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# Achieving sub-50 nm controlled diameter of aperiodic Si nanowire arrays by ultrasonic catalyst removal for photonic applications

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**Abstract.** We report an alternative approach to fabricate the vertically aligned aperiodic Si nanowire arrays by controlling the diameter of the Ag nanoparticles and tuneable ultrasonic removal. The process begins by sputtering the Ag thin film (t=5 nm) on the Si/SiO2 substrates. Followed by Ag thin film, annealed for various temperature (T=300°C, 400°C, 500°C and 600°C) to selectively achieve a high density, well-spaced and diameter controlled Ag nanoparticles (AgNPs) on the Si/SiO2 substrates. The sacrificial layer of AgNPs size indicates the controlled diameter of the Si nanowire arrays. Image J analysis for various annealed samples gives an indication of the high density, uniformity and equal distribution of closely packed AgNPs. Furthermore, the AgNPs covered with Au/Pd mesh (5 nm) as a template, was removed by ultrasonication in the etchant solution for several times in different intervals of preparation. The conventional and facile metal assisted electroless etching approach was finally employed to fabricate the vertically aperiodic sub-50 nm SiNWAs, can be applicable to various nanoscale opto-electronic applications.

## INTRODUCTION

Semiconductor nanowires are promising candidates for future nano-electronics and nano-photonics applications. Silicon nanowires (SiNWs) have taken much attention due to their compatibility with their existing semiconductor technology. Si nanowires fabricated by employing self-assembled patterns are integrated into bottom-up and top-down approaches due to their high-resolution and avoidance of expensive lithographic processes. These approaches have allowed new designs such as silicon nanowire (SiNW) arrays for various applications such as solar cells [1], photodetectors [2], supercapactiors [3] and high-capacity Li-ion battery anodes [4]. Recently, a complex top-down approach has been widely used by indirectly patterning the catalyst by dip coating with a monolayer of silica beads [5], by Langmuir–Blodgett assembly method followed by metal assisted chemical etching approach [6,7]. Although, it approaches to produce SiNW arrays with control diameters, it suffers from the drawback of using the complex processes and also for producing SiNW forests with low areal coverage. In our present work, we have incorporated a reliable, scalable and cost effective technique to pattern the catalysts and fabricate aperiodic SiNW arrays with control diameters by feasible ultrasonic removal of metal nano-catalyst.

## EXPERIMENT

### Material Synthesis

Single crystalline *n*-type Si (100) wfers with $\rho$ =1-10 Ω cm were used to develop SiNWs by using a facile metal assisted electroless chemical etching (MacETch) process. The overall fabrication process is shown in Fig. 1. After a conventional piranha cleaning process, a thin layer of $SiO_2$ was deposited by thermally annealing the Si substrate at

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1000°C for few min under $O_2$ atmosphere. Hereafter, the Ag thin film of 5 nm was sputtered on as-deposited $SiO_2$/Si substrates. The substrate is then annealed for various temperatures from (T=300°C, 400°C, 500°C and 600°C) for 1 hr in a quartz tube under Ar atmosphere (Ar = 50 sccm) to de-wet the Ag film into a monolayer of well-spaced Ag nanoparticles (AgNPs) with a selective range of diameter followed by buffer oxide etching (BOE) of $SiO_2$ layer to lift-off AgNPs from the surface. Hereafter, the Au/Pd coating on AgNPs/$SiO_2$/Si wafers of 5 nm was deposited by sputtering and after that a sacrificial layer of AgNPs were removed by employing an ultrasonication to obtain a Au catalyst mesh. Finally, the Si substrates were etched for few minutes by using an aqueous solution of HF (40%) and $H_2O_2$ (30%) mixture, having a molar ratio of $\rho$[M] = [HF]/([H2O2]+[HF])> 0.80 to obtained a vertically aligned SiNWAs with a self-controlled diameter.

## Material Characterization

Surface morphological study for vertical SiNWs were investigated by field emission scanning electron microscopy FE-SEM (Zeiss, Ultra-55) equipped with EDX (Oxford Instruments). The diameter of the AgNPs were estimated by Image J analysis software.

## RESULTS AND DISCUSSION

Thin-film dewetting is a scalable and robust process for the creation of self-assembled monolayers of metal nanoparticles in the 10–500 nm size range on oxide surfaces [5]. The dewetting behavior has been shown to spontaneously occur for metals such as Ag [8], Co [9], Ni [10], Cu [11], Au [12], and Pt [13] in a few decades. Fig. 2(a)-(d) shows a scanning electron microscopy (FESEM) images of dewetted AgNPs on Si wafer surface. It can be

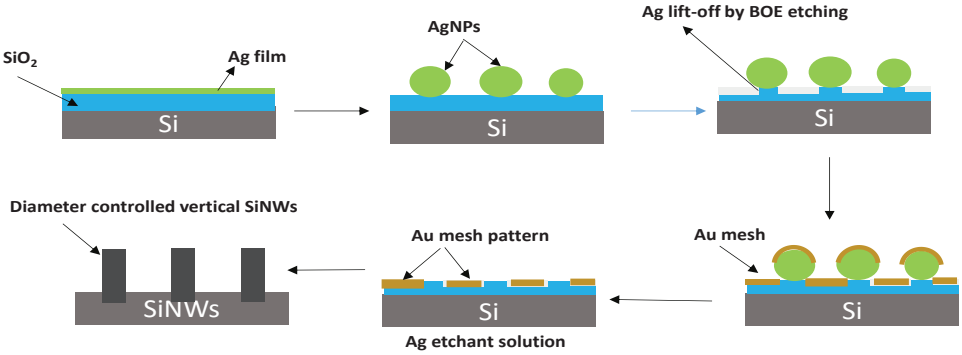


**FIGURE 1:** Represents the schematic diagram of the fabrication process to fabricate SiNWAs with dewetted metal nano-particles.

seen that the nanoparticles are naturally well spaced over the whole $SiO_2$/Si surface. At low temperature the AgNPs grow with a very small diameter, forming a very highly dense and compact structure on the surface. Moreover as the temperature increases, the nanoparticle grows bigger with a very low dense formation with no uniform diameter

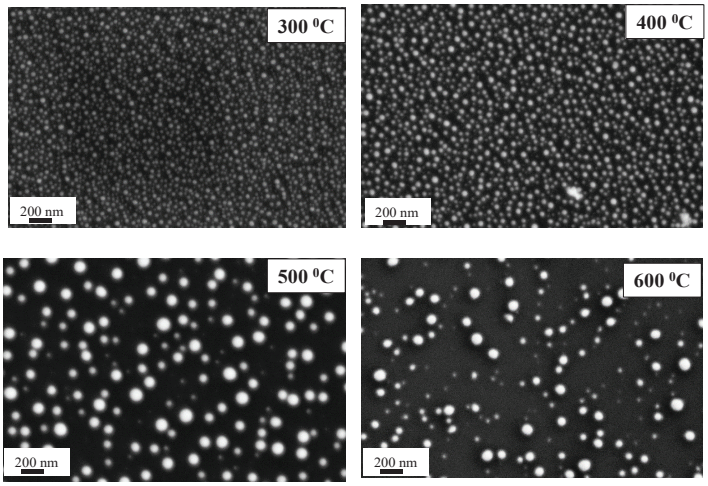


**FIGURE 2:** SEM images of the formation of deweted AgNPs annealing at (a) 300°C (b) 400°C (c) 500°C and (d) 600°C.

separation. Thus, the temperature effect increases the diameter of AgNPs and also increases the spacing between nanoparticles. In addition to Ag, some other metals such as Ni and Au could also form metal particles upon annealing

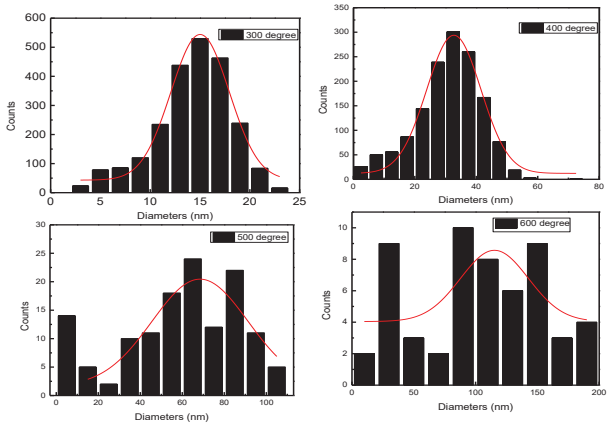


**FIGURE 3:** Various diametric distribution of AgNPs annealed at (a) 300°C (b) 400°C (c) 500°C and (d) 600°C represented by Image J analysis.

as reported in the literature [10,12].

To further elucidate the particle size distribution by varying different temperatures, Image J analysis has been carried out as shown in Fig. 3 (a)-(d). It is clearly seen that at low temperature of 300°C, the diameter of AgNPs are in the range of the 10-20 nm with the very high surface coverage. As we further increase the temperature to 400°C, the particles distribution shift to higher value from 30-50 nm with a sharp Gaussian curve at an optimum surface area as compared to the previous one. Moreover, at 500°C, the particle size increases even more with a very few nanoparticles in the selected region which is in well co-related with the FESEM images. Finally, as we increases to 600°C, there is a non-uniform distribution of diameter of AgNPs in the range of 50-150 nm with the very low surface coverage within the selected region. It is to be noted that, the diameter and the spacing of the SiNWs are determined by the dimensions and the spacing of the sacrificial AgNPs.

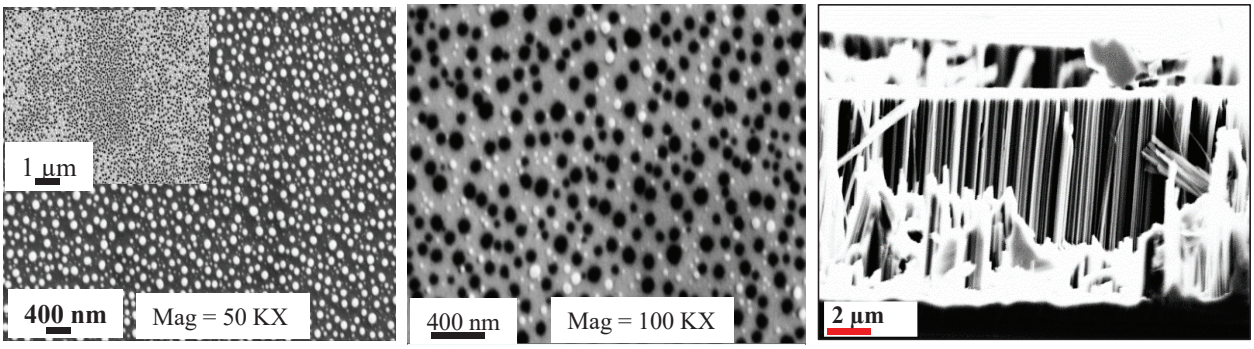


**FIGURE 4:** (a) Surface morphology image of Au/Pd thin film of 10 nm, sputtered on AgNPs. Inset shows the FESEM image of obtained Au/Pd metal mesh after removing the sacrificial AgNPs by ultrasonic removal (b) Demonstrates the magnified SEM image of the Au/Pd metal catalyst and (c) Cross-sectional morphology of SiNWAs fabricated by metal assisted electroless etching technique.

Hereafter, the samples were immersed in a standard buffered oxide etching (BOE) solution ($HF:NH_4F$= 6:1; v:v) in an ice bath with the temperature to as low as 0°C with constant ultrasonic vibration for 30 sec. The process is mainly used in the microelectronic industries for oxide removal on Si substrates. Here, to get an ease of removing the sacrificial metal nanoparticles, the BOE etching of the sample has been carried out, which undercuts the oxide film under the AgNPs and facilitates the subsequent lift-off process [14,15]. Hereafter, the Au/Pd metal mesh of 10 nm has been sputtered onto the AgNPs as a metal mesh pattern on the substrates as seen in Fig. 4 (a). Hereafter, a very facile and easily removal of Ag metal nanoparticles have been incorporated by immersing the samples in an etchant solution ($NH_4OH:H_2O_2$: methanol = 1:1:2; v:v:v) at room temperature and constantly sonicated for 15 min in each interval of time for 4 times. The inset of the Fig. 4 (a) shows the low magnification of FESEM image for AgNPs that are ultrasonic removed and has leave the place vacant with only a Au/Pd metal mesh with a nano holes over the large surface on the $SiO_2$/Si substrates. After sonication it is seen that most of the AgNPs covered with Au/Pd are etched from the surface

leaving behind a gold mesh pattern on the substrates. Fig 4. (b) Shows the extrapolated SEM image of the inset shown in Fig. 4 (b). The $SiO_2$/Si substrates with the patterned Au/Pd metal mesh are finally etched by employing very facile metal assisted electroless etching technique to develop the vertically aligned SiNWs. Fig. 4 (c) demonstrates the highly dense sub-50 nm diameter of vertically aligned aperiodic SiNW arrays. It is found that the SiNWs follow the same pattern as the sacrificial dewetted Ag metal particles. Hence, the diameter of the SiNWs can be controlled by using AgNPs as a sacrificial layer on Si substrates.

## CONCLUSIONS

In summary, we have demonstrated a facile method for the fabrication of aperiodic SiNW arrays with controlled diameters of AgNPs. The method employs a dewetting process to fabricate a well-spaced and compact Ag metal nanoparticles with a large and uniform surface coverage on a Si substrate. The Ag metal nanoparticles are used successfully as a sacrificial template to pattern a catalyst metal mesh by employing ultrasonic catalytic removal process. The Au/Pd metal mesh was finally used to catalyze solution-etching Si underneath it, leaving SiNW arrays. This technique can be easily scaled-up for large production of SiNW arrays at a very low cost for optoelectronic and photonic applications.

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