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Study of seahorse-like Fe-TiO_2 core-shell nanorods obtained in an induction heated MOCVD reactor

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ABSTRACT

This paper presents the growth of Fe-TiO_2 COaxial Heterostructure Nanorods (COHN) by Metal-Organic Chemical Vapour Deposition (MOCVD). The Fe-TiO_2 COHN were grown in one step on silicon based substrates, using titanium isopropoxide as precursor and ferrocene as catalyst. Various growth parameters (deposition time, temperature and substrates) were modified to define a growth model. Samples' morphology and structure were characterized by SEM and Fe-TiO_2 COHN were extensively analyzed by TEM, EDS, SAED and EELS. These techniques show the coaxial structure of Fe-TiO_2 COHN and confirm that the core is pure iron, while the shell is titanium dioxide.

I. INTRODUCTION

Metal oxides are interesting materials with many properties. A lot of these properties are depending on the metal oxides' surfaces or the interfaces between them and other materials [1][2]. TiO_2 is extensively studied because of its interesting chemical, electrical and optical properties. Its applications vary with its form (bulk or nano). TiO_2 layers are used in dye-sensitized photovoltaic cells. Other applications would be protective layers for large scale integrated circuits and optical elements, gas sensors or antireflective coatings [3][4].

There are many ways to prepare TiO_2 layers. Among these preparation methods, the Chemical Vapour Deposition method with organometallic precursors (MOCVD method), is a promising one to obtain nanostructured surfaces. From the variety of TiO_2 nanostructures deposited by MOCVD, original and reproducible 2D (wires) and 3D (membranes, crucibles, trees...) nanostructures can be obtained [5] by varying growth parameters and catalysts.

Fe-TiO_2 COaxial Heterostructure Nanorods were also obtained. This subject will be detailed in this paper. Growth parameters have been varied and their effects on these structures have been studied (deposition time, temperature, SiO_2 layer...) [6]. Also the Fe-TiO_2 COHN were characterized by SEM and TEM techniques.

Some coaxial heterostructure nanowires are presented in literature. However, they are deposited in multiple steps using other technical parameters and materials [7][8]. Other similar coaxial structures would be the filled carbon nanotubes realised in one step. They have a core made out of iron, nickel or cobalt, depending on the used catalyst, but they do not contain any TiO_2 and they are not obtained using induction heating [9][10][11].

Therefore, the growth process of Fe-TiO_2 coaxial heterostructures nanorods in presence of a magnetic catalyst in a magnetic field by MOCVD is part of a new domain that we are going to deepen.

II. MATERIALS AND METALS

Reagents

The precursor, titanium (IV) isopropoxide

($Ti(OC_3H_7)_4$) (99.999% metals basis) and ferrocene ($Fe(C_5H_5)_2$) (98%), were purchased from Sigma Aldrich.

Synthesis of Fe-TiO_2 COHN

Fe-TiO_2 COHN were grown in a home-made MOCVD system. The silicon based substrates were placed on a graphite susceptor inside a silica glass tube, surrounded by an induction heating coil. The induction system, provided by FIVES CELES, is an aperiodic generator HF 6kW working at 400 kHz. In the silica glass reactor, a dynamic vacuum was maintained at 76 torr under N_2 constant flow (1.2 L/min). The titanium isopropoxide source was maintained at 40°C and the ferrocene source at 50°C. These precursors were introduced into the reactor by the carrier gas (N_2) flowing through their containers at a rate of 0.6 L/min each.

When the precursor molecules were in contact with the 550°C heated substrate, they were decomposed by pyrolysis and TiO_2 grew. Without catalysts, TiO_2 columns are usually obtained. In the presence of catalysts, such as ferrocene, original 2D-3D nanostructures were obtained, like the Fe-TiO_2 COHN.

Fabrication method of substrates

In order to have silicon without SiO_2, the substrates were cleaned by sputtering under an argon flow.

A silica glass substrate was used for the pure amorphous SiO_2 substrate. To obtain silicon with amorphous SiO_2 layer, a PVD method at ambient temperature was used. To ensure silicon with crystalline SiO_2, a SiO_2 layer was grown applying a heat treatment to the substrate in an oxide atmosphere at 950°C for 60 min. Another substrate was used without cleaning, leaving the native SiO_2 islands untouched.

Studied parameters

To understand the growth process and eventually build a growth model, the influence of three growth parameters was studied: deposition time, deposition temperature and the substrate type.
The deposition time ranged from 5 to 100 minutes to see the first instants of the growth as well as the morphology of the TiO_2 nanorods at long deposition times.

The deposition temperature varied between 400°C and 750°C, in order to be in the decomposition temperature range of the ferrocene.

Various silicon based substrates were used: silicon without SiO_2, amorphous SiO_2, silicon with amorphous SiO_2 layer, silicon with crystalline SiO_2 layer, silicon with crystalline SiO_2 islands.

Characterisation

Scanning Electron Microscopy (SEM) images were obtained on a JEOL JSM 6400F SEM operating at 20 kV. Transmission Electron Microscopy (TEM) experiments were conducted on a JEOL JEM-2100F microscope operated at 200 kV and fitted with an ultrahigh resolution pole piece achieving a point to point resolution of 0.19 nm. A detailed analysis was carried out with the different features of the TEM: Scanning Transmission Electron Microscopy (STEM), Energy Dispersive Spectroscopy (EDS, Bruker XFlash Detector 5030 spectrometer), Selected Area Electron Diffraction (SAED) and Electron Energy Loss Spectroscopy (EELS, Gatan GIF Tridiem).

III. RESULTS AND DISCUSSION

The results are divided in two sections. The first presents the study growth parameters and their influence on the TiO_2 nanostructures. The second consists of the thorough characterization of Fe- TiO_2 COHN.

Growth parameters

Deposition time

The other growth parameters remain constant: T = 550°C; silicon with crystalline SiO_2 islands substrate. The SEM images (figure 1) show the obtained TiO2 layers when varying the deposition time. By depositing TiO_2 for a short time, 5 - 10 min, the first steps of the growth are visible. The longer deposition times should show how the TiO_2 nanorods react to a longer exposure of precursor inflow and longer heating.

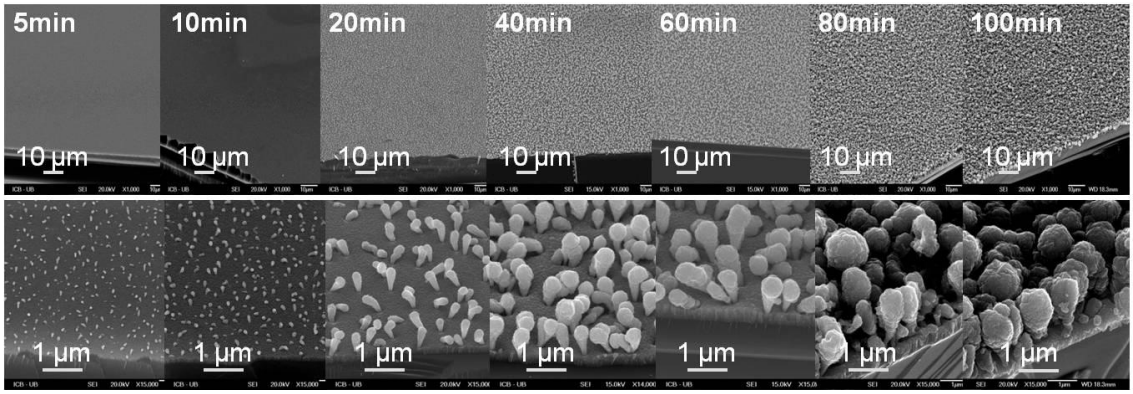

Figure 1 SEM images: Homogeneity of the TiO_2 layer and evolution of height and head diameter of TiO_2 nanorods with time (T = 550°C; silicon with crystalline SiO_2 islands substrate).

For each studied deposition time, a homogenous distribution of TiO_2 nanorods can be observed on the substrate's surface. At higher magnifications, on the silicon with crystalline SiO_2 islands substrate a TiO_2 layer can be observed (figure 2), also seen in depositions without ferrocene, on which TiO_2 nanorods grow. The TiO_2 nanorods are composed of a stem ending in a spherical head.

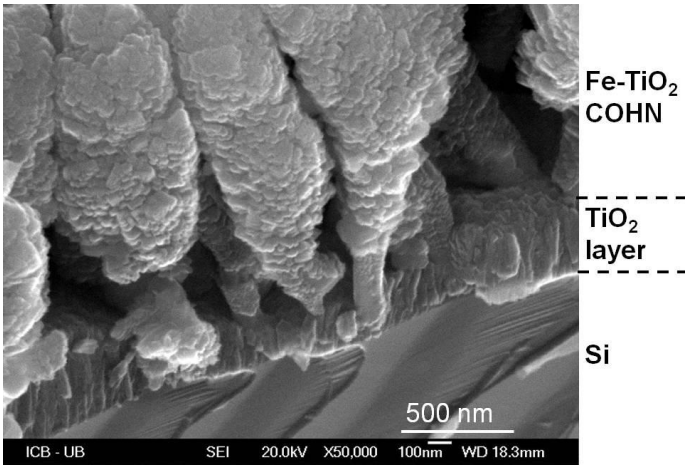

Figure 2 SEM image: TiO_2 layer and TiO_2 nanorods deposited on silicon with crystalline SiO_2 islands substrate, T=550°C, t = 100 min.

For a given deposition time the size distribution of the height and head nanorods is very narrow, thus a quantitative analysis of the nanorods' size with time could be done, as seen in figure 3.

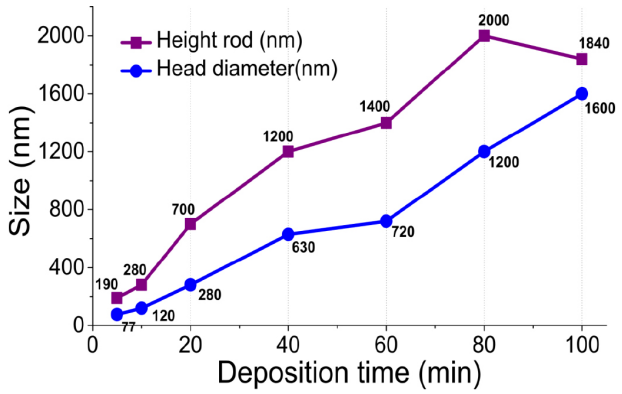

Figure 3 Evolution of height and head diameter of TiO_2 nanorods with deposition time.

After 5 minutes of deposition, TiO_2 nanorods have already a height of 190 nm and a head diameter of 77 nm. With longer deposition times nanorods reach a height of 2 μm and a head diameter of 1.2 -1.6 μm. At 80 – 100 min of deposition time, the heads start to touch each other, resulting in a second TiO_2 layer. This layer presents a superhydrophobic character, where the water drop keeps its round form, but does not slide from the surface.

At the beginning of the deposition, TiO_2 nanorods start to grow in certain nucleation sites. With increasing time of deposition, a higher quantity of reagents will enter the reactor and reach the sample. This matter is deposited on the higher points of the TiO_2 layer, these being the already existing nanorods, especially the heads. The heads will grow until they eventually touch each other, building the second TiO_2 layer seen in figure 2.

Deposition temperature

The other growth parameters remain constant: t = 20 min; silicon with crystalline SiO_2 islands substrate. Knowing that the TiO_2 nanorods start growing at over 550°C, the question was how a different temperature would influence these structures. A step of 50°C was decided starting from 400°C, ferrocene being stable until this temperature. The upper limit was set at 750°C.

Figure 4 shows that at 400°C and 450°C, a TiO_2 layer without any nanorods is created. At 500°C, head like structures begin to appear on a prior formed titanium layer. Above the usual temperature, at 600°C and 650°C, an increase in height is seen, but not in head diameter. Starting from 700°C, the TiO_2 layer structure and morphology changes altogether. It is built of massive TiO_2 crystals.

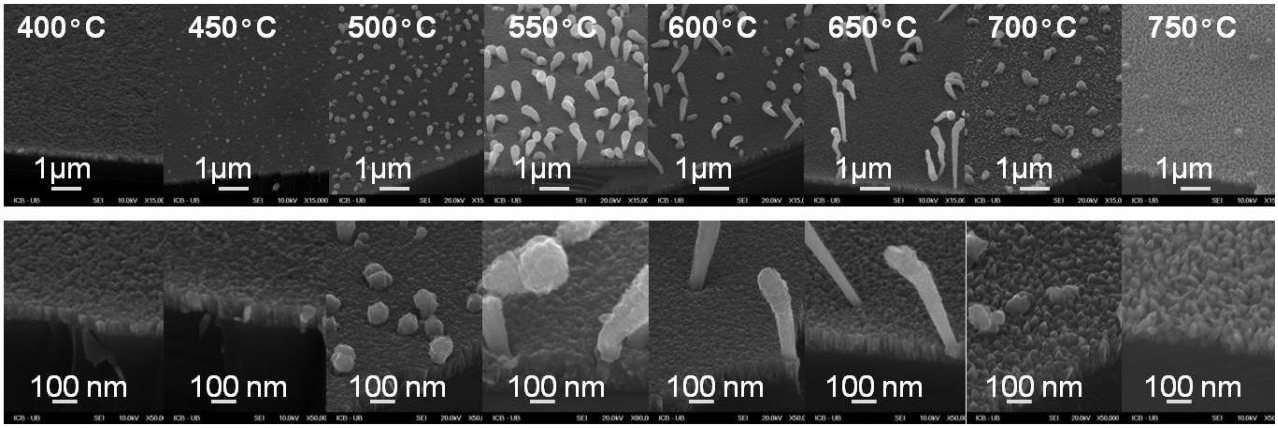

Figure 4 SEM images: Evolution of TiO_2 nanorods with temperature (t = 20 min; silicon with crystalline SiO_2 islands substrate).

The quantitative evolution of both, height and head diameter, of TiO_2 nanorods between 500°C and 650°C is presented in figure 5.

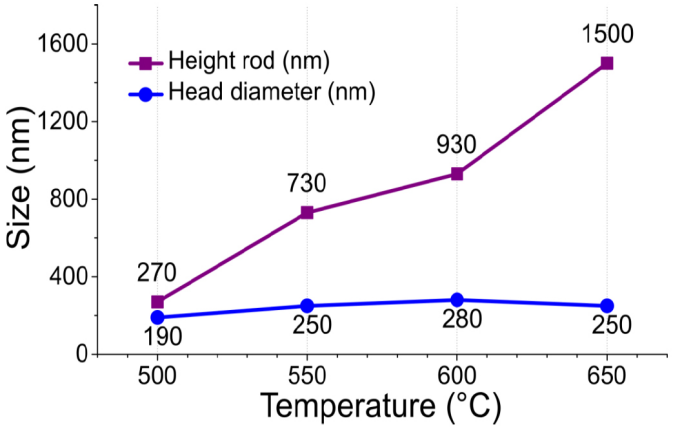

Figure 5 Evolution of height and head diameter of TiO_2 nanorods with temperature.

By varying the deposition temperature the head diameter does not change but the height of the TiO_2 nanorods is highly influenced. For a temperature difference of 150°C the height increases 5 times. It starts at 500°C with a height of 270 nm being almost buried in the TiO_2 initial layer, reaching a height of 1.5 μm at 650°C.

In order to obtain TiO_2 nanorods, a temperature between 500°C and 650°C is necessary. At lower temperatures the catalyst is not yet decomposed and at higher temperatures the structure of TiO_2 layer changes. Also, the increase of deposition temperature results in higher TiO_2 nanorods. This could be explained by the effect that temperature has on the reactions rate. The percentage of reactant molecules that have sufficient energy to react is higher at higher temperatures (the thermal energy being greater than the activation energy $E > E_a$).

Substrates

The other growth parameters remain constant: t = 20 min; T = 550°C. While searching for parameters responsible for the growth of TiO_2 nanorods, the point of interest shifted towards the presence of SiO_2. TiO_2 depositions were realised on different types of SiO_2 layers, amorphous and crystalline as described before. Growth without SiO_2 (Substrate: Silicon without SiO_2) is presented in figure 6.

The TiO_2 layer, that usually appears, can be observed. On the surface there are some small structures, but no nanorods.

Growth on amorphous SiO_2 (Substrate: Silica glass, Silicon with amorphous SiO_2 layer) is presented in figure 7a and 7b.

Figure 7a shows the TiO_2 layer deposited on a silica glass. A structured TiO_2 layer is visible, but no nanorods are present. Figure 7b shows the TiO_2 deposited on silicon with an amorphous SiO_2 layer is presented. The initial TiO_2 layer is present and some isolated seahorse-like seeds show up.

Growth on crystalline SiO_2 (Substrate: Silicon with crystalline SiO_2 islands, Silicon with crystalline SiO_2 layer) is presented in figure 7c and 7d. On both samples, a homogenous distribution of TiO_2 nanorods is clearly recognizable. On the silicon with crystalline SiO_2 islands the nanorods are higher and better developed than on the silicon with crystalline continuous SiO_2 layer.

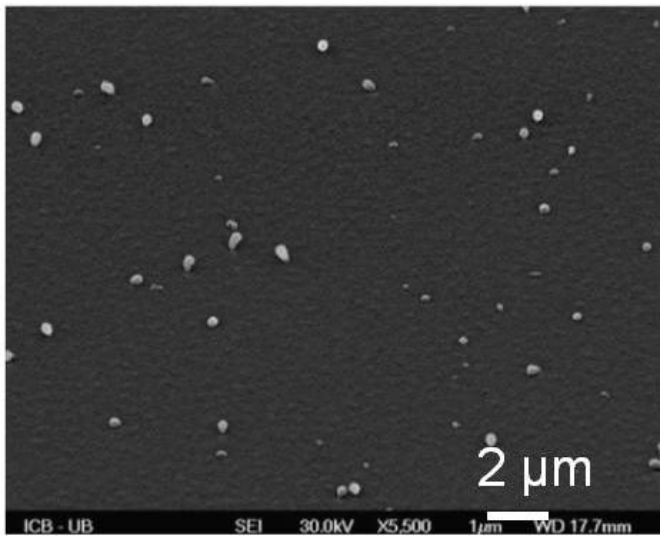

Figure 6 SEM image: TiO_2 layer on Silicon without SiO_2 (t = 20 min; T = 550°C).

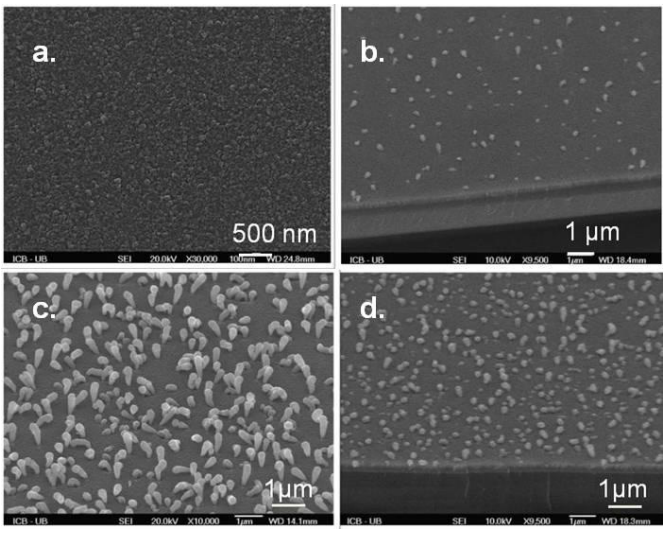

Figure 7 SEM images: TiO_2 layer on silica glass (a), on silicon with amorphous SiO_2 layer (b), on silicon with crystalline SiO_2 islands (c), on silicon with crystalline SiO_2 layer (d) (t = 20 min; T = 550°C).

It is obvious that the presence of crystalline SiO_2 is a necessity for the growth of TiO_2 nanorods. The crystalline SiO_2 layer favors the appearance of Fe-TiO_2 COHN, but in order to have the desired shape of Fe-TiO_2 COHN, crystalline SiO_2 islands are necessary. In literature, a growth model explains the influence of the oxide on the growth: it is called the Oxide Assisted Growth model, where the growth is induced by the oxide and not metal catalysts [12][13]. But, mostly the oxide is present in powder form, not as a layer. Other articles show that a SiO_2 layer can be a guide for the growth direction of nanowires [14].

Characterization of Fe-TiO_2 coaxial heterostructure nanorods.

After analyzing the influence of the growth parameters, the TiO_2 nanorods were thoroughly characterized by transmission electron microscopy (TEM).

Scanning transmission electron microscopy images (STEM) show that the TiO_2 nanorods are made up of two parts: they have a core-shell structure. The two zones are clearly distinguishable: the core which does not exhibit any rugosity on its surface and has a conical shape with a ball at the tip, and the shell with a high rugosity (figure 8 left).

Energy Dispersive Spectroscopy

STEM images are Z (atomic number) and thickness dependent. Thus, the previous micrographs suggest a different chemical composition between core and shell, the iron constituting the core (brighter contrast therefore heavier element) A chemical analysis was thus undertaken including EDS chemical mapping and a quantitative analysis from the chemical map. The results can be seen in figure 8 on the right side and table 1.

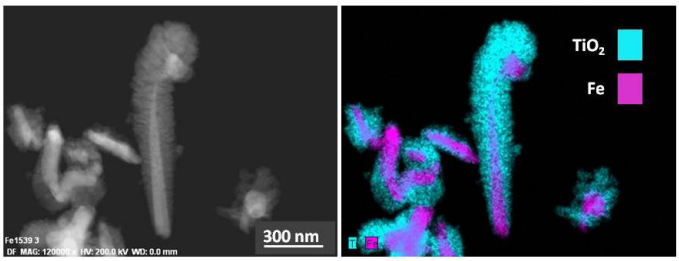

Figure 8 STEM image: Core and shell (left side) and (Ti-Ka ,Fe-Ka) chemical map of TiO_2 nanorod (right side).

Table 1 Quantitative analysis of oxygen, titanium and iron in two areas of seahorse structure of figure 10.

Atomic percentage [at. %]	Spot 1	Spot 2
O	72.6	53.0
Ti	26.0	15.5
Fe	1.4	31.5

As expected from STEM images, the EDS results from area 1, tip of the shell, confirm the pure titanate oxide composition of the shell. The 1.4 atomic percent of iron are certainly coming from the rough sample preparation method: scraping of the sample surface. From area 2, tip of the core, the percentage of titanium decreases to 15%, while the percentage of iron grows to 32%. Because of the titanate shell surrounding the iron core, it is difficult to draw any clear conclusion about the core composition: pure iron or iron oxide. The stem ends suggest that the core is pure iron. Due to environmental pollution/contamination, it is complicated to conclude anything from the oxygen quantification. Titanate oxide is certainly a TiO_2 chemical phase and iron is pure. If so, the excess of oxygen is the same for both areas: around 20%. Crystallographic analyses must be carried out to check the titanate and ferritic phases.

Crystallographic analysis

The shell was analyzed in different places to determine which TiO_2 phase is present. Surprisingly, three different TiO_2 crystallographic phases were observed. Figure 9 present the analyzed crystallites of the shell and their respective diffraction patterns. They confirm the presence of rutile (ICDD card 01-086-0148), anatase (ICDD card 03-065-5714) and brookite (ICDD card 01-076-1934) crystallites in the shell of the TiO_2 nanorods.

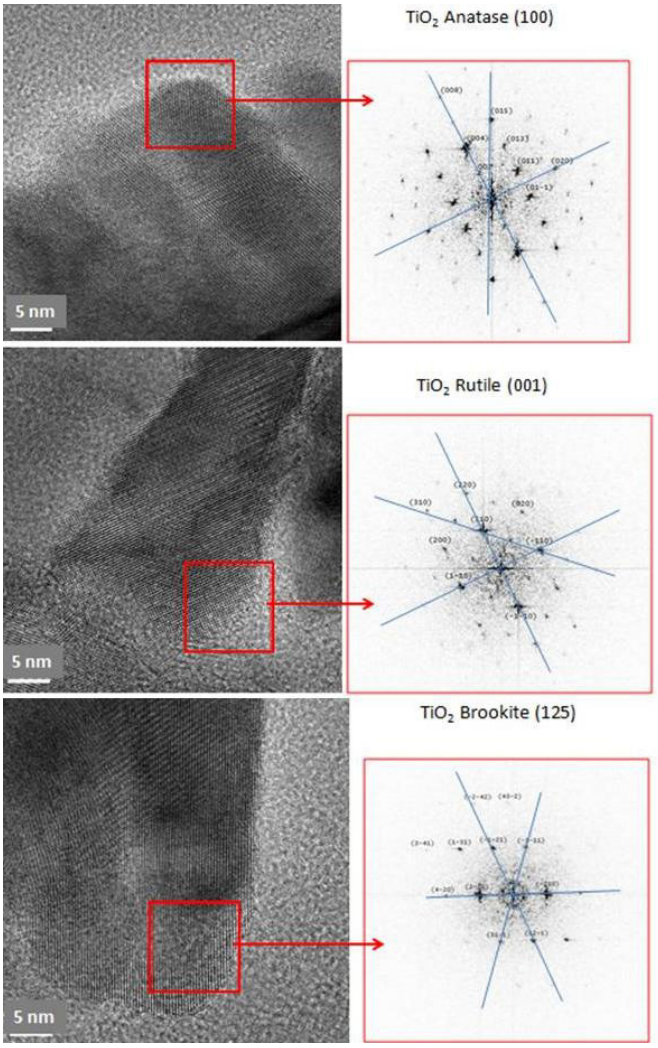

Figure 9 Crystallographic analysis: analyzed crystallite (left side) and experimental diffraction pattern of TiO_2 anatase, rutile and brookite (right side).

The core was also analyzed to check its phase: pure iron or an oxidized phase of iron. The analyzed area and the experimental pattern of ferrite (ICDD card 00-006-0696) is presented in figure 10.

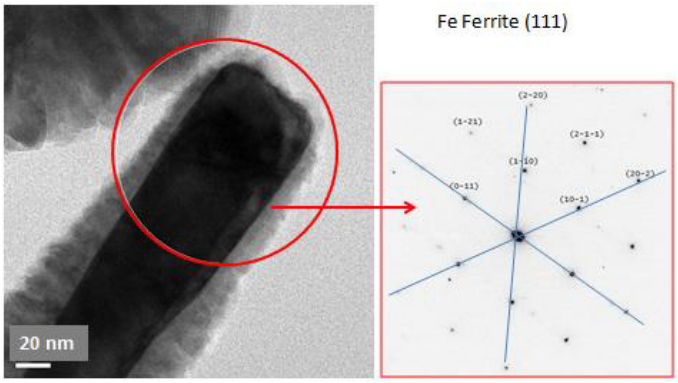

Figure 10 Crystallographic analysis: analyzed core area (left side) and experimental diffraction pattern of Ferrite (right side).

The crystallographic analysis points out that the core is a pure iron phase.

Electron energy loss spectroscopy

To confirm that the core is not an iron oxide, electron energy loss spectroscopy was utilized. This is an analytical technique that measures the change in kinetic energy of electrons after they have interacted with a specimen. When carried out in a TEM, EELS can give structural and chemical information about a solid [15]. Figure 11 shows the analyzed area and its respective EELS spectrum background extracted.

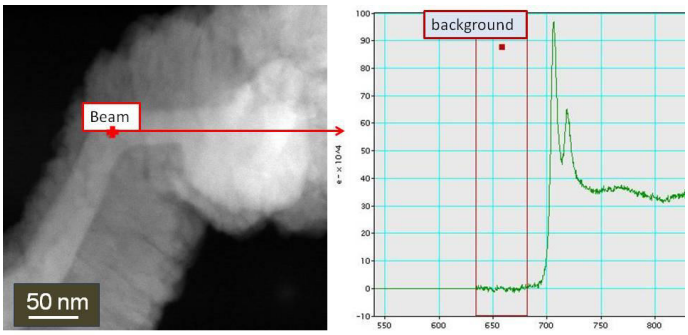

Figure 11 EELS analysis: left: analyzed zone; right: EELS spectrum of L_{23} Fe edge.

The experimental EELS spectrum of L_{23} Fe edge exhibits no pre-edge shoulder (feature commonly observed for iron oxides) as shown in figure 12. This confirms that the core is made of pure iron.

These original Fe- TiO_2 COHN structures are new to the literature. The only similar structures found would be the iron filled CNT. They have the same coaxial form: a shell and a core. The core is also made of iron, because ferrocene is used as a catalyst, but the shell is made of carbon, while in our case the shell is made of TiO_2. The growth models described for the CNT with ferrocene catalyst are the base and tip growth mode. Base growth mode consists in a metal catalyst that remains on the substrate surface while the CNT grows beginning from it. The tip growth mode assumes that the metal catalyst detaches from the substrate and ends up at the tip of the CNT. For iron filled CNT however, the growth mode would be a combined mode: the iron enters through the open tip of the carbon shell, then a larger catalyst particle attaches to the tip, increasing the speed of the growth. This change in pressure causes the large catalyst particle to fall into the CNT and filling it. [19]

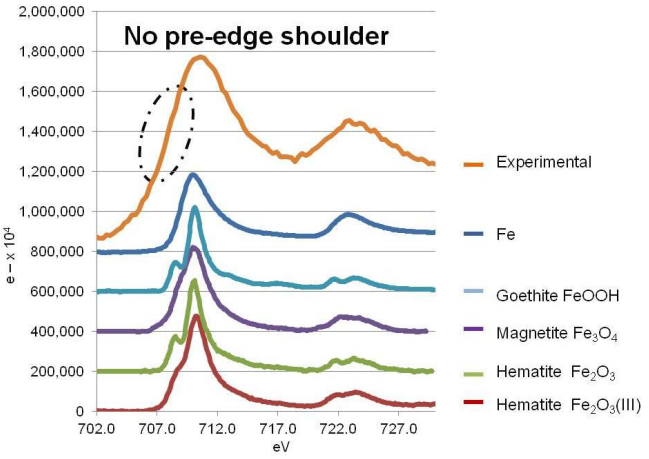

Figure 12 Comparison of the experimental EELS spectrum with the EELS spectrums of iron (Fe) [16], Goethite (FeOOH) [17], Magnetite (Fe_3O_4) [17], Hematite (Fe_2O_3) [17], Hematite (Fe_2O_3) (III) [18] found in literature.

IV. CONCLUSIONS

In the present study reproducible Fe-TiO_2 core-shell nanorods were successfully grown on silicon wafers from titanium isopropoxide precursor, in the presence of ferrocene as a catalyst. Their nanosize and structure was confirmed by techniques as SEM, TEM, EDS, SAED and EELS.

In order to establish a growth model for Fe-TiO_2 COHN, it needs to be considered that the core iron comes from the ferrocene catalyst, which makes the presence of ferrocene a necessity. This limits the deposition temperature interval, because ferrocene needs to be decomposed, but not to totally disappear. Also, on the substrate crystalline SiO_2 islands are needed, and not as a continuous layer.

All Fe-TiO_2 COHN of one sample have the same size and they are built of a TiO_2 shell (anatase, rutile and brookite crystallites) and a pure iron core. Their size (height, head diameter) increases with time, building a second TiO_2 layer.

We propose that the Fe-TiO_2 COHN growth is related to the induction heating method (using a alternative magnetic field). This field would interact with the ferromagnetic catalyst creating "hot spots"- nucleation points. It would also orient the ferromagnetic particles of the catalyst creating the vertical iron cores. This line of thought is yet to be explored in order to define a more precise growth model.

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