the height of the needle. If the FECA/X droplet has very large fraction of X (the fraction of X=Si increases with time), then the difference in electronegativities may be too small for Si, to land on the droplet surface. Low composition X in the R_L species is needed for smooth diffusion of X into the FECA/X droplet. For longer growth times, it is possible that after needle growth saturation there is a deposition of a blanket layer of amorphous Si on the substrate surface, especially since the decomposition of the incoming SiH_4 gas continues to occur at the HWCVD filament while the growth has reached saturation in about 30 min.

SUMMARY

From the experimental observations in this work, SiH_4 flow rate was the critical parameter for direction control, with low substrate temperature preventing substrate degradation (peeling, cracking, scattered metal mass or debris) (Fig. 1). Growth nullification was seen at substrate temperatures ≥700°C (Fig. 4). Au thickness affected the nucleation (Fig. 2) and substrate filament distance was critical to achieve unidirectional high growth yield but affected the nucleation location (Fig. 2). Needle growth in the HWCVD by VLS mechanism suffers from competition with parasitic deposition of amorphous Si (a-Si) especially at low substrate temperatures, high filament temperatures or with oversupply of SiH_4 if the incubation time for VLS growth initiation is high. Optimization of substrate temperature and growth time tilted the competition in favor of needle growth. Growth was limited by saturation possibly due to a reduction in the difference of electronegativities between the Au-Si eutectic alloy droplet and the Si that lands on the droplet. Finally it was established that defect free unidirectional needle growth could take place regardless of the orientation of Si. Needles of similar characteristics grew on Si<100>, Si<111> and polysilicon on insulator substrates.

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