

# A Wireless Sensor Network based on Laser-annealed ZnO Nanostructures for Advance Monitoring in Precise Agriculture

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**Abstract:** Plants own a complex way to communicate with each other based on the exchange of chemical and electrical signals. Indeed, plants are capable of creating extensive communication networks thus warning each other of the presence of pests. In response, plants trigger natural strategy against the infestation. The main tool used by plants for exchanging information is the emission and detection of specific volatile organic compounds in air. To this end, monitoring these compounds can be crucial to reveal the state of health of a cultivation far before visual symptoms arise. In this work, we present a wireless sensor network where each node is based on highly sensitive zinc oxide nanostructures enabling the detection and the discrimination of several chemical gases such as CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, CH<sub>4</sub>, etc. The response of each sensor is tuned by using excimer laser annealing procedure, a technique that changes the electrical and morphological properties of the sensing material. This wireless sensor network can be an appealing solution to capture signals coming from the plants without the usage of bulky and expensive equipment.

## 1 INTRODUCTION

In modern agriculture, the monitoring of the health state of crops is becoming of primary relevance to improve the productivity and reduce both environmental and economic costs. Indeed, preservation of crops in the optimum conditions allows enhancing the production, but in particular means recognizing the first symptoms of any plant disease thus avoiding the broadening of the infection to other part of the crop. A quick intervention allows reducing the cost of phytosanitary intervention and the repercussion on the environment.

From the birth of the farming, the farming fight against crop failure is the main issue, but nevertheless just from the middle of the seventeenth century a scientific approach was applied to the detection of

plant diseases (Martinelli et al., 2015). From the beginning, the visual inspection and the visual symptoms have been the main approaches of diagnosis, but with the technological improvement new methods coming out for early stage diagnostics.

In particular, plants emit in surrounding environments several volatile organic compounds, that are connected with several plant functions such as: growth, communication, lack of nutrients, defence and survival (Baldwin, Halitschke, Paschold, Von Dahl, & Preston, 2006). In particular, appearance or changing in concentration of VOCs are correlated with plant stress or incoming disease and they represent one the most promising markers for early detection (Martinelli et al., 2015).

Besides VOCs, also gaseous pollutant presence affects the plant metabolism and it can be used as

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measurement of the plant stress level. In addition to  $\text{CO}_2$  that is one of the fundamental element of the photosynthesis,  $\text{NO}_2$  presence has many negative effects on the plant metabolism (Kozioł & Whatley, 2016) as well as  $\text{CO}$  concentration (Zimmerman, Crocker, & Hitchcock, 1933).

Up to now, scholars have obtained the estimation of the VOCs or gas pollutant concentration by using classical laboratory instruments such as gas chromatography mass spectroscopy. This kind of instruments are bulky and not appropriate for a continue monitoring in field. To this purpose, in the last year, approaches based on electronic noses have been proposed (Gardner & Bartlett, 1994; Laothawornkitkul et al., 2008). Nevertheless, until now, these approaches are based on single instrument and they are not implemented for a continuous monitoring. Moreover, a plethora of low-cost and high sensitive sensors based on different transduction methods are starting to be proposed as valuable tools to detect specific VOCs and biomolecules. These devices can be assembled combining together commercial sensors (Leccese et al., 2017) or exploiting innovative materials and blend of nanostructures (Kaushal & Wani, 2017; Palneedi et al., 2018) even on flexible substrates (Maiolo et al., 2013; Zampetti et al., 2011).

In this work, we present a wireless sensor network endowed of several sensors, both physical and chemical for the continuous monitoring of the environment of the crop. In particular, a set of gaseous pollutants can be efficiently detected and discriminated such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NO}$  as well as  $\text{NO}_2$ . The paper is organized as follow: in section 2, the materials composing the wireless sensor node are described regarding both electronics and sensors, in section 3, some results of sensor tests are shown and finally section 4 presents the conclusions.

## 2 MATERIALS AND METHODS

### 2.1 Gas Sensor Fabrication

Sensing materials based on nanostructures allows improving and tuning the sensor characteristics (Cuscunà et al., 2012; Galstyan, Comini, Baratto, Faglia, & Sberveglieri, 2015; Polese et al., 2017, 2015; Rickerby & Skouloudis, 2016). In this work, we propose the use of laser annealed ZnO nanostructures as active sensing material.

To fabricate the nanostructured gas sensors proposed, we adopted a standard interdigitated structure where the sensing layer acts as a bridge to

create a variable resistance. To this purpose, a 3-inch silicon wafer with a layer of thermal silicon dioxide  $1\ \mu\text{m}$  thick was used as device substrate. After a surface cleaning procedure in an oxidizing solution of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  (7:4) and HF bath, we deposited a precursor layer of commercial ZnO colloids by spin-coating technique. Subsequently, we grew ZnO nanorods (NRs) by using a recipe explained in previous works and we lithographically defined ZnO NRs islands (Fiaschi et al., 2018). We chose to adopt hydrothermal technique to grow ZnO nanorods since it represents the simplest and the cheapest way to obtain ZnO nanostructures (See Fig. 1) (Fiaschi et al., 2018). This procedure provides disordered ensemble of nanorods with a good crystallinity (e.g. standard wurtzite structure) and a high conductivity under UV irradiation (in the range of  $10\ \text{Ohm/cm}$  in case of lasered samples) (not shown in this paper) (Polese et al., 2019). After the growth of ZnO NRs, we irradiated the sample at two different energy densities ( $75$  and  $100\ \text{mJ/cm}^2$ ) exploiting a XeCl excimer laser ( $308\ \text{nm}$ ), thus obtaining a partially melting of the nanorods tips in the first case and a fully melting of the structures in the second one. The irradiation procedure is provided by lasing five shots on the same point through a beam with a rectangular shape of  $1 \times 70\ \text{mm}$ .

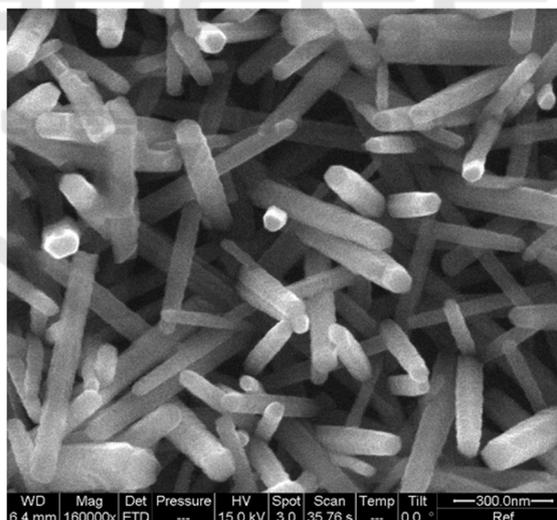


Figure 1: A SEM image of the ZnO NRs grown by hydrothermal technique.

Finally, we patterned interdigitated metal structures on the ZnO NRs islands, cut the samples and glued them onto a PCB. This fabrication flow chart has been adopted to ensure a uniform laser annealing on the material without changing locally the thermal conductivity related to the presence of underlying metal stripes.

## 2.2 Material of the Node

A central unit based on three gas chemical sensors as well as complementary sensors (temperature and humidity) composes each node. The single sensor node has been fabricated on a standard oxidized wafer, then cut and glued on a small PCB. Interconnections are made with wire bonder machine by using a Kulicke and Soffa model 4123. The three gas sensors are based on ZnO nanostructures annealed through an excimer laser irradiation at different energy density to obtain a specific material conductivity and morphology (see Fig.2). Two commercial sensors have been assembled in the board to collect data about temperature and humidity. In particular, we install a SHTC3 by Sensirion (that measures both temperature and relative humidity).

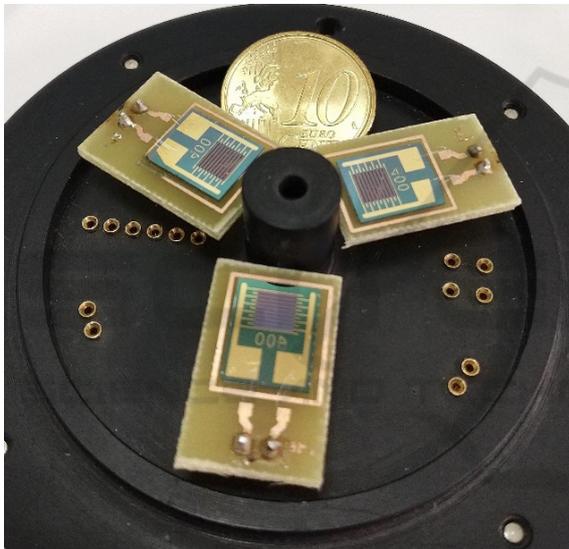


Figure 2: Three sensors of ZnO NRs laser-annealed at different energy densities (0, 75 and 100 mJ/cm<sup>2</sup>) mounted on their respective PCB.

## 2.3 Node Electronics and WSN Architecture

With the intent of maximizing the performance of the node, we considered a set of functions that need to be properly designed: *i*) sensor data acquisition, *ii*) data communication and energy management and harvesting. To this purpose, the node is equipped with electronic interfaces for the custom sensors, a System on Chip (SoC) composed of a microcontroller and a RF interface, a Battery Management (BM) and a Maximum Power Point Tracking (MPPT) circuit for the power management.

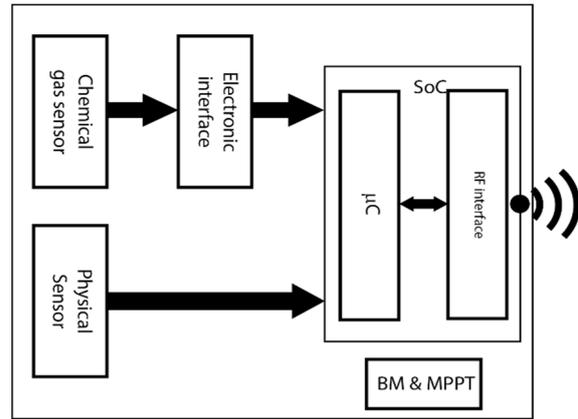


Figure 3: Schematic representation of the node architecture. In the figure, the main parts of the node are highlighted.

A schematic representation of the node structure is sketched in figure 3. With more details, the Texas Instrument CC1352 SoC has been selected for the application. It is composed of an Arm® Cortex®-M4F microcontroller (µC) and a multiprotocol RF interface. The µC can acquire the data coming from the commercial physical sensors (temperature) by means the standard communication digital ports and the data from the chemical gas sensors (RH and volatile pollutant) digitizing the analog value coming from the electronic sensor interfaces. The RF interfaces support several 2.4 GHz protocols and also sub-GHz long range protocols. In particular, our SoC supports the Thread network protocol (<https://www.threadgroup.org>) that allows easily developing mesh networks. Finally, the node has been equipped of a flexible photovoltaic panel (SP3-37 by PowerFilm Solar) and a battery for the energy supply. To optimize the energy consumption, harvesting and storage, a MPPT and a BM circuits have been integrated. They should guarantee a continuous functioning of the nodes in the long period without further maintenance.

Each node has been equipped with a multiband RF interface in order to have both a standard interface at 2.4 GHz for the local data request and, sub-GHz for long range communications. Even if the network is based on sub-GHz carrier, that allows a longer distance of transmission, each node maintains the possibility of being locally interrogated by mean standard Bluetooth interface. This possibility has been maintained for three main reasons: *i*) guarantee the possibility of accessing to the node status (sensors and node status) directly on field with a general-purpose device as a smartphone or tablet; *ii*) allows the download the data from isolated nodes, *iii*) transfer the position information from a mobile GPS

module during the installation procedures. On the other hand, the sub-GHz carrier frequency is useful for long distance communications. Considering the low data rate, due to the slow dynamics of the physical and chemical changes in precise agriculture applications, these quantity can be monitored reaching even distance as long as 1 km. This distance are several order of magnitude larger of the crop information detail that would be reached.

Since each node of the WSN would be placed in the transmission area covered by several other nodes, the characteristics of network reconfiguration of the Thread protocol will be deeply investigated to extend the working period of the network.

### 3 RESULTS AND DISCUSSION

To evaluate the properties of the ZnO nanostructured sensors in detecting low concentrations of pollutants (in the range of tens of ppm) we preliminary tested the device response of each gas in a controlled environment. In particular, we used a customized sealed stain steel chamber with a controlled inlet and outlet to evaluate the sensor response at room temperature. We adopted dry air as carrier gas and we measured the output of the devices under a UV illumination at a frequency of 365 nm and a power density of about  $16 \mu\text{W}/\text{mm}^2$ . We used three different devices with a sensing material based on as deposited ZnO nanorods and two recrystallized structures by using an excimer laser annealing at 75 and 100  $\text{mJ}/\text{cm}^2$ . In figure 4 a score plot shows how it is possible to discriminate all the five analytes (CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, CH<sub>4</sub>) proposed as testing analytes. In this case, we report the sensor response for a gas concentration of 150 ppm. Projection of the data onto principal component plane has also the advantage of allowing the implementation of calibration algorithms among different nodes (Marco & Gutiérrez-gálvez, 2012; Polese et al., 2013; Yan & Zhang, 2015).

In order to estimate the node working life, the power consumption and the energy recharged by the solar panels have to be evaluated. It is important to note that the quantity under monitoring changes slowly during the day, so, a sampling rate every minute is more than enough. Considering a data rate of 250 kbit/s the transmission time is limited to lesser than 1 ms to transmit all the sensors data. In this case the power consumption of the SoC can be limited to less than 100  $\mu\text{W}$ . For the sensors, the main consumption is due to the UV leds that can be estimated in less than 25 mW. On the other hand, the

selected photovoltaic panel can generate up to 70 mW at standard radiation. In these conditions, a long-term operating time could be obtained.

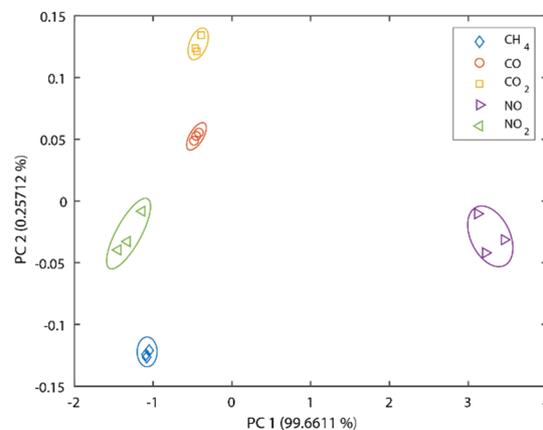


Figure 4: Scores plot of the three ZnO nanostructured sensors. As can be seen, the five analytes measured in the experiments can be easily discriminated.

### 4 CONCLUSIONS

Plants are organisms capable to communicate through a large and complex network of bioelectrical and chemical signals. The possibility to capture this secret language is the key to control and protect cultivation in precise agriculture scenario. A wireless sensor network composed by low cost and highly sensitive devices can be useful to collect signals coming from plants to preventively respond in case of infestation of external harmful stimuli. We proposed a wireless sensor network based on nanostructured zinc oxide sensing material to detect pollutants and VOCs and discriminate these signals in air at room temperature to trigger a proper action in case of starting threat. We adopt excimer laser annealing as unique technique to tune the properties of the sensing materials. We believe that these devices can pave the way to the manufacturing of low-cost sensing systems to be deployed in large cultivation in both greenhouses and open field.

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