Large scale low cost fabrication of diameter controllable silicon nanowire arrays

Leimeng Sun[1], Yu Fan[1], Xinghui Wang[1], Rahmat Agung Susantyoko[1] and Qing Zhang[1]

Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798.

E-mail: eqzhang@ntu.edu.sg

Abstract: We report on a novel solution etching method to fabricate vertically aligned aperiodic silicon nanowire (SiNW) arrays. We begin with a simple dewetting process to fabricate a monolayer of well-spaced metal particles *in situ* on a silicon wafer. The particles function as a sacrificial template to pattern a Ti/Au catalyst film into a metal mesh and the size of particles directly determines the diameter of SiNW. A conventional metal assisted chemical etching process is then carried out with the obtained metal mesh as a catalyst to realize a vertically aligned SiNW array at a large scale and low cost.

1. Introduction

Silicon nanowire (SiNW) arrays have attracted intensive research attention in recent years owing to their great promise in various applications [1-6]. For example, in photovoltaic (PV) devices, due to the extremely strong optical absorption in solar spectrum, SiNW arrays with less than 1% equivalent of Si materials are expected to achieve the same amount of light absorption as traditional planar wafer-based PV devices, greatly reducing the raw materials cost of silicon PV devices [1, 2]. For lithium ion battery (LIB) anodes, SiNW arrays fabricated directly on a stainless steel current collector are shown to be more capable of accommodating significant volume changes of Si during lithiation/de-lithiation processes than traditional bulk or micron sized Si particles, greatly improving electrochemical performance of Si anodes [3, 4].

Basically, SiNW arrays can be fabricated using bottom up and top down approaches. Vapor-liquid-solid (VLS) is a well-established and the most popular bottom up method [7]. It usually produces randomly aligned SiNWs. Vertically aligned SiNWs can also be achieved by either employing a template [8] or using $SiCl_4$ [9] as the precursor. A big problem with the VLS method is the catalyst contamination which could be caused by high temperature diffusion of gold catalyst into SiNWs [10]. The metal defects greatly degrade the life-time and diffusion lengths of minority carriers in the SiNWs and are highly undesirable in electronic applications. In addition, the VLS process is known to be impractical for large scale applications.

Opposite to the bottom up methods in which SiNWs grow up from a substrate, in top down methods, SiNWs are prepared by etching bulk Si. Reactive ion etching (RIE) in combination with a high-resolution-lithography-patterned mask is a CMOS compatible method that offers precise control over nanowire diameters, spacing and locations [11]. The drawback of this method is the limited aspect ratio achievable, especially when the SiNW spacing is small. Moreover, It is an expensive method and unsuitable for large scale applications such as PVs. Another newly developed top down method that has attracted much research interests in recent years is metal assisted chemical etching (MACE) [12, 13]. In a typical MACE process, a Si wafer loaded with

catalyst metals is immersed in an aqueous solution containing HF and an oxidizing agent such as H_2O_2 to perform catalyzed etching. Although detailed etching mechanisms are under argument, a general picture describing the etching process has been suggested: (1) when a Si wafer loaded with catalysts is immersed into the etching solution, the oxidant such as H_2O_2 is preferentially reduced at the surface of the noble catalyst metal due to the catalytic effect of the metal. (2) The holes generated by the reduction reaction inject into Si that is in contact with the catalysts and cause oxidation of Si. (3) The oxidized Si is etched by the HF solution and fresh Si is exposed for oxidation. As the concentration of holes is maximal at the metal/Si interface, the etching rate of the Si beneath the catalysts is much faster than the bare Si. As a result, the Si beneath the catalysts is continuously dissolved. In contrast, bare Si remains almost intact so that SiNWs are formed [13]. Although simple, scalable and cost-effective, SiNW diameter and spacing are not controllable in MACE method, owing to the random distribution of the catalyst metal particles that are prepared through electroless or physical vapor deposition (PVD). It should be pointed that the parameters, like SiNW diameter and spacing, actually play critical roles in many applications. For example, the volume change of Si during charge/discharge processes could be up to 400%, a relatively large inter-wire spacing is therefore essential for SiNWs based anodes to accommodate huge volume changes [3, 4].

To realize SiNW arrays with controlled diameters and spacing, a straightforward approach is to pattern the catalyst film under which silicon is dissolved in the etching process. This has been successfully demonstrated using nanospheres (polystyrene (PS) spheres or silica spheres) [14-16] or anodic alumina membranes (AAMs) [17-19] as the sacrificial templates. Both methods are capable of producing periodic SiNW arrays, but the complicated fabrication processes and limited scalability suggest the techniques are not feasible for large scale low cost applications. In the nanospheres based methods, it is very difficult to assemble a large area closely packed nanosphere monolayer through simple spin coating or drop casting techniques. Although wafer

scale closely packed silica sphere monolayer has been demonstrated using the Langmuir-Blodgett method, precise process controlling still remains challenging [20]. In AAM based method, in addition to AAM fabrication, a critical pattern transfer is employed to transfer AAM pattern to the catalyst metal. Recently, some groups have developed several easier approaches to produce SiNW arrays with controllable diameters. Ruiyuan *et al* [21] dewetted a thin silver film to create pin holes and used the dewetted silver film as the catalyst to etch silicon underneath it. As dewetting process easily turns a silver film into nanoparticles, rather than uniform pin holes on it, the diameters and number density of the pin holes, or resulting SiNWs, are not easily controlled. In contrast, Azeredo *et al* [22] deposited a thin layer of gold onto dewetted silver nanoparticles and they chemically etched the silver nanoparticles, leaving a gold film with many pin holes. Au mesh pattern was employed to etch silicon for SiNWs. However, some of Ag particles could not be removed. Some silver nano-particles were etched, while the Au on them could still remain on the surface. This could result in non-uniformly distributed SiNWs, not suitable for large scale SiNW arrays fabrication.

Here, we demonstrate a reliable, scalable and cost-effective technique to pattern the catalysts and fabricate aperiodic SiNW arrays with controllable diameters and spacing. In this technique, a simple dewetting process is utilized to synthesize a naturally well-spaced metal particle monolayer *in situ* on silicon wafer surface. The monolayer of the metal particles is then used as a sacrificial template to pattern the catalyst film.

2. Silicon nanowire arrays fabrication

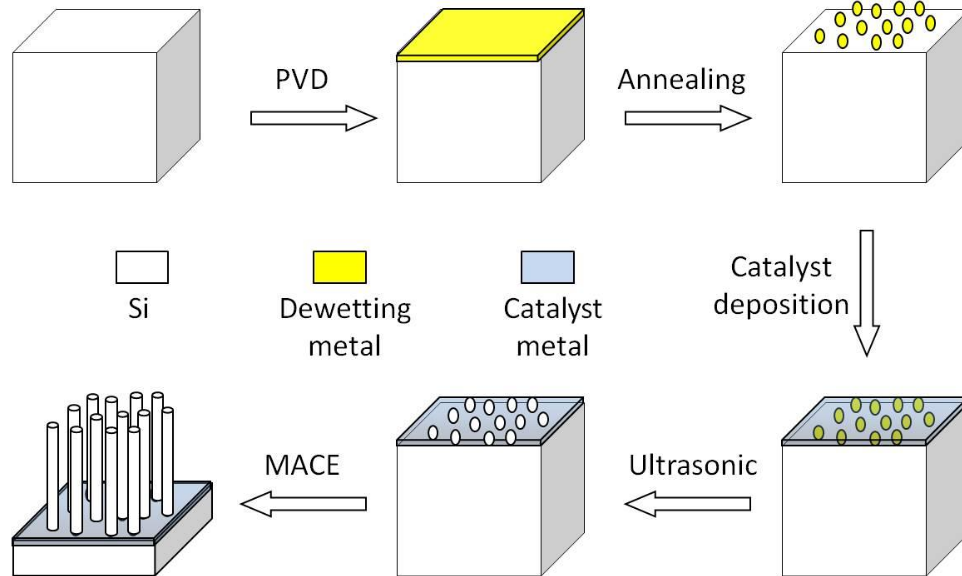

Figure 1. Schematic of the fabrication procedure to realize SiNW arrays with dewetted metal particles as a sacrificial template.

Figure 1 presents a schematic of the fabrication processes. For demonstration, a p-type or n-type Si (1 0 0) wafer is used as the substrate. After a conventional cleaning, a thin layer of Ag is deposited on the wafer by electron beam evaporation. The wafer is then annealed in a quartz tube at ~600°C under Argon atmosphere for several minutes to de-wet the Ag film into a monolayer of well-spaced Ag particles. A Ti/Au bi-layer is sequentially deposited on the Si wafer and the sacrificial Ag particles are removed by ultrasonic to obtain a catalyst mesh. Finally, the wafer is immersed into an etching solution containing deionized water, HF and H_2O_2 to obtain a vertically aligned SiNW array.

3. Results and discussion

Figure 2(a) shows a scanning electron microscopy (SEM) image of dewetted Ag particles on Si wafer surface. The metal particles are naturally well spaced. In addition to Ag, some other metals such as Ni and Au could also form metal particles upon annealing. Figure 2(b) presents the obtained Ti/Au catalyst mesh after removing the sacrificial Ag particles. From this SEM image, one can see that Ag particles are removed so that Ag particles would not affect following etching process. The underlying Ti layer is critical in this technique and it has two functions. First, it greatly enhances the adherence of Au catalyst film onto Si substrates so that Au film could survive the harsh ultrasonic treatment and remain as a continuous film. Second, it promotes the formation of a very thin but uniform Au film. It is observed that the several catalyst metals (e.g. Au, Ag) exhibit very poor adhesion to Si. They could form a continuous catalyst film endurable to structural failure during patterning or transfer processes only when their films are very thick, typically, several tens of nanometres in previous reports.[14, 18] In addition, we find that, with a Ti adhesive inter-layer, Au metal very easily forms a thin continuous uniform film with a thickness down to ~10 nm. It is only with thin uniform Au film that the Ag nanoparticles can be removed completely using ultrasonic treatment. Upon immersion in etching process, the Ti layer is immediately etched away by HF solution so that Au film is directly in contact with Si, performing an active catalyst to etch Si underneath. Figure 2(c) depicts a top-view SEM image of a large area SiNW array fabricated using this method. The SiNWs follow the same pattern as the sacrificial dewetted metal particles. Figure 2(d) shows a tilted angle SEM image of the as-prepared SiNW array. The vertically aligned SiNWs are well spaced with a large inter-wire spacing. The diameter and spacing of the SiNWs are determined by the dimension and spacing of the sacrificial metal particles. In addition, it is noted that the lengths of the SiNWs are very uniform. This is because the etching proceeds precisely underneath of Au layer.

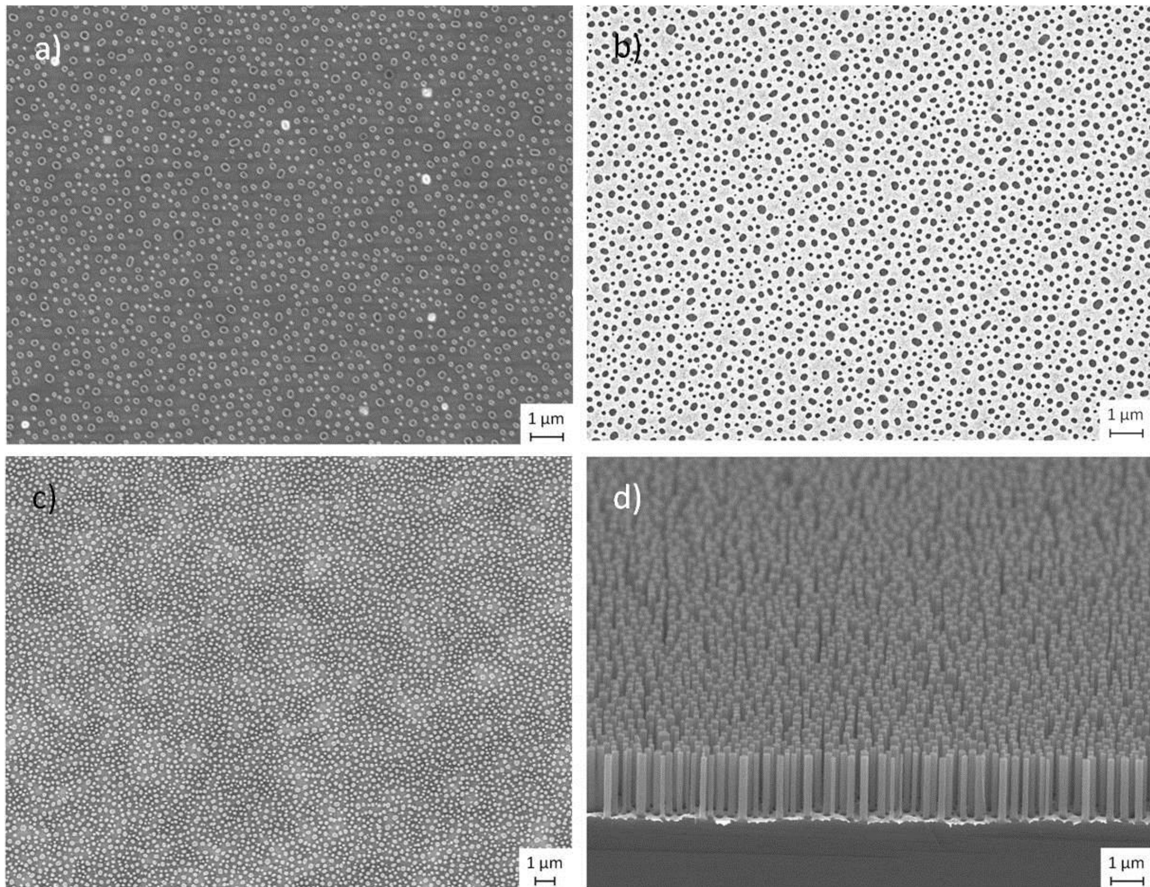

Figure 2. SEM images of (a) the dewetted Ag particles, (b) the obtained Ti/Au metal mesh after removing the sacrificial Ag particles, (c) top view of the obtained SiNW array and, (d) tilted angle view of the SiNW array.

Within this method, the sizes of dewetted metal particles determine the diameters of SiNWs, so changing the thickness of Ag film can directly control the diameters of SiNWs. In Figure 3, it shows different diameters SiNWs with same length produced by depositing different thickness of Ag films. For 10nm thick Ag film, the diameters of SiNWs are in a range from 40nm to 100nm because the diameters are much smaller than the lengths of SiNWs and SiNWs are likely to lean each other forming a SiNWs bundle (Figure 3(b)). Figure 3(d) and Figure 3(f) present the SiNWs produced basing on 30 and 50 nm thick Ag film respectively. 30nm thick Ag film could yield the diameters obviously much larger than 10nm thick Ag film. With the Ag film thickness increasing

from 10 nm to 50 nm, the average diameters of resulting SiNW arrays increase from 90nm to 420 nm, respectively.

The SEM images indicate that with the diameters becoming larger the spacing of SiNW arrays increase but the density of SiNWs goes down. However in spite of various dewetting metal thickness the nanoparticles area coverage remains at a similar value in Figure 4 and, therefore, metal-assisted etching rate could keep at a stable level for even etching different thickness samples so that the length of different diameters SiNWs could be well controlled. As an example of application, the optical anti-reflection of different diameters SiNWs arrays with the same length has been measured. Form Figure 5, one can see the reflectivity of the SiNW arrays decreases along with the thickness of coated Ag films from 10 nm to 50 nm. A certain reflectivity at a specific wavelength could be achieved by adjusting the diameters of SiNWs, suggesting that the SiNW arrays could be a candidate material for light trapping devices.

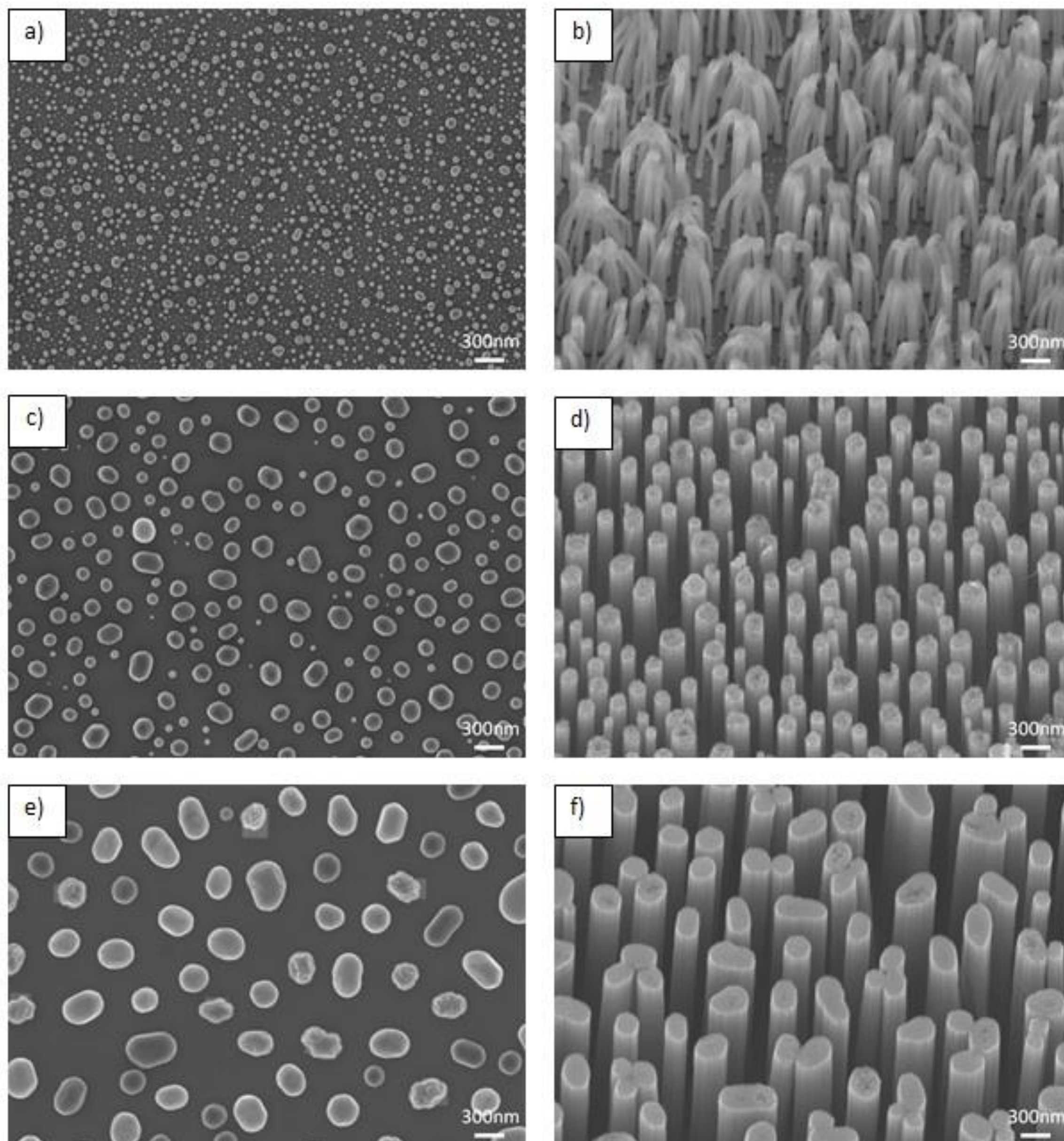

Figure 3. SEM images of (a) dewetted Ag particles formed from 10nm Ag film, (b) SiNWs formed by 10nm Ag film, (c) the dewetted Ag particles formed from 30nm Ag film, (d) the SiNWs formed by 30nm Ag film, (e) the dewetted Ag particles formed from 50nm Ag film and (f) The SiNWs formed by 50nm Ag film.

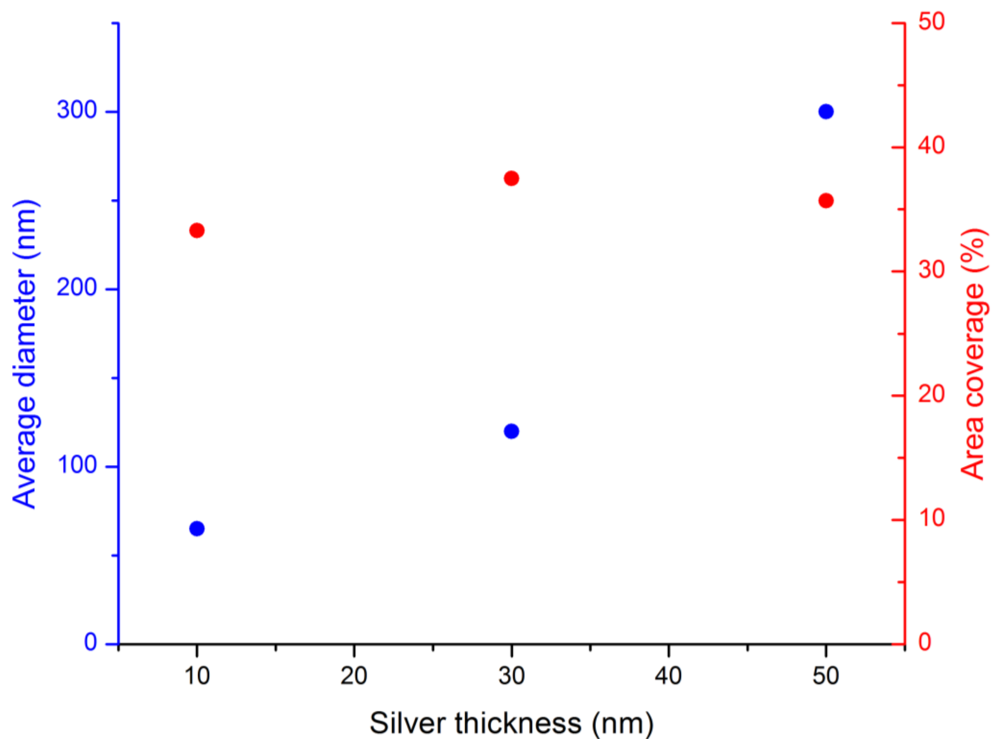

Figure 4. Comparison of silver nanoparticle size: Average diameter (blue) and area coverage (red) as a function of deposition metal thickness.

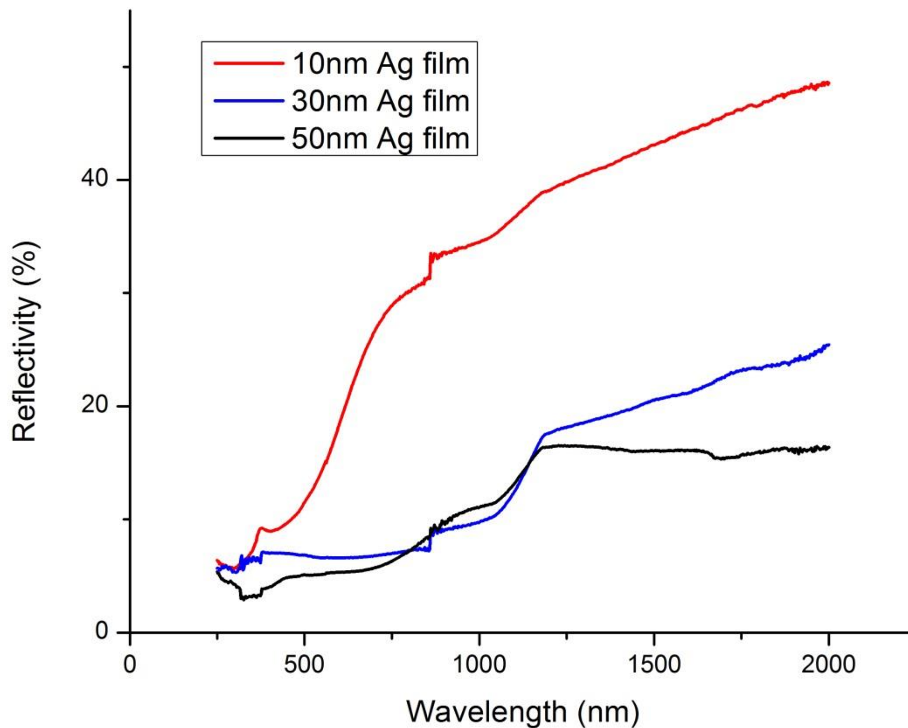

Figure 5. Reflectivity of SiNW arrays produced by 10nm, 30 nm and 50nm thick Ag films.

Compared to previous nanosphere and AAM based methods for periodic SiNWs, the SiNWs fabricated using this method show an aperiodic spacing. Actually, a good periodicity is not necessary in many applications, such as SiNW based LIB anodes, etc. In addition, a recent simulation also predicts that aperiodic SiNW arrays with random spacing for solar cell applications could achieve a factor of 2.35 higher power conversion efficiency than the ordered counterparts [23]. In terms of repeatability and process simplicity, the method presented here is more advantageous than nanosphere or AAM methods when a strict periodicity and a highly diameter uniformity of SiNWs are not necessary. Because dewetting metal and dewetting process to synthesize a monolayer of well-spaced metal particles *in situ* on Si wafer surface are definitely more repeatable and easier to control than the complicated nanospheres assembly and pattern

transfer processes. Moreover, all the processes employed in this method, including physical vapour deposition, dewetting and MACE are easily scalable. Therefore, our method is very promising for large area low cost applications of SiNW arrays.

4. Conclusion

In summary, we have demonstrated a novel method to fabricate large scale SiNW arrays with partly controlled diameters and interspacing. The method employs a dewetting process to fabricate a monolayer of well-spaced metal particles *in situ* on a Si substrate. The metal particles are then used as a sacrificial template to pattern a catalyst metal mesh, which is used to catalyse solution etching Si underneath it, leaving SiNW arrays. This technique can be easily up-scaled for mass production of SiNW arrays at a low cost.

Acknowledgements

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