Water pre-adsorption effect on room temperature SnO2 nanobelt ethanol sensitivity in oxygen-deficient conditions

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Abstract

The water adsorption effects on room temperature ethanol sensitivity of a SnO2 single crystal nanobelt was studied. SnO2 nanobelt showed better electrical conductivity in air than in vacuum. The current increased linearly with relative humidity in air and with water concentration in vacuum. In the presence of water vapor, the SnO2 nanobelt electrical response was quite different, depending on the H2O and C2H5OH molecules adsorption sequence. The current response to ethanol gas increased substantially when water was pre-adsorbed. However, no change was found without water pre-adsorption. This interesting behavior is ascribed to competition between the H2O and C2H5OH molecules trying to adsorb on oxygen sites at the tin oxide surface. Dissociated water acts as the surface conduction channel resulting in better conductivity, while ethanol is physically adsorbed without water pre-adsorption. Based on this sensing mechanism, SnO2 nanobelt can be used as a highly efficient ethanol detector in humid air.

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1. Introduction

One-dimensional (1D) semiconducting metal oxide nanostructures have attracted much attention due to their unique properties and great potential in fabricating highly sensitive and fast responding gas sensors [1–6]. With mass production of high quality single crystal 1D SnO2 nanowires and nanobelts by chemical vapor deposition [7], SnO2 n-type semiconducting nanowires and nanobelts have been widely used as effective and inexpensive chemical sensors for detecting NO2 [8], NH3 [9], CO [10], and H2 [11]. They also exhibit relatively high ethanol sensitivity [12,13], which is often ascribed to their high surface-to-volume ratio associated with the 1D nanostructure. However, the working temperature of the single crystal 1D SnO2 ethanol sensor as reported in the literature, is around 300 °C [14], which limits the breadth of its application. Here, we report room temperature SnO2 nanobelt ethanol sensor operation enhanced by water pre-adsorption.

SnO2 nanowire and nanobelt sensors are less conductive when exposed to air, compared with as-prepared counterparts. This is because electrons from SnO2 are captured by adsorbed oxygen molecules [15]. The ethanol sensing mechanism of SnO2 can be explained by the release of electrons from oxygen ions when they react with reducing ethanol molecules. The high ethanol sensitivity and reversibility could only be achieved at elevated temperatures or UV light exposure. Although there are no literature reports of single crystal SnO2 ethanol sensing at room temperature, the high ethanol sensitivity and reversibility of SnO2 polycrystalline nanowires, under ambient conditions, have been demonstrated by Wang et al. [16]. This indicates that ethanol gas detection by 1D SnO2, even at room temperature, is possible.

H2O and oxygen molecules, main adsorbates in ambient air, both affect 1D SnO2 conductivity and ethanol sensitivity. Adsorbed oxygen depletes the SnO2 surface conduction channel, degrading sensor performance. The water adsorption effect is also very important. Many investigations of SnO2 film sensors proved that both conductivity and sensitivity depend on relative humidity [17,18]. The high sensitivity of SnO2 nanowires high sensitivity to humidity has been reported by Kuang et al. [19]. Zheng et al. [20] recently reported enhanced oxygen sensitivity of individual ZnO tetra-pod sensors caused by water pre-adsorption and ascribed this phenomenon to the adsorption competition between water and ethanol molecules. Similar adsorption competition between these water and ethanol molecules can influence 1D SnO2 ethanol sensing ability, which needs to be understood.

Individual SnO2 nanobelt sensors were fabricated. The effect of water adsorption on room temperature ethanol sensitivity was studied by observing the change in current flowing through the SnO2 nanobelt, when it was exposed to water and ethanol vapor in a vacuum chamber. It was found that water molecule pre-adsorption greatly enhances ethanol sensitivity in the SnO2 nanobelt. However, the same SnO2 nanobelt exhibited almost no ethanol sensitivity when ethanol was adsorbed prior to water. This...
difference was ascribed to competition between H$_2$O and C$_2$H$_5$OH molecules adsorbing on the nanobelt surface.

2. Materials and methods

Single crystal SnO$_2$ nanobelts were synthesized by thermal evaporation of a Sn and SnO powder mixture from an alumina crucible at 1050–1150 °C for 2 h under 300 Torr Ar pressure with 50 sccm flow rate. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize sample morphology and crystal structure (Fig. 1). The following steps were used to fabricate the single crystal SnO$_2$ nanobelt sensor device. As-prepared SnO$_2$ powders were ultrasonically dispersed in ethanol and spread over thermally oxidized Si wafers. Four parallel probes were then patterned on a single nanobelt using electron beam lithography. Thermal evaporation was used to deposit gold electrodes. The length between the two neighboring probes was about 2 μm, as shown in the inset of Fig. 2a. The nanobelt thickness is about 15–20 nm, and its width is 100 nm.

The nanobelt device was placed in a sealed chamber for testing. Current–voltage ($I$–$V$) characteristics of the device were measured both in air and in vacuum using a semiconductor characterization system (Keithley 4200, Cleveland, Ohio, USA). The real-time current change, under different gas conditions, was recorded at a bias voltage of 1 V applied between the two electrodes. The current response to air of different relative humidity was measured first. To eliminate the interference effects of oxygen and other gases on SnO$_2$ nanobelt ethanol sensitivity, the testing chamber was evacuated to $10^{-4}$ Pa and kept airtight before introducing target gases. Subsequently, water and ethanol liquids were injected into the sealed vacuum chamber by a micro-injector and were immediately gasified in the low chamber pressure. Three water and ethanol introduction patterns were used: (I) vacuum → 20 ppm ethanol → 25 ppm water → vacuum; (II) vacuum → 25 ppm water → 20 ppm ethanol → vacuum; (III) vacuum → 20 ppm ethanol and 25 ppm water mixture → vacuum. The chamber was evacuated at the end of each pattern test. In the second pattern, the current response to the same 20 ppm ethanol concentration, at different pre-filled water concentrations of 25 ppm, 50 ppm and 100 ppm, was observed.

3. Results and discussion

SEM image in Fig. 1 shows the morphology of as-grown nanobelts, whose widths are about 30–200 nm and whose lengths are between several tens to hundreds of microns. All diffraction reflections in the XRD pattern of as-grown nanobelts can be indexed to the SnO$_2$ tetragonal rutile structure ($a = 0.474$ nm and $c = 0.318$ nm), according to the 41-1445 JCPDS card. The position and intensity of the reflections, relative to the background signal, are similar to those of the bulk counterpart (Fig. 1(b)). The absence of impurity reflections indicates the high purity of the SnO$_2$ nanobelts. The TEM image and electron diffraction pattern of a single nanobelt rutile structure, in Fig. 1(c) indicate that individual SnO$_2$ nanobelt growth is along the [2 3 1] direction and its surface plane is either (1 0 2) or (1 0 2).

The device linear $I$–$V$ characteristics in Fig. 2 indicate that the contact between the electrodes and the SnO$_2$ nanobelt is nearly ohmic. The device resistance is larger than that reported in reference [12], and is possibly due to high contact resistance between the gold and the SnO$_2$ nanobelt. Additionally, the surface depleting layer, produced by adsorbed oxygen, greatly increased sensor resistance [21]. After thermal treatment at 200 °C for 30 min in vacuum, some of the adsorbed oxygen is desorbed from the SnO$_2$ surface, reducing both the depletion layer thickness, and the belt’s
resistance, significantly (Fig. 2b). The nanobelt resistance will recover again with ageing in air.

Nanobelts’ resistance in air is lower than in vacuum, which is mainly due to the presence of water vapor in air. Further investigation showed that the SnO₂ electrical resistance decreased with higher water concentration, both in air and in vacuum. In Fig. 3, the current increases linearly with the relative humidity of the surrounding air, similar to the results by Kuang et al. [19]. In the vacuum chamber sensor resistance also decreased with increasing water vapor concentration. These results prove the water sensing ability of the SnO₂ nanobelt. Adsorbed H₂O molecules on the SnO₂ surface can accumulate and serve as a conduction channel. Water molecules act as donor-like surface impurities.

Fig. 4 shows the nanobelt sensing response as to water and ethanol are introduced in different sequences. The current response varies greatly with different water and ethanol introduction orders. In vacuum, the current is very stable at 0.15 nA. It is unexpected that almost no sensing response was observed with 20 ppm of ethanol injected into the sealed vacuum chamber, indicating that no electrons were released with the introduction and adsorption of ethanol molecules on the nanobelt surface. Therefore, C₂H₅OH molecules are most likely physisorbed on the tin oxide surface.

With further introduction of 20 ppm of water, the current increased slowly and reached 0.57 nA in 240 s. The vacuum chamber was then evacuated and current immediately reduced to the original vacuum value, showing fast recovery time.

With the opposite introduction order pattern II, the nanobelt sensor exhibits good sensitivity to water, and the current increases to 3 nA in 330 s, with 25 ppm of water injected into the chamber, which is similar to the results measured at different relative humidity in air. It is interesting that the current immediately increases from 3 nA to 10.2 nA in 125 s with further introduction of 20 ppm ethanol gas. Although the absolute current value is not very high, it increases 8 times compared to that measured in vacuum. The response time to ethanol is much faster than to water. It should be mentioned that the current increased by 3 times in 15 s after since ethanol introduction. The recovery time is quite short as the because current reduces to the original vacuum value almost immediately. Therefore, it can be concluded that SnO₂ nanobelt ethanol sensitivity is greatly enhanced by water molecules pre-adsorption.

In the third pattern, water and ethanol mixed gases were introduced into the sealed vacuum chamber (25 ppm of water and 20 ppm of ethanol). The resulting nanobelt current of 0.63 nA for the water/ethanol mixture is lower than that of pure water vapor, and comparable to the first pattern result. In other words, C₂H₅OH adsorption seems to prevail over water molecules adsorption when both are injected in the chamber simultaneously.

SnO₂ nanobelt ethanol sensor characteristics are very repeatable for each pattern, with or without water vapor. The sensor survived dozens of cycles, with good repeatability, during the three days of testing. Similar ethanol sensing characteristics were also exhibited by other SnO₂ nanobelt sensors fabricated using the same process conditions. For example, the current response of another nanobelt sensor is 0.9 nA for water and 11.8 nA for subsequent ethanol introduction into the chamber, according to pattern II. There are multiple factors reasons causing sensitivity differences between the two nanobelts. These factors include nanobelt size, crystal growth direction and the contact area between the gold electrodes and the tin oxide. Among them, the surface state of the tin oxide is the most important factor.

By comparing SnO₂ nanobelt ethanol sensitivity, with or without prior water exposure, it can be inferred that adsorption competition exists between water and ethanol molecules on the SnO₂ nanobelt surface. In pattern I, ethanol molecules are physisorbed on the surface of the depleted SnO₂ nanobelt, in the absence of water vapor. When physically pre-adsorbed, C₂H₅OH molecules can form an insulating layer on the SnO₂ surface. Although H₂O molecules can be dissolved in the ethanol layer, there are fewer less vacant sites left for H₂O molecule adsorption, which is why current increases so slowly with water addition. In pattern III, adsorption competition between water and ethanol is illustrated by the preference toward C₂H₅OH molecule adsorption by the surface of the tin oxide when they appearance in the chamber is simultaneous.

Only in pattern II, when water is introduced first and pre-adsorbed on the SnO₂ nanobelt surface, is high ethanol sensitivity exhibited. It was found that the current increased linearly with ethanol concentration. The SnO₂ nanobelt current response to the same ethanol concentration, with a varying pre-adsorbed water vapor amount, was also investigated. Fig. 5 shows the SnO₂ nanobelt device current response to 20 ppm of ethanol gas when the chamber is pre-filled with 25 ppm, 50 ppm and 100 ppm of water. The corresponding current values are 0.68 nA, 1.14 nA and 2.12 nA, which are 4.5, 7.6 and 14.1 times higher than the current in vacuum, respectively. A similar current–water concentration dependence on relative humidity is exhibited. The ethanol sensing current rapidly increases to 8.85 nA, 15.9 nA and 27.8 nA, respectively, (59, 106, 185 ratios with current in vacuum) when exposed.
to the same 20 ppm ethanol concentration, indicating that ethanol current increases linearly with water concentration (Fig. 6).

Since water is a weak electrolyte, adsorbed water molecules can dissociate on the surface:

$$\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+. \quad (1)$$

OH$^-$ and H$^+$ serve as conductive species. On the other hand, free electrons can also be released due to surface interactions between the SnO$_2$ and the adsorbed H$_2$O molecules. This reaction was discussed by Heiland and Kohl [18]; and their assumptions are related to the presence of hydroxyl groups. A general explanation is that water interacts with the SnO$_2$ lattice oxygen, which results in increased electrical conductivity. Two direct mechanisms were proposed [18]:

$$\text{H}_2\text{O} + \text{Sn}_{\text{lat}} + \text{O}_{\text{lat}} \rightarrow \text{Sn}_{\text{lat}}\text{-OH} + \text{OH}^- + e^- \quad . \quad (2)$$

$$\text{H}_2\text{O}_{\text{gas}} + 2\text{Sn}_{\text{lat}} + \text{O}_{\text{lat}} \rightarrow 2(\text{Sn}_{\text{lat}}\text{-OH}) + V_0; \quad V_0 \rightarrow V^{**} + 2e^- \quad . \quad (3)$$

Reaction (2) includes SnO$_2$ lattice oxygen and ascribes the donor electron to a hydroxyl group, which can be ionized into OH$^-$ and release an electron. The second reaction takes place between a H$^+$ proton and the SnO$_2$. The second lattice oxygen with additional electrons coming from oxygen vacancy ionization. However, reaction (3) will not happen at room temperature because oxygen vacancies are only formed on the SnO$_2$ crystal surface at temperatures higher than 150°C in vacuum [22]. Thus, the current response to water adsorption is based on reactions (1) and (2). It can be concluded that by increasing the number of adsorbed water molecules, the density of the carriers, such as H$^+$ and electrons, is also increased. Therefore, the current flowing through the SnO$_2$ nanobelt is consequently increased.

It is obvious that no electrons are released by adsorption of pure C$_2$H$_5$OH molecules at room temperature. However, the current response to ethanol gas is greatly enhanced by pre-adsorbed water molecules. At the same ethanol concentration, the current shows an increase, which is nearly proportional to the increase in pre-filled water concentration (Fig. 6). There must be some water-dissociated species that facilitate C$_2$H$_5$OH oxidation, then release more electrons, captured by the lattice oxygen, into the conduction channel. Although it is not clear which kind of species, H$^+$ or OH$^-$, is more important for the chemical reaction between the oxygen ions and the C$_2$H$_5$OH molecules, the presence of such species reduces reaction activation energy. A possible mechanism is ethanol dehydration through classical reaction, as described by Whitmore et al. [23]. Preliminary protonation, induced by water dissociation, considerably accelerates the ethanol dehydration reaction rate. This is a donor-like surface reaction. The effect of water pre-adsorption on enhanced SnO$_2$ nanobelt ethanol sensitivity was demonstrated at room temperature. Adsorption competition between water and ethanol molecules is also captured by different current response characteristics (Fig. 4) to the same amount of water and ethanol mixture if the introduction order of these two gases is changed. SnO$_2$ prefers to adsorb ethanol first when both water and ethanol are introduced simultaneously because, otherwise the current response to water/ethanol mixture in pattern III would be as high as in pattern II, when water was adsorbed prior to ethanol. This result will facilitate the designing of room temperature, fast responding and highly sensitive ethanol sensors able to be used in ambient air and other surrounding gases in the presence of water vapor.

4. Conclusions

In summary, SnO$_2$ nanobelts were successfully synthesized and single nanobelt sensors were fabricated by electron beam lithography and thermal evaporation. Single SnO$_2$ nanobelt sensor is highly depleted by adsorbed oxygen at room temperature. The nanobelt device showed better conductivity in air than in vacuum due to the presence of water. Consequently, a linear current dependence on relative humidity was observed. Different sensing characteristics were found, depending on the water and ethanol introduction order. In the absence of water vapor, no ethanol sensitivity was observed, while high ethanol sensitivity was exhibited in the chamber pre-filled with water vapor. Low ethanol sensitivity was exhibited by the same SnO$_2$ nanobelt when water was introduced into the testing chamber simultaneously with the ethanol, or afterwards. This effect was ascribed to the adsorption competition between the H$_2$O and C$_2$H$_5$OH molecules on the tin oxide surface. Water adsorption byproducts, such as hydroxyl groups or H$^+$, played an important role in ethanol molecule chemisorption. This effect can be utilized for making SnO$_2$ nanobelt ethanol sensor with a fast response time and a high sensitivity in the presence of moist air.

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References


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