Influence of annealing temperature on the performance and stability of on-chip hydrothermally grown ZnO nanorod gas sensor toward NO\textsubscript{2}

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ABSTRACT

Nanorod-based gas sensors synthesized at low temperature should generally be stabilized by annealing before usage. However, the influence of annealing on the sensing performance and stability of these nanorods is rarely reported. In this study, we first fabricated gas sensors based on ZnO nanorods grown on-chip on glass substrate using hydrothermal method. Subsequently, these sensors were annealed at either 400, 500 or 600°C in air for 4 h. The gas-sensing performance of the ZnO nanorods toward NO\textsubscript{2} was tested before and after annealing. The sensitivity of the gas sensors to NO\textsubscript{2} decreased, but the stability increased with increase in annealing temperature. Photoluminescence spectroscopy and X-ray diffraction were used to investigate the material structure of ZnO nanorods. Results revealed that the oxygen-atom-related defects in the ZnO lattice in the region close to the surface influenced by annealing process were the most significant factors on the sensing properties and stability of ZnO nanorods.

Keywords: Annealing, defects in nanorods, gas sensor, hydrothermal, zinc oxide.

INTRODUCTION

Urbanization and industrialization are developing rapidly worldwide, thereby increasing the attention given to air quality. NO\textsubscript{2} is a harmful gas for all living forms. In urban environments, 80% of this air pollutant comes from cars and trucks. The remaining NO\textsubscript{2} pollutant originates from other combustion processes. ZnO is an n-type semiconductor with good gas-sensing properties, especially for sensing NO\textsubscript{2}. 1-D nanostructures, such as nanowires or nanorods (NRs), are the most remarkable morphologies of ZnO for NO\textsubscript{2} sensing (Kumar et al., 2015). For example, on-chip hydrothermally grown ZnO NRs have been proven to be highly sensitive and selective to NO\textsubscript{2} (Jiao et al., 2015). Native defects in ZnO have been discussed in detail in a review paper (McCluskey et al., 2008). The n-type semiconductivity of ZnO is determined by its defects. Notably, the gas sensitivity of CVD-grown ZnO nanowires to NO\textsubscript{2} is linearly proportional to the photoluminescence (PL) intensity of oxygen-vacancy-related defects (Ahn et al., 2008). Hydrothermally grown ZnO NRs also present native crystal defects (Tam et al., 2006; Baruah et al., 2010), but the mechanism of how these defects influence the gas-sensing properties toward NO\textsubscript{2} has not been determined. The most common technique used to investigate the defects of semi-conductors is PL spectroscopy (Cheng et al., 2011; Zou et al., 2015; Padilla-Rueda et al., 2012). This technique exhibits numerous advantages. First, PL is a non-destructive method. Second, optical energy gap can be obtained. Third, PL spectroscopy is a self-evident method that is used to obtain comprehensive information about electronic levels.

PL peaks revealed the transition of electrons between two energy levels; hence, the defect is easily identified. Optical properties of ZnO probed by PL were reviewed (Djurišić and Leung, 2006). At room temperature, these spectra commonly consist of three major peaks at 380, 520 and 600 nm, which are referred to as UV, green and orange peaks, respectively. The UV peak is attributed to the exciton recombinaton process, while the green and orange peaks are attributed to intrinsic defects in ZnO (Chandrinou et al., 2009). Therefore, the transition of the
excited electrons from the conduction band to the ground state results in the UV peak and that from the conduction band to a non-ground state yields another peak. The UV peak is well established, but green and orange emissions are disputable. One explanation is that the green peak, centered at 525 nm, is believed to originate from the electron transition from the conduction band to the energy level corresponding to oxygen vacancy (V_o), including singly charged oxygen vacancy V_o^+ and doubly charged V_o^{2+} or to zinc vacancy V_Zn. The orange and red peaks, centered at 600 and 660 nm, respectively, are attributed to the electron transitions from the conduction band to the energy level corresponding to interstitial oxygen O_i (Nguyen et al., 2014).

The electrons on their way down to the ground state are simply trapped by the defects in ZnO. Some researchers found that the green peak at 510 nm originates from singly ionized oxygen vacancies in commercial ZnO phosphor powders (Vanheusden et al., 1996). Nevertheless, most researchers agreed that the peak at 600 nm involves interstitial oxygen ions (O_i^−1) (Green et al., 2003).

Different assumptions regarding the mechanism of the visible emission exist, but the annealing process significantly influences the defects in ZnO (Djurisic et al., 2007; Kwok et al., 2006; Wang et al., 2006; Bae et al., 2001). It is well-known that ZnO NRs must stabilize by annealing prior to its use for gas sensing. Furthermore, when annealed at a temperature above 600°C, the aggregating tendency of NRs between each other also increases (Zhang et al., 2014). Possible defect types in a ZnO crystal are vacancy, interstitial (that is, V_o, V_Zn, O_i, and Zn_i), and antisite of O and Zn. The antisites of O and Zn show remarkably high formation energy and are not present in large quantities (McCleskey et al., 2008). V_Zn and Zn_i usually exist as a result of Frenkel reaction in ZnO sublattice (Han et al., 2002; Lin et al., 2001). However, Zn_i is highly mobile even at room temperature (Janotti and Van de Walle, 2009), thus, it is not durable. Therefore, most attention focuses on V_o, V_Zn, and O_i in terms of the influence of ZnO defects on gas-sensing performance.

Oxygen can only diffuse at less than 100 nm in pure ZnO polycrystalline after 49 h at 900°C (Sabioni et al., 2003). In the present work, we annealed on-chip hydrothermally grown ZnO NRs at only 400, 500 and 600°C in air for 4 h, respectively. Thus, the oxygen diffusion-related defect change should be limited to the considerably shallow depth close to the ZnO NR surface. PL measurement is surface sensitive and can examine the defects at about 50-nm depth (Borseth et al., 2006). Thus, such measurement is a suitable method for the examination of the ZnO NR defects in our case. The response of the ZnO NRs to gases can be explained by the grain boundary and surface charge depletion mechanism (Feng et al., 2005). Nevertheless, this work will not address this depletion layer phenomenon. Instead, the focus will be on the effect of defect change related with the annealing temperature on the sensing performance.

**MATERIALS AND METHODS**

**Sensor fabrication**

Electrodes of the gas sensor were made of layers of 10 nm Cr and 60 nm Pt on a glass substrate by sputter deposition and lift-off patterning. Small round islands with thickness of about 10 nm zinc on 10 nm silicon layer between and on the electrodes were also prepared by using the same technique. These islands were used as seed sites for hydrothermal growth of ZnO NRs. The growth process is similar to that in our previous experiment (Jiao et al., 2015), that is, a two-step process for 16 and 36 h in equimolar solution of 0.005 M Zn(NO_3)_2 and 0.005 M hexamethylenetetramine at 94°C. Annealing was performed in a quartz tube oven with atmospheric air at 400, 500 and 600°C for 4 h.

**Materials characterization**

Morphology of the on-chip grown ZnO NRs was examined by field-emission scanning electron microscopy (FESEM, Zeiss Leo 1550, Germany). X-ray diffraction (XRD) and PL analysis were performed on the same sample before and after annealing at 400, 500 and 600°C to evaluate the crystal structure and defect changes associated with annealing temperatures in the ZnO NRs. PL was performed on the ZnO NRs using Horiba FluoroLog FL3-22 spectrophotometer with a 450 W xenon arc lamp as light resource. The ZnO NRs were excited with 325 nm light. Grazing-incidence XRDs of the samples were performed on parallel beam geometry with X-ray mirrors (Siemens D5000, Germany) at 0.3° incidence angle and Cu Kα radiation.

**Gas test**

The gas sensors were tested with flow-through technique (Jiao et al., 2015) with a standard flow rate of 400 sccm for both dry air and test gas. Switching between dry air and test gas took approximately 1 s. In the experiment, the standard NO_2 gas at 1000 ppm was used. The standard gas was mixed with dry air as carrier using several mass flow controllers. The flow rates of the standard gas and dry air were varied and test gases with low NO_2 concentrations were obtained. Prior to the sensing measurement, dry air flowed through the sensing chamber until a stable sensor resistance was obtained. The resistance of the sensors was continuously measured using a Keithley SourceMeter (Model 2700) and sampled using a computer. The dry air and the test gases were switched on/off each cycle. The
sensor response was defined as $R_{\text{gas}}/R_{\text{air}}$. Response time was defined as the time used to obtain 90% of full response from the base line to the saturated response. Accordingly, recovery time was also defined as the time used to obtain 90% of decrease from the saturated response to the base line.

RESULTS AND DISCUSSION

ZnO structure characterization

Figure 1A shows the overall design of the gas sensor. ZnO NRs grow successfully on-chip from the ZnO seed islands and connect each other. Site-selective growth makes these NRs suitable for gas-sensing application (Jiao et al., 2015; Nguyen et al., 2014). Figure 1B shows the ZnO NRs with high magnification. The ZnO NRs are relatively dense, and they form a dense network between each other. As shown in Figure 1C, the ZnO NRs are relatively porous, which favors gas sensing (Jiao et al., 2015). The ZnO NRs are also tapered; their tops are only 40 to 50 nm, and their bottoms are more than 200-nm wide. The morphology of the ZnO NRs after annealing at 400 and 500°C in air for 4 h remains similar to those of the pristine ones. Hence, the images are not shown in this paper. However, the ZnO NRs start to sinter to each other at the contact points when annealed at 600°C (Figure 1D).

Annealing may induce structure and defect changes on the ZnO NRs grown through hydrothermal method. To clarify this assumption, a sample with ZnO NRs grown under the same condition was examined by performing XRD and PL before and after sequential annealing at 400, 500 and 600°C. Figure 2 confirms that the ZnO NRs possess a hexagonal structure (Reference Code: 01-079-9878). Nevertheless, (103) peak, instead of (002), is predominant, which can be attributed to the sputtered Zn seed layer. Notably, the (103) peak and the other peaks show no remarkable change when annealed at 400, 500 and 600°C. This result suggests that ZnO NRs possess no obvious structural changes when annealed in this temperature interval. If structural change is not responsible for the different sensing behaviors, then it should be the defects in ZnO.
PL Spectroscopy of ZnO

ZnO NRs were excited by 325 nm light and the PL information was collected. The exciting light changes the PL of ZnO, and 325 nm is the most common wavelength to excite ZnO (Djurišić et al., 2006). As shown in Figure 3, two emission bands can be observed. First, the UV peak at 380 nm, which is attributed to the exciton recombination process, decreases remarkably when annealed at 400°C. This peak continues to decrease slightly further at 500°C but increases slightly at 600°C. Second, the visible peak originally located at 550 nm for unannealed ZnO NRs shifts to the infrared region with increasing annealing temperatures. This phenomenon can also be seen in the report of Do et al. (2014). The intensity of the visible peak first decreases when annealed at 400°C and then increases consecutively at 500 and 600°C. Given that the ZnO NRs are grown in alkaline solution and kept in ambient air, OH group exists on the surface of ZnO NRs (Kumar and Sahare, 2012).
Figure 3: PL spectroscopy of ZnO NRs before and after annealing.

Annealing at 150°C can remove the OH group, but H is not removed from the sample until 400°C (Tam et al., 2006). Decrease of both UV and visible peaks when annealed at 400°C can partly result from the removal of the OH group and the oxygen vacancy at the shallow depth of ZnO NRs (Kumar and Sahare, 2012; Leung et al., 2008).

Changes in visible peaks alone are highly related with the transformation of defects in ZnO NRs. Low temperature favors the adsorption of $O^-$ ion (Tam et al., 2006), whereas high temperature (more than 300°C) favors the adsorption of $O^{2-}$ ion (Wang et al., 2006). Moreover, oxygen gases can react with defects in ZnO NRs (Han et al., 2002; Lin et al., 2001) and oxygen atom can diffuse slowly into the bulk of ZnO at increased temperature through interstitial mechanism (Haneda et al., 1999; Soaressabioni, 2004). Therefore, the following reactions can occur when annealed in air at 400, 500 or 600°C, respectively.

\[
\frac{1}{2} O_2 + 2e^- = O^{2-} \quad (1)
\]

\[
\frac{1}{2} O_2 + V_{\text{o}} = O_\text{o} \quad (2)
\]

\[
\frac{1}{2} O_2 = O_\text{o} + V_{\text{zn}} \quad (3)
\]

\[
\frac{1}{2} O_2 + Zn_i = O_\text{o} + Zn_{\text{zn}} \quad (4)
\]

\[
\frac{1}{2} O_2 = O_i \quad (5)
\]

Where $O_\text{o}$ and $Zn_{\text{zn}}$ refer to the neutrally charged oxygen and zinc at the crystal lattice site, respectively. Oxygen diffusion in the ZnO NRs can eliminate $V_\text{o}$ and $Zn_i$ (Equations 2 and 4), and it can also increase $V_{\text{zn}}$ and $O_i$ (Equations 3 and 5). However, $V_{\text{zn}}$ becomes mobile at temperatures higher than 270°C and it can be annealed out at 330°C (Janotti and Van de Walle, 2009). Thus, a remarkable decrease in $V_\text{o}$ and an increase in $O_i$ of ZnO are expected when annealing the ZnO NRs in air. In any case, Equation 2 should naturally precede Equation 5, that is, given that oxygen diffuses into the ZnO bulk, it is needed first for $V_\text{o}$ termination. Afterward, the remaining oxygen will create $O_i$. The lowest annealing temperature in this work is 400°C. Consequently, the following analysis will mostly focus on $V_\text{o}$ and to some extent on $O_i$. 
Oxygen diffusion in bulk ZnO is described by diffusion coefficient, which depends on temperature (Moore and Williams, 1959). High temperature will result in fast oxygen diffusion into the bulk. The oxygen atoms diffuse remarkably shallow into the bulk of the ZnO NRs at 400°C. These newly arrived oxygen atoms will be combined with $V_0$ near the surface and will considerably reduce the green emission that indicates surface defects.

Furthermore, some oxygen atoms can migrate into the lattice of the ZnO NRs and be trapped in the octahedral interstitial site to form $O_i$ defect. $O_i$ in ZnO NRs acts as an electron acceptor, thereby resulting in low exciton emission at 380 nm (Figure 3). The orange emission at 600 nm is related with the defect in the bulk of hydrothermally fabricated ZnO nanostructures (Li et al., 2004). ZnO NRs annealed at 400°C (hereafter written as ZnO NRs_400°C) exhibit no remarkable $O_i$ defect in the bulk; therefore, this peak is weak. At 500 and 600°C, a large amount of oxygen dissociates at the surface and diffuses into the bulk of the ZnO NRs. The amount of interstitial $O_i$ will significantly increase in the ZnO NRs, which increases the intensity of the orange-red peak. Given its recombination with $O_i$, $V_0$ will be completely removed at the surface and to a considerable extent, in the bulk, thereby decreasing the intensity of the green peak.

These two mechanisms, which cause the increase of one light and decrease of the other result in the obtained visible peak moving toward the infrared region, which is similar to the horizontal propagation of a sinus wave; the particles only move up and down in the same positions of the horizontal line. Concurrently, the electrons in the bulk of the ZnO NRs will be taken by $O_i$. When testing for gas sensing, the response of the ZnO NRs_600°C, that is, the sample annealed at 600°C to $O_2$ is significantly lower than that of the unannealed ZnO NRs, because less electrons can be used by $O_2$ due to the depletion effect (Figures 4 and 5). As for the UV peak, an OH group on the surface of one ZnO NR can react with an OH group on the another ZnO NR when both are in contact with each other; this phenomenon is similar to the fusion bonding of two silicon wafers activated by RCA1 cleaning. Consequently, ZnO NRs aggregate at high annealing temperature and their surface states are reduced to some degree, thereby, resulting in a slightly higher UV peak for the ZnO NRs annealed at 600°C as compared with that at 500°C (Shalish et al., 2004).

**Gas sensing results**

Figure 4 shows the dynamic resistance changes of all four ZnO NR gas sensors from the same batch toward NO$_2$. One of them was not annealed. The three others were annealed at 400, 500, and 600°C, respectively. The response/recovery time of each sample to 5 ppm NO$_2$ is summarized in Table 1. This concentration was selected for comparison because the sensors reach saturation at different temperatures. Therefore, the measurement data of this concentration are more reliable than that of the other concentrations.

As shown in Figure 4 and Table 1, both the response time and recovery time of the three annealed sensors decreased, but their ratios (the numbers in parentheses in Table 1) increased in the sensor’s operation temperature, except for the ZnO NRs_400°C at the operation temperature of 400°C (the values in the squared brackets). This exception is attributed to the fact that this sample was annealed at 400°C; when measuring the gas-sensing property at the same temperature, the defects become unstable again, which results in the odd values in the table. The first sample was not annealed, thus, when in operation, it was exposed for annealing at this operation temperature. Therefore, their ratio shows no linear increase despite the same decreasing trend of the response and recovery time versus the increasing operation temperature.

The annealed ZnO NRs exhibit remarkably longer response and recovery time than those of unannealed ZnO NRs, and the time increases with the annealing temperatures. Response time corresponds to the adsorption of NO$_2$ to ZnO NRs, while the recovery time corresponds to desorption of NO$_2$ from ZnO NRs. Thus, two observations were noted: (i) high operation temperature results in easy NO$_2$ adsorption and desorption from ZnO NRs, and the ease of desorption is faster than that of adsorption; and (ii) high annealing temperature results in difficult NO$_2$ adsorption and desorption from ZnO NRs. The defects in the ZnO NRs mostly influence the interaction between NO$_2$ and ZnO NRs. For observation (i), high operation temperature makes NO$_2$ reactive and easy to compete with the oxygen species to adsorb on the surface of the ZnO NRs. When the test gas is switched off for recovery, the dry air, which is switched on at the same time creates a strong gradient of the NO$_2$ concentration between the NR surface and the ambient. Additionally, the high operation temperature helps in pulling the NO$_2$ out fast from the surface of the NRs.

For observation (ii), the increase in the response time and recovery time cannot be explained only by the adsorption mechanism of the NO$_2$ species on the ZnO NR surface. This influence should correspond closely to the change of $V_0$ and $O_i$ in the ZnO bulk. Annealing at higher temperature lowers more the number of $V_0$, especially near the surface, and eventually increases the number of $O_i$. Nevertheless, when measuring the gas response, high operation temperatures will promote the migration of these defects from the deep region to the shallow region of the NRs as a result of their concentration gradient in the material. This migration process causes the measurement to take a longer time to stabilize, in so doing, the long response and recovery time of the samples is annealed at high temperature. The high operation temperature results
in a fast migration as depicted in Table 1.

Annealing influences the defects of the ZnO NRs, which determine the response of the NRs to NO\textsubscript{2}. The response of the unanneled ZnO NRs to NO\textsubscript{2} is shown in Figure 5A. These unanneled ZnO NRs should exhibit a higher number of native defects than those of the three annealed
Table 1: Response/recovery time (s) of each sample to 5 ppm NO₂ at different operation temperatures.

<table>
<thead>
<tr>
<th>Sensors sample</th>
<th>Operation at 300°C</th>
<th>Operation at 350°C</th>
<th>Operation at 400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unanneled ZnO NRs</td>
<td>93/34 (2.7)</td>
<td>84/32 (2.6)</td>
<td>58/19 (3.0)</td>
</tr>
<tr>
<td>ZnO NRs_400°C</td>
<td>314/320 (1.0)</td>
<td>235/162 (1.5)</td>
<td>[62/72 (0.86)]</td>
</tr>
<tr>
<td>ZnO NRs_500°C</td>
<td>323/583 (0.6)</td>
<td>284/376 (0.8)</td>
<td>178/133 (1.3)</td>
</tr>
<tr>
<td>ZnO NRs_600°C</td>
<td>410/597 (0.7)</td>
<td>269/397 (0.7)</td>
<td>221/261 (0.8)</td>
</tr>
</tbody>
</table>

Figure 5: Response of the ZnO NR gas sensors to NO₂ at different temperatures: (A) unannealed, (B) annealed at 400°C, (C) annealed at 500°C and (D) annealed at 600°C.

samples. The highest response of 36.4 occurs for 50 ppm NO₂ at 350°C. The response generally increases with increase of the sensor operation temperature from 300 to 350°C, but it slightly decreases when measured at 400°C. Similarly, the ZnO NRs_400°C presents the highest response of 35 to 50 ppm NO₂ at 350°C and then decreases slightly at 400°C (Figure 5B). This result is attributed to the fact that the operation temperature also exhibits an annealing effect on the material when it is equal or higher than the annealing temperature. Therefore, measurement at lower operation temperatures than 400°C, that is, 300 and 350°C with this sample yield reliable and repeatable results. For the same reason, the sensing performance of the unannealed sample cannot be repeated at the lower operation temperatures than that of the last operation.

Comparatively, both the ZnO NRs_500°C and the ZnO NRs_600°C (Figure 5C and D) show the highest response of only 12.6 and 7.9 to 50 ppm NO₂ at 400°C, respectively, because the remaining V₀ close to the surface of both samples is less than that of the first two samples. Moreover, high operation temperature also facilitates migration of V₀ in the bulk to the surface, as earlier mentioned and it creates many reactive sites, which results in high response to NO₃.

Figure 6 summarizes all of the results for 25 ppm NO₂ from Figure 5 in a 3-D plot, which shows the annealing temperature dependency of NO₂ responses of the tested sensors at different operation temperatures. This concentration was selected for comparison because the data showed clearer tendency than those from the lower
concentrations. From the analysis aforementioned and Figure 5c and d, two observations can be summarized: (i) higher operation temperature results in higher response to NO$_2$; and (ii) higher annealing temperature removes more crystal defects in ZnO NRs causing lower sensing response to NO$_2$ but the ZnO NRs will be more stable in terms of measurement reliability and repeatability. For the high sensor response it should be desirable to have low annealing temperature and high operation temperature. However, the operation temperature cannot be equal but lower than the annealing temperature in order to avoid the annealing-when-in-operation.

**Annealing temperature and stability of the sensing material**

For long-term application, stability is an important property of a sensor. In this study, we compare two measurements of the same sample at present and after 1 week in air. As shown in Figure 7A, the ZnO NRs,400°C samples spend a considerable amount of time to response and recover after 1 week in ambient air. However, the response increases slightly, probably due to significantly increased physisorption of water vapor from air;

Figure 6: Annealing temperature dependency of responses of the tested sensors to 25 ppm NO$_2$ at different operation temperatures.

Figure 7: Response of the ZnO NRs samples annealed at 400 and at 600°C to 10 ppm NO$_2$ in 10 cycles measured at 350°C.
consequently, $\text{HO}_2^+$ and electron hole are produced, as shown in Equation 6 and the density of $V_0$ near the surface is low. By contrast, the ZnO NRs$_{600^\circ C}$ sample is remarkably stable even after 1 week such that the two curves overlap with each other (Figure 7B). However, the sensing response is much lower than that of the ZnO NRs$_{400^\circ C}$ sample. This result is caused by the less oxygen vacancy near the surface of ZnO NRs after annealing at $600^\circ C$, which results in less adsorption of water to the ZnO NRs (Ahn et al., 2004; Kofstad, 1995).

$$V_{O}^{2+} + H_2O (g) = HO_2^+ + h^+ + \frac{1}{2} H_2 (g) \quad (6)$$

Where $V_{O}^{2+}$ is the ionized oxygen vacancy; $\text{HO}_2^+$ is the ionized OH group at the oxygen position and $h^+$ is the electron hole.

Conclusion

We first grew ZnO NRs on-chip through hydrothermal method. Subsequently, we annealed them either at 400, 500 or $600^\circ C$ in air for 4 h prior to their use for NO$_2$ gas sensing. The unannealed ZnO NRs show the highest response to NO$_2$ as compared with those of the three annealed ones. The ZnO NRs annealed at $400^\circ C$ remain highly sensitive to NO$_2$, but are unstable in air. The ZnO NRs annealed at $600^\circ C$ are not as sensitive as the ZnO NRs annealed at $400^\circ C$, but they are more stable in air. Generally, the response time and the recovery time of the sensors toward NO$_2$ tend to increase with increasing annealing temperature. Analysis suggests that when annealing at temperatures higher than $330^\circ C$ ($400^\circ C$ in our case), only oxygen vacancy at shallow depth of the ZnO NRs is the main defect influencing the sensing performance of the ZnO NRs. Thus, high annealing temperature results in less oxygen-vacancy-related defects in the hydrothermally grown ZnO NRs, which makes the sensors less sensitive to NO$_2$ but more stable in air.

Depending on application, a trade-off between sensor response and stability has to be made to determine a suitable annealing temperature. However, the annealing temperature should always be higher than the operation temperature.

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