The electric field effect on the sensitivity of tin oxide gas sensors on nanostructured substrates at low temperature

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A novel low-temperature SnO\textsubscript{2} gas sensor was prepared and studied on silicon nanostructures formed by femtosecond laser irradiation. By applying a bias voltage on the silicon substrate to alter the charge distribution on the surface of the SnO\textsubscript{2}, carbon monoxide (CO), and ammonia (NH\textsubscript{3}) gas can be distinguished by the same sensor at room temperature. The experimental results are explained with a mechanism that the sensor works at low temperature because of adsorption of gas molecules that trap electrons to the surface of the SnO\textsubscript{2}.

Keywords: gas sensor; carbon monoxide; ammonia; SnO\textsubscript{2}; nanostructure; bias-induced selectivity

I. Introduction

Metal oxide semiconductors like SnO\textsubscript{2}, ZnO, In\textsubscript{2}O\textsubscript{3}, Cu\textsubscript{2}O, and Nb\textsubscript{2}O\textsubscript{5} have been used for the detection of combustible and toxic gases for a few decades [1–10]. SnO\textsubscript{2}, an n-type semiconductor, has attracted significant attention because of its low cost and high sensitivity. It has been used to detect ammonia (NH\textsubscript{3}), hydrogen (H\textsubscript{2}), carbon monoxide (CO), and many other gases [1–10]. Different methods have been invented to improve the sensitivity and reliability of the sensors, such as noble metal doping [7], surface modification [8], and the use of SnO\textsubscript{2} nanowires [11]. Most of these sensors work at relatively high temperatures (300–450°C), which increases the energy consumption of the sensor and limits its applications [12]. In our previous work, we successfully fabricated a novel SnO\textsubscript{2} gas sensor on nanospike-patterned surfaces. This sensor operated at temperature lower than 30°C although the sensing mechanism was not clear [13].

In this article, we report that the sensor works at low temperature because of adsorption of gas molecules that trap electrons at the surface of the SnO\textsubscript{2}. We find that an electric field can be used to control the selectivity of this room temperature gas sensor in order to distinguish between different gases, which will greatly enhance the application of such a device in an integrated sensing system. Understanding the gas sensing mechanism and the
electric effect on the sensitivity of the nanostructured SnO$_2$ sensor at low temperatures will allow us to improve the applications of semiconductor gas sensors with other metal oxides [1–10].

II. Experimental

A. Sensor fabrication

The fabrication process of the SnO$_2$ gas sensor, illustrated in Figure 1, is similar to that in our previous work [13]. A cleaned silicon substrate was immersed in water and irradiated by a femtosecond laser with a frequency-doubled output (400 nm wavelength, 100 fs pulse, and 1 kHz frequency) from an amplified Ti:sapphire laser (Quantronix) (Figure 1a). During this process, silicon nanospikes formed on the surface of the silicon substrate [14]. Then the silicon nanospike substrate was placed in a furnace and oxidized at 1000°C, first in dry oxygen for 15 minutes, then in wet oxygen for 30 minutes, and in dry oxygen for another 15 minutes to form a 400-nm-thick dense SiO$_2$ insulating layer on the silicon (Figure 1b) [13]. This dry/wet/dry oxide procedure accelerates the rate of oxide formation and creates a dense SiO$_2$ layer. This was followed by a 150-nm-thick Sn film deposition by thermal evaporation through a mask to form a long rectangular pattern (length 8 mm and width 1 mm) (Figure 1c). The sample was heated on a hot plate at 500°C in air for about 5 hours to oxidize the Sn to a 200-nm-thick tin oxide layer (Figure 1d). Previous research has shown that tin oxide crystalline formed at about 500°C is in the form of SnO$_2$–δ, a non-stoichiometric tin dioxide, when the temperature is lower than 300°C, tin oxide crystalline will be in the form of SnO [15]. We noticed that the crystallinity did not influence the fact that gas sensing with our nanostructures can work at low temperatures. In this work, we do not discuss the tin oxide crystalline dependence of the gas sensing at low temperature. Finally, source/drain electrodes (2 mm × 2 mm) at both ends of the rectangular SnO$_2$ area and the back gate electrode (6 mm × 6 mm) on the bottom of the silicon substrate were fabricated by sputtering a thin layer of gold with about 45 nm thickness (Figure 1d and e). The electric circuit of the sensor is shown in Figure 1f. Although the resultant SnO$_2$ sensing area is 6 mm × 1 mm, the size of the whole sensor can be shrunk for more than ten times into the micro-scale using the present lithography because the sensing SnO$_2$ area consists of structures in the nanoscale as shown in Figure 2.

![Figure 1](https://via.placeholder.com/258x358.png)

Figure 1. The gas sensor fabrication procedure, using (a) femtosecond laser irradiation, (b) oxidation, (c) tin evaporation, and (d, e) oxidation and electrode fabrication. The electric circuit of the sensor is shown in (f).
B. Sensing setup

The electrical measurements on the SnO\(_2\) gas sensor were conducted with an auto-ranging picoammeter (Keithley 6485) equipped with a datalogger (PASCO Xplorer GLX PS-2002). During the electrical measurement, the sensors were sealed in an airtight chamber, a DC voltage of 1.5 V was applied on the SnO\(_2\) channel, and a bias to ground was applied on the back gate to charge the SnO\(_2\) thin film. We choose standard gases to study the reversibility, although the sensor can also work in ambient condition. Standard carbon monoxide (purity 99%) and ammonia (purity 98%) (Airgas Co.), with concentrations of 18 ppm (parts per million) and 50 ppm, respectively (the balance being nitrogen gas with a purity of 99%, to achieve a total pressure of 1 atm), were used for the gas sensing measurements. The relative humidity was measured with a Vaisala DM70 dewpoint meter. The humidity of the three gases used in the present experiments was about 2% at room temperature. The influence of higher levels of water vapor will be investigated separately.

C. Surface characterization

The surface morphologies of the silicon nanospike substrate and the SnO\(_2\) film coated on it were obtained by a field emission scanning electron microscope (FESEM) (JOEL JSM-7401F). Atomic force microscopy (AFM) and electric force microscopy (EFM) images were acquired with a Park AFM XE-150 system to characterize the topology and the surface electric field distribution on the sensor surfaces. The EFM tip was a PointProbe® Plus-EFM (PPP-EFM) non-contact silicon tip with PtIr5/Cr coating on both sides of the cantilever. It had a resonance frequency of 75 kHz and a force constant of 2.8 N/m. During the measurement, the silicon substrate was attached to the AFM stage and the positive electrode of a battery with voltage of 9.1 V was connected to one of the electrodes of the SnO\(_2\) channel. The negative electrode of the battery was grounded. The bias of the EFM tip was set to zero.

III. Results and discussion

A. Surface morphology

Figure 2a shows an FESEM image of the silicon nanospikes fabricated by femtosecond laser irradiation in water [13]. The average diameter of the nanospikes was about 300 nm, and their height was about 800 nm. The FESEM image of the thin SnO\(_2\) film coated on
the silicon nanospikes (cf. Section II) is shown in Figure 2b. The SnO\textsubscript{2} film had a rough surface with many small protrusions or gibbosities.

B. Sensing at low temperature

While traditional sensors can only work at relatively high temperatures, above 200°C [1–11], this SnO\textsubscript{2} gas sensor based on the nanospike-patterned surfaces can operate at room temperature [13]. The nanostructures have a large surface-area-to-volume ratio, so that gas molecules have more chances to interact with the SnO\textsubscript{2} surface than on a flat substrate. Moreover, when current passes through the SnO\textsubscript{2} sensing layer, more electrons may accumulate on the tips of the nanospikes and the gibbosities to maintain the same electric potential; this results in strong local electrical fields around the sharp sites on the SnO\textsubscript{2} and gives rise to a long-range Coulomb interaction with polar molecules, causing them to be attracted onto the tips of the SnO\textsubscript{2} layer. The large surface area and the long-range Coulomb interaction thus enhance the sensitivity of the SnO\textsubscript{2} thin film sensor.

Figure 3 shows the temperature dependencies of the response of our gas sensor to carbon monoxide and ammonia. The SnO\textsubscript{2} gas sensor was put on a hot plate to achieve different temperatures. The inlet gas was preheated to the same temperature as the sensor surface to eliminate the temperature decrease caused by aerating. In both systems, the signals decrease to zero as the temperature increases from room temperature to about 70°C. When the temperature exceeds 100°C, the sensor works again although the responses to the gases are very different from those at temperatures below 100°C. The sensing mechanism above 100°C is the same as that in previous work by others on high-temperature sensors [1–11], except for that the sensitivity of our sensor is much higher (33% versus 19% obtained with conventional sensors which measure CO gas of 12 ppm [15]) because of the surface area enhancements and the long-range Coulomb interaction [16]. The results in Figure 3 suggest a different sensing mechanism as shown in Figure 4 at room temperature.

The occurrence of physisorption versus chemisorption depends principally on the binding energy of the adsorbate to the surface; however, this is not a specific value of energy to distinguish the two kinds of adsorptions strictly. We only consider that CO (or NH\textsubscript{3}) molecules near the sensor surface become adsorbed because the sensor recovers as soon as CO (or NH\textsubscript{3}) gas is off at temperatures lower than room temperatures. The current change (∆I) is proportional to \( n \), the number of electrons in the substrate trapped to the adsorbed gas molecules. The rate equation of the instantaneous number \( n(t) \) at a time \( t \) after the gas was filled in the chamber is:

\[
\frac{dn(t)}{dt} = Am(t) - Rn(t)
\]

where \( Am(t) \) is the adsorption rate of electrons to the adsorbed gas molecules, with \( m(t) \) being the number of gas molecules. \( R \) is the thermal ionization rate, which is given by the Arrhenius-like equation \( R = Be^{-E_c/kT} \), where \( B \) is a pre-factor, \( E_c \) is the binding energy of the electron, \( k \) is the Boltzmann's constant, and \( T \) is the temperature [17,18].

The rate equation of the instantaneous adsorbed gas molecule number \( m(t) \) is described as:

\[
\frac{dm(t)}{dt} = F[N - m(t)] - rm(t)
\]
where $F$ is adsorption rate of gas molecules to an adsorption site, $N$ is the total number of sites, $r$ is the desorption rate given by the Arrhenius-like equation $r = r_0 e^{-E_m/kT}$, where $r_0$ is a pre-factor and $E_m$ is the thermal activation energy for gas desorption.

At equilibrium, it can be assumed that $\frac{dm(t)}{dt} = \frac{dn(t)}{dt} = 0$. Then we have:

$$\Delta I \propto n = \frac{g}{\left(1 + ce^{-\frac{E_e}{kT}}\right)e^{-\frac{E_m}{kT}}}$$  (3)

where $g = NA/B$ and $c = r_0/F$.

Comparison of this model to experimental data on the temperature dependence of the current change (Figure 4b) does not allow a determination of $E_e$ and $E_m$ separately, but we can conclude that $E_e + E_m$ is about 380 meV. From the fact that the oxygen donor binding energy can become as high as 368 meV [19], we know that $E_e$ is much larger than $E_m$.

Furthermore, the bound electron with the adsorbed molecule results in the sensing signal, and the resistance increases. As soon as the bound electron with the binding energy
$E_e$ is thermal exited, the resistance recovers to the original value, and the molecule also becomes free because of its small binding energy $E_m$, as shown for the recovery time in Figure 4c. Considering that the recovery time is proportional to $e^{E_e/kT}$, we estimate $E_e$ to be about 350 meV. We can estimate that $E_e$ and $E_m$ would be approximately 350 and 30 meV, respectively.

In these cases, the gas molecule adsorption is a physisorption, where the gas molecules adsorb to the surface through van der Waals forces at room temperature. As soon as the gas molecules adsorb to the surface, trapping sites form and bind electrons to decrease electric current for the gas sensing. The large surface area and the long-range Coulomb interaction enhance the gas detection with the physisorption.

The exact potential energy for electrically neutral molecules to the substrate surface can be determined by a first principles quantum mechanical calculation. Such a calculation is complicated, and some simple phenomenological forms for the potential are commonly used. The most important features are a strong repulsion at small distance ($r$) and a weak attraction at a larger distance to the substrate surface. The most common phenomenological form is the Lennard–Jones potential:
The value of $\sigma$ is about 0.3 nm [20], and the binding energy $\varepsilon$ is selected as about 30 meV which is similar to $E_m$ in Figure 4. The solid curve in Figure 5 shows the Lennard–Jones potential with a binding energy of about 30 meV for the physisorption of carbon monoxide or ammonia molecules to the SnO$_2$. The interaction of this physisorption is short-ranged compared to the Coulomb interaction.

A strong surface electric field enhancement by the nanospikes plays a critical role in the sensing mechanism at room temperature [13]. Figure 6a shows an AFM image of the topography of the silicon nanospike surface, and Figure 6b shows the EFM image of the electric force distribution over the same area. The electric field distribution on the sensor surface obtained by EFM shows that the aspect ratio of the electrostatic force is much larger than the aspect ratio of the topography itself, which indicates that the electric field is enhanced on the tips of the nanostructures. The electric field strength $E$ at the end of the tip of the nanospike can be estimated from the electrostatic force between the EFM tip and the nanospike tip, $F$, the bias voltage between EFM tip and sample, $V$, and the effective area of the EFM tip, $S$: $E = \sqrt{\frac{2F}{VS}}$. The enhanced electric field $E_z$ at a location of 40 nm from the tip of the nanospike is about $1.1 \times 10^5$ V/m when the bias voltage is 9.1 V. This result is also compatible with results obtained from previous experimental and theoretical calculations [21–26]. The potential energy of a polar molecule in the electric field is:

$$u_d(r) = -pE(r)\cos\theta$$

(5)

where $p$ is the dipole moment of a molecule (0.1 D for CO and 1.4 D for ammonia [27–30]), and $E(r)$ is the magnitude of the electric field, $E(r) = \frac{A}{(a+r)}$, where $a$ is the average radius of curvature of the nanostructures on the surfaces, estimated to be about 2 nm. $A$ can be determined by $E = 1.1 \times 10^5$ V/m when $r = 40$ nm; $\theta$ is the angle between the dipole moment and the electric field, for simplicity, we choose $\theta = 0^\circ$ to consider the...
strongest attractive interaction. The potential energies of a CO and an ammonia molecule in such a field are shown in Figure 5. Although the magnitude of the potential energies at the substrate surface is much smaller than that of the Lennard–Jones potential, the interaction is long-ranged which attracts the molecules to the substrate surface to be physisorbed for detection. The total potential for the molecules near a charged substrate surface enables gas sensing at room temperature.

C. Carbon monoxide sensing

The response of this SnO$_2$ thin film gas sensor to carbon monoxide gas at room temperature is shown in Figure 7. The sensor can operate at room temperature without bias voltage, and a bias voltage affects the sensitivity inversely. During the measurement, CO with a concentration of 18 ppm was introduced into the chamber until the sensor became saturated. Then the CO gas was turned off, and the chamber was purged with nitrogen until the electrical current of the sensor recovered to the initial level. The sensitivity ($S$) of the sensor is defined as $S = \Delta I/I_0 = (I_0 - I_{gas})/I_0$, where $I_0$ is the current going through the sensor without test gas and $I_{gas}$ is the current with the test gas on. As shown in Figure 7a–c, response curves of the SnO$_2$ thin film gas sensors were recorded under different biases. When the bias voltage was set to zero, the current decreased by 0.24% when the CO gas was introduced, with a response time of about 30 s. Although the current change is only 0.24%, the change is obviously larger than the noise in the background of $I_0$. The current decreased less when a positive bias was applied (Figure 7b) and more with a negative bias (Figure 7c), as summarized in Figure 7d.

As discussed above, the sensing mechanism of this room temperature sensor is different from that of those that work at high temperature. In the higher-temperature (300–400°C) model, oxygen molecules from the atmosphere chemisorb onto the sensor surface as O$^-$ ions [31,32]. The incoming CO molecules react with these O$^-$ to form CO$_2$. In this process, an oxygen atom is desorbed from the surface and an electron is released into the conduction band instantly [31–33]. However, at room temperature, the oxygen molecules are much less likely to form O$^-$ ions, and mainly O$_2$$^-$ ions are physisorbed on the SnO$_2$ surface [31,32]. Under these conditions, the traditional sensor cannot detect CO,
whereas our novel sensor can respond to CO at room temperature even in the absence of a bias voltage (i.e., at a bias of 0 V) [13].

It is well known that the CO molecule is polar with a partial positive charge on the oxygen atom and a partial negative charge on the carbon atom [27,28]. When the sensor is exposed to CO gas, the oxygen atoms in the carbon monoxide molecules orient toward and adsorb on the tips of the nanostructures and can be physisorbed because of the electron density and higher electric field on the tips. The number of free electrons in the semiconductor decreases, causing a decrease in the current. Furthermore, when a negative bias was applied on the silicon substrate, more electrons accumulated on the SnO\(_2\) surface and a stronger electric field was present on the tips of the nanospikes. Then, more CO molecules were adsorbed on the SnO\(_2\) surface, more CO binding could occur, and the current decreased more (cf. Figure 6c). On the other hand, if a positive bias was applied on the substrate (Figure 6b), the carbon of the CO molecule may be more likely to be oriented toward the tips of the nanostructures and be bound to the positive charges located there because of the higher electric field on the tips. The bound positive charges include some free holes that are minority carriers because of the property of an \(n\)-type semiconductor. This process does not influence the majority-carrier number of free electrons, and thus, the current changes less than in the case of the negatively charged sensor.
Figure 7d shows the sensitivity of the SnO$_2$ gas sensor to CO gas under various bias voltages. The sensitivity depends linearly on the bias voltage. Here we assume that the change of the electrical current is proportional to the number of gas molecules adsorbed on the sensing surface, which is also proportional to the charge induced by the bias. The charge ($Q$) induced by the bias can be given as $Q = CV_{bias}$, where $C$ is the capacitance of the SnO$_2$–Si system and $V_{bias}$ is the bias voltage. Then, the change of the electrical current can be expressed as:

$$\Delta I = aCV_{bias} + \Delta I_{nb}$$  \hspace{1cm} (6)$$

where $a$ is a constant related to the nature of gas molecules and to the interaction between the gas molecules and sensing surface, and $\Delta I_{nb}$ is the change of the electrical current without bias. For a certain sensing surface, we might therefore distinguish different gases through the value of $a$. Here, the change due to the applied bias in the initial current without test gases ($I_0$) is much lower than that in the current with test gases ($I_{gas}$). The sensitivity can be given as:

$$S = \Delta I/I_0 = (aC/I_0)V_{bias} + S_0$$  \hspace{1cm} (7)$$

where $S_0$ is the sensitivity of the sensor without bias and $I_0$ can be considered constant under certain conditions of measurement. As shown in Figure 7d, the experimental data can be fitted with a straight line with the slope $-0.0020/V$.

D. Ammonia sensing

The responses of the gas sensor to NH$_3$ with concentration of 50 ppm are shown in Figure 8. The response signal can be clearly observed, and a bias voltage affects the sensitivity in accordance. When no bias was applied, the current decreased by about 2.78% with a response time of about 100 s (Figure 8a). The response at positive and negative bias voltages was the opposite of that for the carbon monoxide. The current decreased by 3.09% when a bias of +40 V was applied (Figure 8b) and decreased by 2.09% when a bias of $-60$ V was applied (Figure 8c). As shown in Figure 8d, the sensitivity is also linearly dependent on the bias voltage in this case, with a slope of $+0.0103/V$ obtained through linear fitting of the experimental data. This result is very different from that for CO. The NH$_3$ molecule has a trigonal pyramidal shape and is polar with partial positive charges on the hydrogen atoms and partial negative charge on the nitrogen atom. The nitrogen atom in ammonia molecules strongly interacts with the SnO$_2$ surface [34]. When the sensor surface is positively charged, more NH$_3$ molecules are attracted with their nitrogen atom oriented toward and adsorbed on the surface. At room temperature, ammonia can react with O$_2^-$ ions chemisorbed on the sensor surface to form NO according to [34]:

$$4\text{NH}_3 + 5\text{O}_2^- \rightarrow 4\text{NO} + 6\text{H}_2\text{O} + 5e^-$$

and in the presence of oxygen, the NO molecules can react further to form oxidizing compounds with the general structure NO$_x$ [34]. The latter species increases the resistance of the sensor and results in a decrease in the current [34]. On the other hand, when the surface is negatively charged, the hydrogen atoms in the ammonia molecules may be oriented toward and adsorbed on the sensor surface. The interaction between the hydrogen
atoms and the SnO\textsubscript{2} surfaces may be weaker than that of the nitrogen [34], which would lead to a smaller change of the resistance of the sensor.

In this experiment, we used as-purchased standard 50 ppm ammonia gas as the gas source. The sensitivity to NH\textsubscript{3} is much larger than to CO, but the recovery time is relatively longer for sensing 50 ppm ammonia gas. We find that for lower NH\textsubscript{3} concentrations, the recovery time greatly decreases, as shown in Figure 3d at room temperature that for a lower concentration 5 ppm. The electric field dependence at low concentration is the same as that for sensing 50 ppm in Figure 8. This sensor can thus be used to detect NH\textsubscript{3} at low concentration below 1 ppm.

Although we have clearly shown the difference between the two gasses quantitatively using the above two simple Equations (6) and (7), we need a model to quantitatively explain the difference among different gasses.

\section*{IV. Conclusions}
The sensitivity of low-temperature SnO\textsubscript{2} gas sensors on nanospike-patterned substrates has been investigated. Adsorption and local electrical fields are very important for the gas sensing mechanism at low temperature. Different sensitivities to applied bias voltages for different types of test gases were observed due to the different chemical nature of the gas.
molecules. The bias-induced selectivity can be used to distinguish various gases, which significantly improves the performance and capability of such low-temperature gas sensors.

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