

Synthesis and Growth Mechanism of Amorphous Silica Nano wires Using Humic Acid

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Abstract— *Silica nanowires have been successfully grown directly on the silicon wafers without using either silicon oxide powder as a precursor or metal catalyst to facilitate the silica nanowires growth. A layer of Humic Acid (HA) was spin coated on silicon wafer and annealed in Argon atmosphere at 1050 °C for one hour at atmospheric pressure. The source of the silicon atoms was found to be from the substrate itself; so the nanowires are well attached to the substrate. Scanning Electron Microscope (SEM) investigations showed that the diameter of the silica nanowires was about 60 nm while its length was about 1µm. Transmission Electron Microscope (TEM) showed that the silica nanowires have an amorphous structure. The photoluminescence was measured at the room temperature using the He-Cd laser with the excitation wavelength equal to 325nm. Three emission peaks at 3, 2.86 and 2.3eV have been observed. The growth mechanism of the silica nanowires is twofold: the first part is the acid/base behavior of the HA; the high pH environment could be effective to dissolve the SiO₂ layer on the silicon and making it readily available for growth of nanowires. The second part of the mechanism is the oxidation/reduction reaction that occurs between the carboxylic groups and the bulk silicon substrate, in which the carboxylic groups are reduced to alcohols and Si oxidized to SiO₂.*

Index Terms—Humic Acid, Photoluminescence, Silica Nanowires, Thermal Annealing.

I. INTRODUCTION

One-dimensional nanostructures such as nanotubes and nanowires have been intensively studied during the last decade. Among these nanomaterials, silica nanowires have attracted the scientific community due to the interesting electronic and optical properties; moreover, the promising applications in low-dimensional wave guide and blue light sources [1-10]. Therefore, many methods have been employed for the silicon nanowires production including the top-down approach of nanolithography and bottom-up approach such as laser ablation, chemical vapor deposition and thermal evaporation techniques [11-14]. In most of these methods metal catalyst must be used in order to promote the growth process. For example, in our last work silicon oxide nanowires have been grown over the nickel coated silicon substrate without the presence of powder source material [4]. The source of silicon has been believed to be from the silicon substrate itself. Pan et al. [14] proved that a catalyst is not

essential to produce SiNWs. The growth mechanism is said to be self-induced or oxygen assisted provided that the oxide layer and contamination is removed from the surface of silicon prior to the heating process. Carbothermal evaporation is considered to be a modification of the thermal evaporation method and can be employed in large-scale manufacturing due to the simple procedures and inexpensive equipment. In this method silica nanowires can be synthesized from starting materials of silicon powder mixed with activated carbon. The evaporated silicon is carried by flowing inert gas and collected on silicon substrate. In this method the presence of carbon is essential to promote high purity nanowires being synthesized at high temperature. Gundiah et al. [15] during his attempt to grow silica nanowires showed that the existence of carbon is very important in assisting the growth process of silica nano wires. In this work, amorphous silica nanowires have been synthesized over silicon substrate without using metal catalyst or silicon oxide powder as a starting material. A thin layer of HA was spin coated on the silicon substrate and then annealed in Argon atmosphere at 1050 °C for one hour at the atmospheric pressure. No metal catalyst has been used in order to promote the growth of the silica nanowires; so the silica nanowires in this study does not contain any catalyst contaminations or metal silicide that form when using metal catalyst. We believe that the silicon atoms used to grow the silica nanowires comes from the silicon substrate itself. So the silica nanowires are well attached to the substrate. The acid/base behavior of the HA and the oxidation/reduction reaction that occurs between the carboxylic groups and the bulk silicon substrate could explain the growth behavior of the silica nanowires.

II. EXPERIMENTAL

HA derived from leonardite (1g) was dissolved in 400 ml of deionized water and then ammonium hydroxide was added under the magnetic stirring until the pH stabilizes at 10. The solution was then filtered and sonicated for five minutes and then spin coated over cleaned silicon wafers in order to make thin layer. The coated substrates were placed at the middle part of the tube furnace. Argon gas was introduced into the tube furnace for 20min. before starting the heating process, in order to remove any residual air inside the tube furnace, after that; the furnace was heated to 1050 °C in 49min at the

atmospheric pressure and kept at this temperature for one hour before being slowly cooled down to room temperature. A thin layer of white material was observed on the surface of the silicon substrate. The growth product was then investigated by a field emission scanning electron microscopy (FESEM) equipped with energy dispersive x-ray (EDX) spectrometer (Helios Nano lab 400). A Bruker D8 powder X-ray diffraction unit (with Cu α) was used for collecting powder X-ray diffraction data of samples. The photoluminescence was measured at the room temperature using the He-Cd laser with the excitation wavelength equal to 325nm. The TEM images and diffraction were collected on a JEOL 2010 microscope.

III. EXPERIMENTAL RESULTS

Below 1050 °C, no growth of the silicon nanowires has been observed. Silica nanowires start to grow after reaching this temperature which can be considered as a threshold temperature, which was also observed in our previous work [4]. A typical morphology of the as-grown silica nanowires is shown in the SEM image in Fig. 1a. As one can notice that, there is a relatively high contrast in the diameter of the silica nanowires; while the majority of the silica nanowires have the diameter of about 60 nm, there are some nanowires of higher diameter (~180nm). The length of the nanowire is very close to 1 μ m. Moreover it can be noticed that silica nanowires are aligned in groups in different directions with different angles. Figures b, c and d represent the TEM images of the silica nanowires. It has been noticed that the surface of the nanowires are very smooth. The intensive investigations using the TEM shows that there are no metallic catalytic nanoparticles at the tip or the bottom of the nanowire which give a strong evidence to the catalyst free growth of the silica nanowires. During the investigations of the nanowires under the SEM, we were expecting that these nanowires will be crystalline due to the alignment of the nanowires, because it is difficult for the nanowires to be aligned and has in the same time amorphous structure. Firstly, XRD investigation has been done to the sample but we did not get any useful information from the XRD data maybe because the amount of the nanowires is not thick enough to be detected by the XRD. TEM has been used to study the structure of the nanowires; the electron diffraction reveals the amorphous structure of the nanowire, as shown in the inset in figure 1d. In our previous work also aligned silicon oxide nanowires with amorphous structure has been synthesized [4]. The growth conditions were different from the growth conditions in the present work regarding the catalyst layer. This catalyst layer can help the nanowires to be aligned if it is highly dense so that the nanowires can only grow upward. In the present case there is no catalyst nanoparticles used the reason for this alignment is not clear.

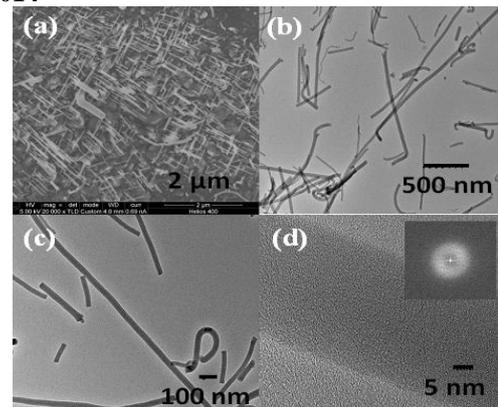


Fig. 1: A typical morphology of the as-grown silica nanowires, a) SEM of silica nanowires over silicon substrate grown using humic acid, b), c), and d) TEM images of the silica nanowires, the inset is the electron diffraction of the silica nanowires which shows that the nanowires has amorphous structure.

Fig. 2 represents the effect of the growth temperature on the formation of the silica nanowires using HA at 1050, 1100 and 1150 °C respectively. As one can see from the figure, the amount and size of the silicon nanowires increases gradually as the growth temperature increased from 1050 to 1150 °C. Fig.2a shows the initial nucleation stage of the silica nanowires. All the white spheres are the early state (nucleation) of the nanowire and it will continue to form complete nanowires. Moreover some of the nanowires grow faster than the other; these nanowires also grow with different angles with respect to the substrate. There are no particles observed at the tip of the nanowires. Some of the nanowire has the needle shape at its tip. The silicon substrates have been used without eliminating the natural oxide layer. After spin coating the HA film was not continuous and does not cover all the surface area. It has been noticed that silica nanowires grow only at the places where there is HA and exhibit a spotty pattern, see Fig. 3. The spotty patterns are likely silica clusters, formed by oxidation of local HA or other oxygen sources that act as nucleation centers for the nanowires growth. Moreover the experiment has been repeated using only silicon substrate without using HA. It has been found that no silica nanowires can grow in this case. This means that existence of HA is essential for the silica nanowires growth and this may be due to the existence of oxide layer which could prevent the diffusion of the silicon atoms from the substrate. Since there is no possible source for the silicon except the substrate, we do believe that the origin of the silicon atoms was from the substrate itself. This suggestion was simply tested by using another substrate (nickel foil) and applying the same procedure to it instead of silicon substrate. We did not find any silica nanowires grown on this substrate which support the idea that the source of silicon atoms was from the substrate and not from the quartz tube or any other source. Fig.4 shows the interface between the silica nanowires and the silicon substrate. As one can see silica nanowires are intimately attached to the substrate.

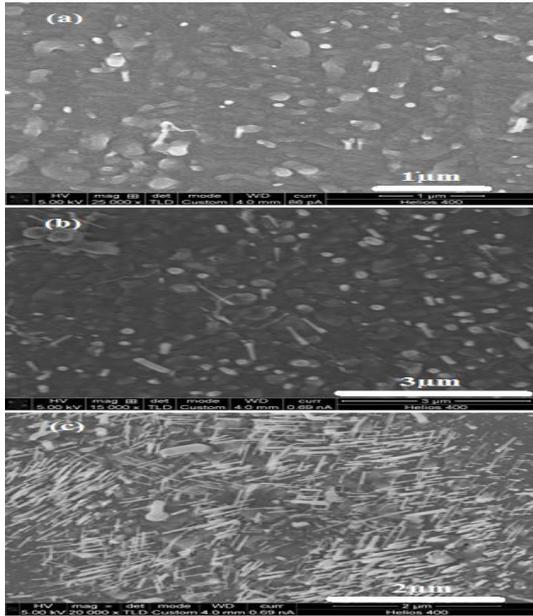


Fig. 2: silica nanowires grown at different temperature, a) 1050°C, b) 1100°C and c) 1150°C

One of the most interesting aspects of the silica nanowires grown by this method is its length. As shown in Fig.4 and Fig.5, not all the nanowires have the same length. There are some nanowires much bigger than others. The short nanowire always lies at the border or edges of the spot covered by the HA. This can be noticed also at the nucleation stage, the nanowire nuclei grow faster when it stand separately with the growth direction perpendicular to the substrate.

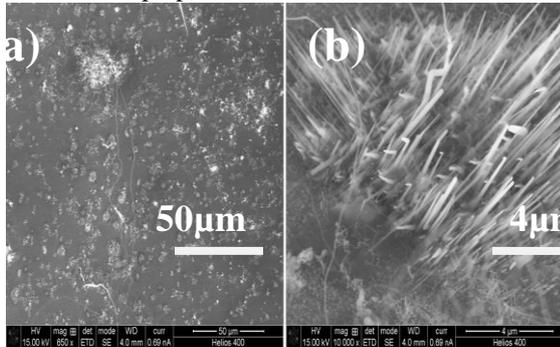


Fig. 3: silica nanowires grown only at the places where there are HA and have spot pattern

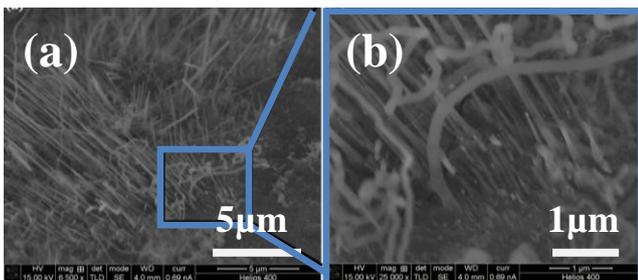


Fig. 4: the interface between the silica nanowires and the silicon substrate.

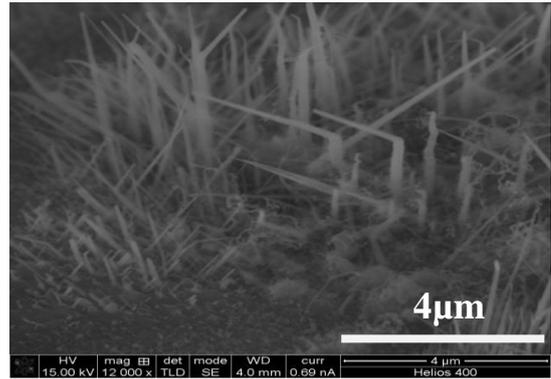


Fig.5: silica nanowires grow in one direction and suddenly change its direction with certain angle.

Moreover in Fig. 5 one can notice that some of the silica nanowires grow in one direction and suddenly changes its direction with certain angle. It is also common to have nanowires with different lengths because of non-uniform nucleation and flux in the system. The growth direction changes that associated with the kink defect may be due to reduced flux of materials, carbon contamination/poisoning, or secondary growth. In the VLS growth mechanism, these kinks can be explained by the instability at the liquid-solid interface [16]. This instability can be induced by the abrupt change in the pressure during the growth process. Hyun et al. showed that the direction of the silica nanowires can be changed by dynamically changing the system pressure during the growth process. When the system pressure is changed the speed of diffusion through the catalyst is changed accordingly and this causes this sudden change in the direction of the silica nanowires [17, 18]. In the present study; we grow the silica nanowires at the atmospheric pressure without using any metallic catalyst. Silica nanowires of quite similar morphology have been reported by Wei et al. by thermal evaporation of mixed powders of zinc carbonate hydroxide and graphite at 1100 °C and condensation on Si substrate without using any catalyst [19]. From the EDAX analysis, figure 6, one can see that only silicon and oxygen can be detected. The atomic ratio was approximately equal to 1:2 which agree with the stoichiometric ratio for the silicon oxide.

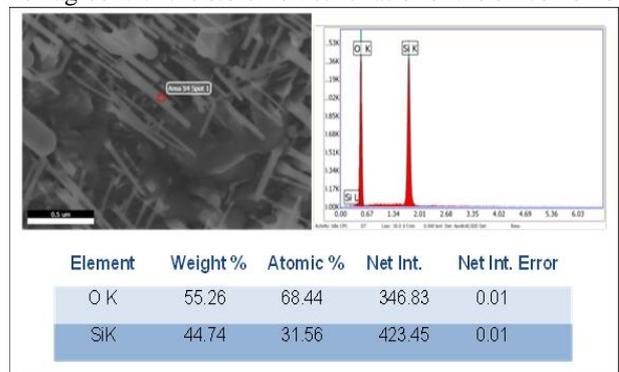


Fig. 6: EDAX analysis for the silica nanowire showed only the presence of silicon and oxygen with atomic ratio approximately equal to 1:2.

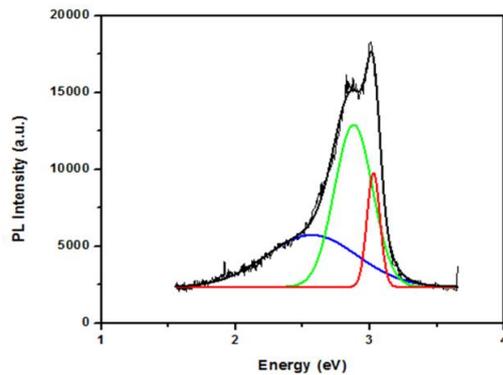


Fig. 7: the PL spectrum of the as-grown silica nanowires, the measurements have been done at the room temperatures temperature using the He-Cd laser with the excitation wavelength equal to 325nm.

Figure 7 depicts the photoluminescence (PL) spectrum of the as-grown silica nanowires. The PL was measured at the room temperature using the He-Cd laser with the excitation wavelength equal to 325nm. During the measurements there was a blue light that can be seen by the naked eye when the sample exposed to the laser beam. The PL of the silicon oxide nanowires was discussed in our previous work [4]; in this work, there are two relatively intensive peaks in the PL spectrum; the first one is intensive and centered at 3eV and the second peak lies at 2.86 eV the third peak is less intensive than the other two peaks and centered at 2.3eV. The first emission peak (3eV) could be explained by the oxygen defect centers and the presence of some intrinsic diamagnetic defect centers. The second peak (2.3eV) could be attributed to the neutral oxygen vacancy and the third peak could arise from the self-trapped excitons [19, 20].

IV. DISCUSSIONS

There are many suggested theories to explain the growth mechanism of the nanowires [4, 19]. The most accepted growth mechanism for the silica nanowires is the vapor liquid solid (VLS) growth mechanism. In this mechanism the silicon vapor diffuses into metal drop (Ni or Au) and accumulated on the other side of the catalyst forming the one dimensional nanowire. However, in this study the growth of silica nanowires was achieved without using any metal catalyst; the above mechanism cannot be used to explain the formation of the silica nanowires in our case. Although the understanding the growth mechanism of the silica nanowires needs more analysis and study; we believe the mechanism of silica nanowires growth is twofold. The first part of the mechanism involves the acid/base behavior of the HA. The HA utilized in this research has a large number of carboxylic acid groups. It is well know that the salt of a weak acid will make water basic. In the case of this research the use of ammonium as the cation mitigates this effect somewhat since it is the conjugate acid of a weak base. Solutions of the ammonium salt of the HA still render the pH of the solution to be close to 10. This high pH environment will be very effective at solubelizing the SiO₂

layer on the silicon and making it readily available for growth of nanowires. From the SEM images one can notice that the amount of SiO₂ available from this source is not sufficient to support the amount of observed silica nanowires growth; so it might be supposed that at the higher temperature (above 1050 °C), the solid silicon oxide can react with the solid silicon from the substrate and form SiO in the gaseous state according to the following reaction $\text{Si (s)} + \text{SiO}_2\text{(s)} \rightleftharpoons 2\text{SiO (g)}$ then the SiO will react with the oxygen and form SiO₂. The second part of the mechanism is the oxidation/reduction reaction that occurs between the carboxylic groups and the bulk silicon substrate. In this reaction the carboxylic groups are reduced to alcohols and Si oxidized to SiO₂. A hypothetical reaction utilizing acetic acid would go as follows.



Although this is a very hypothetical example the presence of large amounts of carboxylic groups on the HA could support a similar reaction to supply the SiO₂ necessary to support the observed growth of nanowires.

V. CONCLUSION

In summary, amorphous silica nanowires have been grown on silicon substrate using HA without using any catalyst metal that can contaminate the nanowires and affect its properties. The diameter of the silica nanowires was about 60 nm while its length was about 1µm. the room temperature photoluminescence showed the existence of two intensive emission peaks at 3eV and 2.86eV and less intensive one at 2.3eV have been observed. The temperature 1050 °C was found to be as threshold temperature for the growth of the nanowires. Both of the HA and the silicon substrate are essential for the growth of the silica nanowire since the nanowires did not grow on the other substrates under the same experimental conditions. The nanowires were suggested to grow from the substrate itself since there are no other sources for the silicon. The growth mechanism of the nanowires could be explained by the acid/base behavior of the HA and the oxidation/reduction reaction that occurs between the carboxylic groups and the bulk silicon substrate.

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