Multifunctional Materials: A Case Study of the Effects of Metal Doping on ZnO Tetrapods with Bismuth and Tin Oxides

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Hybrid metal oxide nano- and microstructures exhibit novel properties, which make them promising candidates for a wide range of applications, including gas sensing. In this work, the characteristics of the hybrid ZnO-Bi_2O_3 and ZnO-Zn_2SnO_4 tetrapod (T) networks are investigated in detail. The gas sensing studies reveal improved performance of the hybrid networks compared to pure ZnO-T networks. For the ZnO-T-Bi_2O_3 networks, an enhancement in H_2 gas response is obtained, although the observed p-type sensing behavior is attributed to the formed junctions between the arms of ZnO-T covered with Bi_2O_3 and the modulation of the regions where holes accumulate under exposure to H_2 gas. In ZnO-T-Zn_2SnO_4 networks, a change in selectivity to CO gas with high response is noted. The devices based on individual ZnO-T-Bi_2O_3 and ZnO-T-Zn_2SnO_4 structures showed an enhanced H_2 gas response, which is explained on the basis of interactions (electronic sensitization) between the ZnO-T arm and Bi_2O_3 shell layer and single Schottky contact structure, respectively. Density functional theory-based calculations provide mechanistic insights into the interaction of H_2 and CO gas molecules with Bi- and Sn-doped ZnO(0001) surfaces, revealing changes in the Fermi energies, as well as charge transfer between the molecules and surface species, which facilitate gas sensing.

1. Introduction

Recent reports have demonstrated attractive sensing properties of single ZnO tetrapods (ZnO-T) or crossed zinc oxide nanorods.[1,2] However, despite the high sensitivity of individual structures, they commonly exhibit several disadvantages, including a slow response rate at room temperature and the need for expensive equipments.[1–6] The connection of ZnO-T into networks can be an effective way to increase the sensitivity and response rate through specific and improved sensing mechanisms considering an increased number of potential barriers between external connections.[7–12] Furthermore, due to the random alignments and the high aspect ratio of the ZnO-T nano- and microstructures, there is high probability for the formation of interconnections allowing continuous paths for current flow through the ZnO-T networks.[7]

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