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The effect of oxygen-vacancy-related defects on gas-sensing properties of ZnO-nanowire gas sensors was investigated. Gas sensors were fabricated by growing ZnO nanowires bridging the gap between two prepatterned Au catalysts. The sensor displayed fast response and recovery behavior with a maximum sensitivity to NO_2 gas at 225 °C. Gas sensitivity was found to be linearly proportional to the photoluminescence intensity of oxygen-vacancy-related defects in both as-fabricated and defect-controlled gas sensors by postannealing in Ar and H_2 atmosphere. This result agrees well with previous theoretical prediction that oxygen vacancies play a role of preferential adsorption sites for NO_2 molecules. © *2008 American Institute of Physics*.
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Ever since Seiyama *et al.*[1] discovered that the electrical conductivity of ZnO could be dramatically changed by the presence of reactive gases in the air, there have been tremendous reports on the applications of metal-oxide semiconductors as gas sensors. In the early stage, metal-oxide-semiconductor gas sensors have been usually fabricated in the form of thin films, in which nanosized powders are screen printed on prepatterned electrodes, followed by firing at high temperature.[2] Recently, one-dimensional nanostructures including nanowires, nanotubes, and nanobelts found their major application into chemical/gas sensors owing to the high surface-to-volume ratios of these nanostructures, as demonstrated with SnO_2-coated carbon nanotube,[3] functionalized silicon nanowires,[4] and ZnO nanowires catalyzed by metal nanoparticles.[5,6]

Like any other semiconductors, deep levels (DLs) affect the electrical and optical properties of ZnO as well. For example, resident and metallization-induced native defects were reported to severely degrade the potential barrier height and ideality factor of metal-ZnO Schottky diodes, acting as a conducting path for charge carriers.[7] For optical applications of ZnO, DLs responsible for so-called green luminescence (GL) have been one of the obstacles for realizing ZnO light emitters. Furthermore, the nature of GL remained controversial for decades. In the early studies it was unambiguously attributed to copper impurities,[8] but strong evidence was later presented in favor of native defects such as V_O or complex defect involving V_O, Zn_i, and O_{Zn}.[9–11] Now, GL is generally accepted to be related to V_O. In spite of numerous reports on the effects of DLs on optical and electrical properties of ZnO-based devices, there have been no satisfactory reports on the correlation between DLs and gas-sensing properties.

Here we report on the effects of V_O-related defects on gas-sensing properties of ZnO-nanowire gas sensor. For this purpose, novel ZnO-nanowire gas sensors were fabricated using a simple and efficient fabrication process and the gas-sensing capability was demonstrated for NO_2 gas. A close correlation was found between GL intensity and gas sensitivity based on which an appropriate mechanism underlying this phenomenon was suggested.

Figure 1(a) shows the schematic illustration for a network of ZnO nanowires floated above SiO_2/Si substrate. For the area-selective growth of ZnO nanowires, 2-nm-thick Au catalyst film was patterned by the conventional photolithography. Since the Au layers were consumed during nanowire growth, we adopted 300-nm-thick Pt acting as contact electrodes between the Au layer and the SiO_2/Si substrate. ZnO nanowires were synthesized by the carbothermal reduction process and the synthesis details were described elsewhere.[12] Figure 1(b) shows a scanning electron microscope (SEM) image of ZnO nanowires, in which one can see that ZnO

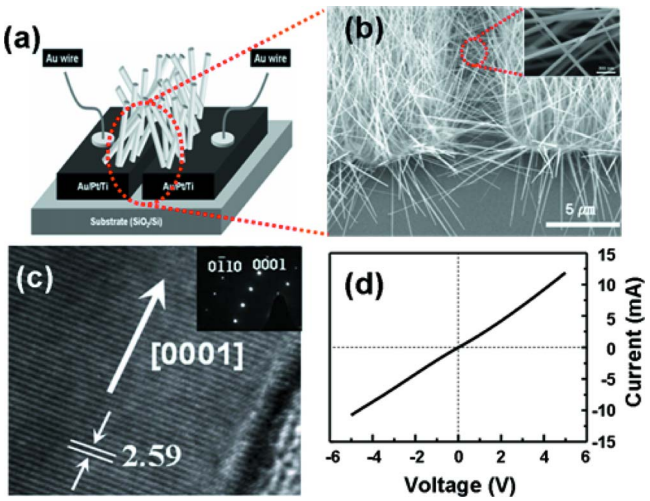

FIG. 1. (Color online) (a) A schematic illustration and (b) SEM images for the network-structured ZnO nanowire floated SiO_2/Si substrate. (c) A high-magnification TEM image of a ZnO nanowire with its corresponding selective-area electron diffraction pattern. (d) Room-temperature *I-V* characteristics of the gas sensor measured under the dry-air condition.

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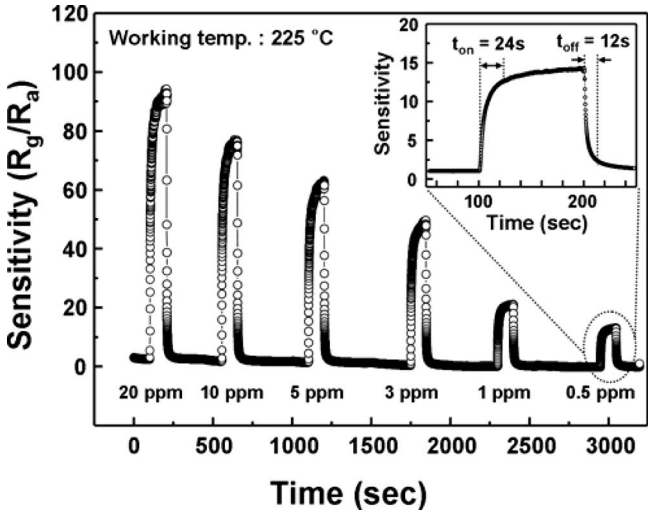

FIG. 2. Gas sensitivity curves of the network-structured SnO_2-nanowire gas sensor under exposure to 20, 10, 5, 3, 1, and 0.5 ppm of NO_2 gas at the measurement temperature of 225 °C. The inset shows the response and recovery behavior of the gas sensor at 0.5 ppm.

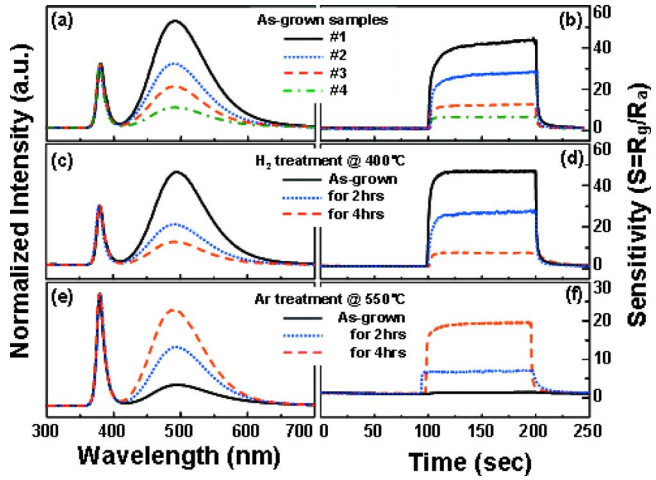

FIG. 3. (Color online) PL spectra and gas sensitivities of four different as-fabricated [(a) and (b)], H_2-annealed [(c) and (d)], and Ar-annealed [(e) and (f)] ZnO-nanowire gas sensors. All PL spectra were normalized to NBE peaks for comparison.

nanowires were selectively grown only on the Au layer. The device structure proposed in this work is very simple and efficient, because the electrical contacts to nanowires are self-assembled during the synthesis of nanowires. From transmission electron microscope studies, ZnO nanowires on the Pt electrode were found to be grown in the *c*-axis orientation, as in Fig. 1(c). Figure 1(d) represents the room-temperature current-voltage (*I-V*) characteristics of the gas sensor in dry-air condition. A good Ohmic behavior was observed, which is very important to the sensing properties because the sensitivity of a gas sensor can be maximized when the metal-semiconductor junction is Ohmic or has a negligible junction resistance. For measuring gas-sensing properties, a sensor was placed inside the quartz tube and then the resistance between two electrodes was measured at 1 V.

The sensor displayed the highest sensitivity (defined as R_g/R_a, where R_g and R_a are the electrical resistances in NO_2 gas and dry air, respectively) at 225 °C as a function of operation temperature. Figure 2 shows the response transient of the ZnO-nanowire gas sensor under exposure to various levels of NO_2 concentration at 225 °C. The sensitivity increases with increasing concentration of NO_2. As seen in the inset, both response and recovery were very fast, taking 24 and 12 s for 90% of full response and recovery, respectively, at 0.5 ppm of NO_2. Especially, the recovery time is much shorter than other types of gas sensors,[13,14] which can be attributed to the unique device structure that ZnO nanowires in the sensor are floated above the substrate, which facilitates the adsorbates to be easily desorbed and swept away from the surface of ZnO.[15] And also the gas sensor developed in this work has similar or even higher sensitivity compared with those based on ZnO nanocrystals,[13] In- and Sn-doped ZnO thin films,[14,16] or ZnO nanowires.[17] The enhanced sensitivity can be explained as follows. When *n*-type ZnO is exposed to the oxidizing gas such as NO_2, oxygen molecules are adsorbed on the surface. The adsorbed oxygen molecules extract electrons from the conduction band and the electron-depletion region is extended from the surface, which increases the resistance of nanowires. However, the sensor in this work has an additional unique feature or nanowire/nanowire junctions at the networking points, which is not available in the usual nanowire-based gas sensors. When exposed to oxidizing gases, a potential barrier develops at the nanowire/nanowire junctions, which blocks the electron flow in a way more efficient than the surface depletion of single nanowires with metal contacts. Thus, the enhanced sensitivity can be attributed to the potential barrier height at the junction as well as surface depletion region of each nanowire.

DLs are known to severely affect the optical and electrical properties of ZnO-based devices. In order to investigate the effects of DLs on gas-sensing properties, photoluminescence (PL) and gas-sensitivity measurements were performed on as-fabricated gas sensors as in Figs. 3(a) and 3(b). PL spectra were obtained by excitation of 325 nm He–Cd laser at room temperature. Two major peaks, a near-band-edge (NBE) emission at 380 nm and V_O-related GL emission at 490 nm, were observed.[10,11] In this plot, all spectra were normalized to NBE peak. Although these samples were prepared at the same run, there were significant variations in the GL intensity. In other words, ZnO nanowires, grown closer to the center of tube furnace, had a lower GL intensity probably because higher growth temperature leads to better crystallinity of ZnO nanowires, which is consistent with the temperature-dependent GL intensity in ZnO thin films grown by metal-organic chemical vapor deposition.[18] The gas-sensing properties of these sensors were measured using 5 ppm of NO_2 at 225 °C, as seen in Fig. 3(b). Contrary to the expectations, the sensitivity linearly *increased* with the GL intensity.

Although there is a trend between V_O-related defects and gas sensitivity of four *different* gas sensors, gas sensitivity can be changed depending on other parameters such as Ohmic contact, crystalline quality of nanowires, and contacting junctions especially in the present device structure. Thus, in order to obtain more reliable evidence on the correlation between V_O-related defects and gas sensitivity, the defect concentration of an *identical* sensor was modified through high-temperature annealing in H_2 or Ar atmosphere. As seen in Fig. 3(c), H_2 annealing significantly reduced the GL emission, which is consistent with previous reports that H_2 an-

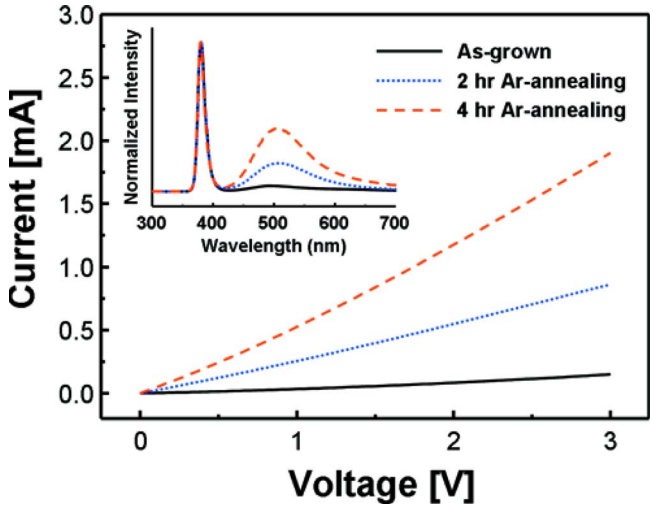

FIG. 4. (Color online) Room-temperature *I-V* characteristics of a ZnO-nanowire gas sensor after as-fabricated and Ar-annealed for 2 and 4 h. The inset shows the corresponding PL spectra.

nealing at a high temperature has a passivation effect on the point defects or impurities since the hydrogen atoms can easily diffuse into the lattice and form strong bonds with various lattice positions.[19] On the other hand, a significant increase in V_O-related defects was observed by annealing the sample under Ar ambient as in Fig. 3(e), which might be explained by oxygen atoms evaporating out of the ZnO lattice. The gas sensitivity of defect-controlled gas sensors showed the same trends [Figs. 3(d) and 3(f)] or gas sensitivity being linearly proportional to the defect density.

The first candidate explanation for this remarkable correlation might be the change in carrier density by the generation of V_O-related defects. Vanheusden *et al.*[10] reported a strong evidence that the electron density in ZnO powders is linearly dependent on the GL intensity based on electron paramagnetic resonance, optical absorption, and PL measurements. Thus, in order to confirm the relationship between the electron density and V_O-related defects, *I-V* characteristics of defect-controlled gas sensors were measured as a function of Ar postannealing time as in Fig. 4. The electrical current was found to be linearly proportional to the intensity of V_O-related defects, which is consistent with the findings of Vanheusden *et al.* Now, it is worthwhile to consider whether higher electron density in ZnO nanowires might result in higher gas sensitivity or not. As explained earlier, higher gas sensitivity means larger modulation in the depletion width of ZnO nanowires. However, the depletion width is inversely proportional to the square root of the free-carrier concentration, which means that the increase in electron density of ZnO nanowire should result in the decrease in the modulation of the depletion width or lower gas sensitivity. Thus, this is not the case.

Another possible explanation is that oxygen vacancies can act as preferential adsorption sites for NO_2 molecules. In fact, there have been several theoretical predictions that surface defects such as oxygen vacancies often dominate the electronic/chemical properties and adsorption behaviors of metal oxide surfaces.[20,21] Very recently, An *et al.*[22] investigated the reaction between NO_2 molecule and the ZnO surface with and without oxygen vacancy using density functional theory and found that the adsorption energy (E_{ad}) of NO_2 on the oxygen-vacancy site is significantly increased to $E_{ad}=-0.98$ eV, three times larger than $E_{ad}=-0.30$ eV on the perfect site and charge transfer from the oxygen-vacancy site to NO_2 adsorbate is much larger than that from the perfect site to NO_2 adsorbate. This means that oxygen vacancies bind more tightly with NO_2 molecules attracting more charge from ZnO surfaces compared with oxygen-vacancy-free ZnO surface, which is in good agreement with the close relationship between the concentration of oxygen-vacancy-related defects and NO_2 sensitivity of ZnO gas sensor observed in this work. This is the first experimental evidence on the correlation between oxygen vacancies and the gas-sensing property of a ZnO gas sensor.

In conclusion, network-structured ZnO-nanowire gas sensors were fabricated and a correlation between the V_O-related defect and gas sensitivity was investigated. Unlike to the general belief that DLs have detrimental effects on electrical and optical properties, V_O-related defects in ZnO-nanowire gas sensor were demonstrated to be exploited to significantly enhance gas sensitivity.

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