Precession Electron Diffraction and Orientation Phase Mapping of Assembled Ag/ZnO Nanoantennas.

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The manipulation of the geometrical and structural arrangement of the constituent's elements on devices at nanoscale level is highly desirable for a precise monitoring of the opto-electrical properties exhibited for these nanomaterials. In fact, a great effort has being made to understand the coupling mechanisms on metal-semiconductors systems, most precisely at interfaces nanoscale level. For instance, it is well known that the multidirectional radiation pattern generated by the active elements on nanoantenna applications is highly dependent on both the structural and orientation distribution of the receiver elements as well as the passive element on the nanoscale device. For example, Wang, et al [1] have synthesized high order nanostructures in a hierarchical configuration to study the photo-induced optical properties of these systems in function of the ZnO concentration distributed along the silver nanowires. However, few is known about the structural coupling mechanisms between this metal-semiconductor heterojunctions. Thus, to understand the dynamic coupling at the interface level in the Ag/ZnO metalsemiconductor heterojunctions we report the epitaxial growing of zinc oxide nanorods on the pentagonal exposes faces of Ag nanowires resembling a hierarchal nanoantenna. Moreover, the studied of the growth mechanism in the active/contact faces of the metal-semiconductor heterojunction has been done by mapping simultaneously the dynamical electron diffraction pattern under in-situ precession electron diffraction at the heterojunction interface Ag/ ZnO nanosystem. Indeed, by indexing the dynamical diffraction patterns using orientational/phase mapping from the precessed electron diffraction data collected an orientational mapping has been retrieved showing the interfacial growing polar planes (0002) of ZnO nanorods on the pentagonal planes of silver nanowires with a mismatch between planes along the coupling interface. For completeness, grazing angle x-ray diffraction measurements on prepared substrates Ag/ZnO systems shown well-defined peaks associated to the main phases of ZnO nanorods and Ag nanowires respectively. A full understanding of the fit faces mechanism between Ag/ZnO along the mismatch direction undoubtedly will allow elucidating the mechanism through which the contact metal-semiconductor behaves at the heterojunction interface.

The figure 1A shows Ag/ZnO metal-semiconductor systems grown by microwave irradiation process as described by *Sanchez et al* [2]. Two main features could be listed in the micrograph; first a constant distribution of ZnO nanorods covering completely the surface area along the silver nanowire and secondly the multi-pentagonal arrangement of ZnO nanorods running through the long axis of the silver nanowire. In fact, figure 1B and 1C SEM reveal the epitaxial distribution more clearly for a lateral view and plan view respectively. Because of the epitaxial distribution, it was indexed the main planes of the crystalline structures at the interface of Ag/ZnO metal-semiconductor nanosystem using precession electron diffraction. Indeed, figure 1 (right) shows a virtual bright field image, for a localized zone at the interface, obtained after applied *precession-assisted crystal orientation mapping technique ASTAR* [3]. Moreover, using *DiffGen* tool, the localized precession diffraction patterns were indexed along the interface Ag/ZnO for phase identification and map orientation distribution [4].

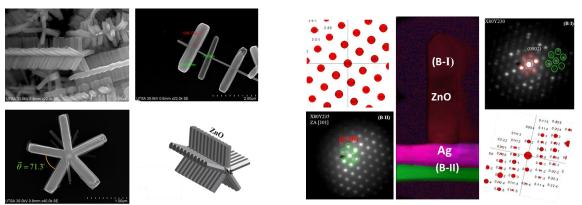


Figure1 (**left**). A multi-pentagonal arrangement showing ZnO nanorods growing perpendicular to the silver nanowires facets. A) and B) low and high magnification micrographs of an experimental nanosystem as obtained using an STEM microscope. C) oriented Ag/ZnO nanostructure. **Figure1** (**right**) ASTAR orientation map of an isolated Ag/ZnO nanostructure, the corresponding electron diffraction patterns are marked along the interface zone. There, it was inferred a misorientation between (0 -2 0) planes and (0002) at the silver nanowires and ZnO nanorods respectively.

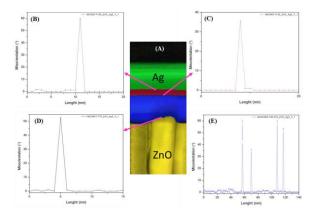


Figure 2. Shows the misorientation between Ag nanowires and ZnO nanorods as a function of the distance along the perpendicular direction to the silver wire on the multi-pentagonal distribution. A) lateral view of the Ag/ZnO nanosystem, three zones (green, wine and blue) could be identified clearly on the virtual bright field image on the silver nanowire. B) and C) misorientation at the interface on the pentagonal faces of silver nanowire. D) misorientation at the Ag/ZnO interface of an isolated Ag/ZnO nanosystem. E) Line profile across the whole system of the Ag/ZnO system.

References

- [1] Shaowu Wang, Yang Yu, Yuanhui Zuo, Chunzhong Li, Jinhu Yang and Conghua Lu, Nanoscale **4** (2012), p. 5763-6074.
- [2] J. E. Sanchez, F. Mendoza Santoyo, J. Cantu Valle, J. Velazquez-Salazar, M. Jose Yacaman, F. J. Gonzalez, R. Diaz de Leon and A. Ponce. J. Appl. Phys. **117**, (2015), p. 0343606-2
- [3] D. Viladot, M. Veron, M. Gemmi, F. Peiro, J. Portillo, S. Estrade, J. Mendoza, N. Llorca-Isern and S. Nicolopoulos, Journal of Microscopy. **252** (2013), p.23
- [4] The authors acknowledge funding from: NSF PREM # DMR 0934218. Scholarship Francisco Jose de Caldas 512 COLCIENCIAS. National Institute on Minority Health and Health Disparities (G12MD007591). Department of Defense #64756-RT-REP and the Welch Foundation Grant Award No. # AX-1615.