Structural analysis of the epitaxial interface Ag/ZnO in hierarchical nanoantennas

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Detectors, photo-emitter, and other high order radiation devices work under the principle of directionality to enhance the power of emission/transmission in a particular direction. In order to understand such directionality, it is important to study their coupling mechanism of their active elements. In this work, we present a crystalline orientation analysis of ZnO nanorods grown epitaxially on the pentagonal faces of silver nanowires. The analysis of the crystalline orientation at the metal-semiconductor interface (ZnO/Ag) is performed with precession electron diffraction under assisted scanning mode. In addition, high resolution X-ray diffraction on a Bragg-Brentano configuration has been used to identify the crystalline phases of the arrangement between ZnO rods and silver nanowires. The work presented herein provides a fundamental knowledge to understand the metal-semiconductor behavior related to the receiving/transmitting mechanisms of ZnO/Ag nanoantennas. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4964719>]

Metal-semiconductor materials with highly ordered matched interfaces have become more attractive in optoelectronic applications because of the unique directionality that exhibit when used as an active element.^{1,2} Crystalline phases matching at the interface junction is a key feature that both metal and semiconductor should exhibit for a controlled epitaxial growth. Most of the metal-semiconductors junctions are designed with the aim of growing the semiconductor material epitaxially from the substrate, which acts as both nucleation center and metal-linked support for electrical applications.^{3,4} Although epitaxial growth normally requires sophisticated pieces of equipment, chemical methods using microwaves can be employed with a high precise control at the nanoscale level. This is done by controlling parameters such as the deposition rate, temperature, and concentration of the species.^{5,6} Furthermore, perfectly aligned nanostructures can be monitored in real time within a transmission electron microscope as demonstrated in a previous work.⁵ Recently, microwave irradiation processes (MIPs) have been employed as an alternative in the chemical synthesis of metallic nanoparticles, quantum dots, and assembled nanostructures.^{7–9} The chemical synthesis using MIP reduces the reaction time and can produce a controlled growth with a good alignment of the crystalline nanostructures.¹⁰ In the present work, the crystalline orientation analysis at the ZnO/Ag interface is reported. ZnO rods grown on lateral faces of the pentagonal cross sectional area of silver nanowires (Ag NWs) are assembled in a hierarchical nanoantenna. The characterization at the interface has been described by precession electron diffraction (PED) through the assisted crystal orientation phase determination system (ASTAR) using transmission electron microscopy (TEM).¹¹ The PED-ASTAR analysis provides crystal phase orientation maps locally at

individual ZnO nanorods (ZnO NRs) and Ag NWs assembled epitaxially at the interface. In addition, X-ray diffraction under grazing angle mode has been performed by analyzing the peaks related to the hexagonal ZnO nanorods (ZnO NRs) and cubic Ag NWs.

Ag NWs have been synthesized using the polyol method as described by Sun *et al.*¹² However, in the present study, the time reaction has been modified in order to control the length and distribution of Ag NWs ranging from few minutes to approximately one hour. The nanowires dimensions were monitored at different times and studied by scanning electron microscopy (SEM). Subsequently, for the self-assembled process to synthesize ZnO NRs on the Ag NWs, 5–25 mM of zinc acetate dihydrate (Zn(Ac)₂, 98% reagent Sigma-Aldrich) and 5–25 mM of Hexamethylenetetramine (HMT) are mixed in a solution. Finally, a multi-mode cavity ETHOS EZ microwave digestion system has been employed to obtain the hierarchical structure of ZnO/Ag nanoantennas. The density of ZnO NRs distributed along the Ag NWs as well as their length has been controlled by changing the three main variables in the chemical process: temperature, power, and reaction time as we reported in detail previously.⁵

In order to understand the mechanism through which the ZnO NRs are coupled to the active faces planes (001) of the Ag NWs, a series of different reaction times were monitored by SEM. Figure 1 shows that the distribution of the ZnO NRs increases as a function of the reaction time. By analyzing the SEM micrographs, we observed that the initial ZnO nanorods are distributed randomly at different locations along the (001) planes of the Ag NWs until they reach the saturation, in which no more empty spaces are available to insert any additional ZnO NRs on the Ag NWs.

The well-defined 3D penta-arrangement shows that the ZnO NRs are similar to an aerial antenna configuration,

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FIG. 1. SEM micrographs taken at different reaction times: in (a)–(c), it is clearly observed the increase in the linear density of ZnO NRs per length of Ag NWs until it reaches the final saturated number of ZnO elements, as shown in (d).

shown in Figure 2. It reveals how the ZnO NRs are epitaxially connected along the (001) planes faces of the Ag NWs, which is indeed the metal-semiconductor heterojunction. In order to describe the rate growth mechanism of the heterojunction as a function of time, the average linear density distribution (ρ) is measured as the number of ZnO NRs deposited along the Ag NWs. The density measured exhibits a value of $\rho = 27$ ZnO NRs/ μm (Ag) (Figure 2(a)) with an average diameter of ZnO NRs around 200 nm and a length of about 900 nm. Subsequently, in order to confirm the epitaxial mechanism during the growth process of the Ag/ZnO interface, the angle between the adjacent ZnO NRs is measured. The measured angle is $71.5 \pm 0.5^\circ$, which matches with high accuracy when it is compared to the internal angles of a pentagon, 72° . This result is combined with the high resolution TEM images. The lattice resolution at the interface shows an epitaxial growth between the ZnO NRs and the Ag NWs, as shown in Figure 2(b).

FIG. 2. SEM images of Ag/ZnO hierarchical nanostructures. (a) The average distribution $\rho = 27$ rods/ μm for a particular time. (b) and (c) Lateral and front views of an actual Ag/ZnO. (c) and (d) The match in the angle θ for a pentagon geometry.

PED-ASTAR is a method developed for the crystalline orientation under quasi-kinematic conditions for the registered electron diffraction patterns and reduces almost totally the forbidden reflections in the diffraction patterns. This orientation phase method is similar to the electron backscatter diffraction (EBSD) coupled in scanning electron microscopes, in which the analysis is within the range of micro-scale.^{13,14} In TEM, PED-ASTAR method (EBSD-like) can obtain crystal orientation maps at the nanometric range, which depends of the probe size of the field emission gun of the microscope.^{11,15,16} PED-ASTAR has become an invaluable tool, not only for the determination of unknown crystal structures but also for the analysis of structural defects such as grain boundaries and twins in nanoparticles. In the current work, the local nanostructure analysis has been obtained at the metal-semiconductor ZnO/Ag interface using the PED-ASTAR method in a JEOL ARM 200F microscope operated at 200 kV. In a previous work, we have shown that after an automated acquisition process of several thousands of electron diffraction patterns, it is possible to complete the actual crystal orientation phase maps for decahedral gold nanoparticle with a barrel-like shape oriented along the five fold symmetry.¹⁷ Phase and orientation identification is performed for each individual pattern, via comparison with the previously generated model templates. Similar work using PED-ASTAR in Ag NWs (synthesized by the same chemical method) has been published in the supplementary material of Alducin *et al.*¹⁸

Figure 3 shows the crystal orientation phase map indexed during the scanning mode and using precession electron diffraction for the Ag/ZnO interface. At the interface between Ag NWs and ZnO NRs, the change in the direction of the indexed diffraction pattern is clearly observed when a line is passing perpendicular to the Ag NWs growing direction [001] and along the ZnO NRs [001] direction. Additionally, Figure 3 shows the triangular color code (obtained from the stereographic projection) for both the Ag *fcc* structure and the ZnO wurtzite crystal structure. The color maps indicate the crystalline orientations of the planes and their crystalline directions.

Figure 4(a) shows a high resolution image of an isolated ZnO NRs, whereas Figure 4(b) shows the crystal orientation phase map of the Ag/ZnO interface. From these images, it is important to highlight the relationship exhibited between the growth direction of both Ag NWs and ZnO NRs. Indeed, from the high resolution transmission electron microscopy image, the growth direction of planes (002) on ZnO NRs with respect to the zones axis [110] is confirmed (inset Figure 4(a)). The coupling at interface can be explained in more detail in Figure 4(b). Also, it is revealed that the orientation phase is mapped as a color code for the five fold symmetry in the cross section of Ag/ZnO and Ag NWs. For instance, the color code in the Ag NWs exhibits three different regions or orientations, two of them along [111] (blue region) and [110] (green region). Similar reports have demonstrated the five fold zone axis symmetry measured on pentagonal nanoparticles by precession electron diffraction.^{17,19} Furthermore, after the automated indexation process, the planes (002) on Ag NWs exhibited a preferential orientation along the [110] direction of the ZnO NRs as shown in Figure 4(b). The color code in Figure 4(b) relates a particular crystalline orientation

FIG. 3. Crystallographic orientation phase maps of ZnO/Ag interface for three different orientations x , y , and z . Arrows mark the directions of the interface and planes of the epitaxial growth. The triangular color code, to the right for both Ag cubic and ZnO hexagonal structures, depicts the crystalline directions exhibited for the corresponding planes. Index maps are added to all orientation maps.

FIG. 4. (a) A high Resolution TEM image of ZnO NRs. The inset shows the Fast Fourier Transform (FFT) of it, where the growth direction of the planes (002) along the direction $\langle 001 \rangle$ of ZnO nanorods is indicated. (b) Crystal orientation maps show the most probable orientation of a particular phase for both ZnO NRs and Ag NWs, depicted with the color code.

with its corresponding preferred orientations within the crystal itself.

Additionally, we have performed high resolution X-ray diffraction (HR-XRD) on the samples and correlated the analyses made by PED-ASTAR. For the analysis, the Ag NWs and ZnO/Ag samples have been studied separately, and they have been deposited on a zero background holder (silicon with high ordered reflections). Figure 5 shows the X-ray diffraction pattern of ZnO/Ag nanoantennas and the inset

FIG. 5. The HR-XRD pattern of the metal-semiconductor Ag/ZnO nanoantennas. The main planes (100), (002), and (101) are associated with the hexagonal phase of ZnO. The inset shows the main planes (111), (002), (022), and (113) marked with *, which correspond to the cubic phase of silver.

shows the Ag NWs pattern. For the Ag NWs, the high order planes (002) revealed on the diffraction pattern are associated with a homogeneous distribution and deposit on the silicon substrate. The lower intensity peak of the Ag NWs corresponds to the (111) planes, which are related to the planes of exposed in the five fold orientation of the nanowires. The X-ray pattern of the ZnO/Ag sample confirms that the highly ordered planes of the Ag NWs act as nucleation centers for the growth of ZnO polar planes.²⁰ The X-ray pattern of the ZnO/Ag sample shows the hexagonal wurtzite crystalline phase for the ZnO. The (111) planes of the Ag NWs show a significant increase in its intensity compared with (002) planes; this change is produced due to the ZnO NRs cover the pentagonal surfaces of the (002) planes of the Ag NWs.

We can conclude that the ZnO NRs interface is assembled epitaxially on the Ag NWs. The crystalline orientations maps showed a preferred orientation in the growth of ZnO NRs on the (001) planes of the Ag NWs. High resolution X-ray diffraction is in agreement with the analyses performed by the PED-ASTAR method. The possibility to fabricate a precise assembling in ZnO/Ag nanoantennas using MIP chemical method will impact in the design and fabrication of other nano-structures used finally for other electronic applications.

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