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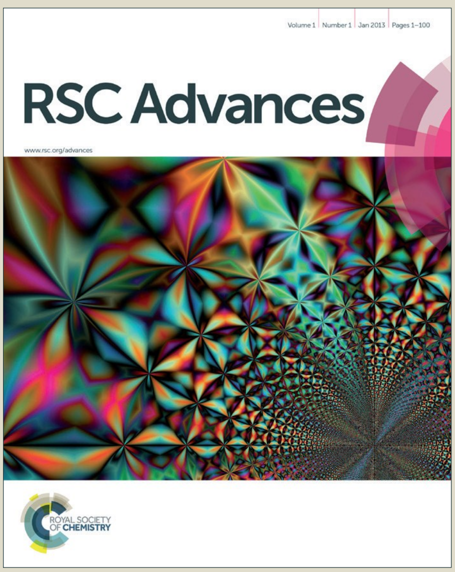

Nano Point Schottky-Gates Array Device: Surface Defect Application and Chemical Molecules Detection

*Jun-Han Song, Tzu-Chiao Chien, Chih-Ming Chang, Chien-Min Chang, and Ping-Hung Yeh**
[*] Prof. Ping-Hung Yeh Corresponding-Author,
Department of Physics, Tamkang University, Tamsui, New Taipei City, 25137, Taiwan
E-mail: ((phyeh331@mail.tku.edu.tw))

Abstract

We have demonstrated the nano point Schottky-gate array device (NPSGAD) for gigantic enhancement of the sensitivity, the signal current output level and the distinguishability by putting numerous ZnO point Schottky-gates in parallel. Using this NPSGAD can improve the current output to mA order and enhance the CO sensor to room temperature detection. NPSGAD can achieve above properties based on several designs, such as point Schottky-gate can enhance detection response, paralleling Schottky-gate can enhance the gas monitor levels and Schottky-gate array can reduce the total resistance to have high signal current output. For UV light detection, the signal current of NPSGAD can achieve to 8 mA. For CO room temperature detection, the signal current can be enhanced above 0.25 mA; these signal level already can be used for commercial application. The gas detection signal also can be improved by increasing operating temperature; the current variation averages of CO detection of NPSGAD are 1.7mA, 10.1mA and 14.9mA under 150℃, 350℃ and 400℃ operation temperature, respectively.

Keywords: Metal Oxide, Schottky-gate, room temperature gas detection, nanosensor

Introduction

Recently, there are lots research reports have gigantic improvement of the photo, gas, chemically-charged molecules detection and antireflective layer, by using core/shell structure, Schottky-gate nanosensor(SGNS) and nanostructure[1-8]. In regard to SGNS, the high resistivity is the major hindrance for increasing the current output level to commercial application. To improve the current output, multi-channel device was used in several research fields, such as photodetectors[9, 10], gas sensors[11, 12], biomolecular detections[13, 14], nanogenerators[15, 16] and solar cells[17, 18]. The greatest advantage for multi-channel device is that it can improve the current output level to commercial application by paralleling numerous nanowires. In addition, some researchers indicate different electronic contact will affect electronic transportation[19]. Due to those reasons, multi-channel device plays an essential role in the future research. In this work, we demonstrated nano point Schottky-gate array device to improve the detection ability of nanosensor. Despite the fact that using multi-channel device to replace single nanowire device is the way to increasing the current level, but there have some unknown issues should be clarified.

Results and discussion

The ZnO NWs can be prepared by the standard solid-vapor process[20, 21] and hydrothermal growth[22]. To investigate Schottky-gate size effect, a series Schottky-gate devices (SGDs) can be fabricated by using crystalline ZnO NWs, which were placed on Pt electrode patterns, and then deposited Pt:Ga on the ZnO NWs to form Ohmic contacts by using the focus ion beam (FIB) system[4-6]. For the Schottky contacts, ZnO NWs placed on a Pt electrode pattern, the natural contacts of which are mainly Schottky type. The current-voltage (I-V) characteristic outputs of different size SGDs (5 and 10 μm) can be shown in Figure 1 (a); in this research work, we provided a nano point

Schottky-gate (NPSG) device and the I-V characteristic output can be seen in Figure 1 (b). All this SGDs show great rectification property. For gas detection, oxygen (O_2) and carbon monoxide (CO) are the gases that deserve to be mentioned. For example, O_2 is an oxidant for classical codices and famous paintings; CO is a toxic gas for human beings, both need high sensitivity and fast response detection. Compare with the CO detection ability of these three SGDs, the response time of NPSG (0.2 μm Schottky-gate areas) is faster than the other two SGDs (5 and 10 μm Schottky-gate areas, as shown in Figure 1 c). The response time of various Schottky-gate areas (10 μm, 5 μm and 0.2 μm) are around 800, 264 and 141 sec. Oxygen absorption on the Schottky-gate can increase the Schottky barrier height (SBH) to have a low current, but when the carbon monoxide absorption on the Schottky-gate can decrease the SBH to have a high current[4]. The SBH variation ($\Delta\Phi$) is equal to the summation of effective SBH and O_2/CO absorption changed barrier height ($\Delta\Phi=\Phi_S+\Phi_{O2}-\Phi_{CO}$), as shown in the inset of Figure 1 (d).

Reducing the Schottky-gate area can compel NPSG to have faster response; it just needs fewer gas molecules to switch the Schottky-gate. The density of surface oxygen vacancies should be consistent for those ZnO NWs (the ZnO NWs were synthesized at same batch), so reducing Schottky-gate area would have fewer oxygen vacancies on the surface and only need less gas amount absorption to tune the SBH for switching the Schottky-gate, as illustrated in Figure 1 (d). But the different CO levels can't be able to monitor. On the contrary, the increasing Schottky-gate area would enhance gas absorption amount and then differentiate the signal of various CO levels (Figure S1). From these three SGDs, we also can see the current will keep rising just like the blue line in Figure 1 (c); the larger Schottky-gate area can detect more gas levels, but the response time will take longer to achieve saturation. The schematic of O_2 and CO_2 absorption relate to surface oxygen vacancy amounts can be illustrated as Figure 1(d). To solve this contradictory, we provide a design to have faster monitor speed and differentiate various gas levels.

In order to differentiate various gas levels, we need to find a solution to increase the Schottky-gate area, but still have faster monitor speed. Base on this purpose, we put two SGDs (5 μm Schottky-gate areas) in parallel to double the Schottky-gate area. The SEM and schematic of ZnO NWs dual-SGDs can be illustrated in Figure 2(a). In this experiment, the total resistance also can be reduced by paralleling the Schottky-gates, namely dual channel dual Schottky-gate device (DCDS). For ZnO NWs SGD, resistances, which include schottky contact resistance (R_s), ohmic contact resistance (R_o) and nanowire resistance (R_w), always be the main issue for dominating signal value of sensor. Based on these three kinds of resistance, the R_s has highest resistance which is the main issue to limit the current output[23]. Typical I-V curves of SGDs indicate that each SGD performs as an excellent diode and well rectification also can be seen under the reverse bias. In the diagrams, the pink and light blue lines in the I-V curve, are represented the individual single channel single Schottky-gate device (SCSS), as shown in Figure 2(b). The output current level of DCDS could be enhanced by decreasing the total resistance; whether decreasing the total resistance will affect the detection characteristics (sensitivity and reset time) of the ZnO SGD or not, which is the task needed to deal with. The DCDS and SCSS were operated at reverse bias (-1V) and preformed repeatable characteristic for UV light sensing, as shown in Figure 2 (c). The signal current output levels of SCSS and DCDS are 90 nA and 174 nA; the signal current output level of DCDS is almost double compared with SCSS. Based on Kirchhoff's circuit law, the current values of DCDS approximately equal to the sum of the current amount of two individual SCSS. The sensitivity of SCSS and DCDS are 1394 % and 1828 %, respectively. From the electric measurement, the ideality factor and Schottky barrier height (SBH) can be calculated[23], the ideality factors of SCSS and DCDS are 1.46 and 1.62, respectively. There are several parameters will affect the ideality factor, such as interface state, thermionic-field emission (TFE), image force lowing, generation/recombination current and temperature . In our experiment, only interface state will be the parameter to vary the ideality factor for these SGDs. The DCDS has much more interface state compared with SCSS, so the ideality factor of DCDS is larger than SCSS. When ideality factor locates between one and two, the electronic transportation behavior would be dominated by the TFE[24]. Using TFE as the electric transportation mechanism, the SBH would be the import parameter for SGD sensing. The SBHs formed by connecting ZnO NWs and Pt electrode of these nanodevices were around 0.54eV, which is close to the ideal SBH[25, 26]. By putting SGDs in parallel(such as DCDS), we not only can low the total resistance to increase signal current output level, but also can increase Schottky-gate area to enhance sensitivity. Five times UV light measurement can show the stability of SCSS and DCDS, such as shown in Figure 2(d). So reducing the total resistance by putting Schottky-gate in parallel will not degrade the detection characteristics (sensitivity and reset time) of the ZnO SGD.

Furthermore, we should clarify if the various gas levels can be differentiated by increasing the Schottky-gate numbers (or area). Firstly, the signal current outputs of these SGDs were measured in the vacuum environment; the current in the vacuum environment can be seen as the base current before O_2 and CO sensing. This step gives us a clean detection environment for O_2 and CO sensing, and simplifies the detection condition without other gases affection. For CO sensing, DCDS has improved both the sensitivity and the signal current output, compares with SCSS. For both DCDS and SCSS, the signal current outputs increased with the CO concentration rising, as shown in Figure 3 (a). DCDS has faster response and enhances the sensitivity from 3000% to 6500% for 320 ppm CO concentration under 250 ^{o}C, compare with SCSS. Based on the monitor data, the various CO levels can be differentiated by using DCDS. But for SCSS device, the CO level can't be differentiated when the CO concentration is above 80 ppm, as shown in Figure 3(b). The reason why DCDS can distinguish the gas concentration difference is that DCDS has larger detection area than SCSS. Proposed mechanisms for the gas absorption of SCSS and DCDS are indicated in Figure 3 (c) and (d). CO sensing mechanism of DCDS, which has twice Schottky-gate area to detect CO molecules and increase gas absorption amount, as illustrated in Figure 3 (c). Once the device is operated in the O_2 environment, plenty of O_2 molecules will be absorbed on the ZnO nanowire and became to O_2^-, it is the reason why the SBH is larger than that in the vacuum environment[1, 2]. On the other hand, CO absorbed the O_2^- on the surface of ZnO nanowire and become carbon dioxide, that's why the SBH can be reduced. We can observe that the sensitivity increased with increasing concentration of CO, consistent with the theory of Scott[27, 28]. Putting two SGDs in parallel to form DCDS, not only can improve the different gas levels monitor ability but also can enhance signal current output level. DCDS just seems to have dual Schottky-gates to detect the gas and control the current flow, as illustrated in Figure 3 (d). In previous and this work, the SCSS can't differentiate the gas concentration over 100ppm[4], but the different gas concentration detection ability of DCDS is much more outstanding than SCSS.

Based on the above data, we need NPSG to have fast response and multi Schottky-gates to have sensitivity and signal current level enhancement. Here, we demonstrated the nano point Schottky-gate array device (NPSGAD) to achieve the room temperature gas detection and enhance the signal output level to mA order (not laboratory level measurement, nA or μA); these two gigantic enhancements can improve the commercial application of ZnO NW device. NPSGAD was designed with two ideas; the first one is nano point Schottky-gate (NPSG), which can enhance the response time because the Schottky-gate can be easily switched if the contact surface narrow down to a nano-point. Secondly, the signal output level would be amplified because NPSGAD puts thousands of NPSG in parallel, which will increase the detection area and low the total resistance to improve the sensitivity/gas monitor levels and signal current output, respectively, as illustrated in Figure 4 (a). The UV light signal current output of NPSGAD enhanced to mA order, which can gigantically improve the commercial potential of NPSGAD, as shown in Figure 4 (b). Otherwise, the room temperature CO detection is the most inspiring enhancement of NPSGAD for commercial application, as shown in Figure 4 (c). Why the current signal will keep increasing is due to the CO molecules keep absorption on the Schottky-gate; the Schottky-gate barrier keeps lowing and then the more electrons can pass the Schottky-gate to form signal current. For our experiment, the NPSG device is extremely sensitive to its environment. The point contact area can create high current density to have Joule heating effect. The Joule heating effect mainly heats the temperature at point contact interface, the Schottky-gate area, which will be gas molecule absorption area. For gas sensor, most articles mentioned that need high operating temperature to increase the gas molecules absorption. NPSG device provides a self-heating effect and just heats the detection area, Schottky-gate, as shown in Figure S2. Based on the above idea, NPSGAD use NPSG as a detection unit and puts thousands of NPSG in parallel, which can reduce the gas absorption temperature and improve the current output level. The signal variation averages of CO detection of PSGAD are 1.7mA, 10.1mA and 14.9mA under 150℃, 350℃ and 400℃ operation temperature, respectively. The gas molecules absorbed on the Schottky-gate might be physical absorption under low temperature (150℃), might be chemical absorption above high temperature (250℃). For NPSGAD, the nano point Schottky-gate is very sensitive, can be triggered with gas absorption, this property is good for gas sensor application.

Conclusion

We have demonstrated the measurement design for ZnO NWs nanosensor to gigantic enhance the sensitivity and the signal current output by putting Schottky-gates in parallel. Using NPSG can enhance the gas detection response; using DCDS for UV light detection, the signal current level and the sensitivity can be improved from 90 nA to 174 nA and 1394 % to 1828 %, compared with SCSS, respectively. For O_2 sensing, DCDS has rapid response and enhances the sensitivity from 130000% to 740000% about six-fold higher than SCSS. For CO sensing, the different gas concentration levels can be monitored by using DCDS. NPSGAD combined several ideas, point Schottky-gate, paralleling Schottky-gates and Joule heating effect, to achieve high speed, various gas levels monitor and room temperature gas detection. Putting numerous nano point Schottky-gates in parallel, not only the total resistance can be lowed to increase the signal current level, but also the Schottky-gates sensing area can be enlarged to enhance the gas monitor levels. Especially when the Shottky-gate narrow to nano-point scale and numbers increase to thousands, the gas monitor ability can be gigantically enhanced to room temperature detection and mA order current output. The illustrated methodology and principle present a unique sensing concept that can be readily and extensively applied to other sensor systems.

Acknowledgement

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Figures

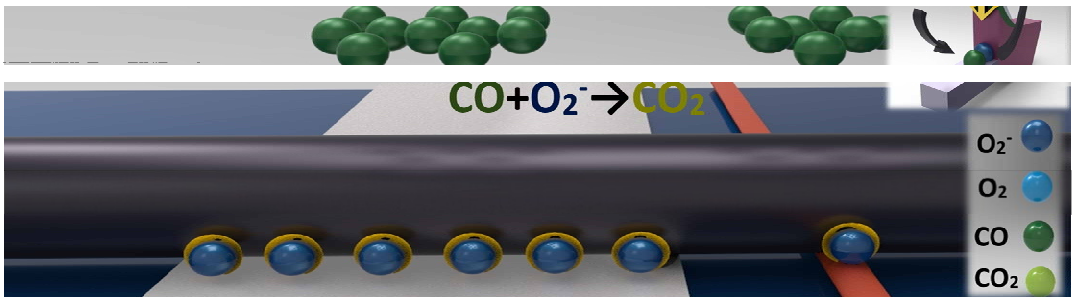

Figure 1. (a) and (b) represent the I-V curves and schematic diagram of 5/10 μm and nano point Schottky-gate devices, respectively. (c) The CO sensing ability of different Schottky-gate size devices under 250℃. (d) The schematic of O_2 and CO_2 absorption relate to surface oxygen vacancy amounts. Small Schottky-gate size can be easily switched by gas molecules.

Figure 2. (a) and (b) show the schematic diagram/SEM image and the I-V curves/basic circuits of Schottky-gate devices, respectively. Pink and light blue line represent the individual current of each single channel single Schottky-gate device (SCSS); while red line represent the current of dual channel dual Schottky-gate device (DCDS). The scale bar of the inset is 5 μm. (c) The UV light detection signal of DCDS (174 nA) is almost twice larger than SCSS (90 nA). Inset: the schematic diagram/basic circuit of SCSS and DCDS. (d) Five times UV light measurement can show the stability of SCSS and DCDS.

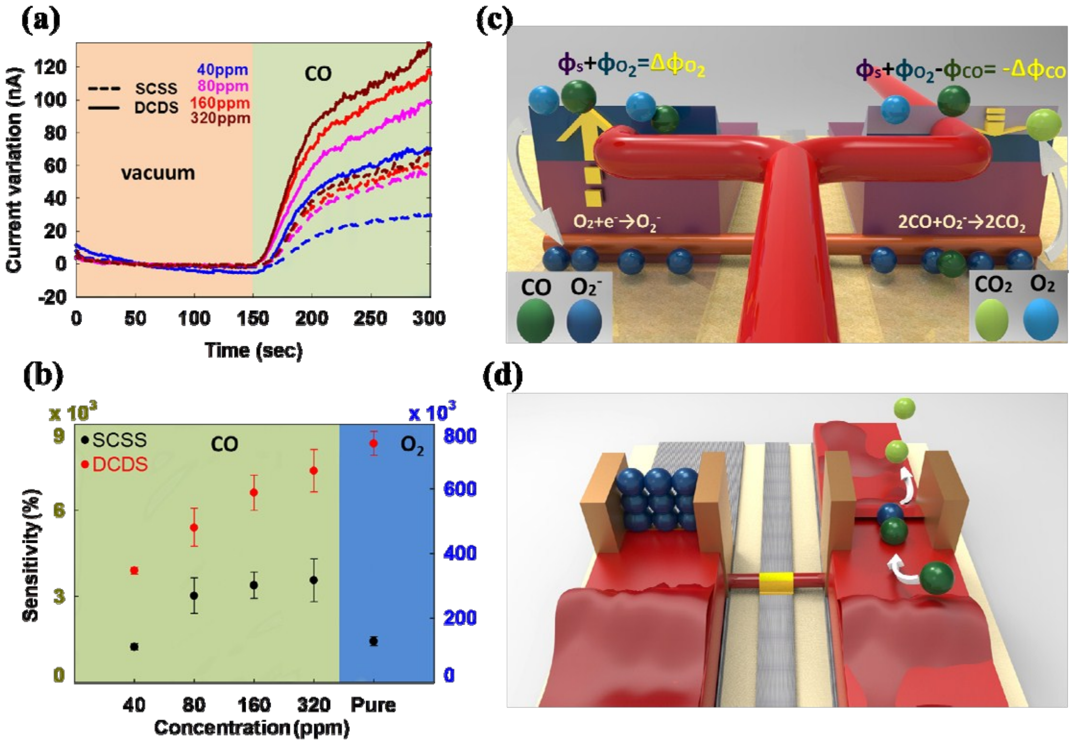

Figure 3. (a) and (b) For CO sensing, DCDS has rapid response and higher sensitivity than SCSS. Proposed mechanisms of the SBH variation controlled SCD are indicated in (c) and (d). DCDS just seems to have dual Schottky-gates to detect the gas and control the current flow. Here just show one Schottky-gate is activated and the other Schottky-gate is steady to illustrate the control ability of DCDS.

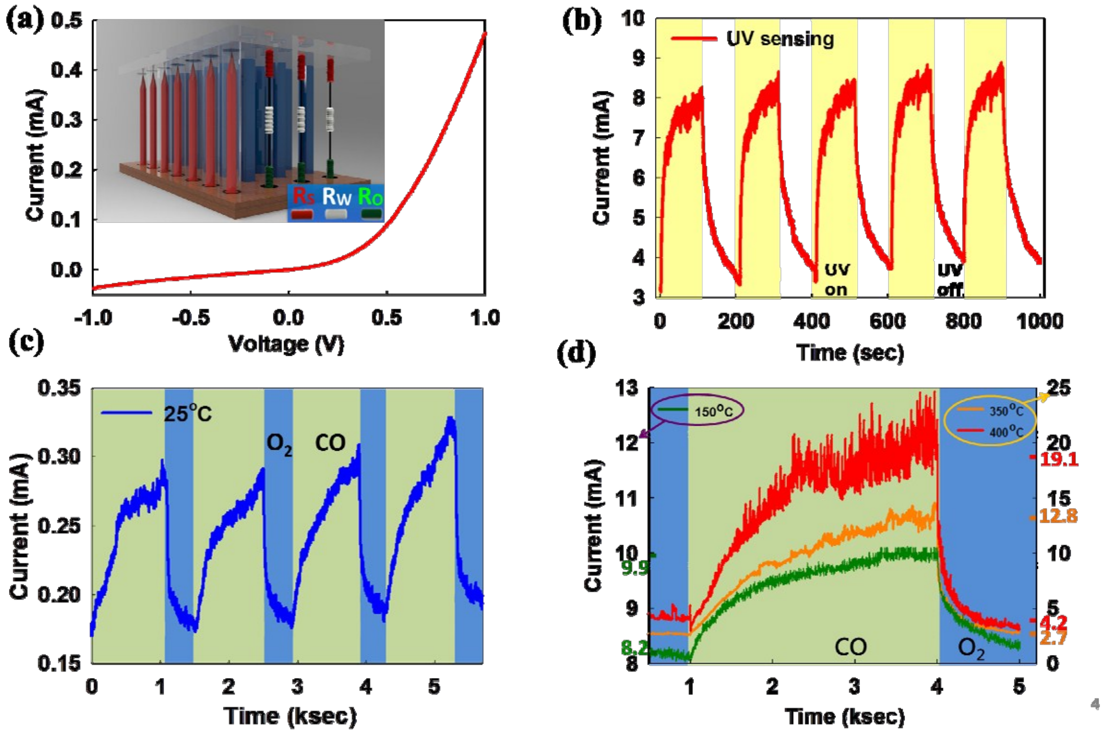

Figure 4. (a) NPSGAD puts thousands of NPSG in parallel, which can increase the detection area and low the total resistance. (b) The UV light signal current output of NPSGAD enhanced to mA order. (c) The room temperature CO detection is the most inspiring enhancement of NPSGAD for commercial application. (d) The signal variation averages of CO detection of PSGAD are 1.7mA, 10.1mA and 14.9mA under 150℃, 350℃ and 400℃ operation temperature, respectively.

TOC: **Nano point Schottky-gate array device (NPSGAD) can gigantically enhance the sensitivity, the signal current output level and the distinguishability.**

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