**ABSTRACT:** Day by day, the demand for portable, low cost, and efficient chemical/gas-sensing devices is increasing due to worldwide industrial growth for various purposes such as environmental monitoring and health care. To fulfill this demand, nanostructured metal oxides can be used as active materials for chemical/gas sensors due to their high crystallinity, remarkable physical/chemical properties, ease of synthesis, and low cost. In particular, (1D) one-dimensional metal oxides nanostructures, such as nanowires, exhibit a fast response, selectivity, and stability due to their high surface-to-volume ratio, well-defined crystal orientations, controlled unidirectional electrical properties, and self-heating phenomenon. Moreover, with the availability of large-scale production methods for nanowire growth such as thermal oxidation and evaporation—condensation growth, the development of highly efficient, low cost, portable, and stable chemical sensing devices is possible. In the last two decades, tremendous advances have been achieved in 1D nanostructure-based chemical/gas sensors ever since the pioneering work by Comini on the development of a SnO2 nanobelt for gas sensor applications in 2002, which is one such example from which many researchers began to explore the field of 1D-nanostructure-based chemical/gas sensors. The Sensor Laboratory (University of Brescia) has made major contributions to the field of metal oxide nanowire chemical/gas-sensing devices. Over the years, different metal oxides such as SnO2, ZnO, WO3, NiO, CuO, and their heterostructures have been grown for their nanowire morphology and successfully integrated into chemoresistive gas-sensing devices. Hence in this invited feature article, Sensor Laboratory research on the synthesis of metal oxide nanowires and novel heterostructures and their characterization and gas-sensing performance during exposure to different gas analytes has been presented. Moreover, some new strategies such as branched-like nanowire heterostructures and core–shell nanowire structures adopted to enhance the performance of nanowire-based chemical sensor are presented in detail.

**INTRODUCTION**

From its beginning, the electronics industry was ruled by silicon. In parallel to its evolution, there is a continuous effort to find alternative materials due to the high cost of silicon-based electronic devices and most importantly to avoid relying on a single material. Thus, as an alternatives, many materials such as organic semiconductors and perovskites have been explored by researchers over the years. In 2010, when the Nobel Prize in Physics was announced, graphene was immediately considered to be the material of the century. However, among all of these, metal oxides (MOXs) were silently doing their job, and nowadays they are used in many modern electronic device applications such as thin film transistors, chemical sensors, biosensors, and solar cells. The reason behind their success is high stability, abundance on earth, and remarkable chemical/physical properties that can be tuned according to the requirements for particular applications.

Among the successful exploitation of MOXs, there are commercially available indium gallium zinc oxide (IGZO)-based high-mobility transistors. MOXs are also considered to be potential candidates for future transparent electronic devices due to their high band gap in the ultraviolet region that makes them transparent in the visible region of the spectrum.

Another important area of application in which MOXs are immensely explored is chemical/gas sensors due to their properties such as low cost, compact size, ease of fabrication, and high abundance on the earth’s crust. For example, tin dioxide (SnO2) is one of the most explored materials in the field of gas sensors. A chemical sensor is a device that convert a chemical signal obtained via the interaction of a chemical analyte with an active sensing materials (such as MOX) into a measurable signal (optical, electrical, and magnetic etc.). In the last two decades, chemoresistive sensors (measurable signal: resistance or conductance) have been extensively investigated to detect a large number of chemical analytes such as volatile organic compounds, toxic gases, explosives, and environ-
The performance of these sensing devices largely depends upon the microstructural properties of the active sensing material. In this regard, nanostructured metal oxide-based gas sensors are attracting attention due to their fast response and high sensitivity. However, the selectivity of these devices is still a major issue, and many different strategies such as surface functionalization have been explored to limit or overcome this challenging issue. Moreover, MOXs in nanostructured form possess a high surface-to-volume ratio, a higher degree of crystallinity, and better stoichiometry. Another important aspect of MOXs is the possibility to grow them with different morphologies such as nanowires, nanobelts, and nanodots. These MOX nanostructures can be grown by using physical, chemical, and solution-processable techniques.

Among these nanostructured forms, 1D MOX nanowires (NWs) possess well-defined crystal orientations and single crystallinity that leads to controlled reactions and increased stability of the sensing devices based on them. The MOX NW gas sensors had faster response dynamics because there was no need for gas diffusion prior to surface reactions. Moreover, very interesting effects such as self-heating, which can be exploited in gas sensing, are effective only for nanowire morphology. For recent developments in nanostructured metal oxide gas sensors, the reader can also refer to other interesting review articles.

In the field of MOX NW-based gas sensors, the Sensor Laboratory (University of Brescia) has done pioneering work concerning the growth, integration, functional characterization, and improvements of the MOX sensing performance. We have grown MOX NWs such as ZnO, SnO2, WO3, TiO2, CuO, and NiO using different techniques and procedures. These techniques are mainly based on two principles: thermal oxidation and vapor-phase growth using vapor–solid (VS) and vapor–liquid–solid (VLS) mechanisms. In all of these cases, laboratory-made equipment has been developed by the Sensor Laboratory.

In this invited feature article, the contributions of the Sensor Laboratory to the development of MOX NW-based chemical/gas sensors will be presented. In particular, the working principles of chemoresistive sensors, the gas-sensing mechanism, the device structure, and the techniques used for nanowire synthesis and their growth mechanism will be described. Moreover, their functional properties, measured using different techniques, will be discussed. In the final sections, their sensing performance and new strategies to enhance their performance will be presented.

**Metal Oxide Gas-Sensing Mechanism and Device Structure of a Conductometric Gas Sensor and Their Working Principles**

**Gas-Sensing Mechanism.** In order to understand the gas-sensing mechanism of n- and p-type semiconductor MOXs, it is important to understand the origin of their semiconducting nature. It is well known that, in Si-based semiconductors, the majority charge carriers (electrons or holes) can be manipulated by doping with donor or acceptors impurities. However, in wide-band-gap MOX, the nonstoichiometry determines the majority charge carriers if no intentional doping has been introduced. For example, the NiO p-type semiconducting character can be explained by the deficiency in metal ions, while SnO2 n-type behavior is a result of the generation of free electrons, as oxygen vacancies are formed. In semiconductor MOX-based chemical/gas sensors, the high response toward specific molecules can be achieved by operating the sensors at a particular optimal temperature that changes the concentration of a majority of the charge carriers and the chemical interaction with the surrounding atmosphere. Furthermore, at elevated temperatures (100–500 °C), oxygen molecules are chemisorbed and ionized (O2−, O−, and O2−) by capturing the electrons from the semiconductor surface. The chemisorption of oxygen ions that occurs on the MOX surface at different temperatures is shown in the following equations:

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\text{O}_2 + e^- \rightarrow \text{O}^- + \text{O}_2^-
\]

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\]
Figure 2. Band-bending phenomenon in n-type metal oxides due to the chemisorption of oxygen. $E_\text{V}$, $E_\text{C}$, $E_\text{F}$, and $E_\text{f}$ represent the vacuum level, conduction band, valence band, and Fermi level energies of the semiconductor.

\begin{align*}
\text{O}_2 (\text{gas}) & \leftrightarrow \text{O}_2 (\text{ads}) \quad (1) \\
\text{O}_2 (\text{ads}) + e^- & \leftrightarrow \text{O}_2^- (\text{ads}) \quad (<100 ^\circ \text{C}) \quad (2) \\
\text{O}_2^- (\text{ads}) + e^- & \leftrightarrow 2 \text{O}^+ (\text{ads}) \quad (100-300 ^\circ \text{C}) \quad (3) \\
\text{O}^+ (\text{ads}) + e^- & \leftrightarrow \text{O}_2^+ (\text{ads}) \quad (>300 ^\circ \text{C}) \quad (4)
\end{align*}

Thus, at temperatures of less than $100 ^\circ \text{C}$, adsorbed oxygen ions capture electrons from the MOX surface and become $\text{O}_2^-$, while in the temperature range of $100-300 ^\circ \text{C}$, $\text{O}_2^+$ captures electrons from the MOX surface and becomes $\text{O}^+$. Finally, at temperatures greater than $300 ^\circ \text{C}$, $\text{O}^+$ exists on the surface of MOX. This adsorption of oxygen ions leads to the formation of an electron core–core–shell configuration. In n-type MOX such as $\text{SnO}_2$, due to oxygen ion sorption, an electron depletion layer (EDL) and a shell around the semiconducting core are formed, while in p-type MOX a hole accumulation layer (HAL) and a shell near the surface and around the insulating core are formed. The core–shell configuration of both n- and p-type semiconductors is shown in Figure 1.39

In order to further elaborate on the formation of the EDL layer in n-type MOX, a band diagram before and after the chemisorption of oxygen is presented in Figure 2.40,43 In vacuum, the bands are flat and the surface states are completely empty. However, when MOX is exposed to air, oxygen chemisorption occurs on their surface. These chemisorbed ions capture electrons from the conduction band of MOX and induce the band-bending phenomenon (upward band bending). The captured electrons trapped on the surface of MOX in the form of negative ions and the EDL on n-type metal oxides is formed.45 On the other hand, the chemisorption of oxygen on p-type metal oxides forms the HAL.

Interestingly, Iwamoto et al.44 have found that the numbers of oxygen ions adsorbed on the surface of n- and p-type semiconductors are considerably different. The total amount of oxygen desorbed below $560 ^\circ \text{C}$ ($V_{560}$) for 16 MOX was measured through the use of temperature-programmed desorption (TPD). The experiments proved that a large number of adsorbed oxygen species (large value of $V_{560}$) exist on p-type metal oxides ($\text{MnO}_2$, $\text{NiO}$, $\text{Co}_3\text{O}_4$, and $\text{Cr}_2\text{O}_3$) in comparison to the n-type ones ($\text{SnO}_2$, $\text{TiO}_2$, $\text{ZnO}$, and $\text{Fe}_2\text{O}_3$). However, among the n-type MOX, transition MOX (i.e., $\text{Fe}_2\text{O}_3$) had the highest $V_{560}$ value since their oxidation state may vary. Thus, the low stability of transition-metal oxides ($\text{NiO}$, $\text{Co}_3\text{O}_4$, $\text{MnO}_2$, and $\text{Cr}_2\text{O}_3$) is the basic reason behind the greater ionosorption of oxygen.44

By taking into account the core–shell configuration of MOX, the resistance of n-type MOX-based chemical/gas sensors is determined by the resistive contacts between shells (shell-to-shell contacts).39 If we define $R_{\text{core}}$ and $R_{\text{shell}}$ as the resistances of a semiconducting core and a resistive interparticle shell, respectively, then the total resistance of the n-type MOX gas sensor will be the series combination of both of these, while in the p-type MOX sensors, the conduction can be explained by the parallel path created between the wide resistive core ($R_{\text{core}}$) and narrow conducting shell ($R_{\text{shell}}$).39 Therefore, when n-type MOXs are exposed to a reducing gas such as carbon monoxide (CO), electrons are transferred to the semiconductor and CO is oxidized by the reaction with the surface-adsorbed oxygen ions. This results in a decrease in sensor resistance (increase in conductance) which is proportional to the gas analyte concentration and can be described by the following equations:

\begin{align*}
\text{CO (gas)} & \rightarrow \text{CO (ads)} \quad (5) \\
\text{CO (ads)} + \text{O}^+ (\text{ads}) & \rightarrow \text{CO}_2 (\text{gas}) + e^- \quad (6)
\end{align*}

The overall effect is a change in the density of adsorbed oxygen ions that is detected as a decrease in sensor resistance. On the other hand, the interaction of n-type metal oxides with a strong electronegative gas such as NO$_2$ (oxidizing gas) increases the sensor resistance as

\begin{align*}
\text{NO}_2 (\text{gas}) & \leftrightarrow \text{NO}_2 (\text{ads}) \quad (7) \\
e^- + \text{NO}_2 (\text{ads}) & \leftrightarrow \text{NO}_2^- (\text{ads}) \quad (8)
\end{align*}

The electron injection into a p-type MOX by the interaction with a reducing gas (CO) decreases the hole concentration in the HAL layer, thus increasing the sensor resistance. According to the literature, n-type MOX sensors generally have a higher response (measured as the change in the sensor resistance/conductance when exposed to the chemical compound relative to its value in air) as compared to p-type MOX.46 This is the basic reason that p-type MOXs have been less-frequently investigated as compared to the n-type ones. It is always a challenge to fabricate highly sensitive p-type MOX chemical/gas sensors. The conduction in p-type semiconductors occurs mainly in the narrow HAL and the hole–electron recombination (electrons donated by the reducing gas) does not affect the overall resistance of the sensor significantly.39 Hence, the response of p-type MOX sensors is usually lower than that of n-type MOX sensors. If $S_n$ and $S_p$ are the responses of p- and n-type MOX sensors for particular gas analytes and semiconductor...
materials with the same morphology, then according to Hubner et al.\textsuperscript{47} they can be related by the following equation:

\[ S_p = \sqrt{S_n} \quad \text{(9)} \]

Hence according to the above equation, it is very difficult to develop a highly sensitive gas sensor based on p-type MOX.

However, p-type metal oxides are still considered to be potential materials for new chemoreisitive gas sensors due to their unique physical/chemical properties. Moreover, due to the advance in the field of nanotechnology, continuous effort has been expended in the development of p-type gas sensors. For example, sensor NiO nanowires were grown for the first time using the VLS mechanism, and they were integrated into conductometric chemical sensors that exhibited remarkable performance toward H\textsubscript{2}.\textsuperscript{48}

To determine the final sensing performances, apart from the chemical reaction and conduction mechanism mentioned above, other important parameters such as the surface morphology, nanocrystalline properties, and the large surface-to-volume ratio have to be taken into account. For this reason, it is very challenging to predict the sensing behavior of an active material without experimental tests. However, in order to understand the gas-sensing mechanism of metal oxides, in situ operando experiments such as X-ray absorption spectroscopy have been performed in the past.\textsuperscript{17,49,50}

**Device Structure and Working Principle of a Conductometric Sensor.** The three main components of a conductometric gas sensor device are the following:

1. An active sensing material that must be deposited on the substrate;
2. Electrodes for the functional measurement; and
3. A heater that keep the sensor at the desired working temperature

These three main components are considered while making conductometric sensing devices. However, the simplest form of a conductometric gas-sensing device can be an active sensing material (thin film, nanowires, and nanobelts) deposited between the two metal electrodes. Thanks to advances in micro/nanofabrication, different structures and dimensions can be achieved. At the Sensor Laboratory, sensing devices were prepared via dc magnetron sputtering having dimensions that were as small as 2 x 2 mm\textsuperscript{2}.\textsuperscript{18} The step-by-step fabrication of a conductometric sensor and the picture of a complete sensing device are shown in Figure 3.

![Figure 3](https://dx.doi.org/10.1021/acs.langmuir.0c00701)

Figure 3. (a) Picture of the real gas-sensing device used in the Sensor Laboratory (UniBs). (b) Step-by-step fabrication of a conductometric device.

In particular, the first step involves the growth of nanowires on insulating substrates, such as aluminum oxide, using different growth techniques. For the electrode deposition, first an alloy of Ti/W and Pt soldering pads was deposited on the substrate using sputtering. Afterward, the interdigitated Pt electrodes were deposited on the nanowires by using shadow masking in order to have higher electrical conductance and mechanically stable gold wire bonding. The pads were used for the electro-soldering of gold wire. For temperature-dependent sensing measurements, Pt heating elements were also deposited using dc magnetron sputtering on the back side of the substrates. To achieve this, the successive deposition of Pt pads (using a Ti/W adhesion layer) and Pt contacts has been performed. Prepared devices were finally mounted on TO packages using electro-soldered gold wires (Figure 3b).

The working principle of chemoresistive gas sensors relies on the change in electrical resistance/conductance of the active sensing materials upon interaction with the gas analyte. The nature of the sensitive materials (n-type or p-type) and the target gas (oxidizing or reducing) governs the increase or decrease in electrical resistance. In the class of solid-state metal oxide-based chemical/gas sensors, conductometric ones are the most investigated and exploited devices and are designed for the detection of toxic as well as inflammable gases in the surrounding atmosphere and for monitoring technological processes.\textsuperscript{51–55} In gas-sensing measurements, the change in electrical conductance or resistance of a sensor upon interaction with the gas is measured at an optimal working temperature. A constant dc voltage whose value may vary depending on the resistance of the sensor is kept constant during the measurement. To find the optimal working temperature of the sensor for a particular gas analyte, the response of the sensor is recorded at different temperatures. The maximum in the response vs temperature plot for a given gas analyte is considered to be the optimal working temperature. The main advantages of metal oxide conductometric sensors are low production cost, ease of fabrication, and simple operation thanks to their intrinsic properties as well as manufacturing techniques.\textsuperscript{54} This implies that mass production at reasonable cost is possible using well-engineered metal oxide conductometric sensors. Brief details of the conductometric gas-sensing measurement setup developed and used in the Sensor Laboratory are described in the Supporting Information.

**Important Sensing Parameters.** In general, the electrical conductance/resistance of the metal oxide-based conductometric gas sensors changes with exposure to the target gas. The nature of the sensitive materials (n-type or p-type metal oxide semiconductors) and the target gas (oxidizing or reducing) governs the electrical resistance increase or decrease. For example, when an n-type semiconductor is exposed to a reducing gas, the resistance decreases, whereas upon exposure to an oxidizing gas, the resistance increases. Figure 5 reports the typical dynamic response curve of a gas sensor. According to this curve, a change in conductance or resistance is registered when it is exposed to a gas analyte (“gas on”). After reaching a stable conductance value in the presence of the gas, the air flow is restored (“gas off”) and the sensor recovers to its initial value (baseline conductance and resistance). In Figure 4, the response and recovery times of sensors can be determined.

Some of the important sensing parameters that are used to characterize the sensing performances are the following:55
1. Sensitivity (S): Sensitivity can be defined as the change in the measured signal per analyte concentration unit (i.e., the slope of a calibration curve). It should be noted that the calibration curve is a log−log graph between the sensor response and the analyte concentration.

2. Selectivity: Selectivity determines whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte. It is generally expressed as

$$selectivity = \frac{\text{response of the sensor to the desired gas}}{\text{response of the sensor to the interfering gas}}$$  

Thus, according to the above equation, selectivity is the ability of the sensor to discriminate the response for a particular gas analyte from other interfering gases.

1. Response time: This is defined as the time required for a sensing device to respond to a step concentration change from zero to a certain concentration value. In addition, the response time can be calculated as the time required for a sensor resistance/conductance to reach 90% of the equilibrium value during exposure to a gas analyte. The response time indicates how fast or slow a sensor can respond when a gas analyte is introduced into the test chamber.

2. Recovery time: When the step concentration changes from a certain value to zero, the recovery time is the time taken by the sensor to return to its initial signal value. In addition, the recovery time can be calculated as the time required for the sensor resistance/conductance to return to 70% of its original value of resistance/conductance in air. The recovery time indicates how quickly or slowly the sensor recovers to its initial conductance when the air flow is restored.

3. Stability: This defines the ability of a sensor to provide reproducible results for a certain period of time.

4. Detection limit: This can be defined as the lowest concentration of gas analyte detected by the sensor under experimental conditions such as temperature. The detection limit can be calculated by fitting the log−log plot of response vs different gas concentrations (calibration curve). It is the minimum concentration that a sensing device can detect under optimized conditions by giving a detectable signal.

5. Optimal working temperature: This corresponds to the temperature at which the sensor gives the maximum response to the gas analyte.

All of the above-mentioned parameters are used to characterize the sensor performance. An ideal sensor should be highly sensitive, selective, and stable with a low detection limit and a short response time. However, it is very difficult to optimize all of these parameters together in a single sensing device, and researchers usually make an effort to approach only some of them.

### Fabrication of Metal Oxide-Based One-Dimensional Nanostuctures and Their Characteristics

For 1D nanostructure fabrication, the most important requirements are dimensions, morphology control, crystalline properties, and uniformity. Furthermore, a preferential growth direction with a faster growth rate and higher yield is mandatory.
One-dimensional nanostructures can be prepared by following two different technologies: bottom-up and top-down. Top-down technology is based on standard microfabrication equipment with the deposition and etching of planar structures to reduce their lateral dimensions down to the nanoscale level. Other techniques such as focused ion beams, electron beams, and X-ray lithography have been used. The major hindrances that come with top-down approaches are the long preparation time and remarkably elevated costs. However, one should not forget the positive aspects of this approach, such as using a well-known technology coming from the semiconductor industry. In addition, the structures can be prepared directly on planar substrates, which allows for easier successive electrical connection with the macro world. In the literature, many reports have been published on the fabrication of 1D nanostructures with a top-down approach.

On the contrary, bottom-up synthesis is based on the assembly of molecular building blocks or chemical synthesis directly into nanosized morphology. This approach presents many advantages such as high purity, crystallinity, and the easy achievement of reduced dimensions of the fabricated materials, in addition to the low cost of the experimental setups together with the possibility to easily vary the intentional doping and formation of junction-based devices. However, the major issue regards the integration into planar substrates necessary to take full advantage of the useful properties. Furthermore, nanostructure patterning and alignment may be difficult.

Thus, bringing together both the bottom-up (for the fabrication of the nanostructures) and top-down (for large scale fabrication) approaches is the most promising scheme for producing highly functional materials.

To grow MOX nanowires, various techniques such as the hydrothermal method, sol–gel chemistry, and electrospinning have been proposed and successfully implemented by the researchers for gas-sensing applications. However, in this review we will mainly focus on the bottom-up growth techniques (i.e., vapor/liquid phase growth methods and thermal oxidation that were used in the Sensor Laboratory).

**Vapor-Phase Growth.** Vapor-phase growth was proposed by Wagner and Ellis in the early 1960s and is one of the first techniques developed for preparing micro- and nanostructures. It consists of the evaporation of source material in a vapor state of the source material, a liquid catalyst droplet, and afterward was adapted for other materials such as metal nanowires. The VS growth takes place when the NW crystallization emerges from the direct condensation of the source material without the presence of any catalyst. In this mechanism, source materials are heated under high temperature from the vapors and directly condensed on the target substrates placed in the relatively low temperature region. Once the condensation process starts, the initially condensed molecules create seed crystals that serve as nucleation sites for the further growth of nanowires.

On the other hand, the VLS mechanism is named after the three different phases of material involved in the growth process: the vapor state of the source material, a liquid catalyst droplet, and the solid crystalline nanostructure that is produced. Catalysts can be deposited on the substrates using different techniques such as colloidal solutions and magnetron sputtering. Liquid metal clusters or catalysts act as favorite adsorption sites for the vapor, and when supersaturation is reached, there is a segregation normally at the bottom of the cluster and the nanowire growth starts. Metal catalysts are essential in the VLS mechanism, but not all metals can be effective. These catalysts need to fulfill some requirements, such as they must be liquid at the deposition temperature, they must be inert to chemical reactions, the vapor pressure of the catalyst component over the liquid alloy should be small, and they must not make intermediate solids.

The most widely used catalysts are noble metals such as gold, ruthenium, platinum, and palladium. The dimensions of the nanowires can be directly related to the size of the catalyst clusters. This can be either by matching the size or by the process involving the catalyst curvature in which lattice matching and strain matching are important.

One-dimensional nanostructure growth via the VLS or VS mechanism can be achieved using a tubular furnace that is able to reach the high temperatures necessary for material evaporation. In order to reduce and control the pressure inside the alumina tube, the system must be connected to vacuum pumps. This will reduce the evaporation temperature and avoid the inclusions of unintentional dopants into the growing nanostructures. In order to ease the mass transport, a gas carrier is normally used, and mass flow controllers inject the carrier gases (normally argon) inside the system. For better reproducibility, a homemade Ni LabVIEW virtual instrument that fully controls the system has been used to control the whole process. MOX powder is placed in an alumina boat, in the middle of the alumina tube, at a temperature which is high enough to induce the evaporation of source material. The growth substrates (with and without catalyst) are placed on the alumina substrate holder in a colder region of the tube. During the heating step, the flow of the carrier gas is restricted to the reverse direction, from the substrates to the powder, in order to avoid any undesired condensation of the powder under undesired growth conditions. As the furnace reaches the desired temperature, the flow is switched to the direct direction, from powder to the substrates, and the deposition begins. The deposition time depends on the different growth parameters such as the amount of material desired, the preferred morphology, and so on. During cooling, the flow is kept in the reverse direction. It is possible to tune the achieved morphology by changing the pressure inside the alumina tube, the condensation temperature, the carrier gas flow, the deposition time, and the catalyst used for the fabrication process.

Different n-type ZnO, SnO2, SnO2, In2O3, and WO3 and p-type NiO metal oxide nanowires deposited on various substrates were successfully used in the Sensor Laboratory with this experimental setup. Some major advantages and disadvantages related to the vapor-phase growth technique in tabular form are presented in the Supporting Information.

**Structural and Morphological Characterization.** Tin dioxide (SnO2) is a MOX that has been extensively exploited for gas-sensing application in many different forms such as thick films, thin films, and nanowires. Our group was the first to present a report on the synthesis of tin dioxide nanobelts using the simple catalyst-assisted evaporation—condensation of source material (in powder form) for gas-sensing application. This work encouraged many researchers worldwide to work in...
the field of nanostructured MOX synthesis for gas-sensing application. Furthermore, in 2007 our group reported on the conductometric gas-sensing application of tin dioxide nanowires grown by VLS and VS mechanisms. For VLS growth, platinum (Pt) is used as the catalyst to promote the nucleation of nanowire growth. The evaporation of source material (SnO exposed to the formation of melted Pt–Sn clusters, which aids nanowire nucleation. HR-TEM reveals that the temperature permits the formation of melted Pt phase technique are very sensitive to the substrate type and observed that the ZnO nanowires grown using the vapor–liquid–solid technique are very sensitive to the substrate type and observed that the ZnO nanowires grown using the vapor–liquid–solid mechanism. The deposited nanowires were long and thin and had a denser morphology with diameters ranging from 16 to 50 nm and were single-crystalline in nature using Au in comparison to other catalysts.

**Thermal Oxidation.** Thermal oxidation is among the easiest and highest-yielding techniques for growing different metal oxide nanostructures. This technique has several advantages such as the production of highly crystalline materials, easy patterning, scalability for a large amount of production with high yields, and possible operation at atmospheric pressure for some materials. However, the major drawback is the time required for the growth process, which can be hours.

For some specific metal oxides such as CuO, the growth mechanism is fully understood. Zappa et al. have described that during the formation of thermally oxidized CuO NWs, first the metallic Cu oxidized to form a CuO film (Cu + O₂ → CuO).
This Cu₂O film further oxidized to CuO (Cu₂O + O₂ → CuO) and produced CuO NWs. Moreover, Arafat et al. 100 have investigated the effect of mechanical stress on thermally oxidized TiO₂ nanowire growth. Indeed, the induced stress has significantly improved the nanowire coverage and confinement. Due to the high thermal energy, the surface reactions are occurring with oxygen atoms present in the atmosphere (Figure 8a,b). 103 The process of nucleation starts due to oxygen atom diffusion inside the metal layer because of the mechanical stress. Furthermore, the nanowire growth is also promoted by the presence of in-phase tensile stresses (Figure 8c), and the uppermost layer is highly defective, porous, and oxidized. For further oxidation, metal atoms find two pathways, lattice or grain-boundary diffusion to reach the interface of oxide/air. Due to the lattice diffusion, the oxide layer thickness increases, while the diffusion at grain boundaries results in nanowire formation (Figure 8d). 103-105

The growth of nanostructures consists of two steps: the deposition of a metallic layer followed by the thermal oxidation shown in Figure 8. For the metal layer deposition, different techniques can be applied such as electrodeposition, magnetron sputtering, and thermal evaporation. The substrate with the patterned metal deposition must undergo thermal oxidation treatment; therefore, it is placed in the tubular furnace in an oxidizing atmosphere (a mixture of oxygen and argon). Controlling different parameters such as the furnace temperature, deposition time, atmospheric composition, and gas flow allow the control of nanostructure morphology and uniformity. Using this technique, ZnO 105 WO₃ 106,107 Nb-doped WO₃ 107 and CuO 109 nanowires have been prepared for the chemical sensing application.

Some major advantages and disadvantages related to the thermal oxidation technique in tabular form are presented in the Supporting Information.

**Structural and Morphological Characterization.** Assorted metal oxide-based nanowires grown by using thermal oxidation techniques are presented in the literature. Adopting this technique also provides the flexibility to fabricate the nanowires directly onto the active transducer. ZnO is one of the most exploited materials in different applications. 80,110,111 Using thermal oxidation, highly scalable ZnO nanowires have been prepared directly on alumina substrate. 105 The morphology largely depends on the oxidation temperature and oxidation time. Figure 9 shows the temperature-dependent morphology of ZnO nanostructures grown using thermal oxidation. Clearly, between 400 and 600 °C, nanowire morphology was observed under a controlled atmosphere of oxygen and argon, while at 200 °C, ZnO nanoparticles are formed.

Larger nanoparticles are obtained at 700 and 800 °C with a porous-like structure. However, ZnO nanostructures obtained by thermal oxidation are less well defined in comparison with the ones prepared by VLS. Furthermore, the oxygen composition strongly affects the morphology. At 400 °C, the decreasing oxygen ratio at atmospheric composition promotes the formation of dense and longer nanowires, although the same composition has no effect on the morphology at lower temperatures. 105

In the case of WO₃ nanowire growth by thermal oxidation, the thickness of the metallic film and the temperature play fundamental roles. 106 This report presents two different metallic tungsten layer thicknesses (18 and 180 nm) and film deposition temperatures (200 and 300 °C) via thermal oxidation in the tubular furnace at 550 °C for 1 h with an oxygen flow of 2 sccm. The morphological investigation shows that the sputtering temperature seems to have a strong influence on the nanowire size. The nanowires have a larger diameter and a longer length for a layer produced at 300 °C than for one produced at 200 °C; however, the average diameter in both cases is 40 nm as shown in Figure 10. The influence is more prominent in the case of the metallic layer prepared at 300 °C rather than 200 °C, which is
due to the abundance of bulk tungsten metal present underneath nanowires (confirmed from the GI-XRD study). However, after the thermal treatment at temperatures of around 400 °C, this metal layer is also oxidized.

In a recent article, a successful attempt to grow Nb-doped tungsten oxide nanowires by thermal oxidation has been reported.\(^\text{107}\) To achieve Nb-WO\(_3\) nanostructures, the metal layer deposition was performed with magnetron sputtering using a target of W with a variable number of niobium insets. An alloy of metallic tungsten−niobium was deposited on an alumina substrate, with a composition that varies with the number of Nb insets. With only four stubs inserted, the presence of Nb was 3 atom %. Increasing the number of stubs to 12, about 9.5 atom % was achieved. Furthermore, the functional analyses showed that Nb-WO\(_3\) nanowires have an excellent hydrogen-sensing capability compared to that of pristine ones. This new and simple perspective of doping nanostructures by the thermal oxidation technique opens a new possibility to change the sensing response of these nanostructured chemical/gas sensors.

Thermal oxidation used for p-type semiconducting material CuO shows a complex process for the nanostructures’ growth. A metallic copper layer (from 300 nm to 3 μm) was deposited by rf magnetron sputtering on alumina substrates at RT and 200, 300, and 400 °C.\(^\text{109,112}\) Copper is a very reactive metal. It reacts with oxygen in the ambient atmosphere and creates a thin layer of copper oxide. This thin layer is pernicious to nanowire growth; therefore, it is essential to remove this layer before thermal oxidation. Techniques such as wet chemical etching and plasma etching can be used to remove this layer.

The complete oxidation process first involves the oxidation of metallic Cu to a CuO film, after which the CuO film is further oxidized to CuO\(_2\), generating CuO nanostructures.\(^\text{113}\) The oxidation temperature has a huge influence on nanowire morphology and uniformity. Figure 11 shows the morphology variation as the oxidation temperature increases from 200 to 600 °C. However, the best growth temperature was found to be around 400 °C for vertically aligned nanowires and 300 °C for randomly oriented nanowires.

As discussed previously, our group\(^\text{83}\) has reported the growth of uniform single-crystalline SnO\(_2\) nanowires using the VLS mechanism on a polycrystalline alumina substrate. This report serves as a benchmark for their further application in chemical sensing. Chemical sensors based on SnO\(_2\) nanowires for the detection of chemical warfare agents (CWAs) such as dimethyl methyl phosphonate (DMMP) were developed.\(^\text{83}\) SnO\(_2\) nanowire sensors showed superior performance (Figure 12) as compared to SnO\(_2\) thin films which were prepared using a rheotaxial growth and thermal oxidation (RGTO) technique. Indeed, the SnO\(_2\) nanowire sensors showed high sensitivity toward a lower concentration of DMMP, even lower than the respective CWAs IDLH values (immediately dangerous to life and health).

In both of the above-mentioned works,\(^\text{83,85}\) Pt was used as a catalyst to grow SnO\(_2\) nanowires. However, recently Zappa et al.\(^\text{114}\) have grown SnO\(_2\) nanowires using three different catalysts...
(Au, Pd, and Sn) with VLS that have been integrated into gas-sensing devices. Interestingly, at high temperatures, Pd-catalyzed SnO$_2$ nanowires exhibited better performance than did Au and Sn nanowires. However, the reason behind this behavior is still not clear.

Furthermore, WO$_3$ nanowires have been grown using both the VLS mechanism and thermal oxidation for chemical sensing applications. In the VLS-grown WO$_3$ nanowires, two different catalysts (i.e., Pt and Au) have been used, and the conductometric sensors based on these nanowires showed remarkable performance with respect to O$_3$ and H$_2$S as compared to the other interfering compounds such as ethanol and acetone (Figure 13).

Kaur et al. have suggested that when H$_2$S gas molecules interact with the surface-adsorbed O$^{2-}$ ions (present on WO$_3$ nanowires), extra electrons are donated to WO$_3$, resulting in a decrease in the depletion layer thickness (Figure 14a) and hence an increase in the conductance of WO$_3$ sensors. The whole process can be explained by the following equation

$$\text{H}_2\text{S} + 3\text{O}^{2-} (\text{ads}) \leftrightarrow \text{SO}_2(\text{gas}) + \text{H}_2\text{O} + 6\text{e}^- \quad (11)$$

When O$_3$ gas molecules interact with the WO$_3$ nanowires, due to their highly accepting character, the concentration of the surface-adsorbed O$^{-}$ ions increases, which increases the electron depletion layer thickness (Figure 14b). Hence, the conductance of the WO$_3$ sensor decreases when interacting with ozone. The whole process can be explained using the following equation

$$\text{O}_3(\text{gas}) \rightarrow \text{O}_3(\text{surf}) + \text{e}^- \rightarrow \text{O}(\text{gas}) + \text{O}^{-}(\text{ads}) \quad (12)$$

It should be noted that the optimal operating temperatures for H$_2$S and O$_3$ were 400 and 200 °C, respectively, which increase the selectivity toward a specific gas by varying the sensor temperature.

On the other hand, WO$_3$ nanowires grown using thermal oxidation showed excellent performance toward gases such as CO and NO$_2$. Interestingly, in this work, the WO$_3$ nanowire sensors prepared from the thermal oxidation of a 180 nm W metal film showed better performance as compared to those prepared from an 18 nm metal film (Figure 15). Zappa et al. suggested that the 180 nm metal film exhibits a higher density of nanowires compared to the 18 nm film. Hence, the increased surface area results in an enhancement of the sensing performance.

Similar to WO$_3$, ZnO nanowires were also prepared using both VLS growth and thermal oxidation and were integrated into chemical sensing devices. Those prepared using VLS showed excellent performance toward acetone and ethanol with a detection limit lower than 1 ppm. Figure 16 shows the response vs temperature graph of thermally oxidized ZnO nanowires for different gases. Here, ZnO_T400 and ZnO_T500 represent the ZnO nanowires grown at 400 and 500 °C, respectively.
p-type MOX semiconductors are consistently classified as secondary choices in several applications. In gas sensing, the trend is also similar.39 At the Sensor Laboratory, in the past few years different p-type metal oxides such as CuO109 and NiO48,90,109 have been explored. NiO exhibits better overall sensing performance comparing to CuO, even though CuO is one of the most studied p-type materials in the literature.115−117 More interesting, as discussed earlier, NiO nanowires were for the first time grown by vapor-phase techniques, and they were successfully integrated into gas-sensing devices.48 The fabricated NiO nanowire-based sensors exhibit a stronger response toward hydrogen at 300 °C; however, their response toward VOCs is very weak (Figure 18).

Furthermore, in a recent study by Kaur et al.,78 the detection of NO2 using the VLS-grown NiO nanowires is reported. These nanowires exhibited superior response and selectivity toward NO2 at an operating temperature of 200 °C in comparison to other gas analyzers (Figure 19a). Indeed, the lower detection limit was found to be at the parts per billion level. The sensor working temperature, type and concentration of gas analyte, sensor response, and technique used to fabricate the metal oxide nanostructures have been presented in Table S2.

STRATEGIES FOR THE IMPROVEMENT OF THE SENSING PERFORMANCE OF ONE-DIMENSIONAL NANOSTRUCTURE DEVICES

To further enhance the sensing performances of the 1D nanostructures, new strategies such as surface functionalization NWs, developing a heterojunction with a high specific surface area, and a full depletion region are auspicious candidates.19,80,119−122 Many recent studies have demonstrated that sensitivity, selectivity, and other chemical sensing properties of chemoresistive metal oxide sensors can be adequately improved by engaging a secondary material to functionalize 1D nanostructures (nanowire doping,107,108 surface functionalization of nanowires,80,123−128 branch-like nanostructures,19,129 and core−shell nanowires130). For instance, as previously discussed, Nb doping in WO3 nanowires enhances the sensing performance with respect to H2.107 In a similar framework, surface functionalization with metal clusters and 2D materials can also be used to further improve the sensing performance. In a recent report, SnO2 nanowires were functionalized with a graphene oxide layer for low-temperature NO2 sensing in the presence of UV light.123 On the other hand, creating a heterojunction by combining two metal oxides on a sensing platform can bring about new possibilities and further improve the sensing performance. The fabrication of composite nanostructures, involving the integration of n-type and p-type metal oxides, allows the combination of the different individual properties into a single system. For 1D
nanostructures, this can be done using various strategies and synthesis techniques, and branched heterostructures or core–shell heterostructures can easily be achieved.\textsuperscript{131–133}

Indeed, branched 1D heterostructures exhibit strong interactions between tightly packed interfaces that can improve their performances, but they are complex to predict. In 2018, Kaur et al.\textsuperscript{19} demonstrated the growth of NiO/ZnO branched heterostructures by a two-step vapor-phase growth method. NiO nanowires grown by VLS act as backbones for ZnO nanostructure condensation. The selected-area electron diffraction data (SAED) demonstrate that the ZnO nanowires were grown epitaxially along (101) planes on the strongly oriented NiO nanowires along (200) crystallographic planes shown in Figure 20.

Their sensing performances were superior to those of different VOCs such as ethanol and acetone in comparison with those of bare NiO nanowires. Calculated detection limits of 7 and 11 ppm have been found for ethanol and acetone, respectively.
Furthermore, the possible interpretation given by the authors for the sensing response enhancement relies on the junction formation by charge transfer as the two Fermi levels come to equilibrium, further extending the charge depletion region. This in turn increases the overall heterostructure resistance, leading to the sensing property enhancement for the heterostructured material. The sensing performance of fabricated NiO/ZnO heterostructures compared with that of NiO nanowires is shown in Figure 21.

Furthermore, 1D-core/shell structures are another promising type of heterostructure that can be exploited in chemical sensing. Several methods were used to create core–shell morphologies.134−138 However, one of the most used and promising is the ALD (atomic-layer deposition) method of depositing a thin layer of a material on top of nanowires. In a recent report, the synthesis of 1D n-SnO2-core/p-NiO-shell nanowires (CSNWs) on an alumina substrate by using vapor phase growth (VLS) and atomic layer deposition techniques was presented.130 The thickness of the NiO-shell layer varies from a range of 2 to 8.2 nm. After the NiO coating on SnO2 NWs, the electrical conductance of the sensors decreases by many orders of magnitude. This suggested that the conductivity of the sensors is majorly dominated by Schottky barrier junctions across the interface of n–p (core/shell). The author presented the gas-sensing response of pristine SnO2 and SnO2/NiO core–shell heterostructure sensors with different NiO-shell thicknesses toward H2 at various temperatures. Three different ALD cycles (50, 100, and 200) were applied to modulate the thickness of NiO on SnO2 nanowires. Comparing the responses showed that SnO2/NiO-100 exhibits the best performance (shell thickness ca. 4.1 nm) due to the maximized radial modulation of the depletion region (Figure 22).

The authors proposed two possible mechanisms for this behavior: (i) a hole-accumulation layer within the NiO shell and (ii) the barrier height at the interface of NiO-SnO2. As in the case of heterostructures, a p–n junction is created at the interface, which results in the Fermi level modulation. This induces band bending and the formation of a depletion region, which leads to an increase in resistance. As the sensor is exposed to air, an oxygen species adsorbs onto the NiO surface, trapping electrons and creating a hole-accumulation layer (HAL) in the near-surface region. The concentration of holes increased in the NiO-shell, which causes the enhancement of the charge gradient near the junction. This leads to an expansion of the depletion region.

Figure 20. (a) HRTEM image of NiO/ZnO heterostructures. (b) FFT of heterostructure reported in (c). Colored representation of NiO and ZnO planes. Adapted with permission from ref 19. Copyright (2018) Elsevier.

Figure 21. (a) Dynamic response of the NiO/ZnO heterostructure sensing device. (b, Left) Dynamic response of the NiO sensing device toward reducing gases (ethanol, black, 5−5−20−50 ppm at 400 °C; acetone, red, 10−10−30−100 ppm at 400 °C) measured at a relative humidity of 50% at 20 °C. (Right) Response of the NiO/ZnO heterostructure and NiO nanowire sensors toward target gases: NiO/ZnO acetone (brown), NiO acetone (yellow), 30 ppm; NiO/ZnO ethanol (blue), NiO ethanol (green), 20 ppm. RH 50% at 20 °C. Adapted with permission from ref 19. Copyright (2018) Elsevier.

Figure 22. Sensing response of the SnO2/NiO-X CSNWs heterostructures as a function of the NiO-shell layer thickness toward 200 ppm of hydrogen at 500 °C. Adapted with permission from ref 130. Copyright (2020) American Chemical Society.
region and increases the barrier height at the junction. Due to this, the overall resistance of the system increases (Figure 23).

Furthermore, in the presence of H₂, it reacts with the adsorbed oxygen ions and releases electrons back into the system. These released electrons recombine with the holes of NiO, which in turn decrease the charge carrier concentration at the junction, resulting in narrowing the space-charge region. Thus, in the presence of the NiO layer the extent in the change of conductance is higher. Another important fact to consider is the shell layer thickness because it affects the depletion region formation at the interface. The highest response was exhibited when the NiO shell thickness was 4.1 nm for the SnO₂/NiO-100 sensors, a value similar to the hole-accumulation layer thickness, which is also related to the Debye length. Further increasing the thickness of the layer decrease the response so that the shell layer is no longer depleted. In Table S3, some interesting reports available in the literature along with our team work are presented.

CONCLUSIONS AND FUTURE PERSPECTIVES

Metal oxide nanowire-based chemical sensors showed remarkable performance and have been explored for the detection of various analytes such as VOCs, toxic gases, environmental pollutants, and explosives. The reasons behind their astonishing performances are high crystallinity, well-defined crystal orientation, controlled electrical properties, and a high surface-to-volume ratio. In the field of 1D MOX nanostructures, the work done by our group in 2002 on the VLS synthesis of tin dioxide (SnO₂) nanobelts for the gas-sensing application inspired many researchers, and afterward tremendous success until now has been achieved. In MOX, the chemisorption of oxygen ions creates the EDL on n-type semiconductors and HAL on p-type semiconductors, which determines their sensing behavior. By operating at different temperatures, these types of chemisorbed ions can be controlled, and the selectivity toward a particular analyte can be achieved. For example, the presence of O⁻ ions on VLS-grown WO₃ nanowires at 200 °C enhanced their reactivity toward O₂, while when sensors operated at 400 °C, they showed excellent performance toward H₂S due to the dominance of O²⁻ ions on the WO₃ surface.

The surface morphology of nanowires, which also play a major role in determining the sensing performance, is largely dependent on the growth technique used. Indeed, MOX nanowires grown using the vapor-phase mechanism were found to be highly crystalline with minimal defects and hence showed remarkable sensing performance. In MOX nanowires growth by VLS, the type of metal catalyst (generally a noble metal) affects the morphology of nanowires, which in turn influences the sensing performance. Hence, the appropriate selection of a metal catalyst in the VLS method is crucial, especially when one works on new material growth. While optimizing ZnO and NiO nanowire growth, it has been observed that the nanowires grown using Au catalysts possesses uniform and dense morphology as compared to other catalysts (Pt, Pd, etc.). On the other hand, thermal oxidation offers the possibility to grow nanowires at relatively low temperatures, which is generally not possible in vapor-phase growth.

A recent achievement of our group is the first-time growth of NiO nanowires using the VLS mechanism and integration into conductometric chemical-/gas-sensing devices for hydrogen and NO₂ detection. Indeed, NiO nanowire chemical-/gas-sensing devices show no major degradation in their devices performance as measured for a period of 6 months. This is remarkable work in the development of NiO-based gas-sensing devices as only limited works have been presented on p-type metal oxides in comparison to n-type.

Moreover, in this feature article we presented an overview of different approaches such as the fabrication of nanowires heterostructures used to further improve the sensing performance of MOX-based gas sensors. Branched-like NiO/ZnO...
nanowire heterostructure sensing devices using the VLS mechanism showed superior performance compared to NiO nanowires for ethanol and acetone detection. The reason behind their superior performance was found to be the formation of junctions between NiO and ZnO, increasing the resistance and in turn enhancing the sensing performance. Moreover, the detailed microstructural investigation reveals the epitaxial growth along the (101) planes of ZnO NWs on strongly oriented NiO NWs. Furthermore, the 1D n-SnO2-core/p-NiO-shell nanowire heterostructure synthesized by the VLS mechanism and ALD showed excellent sensing performance toward hydrogen. The sensing mechanism reveals that the formation of the hole-accumulation layer within the NiO shell and the barrier height at the interface of NiO-SnO2 were the two major reasons behind their excellent sensing behavior.

However, besides the recent advance, the selectivity of the metal oxide-based gas sensor is still an issue which requires further work. We believe that with the availability of an advanced synthesis/characterization technique and other processes such as surface functionalization, this challenging issue will be partially addressed. Indeed, the surface functionalization of MOX nanostructures using self-assembled monolayers (SAM) which is majorly used in biosensing and synthesis of novel supramolecular architecture can also be adopted to improve the selectivity and performance of gas sensors. The reason behind this perspective is the nature of self-assembled monolayers such as silanes that can generate different functional groups on the oxide surface and react only to the specific gas analytes due to their functional properties. Another area that requires further investigations is the theoretical explanation of the chemical sensing mechanism, specifically for 1D nanostructured MOX as the available ones hold for granular morphology. This requires a great deal of work in the investigation of fundamental physical/chemical properties of these materials especially using operando analyses.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00701.

Conductometric gas-sensing measurement setup; advantages and disadvantages of vapor-phase growth and thermal oxidation growth techniques (PDF)

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Notes
The authors declare no competing financial interest.

Biographies

Navpreet Kaur obtained a bachelor of science degree from Govt. College Ropar (Panjabi University, Patiala) in 2010. In 2012, she obtained a master of science in physics (Horns) from Guru Nanak Dev University Amritsar (India). In 2017, she was awarded a Ph.D. degree with her thesis titled “Vapor Phase Growth of NiO, WO3 Nanowires and NiO/ZnO Heterostructures for Gas Sensing Applications” from University of Brescia (Italy). Currently, she is working as a postdoctoral researcher in the Sensor Laboratory (University of Brescia, Italy). The main focus of her research activities are the synthesis and characterization of metal oxide-based nanostructured and heterostructures for gas-sensing applications.

Mandeep Singh obtained his Ph.D. in the chemistry of innovative materials from University of Bari, Italy in 2016. His Ph.D. thesis was focused on “Solution Processable ZnO Based Electrolyte Gated Thin Film Transistor for Prospective Biosensing Applications”. Currently, he is a postdoctoral fellow in the Sensor Laboratory (University of Brescia, Italy). His current research activities including the growth and surface functionalization (using self-assembled monolayers) of different metal oxides for gas and biosensing applications.
Elisabetta Comini received her master’s degree in physics at the University of Pisa in 1996. She received her Ph.D. in materials science at the University of Brescia. In 2001, she was appointed an assistant professor of the physics of matter at Brescia University. In 2016, she became a full professor. She has been the organizer of several symposia in the sensing field for MRS and E-MRS. She was chair of the MRS fall meetings in 2013. She has high productivity as confirmed by numerous publications in international journals (more than 360) and the large number of invited presentations at conferences. She is a researcher specialist in the growth of metal oxides, particularly nanowires, thin films, and the measurement of their electronic, functional, and structural properties. She is also the director of the Sensor Laboratory (University of Brescia) and is a cofounder of NASYS.

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