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Room temperature growth of silica nanowires on top of ultrathin Si nanowires synthesized with Sn-Cu bimetallic seeds

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TEM

Si nanowires (NWs) are grown by the vapor-liquid-solid method using Cu-Sn bimetallic catalysts in a plasma-enhanced chemical vapor deposition (PECVD) reactor. The microstructure of the NWs is analyzed by transmission electron microscopy and energy-dispersive X-ray spectroscopy. An amorphous SiO₂ region, much larger than the native oxide, is present on top of each Si crystalline NW: in SiNWs with diameter below 10 nm, it takes the form of a silica NW of up to 50 nm in length. The new NW separates the initial catalyst particle into one that stays in contact with the SiNW and one or more that lies at the top of the new NW. The former is made of Cu and Cu₃Si and contains no Sn, while the latter keeps amounts of both elements. The observed microstructure appears to be the result of a mechanism of Si oxidation catalyzed by Cu₃Si. The deposit after SiNW growth, in the

PECVD reactor, of a protecting 1-nm thick layer of amorphous hydrogenated Si, completely suppresses this mechanism. This work provides reference for future applications based on Cu-Sn-catalyzed quantum-sized SiNWs.

1. Introduction

Developing quantum size Si nanowires (SiNWs) is of interest for different optoelectronic and photovoltaic applications.^[1-4] Si nanowires with a diameter below 10 nm have a bandgap that increases as their diameter decreases.^[5] Interestingly, they can also adopt the metastable hexagonal diamond crystalline structure,^[6] the calculated electronic structure of which would have specific and interesting opto-electronic properties (increased absorption).^[5] In other respects, Si nanowires may be good conductors when properly doped; they can act as efficient collectors for radial junction solar cells^[7] for instance.

Obtaining quantum-sized SiNWs with a small diameter distribution has been the object of a number of studies. Some authors have achieved the synthesis of small diameter SiNWs, using well-defined gold nanoclusters as catalysts in a vapor-liquid-solid (VLS) growth process or in a supercritical hexane solution-phase.^[3, 8-10] However, these methods deliver a small fraction of NWs with sufficiently small diameters. Moreover, the use of gold brings undesirable impurities. In order to consider using large area quantum wire devices, gold-free catalysts are needed. We have achieved to grow very dense quantum wire arrays with average diameter around 6 nm using a plasma-enhanced chemical vapor deposition (PECVD) method with a novel Sn-Cu mixed catalyst and a liquid-assisted vapor-solid-solid (LAVSS) mechanism.^[11] This work is the object of a forth-coming paper.

However, these NWs systematically wear an amorphous cap, which can become an actual NW on top of the Si NWs. We show in this paper that this amorphous cap or NW is the result of the oxidation of the SiNW, catalyzed by Cu in air, as indeed, Cu is a catalyst of Si

oxidation.^[12-14] Thus, when the nanowires are taken off from the growth reactor and come into contact with ambient air, the catalyst nanoparticles at their top catalyze the NW oxidation. What makes it particularly interesting is that this oxidation develops at the interface between catalyst and nanowire, where, in nanowires with diameter below 10 nm, it ends up by making – at room temperature in air – a whole Si oxide nanowire.

Silica nanowires, by the way, have been the object of intense efforts these last two decades, due to their wide range of potential applications, from intensive blue-light emitters^[15-17] to separator for Li-ion batteries^[18] or biosensors.^[19] Regarding Si-silica heterostructures, the coupling of silica nanostructures with SiNWs has been demonstrated to strongly enhance or modify the NW luminescence.^[20-22]

In this paper however, we focus on the characterization of the silica NW and on the way of avoiding its formation. We analyze the NW microstructure by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). We manage to suppress the formation of the silica nanowire by coating the SiNWs with an *a*-Si:H thin film in the PECVD reactor.

In the following, we start by showing the structure and chemical composition of silica NWs and of the separated parts of the original catalyst particle; then we discuss the formation of the amorphous oxide NW in between the crystalline SiNW and the remnants of the catalyst, in the light of literature on Cu-catalyzed oxidation of Si wafers.

2. Results

2.1. TEM analysis

The SiNWs discussed in the following were grown using a mixed catalyst of 0.1 nm Sn/0.1 nm Cu (70 at. % Cu) with the typical PECVD conditions (see Experimental Section). They have diameters ranging from 4 to 9 nm with an average diameter of 6.3 nm (measured by

TEM based on 89 SiNWs); the average diameter of their crystalline core is around 4 nm.^[11] They have thus the size where the band gap depends on wire diameter. TEM observation shows that these thin SiNWs systematically have a special structure with an amorphous nanowire separating the initial single-particle catalyst into several nanoparticles (NPs). That amorphous NW was present in all the 89 SiNWs observed; its length could vary from 10 to 50 nm: **Figure 1a** & **b** shows typical configurations. The HRTEM image in **Figure 1c** presents a SiNW in [110] zone axis, where the differences in structure between the crystalline core of the Si NW and its amorphous tip and shell are well visible (see schematic in **Figure 1d**). There is a catalyst NP (catalyst 1) connected to the crystalline core. However, this is not the end of the NW; we can see that there is still an amorphous part with a length around 10 nm above the crystalline core, on top of which lies catalyst 2 (with one or more catalyst NPs).

Let us add here that the substrate appears to play no role: the amorphous NW was found on SiNWs grown on (100) Si (**Figure 1a**) or on the amorphous C-membrane of TEM grids (**Figure 1b, c**), or on the metallic grids themselves. The only limitation we noticed was that of size: the starting particles had to be smaller than ~10 nm for an actual amorphous wire to develop.

This catalyst separation phenomenon along with the growth of the amorphous NW has only been observed in the SiNWs synthesized with Sn-Cu and In-Cu mixed catalysts, never in SiNWs synthesized with pure Sn or Au catalyst.^[11] (Let us mention that SiNWs cannot be grown with pure Cu catalysts under the current PECVD conditions.^[11])

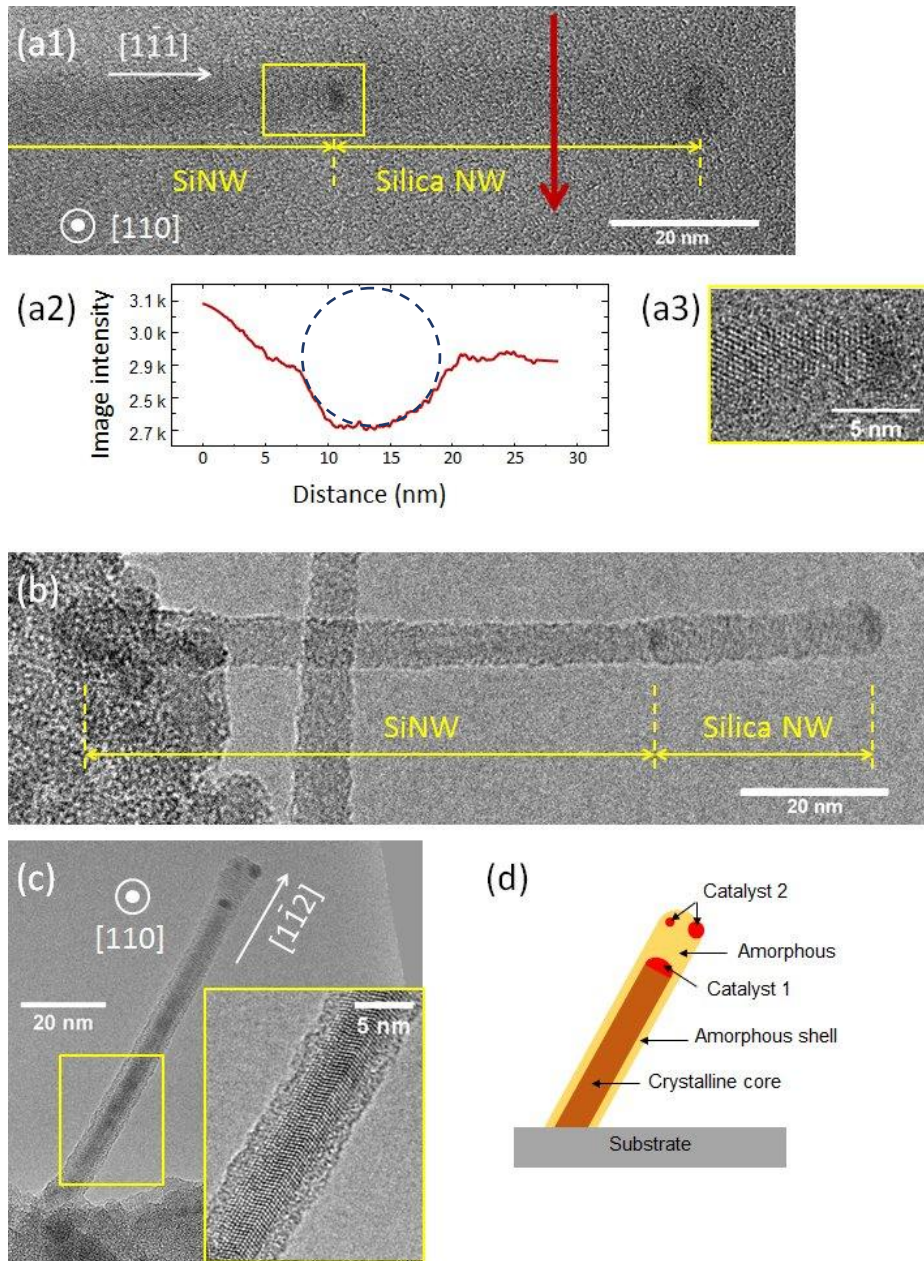


Figure 1. Typical examples of silica NWs grown on top of SiNWs. a) NW synthesized with 0.1 nm Sn/0.1 nm Cu as catalyst on (100) Si then scratched and deposited on the amorphous C-membrane of a TEM grid; TEM close to [110] zone axis of the SiNW, showing its $\langle 111 \rangle$ orientation; a2) intensity profile over the red arrow in (a1), integrated over the length of the amorphous NW, showing its presence (dashed circle); a3) enlargement of squared area in (a1). b) Same catalyst and same recipe with growth directly on the TEM grid amorphous

membrane (SiNW out of zone axis); same scale as (a1). c) [110] zone axis image of a similar SiNW, showing its $\langle 211 \rangle$ orientation; the enlarged area shows the details of the twinned crystalline core. d) Schematic of (c).

2.2. EDX analysis

Due to irradiation damage, we were not able to record X-ray maps of the NWs: the objects would become irreversibly damaged before a sufficient signal-to-noise-ratio had developed. Thus, we carried out point analyses, obtained by leaving a non-focused beam a short time on the NWs. In **Figure 2**, we show an EDX analysis on two separated catalyst NPs as well as on the amorphous part between them, in the case of a thin SiNW grown in the same run with 0.1 nm Sn/0.1 nm Cu bimetallic catalyst. In area 1, the catalyst NP in contact with the crystalline NW, O, Si and Cu are found. Cu has a strong signal. No trace of Sn is found in this catalyst NP. In area 2, the amorphous part, O and Si are mainly detected. The atomic ratio of O and Si is 9:4, close to the ratio in SiO₂. Therefore, it is reasonable to speculate that the part between the two catalyst NPs is SiO₂. The signals of Cu and Sn in this area are relatively low, just above the background noise. On the top particle of the NW in area 3, the presence of O, Si, Cu and Sn are confirmed. Putting aside the signals from Si and O, that are influenced by the proximity of the SiO₂, one can measure the atomic fractions of Cu and Sn in this area. As the Cu signal is at about twice the noise level, the uncertainty on its value is large. These fractions come at 20±15 % and 80±15 % respectively: Sn is present in contrast to its absence in the other part of the catalyst and, compared to the starting atomic ratio of 70 % the amount of Cu has drastically decreased. Thus, some Cu has diffused away from the original catalyst to form a new one at the interface between *c*-Si and *a*-SiO₂.

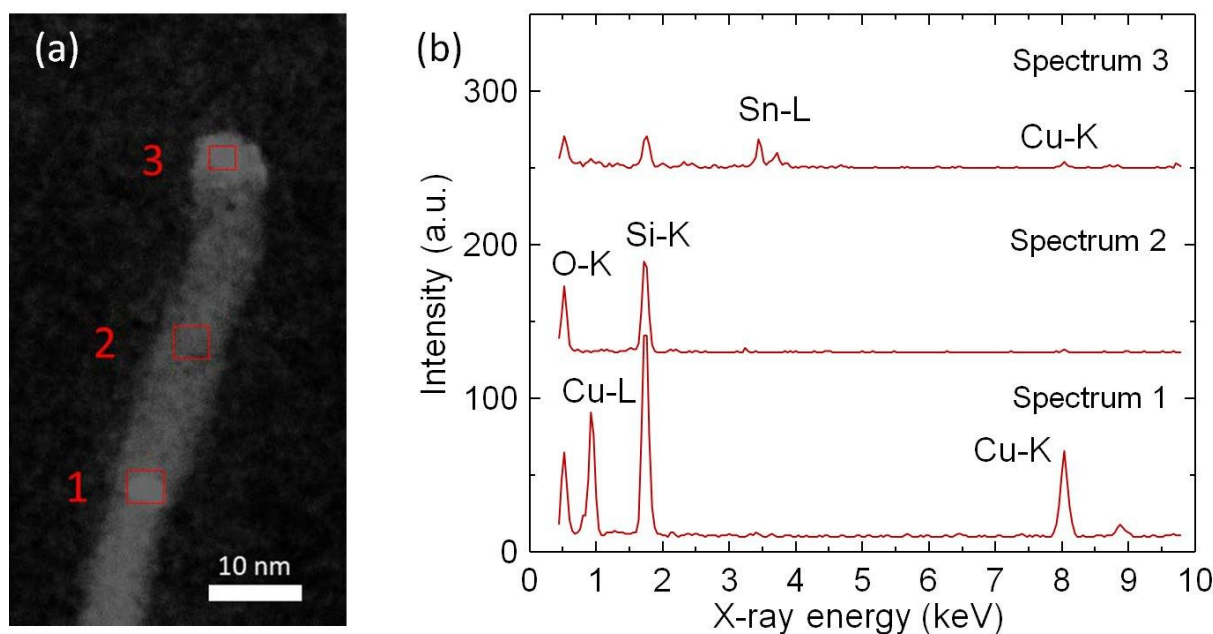


Figure 2. EDX analysis on a silica NW and a split catalyst. **(a)** STEM-HAADF image; **(b)** EDX spectra. Area and spectrum 1 correspond to the catalyst part that is connected to the SiNW, area and spectrum 2 to the amorphous part between the two catalyst NPs, and area and spectrum 3 to the top catalyst NP. The SiNW is synthesized with 0.1 nm Sn/0.1 nm Cu co-catalyst at the typical conditions.

2.3. Eliminating post-growth oxidation

In order to verify whether the formation of the silica nanowires has occurred during processing in the PECVD reactor chamber, or after NW growth in the atmosphere, we performed the following growth experiment. Immediately after NW growth in exactly the same conditions as those mentioned above, we decreased the substrate temperature to 185 °C, and deposited a thin layer of hydrogenated amorphous Si (*a*-Si:H) on the SiNWs, thus “freezing” the original structure and protecting it from exposure to the air when the chamber was opened. A TEM image of a SiNW with amorphous silicon layer is shown in **Figure 3**.

The SiNW has a total diameter of 10 nm and the shell around the NP has a thickness around 2 nm. At the top of this NW, we only find one catalyst NP and no oxide NW. We have observed the structures of 30 SiNWs, and none of them had several catalyst NPs separated by amorphous matter. Therefore, we can conclude that *i*) catalyst separation and the growth of the silica NW happen after SiNW growth in the ambient air and *ii*) the deposit of *a*-Si:H in the PECVD reactor immediately after SiNW growth is an efficient way of suppressing all post-growth oxidation phenomena.

Thus, for preparing unoxidized quantum-sized SiNWs with such catalysts, the deposit of *a*-Si:H in the same reactor appears as a mandatory step. As, moreover, *a*-Si:H is known to electrically passivate crystalline Si surfaces ^[23], the present protection process, which implies only a light treatment in the same reactor, would be a good solution for future measurements of the optical properties or use in devices.

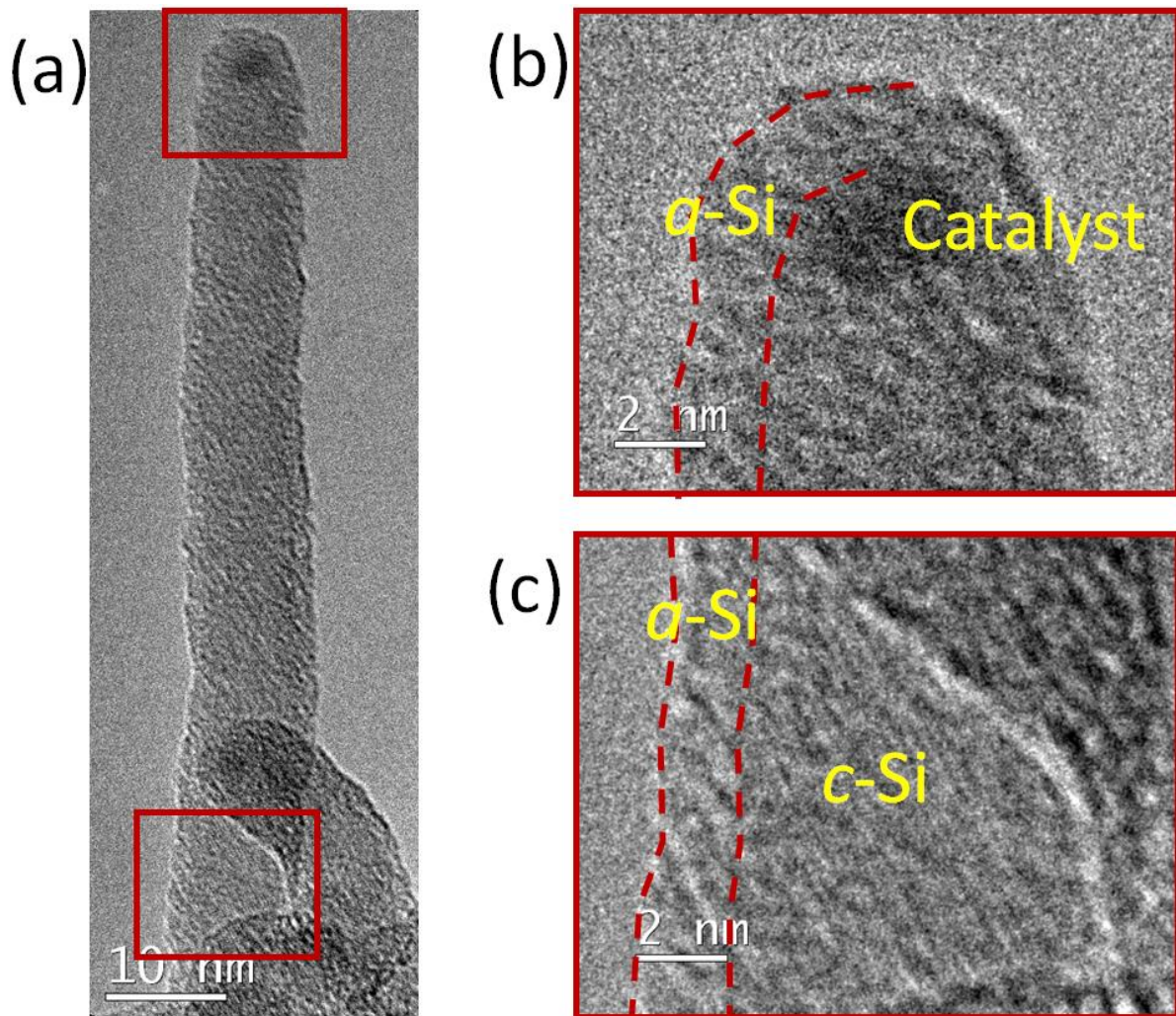


Figure 3. a) TEM image of a SiNW with a thin layer of amorphous Si deposited immediately after NW growth. b) Enlargement of the top squared area in (a) showing the a-Si:H layer around the catalyst. c) Enlargement of the bottom squared area where the lattice fringes are visible, so that crystalline Si can be differentiated from a-si:H and the thickness of the deposited a-Si:H can be measured directly: its value is 2 nm.

3. Discussion

To evaluate the possible formation mechanism of the silicon oxide NWs and the catalyst splitting, let us make a brief review of the literature. Several authors have demonstrated that Cu_3Si can catalyze the oxidation of crystalline silicon at room temperature,^[12-14, 24-25] producing SiO_2 . Harper *et al.*, for example, obtained Cu_3Si films by sputtering Cu onto (100) Si at 200 °C. They observed the formation of a thick layer of SiO_2 under a copper-rich surface

after exposure to air at room temperature for a few weeks. They found Cu_3Si NPs at the SiO_2/Si interface.^[12] This is similar to what has happened in our SiNWs: Cu and Cu-silicide nanocrystals have been found in the separated catalyst NPs (see supplementary information, Fig. S1), and between the NPs there is SiO_2 according to the TEM characterizations and the EDX analysis. **Figure 4** summarizes the reactions that occur in the SiNWs in the air after PECVD growth. We have shown that, during SiNW growth, the mixed Sn-Cu catalyst NPs consist of a crystalline core of Cu_3Si and a Sn-rich shell.^[26] The SiNWs grown with the current PECVD conditions mostly have single crystalline structure (Figure 4a). When the reactor chamber is open and the NWs are exposed to the air, Cu_3Si in the catalyst first reacts with oxygen to form SiO_2 and Cu: $\text{Cu}_3\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 + 3 \text{Cu}$. This produces a layer of SiO_2 between the catalyst NP and the crystalline SiNW (Figure 4b). Then the Cu atoms released by oxidation of Cu_3Si diffuse through the SiO_2 to the SiNW (Figure 4c) and give rise to the second reaction: $3 \text{Cu} + \text{Si} \rightarrow \text{Cu}_3\text{Si}$ (Figure 4d). The Cu and Cu-silicide crystals found at the interface with the Si NW have different orientations (see Fig. S1), and the Cu_6Sn_5 planes of the top NP are always found perpendicular to the growth direction of the SiNWs (Fig. S1); this shows that the latter are the remnants of the original catalyst, active during growth, while the former have developed afterwards. In addition, no Sn has ever been found in these parts at the interface with the SiNW. Therefore, we think that the Cu silicide nanocrystals connected to the crystalline NW core have formed due to the reaction of Cu and Si after the growth.

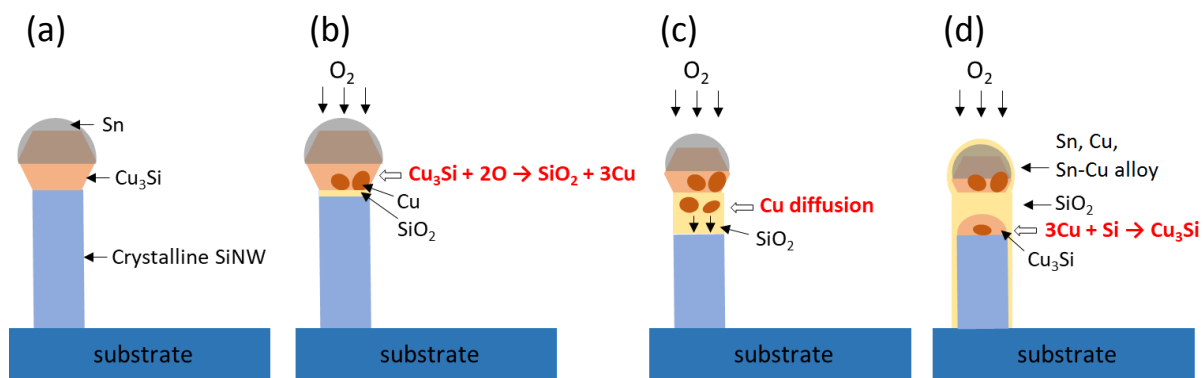


Figure 4. Schematic diagram of formation of a silica NW catalyzed by Cu_3Si , following the model developed by Harper *et al.* for the room-temperature oxidation of bulk Si.^[12, 24] a-d) Time evolution during exposure to air.

However, this reaction sequence does not continue catalytically until the whole SiNW is consumed and has become a SiO_2 NW. One may assume that it stops when the Cu silicide reservoir at the top is exhausted (i.e. when all the Si from the silicide has been oxidized). In other respect, this reaction seems to be limited in thick nanowires (we only found separated catalyst NPs in SiNWs with diameters smaller than 24 nm); the explanation could be related to the fact that, to feed the production of SiO_2 , oxygen from the air must diffuse through the interface between Cu_3Si and the existing SiO_2 , down to the center of the wire, over a distance worth a wire radius. That distance would just become too long in thick wires. This is different from the experiments on Si wafers, where oxygen would come from the top; here, after some Cu has diffused through the oxide, Sn becomes majority element at the top (see Figure 2) and Cu_6Sn_5 replaces the initial Cu_3Si (see Fig. S1), preventing air oxygen to get in contact directly with Cu silicide.

4. Conclusions

In this work, we have evidenced the growth, at room temperature in air, of silica nanowires on top of thin SiNWs catalyzed by Sn-Cu mixed catalysts: the catalyst particle that remains connected to the crystalline NW core is not anymore at the end of the NW, an amorphous silicon oxide has developed above the crystalline core, on top of which lies another one or more catalyst particles. The initial catalyst particle has split into two or more new particles. This appears to be due to the oxidation of the Cu-silicide inside the initial particle in the air after growth: Cu_3Si first reacts with oxygen to form SiO_2 and Cu; then the Cu atoms released by oxidation of Cu_xSi move towards the SiNW through SiO_2 and react with Si to form new Cu_3Si . It thus adds silica NWs on top of the original SiNWs, which may drastically extend and enhance the luminescence of such objects.^[20-22] This, in turn offers new prospects of applications. Inversely, we also showed that the development of the silica NW can be totally inhibited by the deposition, in the same growth reactor, of an α -Si:H passivating layer. As the latter, in turn, would also suppress surface recombination of minority carriers, we believe that this treatment could be used in future Si quantum wires prepared with Cu-based catalysts. This work provides reference for future applications based on Cu-Sn-catalyzed quantum-sized SiNWs.

5. Experimental section

We used a mixed catalyst of Sn and Cu prepared in a Boc Edwards Auto 306 Evaporator FL 400 to obtain small-diameter SiNWs. Cu was first evaporated on the substrates and then Sn was evaporated on top of Cu to act as the Sn-Cu mixed catalyst. The nominal thickness of the evaporated catalyst was measured by a quartz microbalance in the thermal evaporator. The catalysts were evaporated either on (100) Si wafers or on the amorphous carbon membrane of carbon-coated gold TEM grids for the convenience of TEM observation. SiNWs were synthesized in a radio frequency (RF) PECVD reactor. After the vacuum reached 5×10^{-5}

mbar, a hydrogen plasma treatment was carried out at 200 °C to remove the native oxide formed around the catalyst NPs before the SiNW growth. During the treatment, the H₂ flow rate, the gas pressure P , the RF plasma power density and the duration time t were 100 sccm, 0.8 mbar, 57 mW cm⁻² and 2 min, respectively. Then SiNWs were grown at 416 °C by adding a SiH₄ flow of 5 sccm and changing the process parameters to the following values: P of 1.42 mbar, RF power density of 17 mW cm⁻² for $t = 3$ min. After SiNW growth, the substrate temperature was either: *i*) decreased to 140 °C, at which point we open the chamber (this set of conditions is referred as the “typical PECVD conditions” in the text); or *ii*) decreased to 185 °C, at which point an amorphous silicon layer was deposited on the SiNWs and their catalysts, to inhibit oxidation of the latter. The PECVD parameters used in this process were: 10 sccm for SiH₄ flux, 0.17 mbar for gas pressure, 1 W for RF power, and 30 s for time duration. The chamber was opened after the substrate had cooled down to 140 °C. The purpose of coating the SiNWs with an amorphous silicon layer was to prevent the catalyst and the crystalline NW from oxidation in the air and ascertain the origin of silica NW formation. The SiNWs were characterized by transmission electron microscopy (TEM) for high resolution (HR) imaging and Energy Dispersive X-ray spectroscopy (EDX) analysis using a Jeol 2010F and a Thermo Fisher Titan 80-300. The acceleration voltages utilized were 200 kV for the Jeol 2010F TEM (0.16-nm information limit), and 300 kV for the Titan TEM (0.12-nm information limit), respectively. Some high-angle annular dark-field (HAADF) images were recorded in scanning TEM (STEM) mode, prior to EDX analysis with the Titan. EDX was performed using an INCA system from Oxford Instruments, equipped with a silicon drift detector. The use of Au TEM grids (instead of standard Cu-grids) warranted that the Cu signal genuinely came from the sample.

Supporting Information: Supporting Information is available from the Wiley Online Library or from the author: it includes Figure S1: HRTEM structural analysis of split catalyst particle.

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