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Functionalized Pd/ZnO Nanowires for Nanosensors

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A method for surface doping and functionalization of ZnO nanowires (NWs) with Pd (Pd/ZnO) in a one-step process is presented. The main advantage of this method is to combine the simultaneous growth, surface doping, and functionalization of NWs by using electrochemical deposition (ECD) at relatively low temperatures (90 °C). Our approach essentially reduces the number of technological steps of nanomaterial synthesis and final nanodevices fabrication with enhanced performances. A series of nanosensor devices is fabricated based on single Pd/ZnO NWs with a radius of about 80 nm using a FIB/SEM system. The influence of Pd nominal composition in Pd/ZnO NW on the H_2 sensing response is studied in detail and a corresponding mechanism is proposed. The results demonstrate an ultra-high response and selectivity of the synthesized nanosensors to hydrogen gas at room temperature. The optimal concentration of $PdCl_2$ in the electrolyte to achieve extremely sensitive nanodevices with a gas response (S_{H2}) $\approx 1.3 \times 10^4$ (at 100 ppm H_2 concentration) and relatively high rapidity is 0.75 μM. Theoretical calculations on Pd/ZnO bulk and functionalized surface further validated the experimental hypothesis. Our results demonstrate the importance of noble metal presence on the surface due to doping and functionalization of nanostructures in the fabrication of highly-sensitive and selective gas nanosensors operating at room temperature with reduced power consumption.

Nanoscale sized clusters of noble metals such as Pd, Pt, Au, Ag, Rh, and Ru, are known to act as effective catalysts[1,2] and play a vital role in the improvement of the semiconducting oxides sensing properties and photocatalytic activities.[3–5] A number of methods has been proposed to incorporate these metals into semiconducting oxides micro- and nanostructures in order to improve their UV- and gas-sensing properties in the most efficient way. The most well-documented methods are adsorption, doping,[6,7] surface functionalization (decorating, hybridization, loading, impregnating),[3,8] and composing.[9] Among all noble metals, Pd-doping/incorporation has been demonstrated to show the highest efficiency in the detection of H_2 gas.[2,5,10] Such radically improved performances can be attributed to both chemical and electronic sensitizations.[5] The presence of Pd nanoparticles on ZnO greatly improves the room temperature catalytic activity due to the high H_2 solubility in Pd which gives higher concentration of clusters (catalytic centers) and lowers the saturation rate of response and recovery processes.[11]

The detection mechanism of sensors based on NWs in most cases is based on the modulation of the conduction channel/electron depleted region (EDR).[3,6] In the case of surface functionalization, the Schottky barriers are formed at the Pd/semiconducting oxide interface due to higher work function of Pd compared to ZnO,[3,12] leading to more narrowed conduction channel (extension of EDR). After exposure to H_2 gas, the formation of PdH_x phases with lower work function can take place,[2,12] which lower the height of the Schottky barrier and expand the conduction channel width (suppression of EDR).[6,12] This type of mechanism is related to electronic sensitization.[5] Another important sensing mechanism is related to chemical sensitization and is based on dissociation of H_2 molecules into H atoms,[2,13] which interact with adsorbed oxygen species onto the surface of semiconducting oxide nanostructures. It is not well understood yet which mechanism is more dominant under different operating conditions.[3,14] However, in the case of surface functionalization with noble metal nanoparticles (NPs) due to the dependence of gas response on size and homogeneity of NPs, density, and space distribution, some issues still need to be resolved in order to improve long term stability and repeatability of sensors.[3,14] Thus, different methods for efficient control of the NPs deposition are still investigated.[14]

In this study we demonstrate the outstanding increase in hydrogen gas sensing properties of a single Pd/ZnO NW based nanosensor after surface doping and functionalized with Pd NPs. Both surface doping and functionalization are performed

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