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Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts

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Gas sensors have been fabricated using the single-crystalline SnO_2 nanobelts. Electrical characterization showed that the contacts were ohmic and the nanobelts were sensitive to environmental polluting species like CO and NO_2, as well as to ethanol for breath analyzers and food control applications. The sensor response, defined as the relative variation in conductance due to the introduction of the gas, is 4160% for 250 ppm of ethanol and -1550% for 0.5 ppm NO_2 at 400 °C. The results demonstrate the potential of fabricating nanosized sensors using the integrity of a single nanobelt with a sensitivity at the level of a few ppb. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1504867]

Conductometric metal–oxide–semiconductor thin films are the most promising devices among solid state chemical sensors, due to their small dimensions, low cost, low power consumption, on-line operation, and high compatibility with microelectronic processing. The application field spans from environmental monitoring, automotive applications, air conditioning in airplanes, spacecrafts and houses, to sensors networks. The progress made on Si technology for micromachining and microfabrication foreshadows the development of low cost, small sized, and low power consumption devices, suitable to be introduced in portable instruments and possibly in biomedical systems.

The fundamental sensing mechanism of metal oxide based gas sensors relies on a change in electrical conductivity due to the interaction process between the surface complexes such as O^-, O_2^-, H^+, and OH^- reactive chemical species and the gas molecules to be detected. Although many different oxides have been investigated for their gas sensing properties, commercially available gas sensors are made mainly of SnO_2 in the form of thick films, porous pellets, or thin films. The effects of the microstructure, namely, ratio of surface area to volume, grain size, and pore size of the metal oxide particles, as well as film thickness of the sensor are well recognized. Lack of long term stability has until today prevented wide application of this type of sensor.[1] The most recent research has been devoted towards nanostructured oxides,[2–6] since reactions at grain boundaries and complete depletion of carriers in the grains can strongly modify the material transport properties. Unfortunately the high temperature required for the surface reactions to take place induces a grain growth by coalescence and prevents the achievement of stable materials.

Nanobelts of semiconducting oxide,[7,8] with a rectangular cross section in a ribbon-like morphology, are very promising for sensors due to the fact that the surface-to-volume ratio is very high, the oxide is single crystalline, the faces exposed to the gaseous environment are always the same and the size is likely to produce a complete depletion of carriers inside the belt. Not only is the deposition technique very simple and cheap, but the size and shape can be easily controlled. In the polycrystalline and thick film devices, only a small fraction of the species adsorbed near the grain boundaries is active in modifying the device electrical transport properties. In the new sensors based on single crystalline nanobelts, almost all of the adsorbed species are active in producing a surface depletion layer. Free carriers should cross the belt's bulk along the axis in a field emission transistor (FET) channel-like way. In addition, since the size of the depletion layer for tin oxide, due to oxygen ionosorption, penetrates 50 nm or more through the bulk, the belts are probably almost depleted of carriers as a pinched-off FET because belt thickness is typically less than 50 nm. The presence of poisoning species should switch the structures from a pinched-off to conductive channel, strongly modifying the electrical properties. A further reduction of belt size could lead to the development of quantum confined structures and nanodevices.

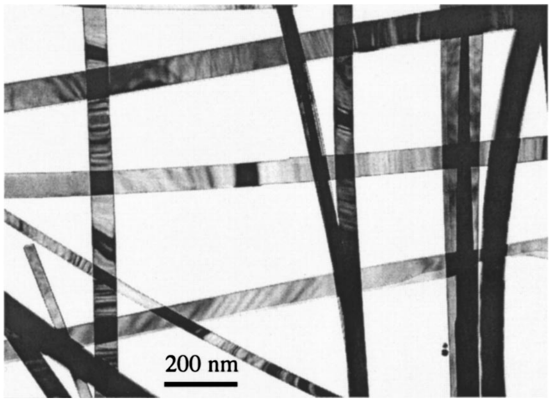

FIG. 1. TEM image of the as-synthesized SnO_2 nanobelts.

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TABLE I. Structural characteristics of SnO_2 nanobelts.

Nanobelts	Crystal structure	Growth direction	Top surface	Side surfaces
SnO_2	Rutile	[101]	$\pm(10\bar{1})$	$\pm(010)$

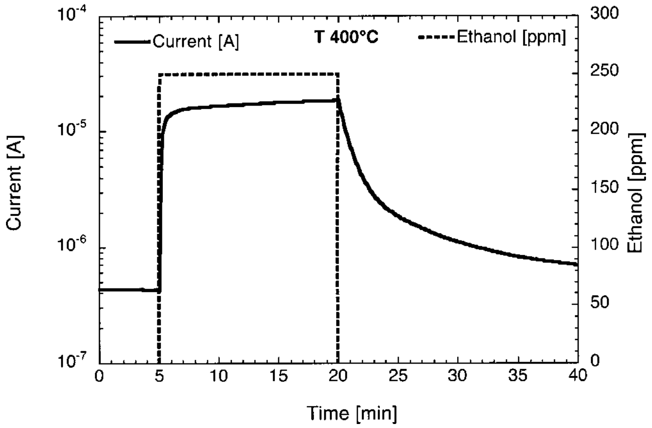

FIG. 3. Response of the SnO_2 nanobelts to ethanol at a working temperature of 400 °C and 30% RH.

In this letter, gas sensors have been fabricated using the SnO_2 nanobelts. The responses of the sensors have been characterized for gaseous polluting species like CO and NO_2 for environmental applications, as well as for ethanol for breath analyzers and food control applications. The extremely high sensitivity demonstrates the potential for developing a new class of stable and very sensitive nanosized sensors using the integrity of individual nanobelts.

Semiconducting oxide nanobelts were synthesized by thermal evaporation of oxide powders under controlled conditions without the presence of a catalyst. The desired oxide powders obtained commercially were placed at the center of an alumina tube that was inserted in a horizontal tube furnace, where the temperature, pressure, and evaporation time were controlled. Ultralong nanobelts have been successfully synthesized for ZnO, SnO_2, In_2O_3, CdO, Ga_2O_3, and PbO_2 by simply evaporating the desired commercial metal oxide powders at high temperatures. A detailed introduction to the synthesis process and the microstructures of the nanobelts can be found elsewhere.[7,8]

Figure 1 gives a transmission electron microscopy (TEM) image of SnO_2 nanobelts. Each nanobelt is a single crystal without the presence of dislocations; its morphology and structure, such as growth direction and surface planes, are well defined (see Table I), and their surfaces are clean and atomic flat. The nanobelts have a rectangular-like cross section with typically an average width of ~200 nm, width-to-thickness ratios of 5–10 and lengths of up to a few millimeters. The contrast observed in the TEM image is due mainly to strain contrast.

For the fabrication of sensors, a platinum interdigitated electrode structure was made using a metal deposition technique with shadow masking on an alumina substrate. A platinum heater was deposited on the back side of the substrate in order to control the working temperature of the sensor. Next, a bunch of nanobelts was placed onto the electrodes for measuring their electric conductance, and $I-V$ measurements confirmed that the contact is ohmic and that good carriers injection is obtained. The flow-through technique is used to determine the gas-sensing properties of the thin films. A constant flux of synthetic air equal to 0.3 l/min, mixed with the desired amount of gaseous species, flows through a stabilized sealed chamber at 20 °C, atmospheric pressure, and controlled humidity. Electrical characterization was carried out by a volt-amperometric technique at constant bias of 1 V, and a picoammeter measured the change of electrical current.

Figure 2 reports the isothermal response of the current flowing through the tin oxide nanobelts as two square concentration pulses of CO (250 and 500 ppm, respectively) are fed into the test chamber, at a working temperature of 400 °C and 30% RH (relative humidity at 20 °C). The electric current increases for about 60% and 100% with the introduction of 250 and 500 ppm CO, respectively. The sensor response, defined as the relative variation in conductance due to the introduction of gas, is about $\Delta G/G=0.9$.

Figure 3 is the isothermal response of the sensor to 250 ppm of ethanol at 400 °C and 30% RH. The response $\Delta G/G=41.6=4160\%$ is extremely high. Figure 4 shows the isothermal response of the current flowing through the nanobelts as a square concentration pulse of 0.5 ppm nitrogen dioxide is fed into the test chamber, at a working temperature of 400 °C and 30% RH. The sensor response is $\Delta G/G=-15.5=-1550\%$, which is extremely high and sensitive.

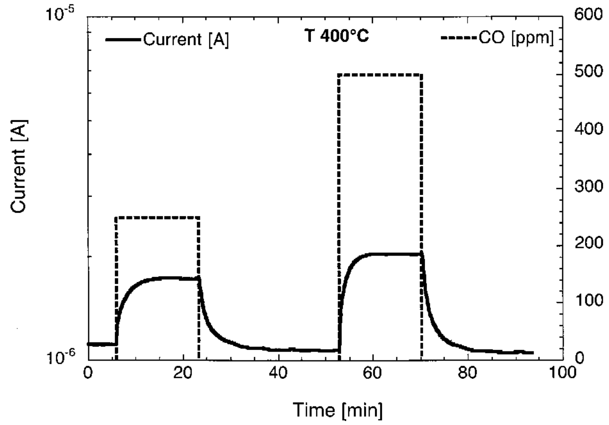

FIG. 2. Response of the SnO_2 nanobelts to CO at a working temperature of 400 °C and 30% RH.

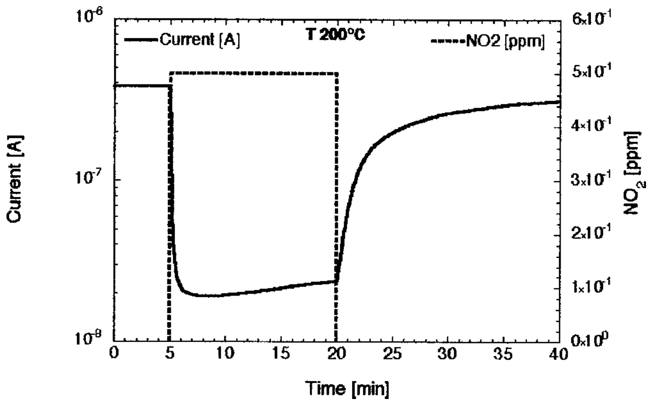

FIG. 4. Response of the SnO_2 nanobelts to NO_2 at a working temperature of 200 °C and 30% RH.

This means that the sensitivity of the sensor is at the level of a few ppb.

In general, the selectivity of the oxide is a concern. This may be improved by fabricating sensors using several different types of nanobelts, or by functionalizing the surfaces of the nanobelts. It is, however, very important to note that CO and ethanol increase the conductivity, while NO_2 decreases the conductivity of the SnO_2 nanobelts.

In conclusion, based on the SnO_2 nanobelts synthesized by thermal evaporation of oxide powders under controlled conditions, we have fabricated gas sensors. Electrical characterization showed that the contacts were ohmic and the nanobelts were sensitive to gaseous polluting species like CO and NO_2 for environmental applications, as well as to ethanol for breath analyzers and food control applications. The results demonstrate the development of a new class of stable and very sensitive nanostructured materials for gas sensing. It shows the experimental feasibility of fabricating nanosized sensors using the integrity of individual nanobelts.

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