

PECVD synthesis of Si nanowires.

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ABSTRACT

Silicon nanowires 42 nm in diameter and up to 70 micrometer long have been obtained by utilizing a common (for an average nanofabrication facility) plasma equipment set that did not require special modifications. Further studies are needed to improve the synthesis process parameters and gold catalyst particle distribution.

Keywords: Si nano-wire, PECVD, gold catalyst, nano-particle

1 INTRODUCTION

Since the discovery of carbon nanotubes, other one-dimensional as well as differently nanostructured systems have been attracting increasing attention due to potentially unlimited technological applications. These materials are expected to help overcome existing technological limits of the semiconductor industry [1] and provide new venues to obtain higher device density and to develop new devices (e.g. single-electron [2]) that utilize new unexplored principles. Silicon nanowires (SiNWs) have already been employed to create test prototypes of field effect transistors [3,4], nanosensors [5,6] and thermoelectric devices [3]. Besides, due to quantum confinement SiNWs manifest properties of a direct band-gap semiconductor [7,8] that, unlike bulk Si, may be of interest for optoelectronics applications.

A number of Si nanowire growth methods such as laser ablation [9], thermal evaporation [10], CVD [11], plasma enhanced CVD (PECVD) [12,13], have already been reported. The CVD methods require assistance of heavy metal catalysts such as Au, Cu, Ag, Ni, Ga, In [11-14]. Catalytic growth gives the benefit of lower synthesis temperatures and flexibility in choosing the sample areas where the wires are needed. If the PECVD method is chosen the precursor gas molecules are already dissociated in the plasma discharge, so the temperature required is only slightly above of Si-catalytic metal eutectic point.

2 EXPERIMENTAL

It is an unfortunate but established fact that conducting nano-scale research requires expensive and complex instrumentation that an average research laboratory rarely can afford. Therefore, there is trend to concentrate

equipment, expertise and highly skilled dedicated staff in user facilities that allow uninterrupted operations and experience transfer. On the other hand, continuous flow of diverse ideas, tasks, and users compounded by competition among research groups often exclude time consuming or highly specialized modifications to existing equipment that put additional strain on researchers and staff members to find ways to fully utilize and/or expand available capabilities. This work is a result of such explorations.

A commercial STS310PC plasma enhanced CVD system (PECVD) initially designed to deposit silicon oxides and nitrides was utilized to synthesize SiNWs. The precursor gas was 2% silane diluted with nitrogen. The hot flat bottom electrode where the substrates are located during deposition is grounded. The other electrode which also serves as a gas shower head is located about 2 cm above.

Silane/nitrogen mixture flow, gas process pressure and the process temperature were variable. The 13.56 MHz RF power was kept constant at 30W. The deposition time was usually 2 minutes. The process temperature was set at 380°C.

A KJL CMS-18 multi-target sputtering deposition system along with a Unaxis RIE-ICP etcher was needed to create catalyst particles on the sample surface. Process pressures in both systems were 5 mtorr.

Gold was selected as the catalytic material. The Au-Si eutectic temperature is 363°C which is within working temperature range of the PECVD system. To prevent gold diffusion into the sample bulk the substrates (20x20 mm pieces of Si(100) wafer) were coated with a 1 micrometer thick PECVD silicon oxide. The substrates were deliberately made larger to compare SiNWs growth condition on the sample flat surface and near its edge where the plasma electrical field was disturbed.

It has been reported recently that in co-sputtered Au/SiO₂ films, gold will precipitate in bulk even at room temperatures and create nanometer-size particles in the SiO₂ matrix if Au/Si atomic ratio exceeds a critical value [15].

In this work, a 500 nm composite film was deposited by simultaneous sputtering from SiO₂ and Au targets. The sputtering rates were adjusted in such a way that the Au/Si atomic ratio would be close to 1. The resulting film was etched back 60 nm in the RIE-ICP system by using a CHF₃-based chemistry. The process parameters were tuned to obtain isotropic SiO₂ matrix etching. SEM inspection of

the resulting surface revealed exposed clusters averaging 15 nm in size (Fig.1).

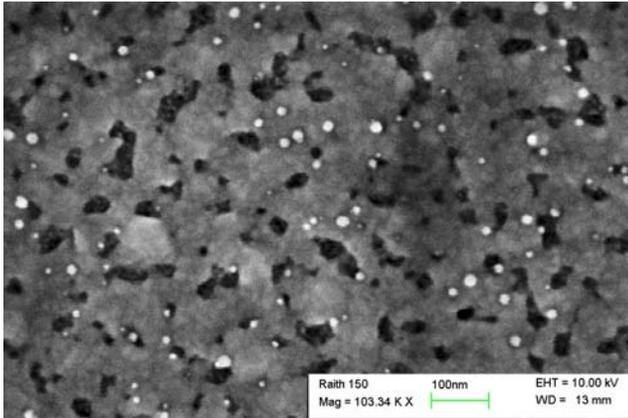


Figure 1. Catalyst particles after plasma surface preparations.

3 RESULTS AND DISCUSSION

First attempts to grow silicon nanowires were not successful due to a very high deposition rate. Resulting films were unstructured masses of amorphous silicon. Only after gas flow and process pressure were reduced to the lowest possible values when the plasma was still stable, were the SiNWs obtained (Fig.2). As it can be seen from the picture the catalytic particle is at the tip of the nanowire indicating the tip-growth mechanism which in this case may be described by the VLS model [16], according to which Si diffuses into a particle before solidifying in the shape of wire.

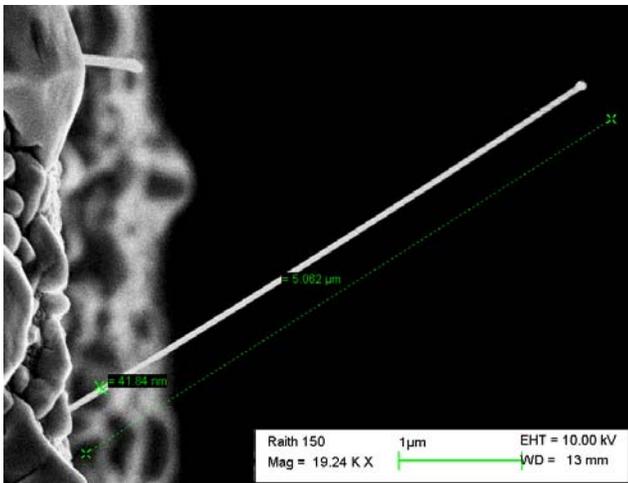


Figure 1. A 5 micrometer long silicon nanowire. The size of the wire at the root and at the tip is the same, 42 nm across. The catalyst particle is visible at the top.

It should be noted that the wires were observed only at the edges of the substrate. SEM inspections of the sample

areas away from the edge revealed interwoven worm-like structures (Fig.3a) occasionally dotted with protruding short stubs of nanowires (Fig.3b). This indicates that the nanowire growth was hindered by the incoming flux of ions and other radicals to the surface, causing a random movement of the catalyst particles over the sample surface and resulting in the worm-like shapes of crystallized silicon.

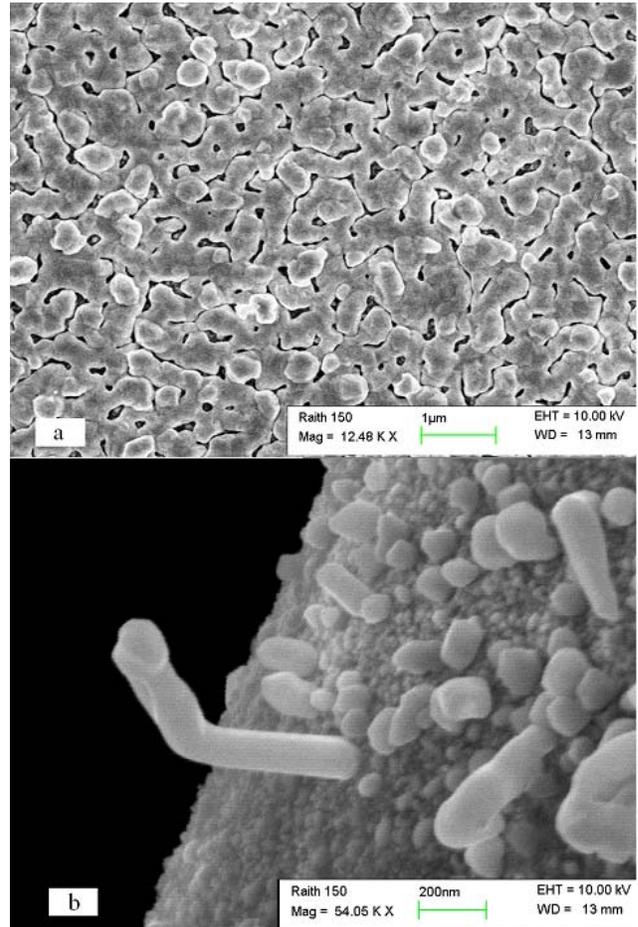


Figure 3. A typical sample surface after PECVD plasma process.

At the same time, different plasma conditions at the sample edges were more favorable for the SiNWs growth. To test these assumptions a grounded cage made of 100x100 tungsten mesh was placed over the substrates during deposition. Although it did not lead to the nanowire growth on the flat areas of the samples, the density and length of SiNWs were visibly bigger at the edges (Fig.4). A nanowire as long as 70 micrometers long was discovered that amounts to a 35microns/min growth rate. It was also observed that the wires were not tapered, i.e. the thickness at the root and at the tip was the same (around 40 nm) indicating a negligible mass loss by the gold particle as it was moving along the wire during the growth.

To complete this paper a different attempt of growing Si nano-structures should be mentioned. A piece of Si(100) wafer with a native silicon oxide intact was sputter coated with a thin (7.5 nm) gold film and processed in the PECVD system with parameters identical to the experiments when the SiNWs shown in Fig.4 were obtained. SEM inspections of the sample did not discover any nanotubes but, instead, revealed a self-organized array of interconnected 270 nm diameter nanoballs (Fig.5). It is too early to speculate on origin and the growth mechanism of these Si-based nanostructures, but one can already come to the conclusion that possibilities of obtaining a variety of structures through process parameters changing and catalyst tailoring look promising.

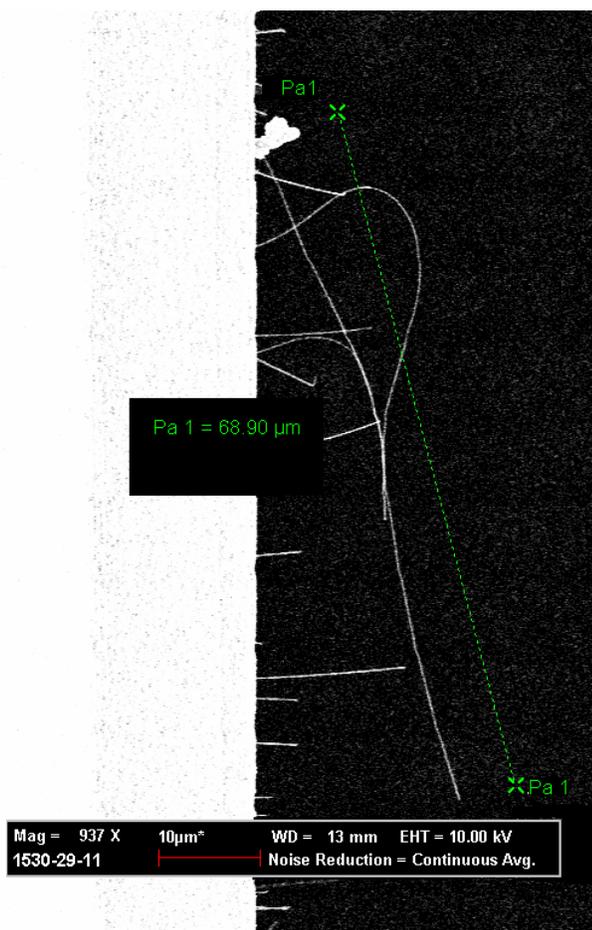


Figure 4. A 70 micrometer long silicon nanowire.

4 CONCLUSIONS

This paper shows that with a proper catalyst conditioning it is possible to grow silicon nanowires and other Si-based nanostructures in a typical nanofabrication facility. Tens-of-micrometers-long wires and a high growth rate are achievable with help of commercially available PECVD equipment.

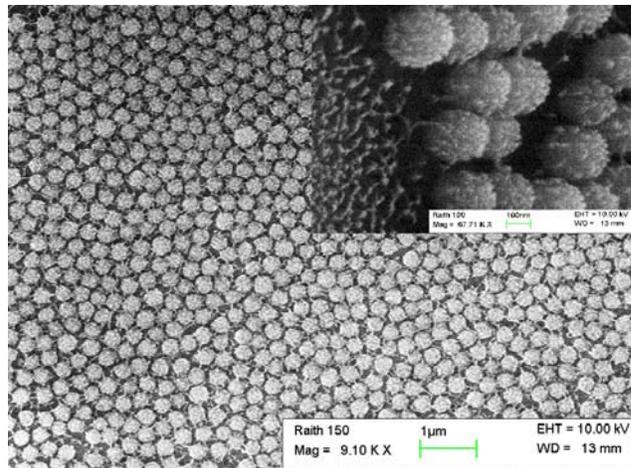


Figure 5. An array of 270 nm diameter nanoballs grown on Si surface.

REFERENCES

- [1] L.E.Brus, Appl.Phys.A 53, 465, 1991
- [2] A.Tilke, R.H.Blick, H.Lorenz, J.P.Kotthaus, J.Appl.Phys. 89, 8159, 2001.
- [3] Y.Cui, C.M.Lieber, Science, 291, 851, 2001
- [4] M.C.McAlpine, R.S.Friedman, S.Jin, K.-H.Lin, W.U.Wang, C.M.Lieber, Nano Lett, 3, 1531, 2003.
- [5] Y.Cui, Q.We, H.Park, C.M.Lieber, Science, 293, 1289, 2001
- [6] J.H.Hahm, C.M.Lieber, Nano Lett, 4, 51, 2004.
- [7] L.T.Canham, Appl.Phys.Lett., 57, 1046, 1990.
- [8] G.D.Sanders, C.Yia-Chung, Phys.Rev.B, 45, 9202, 1992.
- [9] A.M.Morales, C.M.Lieber, Science, 279, 208, 1998.
- [10] H.Pan, S.Lim, C.Poh, H.Sun, X.Wu, Y.Feng, J.Lin, Nanotech., 16, 417, 2005.
- [11] J.Westwater, D.P.Gosain, S.Tomiya, S.Usui, H.Ruda, J.Vac.Sci.Tech.B, 15, 554, 1997.
- [12] S.Hoffman, C.Ducati, R.J.Neill, S.Piscanec, A.C.Ferrari, J.Geng, R.E.Dunin-Borkowski, J.Robertson, J.Appl.Phys., 94, 6005, 2003.
- [13] H.Griffiths, C.Xu, T.Barrass, M.Cooke, F.Iacopi, P.Vereecken, S.Esconjauregui, Surf.&Coat.Tech., 201, 9215, 2007.
- [14] G.A.Bootsma, H.J.Gassen, J.Cryst.Growth, 10, 223, 1971.
- [15] K.-H. Jung, J.-W.Yoon, N.Koshizaki, Y.-S.Kwon, Current Appl.Phys. in press, 2007
- [16] R.S.Wagner, W.C.Ellis, Appl.Phys.Lett., 4, 89, 1964.