Room-Temperature Chemiresistive Effect of TiO$_2$ – B Nanowires to Nitroaromatic and Nitroamine Explosives

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Abstract—Semiconducting TiO$_2$ – B nanowires were synthesized and their chemical sensor performance was studied. It was found that the TiO$_2$ – B nanowires exhibited a large and reversible change in electrical resistivity when exposed to trace vapor of nitroaromatic and nitroamine explosives. The sensor showed high sensitivity and fast response at room temperature. The chemiresistive effect was attributed to the adsorption of high electronegativity explosives on the TiO$_2$ – B nanowires and a consequent depletion of charge carriers in the nanowires by surface states created by the explosive molecules. The role of the TiO$_2$ – B nanowires is to impart both an extremely large surface area for the adsorption of gas molecules and a surface enriched in hydroxyl groups which connect to nitro groups of the explosive molecules. Chemiresistive sensors made of TiO$_2$ – B semiconducting nanowires promised to achieve micro-sized devices with several orders of magnitude reduction in dimensions, weight, and power consumption over current explosive detectors.

Index Terms—Charge transfer, chemiresistive sensor, surface depletion layer, TiO$_2$ – B nanowires, trace explosives detector.

I. INTRODUCTION

V APOR detection is a common approach to detect hidden explosive devices to protect society from terrorist attacks. Most high explosives are nitroaromatic and nitroamine compounds. The vapors of such compounds are known to be highly difficult to detect due to their extremely low vapor pressure. As a result, detecting trace explosives usually requires complicated technologies involving ionization and fluorescent sensing materials, making detection systems bulky and having high-power consumption, limiting their applications. There are fundamental limitations to significantly reducing the size and power consumption of existing technologies. It is highly desirable that explosive detectors be made with microelectronic technology and be monolithically integratable with silicon microelectronics circuits. Nanotechnology holds great promise to meet this need.

In this paper, TiO$_2$ – B nanowires were studied to work as a chemiresistive sensor material for a detection of the nitroaromatic and nitroamine explosives. It was found that, in a chip-size device with greatly reduced size, weight, and power consumption, both the sensitivity and response speed of the TiO$_2$ – B nanowire sensor had surpassed those of current technologies [1]–[3]. TiO$_2$ – B is one of the crystal polymorphs of TiO$_2$ [4]. Single crystalline TiO$_2$ – B nanowires of well controlled length and diameter can be chemically synthesized in relatively large quantities [5]–[11]. The achievement of TiO$_2$ – B nanowires in detecting explosives is related to two common characteristics of the nitroaromatic and nitroamine explosive compounds: 1) high electronegativity due to strong oxidizing chemical groups and 2) strong tendency to adsorb on the surfaces of objects exposed to their vapor. Therefore, to effectively detect these explosive compounds, it is desirable that the sensing material has a high surface-to-volume ratio as well as a large surface area for molecule adsorption and, moreover, must be able to facilitate a strong surface charge transfer interaction with the molecules. It was demonstrated that semiconducting TiO$_2$ – B nanowires might meet these requirements very well and presented both a strong and fast response when exposed to the vapors of explosives, by means of a change in the electric conductance. In addition, the inorganic nature of the material offers good stability, important for practical applications.

II. MATERIAL SYNTHESIS AND DEVICE FABRICATION

A. Material Synthesis

The TiO$_2$ – B nanowires were synthesized with a hydrothermal method [6]–[10]. Typically, a suspension containing 0.5 g of commercial anatase TiO$_2$ powder (J. T. Baker Chemical Company) dispersed in 20 ml of 10 M NaOH aqueous solution was prepared as a precursor. After vigorous stirring for 5 ~ 10 min, the suspension was transferred to a Teflon vessel and placed in a hermetically sealed autoclave and heated at 180 °C for 32 h. The precipitate produced was washed with 0.1 M HCl several times and then with DI-water until the pH value reached 7. This treatment removes Na$^+$ ions remaining in the titrate nanoproducts and results in the formation of H$_2$TiO$_3$ nanowires. A following post-treatment at 450 °C for...
Fig. 1. Schematic sketch of the chemiresistive effect of TiO$_2$–B nanowires to nitroaromatic and nitroamine explosives. Inset is a SEM image of the TiO$_2$–B nanowires film. The film is fabricated on glass substrate and its resistance is modulated as the vapor (TNT) switches between “on” and “off.”

Fig. 2. SEM image of the interconnected 3-D mesh structure of a TiO$_2$–B thin film.

1 h was carried out to promote the phase transformation from H$_2$TiO$_3$ to TiO$_2$–B [6]. The length of the nanowires could be controlled by an ultrasonic treatment of the suspension of TiO$_2$ nanoparticles, as described in literature [8]. The diameter of the nanowires was determined by the temperature during hydrothermal growth.

B. Device Fabrication

As-synthesized nanowires were dispersed in ethanol to form a suspension. This suspension was then drop-cast on glass substrates and heated at 70 °C to attain a thin film of nanowires about 10 μm in film thickness. To fabricate a sensor, as shown in Fig. 1, patterned titanium electrodes were deposited through a shadow mask over the nanowire film by sputtering. The titanium electrodes have a circular shape and are 4 mm in diameter. The spacing between contacts is 1 cm for the convenience of shadow mask patterning and probing during testing. The nominal thickness of the titanium electrodes is 200 nm.

C. Test of Sensor Performance

Vapors of equilibrium concentration at room temperature were generated using glass beads coated with various explosives (Inert Products, LLC.) and a vapor generator based on [12], and confirmed by an HP 5797 gas chromatography-mass spectrometry (GC-MS). Vapor of lower concentration is obtained by diluting the saturated explosive vapor with air at the required ratio. The resistance change and response time of the sample is determined by measuring its resistance between two metal contacts with an electrometer (Keithley 617) when the gas applied to the thin film sample is cycled between air with vapor and pure air. The electrometer applies a constant current of 1 nA through the sample during resistance measurement, and the voltage across the sample is typically below 1 V.

III. RESULTS AND DISCUSSION

Single crystalline TiO$_2$–B nanowires synthesized through the high-yield hydrothermal method have a consistent diameter. A scanning electron microscopy (SEM) observation, as shown in Fig. 2, revealed that the film was made of a three dimensional mesh of randomly orientated and interconnected nanowires. These nanowires were several micrometers in length and 50–100 nm in diameter, depending on the condition of the nanowire synthesis. The large amount of free space between wires makes the thin film highly permeable by vapors of analytes for rapid response. Shown in Fig. 3 are energy dispersive
Fig. 4. Typical resistance change of a TiO$_2$—B nanowire thin film in response to vapors. (a) 1 ppb of 2, 4, 6-trinitrotoluene (TNT). (b) 5 ppt of 1, 3, 5-Trinitrohydro-1, 3, 5-triazine (RDX) at ambient conditions.

The sensing performance of nanowire samples were tested in ambient air, except for tests of temperature effects. During the test, the resistance of the sample was recorded while air flow to the sample was switched between pure air and air that contained explosive vapor at intervals of several seconds to a few tens of seconds. The chemiresistive response is defined as $S = (R_v - R_0)/R_0$, where $R_v$ is the resistance when the sample is exposed to the vapor, and $R_0$ is the resistance of the fresh sample before it is exposed to any explosive vapor [13]. The resistance of the nanowires increases to $R_v$ upon exposure to explosive vapor. After the sample is returned to fresh air, its resistance decreases and reaches a stabilized value $R_s$, which is usually 0% to 100% higher than $R_0$ and is likely due to incomplete desorption of explosive molecules from the surface of nanowires. Subsequent switching cycles between vapor of the same concentration and pure air make the resistance vary between $R_v$ and $R_s$, as shown in Figs. 4 and 5. The recovery time of the resistance after the explosive vapor is replaced by pure air is almost the same as the response time to the vapor. The incomplete desorption mentioned above can be eliminated by heating the sample at 80°C to 100°C for several minutes, and the resistance of the sample returns to $R_0$. Although the base resistance has a drift from 0.6 GΩ to 1.5 GΩ, the resistance change between $R_v$ and $R_s$ is found to be highly consistent over a long-term test of 15000 switching cycles (Fig. 5). It demonstrated the exceptional stability of sensing performance. The sample was at ambient temperature throughout the test.

Table I lists the percentage resistance change and response times of the TiO$_2$—B nanowire thin film for vapor of representative explosive compounds at equilibrium concentrations, where the values of equilibrium vapor concentration are refer-
Nanowires have been used for determining the lengths of the nanowires. Test results showed that nanowire diameters were 50 nm, as shown in Fig. 8(a) and (b), compared. The nanowire length is controlled by an ultrasonic meter but different lengths were fabricated and their test results were analyzed by HP 5797 GC-MS spectrum and compared with the results in literature [15] (Fig. 7). Note that molecules of less mass produce faster response, because the response time is limited by the diffusion of the vapor molecules through the nanowire thin film and smaller molecules permeate the 3-D matrix of nanowires faster.

In order to determine whether the response is due to charge transport within individual wires or across junctions between connecting wires, test samples of nanowires of the same diameter but different lengths were fabricated and their test results compared. The nanowire length is controlled by an ultrasonic treatment of TiO2 nanoparticles prior to the hydrothermal synthesis of the nanowires [8]. As shown in Fig. 8(a) and (b), the nanowire diameters were 50 nm ± 10 nm. The lengths of the longer nanowires were 2.4 ± 0.5 μm, and the lengths of the shorter nanowires were 1.8 ± 0.3 μm. Test results showed that the length of the wires has no significant effect on the chemiresistive response. However, shorter wires respond to the vapor at a slower rate. The slower response can be attributed to the denser packing of shorter nanowires and the consequent slower permeation of the thin film by vapor. Since the test samples have the same separation between the electrodes, the average path length for an electron to travel from one electrode to the other electrode is largely independent of the length of nanowires. However, the average number of junctions between connecting nanowires in the path of the electron is strongly dependent on the length of individual wires. In the film made of shorter wires, electrons need to pass through a greater number of junctions. The fact that the response is not affected by the length of nanowires indicates that junction between nanowires does not play a significant role in the sensing process. In addition, different metal electrodes including gold, aluminum copper, and titanium have been used for the electrodes. Different types of metals did not change sensitivity and response time, indicating that the interface between the metal electrodes and nanowires did not play a significant role in the chemiresistive response. Test samples with titanium electrodes exhibited a more linear current-voltage (I-V) relationship, characteristic of a good ohmic contact between the metal electrode and nanowires. Based on these observations, it can be concluded that the electrical response is dominated by the charge transport within individual nanowires.

Previously, nanowires of semiconducting metal oxides, such as ZnO [16]–[18] and SnO2 [19], [20], have been used for sensors to detect gases such as oxygen, ethanol, and NO2. However, these gas sensors operate at elevated temperatures of 200–500 °C, and their sensitivity is only at parts-per-million level with a slow response on the order of a minute [16], [19], [21]. Their sensing mechanism at elevated operating temperatures was attributed to the chemical reduction-oxidation reactions taking place on the nanowire surface [22]. Since the detection of explosives based on TiO2 – B nanowires was realized at room temperature, the interaction between explosive molecules and TiO2 – B nanowires should be quite different from previous metal oxide gas sensors. Explosive molecules are unlikely to be capable of producing significant and fast chemical reduction-oxidation reactions at room temperature to produce sensitivity below ppt level (Fig. 4) and a fast response on the order of a second. Cyclical current-voltage measurements showed a linear relationship between the current and voltage no matter whether the test sample is exposed to explosive vapor or pure air. The current-voltage scans do not show any cyclical voltametric peaks indicative of red-ox processes. The synthetic TiO2 – B nanowires have relatively higher charger carrier transfer ability than anatase TiO2 [23], less compact structure and higher level of oxygen vacancies due to Ti4+ ions. The Ti4+ ions can be coordinated by hydroxyl groups and form hydroxyl terminated surfaces [24]. The surface hydroxyl groups can trap electrons and facilitate adsorption of explosive compounds via their nitro groups. This indicates that the hydroxyl groups on the TiO2 – B nanowires surface may play an important role in determining the explosive gas sensing properties at room temperature and further study is needed. Previous studies have shown that titanium oxide is an n-type semiconductor due to oxygen vacancies [25], [26]. It is also known that nitroaromatic compounds and most high explosive compounds are highly electronegative, meaning that...
they tend to attract electrons from other molecules through charge transfer interactions from nitro groups in explosives to hydroxyl groups on TiO$_2$—B nanowires surface. When explosive molecules adsorb on the surface of n-type semiconductor nanowires, the explosive molecules can trap charge carriers via surface hydroxyl groups and create a carrier depletion region near the TiO$_2$—B nanowires surface. This could explain the increase of the resistance when the nanowires are exposed to explosive vapors.

The surface depletion being the origin of the chemiresistive response is confirmed by the effect of wire diameter on the response. Samples made of films with two different wire diameters were prepared [27] and tested. The lengths of the nanowires were 1.8 ± 0.3 μm for both diameters employed [see Fig. 8(a) and (c)]. The same film thickness and electrode spacing were used for all test samples. Wires of 50 nm ± 10 nm in diameter produced a response of 30%, higher than the 22% response observed for wires of 100 nm ± 20 nm in diameter. This observation supports the surface depletion hypothesis because thinner wires are more susceptible to surface depletion [28]. The response time is found to be largely independent of the diameter of nanowires. Because the band-gap of TiO$_2$ is much greater than the thermal energy, the chemiresistive response of TiO$_2$—B nanowires to explosive trace vapors is found...
to be reliable and insensitive to temperature. There is only a few percent decrease in (Rv-Rs), and a slightly faster response at 75 °C over 25 °C. Such stability is the key to reliable sensors for practical applications. The nanowires are also found to have good specificity (Fig. 9) and be not sensitive to chemicals that are unrelated to explosives that often cause false positives to other explosive detectors such as inert chemicals that have high nitrogen content (for example, urea).

IV. CONCLUSIONS

In summary, a large and fast increase of the electrical resistivity of TiO$_2$-B nanowires in response to sub-trace vapors of nitroaromatic and nitroamine explosive compounds at room temperature has been observed. Experimental results indicate that the response originates from a depletion of electron carriers by the surface states produced by adsorbed molecules of electrogeneative explosive compounds on TiO$_2$-B nanowires surface.

REFERENCES

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