ON THE STRUCTURE OF PENTAGONAL CROSS-SECTIONS NANOWIRES

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Abstract

In this work we comment and discuss the structure of pentagonal cross-section nanowires such as those reported for the case of silver, gold and copper and we show that all of them are closely related to a decahedron-base structure.

Key words: Silver and gold nanowires, electron microscopy, electron diffraction patterns.

Introduction

One of the most interesting features of the silver nanowires produced by the polyol method in presence of PVP is their remarkable structure. Their cap resembles a decahedron and there is experimental evidence of a pentagonal cross-section all along the long axis of the nanowire (1, 5). These features have been also reported in nanowires of gold and copper. Based on these observations, it has been proposed that they evolved from a multi-twin decahedral nanoparticle growing in the [110] direction with the capping agent assisting to direct the structure by stabilizing more effectively the new formed {100} facets than the {111} facets. However, up to today there is not a complete explanation of all the features presented in the electron diffraction patterns obtained from the long axis of this type of nanowires. Herein, we present a comprehensive transmission electron microscopy (TEM) analysis on the structure of these penta-twinned nanowires (Dh-NWs).

Pentagonal arrangement in the multiple twinned particles (MTP) is quite known. MTP nanoparticles of transition metals with face-centered cubic (FCC) lattice (7-9) and some related materials such as carbon (9) and silicon (10) have been reported. Based on these studies, the basic structure of a decahedral particle can be described as the junction of five tetrahedron single crystals with twin-related adjoining faces. The theoretical angle between two (111) planes is ~70.5°, so by joining 5 tetrahedrons, which are bounded by {111} facets, a gap of ~7.5° is generated. Thus, to fill this gap some form of internal strain is necessary, giving place to dislocations and other structure defects (7-9). These defects have been observed in the TEM cross-sectional images of the mentioned penta-twinned nanowires (1).

Therefore, the structure of these Dh-nanowires has been described as five triangular prisms joined in such a way that they show the {100} planes on their sides and are capped by {111} planes, growing along the [110] direction (1, 4-6). However, up to now it is not clear the actual physical mechanism that allows the growth of such structure having a decahedral cap and be energetically stable. It is clear that a comprehensive understanding of the structure is required to elucidate the growth mechanism.

In this work, we present and discuss the structure of this type of nanowire through the analysis of the high resolution TEM (HRTEM) images and of the selected area electron diffraction (SAED) patterns from silver nanowires, but all say in this case is also valid for gold and copper. We have found that both the HRTEM images and the SAED patterns can be easily interpreted in the basis of a decahedron.

Experimental Procedure

The synthesis for silver nanowires has been reported elsewhere. Silver nanowires were synthesized by the polyol reduction of silver nitrate ($AgNO_3$) in presence of PVP. Scanning electron microscopy of the nanowires was conducted using the scanning electron microscopes (SEM) Hitachi 4500F. Transmission electron microscopy was conducted in a HRTEM JEOL 2010F microscope equipped with Schottky-type field emission gun, ultra-high resolution pole piece (Cs = 0.5 mm), and a scanning transmission electron microscope

(STEM) unit with high angle annular dark field (HAADF) detector operating at 200 kV. For digital image processing the Digital Micrograph (GATAN) software was used. To simulate the electron diffraction patterns, the SimulaTEM software (11) was employed.

Results

We have already shown that the HRTEM images of the silver nanowires can be interpreted as a Moire pattern contrast based on a penta-twinned decahedron and that their SAED patterns can be also completely generated through the same decahedron basis (12).

SAED patterns along the long axis of individual pentagonal nanowires are presented in Figure 1. The TEM analysis of these SAED patterns revealed a rotational periodicity of 18° between them. This is an expected characteristic due the pentagonal cross-section symmetry of the nanowires. Both SAED patterns are easily interpreted as the overlapping of the [100] and [112] zone axes of the silver FCC unit cell in the case of Figure 1a, and the overlapping of the [111] and [110] zone axis for Figure 1b. The presence of an aperiodic sequence of diffraction spots in Figure 1a is of notorious relevance but it is produced by the combination of double diffraction due to twinning and nano-size-dimension effects, as indicated in figure 2.

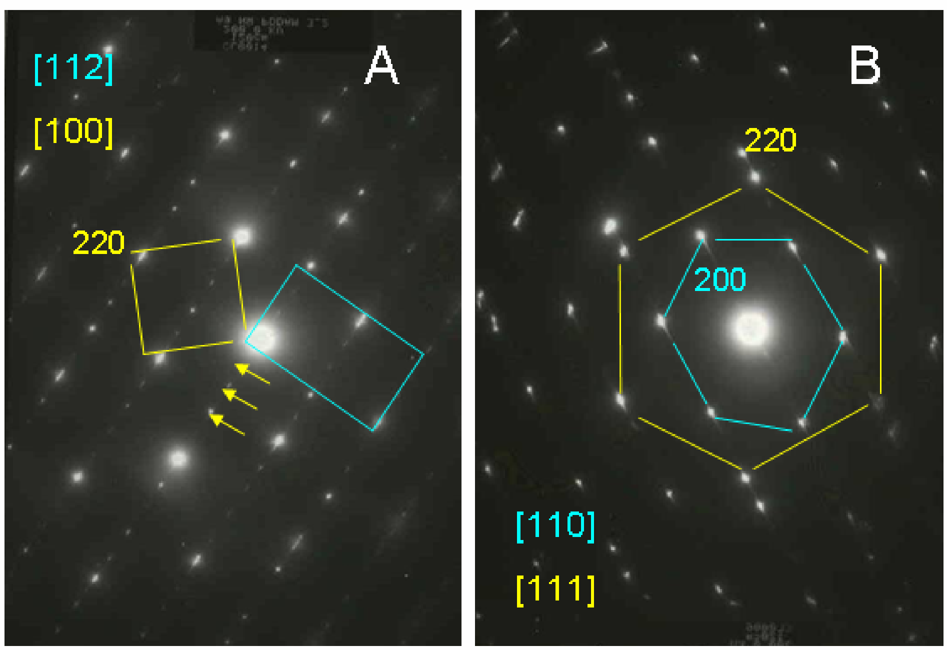

Fig. 1. Characteristic selected area electron diffraction (SAED) patterns of the Dh-NW. Their indexation indicates that they correspond to the overlapping of [100] and [112] zone axes in (A), and the overlapping of [111] and [110] zone axes in (B). Note the existence of an aperiodic sequence (indicated by arrows) of diffraction spots in (A).

In figure 2 the analysis of the diffraction pattern shown in Figure 1A is presented. Because the nanometric size of the nanowire along its cross-section, which produce enlarged reciprocal spots, it is easily deduced that some of the spots composing this SAED pattern are in fact belonging not only to the Zero Order Laue Zone (ZOLZ) but also to the First Order Laue Zone (FOLZ). Some others are produced by double-diffraction effect.

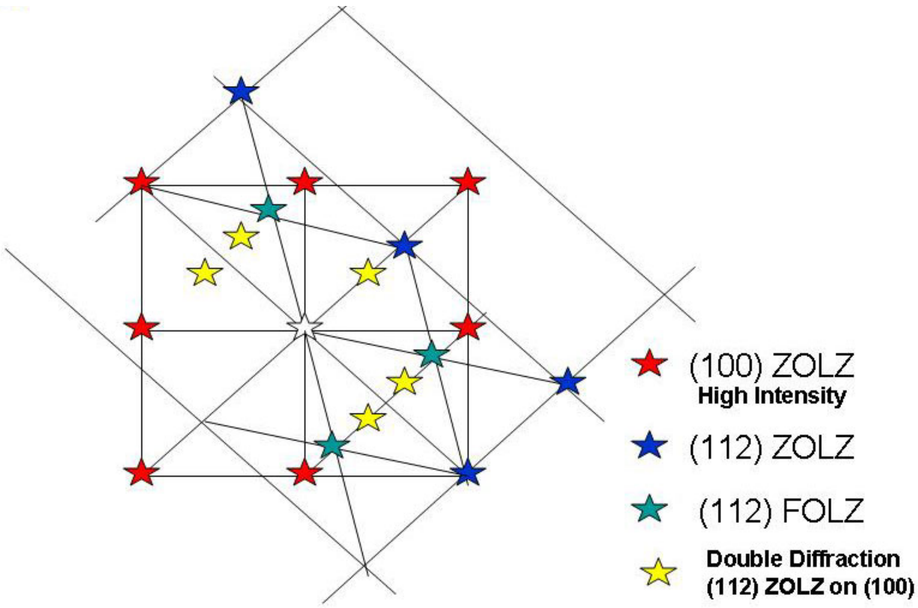

Fig. 2. Analysis of the diffracted spots observed in figure 1A. Some of them are ZOLZ spots while others are FOLZ and double diffraction spots.

As commented previously, the Dh-NW habit has been described as an elongated pentagonal dipyramid (13). However, there are different ways to build this Johnson Solid. One is that currently reported as the structure of the Dh-NW, which consists of five triangular prisms in such a way that they present {100} planes on their sides and are capped by {111} planes, growing along the [110] direction (1, 5). We generated this model and obtained its corresponding electron diffraction pattern using the SimulaTEM software (11). The results are presented in Figure 3; note the similarity between these patterns and those shown in figure 1.

The model is a polyhedron of twelve vertexes (two poles and ten vertexes at the waist), twenty five edges, ten equilateral triangular faces, and five squared lateral faces. It was grown from a decahedron by adding a great number of layers. Each layer was composed by two sub-layers: one that is the waist of the decahedra and the other that is the immediate layer over the waist. The final model is composed of 24,739 atoms with twenty intermediate (110) planes.

Making the comparison among the simulated diffraction patterns show in Figure 3 and the experimental ones shown in figure 1, we noted that although there is presence of an aperiodic sequence of diffracted spots, this sequence is not completely equal to the observed in the experimental patterns. Therefore, the model presented in Figure 3 does not reproduce to the fully extent the features of the electron diffraction patterns shown in Figure 1. Therefore, an alternative idea is necessary.

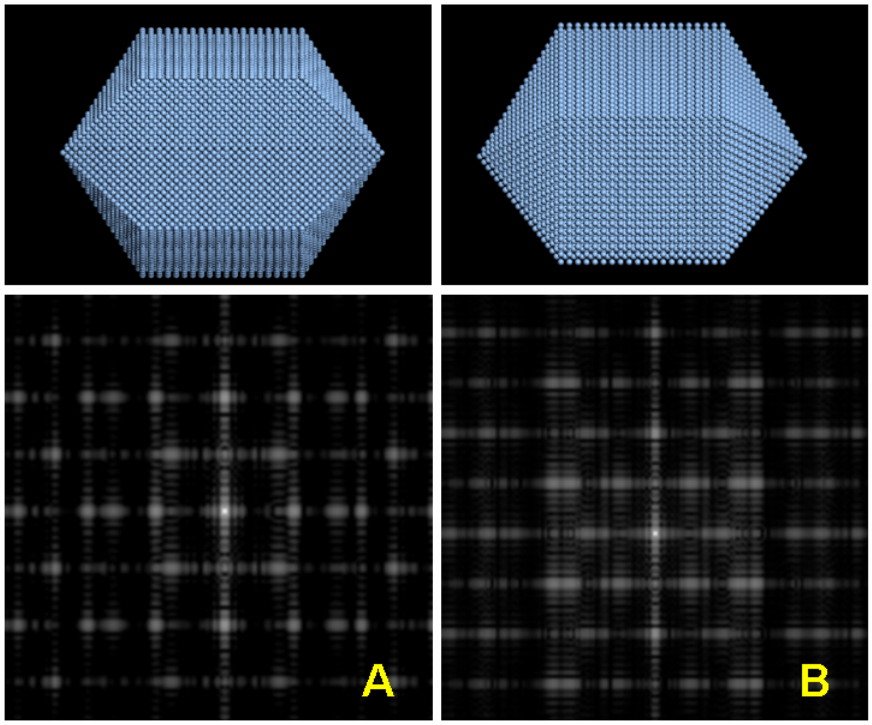

Fig. 3. Model of a Dh-NW structure consisting of 5 triangular prisms based on the Ag FCC unit cell joined along the common [110] edge and their corresponding simulated SAED patterns. A) Structure along one of the five [100] directions. B) The same structure as in (A) but rotated by 18o around the five-fold pentagonal axis. This model generates a different aperiodic sequence than the one observed in figure 1.

Let us back to the decahedron formulation. As for the case of the previous model, we generated a model for a five-twinned silver decahedron and simulate the corresponding electron diffraction pattern along the same directions as for the previous simulated structure. These results are shown in Figure 4.

For this model, we started from a decahedron without a central site that has only seven vertexes in two layers. The first layer (order 1) is covered by a second layer (order 2), with a shell of forty seven sites distributed as follows: seven vertex sites of two types, thirty edge sites in three layers (ten sites of one type and the equator), and ten at the triangular faces, for a total of fifty four sites in the cluster. Decahedra of superior order were formed by covering this cluster with successive shells to obtain a final decahedron composed of 6,670 atoms. Figure 4c shows the corresponding SAED pattern to the direction 18^{o} from figure 4b.

The comparison between the simulated diffraction patterns of the 5-twinned silver decahedron and the experimental ones from the Dh-NW presented in Figure 1 demonstrates that there is an almost perfect match among them.

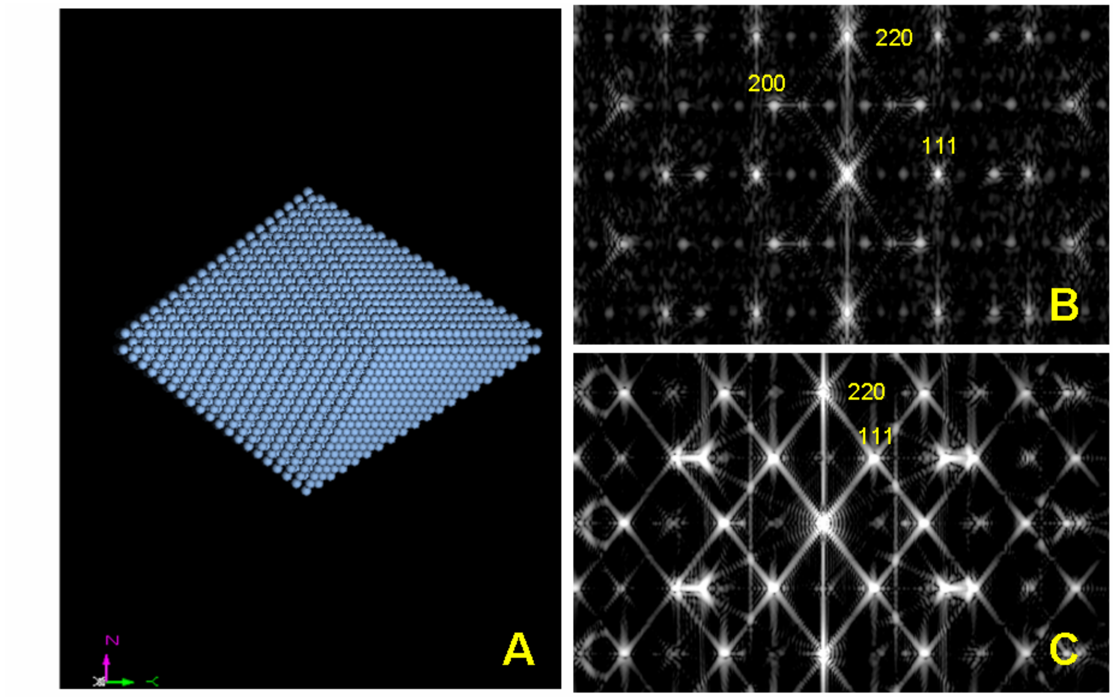

Fig. 3. A) Simulated silver decahedron. This structure consists of 5 tetrahedra based on the Ag FCC unit cell joined along the common [110] edge. B) Simulated SAED pattern along one of the five [100] edges. (C) Simulated SAED pattern after rotating the direction of (B) by 18^o around the five-fold pentagonal axis.

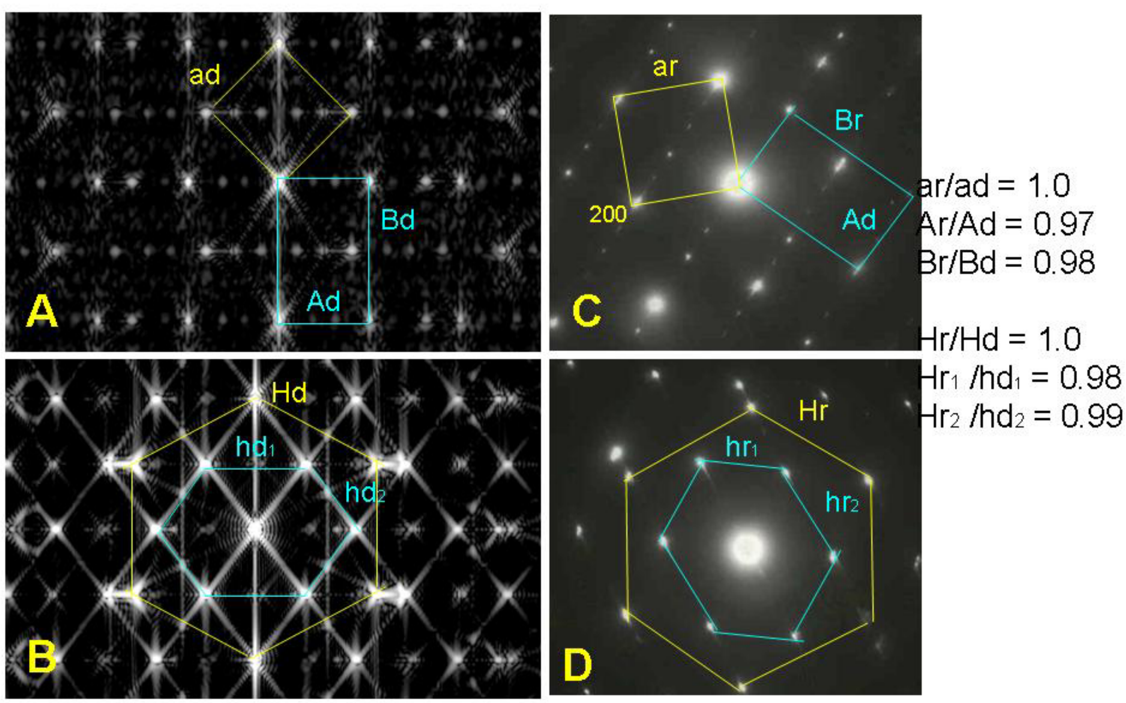

Fig. 4. Comparison of the simulated SAED patterns (A, B) of Figure 3 with the experimental ones (C, D). The aperiodic sequence observed in the experimental patterns is fully reproduced.

Nevertheless, let us make the comparison of the simulated SAED patterns of the decahedron with the experimental ones. This is done in Figure 4. The measurements indicates that, making ar/ad = 1.0 and Hr/Hd = 1.0, the ratios Ar/Ad = 0.97 (i.e. 3% of difference), Br/Bd = 0.98 (2%), hr_1/hd_1 = 0.98 (2%), and hr_2/hd_2 = 0.99 (1%). We also noted that the generated aperiodic sequence of diffracted spots is equal to the observed in the experimental patterns. But not only this, IT IS SIMILAR IN POSITIONS AND IN INTENSITY. Therefore, the experimentally observed diffracted aperiodic sequence is produced by the twinning relationship of the 5 crystals that are forming the decahedral nanostructure and all the images described so far, correspond to a structure based on a 5-twinned decahedron.

We have already proposed that one way of see the structure of the Dh-NWs could be as a chain of decahedra joined along the vertex (which is parallel to the 5-fold symmetry) (12). In such a model, the Dh-NWs will be always growing along the [111] direction. However, there is a lot of work to be done in this direction.

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