

Self-Powered Solar Diode Gas Sensors

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Abstract

A novel sensing concept was developed; namely solar diode sensor (SDS), based on the integration and correlation of complementary functionalities originating from multiple junctions in a singular nanostructure to enable self-sustained gas sensors working without any external power sources except solar light. In this work, the gas sensing and solar energy harvesting abilities of metal oxide semiconductors were utilized to deliver a self-generated sensing signal. The fabricated sensors, based on CdS@n-ZnO/p-Si nanoelements, were capable of detecting oxidising and reducing gases with reproducible response at room temperature by solely using solar illumination. A new sensing mechanism (change of open circuit voltage, ΔV_{oc}), in comparison to the well-known conductometric sensors (change of resistance, ΔR), was demonstrated and explained in terms of gas-material surface interactions and the subsequent changes in the doping level (N_D) of metal oxides, which is manifested in the variation of V_{oc} at the n-ZnO/p-Si heterojunction diode. Furthermore, the generality of the concept was demonstrated by extending the new sensing approach to other systems such as thin-film based heterojunctions and core-shell radial heterojunctions. The here reported gas sensors are promising candidates for the development of a new generation of commercially appealing, technically feasible and easy to use self-powered gas sensor nanodevices.

1. Introduction

Air pollution and environmental problems are of critical importance due to their impact and harmful effects on human health besides other safety concerns. Gas sensors have been developed for environmental application including air pollution monitoring, and detection of harmful and explosive gases [1]. Low power consumption, low operating temperature and cost effective production are the most challenging issues in gas sensor technologies [1].

Among the different gas sensor technologies, conductometric sensors based on semiconductor metal oxides unify the highest robustness level and minimum costs [2]. Nevertheless the continuous supply of the energy needed, on one side to provide a constant voltage or current for signal generation, on the other hand to activate the chemical interaction between analyte gases and the metal oxide surface, either in the form of heat or light, demands new concepts for energy harvesting units that can be combined as a built-in module to realize autonomous sensors [3].

Pristine ZnO, an intrinsic n-type semiconductor, grown on p-doped silicon substrates produces heterojunctions interesting for applications such as solar cells or photodiodes due to low production costs and good photon-to-electron conversion efficiency [3].

Recent reports have shown that CdS quantum dots, assembled on ZnO nanorods can be used as effective visible light harvesting components in quantum dot solar cell devices. The presence of a narrow band gap CdS sensitizer (2.4 eV) on the surface of ZnO extends the photo-response of ZnO (3.37 eV) into the visible-light region [3].

Based on these considerations, CdS@n-ZnO/p-Si was grown in order to combine a photo-activated gas sensing unit (CdS@n-ZnO) with a p-n junction (n-ZnO/p-Si) capable of harvesting the energy required to operate the sensor (as shown in figure 1).

3. Results and discussion

The SDS prototype devices, schematically represented in figure 1, were fabricated by using a conductive glass (F:SnO₂, FTO) as a transparent top contact on the vertically aligned ZnO nanowires arrays whereas the p-Si substrate was contacted as the back electrode.

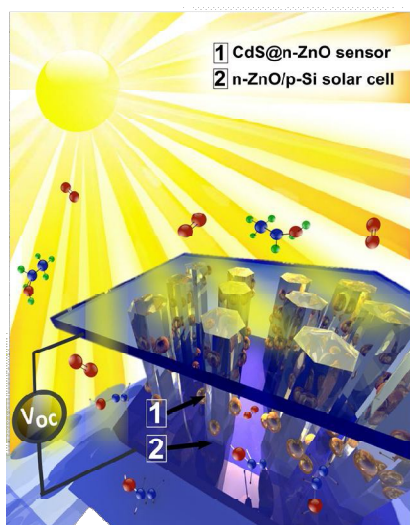


Fig. 1 Schematic representation of the SDS device based on CdS@n-ZnO/p-Si system.

Gas sensing properties

When a constant current is applied to the SDS device (CdS@n-ZnO/p-Si), the sensing mechanism is the same as for simple conductometric (n-type) gas sensors, in which the resistance is increased when an oxidizing gas such as oxygen is introduced (under solar illumination). Remarkably, the CdS@n-ZnO/p-Si showed significant gas sensing responses even at zero bias current, i.e., no external electric power applied. The response at zero bias current is opposite to those of bias currents, indicating a different sensing mechanism. As can be seen in figure 2c, the value of open circuit voltage (V_{oc}) decreases in oxygen (about 41%) in comparison to nitrogen atmospheres (the reference gas).

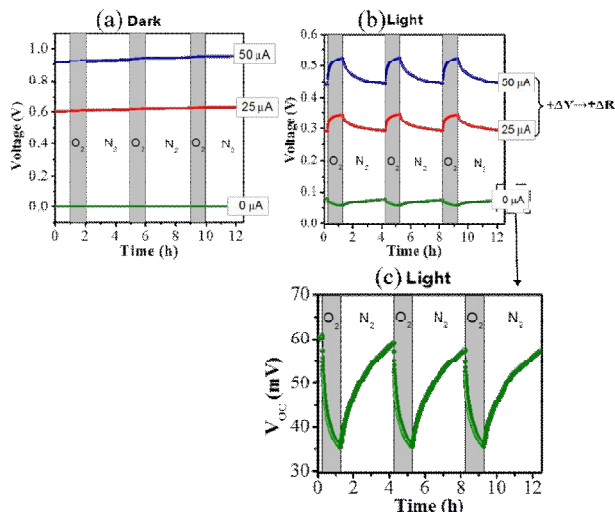


Fig. 2 Gas sensing characteristics of CdS@n-ZnO/p-Si system. ON/OFF curves (oxygen / nitrogen) recorded at different constant currents in (a) dark and under (b) solar illumination. (c) ON/OFF (oxygen / nitrogen) curve recorded with open circuit voltage V_{oc} ($I = 0$ A) under solar illumination condition.

Figure 3 show the V_{oc} signals of CdS@n-ZnO/p-Si in dark and under solar illumination conditions upon exposure to a sequence of ethanol pulses diluted in synthetic dry air. Under dark conditions, no V_{oc} sensing signal was obtained. Upon illumination, the CdS@n-ZnO/p-Si showed significant dependence of V_{oc} on the ethanol concentration (inset of Figure 3b). Evidently, V_{oc} is an auto-generated signal that correlates with the atmospheric composition.

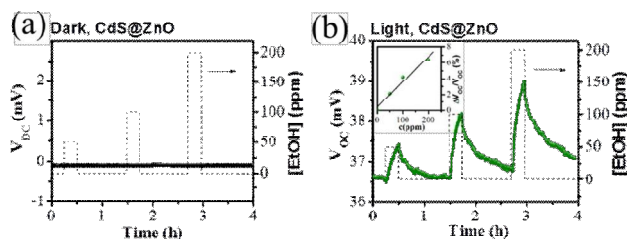


Fig. 3 ON/OFF (ethanol / air) curves of CdS@n-ZnO/p-Si recorded in (a) dark and under (b) solar illumination

The dependence of charge carrier density (N_D) monitored in different gas environments were studied with the help of capacitance–voltage (C–V) measurements (see figure 4). It was proven that the change of V_{oc} is due to the variation of charge carrier density (N_D) that is directly affecting the built in potential (V_{bi}) of the p–n– junction.

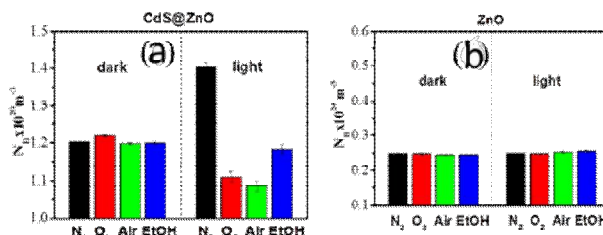


Fig. 4 Environmental dependent N_D of (c) CdS@n-ZnO/p-Si and (d) n-ZnO/p-Si recorded in dark and under solar illumination.

3. Conclusions

The results presented here demonstrated that the inclusion of a solar cell (n-ZnO/p-Si) and an active gas sensing material (CdS@ZnO) enabled a self-generated sensing signal, whose intensity is dependent on the chemical nature of the surrounding gas and its concentration. Self-powered sensor concepts could become extremely interesting in the future for emerging ubiquitous environmental sensing.

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