Advanced Transmission Electron Microscopy Investigation of Epitaxy-Enabled Morphology Controling ITO Nanowires

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1. INTRODUCTION

Controlling nanowire morphology in bottom-up synthesis and allowing the assembly of nanowires on planar substrates is of tremendous importance for device applications in electronics, photonics, sensing and energy conversion. To date, there has however been only limited success in reliably achieving these goals, hindering both the fundamental understanding of the growth mechanism and the integration of nanowires in real-world technologies. In this work, we will show the impact of transmission electron microscopy (TEM) on this domain, as an extremely versatile and powerful technique.

2. RESULTS

Novel dual-metal Au-Cu alloy nanoparticles were used as a catalyst for tin-doped indium oxide (ITO) nanowire growth. The enhanced mobility of the catalyst nanoparticles (NPs) enables *in situ* seeded growth of branched ITO nanowires (NWs). The dynamically tuned chemical potentials in the catalyst NPs selectively stabilize a rare cubic indium-tin-oxide phase (ISO), forming epitaxial heterojunctions within individual NW branches. This methodology of selecting phases and forming compositionally abrupt axial heterojunctions in NWs departs from the conventional synthesis routes, giving unprecedented freedom to navigate phase diagrams and promising novel nanomaterials and devices [1]

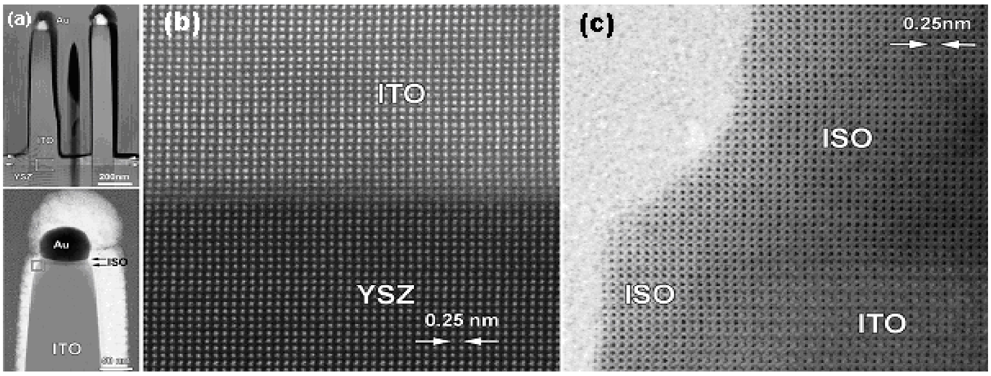

Fig.1 (a) Low magnification ADF STEM (top) and BF TEM(bottom) images of off-plane ITO NWs, (b) - high resolution HAADF-STEM image of the ITO-YSZ interface, (c) ABF-STEM image of the top part of an ITO NW. Notice the presence of the ISO phase.

Here we report that growth of planar, vertical and randomly oriented ITO nanowires can be realized on yttria-stabilized zirconia (YSZ) substrates via the vapor-liquid-solid (VLS) mechanism, by simply regulating the growth conditions, in particular the growth temperature. [2]. TEM and reciprocal space mapping experiments reveal the indispensable role of substrate-nanowire epitaxy in the growth of oriented planar and vertical nanowires at high temperatures, whereas randomly oriented nanowires without epitaxy grow at lower temperature. Further control of the orientation, symmetry and shape of the nanowires was achieved through use of YSZ substrates with (110) and (111), in addition to (001) surfaces. Conforming to the principles of energy minimization and interfacial epitaxy, ITO nanowires exhibit triangular, rectangular or trapezoidal cross sections, as a well as a novel "tie"-like morphology with dimension modulation along the length of nanowires. In terms of structure, little deformation and few defects were detected in our systematic TEM experiments, and the effect of strain due to bulk lattice mismatch is locally confined at the ITO/YSZ interface. Based on these insights, we succeeded in growing regular arrays of planar ITO nanowires from patterned catalyst nanoparticles. Overall, our discovery of unprecedented orientation control in ITO nanowires advances the general VLS synthesis, providing a robust epitaxy-based approach towards rational synthesis of nanowires.

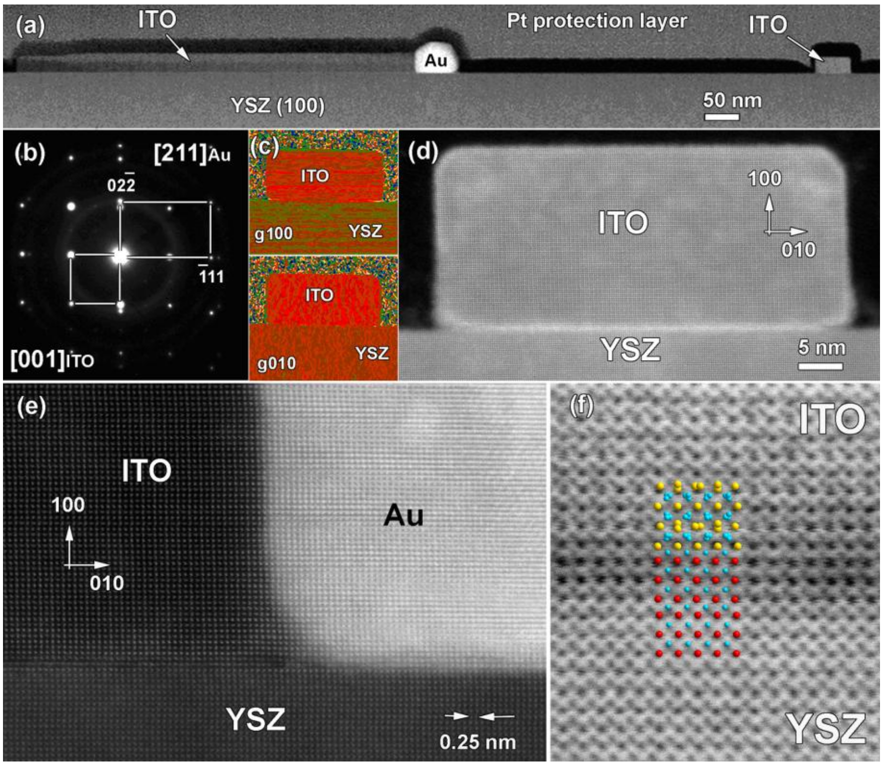

Figure 2 (a) Low-magnification STEM-HAADF image of the in-plane nanowires and (b) corresponding SAED pattern (c) GPA patterns along [100] and [010] directions. (d) HR STEM-HAADF cross-section image of ITO nanowire.(**e**) STEM-HAADF image of the tri-junctions of the ITO, YSZ and Au particle. (**f**) STEM-ABF image of ITO / YSZ interface with overlayed structural model

As demonstrated by our results, the unprecedented freedom of producing nanowires with diverse morphology open doors towards not only general fabrication of advanced nanostructure and devices but also better understanding on the rich mechanisms of general nanowire growth.

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