

Synthesis of Amorphous SiO_x Nanowires and Nanofibers by Thermal Evaporation with Gold as Catalyst

Majid.S.Al-Ruqeishi*, Roslan Md Nor, Yosuff Mohd Amin and Khalifa Al-Azri

Department of Physics, Faculty of Science, University Malaya, 50603 Kuala Lumpur.

* majidruq@yahoo.com (corresponding author)

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ABSTRACT The growths of SiO_x nanostructures (nanowires and nanofibers) on Au-coated n-type-Silicon (100) substrate via thermal evaporation were studied. Based on SVLS growth mechanism, the obtained diameter of the nanowires varies between 13 nm and about 243 nm and the diameter of nanofibers found to be around 8 nm to 30 nm. The SiO_x nanowires are 194 nm to several microns in length, but the length of SiO_x nanofibers are 50 nm to several microns. It was found that the carbo-thermal reactions played an important role to accomplish the growth.

(Keywords: Thermal evaporation, SiO_x nanowires, SiO_x nanofibers.)

INTRODUCTION

One-dimensional SiO_x nanostructures have recently attracted considerable research attention due to their unique properties and promising applications [1-7]. The stable and bright blue emission of SiO_x nanowires makes them potential sources of high-intensity light, near-field optical microscope probes and waveguides. Many studies prefer to use gold [1-3] as a catalyst for SiO_x growth. The Vapor- Liquid-Solid (VLS) growth mechanism was pointed out as based mechanism when the growth species comes as a vapor form [4]. Another mechanism is used to explain the growth when the main source of Si atoms diffused from the substrate, which called the Solid-Liquid-Solid (SLS) [3]. The later argument cannot be accepted as there is no thermodynamic (energetic) reason for the silicon of the wafer to supersaturate from the binary liquid phase. Then a Solid-Vapor-Liquid- Solid (SVLS) mechanism was suggested by Bahloul [5], which is similar to VLS mechanism, but differs in the starting phase of silicon whether it is solid or vapour.

EXPERIMENTAL SETUP

The source was a mixture of 0.5 g of TiO₂ powder and 0.5 g of graphite powder. The mixture was loaded into the center of a 2.2 cm-inner diameter quartz tube. *N-type* Si (100) of resistivity 5.15 Ω.cm⁻² substrates were ultrasonically cleaned in acetone and in methanol for 5 min, and then dried in air. A thin layer of gold was thermally deposited by sputtering on the substrate for 60 sec, which was then placed 2 cm apart from source. The system was pumped down to 150 mTorr and the argon gas was flushed into the

quartz tube and then kept at constant flowrate of 10 sccm. The furnace temperature was set at 1200°C with a heating rate of 1.4 C/sec and maintained for 1h. After cooling down to room temperature, a thin layer of gray color was found on the surface of the substrate. The nanostructures were characterized using field-emission scanning electron microscopy (FESEM) energy-dispersed X-ray spectroscopy (EDX) and X-ray diffraction (XRD).

RESULTS AND DISCUSSIONS

The nanostructures (nanowires and nanofibers) obtained are smooth with a cap of Au-Si alloy on the top of the wire. The SiO_x nanowires were 13 nm to about 243 nm in diameters and 194 nm to several microns in length. The nanofibers look like comet and tree roots in shape, which started to grow beneath the nanowires with diameter between 8 nm to 30 nm and around 50 nm to several microns in length. These nanostructures, shown in Figure 1(a) with the EDX spectrum shown in (b) reveals that the nanostructures consist of Si, O, Au (the catalyst) and the carbon peak partially could comes from the graphite powder used in the source.

In Figure 2, the FESEM images give a closer view of the SiO_x nanostructures. Figure 2(a), shows that the product is composed of a large number of comet-like objects with long tails. Most samples consist of a short rod (white part) and a long tail (grey part) distributed on each side of a plate-like object (white part). In addition, there are some small plate-like objects attached to the tips of the short rods. The length of SiO_x nanofibers is between around 50 nm to 2.5 μm. Figure 2(b), shows the enlarged image of

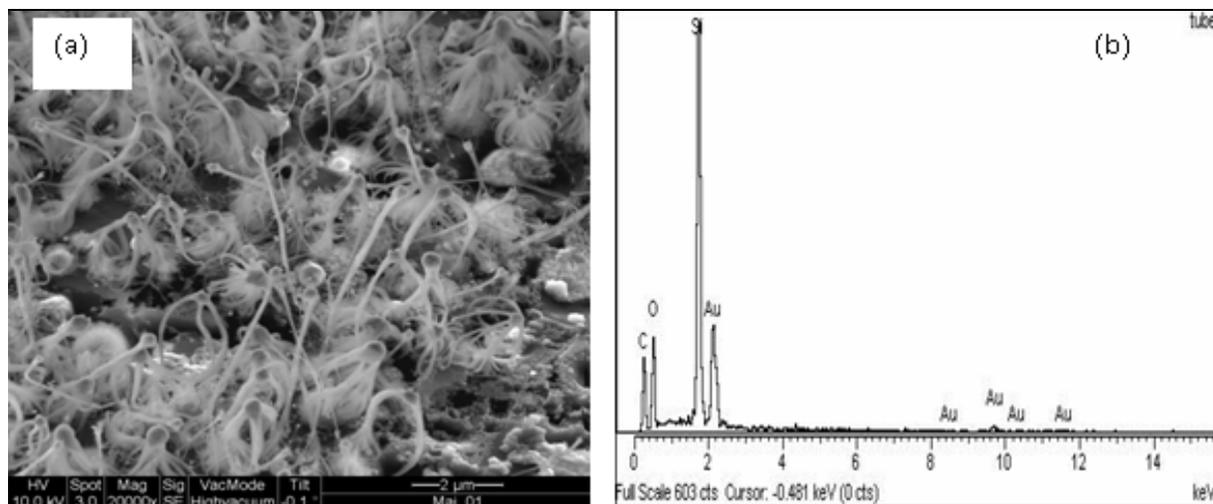


Figure 1. (a) FESEM image nanostructures on Au-SiO₂ substrates and (b) EDX spectrum of SiO_x Nanostructures.

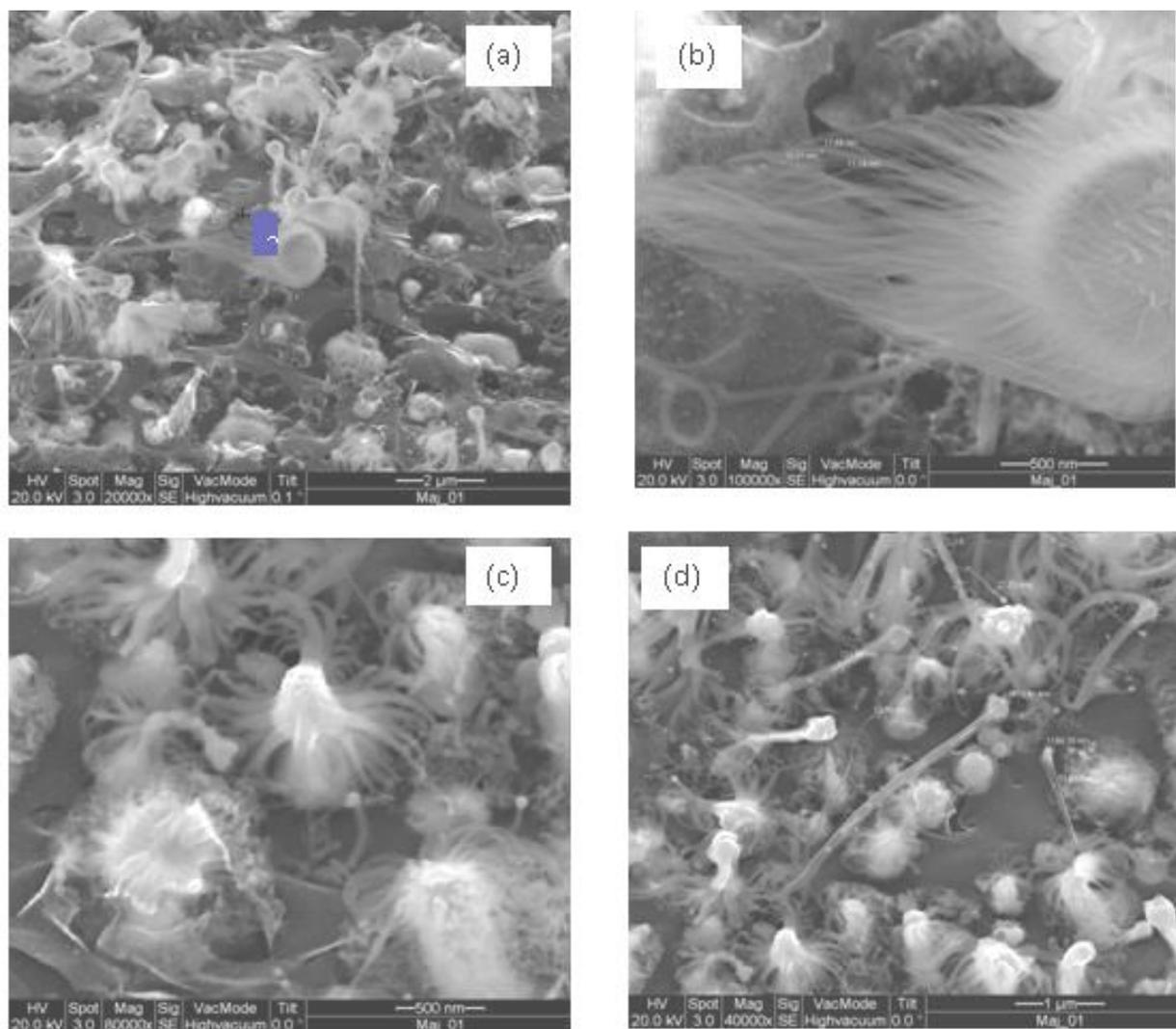


Figure 2. FESEM images (a) and (b) SiO_x comet-like objects low magnification, (c) tree-like nanostructure attached to a rod (white), (d) SiO_x nanowires tree-roots base formation.

comet-shaped nanofibers. Further more root-like nanostructure; see Figure 2(c), which reveals hollow nanotubes attached to the tip of the short rod. After applying more concentration one the FESEM image, Figure 2(d), we can see all SiO_x nanowires bases have tree roots.

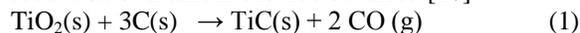
In Figure 3, the SiO_x nanowires have a spherical cap or tip. Some of these wires were embedded with gold which can be seen clearly in Figure 3(a) and (b). The obtained embedded nanowires are similar to the work of Wu *et.al* [6] and Hu *et.al* [7]. We suggest, the deposited Au nanoparticles are attached to the surface of a Si nanowire. Upon heating the coated Si nanowires, the Au nanoparticles tended to move into the core, together with the motion of the Si–SiO_x interface of the wire so as to reduce the surface area and thus the surface energy. As the annealing temperature was slightly below the melting point of Au, the Au nanoparticles would be in a semi-liquid state. The crystalline structure of silicon was changed to an amorphous structure, which is soft enough to allow the diffusion of Au nanoparticles into the core of the nanowire. Fletcher *et al* [8] grown Au embedded SiO_x nanowires with roughly same condition like our study but they used inert gas mixed with oxygen and our approach to explain the gold embedded phenomena agreed with there explanation. The XRD were carried out on three different samples, the cleaned (SiO₂/Si) substrate, the Au coated substrate before experiment and the resultant SiO_x nanostructures. In Figure 4(C), we can observe the amorphous structure of the SiO_x nanostructures. All peaks in the Au coated substrate reveal the attendance of gold with different facets; see Figure 4(B).

The growth mechanism starts when the Au thin film melted and aggregate to form spherical ball with diameter about hundreds of nanometres due to the effect of annealing on the surface tension. The Au catalyst dot served as a nucleation seed for the subsequent nanowire growth. Thus, the annealing step can be termed as the catalyst formation, see Figure 5 stage (1). Even we are not showing temperature as variable condition in this study but the effect of Ar flow gas is very important in growth initial timing. Therefore, in the same condition we got the SiO_x nanowires grown at different stages as in Figure 1 (a). That's because the flowing Ar may cause the substrate surface temperature to changed or fluctuated. This tiny temperature fluctuation have great effect in the growth of nanowires because when the temperature suddenly goes down the growing object can solidify with wider diameter before it complete the other step, which can be seen in Figure

5 stage (1). Here, the droplet diameter should reach critical amount to establish the growth processes [9]. For example, the FESEM shown in Figure 5 stage (1) reveals the diameter of cone like object or droplet is around 350nm. So bigger droplets diameter can not involved in the production of the SiO_x nanowires.

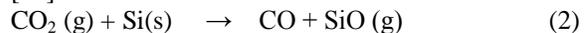
After that the furnace switched off and the temperature drops down until it reached Au-Si eutectic temperature at ≈ 363°C to form Au-Si alloy. Silicon and oxygen atoms start to diffuse into the droplet from the oxide layer of the substrate because of silicon concentrations differences between the alloy and the substrate see Figure 5 stage (2). As the duration time increased, more and more silicon and oxygen diffused and dissolved into the droplet until supersaturated. The substrate provides the droplet with silicon until it get saturated and hence, no more silicon atoms were attracted [5]. Therefore, the SLS mechanism is not responsible of SiO_xNWs complete growth processes.

To under stand the other source of Si atoms lets consider the carbothermal effect of our mixed TiO₂ and graphite powders. Firstly, the carbothermal reduction of titanium dioxide occurred [10]:



This reaction is rapid at temperatures higher than 1000°C and their rates are limited by the volumic diffusion of oxygen inside the oxide grains [10].

The CO gas will react with oxygen to be CO₂, and it can enhanced silicon monoxide to evaporate from the substrate surface through equation (2) at > 900°C [11].



That means the first growth stage is responsible of the SiO gas and the gold droplet diameter. Also, having Si in form of unstable SiO gas emphasized the droplet to dissolve silicon and oxygen and then precipitate and germinate from the edge of the droplet. Finally, SiO_x nanowires start to grow. The core of these wires is mixture of gold, silicon and oxygen as shown in Figure 5 stage (2). Here, the EDX results reveal that the mass ratio of Au to Si is > 1 at the middle of the wire but the outer layer is only SiO_x as in EDX mass ratio shown in Figure 5 stage (4).

The growth of SiO_x nanowires continue to deposit many branches tree-like or comet-shape nanofibers structured forms beneath the Aggregated Au-Si cap, stage (3). If the SiO gas not enough to dissolve into the droplet the growth will stop and the final shape will look like tree roots or comet shape, but if the deposition time is more enough, these Au balls will aggregates and form bigger ball as in stage (4), which

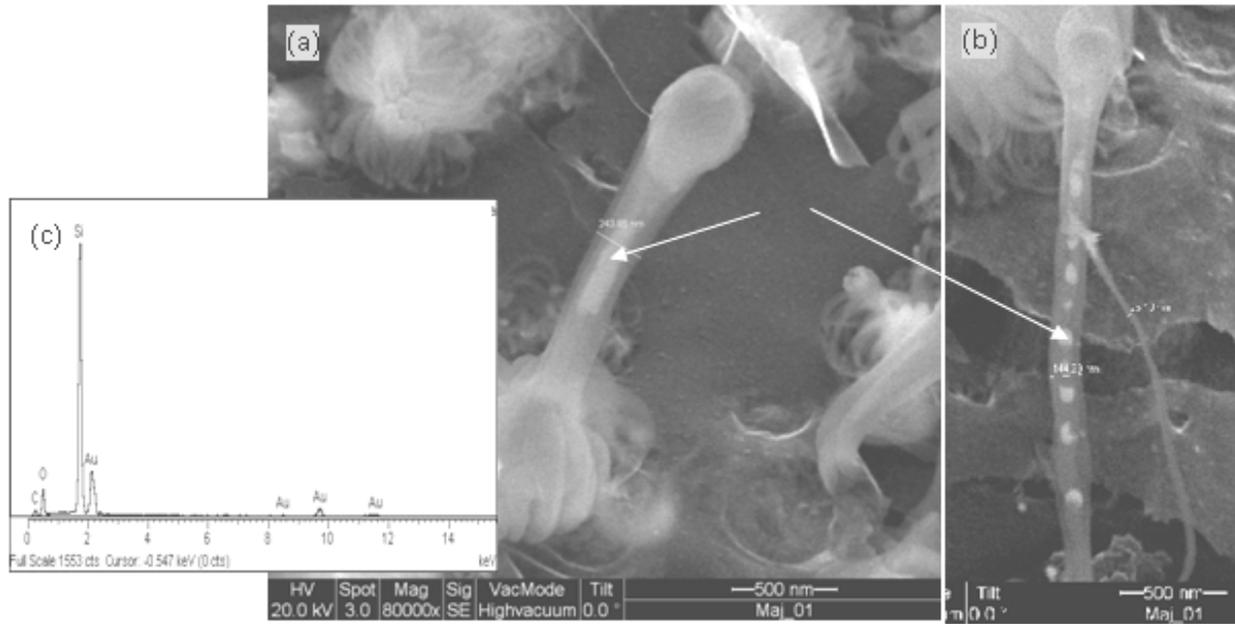


Figure 3. FESEM of (a), (b) The SiO_x Nanowire embedded with gold and (c) the EDX spectrum in the middle of the wire.

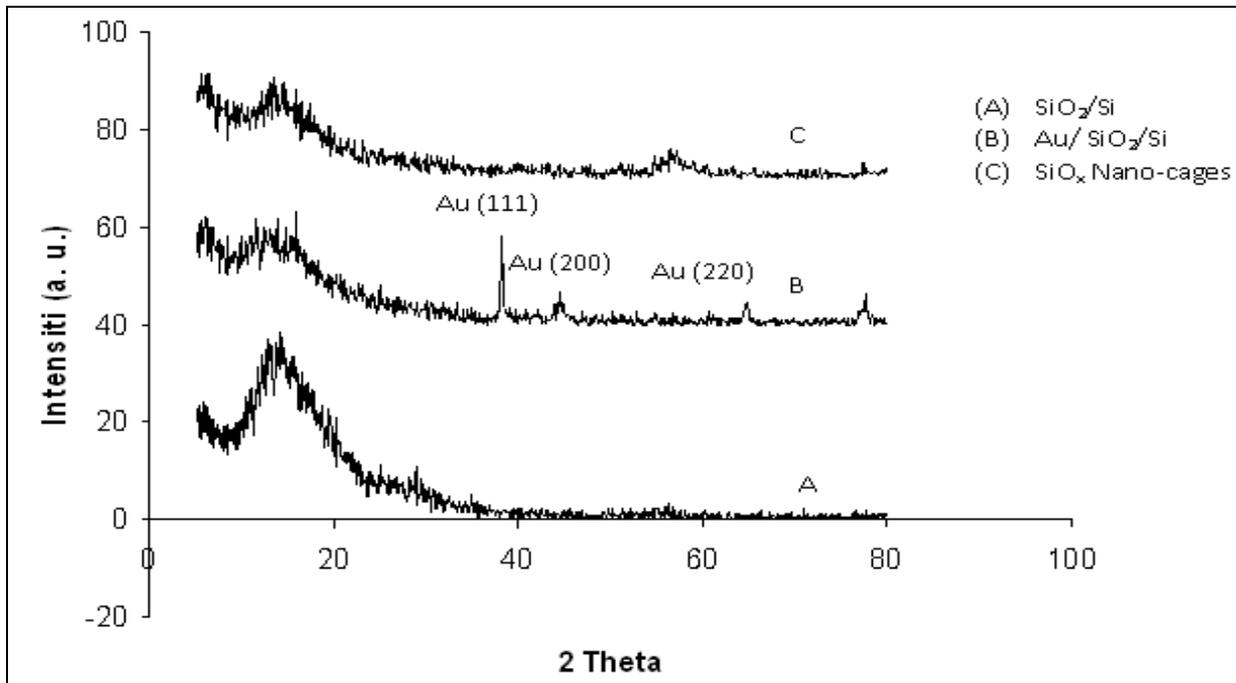


Figure 4. XRD spectrums of (A) SiO₂/Si, (B) Au/SiO₂/Si and (C) SiO_x Nanowires at 1200°C heating temperature for 1h.

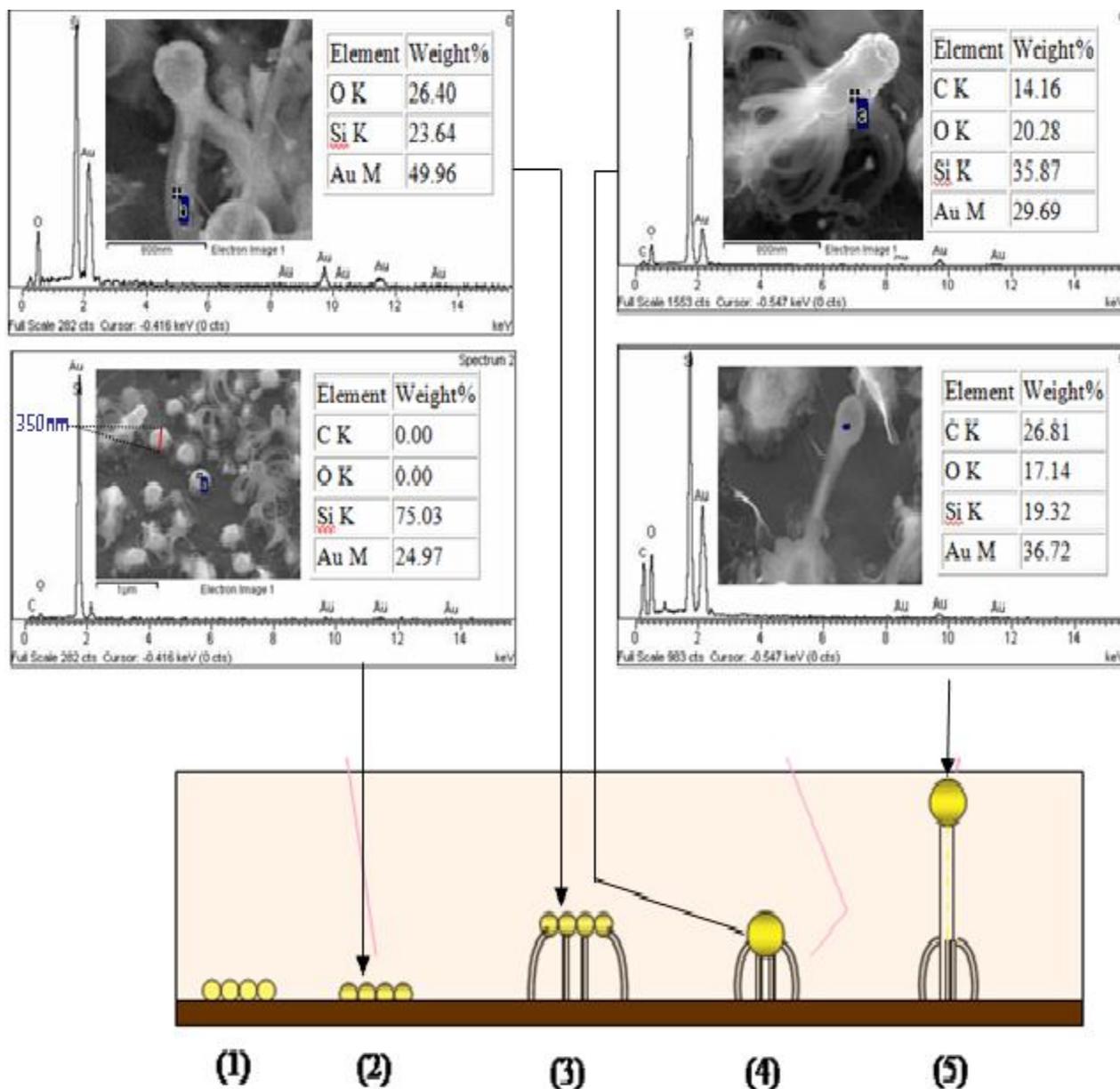


Figure 5. A schematic diagram of SiO_x nanostructures growth mechanism.

then let the wires continue to rise and form SiO_x nanowires with Au cap at the end of the wire, see stage (5). The percentage of gold is changing in the same wire or a fiber depending on the location.

CONCLUSIONS

The gold catalyst works as an essential part of SiO_x nanostructures growth. The SiO_x nanostructures (nanowires and nanofibers) have been synthesized by using catalyst gold and silicon wafers as Si source by thermal evaporation technique. The diameters of the nanowires are (13 nm - 243 nm) and the diameter of

nanofibers is between 8 nm to 30 nm. SiO_x nanowires are 194 nm to several microns in length, but the length of SiO_x nanofibers is between 50 nm to several microns.

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