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Porous tungsten oxide films were deposited onto a sensor substrate with a Si bulk-micromachined hotplate, by drop-coating isopropyl alcohol solution of highly crystalline tungsten oxide ($WO_{2.72}$) nanorods with average 75 nm length and 4 nm diameter. The temperature-dependent gas sensing characteristics of the films have been investigated over the mild temperature range from 20 to 250 °C. While the sensing responses for ammonia vapor showed increase in electrical conductivity at temperatures above 150 °C as expected for *n*-type metal oxide sensors, they exhibited the opposite behavior of unusual conductivity decrease below 100 °C. Superb sensing ability of the sensors at room temperature in conjunction with their anomalous conductivity behavior might be attributed to unique nanostructural features of very thin, nonstoichiometric $WO_{2.72}$. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1929872]

Miniaturized solid-state chemical sensors have played an important role in chemical process controlling, pollutant monitoring, personal safety, medical diagnosis, and sensor networks. In particular, metal-oxide-semiconductor (MOS) sensors are very promising due to their high sensitivity, small dimensions, low cost, and good compatibility with the fabrication process for microelectronic devices. They operate on the basis of the modification of electrical conductivity of metal oxide layers, resulting from the interactions between ionosorbed moieties such as O_2^-, O^-, and O^{2-} species and gas molecules to be detected. In conventional MOS sensors consisting of polycrystalline metal oxide particles typically with the average size of 10 nm–1 μm, only the species adsorbed near grain boundaries are operative in modifying the electrical transport properties and therefore the gas-sensing ability has been greatly hampered by low surface-to-volume ratio.

One-dimensional (1D) nanostructures with high surface-to-volume ratio and small grain size have attracted much current attention as candidate materials for solid-state gas sensors. Recently, nanosensors fabricated by using individual carbon nanotube,[1] SnO_2 nanoribbon,[2] or nanowire,[3] and In_2O_3 nanowire[4] exhibited properties such as high sensitivity, fast response time, and room temperature operation, which are unattainable by the conventional materials. The major drawback, however, remains due to difficulties in mass production of sensors based on individual 1D nanostructures. Alternative promising approach is to prepare porous structures from highly crystalline and phase-pure 1D nanomaterials. These films could be easily fabricated by wet processes and their sensing characteristics were found to be superior to those of conventional MOS.[5] In addition, the compatibility of wet processes with microelectronic fabrication offers particular opportunities for development of inexpensive sensor systems in the cost-conscious gas sensor market.

Nanosized tungsten oxide particles have been found useful in fabricating gas sensors for the detection of nitrogen oxides,[6] ammonia,[7] and hydrogen sulfide.[8] Current research, however, has focused on the use of polycrystalline tungsten oxide systems for these applications, and thus important sensor requirements such as high sensitivity and reproducibility, which can be obtained only by using size-controlled pure nanomaterials, have not been accomplished. We have recently reported a single step, large scale preparation of single crystalline, size-controlled tungsten oxide nanorods,[9] thus providing a singular research opportunity for tungsten oxide-based gas sensor development. In this letter, we report fabrication of a MOS gas sensor, which entails drop coating of $WO_{2.72}$ nanorod solution on the Si bulk-micromachined membrane equipped with a hotplate for temperature regulation, as well as its unusual gas sensing behavior dependent on operation temperatures.

Sensor substrates were fabricated on Si wafers by using microelectromechanical system (MEMS) and silicon technology, as previously reported in detail.[10] They have a square membrane (2×2 mm^2) embedded with interdigitated detection electrodes and a Pt microheater, which enables temperature regulation of a sensing layer under minimized power consumption. Figures 1(a) and 1(b) show a cross-sectional schematic diagram and a plane-view optical-microscope image of the sensor device, respectively. The well structure with the membrane was fabricated by the anisotropic wet

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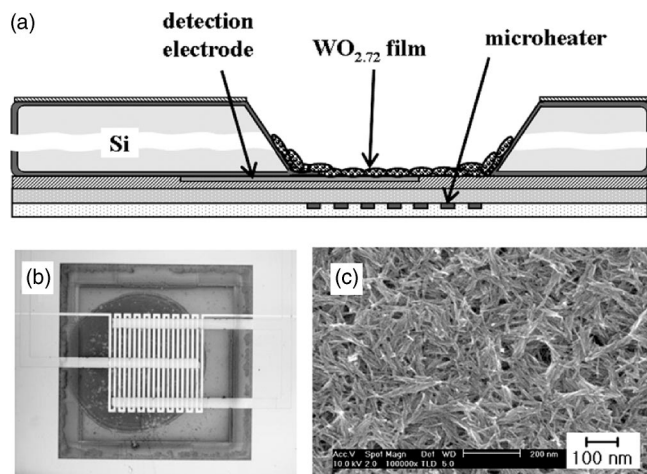
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FIG. 1. (a) Cross-sectional schematic diagram for well structure of a sensor substrate with a membrane-based hotplate, (b) plane-view optical-microscope image of a fabricated sensor equipped with interdigitated detection electrodes, a microheater, and a sensing film, and (c) surface SEM image of the sensing layer deposited by drop coating of $WO_{2.72}$ nanorod-based solution.
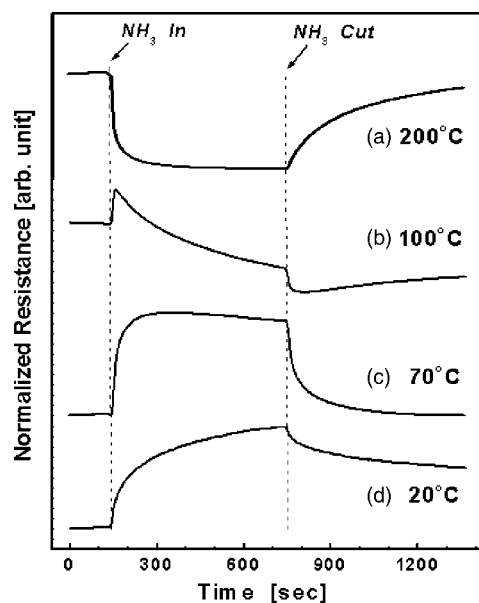

FIG. 2. Variation of the magnitude of normalized resistance as a function of measurement time at the operation temperature of (a) 200, (b) 100, (c) 70, and (d) 20 °C when tungsten oxide nanorod sensors are exposed to 100 ppm NH_3.

etching of bulk Si using 5 wt. % tetra-methyl ammonium hydroxide (TMAH) solution. The interdigitated detection electrodes have 100 μm width and 300 μm spacing. The heater line (25 μm width and spacing) simultaneously acts as a temperature-measuring resistor. The sensing layer displayed as a circle-shape blot at center of Fig. 1(b) was formed by using the tungsten oxide nanorods with 4 nm diameter and aspect ratio of ~20, which were synthesized according to our colloid-based synthetic approach.[9] The isopropyl alcohol solution of tungsten oxide nanorods prepared by ultrasonic treatment was dispensed onto the membrane, and then the membrane was dried at 100 °C under vacuum for 10 h. The well structure allows dropped solution to be placed reproducibly in a specific, well-constrained area.

Figure 1(c) shows a scanning electron microscope (SEM, Philips XL-30) image of a tungsten oxide nanorods film. The film was fabricated under the same experimental conditions on a silicon substrate instead of on the Si-based membrane due to the difficulties in sample handing and availability. The resulting porous film consists of randomly arranged linear aggregates which are formed by parallel alignment of individual $WO_{2.72}$ nanorods. The x-ray diffraction (XRD, Rigaku D/MAX-RC) patterns recorded for this film demonstrated the (010) peak of monoclinic $WO_{2.72}(W_{18}O_{49})$, assigned to the growth direction of the rods,[9] in addition to broad background peaks resulting from the small nanorod size of 75 nm length and 4 nm width. Furthermore, the Raman shift bands observed at 264, 325, 709, and 805 cm^{-1} give further evidence to the monoclinic tungsten oxide structure.[11] The constituents of the films were also analyzed by XPS (VG Scientific, ESCALAB 200R) and found to be composed predominantly of tungsten and oxygen atoms together with only small amount of carbon impurities, which could be easily introduced from carbon dioxide at atmosphere or from solvents and reactants at the synthesis step. Consequently, the tungsten oxide nanorod film used as a sensing element can be considered simply as the condensed collectivity of randomly arranged bundles of monoclinic $WO_{2.72}$ nanorods with high porosity and little carbon impurities.

Gas-sensing measurements were carried out by placing a sensor sample in a small chamber with electrical feedthrough, and by blowing diluted analyte vapor over it with the flow rate of 500 ml/min while monitoring the resistances of the sensing layer and the heater. Figure 2 shows the variations of normalized resistances at four different operation temperatures for air-diluted 100 ppm NH_3 exposure. The measurements were performed sequentially with decreasing the temperature from 250 to 20 °C.

Upon exposure to ammonia gas, decrease in resistance was observed at the operation temperature of 150–250 °C [see Fig. 2(a)]. This is understandable because tungsten oxide sensors are known to behave as an *n*-type semiconductor.[6–8] Current in *n*-type MOS sensors is carried by conduction band electrons, and adsorbates formed by atmospheric oxygen at a grain boundary capture the electron carriers. Upon exposure to reducing chemicals such as ammonia, the arrested electrons are released by the reactions between the reducing gas and the negatively charged oxygen adsorbates, leading to the decrease in resistance. Completely opposite behavior, however, was observed for gas sensing at below 70 °C; the resistance of the sensor film increases upon exposure to ammonia gas as displayed in Figs. 2(c) and 2(d). The sensor response at 100 °C shows a complex pattern [Fig. 2(b)]; rapid increase in resistance for NH_3 injection, slow resistance decrease for duration of NH_3 pulsing, and the rapid decrease followed by slow increase for recovery period. This variation can be understood by summing up the positive (abnormal) and the negative (ordinary) responses observed at low and high operation temperatures, respectively. This kind of temperature-dependent response reversal was also observed for the reducing ethanol analyte.

Further experiments were performed under different atmosphere conditions for various analytes at room temperature in order to clarify the gas sensing characteristics of our $WO_{2.72}$ nanorod sensor. Figures 3(a) and 3(b) show the sensor responses for 2% N_2 (or air), 1000 ppm ethanol, 10 ppm NH_3, and 3 ppm NO_2 exposures in dry air and nitrogen at-
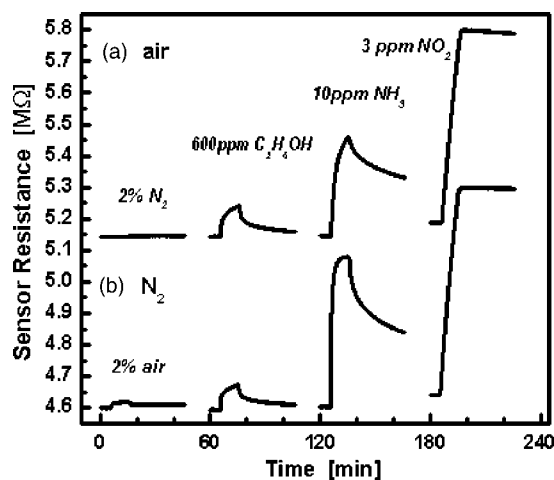
FIG. 3. Sensor responses for 2% N$_2$ (or air), 1000 ppm ethanol, 10 ppm NH$_3$, and 3 ppm NO$_2$ exposures in (a) dry air and (b) nitrogen atmosphere at room temperature.

mosphere, respectively. All of them display the positive response of increase in resistance except for the case of N$_2$ injection with no discernable change, irrespective of reducing and oxidizing analyte gases. Their response magnitudes ascend in the order of air, C$_2$H$_5$OH, NH$_3$, and NO$_2$ exposures, which seems to be correlated with the interaction strength between the analyte vapors and the sensing layer. Since the desorption rate of adsorbed analytes greatly depends on the bound interaction energy, the recovery time becomes longer in the case of having the stronger interaction strength, namely, the larger response. The recovery process was found to be accelerated by heating the sensing materials at around 100 °C for short duration (<60 s) or by illuminating 365-nm-UV light for about 10 s. These phenomena are probably due to the activated desorption process of adsorbent species by imparted thermal or photon energy, as previously reported in other 1D nanostructural MOS systems.[2,12] In addition, other volatile organic compounds such as toluene, *n*-heptane, and acetone were also possible to detect at low concentration less than 5 ppm at room temperature.

For porous WO$_{2.72}$-based sensors, the highly sensitive increase in resistance under ambient conditions must be mainly caused by the competition adsorption between ambient molecular oxygen and analyte vapors on the surface of the active layer. The molecular oxygen had been observed predominantly as initial adsorbates instead of the ionosorbed moieties at below 150 °C.[13] The nonstoichiometric WO$_{2.72}$ films should have more favorable absorption sites due to its oxygen-deficient defect structure than the stoichiometric WO$_3$ with several active sites.[14] We believe that the high sensitivity is attributed to the very small grain size and high surface-to-volume ratios associated with the WO$_{2.72}$ nanorod structures. These nanostructural features allow the sensors to be operated in the most sensitive, grain-controlled mode having the completely depleted space charge region.[15] However, the abnormal resistance increase upon exposure to reducing analytes cannot be explained with the conventional space

charge model. One of the conceivable mechanisms is the adverse effect of adsorbed analytes on the mobility of free charge carriers. The number of collision experienced by the carriers in the bulk of the grain becomes comparable with the number of surface collisions because of the comparable dimension between the mean free path of the carriers and the very thin nanorod thickness. The adsorbates may function as active scattering centers, thus suppressing the electrical conduction of free carriers, i.e., resulting in the resistance increase for both oxidizing and reducing analyte exposures.

In conclusion, we have fabricated tungsten oxide gas sensors by using highly crystalline, tiny WO$_{2.72}$ nanorods. They show highly sensitive sensing ability for various reducing and oxidizing analytes even at room temperature. When reducing gases exposure, the temperature-dependent response was reversed from decrease in the sensor resistance at higher temperature to resistance increase at lower temperature. Such unusual behavior, unprecedented for *n*-type MOS, might be due to the unique structural features of nonstoichiometric WO$_{2.72}$ nanorod-based films with a high surface-to-volume ratio and active adsorption sites. The facile vapor detection of WO$_{2.72}$ nanorod sensor at ambient temperatures might be successfully employed for the miniaturized sensing system, fulfilling the requirement of low power consumption.

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