Experimental Investigations of Acetone Sensors Based on Tin Dioxide

V. M. Aroutiounian

Yerevan State University, Armenia

ABSTRACT

Results of investigations of metal oxide chemical sensors for detection of acetone made of tin dioxide were discussed in this review paper. There are several possibilities and technologies to manufacture of such sensors. Pure (without impurities) SnO$_2$ and other metal oxide have low sensitivity to gases at its rather high pre-heating (operation) temperature. Doping of tin dioxide with some metals or carbon nanotubes is one way of improving the sensitivity of such metal oxide sensors. Another way is the preparation of nano-sensors.

Keywords: Tin dioxide; Acetone; Metal oxide; Gas sensor; Sensitivity; Doping, Carbon nanotube

INTRODUCTION

Acetone is the important volatile organic compound (VOC), that have high vapor pressure in ambient conditions. Acetone is present in the organism of a people and exhaled by him breath. Acetone can affect human body and can damage the nervous system by acute poisoning [1,2]. In low value of gas concentration, the damage of acetone is not so much high, but at higher concentration it can lead to coma or even death. Inhalation of acetone can cause headaches, allergies, fatigue, and even narcosis, and can be harmful to the nervous system. The use of exhaled acetone gas from humans to diagnose (identification) of diabetes and monitoring health conditions as well as treatment of diabetic patients are very important. Such type of the identification of diabetes has great promise as it is non-invasive. Acetone can be used for a fast, risk-free and inexpensive diagnosis of diabetes. The concentration of acetone in healthy individuals’ breath varies from 0.3 to 0.9 ppm and in the exhaled air of diabetic patients exceeds 1.8 ppm. Note that a resistive type sensor using tin dioxide SnO$_2$ is considered as an exhalation gas sensor because of its excellent reactivity with VOCs, non-difficult fabrication processes, and the possibility of its miniaturization.

Note that possibilities to the use of semiconducting metal oxide sensors for detection of different gases are in the focus of attention of many researchers [3-5]. Note that a sensitivity, that is, a change of measured signal (voltage, current, etc.) per the analyte unit; selectively to a single analyte; the ability of a sensor to provide reproducible results in time (stability), response and recovery times, operation (working) temperature (pre-heating temperature of a substrate) are main parameters of all types of chemical sensors. The widely used gas-sensing metal oxide materials, such as SnO$_2$, ZnO, TiO$_2$, In$_2$O$_3$, Ga$_2$O$_3$ and Fe$_2$O$_3$, are very promising. The pure SnO$_2$ and other metal oxide thin film without any catalyst exhibits a poor sensitivity to gases and need in pre-heating of its at rather high temperature (up to 350-400 °C). Therefore, rather large consuming electric power for the detection of a gas is necessary.
Different versions of acetone tin dioxide sensors will be discussed below. Doping is one way of improving the sensitivity of a metal oxide sensors. Their sensitivity can be greatly improved by doping of the volume during a sensitizing of a material or dispersing on the oxide surface a low concentration of Co, Au, Pd, Pt, etc. For example, compared with sensors loaded with pure SnO₂ nanofibers, the Co-SnO₂ nanofiber sensors exhibited improved acetone sensing properties with high selectivity and rapid response and recovery times. Pure SnO₂ nanofiber-based flat sensors have similar responses to acetone and ethanol. The Co-doped SnO₂ nanofiber-based flat sensors had more than five times larger response (sensitivity) than that of the sensors to ethanol. These results suggest that the addition of Co is beneficial to the selective acetone sensing properties of SnO₂ nanofibers [6].

It was found also that the controlling particle size and porosity of the material can enhance the sensitivity of the material. Metal oxides with small grains, nanorods, nanotubes, nanowires and so on can lead to higher sensitivity of sensors made from them. Average grain size was reduced to several nanometers [7]. Tin oxide powders show higher sensor performance than corresponding metal oxide powder materials, which have lower specific surface area. Microstructure plays a crucial role, and a sensor’s sensitivity can be significantly increased by using materials with very small grain sizes [7]. Note that nanosensors made from metal oxides doped with carbon nanotubes (CNTs) have higher sensitivity and better stability of the sensor [8].

Properties of semiconducting tin dioxide acetone sensors are reported below. At first, we will report results of investigations of sensors made of doped tin dioxide, then sensors with lower dimension. After that tin dioxide sensors activated with carbon nanotubes (CNTs) are considered.

**DOPED SNO₂ SENSOR FOR DETECTION OF ACETONE**

Acetone sensors made from SnO₂ doped with different impurities. A series of Co₃O₄-loaded tin dioxide nanocomposite thick films were prepared by grinding, screen-printing and sintering in [9]. The composite films exhibited good response to acetone at pre-heating temperature of the substrate 300°C. At this temperature, the maximum sensor response to acetone (1000 ppm in air) was 235, which was about 5 times as large as that of the pure SnO₂. The selectivity to acetone over H₂ and CO was also promoted by the addition of Co₃O₄ to SnO₂. Though Co₃O₄ is a p-type conductor and SnO₂ is a typical n-type conductor, the small mole rate of Co₃O₄ does not change it to a p-type. Measurements show n-type response to reducing gases (the electrical resistance decreases on exposure to reducing gas) in air. The gas sensitivity exhibits a volcano-shaped relation with the operating temperature, reaching a maximum at 300°C in each case. The addition of Co₃O₄ does not result in a shift of the volcano-shaped correlations between gas response and temperature toward the lower temperature side. This is different from Ag₂O- and PdO-loaded SnO₂ sensors which make the best operating temperature shift toward the lower temperature side [10,11].

Acetone vapor sensing characteristics of cobalt-doped SnO₂ thin films were reported in [12]. Structural and micro structural studies of PbO-doped SnO₂ sensor for detection of methanol, propanol and acetone were carried out in [13]. The thick films of undoped, zinc, ceria and zinc with ceria doped SnO₂ nanopowders were tested in [14] for gas sensing characteristics at various temperatures and concentrations of LPG, ethanol, ammonia and acetone vapour. The response, selectivity, optimum operating temperature, response time and recovery time were investigated for zinc, ceria, zinc with ceria
doped and undoped SnO$_2$. Gas sensors based on samarium oxide loaded mulberry shaped tin oxide for highly selective and sub ppm-level acetone detection were investigated in [15].

**SENSORS WITH LOWER DIMENSION**

We discuss in [7] dimensional effects in small-size nanosensors. They are very important for modern micro- and nanoelectronics. Today the following small-size nanosensors are known: zero dimensional (0D); one dimensional (1D) nanorods and nanowires (NWs); two dimensional (2D) nanosheets and films; three dimensional (3D) porous nanostructures; three dimensional (3D) nanostructures functionalized (decorated) with nanotubes. It is known that electrons in 1D nanomaterials are confined in the 2D, but can delocalize along the long axis. For 2D nanomaterials, electrons conduct across the thickness but are delocalized in the plane of the nanomaterial. Regardless of the dimension of the nanomaterial, the surface of the nanomaterial is homogenous in an electron depleted region within the nanomaterial at a distance known as the Debye length. For example, when a volatile organic compound introduced to a sample, the neutralization of oxygen species and subsequent release of trapped electrons causes a large change in the value of the resistance. This mechanism is well understood for gas sensors made from many nanomaterials. Introducing different dopants to improve response and recovery kinetics allows preparing the device greater selectivity toward a define gas. Researchers have possibilities to produce nanorods, nanowires, nanofilms, and nanosheets with nanoparticles as well as form nanoscale multiple p•n heterojunctions between the two nanomaterials at its interface. We will focused on reporting here new information about nanosensors made of various SnO$_2$ based gas sensor with different morphology such as nanobelt [16-19], multishelled hollow microspheres [20], flower-like structures [21-23] and etc. To improve sensitivity and selectivity towards acetone and also reduce their operating temperature of SnO$_2$ based chemiresistor, as usually, noble metals such as Au [24], Pt [25], Ag [26], as well as reduced graphene oxide [27-29] have been doped to the SnO$_2$ substrate.

Li et al. [17] synthesizes 3D Au-sensitized SnO$_2$ hollow microspheres via hydrothermal method. The catalytic effect of Au and the enhanced electron depletion at the surface of SnO$_2$ hollow microspheres were responsible for improvement in acetone-sensing. Templating route using polystyrene (PS) colloid and bioinspired protein (apoferritin) was suggested for producing both meso/macro pores and catalyst loaded thin-walled SnO$_2$ nanotubes (NTs) by Jang et al. [25-29].

Co-SnO$_2$ composite nanofibers were synthesized in [6] by an electrospinning. Gas sensors were fabricated by spinning these nanofibers onto flat ceramic substrates, which had signal electrodes and heaters on their top and bottom surfaces, respectively. The response was 33 when the sensors were exposed to acetone at 330°C. The response and recovery times to acetone were about 5 and 8 s, respectively.

A heterostructure acetone sensor based on NiO-doped SnO$_2$ hollow NFs with porous structures through the combination of electrospinning technique and calcination procedure were developed [30]. The excellent sensing performances of the proposed sensor were ascribed to its hollow-core structure and Ni doping. In fact, the presence of hetero junctions which formed by the combination of p-type NiO and n-type SnO$_2$ increased the sensor resistance and sensory responses to acetone vapor. The enhanced acetone sensing can be ascribed to the formation of p-n junction between p-type NiO and n-type SnO$_2$ grains. The gas sensor based on NiO-SnO$_2$ nanofibers has a maximum gas response at the operating temperature of 275°C, while the sensor based on NiO shows highest responses at 325°C. NiO-SnO$_2$ exhibits a better selectivity than NiO, having a preferential response to acetone. Therefore, the NiO-SnO$_2$ nanofibers could be used for selective acetone detection. Furthermore, the long-time stability of NiO
and NiO-SnO2 are also measured. Both sensors exhibit good stability towards 20 ppm acetone in 60 days [31]. Highly sensitive acetone sensor based on Eu-doped SnO2 electrospun nanofibers are reported in [31]. Work temperature is 280oC for such sensors. Y-doped SnO2 nanosensors were developed in [32,33]. The nanocrystalline SnO2 powders were prepared in [32] by a co-precipitation method. Diameters of SnO2 nanoparticles were 5.7 to 14.3 nm. Thick-films were made from these nanoparticles. Its response characteristics as a function of the operating temperature in the range 140-260°C at 0.5 ppm of acetone vapor in air is shown in Figure 1.

Figure 1. The response characteristics of the SnO2 thick-films as a function of the operating temperature.

SnO2 can be used as a sensing material for the detection of acetone at low concentrations. The responses of all SnO2 samples initially increase and attain the highest value and then decline with the increase in operating temperature. This behavior can be explained from the kinetics and mechanics of gas adsorption and desorption on the surface of SnO2. The quantity of the chemically adsorbed gas species on the surface gradually increases with an increase in the operating temperature until the rate of desorption becomes equal to that of adsorption. The maximum amount of chemisorption is reached at the temperature with the highest gas response. If the temperature is further increased above this temperature, the balance will move to desorption, as the chemisorption is an exothermic reaction. Then, the amount of adsorbed gas is reduced, resulting in a decreased gas response. The response of the SnO2

samples annealed at 400°C and 500°C attained a maximum value at 220°C and the corresponding responses were 1.073 and 1.035, while the SnO2 samples annealed at 600°C, 700°C, and 800°C attained the maximum value at 180°C and the corresponding responses are 1.582, 1.477, and 1.358, respectively. Therefore, 600°C is the optimum annealing temperature and 180°C is the optimum operating temperature. The optimum operating temperature of SnO2 shifts to a lower optimal working temperature when annealed at 600°C, 700°C, and 800°C. The reduction of the optimal operating temperature of SnO2 may be caused by the large specific surface area, which increases the concentration of chemisorbed oxygen. Compared to others annealed at a higher temperature, the SnO2 sample annealed at 600°C exhibits the highest acetone response. This may be ascribed to the smaller particle size of the SnO2 sample annealed at 600°C. At 180°C, the responses are 1.582, 1.477, and 1.273 for SnO2 sensors annealed at 600°C, 700°C, and 800°C with 0.5 ppm acetone. Hereafter, we mainly conducted the gas sensing investigations of SnO2 sensors annealed at 600°C.

The response of the SnO2 sensor annealed at 600°C to different concentrations of acetone in relation to the operating temperature is shown in Figure 2. TA is the annealing temperature. We can see that the response increases continuously with an increase in the acetone concentration. This is attributable to the increased surface coverage of the acetone molecules on the membrane at higher concentrations, which promotes a subsequent reaction between acetone and atmospheric oxygen on the membrane surface, leading to a rapid chemical reaction and thus increasing the response. At the optimal operating temperature (TO) of 180°C, the response of the SnO2 sensor was 3.333, 3.936, 5.043, and 7.274 for 1, 3, 5, and 10 ppm acetone gas, respectively.
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At the optimal operating temperature of 180 °C, the relationship between the sensitivity of the SnO2 thick film and the acetone vapor concentration is shown in Figure 3. The SnO2 nanosensor is sensitive to low concentrations of acetone.

Figure 3: The response dependence on the acetone concentration for SnO2 powders at the operating temperature of 180 °C.

As was mentioned above, the selectivity is another important factor for gas sensors. The sensor selectivity was tested by exposing it to 1 ppm of different gases at 180°C, and the test results are shown in Figure 4. It can be seen that the sensor shows remarkable higher response to acetone compared to other gases. The results indicate that the SnO2 based nanosensors show good selectivity for acetone. Measurements in [32] are shown that the SnO2 nanosensors annealed at 600°C have long-term stability, which benefits its practical application. Choi et al. [29] utilized SnO2 nanofibers functionalized with reduced graphene oxide (RGO) for detection of acetone. The sensitive acetone detection was achieved by increasing the RGO loading to 5 wt% and raising the operation temperature to 350°C. The detection limit of these sensors was predicted to be as low as 100 ppb for acetone. At the loading level (5 wt%), probably, the RGO formed continuous percolation pathways which controlled the electrical transport in the nanofiber.

Highly selective acetone sensing performances were due to the combined synergistic effect of porous nanotubular morphology and uniform distribution of Pt/PtOx nanocatalysts on thin walled SnO2 NTs, which can offer both chemical and electronic sensitizations. Furthermore, they designed sensor arrays with 3 different sensing layers (Pt-RGO-SnO2 NTs, Pt-SnO2 NTs, and RGO-SnO2 NTs). Thin SnO2 NTs were successfully examined for the analysis of diabetic people breath [34-38].

Figure 4: The response of the SnO2 thick film to different gases with a concentration of 1 ppm at 180 °C.

ACETONE SENSORS MADE FROM SNO2-MWCNT NANOCOMPOSITES

It was shown in Yerevan State University [39] that the functionalization of multi-walled carbon nanotube (MWCNT)/SnO2 thick-film structures with Ru leads to considerable increase in response signal to methanol and ethanol vapors as well as to i-butane gas (Figure 5). The VOCs sensing properties of various ruthenated MWCNT/SnO2 nanocomposite structures as thick films were reported. Structures were obtained by hydrothermal synthesis and sol-gel techniques as well as their combination. The choice of corresponding treating conditions and regimes for
CNTs functionalization as well as thick films surface modification with Ru catalyst were focused in [39] on obtaining the sensitivity to such target gases as ethanol, methanol, acetone and toluene. Results of measurements and samples codes with corresponding synthesis methods are summarized in Table 1.

Figure 5: Response to 1000 ppm methanol and ethanol vapors at the operating temperature 200°C.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Process parameters</th>
<th>( \frac{R_{\text{air}}}{R_{\text{meth}}}, R_{\text{air}}/R_{\text{eth}} )</th>
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<td>KCS2-2</td>
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<td>ZCS-200</td>
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Table 1: The response of studied MWCNT/SnO\(_2\) samples to 1000 ppm of different gases at the operating temperature 200°C.

The testing of all samples at different operating temperatures in other to compare responses to various considered here target VOCs was carried out. Results of these investigations fulfilled for set of ECS7-2 series samples summarized in Figure 6. The relatively high 1000 ppm concentration was chosen. The selectivity relative to other VOC and high response values are registered at methanol and ethanol vapors exposure at the operating temperature 200°C. Unfortunately, separate detection of methanol and ethanol vapors is not come in as yet. The selectivity at the operating temperature 250°C is absent though at that relatively we were carried out the testing of all samples at different operating temperatures in other to compare responses to various considered here target VOCs. Results of these investigations fulfilled for set of the ECS7-2 series samples summarized in Figure 6. As for the EKCS3-2 set of samples made by applying of the hybrid technology, it should be noted that the high response to acetone and toluene vapors of these sensors appears at 200°C but selectivity at that is poor. The selective response to toluene vapors is observed at 150°C (Figure 7). Thus, the KCS1-3 and EKCS3-2 series samples functioned at relatively low operating temperature (150°C) could be use as toluene and acetone vapors sensors, respectively. Sufficiently selective response to acetone vapors is registered by ZCS1-200 set of samples at all operating temperatures in the range of 150-300°C. Results of the test measurements are shown in Figure 8.
Results of measurements of the sensitivity of all studied samples at different work temperature are collected in Table 2.

The largest and sufficiently selective response to acetone vapors (Ra/Rg = 1002) at their concentration 1000 ppm is achieved at samples with 1:200 mass ratio of the components. The largest response to acetone vapors (Ra/Rg=555,62) is fixed for the ZCS1-200 set of samples with 1:200 mass ratio of the components to acetone vapors exposure 1000 ppm at 250°C operating temperature. Selective sensitivity of acetone vapors sensors with 1:50 mass ratio of the components appears only at the 300°C operating temperature. As an example, the dependence of the ZCS1200 sensor response vs acetone vapor concentration at 150°C is presented in Figure 9.

Note that the gas response increases linearly with acetone vapor concentration in its large range. It opens a possibility to realize easy a detector/measurer of the concentration of acetone in air or breathe gas of men.

It is obvious today that the doping of metal oxide with CNTs leads to better sensitivity and lower preheating of the work body of a hybrid sensor. Note that several complicate phenomena processes take place in such functionalized nanocomposites. The full picture is not possible to propose today, but we have to take into account the following: MWCNTs have a huge specific surface area and a nanoscale structure, which exposes a large number of sites at which the gases can react. Detection of various gases can be provided at low temperatures of preheating of the work body of a sensor. The electric conductivity of CNTs is much higher in comparison with the conductivity of metal oxides. Therefore, CNTs reduce the resistance of the sensing metal oxide materials and opens possibility for the percolation of charge carriers through the sample. Since a metal oxide film has mainly n-type semiconductor characteristics and MWCNTs have p-type semiconductor characteristics, there are two depletion layers in such hybridized gas sensors as the decrease in the work function (barrier height) or increase in the conductivity of the metal.
oxide sensitive layer lead to the improvement in the performance of the gas sensor at low operating temperature [40,41]. Apparently, the discussed possible mechanisms require further experimental and theoretical investigations.

The weight ratio of MWCNT to SnO$_2$ was varied in [42] from 0.0-0.75% to synthesize powder with different compositions. The response of prepared sensor toward 1ppm acetone vapor at 250°C was presented in Figure 10(a). It is shown that the resistance decreases very sharply after the exposure of acetone. The addition of MWCNTs improves significantly the sensitivity of SnO$_2$. The sensitivity study was carried out for different concentrations of MWCNT to get the highest response as shown in Figure 10(b). It is to be noted that highest sensitivity was achieved for SnO$_2$ loaded in 0.25% MWCNTs. Over-addition of MWCNTs in the composite decrease the resistance of the sensor sharply. For over-addition of MWCNTs, the increasing number of electrons in the grain boundary reduce the resistance and increase the sensitivity of the sensors. Similar behavior is also reported for NO$_x$ by Sharma et al. [43]. The response toward acetone vapor was jumped to 72% after addition of 0.25% MWCNT. The response of sensors made from pure nanocrystalline SnO$_2$ and SnO$_2$ loaded in 0.25% MWCNTs toward 1 ppm acetone for different operating temperatures is shown in Figure 10(c). 0.25% MWCNT loaded SnO$_2$ sensor showed a much better response at the lower temperature. The sub-ppm level acetone sensing at 350°C is presented in Figure 10(d).

Note that acetone concentration in the exhaling breath is always below 0.9 ppm for normal human being, and value between 1 and 2 ppm indicates a tendency of high blood sugar. If concentration of acetone in exhaled breath is above 5 ppm, then the person probably is diabetic one. It showed that a distinct resolution at this trace level of acetone is required for the prediction of diabetes which is achieved in the sensor. The study was repeated for many times which gives steady results. It indicates the excellent device reliability without

<table>
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<th>KCS1-3</th>
<th>EKCS3-2</th>
<th>ZCS1-200</th>
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Table 2: Acetone and toluene vapors responses of all studied samples vs operating temperature.

![Figure 10](image-url)
any protective layer. The sensor on nanocomposites could be a very promising material for the development breath analyzer for monitoring diabetes. The sensitivity has been carried out for different gases and VOCs at 250°C to check the cross sensitivity and presented in Figure 11. The comparative response toward 1ppm acetone, 1ppm alcohol, 500ppm butane, 5000ppm methane, 30ppm CO and saturated moisture has been shown in Figure 11. It clearly delineates that prepared sensor was very much selective for acetone. Long-term stability study of SnO2-0.25% MWCNT nanocomposite sensor is shown on the inset to Figure 11.

Note that nanosensors to hydrogen dioxide made from SnO2/ MWCNT were reported also in [7,8,41-44] and ZnO/CNT-in [45].

DEVELOPMENT OF DETECTORS OF GASES IN YSU

An intensive work has been started on a manufacture of corresponding new small-sized equipment for medical applications using semiconductor gas nanosensors. Note that at Yerevan State University (Department of Semiconductor Physics and Microelectronics and the Scientific Center for Semiconductor Devices and Nanoelectronics) as a result of many years of research, semiconductor sensors of various gases have been developed [1]. Developed in YSU small-sized detectors of acetone, hydrogen and alcohols were reported [1, 46-49]. In particular, acetone detector using Arduino NANO is made. Earlier, we developed also a device, which allows us to measure simultaneously three gases - methane, carbon monoxide, and hydrogen [50]. Now we worked on development of small-size acetone detector.

REFERENCES


