Improving the NH$_3$ gas sensitivity of ZnO nanowire sensors by reducing the carrier concentration

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Abstract

We report a method to improve the sensitivity of a zinc oxide (ZnO) nanowire gas sensor towards ammonia (NH$_3$) without the use of catalyst nanoparticles on the nanowire surface. This improvement is achieved by lowering the nominal carrier concentration in the as-grown ZnO nanowires. The carrier concentration in the as-grown ZnO nanowires can be tuned by treating these nanowires to either an oxidizing gas plasma or a reducing gas plasma, as observed from the measured current–voltage (I–V) characteristics response. We demonstrate that a ZnO nanowire sensor device that has been subjected to oxygen plasma treatment, thereby having a reduced carrier concentration, exhibits a sensitivity towards 0.75% NH$_3$ gas that is improved by approximately four times. The origin of this gas sensitivity improvement is discussed based on x-ray photoelectron spectroscopy analysis results of the plasma-treated ZnO nanowires.

1. Introduction

Zinc oxide (ZnO), an intrinsically n-type metal oxide semiconductor, has a long history as a suitable candidate for solid state gas sensing owing to its high chemical stability, low cost and sensitivity to a variety of gases such as NH$_3$, O$_3$, NO$_2$, CO, H$_2$ and other species [1, 2]. In recent years, attention has been placed on the investigation of ZnO nanowires as ultra-miniature gas sensors. This is due to their high surface-to-volume ratio and distinctive properties originating from their nanometer diameter that may have great influence on their gas sensing performance [3, 4]. Furthermore, to enhance the performance of these ZnO nanowires, the surfaces are often deposited with small amounts of noble metals such as nanoparticles of platinum (Pt) or palladium (Pd). It is reported that these metallic nanoparticles can act as catalysts that increase the dissociation efficiency of the molecular test gas to its more reactive atomic form for enhanced surface reaction during gas sensing [5, 6].

The commercial viability of ZnO nanowire gas sensors can be increased significantly if they can be produced with standard semiconductor technologies in existing silicon-based fabrication plants. However, nanowires incorporating metallic nanoparticles are generally difficult to subtractively pattern using existing standard semiconductor processing. Furthermore, metallic nanoparticles may be a source of contamination that is detrimental to silicon device performance and are not welcome in existing silicon-based fabrication plants. For example, metals such as Pt can introduce deep level traps in the bandgap of silicon that act as efficient recombination centers, causing high junction leakage in periphery silicon metal oxide semiconductor (MOS) devices [7, 8]. Thus, the use of such metallic nanoparticles in ZnO nanowire gas sensors is best avoided if these devices are to be manufactured by leveraging on existing fabrication technologies and facilities.

In this work, we propose an alternative way to increase the sensitivity of ZnO nanowires towards NH$_3$ gas, while avoiding the use of metal catalyst nanoparticles on the surface of these nanowires. The method uses oxygen (O$_2$) plasma treatment to reduce the conductance of the as-grown ZnO nanowires, thereby lowering the nominal carrier concentration, to achieve an improved gas response. To illustrate how gas sensitivity is related to the carrier concentration in ZnO nanowires, we consider the following.

The conductance of a ZnO nanowire gas sensor is given by [9]

\[ G = n_o e \mu \pi R^2 L \] (1)
investigate the origin of this gas sensitivity improvement. The carrier concentration in the as-grown ZnO nanowires was found to be reduced by a factor of four times. X-ray photoelectron spectroscopy (XPS) analysis further demonstrated that the carrier concentration in the as-grown ZnO nanowires was reduced by a factor of four times. X-ray photoelectron spectroscopy (XPS) analysis was used to investigate the variation in carrier concentration in these nanowires.  

To study the improvement in gas sensitivity of the ZnO nanowire sensor as a result of its reduced carrier concentration from oxygen plasma treatment, we fabricated another device (sample C). This sample has a similar structure to that shown in figure 1 and was subjected to the same oxygen plasma treatment condition as described above. NH3 gas sensing characterization was performed on this device. The gas sensing response of the device was measured using a Keithley 4200 semiconductor parameter analyzer. The device was biased at 4 V and operated at 300 °C in a temperature-controlled quartz tube furnace at atmospheric pressure. 200 sccm argon (Ar) was introduced to the gas ambience for a period of 180 s, followed by introduction of 0.75% NH3 in Ar for 10 min. Thereafter, 200 sccm O2 was used to reset the device. The initial exposure to Ar gas acted as a control to ensure that the device did not change its conductance when exposed to an inert gas. The gas sensing response of the as-fabricated nanowire sensor towards 0.75% NH3 was compared with its response when the experiment was repeated after the sample was subjected to O2 plasma treatment.

2. Experimental details

To illustrate that the carrier concentration in ZnO nanowires can be tuned via oxidizing/reducing gas plasma, we fabricated two ZnO nanowire sensor devices (sample A and sample B) for this study. The ZnO nanowires were synthesized by a direct thermal oxidation of patterned Zn metal in air through a ‘self-catalyzed’ growth process as described in our previous works [11, 12]. Figure 1(a) shows an optical micrograph of a typical fabricated ZnO nanowire gas sensor device consisting of an array of an interconnected mesh of ZnO nanowires contacted at both ends by electrode pads. Figure 1(b) is a field-emission scanning electron microscopy (FESEM) (Phillips XL30 FEG) image showing a mesh of interconnected ZnO nanowires spanning across the patterned array. In brief, the device is fabricated on an insulated silicon substrate by two-layer selective lithography and metalization processes: the first layer selectively patterns an array of zinc metal which seeds the ZnO nanowire growth, whereas the second layer defines the Cr/Au metal contact electrodes which directly contact the underlying Zn seed layer. Thereafter, the sample is subjected to thermal oxidation in a quartz tube furnace at atmospheric pressure in air at a growth temperature of 500 °C for 3 h before cooling down to room temperature. ZnO nanowires grow and bridge the patterned array by self-assembly to form a large nanomesh of interconnected nanowires. The nanowires have diameters of around 20–40 nm. The x-ray diffraction peaks of these nanowires can be well indexed to the wurtzite hexagonal ZnO crystal structure, and high-resolution transmission electron microscopy (HRTEM) shows that the nanowires grown by this method are single crystalline (as reported in our previous works [11, 12]).

Sample A and sample B were treated with O2 (oxidizing gas) and NH3 (reducing gas) plasma respectively, at a flow rate of 50 sccm for 10 min in 1.8 mbar pressure and 30 W RF power in a reactive ion etching system. Since the electrical conductivity of ZnO nanowires is directly proportional to the carrier concentration [13, 14], we measured the conductance of ZnO nanowires is directly proportional to the carrier concentration [13, 14], we measured the conductance of ZnO nanowires before and after the respective gas plasma treatment using a Keithley 4200 semiconductor parameter analyzer to investigate the variation in carrier concentration in these nanowires.

To study the improvement in gas sensitivity of the ZnO nanowire sensor as a result of its reduced carrier concentration from oxygen plasma treatment, we fabricated another device (sample C). This sample has a similar structure to that shown in figure 1 and was subjected to the same oxygen plasma treatment condition as described above. NH3 gas sensing characterization was performed on this device. The gas sensing response of the device was measured using a Keithley 4200 semiconductor parameter analyzer. The device was biased at 4 V and operated at 300 °C in a temperature-controlled quartz tube furnace at atmospheric pressure. 200 sccm argon (Ar) was introduced to the gas ambience for a period of 180 s, followed by introduction of 0.75% NH3 in Ar for 10 min. Thereafter, 200 sccm O2 was used to reset the device. The initial exposure to Ar gas acted as a control to ensure that the device did not change its conductance when exposed to an inert gas. The gas sensing response of the as-fabricated nanowire sensor towards 0.75% NH3 was compared with its response when the experiment was repeated after the sample was subjected to O2 plasma treatment.

3. Results and discussion

Figures 2(a) and (b) show the current–voltage (I–V) curves from sample A and sample B respectively in a sweep voltage range.
Figure 2. (a) I–V curve of sample A showing as-fabricated characteristics and characteristics after the sample had been treated with $O_2$ plasma. (b) I–V curve of sample B showing as-fabricated characteristics and characteristics after the sample had been treated with $NH_3$ plasma.

The conductance decreased after sample A was subjected to $O_2$ plasma. In contrast, sample B experienced an increase in conductance following $NH_3$ plasma treatment.

The observed conductance changes may be explained in terms of the oxidizing/reducing gas effect on the ZnO nanowires. The coverage of chemisorbed gases on the ZnO nanowire surfaces can modify the electronic surface states, vary the electron concentration and modify the band structure. These are schematically shown in figure 3 using a single ZnO nanowire as an illustration. When a ZnO nanowire is exposed to an oxidizing gas plasma, e.g. $O_2$, the ionosorbed (ion-chemisorbed) $O_2$ acts as surface acceptors and binds electrons at the surface of the ZnO (figure 3(a)), creating a depletion layer below the surface and reduces the carrier concentration (figure 3(b)). The electrostatic potential of the space–charge that is formed thus induces a band bending upwards from the conduction band (figure 3(c)). In this way, the conductance and the carrier concentration of the ZnO nanowires are reduced. On the other hand, when the ZnO nanowire is exposed to a reducing gas plasma, e.g. $NH_3$, the ionosorbed $NH_3$ acts as surface donors and donates electrons to the surface of the ZnO (figure 3(d)), creating an accumulation layer below the surface and increases the carrier concentration (figure 3(e)). This induces a band bending downwards from the conduction band as illustrated in figure 3(f). Thus, the conductance and the carrier concentration of the ZnO nanowires are increased. Similar observations of conductance variation in ZnO nanoneedles resulting from carrier concentration variation caused by hydrogen plasma gas treatment is reported in [13]. Thus the lowered conductance measured across our ZnO nanowire device when subjected to $O_2$ plasma treatment implies that the ZnO nanowires have a lower carrier concentration compared to their as-grown state. The possibility that the physical bombardment of the plasma affects the response of the ZnO nanowires is eliminated, based on two reasons. First, both sample A and sample B were treated with exactly the same plasma conditions, except with a different gas for each case. The I–V results shown in figure 2 which indicate a difference in response—a decrease in conductance for sample A and an increase in conductance for sample B—imply that it is the gas, not the plasma, that affects the response of the nanowires; else both will show similar responses as they were treated with the same plasma conditions. Second, the morphology of the nanowires after plasma treatment was checked using FESEM, and it was observed that there was no significant physical difference from those before plasma treatment.

Figure 4 shows the measured current versus time response of the ZnO nanowire sensor (sample C) towards $NH_3$ gas sensing. The response of the as-fabricated nanowire sensor (sample C) (figure 4(a)) is compared with its response when the experiment was repeated after the device was subjected to $O_2$ plasma treatment (figure 4(b)). The measured sensitivity of the untreated device to 0.75% $NH_3$ gas is about 1.1. For the treated device, the measured sensitivity increased to 4.9, showing an improvement in gas sensitivity of about four times. The result is repeatable, as illustrated by the two cycles of gas treatment.

1 Sensitivity as defined in this experiment is a ratio of the conductance of the sensor before introduction of $NH_3$ to the conductance of the sensor after introduction of $NH_3$. For a fair comparison, the conductance is taken at a fixed duration of time in all cases.
sensing shown in figure 4(b). Though in our experiment an improvement towards NH3 gas sensitivity of our ZnO nanowire sensor was obtained after oxygen plasma treatment, the sensitivity performance still may not be comparable to reported sensitivities of above 70 [15, 16] towards NH3 gas sensing. Reports have shown that the diameter of ZnO nanostructures can greatly affect the gas sensitivity performance [16–18]. For instance, Chen et al [17] reported that their small diameter one-dimensional ZnO nanostructures (15 nm) exhibited an improvement of about 4 to 5 times gas sensitivity towards ethanol vapor compared with those whose diameters range from 50 to 150 nm. Taking this into consideration, one possible reason for the low gas sensitivity of our ZnO nanowire sensor may be related to the size of our nanowires (20–40 nm in diameter). Thus, it is proposed that further work to synthesize smaller diameter ZnO nanowires could be a possible way to improve the gas sensitivity performance of our sensor.

The origin of the improvement in gas sensitivity of the ZnO nanowires was investigated by characterization of the surface composition and chemical binding state of these nanowires using an x-ray photoelectron spectroscopy (XPS) system (VG ESCALAB 220i-XL system). XPS analysis was carried out on ZnO nanowires that had been subjected to O2 plasma treatment (sample E) and NH3 plasma treatment (sample F) and compared against an as-grown nanowire sample (sample D). All the XPS spectra are calibrated against the C 1s peak (284.6 eV) as reference. The XPS spectra for Zn 2p3/2 of the three samples are shown in figure 5(a). The approximately symmetrical Zn 2p3/2 spectrum centered at ∼1022 eV for all three curves can be assigned to Zn 2+ in ZnO [19, 20]. The XPS spectra for the O 1s spectra of all three samples as shown in figure 5(b) are asymmetric curves, which is typical for ZnO [21, 22]. The O 1s curves were fitted with a Gaussian–Lorentzian distribution (dash–dot lines). Two peaks (O1 and O2) are sufficient to obtain a good fit for the O 1s spectra for all the curves. The lower energy peak (O1) (the position of this peak varies from 529 to 530.7 eV in different reports) is typically attributed to O2− ions in the wurtzite ZnO structure. The higher energy peak (O2) (with typical positions at 531–532 eV) is normally assigned to O2− ions in oxygen-deficient regions on the surface [21, 22]. To analyze the effect of oxidizing/reducing gas plasma on the ZnO nanowires, we calculated the ratio of the O1/O2 peaks for samples E and F and compared their values against those of the as-grown control sample (sample D). It was found that the O2 plasma-treated sample (sample E) has a O1/O2 ratio of 0.40, which is lower than that of the as-grown control sample (sample D), with a ratio of 0.51. This implies that the oxidizing gas in the plasma had bound the electrons on the
surface of the ZnO nanowires to create more surface \( O^{2-} \) ions. This effect would inadvertently reduce the nanowire’s original carrier concentration (\( n_o \)), as illustrated in figure 3. With a smaller \( n_o \), \( \Delta G / G \) or sensitivity will be increased.

Furthermore, it is known that the sensing mechanism of ZnO nanowires towards NH\(_3\) gas depends on the interaction between the reducing gas and the negatively charged \( O^{2-} \) ions on the nanowire surface, thereby causing a variation in conductance, as described by equation (4) [23]:

\[
2\text{NH}_3 + 3\text{O}^{2-} \rightarrow 3\text{H}_2\text{O} + \text{N}_2 + 3e^{-}.
\] (4)

Thus, a higher availability of the \( O^{2-} \) ions on the surface of the nanowire after \( O_2 \) plasma treatment may allow more effective NH\(_3\) to \( O^{2-} \) ion interaction and thereby may result in a higher sensitivity of the ZnO nanowire sensor towards the reactant gas.

The \( \text{O}_1/\text{O}_2 \) ratio for the NH\(_3\) plasma-treated sample (sample F) is calculated to be 0.78, which is higher compared to the as-grown control sample (sample D) (with a ratio of 0.51). This implies that the NH\(_3\) plasma-treated sample has fewer \( O^{2-} \) ions on the surface of the ZnO than the as-grown sample, which is consistent with the notion that the reducing gas in the plasma acts as surface donors and donates electrons to the space charge layers, thereby freeing up the \( O^{2-} \) ions on the surface of the ZnO nanowires.

4. Conclusion

In summary, we have proposed a route to improve the gas sensitivity of an as-fabricated ZnO nanowire sensor towards ammonia without using catalyst nanoparticles. This improvement is achieved by lowering the nominal carrier concentration in the as-grown ZnO nanowires. We have demonstrated that the carrier concentration in these nanowires can be tuned by treating them to an oxidizing gas plasma or a reducing gas plasma. \( I-V \) measurement across a ZnO nanowire device that was subjected to an oxidizing gas plasma treatment shows a conductance decrease, whereas an increase in conductance was measured across another ZnO nanowire device that was subjected to a reducing gas plasma. We further demonstrate as a proof-of-concept that the ZnO nanowire device that has been subjected to an \( O_2 \) plasma treatment, thereby having a reduced carrier concentration, exhibits a gas sensitivity improvement of approximately four times towards 0.75% NH\(_3\) gas sensing. This improvement in sensitivity can be attributed to a lowered carrier concentration in the ZnO nanowires and a higher availability of the \( O^{2-} \) ions on the nanowire surface as inferred from the XPS analysis results, when these nanowires were subjected to oxygen plasma treatment, which enables a more effective NH\(_3\) to \( O^{2-} \) ion interaction during gas sensing.

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