

METALLIZATION OF SILICON NANOWIRES AND SERS RESPONSE FROM A SINGLE METALLIZED NANOWIRE

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ABSTRACT

A simple method was developed to metallize silicon nanowires using an electrodeless displacement deposition reaction. The resulting metal nanoparticles were self-assembled along a nanowire core to get a metal covering. The silver nanoparticles array aggregated along the nanowire was used as a SERS substrate. The enhancement for SERS response was high even from a single metallized nanowire. The significantly high enhancement came from the close interdistance among the neighbouring nanoparticles aggregated along nanowire by self-assembly.

KEYWORDS: silicon nanowire, metallization, SERS substrate, enhancement

INTRODUCTION

Interest in semiconductor nanowires, from silicon to germanium, has accelerated recently due to their lots of amazing properties. The further research is highly desirable, no matter the nanowires are used as sensor or as electric contact in microcircuit. The metallized nanowire, which is a kind of nanocomposite materials, has also attracted significant attention [1]. The existed metallization method, however, is seemingly complicated, such as vapor vacuum implantation, silver mirror reaction, and argon-ion sputtering [2]. Some simple methods were also reported, but the density and size of the nanoparticles formed onto nanowire surface were uncontrollable [2, 3]. Herewith we demonstrate a simple method to metallize silicon nanowire by dipping into an aqueous solution. The application was also studied by using as a SERS (Surface-Enhanced Raman Scattering) substrate.

EXPERIMENTAL

All the silicon nanowire arrays (chips) were produced at IME (Institute of Microelectronics), A*Star, Singapore [5]. The oxide layer on silicon nanowires surface was removed by dipping into Ammonium Fluoride Etchant. Then the metallization was immediately conducted by dipping into a fresh deposition solution with slightly shaking for different period of time.

RESULTS AND DISCUSSION

Since silicon is a known reducing reagent in the presence of metal ions, it is possible to deposit nanoparticles directly onto the silicon nanowires surface by a redox displacement reaction. The challenge is the native oxide layer on the nanowire surface, which inhibits the reaction by barricading the electron exchange process [4]. In the presence of HF in the deposition solution, the formed oxide layer was simul-

taneously dissolved into the solution, so that a sustainable and controllable reaction was obtained [3]. The concentration of HF or metal ion, here is Ag^+ , has been optimized and the growth process of the nanoparticles onto nanowire is presented in Figure 1.

The nucleation process of silver onto nanowire surface is not an instantaneous, but a progressive one, at least within the first 30 s (Figure 1 (a - d)). There are only several nuclei at the very beginning, but the number increases with the prolonging of the deposition time. After nucleation, growth process is also complicated. Although a universal mechanism is not yet completely understood, it is well accepted that there are two kinds growth processes, Coarsening and Aggregation [6]. From Figure 1 (d) to (f), the homogeneous growth of each individual nanoparticle is observed, suggesting the aggregation is the dominant growth process. In Figure 1 (g, h), the morphology of the resulting nanoparticles on the edge nanowire is different from the rest in central part, indicating the influence of transportation process. The extremely high surface area of nanowire means the transportation of metal ion is crucial [14].

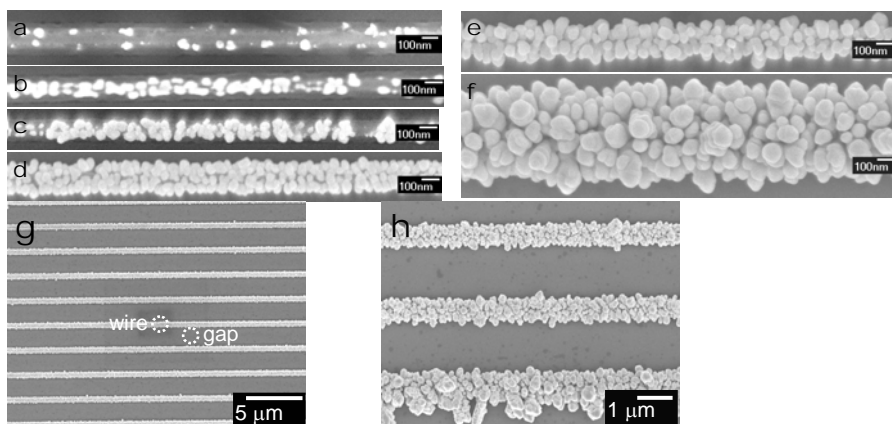


Figure 1. Dependence of nucleation and growth process on deposition time. All in $1 \times 10^{-3} \text{ M HF} + 1 \times 10^{-4} \text{ M AgNO}_3$ for different period of deposition time, a) 1 s; b) 5 s; c) 10 s; d) 30 s; e) 1 min; f, g, h) 5 min, respectively. Picture (g) is the central part of the nanowire array whereas (h) the edge part. The dashed-line circles in (g) indicate the laser spot position for SERS shown in Figure 2 (b).

The aggregated silver nanoparticles are used as a substrate for SERS, as shown in Figure 2. Rhodamine 6G (R6G) was selected as the Raman probe. Detection limit of 1 nM was reach (Figure 2 (a)). The laser was focused onto the substrate to get a spot with an area size of about $1.0 - 1.5 \mu\text{m}^2$. Therefore, all collected Raman signal comes from only one metallized nanowire since the interdistance between two neighbouring nanowires is $2 \mu\text{m}$ [5]. Only the aggregated nanoparticles along nanowire make the great contribution for SERS signal (Figure 2 (b)). In Figure 1 (f), there are utmost 500 nanoparticles within this laser spot area, which is closed to the single nanoparticles analysis. On the other hand, the concentration of R6G was

1×10^{-7} M and the volume was 0.2 μ L (Figure 2 (b)). Therefore, even all the R6G has been uniformly adsorbed onto the whole array area (ca 0.2 cm^2), there were about 600 R6G molecules located into the area of laser spot.

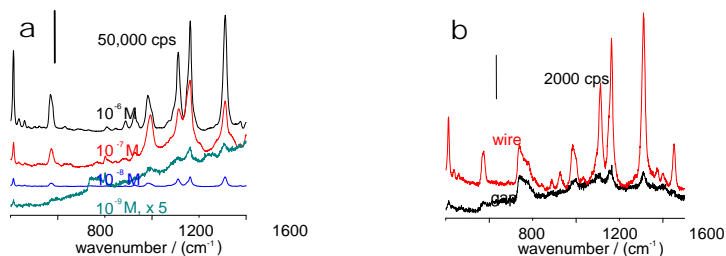


Figure 2. Dependence of SERS spectra on the concentration of R6G in the incubation solution (a), or on the laser spot position (b) on nanowire array indicated in Figure 1 (g). The structure of the employed metallized nanowire is shown in Figure 1 (f). The incubation in about 5 mL solution was lasted for 3 h in the presence of 1 mM NaCl. After then, it was washed with deionic water, dried with N_2 blow (a); or 0.2 μ L 1×10^{-7} M R6G was dropped onto the nanowire array and dried at 37 $^{\circ}$ C (b).

The possible reason of the high enhancement is due to the fact the aggregated nanoparticles along nanowire by self-assembly provides the close interdistance among the neighboring nanoparticles. The size of nanowire (cross-section 50 nm \times 50 nm) is comparable with that of silver nanoparticles (50 – 100 nm) [7]. On the other hand, nanowire supplied the extremely high surface area for the deposition reaction to produce nanoparticles [2, 3].

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