A new approach of the synthesis of SiO₂ nanowires by using bulk copper foils as catalyst

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Abstract

A novel procedure for the growth of SiO₂ nanowires (SiO₂NWs) directly from polycrystalline copper foils is reported. The single-step synthesis procedure consists of a thermal treatment at 900 °C without the need for additional catalysts. As a result, nanowires with an average diameter of 100 nm are synthesized. A systematic study undertaken at different stages of the SiO₂NWs growth confirmed the generation of nucleation centers on the Cu surface, as well as revealed the existence of an intermediate gaseous SiO species at the synthesis temperature. On the basis of these evidences, the vapor-liquid-solid (VLS) route has been proposed as the mechanism responsible for the growth.

Keywords: Silica nanowires; catalytic Cu centers, VLS process; CVD; gaseous SiO species, nanowires protective against Cu oxidation.

1. Introduction

Especially numerous and varied are the procedures for the growth of SiO₂NWs, being one of the most employed the so-called vapor-liquid-solid (VLS) method. By this mechanism, firstly described by Wagner and Ellis [8], the nanowires grow from a metal nanoparticle when the adequate gaseous precursor is added. However, the main drawback of this mechanism resides in the need of a silicon substrate for the synthesis of the SiO₂NWs.

Moreover, the widespread use of this mechanism for the synthesis of silicon-based nanowires has shown that, apart from the original Au-Si system, a broad variety of other metals such as Fe [9], Co [10], Ni [11] or Cu [12-14] may act as catalysts for the growth. Particularly, it has a special interest the case of copper, which is present in a large majority of electronic devices as well as in the tracks of printed circuit boards. Furthermore, the Cu-Si phase diagram [15] shows a eutectic point at 802 °C (16 wt% of silicon) promoting the formation of a liquid alloy at an accessible temperature for a relatively low concentration of silicon in copper.

With regard to all these considerations, this work presents a novel procedure for the growth of SiO₂NWs via a catalytic process directly from polycrystalline copper foils. This mechanism consists of a single-step thermal process with Cu as catalytic agent that allows the growth of SiO₂ nanowires over metallic substrates, granting an adequate interconnection between both surfaces.

2. Materials and methods

2.1 Materials

Polycrystalline copper foils (0.3 mm thickness, 99.9 %, Goodfellow) were used as substrates, after careful cleaning with ethanol (99.8 %, Panreac).

Single crystal silicon wafers, Si <100>, (300 µm thickness, p-type, single-side polished, Sievert Wafer) were used as sole precursor of silicon source. With this purpose, the wafers were cleaned with ethanol and properly cut in a size larger than of the Cu substrates. Subsequently, a 5 nm-thick gold film was deposited by sputtering (Sputter Quorum, Q150T-S) on the polished side of the Si<100> fragments.

Additionally, square-mesh copper grids (3.05 mm of diameter, 300 lines/inch, Gilder Grids) were used as substrates at the last stage of the study, in order to directly observe the grown nanowires by Transmission Electron Microscopy (TEM).

2.2 Synthesis Setup and Thermal Study

The synthesis of the nanowires was carried out in a tubular quartz furnace equipped with a controllable gas inlet system, at atmospheric pressure. The Cu substrates were arranged in a quartz boat according to the scheme shown in Fig 1a. Under this arrangement, a silicon fragment with the gold-coated face down was placed about 4 millimeters over the Cu substrate, elevated by two pieces of mica (Fig 1b). From now on, this silicon fragment will be referred as *Si-hat* to shortening. The gap between substrate and *Si-hat* was required to prevent both substrates merging during the heating process. It should be noted that mica was selected as spacer due to its high melting point and chemical inertness to the gases involved in the synthesis.

The quartz boat, with the substrates arranged as described, was placed in a quartz reactor and subsequently inserted into the center of the quartz tube furnace. Following this, the system was purged with Ar for several minutes. The samples were then ramped to a temperature of 900 °C followed by one hour plateau, while flowing a mixture of H₂ (99.9992 %) and Ar (99.9992 %) in a proportion of 3:1 in volume. To conclude the reaction, the furnace was turned off and the setup was allowed to cool to room temperature while passing 600 mL/min of Ar flow for 60 minutes. Reaction temperatures at 700 °C, 800 °C and 900 °C were also investigated. The experimental details of the nanowires synthesis process, as well as the subsequent thermal treatments, are summarized in Fig 1c.

Fig. 1. (a) Arrangement of the Cu substrate in the quartz boat. (b) Schematic representation of the setup outlining the different components. (c) Diagram illustrating the processes used for the nanowires synthesis (black) and the intermediate stages of the growth at: 700 °C (blue), 800 °C (green) and 900 °C (red). The gas flows are depicted by different shading.

2.3 Analysis

The morphology of both substrates and *Si-hats* were analyzed by Field-Emission Scanning Electron Microscopy (FE-SEM, Philips XL30 S-FEG) after the different thermal processes. Pretreatment of samples for SEM analysis was not required.

The chemical composition of the substrates was analyzed by Energy Dispersive X-ray Spectroscopy (EDX, Oxford INCAx-sight) and X-ray Photoelectron Spectroscopy (XPS). The XPS measurements were performed on a PHI 3027 ESCA system using non-monochromatic Mg K α radiation (1253.6 eV) of a twin anode, in the constant analyzer energy mode, at a scanning step size of 0.5 eV for the survey and 0.2 eV for the high-resolution spectra. The shifting produced by charging was corrected by using C 1s peak set to 284.5 eV coming from adventitious carbon.

The evolution of the crystalline structure upon annealing was conducted using a Siemens D5000 HR diffractometer in the Grazing-Incidence X-ray Diffraction configuration (GIXRD) with a Cu-K α radiation ($\lambda=1.54$ Å) at a fixed angle of 1° with increments of $\Delta\theta=0.04$ ° (accumulation time of 4 s).

The nanowires were further analyzed by EDX elemental analysis by scanning and transmission electron microscopy. The EDX analysis performed by SEM was carried out in a Zeiss Ultra Plus system (CRANN, AML, Dublin, IE) equipped with an Oxford Instruments INCA spectrometer at an accelerating voltage of 5 kV. Scanning transmission electron microscopy (STEM) images of the nanowires were collected using a FEI Titan instrument (CRANN, AML, Dublin, IE) equipped with an EDAX EDAMIII spectrometer (ultra-thin window, detector resolution 135 eV), by using a high angle annular dark field (HAADF) detector.

3. Results and discussion

The thermal treatment parameters described in previous works [16, 17] for the synthesis of SiO_2 nanowires have been applied, but in this case using polycrystalline copper foils as substrates instead of crystalline silicon wafers. Fig 2a and 2b show the standard growth of SiO_2 NWs when a silicon substrate is used [16,17]. In this synthesis gold is required as catalytic particle for the generation of the nanowires. SiO_2 NWs grown under these conditions showed diameters of around 20 nm and lengths of several micrometers (Fig 2b).

Fig. 2. (a) SEM image showing the standard growth of NWs on Si substrates. (b) Higher magnification of area outlined in 2a. (c) SEM image showing the Cu substrate after the synthesis of the nanowires. (d) Magnification of the outlined area in 2c showing the NWs at a grain boundary. FE-SEM images of the nanowires in top view (e) and at 30 ° tilt angle (f).

By contrast, Figs 2c to 2f show the result of the synthesis when the same thermal treatment (detailed in Fig 1c as *NWs synthesis* curve) is performed by using Cu foils as substrates instead of Si wafers. In this process the Cu substrate is placed as described in Fig 1a. The system Si-Au is equally present under this configuration (*Si-hat*), but only as precursor of the silicon source. The nanowires synthesized by this method start growing from the copper surface and merge with each other in the immediate vicinity creating a dendritic distribution ending up in a common point, as shown in Figs 2e and 2f. These branched nanowires, thinner at the beginning and thicker at the end, have diameters ranging from 50 to 100 nm. Additionally, as observed in Figs 2c and 2d, the nanowires cover totally the Cu surface regardless of the crystallographic orientations of the grain domains, and no preferential growth directions are observed. It therefore follows that the crystallinity of the substrate has no influence on the mechanism of nanowires growth.

The XPS analysis evidences the complete coverage of the substrate by the nanowires, since neither in the survey (Fig 3a) nor in the high-resolution Cu 2p spectrum (Fig 3b) Cu peaks were observed. In fact, the only peaks found corresponded to Si, O and C elements. The Si 2p spectrum (Fig 3c) as well as the O 1s spectrum (Fig 3d) show unique contribution at binding energies of 103.5 eV and 532.5 eV, respectively. The positions of these peaks were consistent with a Si-O bonding corresponding to a SiO₂ phase [18], as was also confirmed by the O 1s/Si 2p peak area ratio (see Supplementary Information 1) [19].

Fig. 3. (a) XPS survey spectrum performed on the Cu substrate after the synthesis of nanowires. The inset images show the high-resolution spectra of Cu 2p (b), O 1s (c) and Si 2p (d).

The formation of SiO₂NWs on the Cu substrate supports the role of the *Si-hat* as unique possible source of silicon for the generation of the nanowires. According with this

assumption, it is also clear that a new gaseous species is created during the thermal treatment, since Cu and Si were not in direct contact during all the process. Under these conditions, the most convincing explanation for the process consists in the generation of a gaseous SiO species.

Several thermodynamic and kinetic experiments [20-22] performed under ultra-high vacuum conditions have shown that at low oxygen pressures and high substrate temperature, the Si surface can be rapidly etched by the O₂ while producing SiO vapor, via the active oxidation reaction:

In addition, recent reports have proved that these conditions may be also achieved at medium vacuum [23] or even at atmospheric pressure [24, 25], using high purity gases (in other words, low O₂ residual concentrations). Among them, our previous work [17] provides experimental proofs which evidence the presence of this new phase when the SiO₂NWs synthesis process is performed.

Bearing this in mind, intermediate reaction temperatures were also investigated in order to observe the gradual growth of the SiO₂NWs as well as the morphological changes produced on the Cu surface. The details of these processes are summarized in Fig 1c. After the different thermal treatments, both the Cu substrates and the *Si-hats* were analyzed by FE-SEM (Fig 4a).

As can be observed in the evolution of the *Si-hat*, the nanowires synthesized by the Au catalytic nanoparticles start to grow at 800 °C until covering the entire surface at 900 °C. Inasmuch as the presence of these nanowires is indicative of the generation of SiO gas, it is deduced that the highest gas production is reached at 900 °C. Therefore, since both the nanowires on the *Si-hat* and the SiO₂NWs on the Cu substrate are generated via the same precursor, no SiO₂NWs were expected to grow on the Cu substrate until reaching 900 °C.

On the Cu substrate, two regions could be easily distinguished: a nanorough darker zone and a brighter region composed of clusters, this latter being larger at higher temperatures. In order to clarify the composition of these two regions, an EDX analysis was performed on the Cu substrate treated at 800 °C (Fig 4b). Different accelerating voltages (AV) were employed to observe the chemical composition at different X-ray generation depths. The analysis conducted on the granulate region showed a uniform in-depth composition (Cu 67 at %, O 33 at %) corresponding to a Cu₂O phase, which was also in agreement with the description of the cuprous oxide in the literature [26,27], depicted as a thick layer of perpendicular grains. The smooth region instead showed very low concentration of oxygen in bulk (Cu 86 at %, O 14 at %) increasing this amount on the surface at AV of 5 kV. This result may be consistent with a bulk copper region covered by a native oxide layer, as a result of the air exposure during the sample manipulation prior the analysis. This leads to the assumption that the SiO₂NWs started to grow from the regions described

as clean Cu, as shows the zoomed FE-SEM image on the Cu substrate at 900 °C (Fig 4a), remaining the rest oxidized.

Fig. 4. (a) SEM images of the Cu substrates and the Si-hats at different stages of the SiO₂NWs growth. (b) In-depth EDX analysis of the granulate and smooth regions, performed on the 800 °C Cu sample.

To support this hypothesis, a GIXRD study was performed on the Cu substrates after the different thermal treatments. Fig 5a shows the presence of Cu₂O peaks at all intermediate stages of the synthesis. The enlarged images of the spectra, depicted in Fig 5b, show the intensity evolution of the peaks corresponding to the Cu₂O phase with temperature. An incipient peak corresponding to the CuO (111) is also detected in the sample at 900 °C. The presence of these oxidized species can be explained, regardless of the high purity of the gases, to the fact that after the end of the gas flow, the temperature in the furnace was significantly high (see Fig 1c). This remaining temperature, between 350 °C and 100 °C depending on the processes at 900 °C, 800 °C or 700 °C, would be enough to slightly oxidize the Cu surface [28, 29].

Significantly, the sample in which the SiO₂NWs synthesis was carried out did not show any presence of oxide, as evidence the GIXRD spectra of Figs 5a and 5b. This result implies that Cu remained oxide-free prior the start of the SiO₂NWs growth, thus maintaining until the process ends. Otherwise, the peaks corresponding to the Cu₂O phase observed in the other samples should also appear in this case. This fact evidences that the SiO₂NWs indeed grow from the smooth regions, which remain oxide-free during the synthesis. It can be clearly observed in Fig 4a (Cu 900 °C) where grains belonging to the Cu₂O phase cover the whole surface except for the areas where the nanowires are grown. It follows therefore that the SiO₂NWs act as protecting layer against oxidation.

From the above discussion it was reasonable to assume the existence of a Si-Cu alloy during the thermal treatment, which promotes the growth of the SiO₂NWs via a VLS mechanism.

Fig. 5. (a) X-ray diffraction patterns recorded at 1° glancing angle of the Cu substrates after the different thermal treatments, compared to the untreated Cu. (b) A detailed observation of the grouped patterns peaks show the evolution of the Cu₂O phase as the temperature increases. No presence of this phase is observed on the untrated Cu and the sample with the SiO₂NWs.

In order to validate such an assumption, a TEM copper grid used as substrate was subjected to the SiO₂NWs synthesis process (equal configuration of Fig 1a). As a result, the same SiO₂NWs observed in the Cu foils were synthesized throughout the mesh of the TEM grid. The SEM image of Fig 6a shows the nanowires grown edgewise in a hole of the mesh. The EDX elemental maps performed on this area verify the presence of Si and O in the regions covered with the nanowires (Figs 6b and 6c), in contrast with the Cu signal (Fig 6d) that seems to come exclusively from the substrate. Fig 6e shows an EDX line scan conducted along one of the nanowires. It is clearly visible that the signals of Si and O are completely correlated and more intense at half height of the nanowire. Significantly, the signal of Cu that was considered to come only from the substrate, was present from half way down the SiO₂NW. Therefore, these evidences suggested the existence of a protrusion of the copper substrate under the nanowire.

Fig. 6. (a) In-Lens SEM image of the SiO_2NWs at the edge of a hole in the TEM copper grid and corresponding EDX elemental mapping images of Cu (b), Si (c), and O (d), acquired at 5 kV. (e) In-Lens zoomed SEM image of the SiO_2NWs and overlapped EDX line scan along a vertical nanowire.

A subsequent study of the TEM grid via scanning transmission electron microscopy was performed. HAADF-STEM image of Fig 7a shows a protrusion of around 200 nm in diameter excelling from the Cu substrate (in bright contrast) just under the nanowire (in dark contrast). EDX elemental maps performed on the inset area confirms the presence of Cu at the bottom of the nanowire (Fig 7b). Meanwhile, Figs 7c and 7d show a homogeneous distribution of Si and O across the whole nanowire. It should be noted that these signals come also from the region of the Cu protrusion. However, inasmuch as the protrusion is located inside the nanowire, it is not possible to determine whether a combination between Si, O and Cu elements is taking place.

Fig. 7. (a) HAADF-STEM image of a SiO_2NW at the edge of a hole in the TEM grid and the corresponding EDX elemental mapping images of Cu (b), Si (c), and O (d).

It is clear the relevance of these protrusions in the process, since they are present within all the nanowires (see Supplementary Information 2). In this respect, the protuberances produced during the thermal treatment, would act in some catalytic form to generate the SiO_2NWs . As a consequence, the SiO vapor coming from the *Si-hat* is incorporated into these catalytic Cu centers, possibly forming Cu-Si alloys, until reaching the nucleation and subsequent bottom-up growth of the nanowire via a mechanism similar to the VLS method. Although the existence of these alloys Cu-Si will require additional verification, the evidence obtained so far clearly point to this possibility. In fact, as seen in the XPS results shown in the Supplementary Information 3, after completely removing the silicon oxide by treatment for 12 minutes in the presence of HF, a clear contribution of silicon is still observed. Obviously, this contribution must be due to Si-Cu alloy.

Fig. 8. FE-SEM images corresponding to different steps (from left to right) of the growth process: i) the image on the left shows the initial growth, generated from the protrusions of the substrate; ii) the center image shows a more advanced state of growth; iii) the right image shows that adjacent nanowires together to form dendritic-like arrangements. The scheme of the growth process is shown in the top of the figure (from left to right).

It is worth mentioning that the observation of the evolution of growth of nanostructures is a very difficult task. This is because, when the heating process is stopped, if the substrate is not protected by SiO nanostructures, quickly generates a Cu_2O layer covering the substrate. The roughness of the oxide layer does not allow to observe the underneath nanostructures (as shown in Fig.4). This roughness significantly complicates monitoring the growth process. Nevertheless, to understand the growth phenomena we studied the growth evolution of the SiO_2NWs when using Cu grids as substrates. In this case, the SiO gas flow was not the same over the entire surface, probably due to the irregular surface and the position of the *Si-hat* above it. This arrangement allowed us to detect low and high SiO gas exposure areas during the heating treatment of Cu substrate and, therefore, to

observe different stages of the growth evolution. Figure 8 shows the SEM images of the nanowires in different states of growth, including a schematic of the growth model. Based on the above results, the following growth mechanism is proposed. First Cu protrusions act as catalytic centers for the incorporation of SiO gas, forming an alloy (Fig. 8, left image). At this point, SiO₂NWs grow from the catalytic Cu centers via a VLS mechanism being strongly anchored to the Cu substrate via the protrusions. These SiO₂ structures merge with each other in the immediate vicinity creating a dendritic-like arrangement (Fig. 8, right image). These evidences suggest that SiO₂NWs grow via a VLS mechanism by successive adsorption of SiO vapor through the bottom of the nanowires.

4. Conclusions

This research presents a novel procedure for the growth of silica nanowires in a dendritic distribution over bulk polycrystalline copper, via a thermal treatment process, in atmosphere of Ar-H₂. The nanowires, with an average diameter of 100 nm, grow uniformly throughout the substrate indistinctly of any crystallographic orientation.

The mechanism of the nanowires growth is supported by two main parallel processes. On the one hand, the residual O₂ present in the atmosphere reacts with the Si of the wafer, via an active oxidation reaction, to generate gaseous SiO species. On the other hand, protrusions of around 200 nm in diameter are generated on the Cu substrate, providing adequate nucleation centers for the incorporation of SiO vapor. These evidences suggest that SiO₂NWs grow via a VLS mechanism by successive adsorption of SiO vapor through the bottom of the nanowires. Moreover, the close physical proximity between nucleation centers would cause the collapse of adjacent nanowires on a larger one, providing a branched structure.

Finally, the GIXRD analysis performed on the SiO₂NWs/Cu sample showed no presence of copper oxide peaks, which evidences the potential application of the nanowires as a good protective layer against oxidation of copper surfaces exposed to environmental conditions.

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