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Fabrication at wafer level of miniaturized gas sensors based on SnO_2 nanorods deposited by PECVD and gas sensing characteristics

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Abstract

SnO_2 nanorods were successfully deposited on 3″ Si/SiO_2 wafers by inductively coupled plasma-enhanced chemical vapour deposition (PECVD) and a wafer-level patterning of nanorods layer for miniaturized solid state gas sensor fabrication were performed. Uniform needle-shaped SnO_2 nanorods *in situ* grown were obtained under catalyst- and high temperature treatment-free growth condition. These nanorods have an average diameter between 5 and 15 nm and a length of 160–300 nm. The SnO_2-nanorods based gas sensors were tested towards NH_3 and CH_3OH and gas sensing tests show remarkable response, showing promising and repeatable results compared with the SnO_2 thin films gas sensors.

Keywords: Nanorods, Plasma-enhanced chemical vapour deposition (PECVD), SnO_2, Gas sensors

1. Introduction

Nanoscience and nanotechnology are devoting great efforts to the development of novel materials termed as nanostructured materials, 1D and quasi 1D nanostructures, such as wires, rods, belts, that, due to their promising properties, suitable for future applications in many areas such as nanoscale electronics, magnetism, optics, energy storage, electrochemistry, biomedical science and sensing devices [1,2].

In the field of chemical micro- and nano-gas sensors, the development of novel functional materials has leaded to the realization of a variety of nano-sized materials.

Different approaches are used in order to realize 1D structures, so called top down approach, with which a larger scale structure is created and nanoscale characteristics are obtained by etching or by microelectronic fabrication, employing facilities as e-beam or focused-ion-beam writing, X-ray or extreme-UV lithography, and a bottom up approach, with unconventional methods, as wet-chemical synthesis, templates methods, vapour phase transport process, based on chemical synthesis [3,4] that might provide an alternative and interesting strategy for generating low dimensional nanostructure [5].

Among semiconductor materials, metal oxides stand out as one of the most versatile materials, owing to their diverse properties and functionalities [6]. In fact, their 1D structures not only inherit the fascinating properties from their bulk form such as piezoelectricity, chemical sensing, and photodetection, but also possess unique properties associated with their highly anisotropic geometry and size confinement [7]. So, the application of nanocrystalline metal oxides films in semiconductor gas sensors is bound to the obtained enhanced performances. In fact, the advantages connected to employ nanocrystalline metal oxides are due to their very high surface-to-volume ratio and the possibility to realize single crystalline structures (with expected high stability), the faces exposed to the gaseous are always the same and to the grain size (few nanometers) which is likely to produce a complete depletion of the carriers inside the nanostructures.

So, taking into account both their typical features and the gas detection mechanism based on adsorption/charge transfer processes, high efficiency and high performance gas sensors are expected to be produced by using such nano-structured semiconductors.

In fact, in metal oxide 1D nanostructures, when the grain size decreases, the reaction at grain boundaries and the complete depletion in the grain can strongly modify the material transport properties [8]. So the reduction in grain size becomes one of the main factors in enhancing the gas-sensing properties of semiconducting oxides. SnO_2 is an important n-type semiconductor and has been extensively investigated for application in solid-state gas sensors [9] due to its suitable physicochemical properties, such as high stability, high reactivity to reducing gas at relatively low operating temperature, and the possibility to improve sensitivity through the introduction of different metal dopings [10]. The development of one-dimensional SnO_2 nanostructures [11], have been extensively studied and carried out in the field of chemical gas sensor together with the utilization of silicon manufacturing technology in the fabrication of gas sensors in order to achieve small size, low cost, low power consumption, high reproducibility gas detection systems [12]. Various synthesis methods have been reported to prepare 1D SnO_2 nanostructures, such as wet chemical routes [13], thermal evaporation [14], spray pyrolysis [15], template-based growth [16]. In this work, deposition of SnO_2 nanorods was carried out with a custom designed inductively coupled plasma-enhanced chemical vapour deposition (PECVD), used as an alternative manufacturing approach for nanostructured materials and a wafer-level patterning of nanorods layer for miniaturized solid state gas sensor fabrication was performed.

Gas sensing properties of these nanorods SnO_2-based chemoresistive gas sensors were investigated. It was found that SnO_2 based sensor had very good performances for ammonia and methanol detections.

2. Experimental

The setup used to deposit SnO_2 nanorods is a custom-designed cold wall, horizontal inductively coupled PECVD system. The details of the setup have been described elsewhere [17]. The inductively coupled plasma was generated by a 13.56 MHz RF generator with rated power up to 2 kW. Dibutyltin diacetate (DBTDA) (Aldrich, 98% purity) $(C_1H_9)_2Sn(OOCCH_3)_2$ was used as the precursor source. The precursor was maintained at 90 ℃ and its vapour was carried out into the chamber by argon at a flow rate of 50 sccm. Oxygen was used as the reaction gas at a flow rate of 50 sccm.

The fabrication process of integrated gas sensors have been carried out on a 3″ SSP (single side polished) silicon wafer, p-type, 380 μm thick, with 500 nm of grown thermal oxide. Two different photolithographic steps defined both the active area of device (SnO_2 nanorods) and front side electrical contacts, embedded thermometer and heater. The sensitive layer of uniform needle-shape SnO_2 nanorods has been patterned by chemical wet etching before contact-deposition on front side of the wafer. This step leads to an high reproducibility of measured current across the metal oxide film, with an easy coupling of these sensors with electronic interfaces for signal reading and processing. For wet etching process a positive resist mask has been used for selected area protection. After sensitive layer patterning at wafer level, 400 nm/20 nm thick Pt/Ti heater, thermometer and interdigitated contacts have been deposited by RF sputtering and patterned by lift-off technique.

Due to the chemical wet etching supported by a simple photolitographic step, the final fabricated gas sensors (about 800 samples/3″ wafer) present a well patterned area of nanowires layer. This procedure avoid large baseline current spread among different devices and clean substrate surface outside sensors sensitive areas.

A Leo 1550 FESEM was used to observe the morphology of the SnO_2 nanorods. The microstructure of the SnO_2 nanorods was studied using a JEOL-JEM-2100F high-resolution TEM.

For gas sensing tests, the devices were soldered onto a commercial TO-39 socket and were hosted in a test chamber. The micro-sensors were heated at different operating temperatures by supplying a given voltage to the heating element. The sensor responses towards gases were carried out by applying a constant voltage of 2 V between the sensor electrodes and by monitoring the current by means of an electrometer (Keithley 6517A) equipped with a multiplexer module. A PC via Labview National Instruments software controlled the entire process. The desired gases concentrations were obtained starting from certified cylinders by means of a mass flow controller (MKS mod. 647B) and of mass flow meters. A total flow of 100 sccm was fixed during the measurements.

3. Results and discussion

Morphological investigation was carried out by both scanning electron microscope (SEM) and transmission electron microscope (TEM).

Fig. 1 shows the FESEM micrograph of the (a) plane-view and (b) cross-sectional view of the SnO_2 nanorods deposited by PECVD. The SnO_2 nanorods were directly grown from the SiO_2/Si substrate and randomly directed. The average diameter and length of the nanorods estimated from microscopy images is 5–15 and 160–300 nm, respectively. Fig. 2 shows the TEM images that highlights the structural features of the nanorods. Fig. 2(a) shows a SnO_2 nanorods cluster that correspond well with the SEM images, the nanorods are 5–16 nm in diameter and 160–250 in length. The Fig. 2(b) shows a high-resolution TEM image of a SnO_2 nanorod. The lattice image observed by HRTEM confirm that the nanorod is a single crystal. The interfacial spacing of the nanorod is 3.3 Å, that is close to that of bulk SnO_2 (3.347 Å). The [1 1 0] direction was found parallel to the long axis of the rod, indicating the [1 1 0] direction is the growth direction for the SnO_2 nanorods.

The XRD analysis not present here, but of which the reference is reported [18], shows SnO_2 nanorods well crystallized and all major XRD peaks indexed by Casserite SnO_2 with tetragonal rutile structure.

The sensing properties of nanorods SnO_2-based sensors were evaluated by exposing them to NH_3 (100–1000 ppm) and CH_3OH (10–100 ppm). Fig. 3 shows fabricated gas sensor layout used for gas sensing characterization. Tests were made at different temperatures in order to find the optimum operating temperature for each gas and at different concentrations of each analyte gas. The relations between working temperature and response toward different gases are shown in Fig. 4 for a settled concentration of each target gas. The sensor responses have been calculated as $I_{gas}-I_{air}/I_{gas}$, where I_{gas} and I_{air} are the electrical current of the sensor in the mixture of the gas and the air respectively.

As shown in this figure, obviously, the response of the SnO_2 sensor is greater toward NH_3. Best responses towards this gas is obtained at 200 °C. At higher temperatures a significant decreases of the sensor responses takes place, while the responses towards methanol are higher at high temperature (350 °C).

Fig. 5 shows, as an example, the dynamic response of six similar sensors to a sequence of different NH_3 concentrations at 200 °C of temperature. The sensors result show that they are very sensitive to NH_3 and the responses are comparable, showing in this way a repeatability of the devices properties.

As it is known, the semiconductor sensing properties are based on reactions between the semiconductor and the gases in the atmosphere, which cause a change in the semiconductor's electrical resistance due to charge transfer between the adsorbate and the adsorbent. This conventional metal oxide semiconductor theory is extended for the case of nanometric sizes [19]. In particular, the sensing action by metal oxides depends on several factors, such as grain size, surfaces states, as well as the efficiency with which the test gas molecules adsorb on the surface [20]. When the grain size of the metal oxide in nanocrystalline gas sensors decreases, the interaction between adsorbate and adsorbent gives rise to reactions at grain boundaries and to complete depletion of carriers in the grains, with subsequent modification of the materials transport properties, that leads to an huge improvements of gas sensing performances. In case of size of the rods it is likely to produce a complete depletion of the carriers inside the rods. In fact, in polycrystalline and

thick film devices, only a small fraction of the species adsorbed near the grain boundaries is active in modifying the devices electrical transport properties. However, in the new single crystal nanorods based sensor, almost all of the adsorbed species are active in producing a surface depletion layer. Free carriers should move in the bulk part of the rod, along the axis, in a channel-like way.

For these specific sensing applications, in principle, a metal oxide can adsorb oxygen present in the atmosphere both as O_2^- and O^- species. The adsorbed oxygen due to electron trapping from the metal oxide bulk produces the formation of a charge depletion layer on the surface of the oxides. In this way, the adsorbed oxygen plays a crucial role in the sensing ammonia.

$$2NH_2 + 3O_{(ads)}{}^- \rightarrow N_2 + 3H_2O + 3e^- \quad (1)$$

As expected from Eq. (1), the resistance of nanostructured material decreases on contact with ammonia. If the size of the nanorods is closer to the size of the depletion layer, electrons in the nanostructures are fully depleted due to the oxygen adsorption from air. Electrons are released with the exposition to the ammonia, leading to an increase in the conductance according to Eq. (1) [20].

Also the responses towards methanol (Fig. 6) are fast, reversible and comparable. In the particular cases of methanol, once VOCs are introduced, the oxidation reaction takes place on the surface of films as follows [21]:

$$VOCs + O^- \rightarrow VOCs - O + e^- \quad (2a)$$

$$VOCs + O^{2-} \rightarrow VOCs - O + 2e^- \quad (2b)$$

Also in this case, the sensitivity is greatly dependent on the amount of chemisorbed oxygen.

Moreover, in all gas sensing tests, the sensors provide a very stable signal and reach their original baseline after each gas exposure cycle has been completed. These results are attributed to the preparation of nanosize structures and to their processing for the device realization. The results obtained are generally better than those reported in the literature [20,22] and are very promising and stimulating further development of SnO_2 nanorods-based sensor devices and nanowires structures device integration.

4. Conclusions

SnO_2 nanorods were successfully deposited on 3″ Si/SiO_2 wafers by inductively coupled plasma-enhanced chemical vapour deposition (PECVD). Nanorods SnO_2-based chemoresistive gas sensors were realized and gas sensing properties were investigated. Fabricated gas sensors (about 800 samples/3″ wafer) present a well patterned area of nanowires layer defined by chemical wet etching supported by a simple photolitographic step. The gas sensing tests show remarkable response to NH_3 even at very low operating temperatures and good responses towards methanol. This result is attributed to the preparation of highly nanosized material and to the processing for the device realization.

The results obtained are very promising and stimulating further development of SnO_2 nanorods-based sensor devices and nanowires structures device integration. Next step of the process will be the integration of tin oxide nanorods film into micromachined hotplates-based gas sensors.

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Biographies

Angiola Forleo received the degree in physics from the University of Lecce in April 2000 with a thesis on semiconductor gas sensors. In 2000, she was with the Department of Physics, University of Lecce, where she was involved in deposition of thin films making use of the pulsed laser deposition technique. Since 2001, she is working at the IMM-CNR Institute of Lecce. She researches the interactions between gases and mixed oxides and the electrical and optical characterizations of thin films for organic and inorganic gas sensors. At present, she works in the field of structural and electrical characterization of innovative nanostructured materials for gas sensors application.

Luca Francioso received the degree in physics in April 2001 at the University of Lecce. Since 2001, he works in the Institute for Microelectronic and Microsystems of the Italian National of Research Council (C.N.R.-I.M.M.) in Lecce (Italy) in the field of silicon micromachined systems and thin film gas sensor, in charge to develop fabrication processes and new sensor designs. Since February 2002, he is in the position of researcher working on within silicon technology and integration of sol–gel process into silicon devices. At present he works in the field of combustion control sensors with implementation of thin film based gas sensors and development of micromachining process of metaloxide layers.

Simonetta Capone graduated cum laude in physics at the University of Lecce in 1996 with a thesis on semiconductor gas sensors. In January 2001 she received the PhD degree in physics by discussing a thesis on metal oxide based gas sensors for applications in Electronic Nose. At present she held a permanent position as a researcher at the Institute for Microelectronic and Microsystems of the Council National of Research (C.N.R.-I.M.M.) in Lecce (Italy). Her main research interests are in the field of metal oxide and novel nanomaterials, their development and characterization for various gas sensing applications. At current time she is co-author of numerous scientific papers published in national and international journals.

Flavio Casino works as a technician at the Institute for Microelectronic and Microsystems of the Council National of Research (C.N.R.-I.M.M.) in Lecce (Italy) since 1994. He is involved in the realization of ultra-high vacuum systems. Their employment for thin films deposition techinques and in the implementations of experimental setup for characterization of chemical and optical gas sensors.

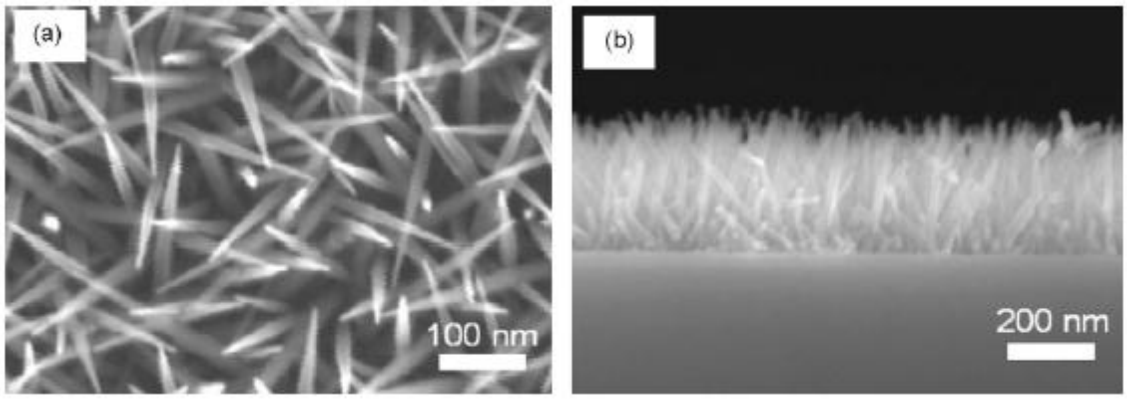
Dr. Pietro Siciliano, physicist, senior researcher, received his degree in physics in 1985 from the University of Lecce. He took his PhD in physics in 1989 at the University of Bari. During the first years of activities he was involved in research in the field of electrical characterization of semiconductors devices. He is currently a senior member of the National Council of Research in Lecce, where he has been working from many years in the field of preparation and characterization of thin film for gas sensor and multisensing systems, being in charge of the Sensors and Microsystems Group. He is responsible for several national and international projects at IMM-CNR in field of sensors and microsystems, mainly for environmental, automotive and agro-food applications. He has been organiser and chairman of International Conferences and director of International Schools on Sensors and Microsystems. He is member of the

Steering Committee of AISEM, the Italian Association on Sensors and Microsystems. At the moment he is director of IMM-CNR in the Department of Lecce.

O.K. Tan (S'82–M'83–SM'03) received the PhD degree from the Nanyang Technological University (NTU), Singapore, the MSc degree from the University of Edinburgh, Edinburgh, U.K., and the BEng degree (1st class Hons.) from the National University of Singapore. He is currently a professor and the associate chair (curriculum and graduate studies) in the School of Electrical and Electronic Engineering at NTU. He has been actively involved in the Sensors, Actuators, and Smart Materials Research Group in the Microelectronics Center, EEE, NTU. His recent work has seen excellent results in semiconductor gas sensors. He also has worked in IC design for many years. His interest is in silicon IC designs, thick- and thin-film devices, especially semiconductor and ferroelectric films, nano-sized materials for sensor and actuator application, integration on silicon, and biochemical sensors. Dr. Tan has been appointed as a member of the International Steering Committee for the East Asian Conference on Chemical Sensors.

Hui Huang received the BEng and MEng degrees in material science from the Northwest Institute of Light Industry (NILI), China, and the PhD degree from the Xi'an Jiaotong University, China. He is currently a research fellow in the School of Electrical and Electronic Engineering, Nanyang Technological University (NTU), Singapore. His research interests are in the area of multifunctional nanostructured thin-film preparation and applications, low dimensional functional materials, semiconductor sensor and actuator, ferroelectric/dielectric materials and devices, and plasma processing of materials.

List of Figures



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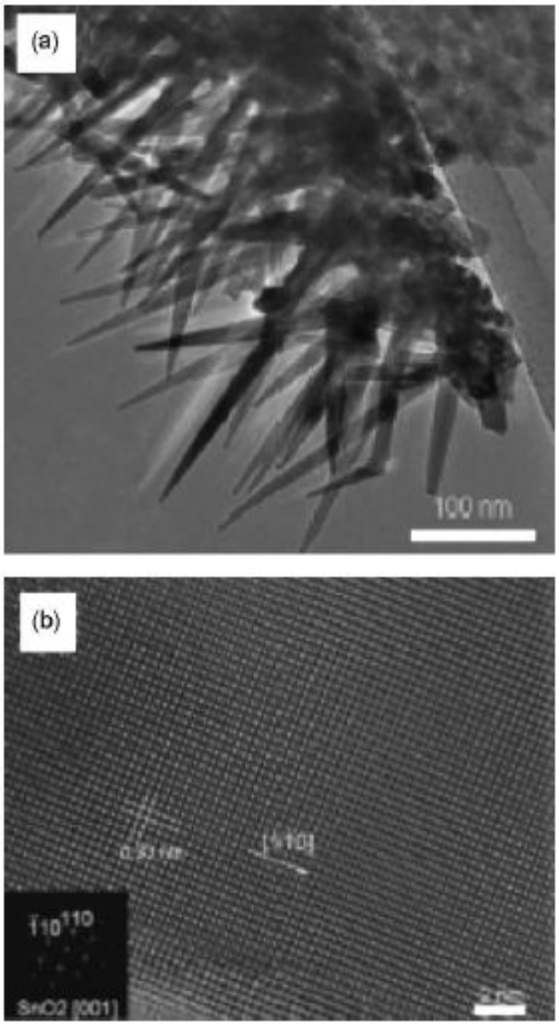
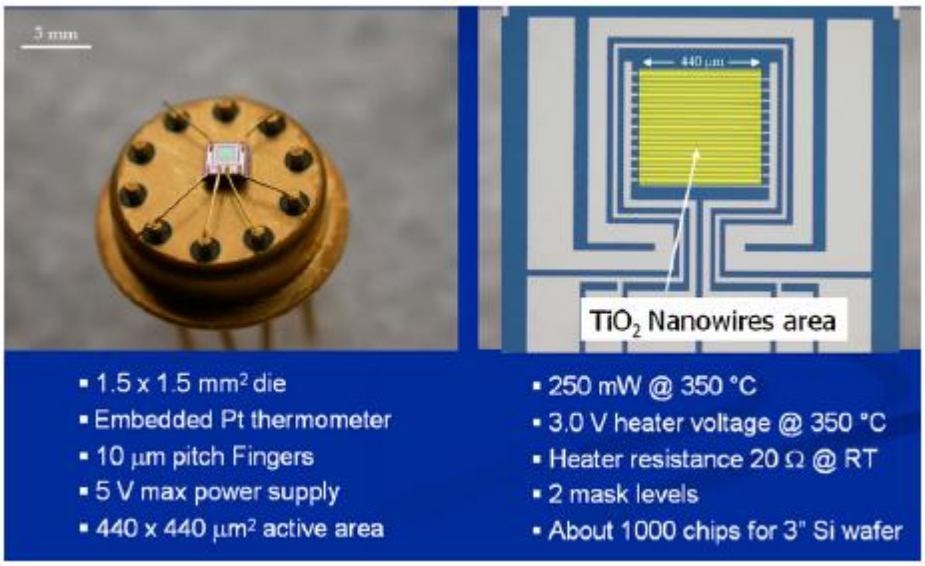


Fig. 2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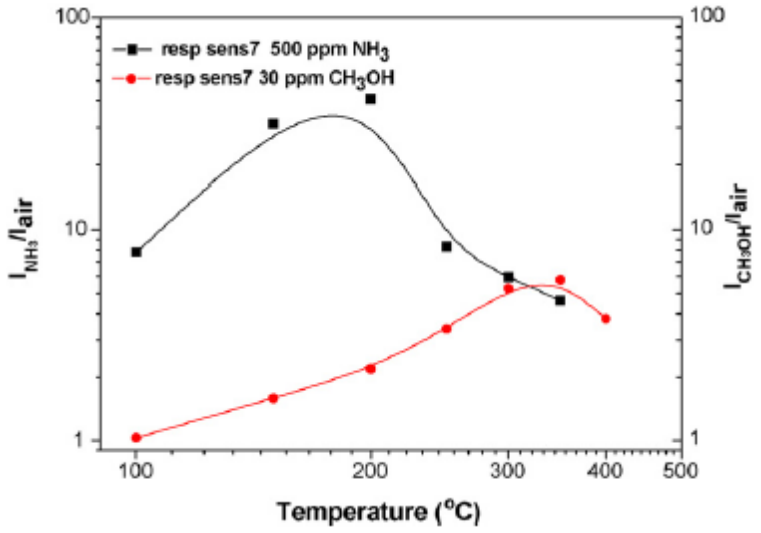
440 µm
TiO2 Nanowires area
▪ 1.5 x 1.5 mm² die
▪ Embedded Pt thermometer
▪ 10 µm pitch Fingers
▪ 5 V max power supply
▪ 440 x 440 µm² active area
▪ 250 mW @ 350 °C
▪ 3.0 V heater voltage @ 350 °C
▪ Heater resistance 20 Ω @ RT
▪ 2 mask levels
▪ About 1000 chips for 3" Si wafer

Fig. 3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resp sens7 30 ppm CH3OH
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I_NH3/I_air
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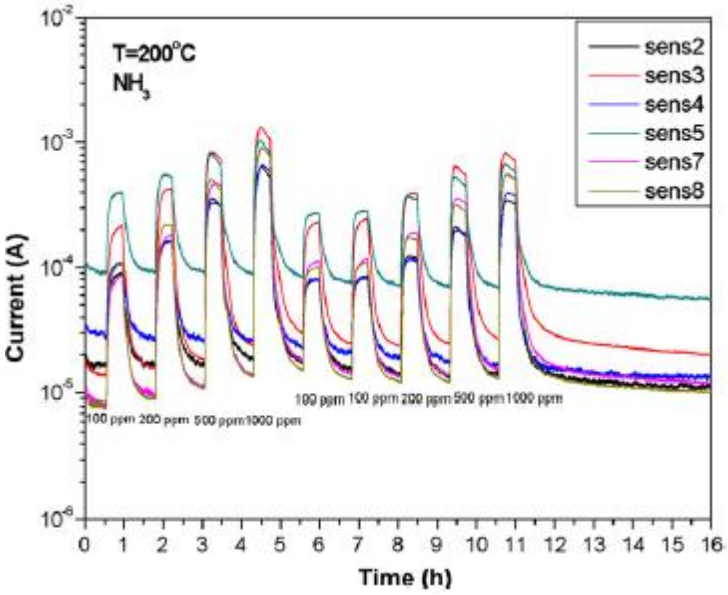
Fig. 4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NH3
sens2
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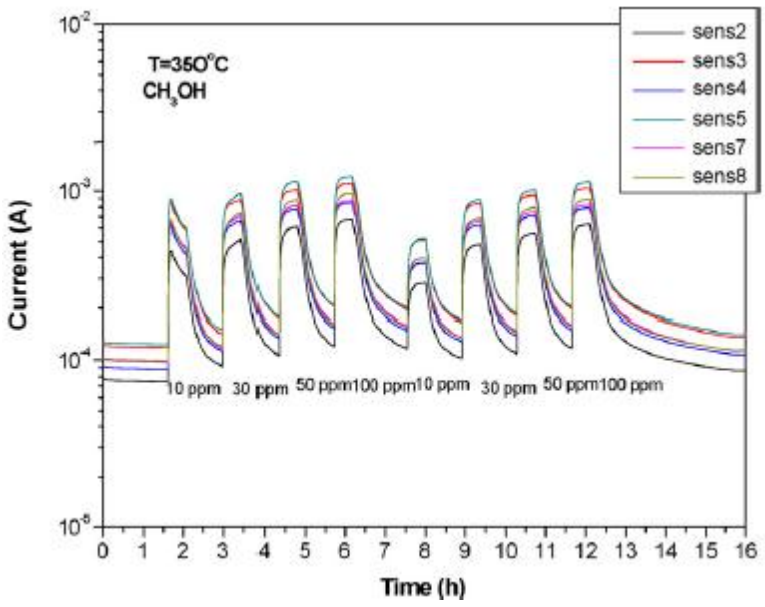
Fig. 5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30 ppm
50 ppm
100 ppm

Fig. 6